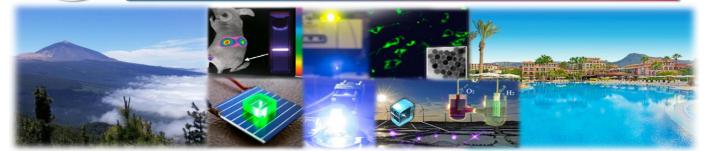


Spectral shaping for biomedical and energy applications

November, 13-17, 2017/Tenerife, Canary Islands, Spain.





PROGRAMME AND BOOK OF ABSTRACTS



"If I have seen further, it is by standing upon the shoulders of giants"

(Isaac Newton, 1643-1727)







Dear Friends and Colleagues,

On behalf of the organizing committee of SHIFT 2017, we kindly welcome you to Tenerife (Canary Islands, Spain) to attend this international conference about spectral shaping ground-breaking applications in both energy and biomedical fields.

Spectral shaping of light is an emerging route for enhancing the efficiency of various solar energy harvesting, storage and conversion processes facing the increasing demand for energy supply, from photovoltaics to photocatalysis, natural and artificial photosynthesis and solar fuels generation, where usually large parts of the solar spectrum are not efficiently utilized. Moreover the use of light in life sciences, within the well-known infrared therapeutic windows (deeper penetration and lower tissue damage) and subsequent wavelength transformation to higher or lower energies provides ground-breaking applications in photodynamic cancer therapy and bio-imaging. Interdisciplinary efforts from physics, chemistry, biology, medicine, materials science and engineering will certainly be required to overcome current challenges leading the way for spectral shaping of light to be a future key technology.

SHIFT 2017 shows up as a cutting-edge multidisciplinary platform to gather presentations and discussions of recent achievements by leading researchers in wavelength shifting luminescence processes (quantum cutting, down-shifting, up-conversion...), as a very promising and not yet fully explored route. We are convinced that SHIFT2017 will provide an unparalleled forum for fruitful scientific discussions at an outstanding warm and sunny destination, to make a significant shift to state-of-the art spectral shaping for biomedical and energy applications. The SHIFT happens in Tenerife!

Undoubtedly, this is not another more conference in the calendar; our list of renowned confirmed invited speakers at the frontiers of renewable energy and biomedicine supports this assumption. At SHIFT2017 you will also have the important opportunity to gain first-hand knowledge about special low tax zone and tax incentives to R+D that Canary Islands offer. Moreover you will be also able to meet some of our technology-based companies and scientific divisions at Canary Islands in the fields of photonics for imaging and biomedical. Besides during our social program, you will also be able to visit important large scientific facilities at Tenerife like ITER, Institute of Technology and Renewable Energies of Tenerife, and the impressive IAC, Astrophysics Institute of Canary Islands, located in El Teide National Park, and of course to enjoy our island's landscapes and touristic attractions.

May the SHIFT be with you! Yours sincerely,



Dr. Jorge Méndez-Ramos jmendezr@ull.es Universidad de La Laguna (Tenerife, Canary Islands, Spain) Conference Chairman SHIFT2017

International Organizing Committee: Ruud Schropp (Eindhoven University of Technology, the Netherlands) Eva Hemmer (University of Ottawa, Canada) Stefan Fischer (Stanford University, USA) Jose Marqués-Hueso (Heriot-Watt Univ., UK) Luca Salassa (DIPC Donostia Int. Physics Center, Spain) Marta Quintanilla (CIC-biomaGUNE, Spain)



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In Memoriam (1970-2017) Juan Carlos Ruiz-Morales

Grupo de Nano y Microingeniería de Materiales <u>www.sofc.es</u>

Instituto de Materiales y Nanotecnología, IMN, University of La Laguna, Spain

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Canarias avanza Gob

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PLOCAN (Plataforma Oceánica de Canarias), ITER (Instituto de Energías Renovables de Tenerife), IAC (Instituto Astrofísica de Canarias), European Upconversion Network, BIOSIGMA, Obra Social "La Caixa", CEOE-Tenerife, J. Mater Chem A & B (RSC Editors), Optical Materials (Elsevier), CIENCI@ULL





PROGRAMME OUTLINE

Scheduled timeline SHIFT2017 Scientific Programme:

Hotel Venue: Hotel Iberostar Anthelia

Time slots (min: talk + questions):

Plenary (45 min: 40+5), Keynote ("K", 30 min: 25+5), invited talk ("I", 25 min: 20+5) and contributing speakers ("O", 20 min: 15+5)

Plenary Sessions: "Sala Orfeo"

2 Parallel sessions: "Biomedical applications" ("B"): "Sala Perseo";

"Energy Applications" ("E"): "Sala Athenea"

(talks code, e.g: "KB1" for Keynote Biomedical 1; "OE12" for Oral Energy 12, and so)



Social Program:

-Monday, 13th (Welcome Reception at Hotel Venue, included in fee, free of charge)

-Wednesday, Nov 15th ("Big Wednesday", FULL DAY EXCURSION "SHIFTING TENERIFE", 8:30h-18:00h, included in fee, <u>registration required only for accompanying persons</u>)

#Important notice: During the visit to the ITER (Institute of Technology and Renewable Energy), and for security reasons it is mandatory to register before entry. Therefore we need to provide them *your passport or identity card number in advance*, to allow them to prepare the passes to enter the institute. Please contact Technical Secretariat shift2017@magnacongresos.es with your passport / ID card number.

-Thursday, 16th: "Spectral conversion Dinner", Gala Dinner at Hotel Venue, registration required

Monday, Nov 13th			
9:00-9:30 h	Opening ceremony ("Sala Orfeo") SHIFT happens!		
9:30-10:15 h	PLENARY speaker ("Sala Orfeo") Chair: J Méndez-Ramos John Capobianco (Concordia University, Canada)		
10:15-10:25 h		iness development con nd Special Zone, ZEC, E	
10:25-10:50 h		Coffee Break	
Parallel Sessions	BIO ("Sala Perseo") Chairs: E. Hemmer / Luis D. Carlos		RGY ("Sala Athenea") B.S. Richards / I.R. Martín
10:50-11:20 h	Keynote: S. Wu (KB1)	10:50-11:15 h	Invited (IE1) G. Westin
11:20-11:40 h	Oral (OB1) T. Giraldez	11:15-11:35 h	Oral (OE1) B. González-Díaz
11:40-12:00 h	Oral (OB2) F. Lahoz	11:35-11:55 h	Oral (OE2) J. Swabeck
12:00-12:25 h	Invited (IB1) U. Resch-Genger	11:55-12:25 h	Keynote: M. Ferrari (KE1)
12:30-14:00 h	Networking Lunch		
14:00-14:45 h		ker ("Sala Orfeo") s chmidt (Fraunhofe	
	Chairs: Luca Salassa / V. Lavín		Chairs: S. Fischer / G. Westin
14:50-15:20 h	Keynote: A. Bednarkiewicz (KB2)	14:50-15:10 h	Oral (OE3) F. Enrichi
15:20-15:40 h	Oral (OB3) J. Hu	15:10-15:30 h	Oral (OE4) S.F.H. Correia
15:40-16:00 h	Oral (OB4) T. Hirsch	15:30-16:00 h	Keynote: P. Balling (KE2)
16:00-16:20 h		Coffee Break	
	Chairs: A. Bednarkiewicz / S. Wu	Chairs	: P. Balling / A. Menéndez
16:20-16:40 h	Oral (OB5) T. Grzyb	Or	al (OE5) C. Roscini
16:40-17:00 h	Oral (OB6) A. Szczeszak	Or	al (OE6) J. Sanchiz
17:00-17:25 h	Invited (IB2) B. Cohen	Invite	ed (IE2) D. W. Shaffer
17:25-17:45 h	Oral (OB7) D. H. Ortgies	Oral	(OE7) M. Oldenburg
17:45-18:05 h	Oral (OB8) L.M. Wiesholler	Ora	l (OE8) H. Lakhotiya
18:30-20:00 h	Hote	Welcome Reception I Venue Iberostar Anthelia oducts gastronomic degustation)	



Tuesday, Nov 14th			
9:00-9:45 h	PLENARY speaker ("Sala Orfeo") Chair: J Méndez-Ramos Rod Eggert (Critical Materials Institute, USA)		
Parallel	BIO ("Sala Perseo")		RGY ("Sala Athenea")
Sessions	Chairs: D. Jaque /L. Salassa		Goldschmidt / L .Wondraczek
9:50-10:20 h	Keynote: L.D. Carlos (KB3)	9:50-10:15 h	Invited (IE3) B.S. Richards
10:20-10:45 h	Invited (IB3) M. Haase	10:15-10:45 h	Keynote: N. Martín (KE3)
10:45-11:10 h		Coffee Break	
	Chairs: E. Hemmer / M. Haase		Chairs: N. Martín / J. Méndez-Ramos
11:10-11:30 h	Oral (OB9) L. Labrador-Páez	11:10-11:40 h	Keynote: G.W. Ho (KE4)
11:30-11:55 h	Invited (IB4) C. Wickleder	11:40-12:05 h	Invited (IE4) A. Menéndez
11:55-12:25 h	Keynote: K. Soga (KB4)	12:05-12:25 h	Oral (OE9) I. Menéndez
12:30-14:00 h		Networking Lunch	
	BIO ("Sala Orfeo") Chairs: K. Soga / K. T. Lee		Chairs: J.C Hummelen / D. W. Shaffer
14:00-14:30 h	Keynote: G. Hong (KB5) (Chairs: D. Jaque / J. Méndez-Ramos)	14:00-14:20 h	Oral (OE10) C. Montes (Presentation of ITER-Tenerife)
14:30-14:50 h	Oral (OB10) C.D.S. Brites	14:20-14:40 h	Oral (OE11) P. Acosta-Mora
14:50-15:10 h	Oral (OB11) S.V. Eliseeva	14:40-15:10 h	Keynote: L. Wondraczek (KE5)
15:20-15:35 h		esentation (Wooptix S.L D, Jose M. Rodríguez-Ra	
15:35-15:45 h	Company's presentation	on (CEAMED) G. Mcnaugth	non-Smith ("Sala Orfeo")
15:45-16:30 h		aker ("Sala Orfeo") Jionne (Stanford Uni [.]	
		Coffee Break and	
16:30-17:30 h	POSTER SESSION (Bio and Energy)		
18:30-20:00 h	"The S	cience Behind SHI	T2017"
Public Session*	Café Científico SHIFT2017-Tenerife		
(Optional) Round Table:	Santa Cruz de Tenerife,		
Educational event	TEA, Tenerife Espacio de las Artes		
(*in Spanish)	Ponentes: Nazario Martín, Daniel Jaque,	Amador Menéndez, Javie	r Concepción, Catalina Ruiz, Jorge Méndez





Wednesday, Nov	15th ("Big Wednesday", Full day Excursion "SHIFTING TENERIFE")
8:30 h	Bus departure from Hotel Venue (Iberostar Anthelia, Costa Adeje)
9:00-11:00 h	Visit to ITER (Institute of Technology and Renewable Energies of Tenerife) Coffee Break at ITER Image: State of Technology Image: State of Techn
12:30 h	**El Teide" National Park Conference Photo **El Teide" N
13:00-15:00 h	Parador Nacional de El Teide" Conference lunch
	Visit to IAC (Astrophysics Institute of Canary Islands) (Observatorio de "El Teide")
15:30-16:30 h	
	Descending through north face of the island (expected arrival time Hotel Venue 18:00 h)
16:30 h	
10.30 11	

Thursday, Nov 16th				
9:00-9:45 h	PLENARY speaker ("Sala Orfeo") Chair: D. Jaque			
	Xiaogang Liu (National University Singapore)			
Parallel	BIO ("Sala Perseo") ENERGY ("Sala Athenea")			
Sessions	Chairs: N. Martín / R. Balda		hairs: R.E.I. Schropp / S. Fischer	
9:50-10:20 h	Keynote: J.C Hummelen (KB6)	9:50-10:15 h	Invited (IE5) X. Zhang	
10:20-10:45 h	Invited (IB5) K.T. Lee	10:15-10:45 h	Keynote: A. Meijerink (KE6)	
10:45-11:05 h		Coffee Brea		
	Chairs: J.Fernández/J.Méndez-Ramos		Chairs: S. McCormack / R.M. Almeida	
11:05-11:25 h	Oral (OB12) P. Haro-González	11:05-11:25 h	Oral (OE12) A. Speghini	
11:25-11:45 h	Oral (OB13) A. Lay	11:25-11:50 h	Invited (IE6) J. Agustynski	
11:45-12:10 h	Invited (IB6): J. García-Solé	11:50-12:10 h	Oral (OE13) D. Hudry	
12:10-12:35 h	Invited (IB7) M. Maynar	12:10-12:35 h	Invited (IE7) S.J.L. Ribeiro	
12:40-14:50 h	Networking Lunch			
	Chairs: S. Fischer / D.H. Ortgies Chairs: A. Meijerink / D. Hudry		Chairs: A. Meijerink / D. Hudry	
14:50-15:10 h	Oral (OB14) R. D. Mehlenbache	r 14:50-15:20	h Keynote: W.G. van Sark (KE7)	
15:10-15:30 h	Oral (OB15) P. Rodríguez-Sevilla	15:20-15:50	h Keynote: S. Schweizer (KE8)	
15:30-15:50 h	Oral (OB16) C. Würth	15.20-15.50	Reynote. 3. Schweizer (RE8)	
15:50-16:10 h		Coffee Brea	ık	
	Chairs: F. Vetrone / P. Haro-González		Chairs: W.G. van Sark / M. Oldenburg	
16:10-16:40 h	Keynote: S. Bonnet (KB7)	16:10-16:35	h Invited (IE8) R. M. Almeida	
16:40-17:00 h	Oral (OB17) S. Alonso-de-Castro	16:35-17:00	h Invited (IE9) S. McCormack	
17:00-17:25 h	Invited (IB8) R. Balda	17:00-17:20	h Oral (OE14) K.W Krämer	
17:25-17:45 h	Oral (OB18) M.S. Wickleder	17:20-17:40	h Invited (IE10) P. Loiko	
17:45-18:45 h	POSTER SESSION (Bio and Energy)			
20:00-22:30 h Gala Dinner [*] ([*] registration required)	Gala Dinner "SHIFT2017-Tenerife" Hotel Venue Iberostar Anthelia <i>"Spectral Conversion Dinner"</i>			



Friday, Nov 17th				
9:00-9:45 h	PLENARY speaker ("Sala Orfeo") Chair: J. García-Solé Daniel Jaque (Univ. Autónoma Madrid/IRyCIS, Spain)			
Parallel Sessions	BIO ("Sala Perseo") Chairs: A. Speghini / S. Alonso-de-Castro ENERGY ("Sala Athenea") Chairs: J. Marqués-Hueso / R.E.I. Schropp		• •	
9:50-10:20 h	Keynote: F. Vetrone (KB8)	9:50-10:15 h	Invited (IE11) G.E. Arnaoutakis	
10:20-10:40 h	Oral (OB20) E. Martín-Rodríguez	10:15-10:45 h	Keynote: D. Sinton (KE9)	
10:40-10:55 h		Coffee Bre	eak	
Parallel Sessions	BIO ("Sala Perseo") Chairs: S. Bonnet / J. García-Solé		BIO ("Sala Athenea") Iartín-Rodríguez / R. D. Mehlenbacher	
10:55-11:20 h	Invited (IB9) J. Fernández	10:55-11:20 h	Invited (IB10) S. Lis	
11:20-11:40 h	Oral (OB21) M. Díaz	11:20-11:40 h	Oral (OB23) C. Hazra	
11:40-12:00 h	Oral (OB22) S. Petoud	11:40-12:00 h	Oral (OB24) O.Q. De Clercq	
12:05-13:00 h	SHIFT2017 Final Round Table ("Sala Orfeo") Podium Discussion: Present and future outlook of spectral shaping approach in energy and life sciences			
13:00-13:30 h		Closing ceremony (* - Poster Aw J.Mater Chem A & - Special Is: Optical Materials Call for pap May the SHIFT be	ards: &B (RSC) sue: (Elsevier) ers Chemistry A Journal of Materials Chemistry B Optical Materials	

PLENARYS



	Plenary		
	Presenting author	Affiliation Presenting author	Title
	Iohn A Canobianco	Department of Chemistry and Biochemistry, Centre for NanoScience Research, Concordia University, Montreal, Canada	Upconversion: Odyssey
	Jan C. Goldschmidt	Fraunhofer Institute for Solar Energy Systems, Germany	Upconversion for Photovoltaics – From Devices to Photonic Enhancement
	Rod Eggert	Professor, Colorado School of Mines, USA; Deputy Director, Critical Materials Institute, USA	Critical Elements and Energy Materials
4	Jennifer Dionne	Department of Materials Science and Engineering, Stanford University, USA	New upconversion schemes for efficient solar harvesting and biological force sensing
	Xiangang Lili	Department of Chemistry, National University of Singapore, Singapore 117543 and Institute of Materials Research and Engineering, A*STAR, Singapore	The Trajectory of Upconversion: A Chemist's View
	Marco Bettinelli	University of Verona,	Shifting the emission colour in Tb-based phosphate hosts by Tb3+ to Eu3+ energy
	Marco Dettinem	Our condolences to our friend Marco	transfer: a spectroscopic study
	Daniel Jaque	Fluorescence Imaging Group, Departamento de Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid, Spain; Instituto Ramón y Cajal de Investigación Sanitaria, Spain	Luminescent nanothermometers for new in vivo diagnosis and therapy.



ong Hong

Wilfried van Sa

David Sinte

Si Wu

Peter Balling

A. Bednarkiewicz Stefan Schweizer

	Keynote		
Code	Presenting author	Affiliation Presenting author	Title
KB1	Si Wu	Max Planck Institute for Polymer Pesearch, Germany	Remote Control of Nanomaterials Functionalized with Ru Complexes Using Near-Infrared Light for Deep-Tissue Biomedical Applications
KB2	Artur Bednarkiewicz	Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw Research Centre EIT+, Wroclaw, Poland	Spectral Shaping in Active-Core-Active-Shell Up-converting Nanoparticles
КВЗ	Luis D. Carlos	Departamento de Física and CICECO-Aveiro Institute of Materials, Universidade de Aveiro, Portugal	Shedding Light on Luminescent Nanothermometry
KB4	Kohei Soga	Department of Materials Science and Technology, Tokyo University of Science, Tokyo, Japan Frontier Imaging Center, Tokyo University of Science, Chiba, Japan	Biophotonics in Infrared Therapeutic Windows
KB5	Guosong Hong	Department of Chemistry and Chemical Biology, Harvard University, USA	In Vivo Deep-Tissue Fluorescence Imaging in the Second Near-Infrared Window
KB6	Jan C. Hummelen	Stratingh Institute for Chemistry, University of Groningen, The Netherlands	Dye-sensitized upconversion
KB7	Sylvestre Bonnet	Leiden Institute of Chemistry, Leiden University, The Netherlands	Triplet-triplet annihilation upconversion vesicles and their biological applications
KB8	Fiorenzo Vetrone	Institut National de la Recherche Scientifique (INRS), Centre Énergie, Matériaux et Télécommunications, Université du Québec, Canada	Hybrid Nanoplatforms Based on Rare Earth Doped Nanoparticles
KE1	Maurizio Ferrari	Centro di Studi e Ricerche "Enrico Fermi", Roma, Italy. IFN-CNR CSMFO Lab. and FBK Photonics Unit, Trento, Italy	Glass photonic structures for photon management applications
KE2	Peter Balling	Department of Physics and Astronomy, Aarhus University, Denmark. Interdisciplinary Nanoscience Center (INANO), Aarhus University, Denmark	Improving the efficiency of solar cells by upconverting sunlight using field enhancement from optimized nano structures (SunTune)
KE3	Nazario Martín	Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, Spain. IMDEA-Nanoscience, Madrid, Spain.	Highly Efficient Hole and Electron Transporting Materials for Perovskite Solar Cells
KE4	Ho Ghim Wei	Department of Electrical & Computer Engineering, National University of Singapore (NUS)	Photothermal Harnessing for Photocatalysis and Vaporization
KE5	Lothar Wondraczek	Otto Schott Institute of Materials Research, University of Jena, Jena, Germany Center of Energy and Environmental Chemistry – CEEC, University of Jena, Jena,	Solar spectral conversion and structured illumination in photosynthesis and photochemical energy storage
KE6	Andries Meijerink	Debye Institute, Utrecht University, The Netherlands	Multi-photon Phosphors
KE7	Wilfried van Sark	Utrecht University, Copernicus Institute, Utrecht, The Netherlands	Nanoparticles for Luminescent Solar Concentrators
KE8	Stefan Schweizer	Fraunhofer Application Center of Inorganic Phosphors, Branch Lab of Fraunhofer Institute for Microstructure of Materi-als and Systems IMWS, GermanyDepartment of	Lanthanide-doped glasses as frequency converter for high-power LED applications
KE9	David Sinton	Mechanical and Industrial Engineering, University of Toronto, Canada	Optofluidics for Energy and Environmental Applications

INVITED SPEAKERS



	Invited		
Code	Presenting author	Affiliation Presenting author	Title
IB1	Ute Resch-Genger	Federal Institute for Material Research and Testing (BAM), Germany	Challenges and Examples for Quantitative Fluorescence Measurements > 800 nm with Semiconductor and Lanthanide-Doped Nanocrystals
IB2	Bruce E. Cohen	The Molecular Foundry, Lawrence Berkeley National Laboratory, USA	Low fluence multiphoton imaging with alloyed lanthanide nanocrystals
IB3	Markus Haase	Institute of Chemistry of New Materials, University of Osnabrueck, Germany	Control of Growth, Nucleation and Size of Monodisperse Core/Shell Upconversion Nanocrystals for Bioimaging
IB4	Claudia Wickleder	University of Siegen, Germany	Shifting Eu2+ Emission Bands to low Energies
IB5	Kang Taek Lee	Gwangju Institute of Science and Technology (GIST)	Upconverting nanoparticles (UCNPs): A platform for multiplexed 3D and super-resolution imaging
IB6	José García Solé	Fluorescence Imaging Group, , Universidad Autónoma de Madrid, Spain.	Shaping nanoparticles for enhanced cardiovascular imaging
IB7	M. Maynar	Chair of Medical Technologies, University of Las Palmas de Gran Canaria (ULPGC), Spain	Technological Progress, a Gate to a New Era: the 4 th Space
IB8	Rolindes Balda	Universidad del País Vasco, Bilbao, Spain	Optical temperature sensing using upconversion emission of erbiumdoped lanthanum oxysulfide powders
IB9	Joaquín Fernández	Universidad del País Vasco and Donostia International Physics Center, Spain	A performance study of Nd-based stoichiometric random lasers
IB10	Stefan Lis	Adam Mickiewicz University, Poland	Nanomaterials containing rare earths ions: chosen luminophores, core-shell surface functionalized nanoparticles and multifunctional hybrids; from synthesis to applications
IE1	Gunnar Westin	Uppsala University, Sweden	Solution based synthesis of complex shape and composition nano-structures for energy applications
IE2	David W. Shaffer	Brookhaven National Laboratory, USA	Fast single-site molecular water oxidation catalysts: one site is still enough
IE3	Bryce S. Richards	Institute of Microstructure Technology (IMT), Karlsruhe Institute of Technology (KIT), Germany	Application of Up-Conversion Materials for Plastic Recycling
IE4	Amador Menéndez-Velázquez	ITMA Materials Technology, Principado de Asturias, Spain	Luminescent solar concentrators: from BIPV to mobile electronics
IE5	Xiaodan Zhang	Nankai University, China	Upconversion Material and its Application in Solar cells
IE6	Jan.Augustynski	Centre for New Technologies, University of Warsaw, Poland	Metal-oxide semiconductor photoanodes for sunlight-driven water splitting
IE7	Sidney J.L. Ribeiro	São Paulo State University (UNESP), Brazil	Upconversion nanoparticles modified by sol-gel methods for applications in UV-Vis light activated processes
IE8	Rui M. Almeida	Universidade de Lisboa, Portugal	Photonic crystal assisted rare-earth doped frequency conversion in solar energy applications
IE9	Sarah J. McCormack	Trinity College Dublin, Ireland	Advanced materials for luminescent photovoltaic systems
IE10	Pavel Loiko	KTH - Royal Institute of Technology, Sweden; ITMO University, Russia	Complex Fluorides of Yttrium and Alkali Elements as Efficient Up and Down-Conversion Materials for Versatile Applications
IE11	Georgios Arnaoutakis	Alexandre Yersin Dept. of Solar Energy and Environmental Physics, Ben-Gurion University of the Negev, Israel	Spectral conversion under high solar concentration

	Oral		
code	Presenting author	Affiliation Presenting author	Title
OB1	Teresa Giraldez	Department of Medical Sciences-Physiology, ULL Medical School; Institute of Biomedical Technologies (ITB);	Structural dynamics of large conductance calcium-and voltage-gated potassium channels revealed by Patch-Clamp Fluorometry
OB2	F. Lahoz	Departamento de Física, Instituto de Estudios Avanzados en Atómica, Molecular y	Control of laser induced temperature increase in bacteria through Green Fluorescent Protein nanothermometers
ОВЗ	Jie Hu	Fluorescence Imaging Group, Universidad Autónoma de Madrid, Spain.	Quantum Dots emitting in the third bio-window as potential contrast agents for bimodal intracoronary imaging
OB4	Thomas Hirsch	University of Regensburg, Germany	Upconversion nanoparticles for monitoring of enzymatic reactions in human serum
OB5	Tomasz Grzyb	Adam Mickiewicz University, Poland	Nanocrystalline alkaline and rare earth M2REF7 fluorides (where M = Ca, Sr, Ba and RE = Y, La, Gd, Lu) for upconversion and bioapplications
OB6	Agata Szczeszak	Adam Mickiewicz University, Poland	Tunable upconversion emission in inorganic nanomaterials based on rare earth fluorides and borates
OB7	Dirk H. Ortgies		Multifunctional Upconverting Nanoparticles for the Activation of Organic Photocatalysts
OB8	Lisa M. Wiesholler	University of Regensburg, Germany	Design, Synthesis, and Theranostic Application of Upconversion Nanoparticles with Tandem Sensitization
OB9	L. Labrador-Páez		Ion exchange between luminescent nanoparticles evidences temperature-induced crossover in water molecules behavior
OB10	Carlos D.S. Brites		Tethering Luminescent Thermometry and Plasmonics to Assess Real-Time Thermal Flow in Nanoarchitectures
OB11	Svetlana V. Eliseeva	Centre de Biophysique Moleculaire, CNKS , France	Lanthanide(III)-Based Metallacrowns: Photophysical Properties and Biological Applications
OB12	P. Haro-González	Fluorescence Imaging Group, Universidad Autónoma de Madrid, Spain	Increasing optical trapping forces by means of photonic nanojets
OB13	Alice Lay	Department of Applied Physics, Stanford University, USA	In Vivo Application of Upconverting Force Sensors to Elucidate Neuromuscular Pump Action in C. elegans
OB14	Randy D Mehlenbacher	Department of Materials Science and Engineering, Stanford University, USA	Electric field sensitive upconverting nanoparticles for in vivo action potential imaging
OB15	Paloma Rodríguez-Sevilla	Fluorescence Imaging group, Universidad Autónoma de Madrid, Spain.	Cancer drug control by UCNPs-based intracellular microrheometry.
OB16	Christian Würth	BAM Federal Institute for Materials Research and Testing, Germany	Systematic Investigation of P-dependent Quantum Yields, Excited State Lifetimes and Emission Spectra of Yb3+, Er3+ doped ß-NaYF4 Nanoparticles: Influence of Size, Microenvironment, Surface-Chemistry and Resonance Energy Transfer
OB17	Silvia Alonso-de Castro	CIC biomaGUNE, Donostia, Spain	Phosphonate-Functionalized Upconverting Nanoparticles As Multimodal Imaging Probes
OB18	Mathias S. Wickleder	University of Cologne, Germany	Synthesis and Characterization of Rare Earth-doped ZrO2 Nanoparticles
OB19	Ana-Maria Albu	University POLITEHNICA of Bucharest, Romania	Structural Peculiarities of the Polymer- DNA Assembles
OB20	Emma Martín Rodríguez	Fluorescence Imaging Group, Universidad Autónoma de Madrid, Spain; Instituto Ramón y Cajal de Investigación Sanitaria IRVCIS	Long-luminescence-lifetime nanoparticles for time-gated autofluorescence-free bioimaging
OB21	Mario Díaz	Dpto. Biología Animal, Universidad de La Laguna, Spain	Opto-Chemical and Laser Properties of a Novel Fluorescent Antiestrogen Derivative and its Potential Applications in Breast Cancer Photodynamic Chemotherapy
OB22	Stéphane Petoud	Centre de Biophysique Moléculaire, CNRS, France	Polymetallic Lanthanide Near-infrared Emitting Compounds for Optical Microscopy: Dendrimer Complexes and Metal Organic Frameworks
OB23	Chanchal Hazra	llnstitute of Chemistry, São Paulo State University (UNESP), Brazil	Enhanced NIR-I Emission from Water Dispersible NIR-II Dye-Sensitized Core/Active Shell Upconverting Nanoparticles
OB24	Olivier Q. De Clercq	Center for Nano- and Biophotonics (NB-Photonics), Ghent University, Ghent, Belgium	Trapping in the LiGa5O8:Cr infrared emitting persistent phosphor

OE1	Benjamín González-Díaz	Departamento de Ingeniería Industrial, Universidad de La Laguna, Spain	Durability analysis of polymeric Eu3+ down-shifter on Si-based solar modules under outdoor conditions.
OE2	Joseph Swabeck	Department of Materials Science and Engineering,, Department of Chemistry, University of California Berkeley, USAMaterials Sciences Division, Lawrence Berkeley National Laboratory, USA	Lanthanide decorated semiconductor quantum dots for use as broadly absorbing downshifters
OE3	F. Enrichi	Luleå University of Technology,, Sweden. Museo Storico della Fisica e Centro Studi e Ricerche Enrico Fermi, Italy	Downconversion enhancement by Ag nanoaggregates in Tb3+/Yb3+ doped sol-gel glass and glass-ceramic films for solar cell applications
OE4	Sandra F. H. Correia	Department of Physics, CICECO - Aveiro Institute of Materials and Instituto de Telecomunicações, University of Aveiro, Portugal;	Large area tunable visible-to-NIR luminescent solar concentrators based on organic-inorganic hybrids
OE5	Claudio Roscini	Catalan Institute of Nanoscience and Nanotechnology (ICN2), Barcelona, Spain.	Spectral shifts in waxes
OE6	Joaquín Sanchiz	Departamento de Química, Instituto de Materiales y Nanotecnología. Universidad de La Laguna	Highly Luminescent Films as Enhancer of Photovoltaic Devices
OE7	Michael Oldenburg	Institute of Microstructure Technology (IMT), Karlsruhe Institute of Technology (KIT), Germany	Up-conversion Thresholds: Describing the Power Dependence of Up-Conversion from Triplet Annihilation Systems to Lanthanide Core-Shell Nanoparticles
OE8	H. Lakhotiya	Department of Physics and Astronomy, Aarhus University, Denmark	Near-infra-red plasmonic nano structures for upconversion enhancement
OE9	Inmaculada Menéndez	IOCAG, Instituto de Oceanografía y Cambio Global, Universidad de Las Palmas de Gran Canaria, Spain	Exploration of REE-bearing mineral resources at the Canary Island Volcanic Province: Gran Canaria Island and neighboring seamounts of Amanay, Banquete, and Conception Bank
OE10	C. Montes	ITER, Instituto de Energías Renovables de Tenerife, Spain	Manufacturing of thin film photvoltaic solar cells based on perovskites in a clean room environment
OE11	P. Acosta-Mora	Departamento de Física, Instituto de Materiales y Nanotecnología IMN, Universidad de la Laguna, Spain	A bridge over troubled gaps: evidences of up-conversion driven photocatalysis for H2 generation and organic dye degradation
OE12		Nanomaterials Research Group, Department of Biotechnology, Università di Verona and INSTM, Italy	NIR to Visible Upconversion of composite polymeric aerogels
OE13	D. Hudry	Karlsruhe Institute of Technology, Institute of Microstructure Technology, Germany.	Crystal structure and chemical interfaces in core@shell upconverting nanocrystals: there is still plenty of room.
OE14	Karl W. Krämer	Department of Chemistry and Biochemistry, University of Bern, Switzerland	Room temperature synthesis and luminescence of $\beta\-NaGdF4$: Eu3+, Er3+, and Yb3+, Er3+ nanocrystals
OE15	Tuhin Samanta	Department of Chemical Sciences, Indian Institute of Science Education Research (IISER), India	Enhanced Ln3+ lons Luminescence from Ln3+-Doped Nanocrystals via Sensitization and Its Application in Silicon Solar Cell

Poster		
Presenting author	Affiliation Presenting author	Title
Minnea Tuomisto	Department of Chemistry, University of Turku, Finland. University of Turku Graduate School (UTUGS), Turku, Finland.	Yb,Er up-conversion luminescence from molecular hybrid thin films prepared by ALD/MLD
Antonio D. Lozano-Gorrín	Departamento de Física, Universidad de La Laguna, Spain. MALTA Consolider Team, Universidad de La Laguna, Spain.	Nanothermometry and nanoheating applied to biomedicine. Near-infrared emitting rare-earth doped nano- garnets
Yo Han Song	Department of chemistry, Gwangju Institute of Science and Technology (GIST), Korea.	Upconversion nanoparticle labeling of EGFR using click chemistry and three-dimensional live-cell imaging
Isabella Norrbo	Department of Chemistry, University of Turku, Finland	The use of synthetic hackmanites in storing UV radiation and X-rays
M.A. Hernández-Rodríguez	Departamento de Física, Universidad de La Laguna, Spain. MALTA Consolider Team, Universidad de La Laguna, Spain.	Nanoperovskites doped with RE3+ ions as optical temperature sensors working in the near infrared region
Karina Nigoghossian	Laboratory of Photonic Materials, Institute of Chemistry, São Paulo State University. Centre d'optique, photonique et laser, Université Laval Canada. Department of chemistry, Université Laval, Canada.	UV and temperature-sensing based on NaGdF4:Yb3+:Er3+@SiO2-Eu(tta)3 nanoparticles
Yeongchang Goh	Department of Chemistry, School of Physics and Chemistry, GIST.	Multiplexed 3D Tracking of Single Upconversion Nanoparticles (UCNPs) in Living Cells
Ángel Acebes	Centre for Biomedical Research of the Canary Islands, Institute of Biomedical Technologies, University of La Laguna, Spain.	New advances in 3D-technology applied to Biomedicine
Eunsang Lee	Department of Chemistry, School of Physics and Chemistry, GIST.	Distinct Mechanisms for The Upconversion of NaYF4:Yb3+,Er3+ Nanoparticles Revealed by Stimulated Emission Depletion
J. del-Castillo	Departamento de Física, Universidad de La Laguna, Spain.	Ultraviolet and visible up-conversion in SiO2-BaY0.78-xYb0.2Tm0.02GdxF5 doped glass-ceramics under 980 nm excitation
Dragana Jovanović	Vinča Institute of Nuclear Sciences, University of Belgrade, Serbia.	Nd3+-sensitized up-conversion emission in GdVO4:Er3+ and GdVO4:Ho3+ nanoparticles
Maria Tesa	Edinburgh Instruments, Bain Square, Livingston, United Kingdom.	Characterisation of Upconversion Materials by Spectral and Time-Resolved Luminescence
Marcel Popa	Gheorghe Asachi Technical University, Faculty of Chemical Engineering and Environmental Protection, Romania.	Photoluminescent polymer aerogels based on poly(N-Isopropylacrylamide) - rare earth complexes
A. Bouajaj	Laboratoire des Technologies Innovantes,LTI, Département de Génie Industriel ENSA-Université de Tanger, Morocco.	Luminescent 70SiO2-30HfO2 layers doped rare earth ions for enhanced silicon solar cell performance by using Down-Conversion process.
Marta Sierra	Departamento de Química, Instituto de Materiales y Nanotecnología. Universidad de La Laguna, Spain.	Design and Preparation of Luminescent Films Applied to Photovoltaic Technologies
Tamara Gavrilović	Vinča Institute of Nuclear Sciences, University of Belgrade, Serbia.	The impact of nanoparticles size on luminescent properties of LaPO4: Eu3+ system
Jiaren Du	LumiLab, Department of Solid State Sciences, Ghent University, Belgium.	LaAIO3: Mn4+ as near-infrared emitting persistent luminescent phosphor for medical imaging
Ana R. Frias	Department of Physics and CICECO - Aveiro Institute of Materials. Instituto de Telecomunicações, University of Aveiro, Portugal.	Chlorophyll-based luminescent solar concentrators
Aleksandra Pilch	Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna, Poland.	Heterogeneously Nd3+ Doped Single Nanoparticles for NIR-induced Heat Conversion, Luminescence, and Thermometry
C. Montes	Instituto Tecnológico y de Energías Renovables, S. A. (ITER),Granadilla de Abona. Departamento de Ingeniería Industrial, Universidad de La Laguna, Spain.	Optical characterization of perovskite thin layers produced by one-step deposition method for solar light harvesting
K. Elzbieciak	Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna, Poland.	The influence of structural changes in Y3AI5-xGaxO12 on the sensitivity of Cr3+ based luminescent nanothermometers
Kyujin Shin	Department of chemistry, Gwangju Institute of Science and Technology (GIST), Korea	Cooperative bidirectional motion of motor proteins revealed at the single particle level
K.Kniec	Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna, Poland.	The influence of grain size and dopant concentration on the spectroscopic properties of YAG: V3+, Eu3+ nanocrystalline luminescent thermometers
Giacomo Lucchini	Dipartimento di Biotecnologie, Università di Verona and INSTM, UdR Verona, Italy.	Upconversion ratiometric thermometer based on Nd3+ excited state absorption
M.A. Rodriguez-Florido	Chair of Medical Technologies, University of Las Palmas de Gran Canaria (ULPGC), Spain.	Technological Challenges for the Optical Physics in the Diabetes-Related Lower Extremity Disease
Philipp Weis	Max Planck Institute for Polymer Research, Germany.	Visible-Light-Responsive Azopolymers for Photopatterning and Solar Energy Storage
Suman Devi	Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, India.	Lanthanide doped Upconversion Nanoparticles for Biological Applications
Katarzyna Zawisza	Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna, Poland.	Phosphate doped with lanthanide ions embedded into polylactic acid composite – spectroscopic properties
Daniel Avram	National Institute for Laser, Plasma and Radiation Physics, Magurele, Ilfov, Romania	X-ray and Near-Infrared Excitation of Luminescence in Ln doped Nanoparticles for Bio-imaging Applications
Sergei Popov	Department of Applied Physics, KTH – Royal Institute of Technology, Sweden	Cooperative Up- and Down-Conversion in Y2O3:Eu,Yb and Y2O3:Tb,Yb Nanoparticles
Paulina Sobierajska	Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna, Poland.	Rare Earth doped Nanostructured Apatites for Theranostic Applications
Wiktor Matysiak	Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego, Gliwice, Poland.	Polymeric nanofibers filled by TiO2 NWs – synthesis, structural and optical investigation of the novel type of nanocomposite material
Tomasz Tański	Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego, Gliwice, Poland.	Optical analysis of PAN/TiO2, PAN/Bi2O3, and PAN/SbSI electrospun composite fibrous mats
K.Trejgis	Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna, Poland.	Spectroscopic properties of YAG:Mn,Nd nanocrystals as a new luminescent thermometer
L. García-Rodríguez	Departamento de Física, Universidad de La Laguna, Spain	Nanoperovskite doped with Yb3+ and Tm3+ ions used as optical upconversion temperature sensor
L. de Sousa-Vieira	Departamento de Física, Universidad de La Laguna, Spain	Whispering Gallery Modes in a holmium doped glass microsphere: temperature sensor in the second biological window
K. Grzeszkiewicz	Institute of Low Temperature and Structure Research, Department of Spectroscopy of Excited States,	Investigation of quantum cutting process followed by energy transfer in Mn2+, Pr3+ co-doped SrF2 and CaF2 nanoparticles
	separtment of spectroscopy of Excited states,	nanoparucies



ABSTRACTS

PLENARY KEYNOTES INVITED ORAL CONTRIBUTIONS POSTER CONTRIBUTIONS

Shift2017 Spectral sHapIng For biomedical and energy applicaTions November, 13–17, 2017/Tenerife, Canary Islands, Spain.

Universidad de La Laguna

Upconversion: Odyssey

John A. Capobianco

Plenary Speaker

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The field of upconversion in ion doped system can be traced back to an idea of Bloembergen in 1959. Bloembergen proposed that IR photons could be detected and counted through sequential absorption(ESA) within the levels of a given ion in a solid. Prior to the 1960s, all anti Stokes emissions, which were known to exist, involved emission energies in excess of excitation energies by only a few kT. Thus they were linked to thermal population of energy states above excitation states by such an energy amount. Role of energy transfer in upconversion was recognized by Auzel in 1966. The period 1970-1990 was rich in the research of upconversion in single crystals, glasses and glass ceramics. The driving force was the search for new laser materials using upconversion. We witnessed the synthesis of many of the bulk materials such as LiYF4, CaF2, NaYF4, NaGdF4, YF3, LaF3, LiSrAIF6, LiCaAIF6, LiSrGaF6, LiLuF4, BaY2F8, BaLuF8, for potential applications as laser host materials. This area of research continued to flourish, however there was a change appearing on the horizon with the development of nanomaterials. From late 1990s to early 2000 we witnessed an interest in studying upconversion in nanomaterials. Initially, oxides were synthesized and many studies were performed on their upconversion properties. Y2O3 was one of the material studied initially and in time gadolinium gallium garnet, YVO4 etc. were included to the list. The mid 2000 to today has witnessed an exponential growth in publications on fluoride based nanoparticles due to their efficient upconversion but principally for their potential applications in nanobiomedicine (bioimaging, drug delivery, nanothermometry, photodynamic therapy and multifunctional platforms).

Upconversion for Photovoltaics – From Devices to Photonic Enhancement

Jan Christoph Goldschmidt^{1*}, Clarissa L. M. Hofmann^{1,2}, Benedikt Bläsi¹, Emil H. Eriksen³, Elena Favilla⁴, Stefan Fischer⁵, Christian Reitz⁶, Bryce S. Richards^{2,7}, Mauro Tonelli⁴, Deniz U. Yazicioglu¹

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Upconversion (UC) can convert two, or more low-energy sub-bandgap photons into one high energy photon, which then could be used in a silicon solar cell. In my talk, I will present measurements of upconverter solar cell devices (UCPVDs) showing record values for the relative increase in shortcircuit current density due to upconversion. To further increase upconversion performance, we apply photonic structures that combine local irradiance enhancement and resonant emission amplification via a modification of the local density of optical states (LDOS). We have identified 1-D photonic crystal, more specifically Bragg stacks, as very promising for this purpose as they combine the potential for strong upconversion luminescence enhancement, with the possibility for high loading with upconverter material and potentially cheap processing.

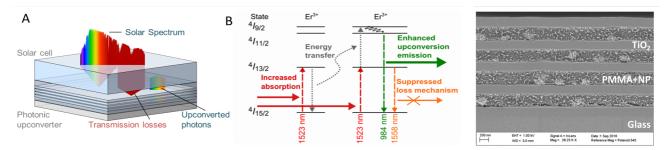


Fig. 1. A: Schematics of a solar cell combined with a photonic upconverter. B: Simplified energy scheme of the UC process in Er^{3+} including the photonic effects of increased absorption by an enhanced energy density and tuned spontaneous emission probabilities by a modified LDOS. C) SEM cross section of a realized Bragg stack e made of TiO₂ and 4 active layers of PMMA with embedded upconverter nanoparticles.



Critical Elements and Energy Materials

Rod Eggert^{1,2,*}

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Modern energy systems depend on raw materials whose properties provide essential functionality to these systems. Some of these elements have few if any good substitutes and, additionally, are subject to supply-chain risks. Such materials are known as critical materials or elements. Examples include several of the rare-earth elements in permanent magnets used in high-efficiency motors and direct-drive wind turbines, and in phosphor materials in fluorescent and LED lighting; lithium, cobalt and graphite in batteries; and silver, indium and tellurium in photovoltaic materials. This paper reviews the critical elements on which modern energy systems depend and how innovation can help overcome supply-chain risks through advancements that increase and diversify supplies, reduce wastes through improvements in manufacturing efficiency and recycling, and foster substitution away from materials with supply-chain risks.

New upconversion schemes for efficient solar harvesting and biological force sensing

Universidad de La Laguna

Jennifer Dionne Department of Materials Science and Engineering, Stanford University *jdionne@stanford.edu

Please indicate preference: ___Poster Oral _x_ Invited Speaker Specify Technical Area: <u>x</u> Biomedical _x_ Energy

Upconvertering nanomaterials hold significant promise for photovoltaics, photocatalysis, photodetection, bioimaging, and security applications, but suffer from two notable limitations: 1) their efficiency is rather low, in many cases not exceeding a few percent, and 2) their upconverted intensity or color cannot be modulated with an external force or field. Here, we introduce efficient and tunable upconverting materials that address each limitation, and show how they can be utilized for improved solar energy generation and in vivo biological force sensing. First, we develop a new upconverting scheme based on hot-carrier injection from a plasmonic absorber to an adjacent semiconductor. Low-energy photons incident on a plasmonic particle generate hot electrons and hot holes, which are injected into a semiconducting quantum well and subsequently radiatively recombine. Importantly, the bandgap of the quantum well can be higher than the energy of the incident photon, enabling upconversion. This scheme does not require coherent illumination, is a linear process, and can be broadband, paving the way towards higher-efficiency upconversion. Then, we develop upconverting nanoparticles that can be used as in vivo optical sensors of nano-tomicroNewton forces. These upconverting force probes are small, bio-compatible, do not bleach or photoblink, need not be genetically encoded, and exhibit reversible changes in their color with an applied pressure. We deploy these upconverting nanoparticles in C. elegans to generate highresolution in vivo force maps. In particular, we focus on the forces generated by these tiny roundworms as they feed and digest their bacterial food, to visualize how digestive tract forces vary across space and time. These force measurements are coupled with electrical measurements of muscle contractions in both wild-type and mutant animals, providing insight into the interplay between mechanical, electrical, and chemical signaling in vivo.



The Trajectory of Upconversion: A Chemist's View

Universidad de La Laguna

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Plenary Speaker

Lanthanide-doped nanoparticles exhibit unique luminescent properties, including a large Stokes shift, a sharp bandwidth of emission, high resistance to optical blinking, and photobleaching. Uniquely, they can also convert long-wavelength stimulation into short-wavelength emission. These attributes offer the opportunity to develop alternative luminescent labels to organic fluorophores and quantum dots. In recent years, researchers have taken advantage of spectral-conversion nanocrystals in many important biological applications, such as highly sensitive molecular detection and autofluorescence-free cell imaging. With significant progress made over the past several years, we can now design and fabricate nanoparticles that display tailorable optical properties. In particular, we can generate a wealth of color output under single-wavelength excitation by rational control of different combinations of dopants and dopant concentration. By incorporating a set of lanthanide ions at defined concentrations into different layers of a core-shell structure, we have expanded the emission spectra of the particles to cover almost the entire visible region, a feat barely accessible by conventional bulk phosphors. In this talk, I will highlight recent advances in the broad utility of upconversion nanocrystals for multimodal imaging, bio-detection, display and photonics.



Xiaogang Liu earned his B.E. degree (1996) in Chemical Engineering from Beijing Technology and Business University, P. R. China. He received his M. S. degree (1999) in Chemistry from East Carolina University under the direction of Prof. John Sibert and completed his PhD (2004) at Northwestern University under the supervision of Prof. Chad Mirkin. He then became a postdoctoral fellow in the group of Prof. Francesco Stellacci at MIT. He joined the faculty of the National University of Singapore in 2006. He holds a joint appointment with the Institute of Materials Research and Engineering, Agency for Science, Technology and Research. Currently, he sits as an Associate Editor for Nanoscale and serves on the editorial boards of Chemistry - An Asian Journal, Advanced Optical Materials, and Journal of Luminescence. His research encompasses optical nanomaterials and energy transfer and explores the use of luminescent nanocrystals for photocatalysis, sensing and biomedical applications.

Shifting the emission colour in Tb-based phosphate hosts by $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer: a spectroscopic study

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Energy transfer processes involving trivalent lanthanide ions (Ln³⁺) are crucial for the development of novel luminescent materials and devices such as phosphors, scintillators, materials for solar cells, nanothermometers or probes for optical bioimaging. All these materials and devices are strongly linked to energy and/or biomedical applications.

In the case of the energy transfer of the type $Tb^{3+} \rightarrow Eu^{3+}$ in Tb-based materials containing Eu^{3+} as a dopant, different types of behaviour can be observed in different systems due to structural peculiarities of the host. These differences determine the emission colour of the material, since this is strongly related to the presence or absence of energy transfer (both $Tb^{3+} \rightarrow Tb^{3+}$ and $Tb^{3+} \rightarrow Eu^{3+}$) [1, 2].

In this contribution we present and discuss the luminescence spectroscopy of polycrystalline $Ca_9Tb(PO_4)_7$ (rhombohedral structure, whitlockite family) and TbPO₄ (tetragonal structure, zircon family) both undoped and doped with Eu^{3+} . In the case of Eu^{3+} -doped TbPO₄ powders, a very fast and efficient $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer is present upon near UV excitation in the levels of the Tb^{3+} ion. This shifts the emission colour of the material from green to red, even by addition of very small amounts of dopant ions. On the contrary, in the Eu^{3+} -doped $Ca_9Tb(PO_4)_7$ materials the overall $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer process is not efficient and the resulting emission colour of the Eu^{3+} -doped materials appears to be yellow, even for high europium doping levels. This appears to be related to the disordered and multisite nature of the whitlockite host [3].

The experimental results will be discussed on the basis of the impact of different crystal structures on the energy migration rates in the Tb^{3+} donor subsets.

We would like to thank the European Commission for funding through the Marie Curie Initial Training network LUMINET, grant agreement No. 316906.

References

- [1] I. Carrasco, K. Bartosiewicz, M. Nikl, F. Piccinelli, M. Bettinelli, Opt. Mater. 48 (2015) 252-257.
- [2] I. Carrasco, F. Piccinelli, M. Bettinelli, Opt. Mater. Express 6 (2016) 1738-1746.
- [3] I. Carrasco, F. Piccinelli, M. Bettinelli, submitted for publication.

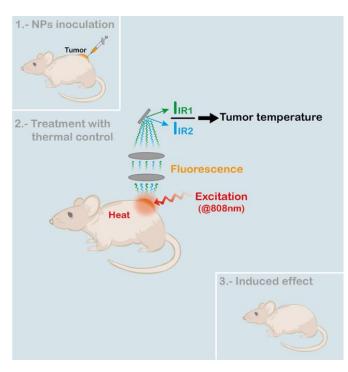
Luminescent nanothermometers for new in vivo diagnosis and therapy.

Daniel Jaque

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Over the last few years, the scientific community has witnessed a remarkable advance in the design, synthesis, and implementation of luminescent nanoparticles for bio-imaging and bio-sensing applications. Some of the old, unrealizable dreams have become possible thanks to the appearance into scene of novel advanced materials with never before imagined properties. This is the case of luminescent nanothermometers, nanoparticles capable of provide a contactless thermal reading through their light emission properties. As you are aware, luminescent nanothermometers have made possible to measure temperature inside a living cell or, even, inside a cancer tumor in animal models. These achievements demonstrated the crucial role that luminescent nanothermometers



could have in modern biomedicine as they emerge as an unique diagnosis tools as well as fundamental control agents during, for instance, hyperthermia treatments.

Universidad de La Laguna

In this work we will summarize the latest results at the in vivo level obtained by using luminescent naothermometeres as both imaging and diagnosis probes. Furthermore, the use of luminescent nanothermometeres in novel. accurate and minimally invasive therapies will be also discussed. А representative example is included in the Figure at left, in which the use of luminescent nanothermometers as thermal controllers in photo-thermal therapies of cancer tumors is schematically indicated. In this work we will fully demonstrate the potential of luminescent nanothermometers as new multifunctional thermal probes without competition to lead a

new era of biomedicine founded on thermal imaging based diagnosis and therapies.

Remote Control of Nanomaterials Functionalized with Ru Complexes Using Near-Infrared Light for Deep-Tissue Biomedical Applications

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The near-infrared (NIR) region is called "therapeutic window" because NIR light can deeply penetrate into tissue. In this talk, I will present our recent work about NIR light-responsive nanomaterials based on Ru-containing block copolymers (BCPs) and Ru-complex-functionalized upconverting nanoparticles (UCNPs).^[1-8]

Photoactivatable Ru complexes are introduced to the side chains and backbone of BCPs. The Ru complexes in the BCPs act as photocleavable moieties, singlet oxygen sensitizers, and anticancer agents. Depending on the molecular weight and chemical structure, the BCPs assembled into micelles, vesicles, large compound micelles and other nanostructures. The BCP assemblies can be taken up by cancer cells. Red light can pass through tissue and activate the Ru-containing BCP assemblies. We demonstrated anticancer activities of photoactivatable Ru-containing BCPs in vitro and in vivo.

Photoactivatable Ru complexes are combined with UCNPs to prepare NIR light-responsive nanomaterials. UCNPs convert NIR light to visible light that can trigger cleavage of Ru complexes. We used Ru-complex-functionalized UCNPs for NIR-controlled drug delivery, protein adsorption, and actuation of hydrogels.

References

[1] W. Sun, S. Li, B. Häupler, J. Liu, S. Jin, W. Steffen, U. S. Schubert, H.-J. Butt, X.-J. Liang,* S. Wu*, *Adv. Mater.* 2017, 29, 1603702.

[2] S. Wu*, J. P. Blinco*, C. Barner-Kowollik*, *Chem. Eur. J.* 2017, in press, DOI: 10.1002/chem.201700658.

[3] S. Wu*, H.-J. Butt*, Adv. Mater. 2016, 28, 1208.

[4] Z. Chen, Y. Xiong, R. Etchenique, S. Wu*, *Chem. Commun.* 2016, 52, 13959.

[5] W. Sun, M. Parowatkin, W. Steffen, H.-J. Butt, V. Mailänder, S. Wu*, *Adv. Healthcare Mater.* 2016, 5, 467.

[6] Z. Chen, S. He, H.-J. Butt, S. Wu*, Adv. Mater. 2015, 27, 2203.

[7] S. He, K. Krippes, S. Ritz, Z. Chen, A. Best, H.-J. Butt, V. Mailänder, S. Wu*, *Chem. Commun.* 2015, 51, 431.

[8] Z. Chen, W. Sun, H.-J. Butt, S. Wu*, Chem. Eur. J. 2015, 21, 9165.

KB1

Spectral Shaping in Active-Core-Active-Shell Up-converting Nanoparticles

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Conventionally, the optimization of lanthanide doped luminescent (nano)materials is carried out in the field of brightness and it is performed by either selecting host material or dopants type and concentration. By selecting the host matrix one decides about phonon spectrum, crystallographic structure, coordination number etc., while by selecting dopants (i.e. absolute or relative concentration of co-dopants), one decides about available luminescence spectrum, color and intensity. There are also some fundamental limitations of lanthanide doped (nano)materials which owe to forbidden character of the *f-f* transitions at fixed energy levels, which in consequence lead to long luminescence lifetimes and efficient cross-relaxation (i.e. concentration quenching). These limitations are barely manageable by conventional chemical approaches in homogenously doped materials. The solution to the above mentioned issues, nanotechnology and engineering offer novel, unprecedented possibilities. This means, that further progress in new materials development and bringing these materials to real-life application cannot be achieved with chemistry alone, and require deep understanding of physics and involvement of chemical engineering as well as engineering of excitation and detection paths of optical instrumentation.

Among a few novel possibilities, the intentional design and fabrication of luminescent nanoparticles with desirable morphology and composition, with multiple functionalities have emerg ed over the last couple of years as a very active field of research. This can be achieved by synthesis core–(multi)shell heterogeneous nanoparticle. Such approach provides new opportunities in searching for new properties and broadening functionalities, which are neither present or barely available in bulk materials or homogenous nanoparticle counterparts. In this work we show a few examples, where the core-shell design of Ln³⁺ doped heterogeneous nanoparticles demonstrate improved functionalities or enhanced properties. Future trends and perspectives of the development of the core-shell heterogeneous (nano)materials will be also provided.



Shedding Light on Luminescent Nanothermometry

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Specify Technical Area: Biomedical

Luminescent ratiometric thermometers combining high spatial and temporal resolution at the micro and nanoscale, where the conventional methods are ineffective, have emerged over the past decade as an effervescent field of research, essentially motivated by their potential applications in nanotechnology, photonics and biomedicine [1]. Examples are based on both individual thermal probes, *e.g.* organic dyes, polymers, QDs, Ln³⁺-based materials and more complex structures formed by probes encapsulated into polymer and organic-inorganic hybrid matrices.

One of the main challenge that is currently facing scientists in the field is to use luminescent thermometry as a tool for unveiling thermometers' local surrounding properties.

After a general historical perspective of the work done on ratiometric luminescent nanothermometers since the explosion of the field at one decade ago, the lecture will be focused on recent examples illustrating how powerful is the technique to unveil the thermometers' local surrounding properties, as, for instance, the instantaneous ballistic velocity of Brownian nanocrystals suspended in both aqueous and organic solvents [2] or the thermal conductivity of SiO₂ and SiO₂ mesoporous nanolayers [3].

[1] C. D. S. Brites, A. Millán, L. D. Carlos, in *Handbook on the Physics and Chemistry of Rare Earths*, J.-C. Bünzli, V. K. Pecharsky, Eds., Amsterdam: Elsevier Science B.V., Vol. **49** (2016), 339–427.

[2] C. D. S. Brites, X. Xie, M. L. Debasu, X. Qin, R. Chen, W. Huang, J. Rocha, X. Liu, L. D. Carlos, *Nature Nanotech.* **11** (2016) 851–857.

[3] C. D. S. Brites, M. C. Fuertes, P. C. Angelomé, E. D. Martínez, P. P. Lima, G. J. A. A. Soler-Illia, L. D. Carlos, *Nano Lett.* (2017), 10.1021/acs.nanolett.7b01433

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Biophotonics in Infrared Therapeutic Windows

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Please indicate preference: ___Poster ___Oral <u>X</u> Invited Speaker Specify Technical Area: <u>X</u> Biomedical ___Energy

Near infrared (NIR) with wavelength over 1000 nm (OTN) has been known as transparent optical window for biological objects with various designations such as the "second biological window," "NIR II/III" or OTN-NIR. The author's group has developed materials and imaging systems in the OTN-NIR window since 2005. Major OTN-NIR fluorescent agents are dyes, quantum dots, carbon nanotubes and rare-earth doped ceramic nanoparticles (RED-CNPs). The agents must be installed to proper probe materials to be functionalized in biological objects such as cells or animals. The paper will at first review the materials design for the OTN-NIR fluorescence bioimaging. Some more interesting feature of the materials design is to give multiple functions to the imaging probes. We are developing multimodal imaging probes, nanothermometry probes and theranostic functional nanostructure for simultaneous imaging and photodynamic therapy in the OTN-NIR window. Followed by the above fluorescent probes, the multifunctional design of the nanobio materials will be reviewed. The last part of talk will be introducing the application of OTN-NIR hyper spectral imaging. Not only more transparent in the OTN-NIR window than shorter or longer wavelength range, it contains very weak absorption by molecular vibration. It is the overtone range of the mid infrared absorption by molecular vibration and essentially the absorption is forbidden with the harmonic oscillator model. The analysis of almost 100 times weaker absorption than that in the mid-infrared range of molecules will give the compositional information of molecules. As well, the observation can reach cm depth. However, the spectra in this range is much more complicated than those in the mid-infrared since overtones are generated from various combinations of the fundamental vibrational modes. The author's group is applying machine learning for utilizing the spectra for diagnostic applications.

In Vivo Deep-Tissue Fluorescence Imaging in the Second Near-Infrared Window

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Please indicate preference: ___Poster ___Oral <u>v</u> Invited Speaker Specify Technical Area: v Biomedical ___ Energy

In vivo fluorescence imaging in the traditional visible (400-750 nm) and near-infrared (NIR, 750-900 nm) windows has limited penetration depth due to scattering and absorption of photons in most mammalian tissues, leading to compromised resolution and contrast with increasing tissue depth. To address this dichotomy between penetration depth and resolution, the Dai lab at Stanford University has pioneered in vivo fluorescence imaging in the second near-infrared window (NIR-II, 1,000-1,700 nm) to achieve high spatial resolution and crisp contrast at deep tissue penetration.

In this talk, I will give a historical overview of a 10-year development of in vivo NIR-II fluorescence imaging that originated from Prof. Hongjie Dai's prescient conception of this new paradigm of biomedical imaging to overcome the limitations of conventional fluorescence imaging. Implementation of this visionary conception has led to the constant evolution of a broad palette of biocompatible NIR-II fluorophores ranging from nanomaterials to organic molecules, and wide applications of in vivo NIR-II fluorescence imaging for cancer, cardiovascular disease and neurological disorders (Figure 1). Specifically, I will highlight the recent development of small organic molecule based NIR-II fluorophores with preferable in vivo pharmacokinetics [1-3], as well as deep-tissue ultrafast imaging of cardiovascular hemodynamics and deep-brain fluorescence imaging through the intact scale and skull in the NIR-II.

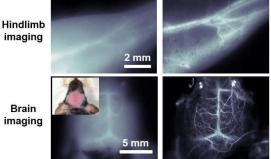
imaging through the intact scalp and skull in the NIR-II window [3-6]. With the superior spatial resolution at deep tissue penetration, in vivo NIR-II fluorescence imaging opens up exciting opportunities for real-time investigation of fast physiological processes in living organisms, understanding of brain functions with all optical NIR-II electrophysiology in behaving animals, and realization of non-invasive brain-machine interfaces (BMIs) using NIR-II photons as the medium.

References

- [1] H. Dai, et al. Nat. Mater. 2016, 15, 235-242.
- [2] H. Dai, et al. Proc. Natl. Acad. Sci. USA 2017, 114, 962-967.
- [3] H. Dai, et al. Nat. Commun. 2017, 8, 15269.
- [4] H. Dai, et al. Nat. Photonics 2014, 8, 723-730.
- [5] H. Dai, et al. Angew. Chem. Int. Ed. 2015, 54, 14758-14762.
- [6] H. Dai, et al. Nat. Commun. 2017, 8, 737.



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Spectral sHapIng For biomedical and energy applicaTions November, 13–17, 2017/Tenerife, Canary Islands, Spain.

Dye-sensitized upconversion

Universidad de La Laguna

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Up conversion is a very versatile tool for biomedical and energy applications. Mixed lanthanide nanoparticles are relatively efficient upconversion materials, but they generally suffer from extremely low and narrow light absorption. In 2012 we have shown that this limitation can be overcome by introducing antenna molecules on the surface of the nanoparticles. Hence, the proof of principle of dye-sensitized upconversion was realized.¹

In the past four years, dye-sensitized upconversion has been extended, improved and applied by a number of research groups. We and others have shown that the principle can be extended to co-sensitized systems using various antennas on the nanoparticles. The applications of dye-senstized upconversion are both in energy and in biomedicine. In the field of energy, the main application is in third generation photovoltaics, where the holy grail is to beat the Shockley-Queisser limit for the power conversion efficiency of single junction solar cells. In the field of biomedicine, the main applications described thusfar are already of a much wider nature, e.g. combined photothermal and photodynamic therapy, bio-imaging, and optogenetics. Thus, it is becoming clear that the principle of dye-senstized upconversion is of great potential for a wide palette of interesting and important applications.

An overview of these recent and exciting developments in the field of dye-sensitized upconversion will be given during the lecture.

¹ "Broadband Dye-Sensitized Upconversion of Near-IR Light" W. Zou, C. Visser, J. Maduro, M.S. Pshenichnikov, and J.C. Hummelen, *Nature Photonics*, 6, 560-4 (2012). Highlight article: X. Xie and X. Liu, "Upconversion goes broadband", *Nature Materials*, (11), 842-843 (2012)

Triplet-triplet annihilation upconversion vesicles and their biological applications

Universidad de La Laguna

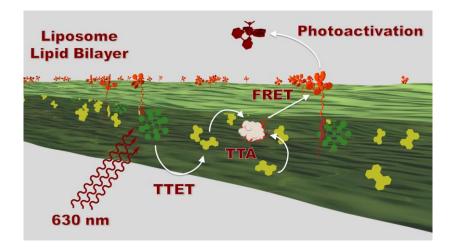
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Invited Speaker Technical Area: Biomedical

Photopharmacology consists in activating medicinal compounds *in vivo* with light in order to circumvent the biological action of the drug in space and time. In cancer research light activation of chemotherapeutic prodrugs is regarded as a promising alternative to chemotherapy as it might limit side effects and increase treatment efficacy. However, many photosensitive compounds are sensitive to UV or blue light, which penetrates sub-optimally in biological tissues. We have developed upconverting liposomes¹ and polymersomes² that can produce blue light upon red light irradiation to activate blue-light sensitive ruthenium compounds.^{3,4} The use of such upconverting nanovesicles for the activation of light-activatable ruthenium compounds will be be discussed.



References:

- S. H. C. Askes, A. Bahreman, S. Bonnet, Angew. Chem. Int. Ed. 2014, 53, 1029; S. H. C. Askes, M. S. Meijer, T. Bouwens, I. Landman, S. Bonnet, Molecules 2016, 21, 1460
- 2. S. H. C. Askes, W. Pomp, S. L. Hopkins, A. Kros, S. Wu, T. Schmidt, S. Bonnet, *Small*, **2016**, *12*, *5579*
- 3. R. E. Goldbach, I. Rodriguez-Garcia, J. H. van Lenthe, M. A. Siegler, S. Bonnet, Chem. Eur. J. 17 (2011) 9924
- 4. L. N. Lameijer, S. L. Hopkins, T. G. Brevé, S. H. C. Askes, <u>S. Bonnet</u>*, *Chem. Eur. J.* **2016**, *22*, 18484

Hybrid Nanoplatforms Based on Rare Earth Doped Nanoparticles

Universidad de La Laguna

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Please indicate preference: ___Poster ___Oral __X_ Invited Speaker Specify Technical Area: __X_Biomedical ___ Energy

Nanoparticles excited in the near-infrared (NIR), in particular rare earth doped nanoparticles, are quickly emerging as useful tools in diagnostic and therapeutic medicine. In particular, the usefulness of these nanoparticles for applications in biology stems primarily from the fact that NIR light is silent to tissues thus minimizing autofluorescence, possesses greater tissue penetration capabilities, reduced scattering, and does not cause photodamage to the specimen under investigation. Moreover, tailoring of the nanoparticles' absorption and emission wavelengths allow them to operate within the so-called "biological windows", regions of the spectrum in which tissues are partly transparent. Here, we present the synthesis and surface functionalization of various rare earth doped nanoparticles and show how they can be used as building blocks in the development of multifunctional hybrid nanoplatforms through intelligent combination with other optically active nanostructures, for the potential diagnostics and therapeutics of disease.

Spectral sHaping For biomedical and energy applications November, 13-17, 2017/Tenerife, Canary Islands, Spain.

Glass photonic structures for photon management applications

Universidad de La Laguna

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The development of optically confined structures is a major topic in both basic and applied physics including information engineering, biological and medical sciences, sensing, lightning, energy and quantum optics. Glasses and glass-ceramics as well as microresonators and microcavities activated by rare earth ions are the bricks of such structures. The contribution given by functionalized glasses is well recognized for the outstanding results obtained in integrated optics, quantum cutting, downshifting and luminescent devices. Glass-ceramics are nanocomposite systems that exhibit specific morphologic, structural and spectroscopic properties allowing to develop interesting new physical concepts, for instance the mechanism related to the transparency, as well as novel photonic devices

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based on the enhancement of the luminescence. Looking to application, the enhanced spectroscopic properties typical of glass ceramic in respect to those of the amorphous structures constitute an important point for the development of photonic structures based for instance on and up and down converters and frequency converters for photovoltaics. Other important photonic structures for photons management applications are microcavities and microresonators. One-dimensional photonic crystals have been widely investigated and remain an outstanding tool for new photonics, being the simplest system to exhibit a so-called photonic bandgap and therefore one of the easiest to handle to obtain tailored optical devices. Just few examples are 1D photonic crystals allowing luminescence enhancement, disordered 1D photonic structures that are very interesting for the modeling and realization of broad band filters and light harvesting devices; 1D microcavities, leading to low threshold coherent emission. Whispering gallery modes, characteristic of spherical resonators, which are very known for their applications in sensing and metrology have already demonstrated appealing improvements in photovoltaics.

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The research activity is performed in the framework of COST Action MP1401 Advanced fibre laser and

coherent source as tools for society, manufacturing and lifescience (2014-2018), ERANET-LAC FP7 Project RECOLA - Recovery of Lanthanides and other Metals from WEEE (2017-2019) and Centro Fermi PLANS project. Lam Thi Ngoc Tran acknowledges the scholarship of the Ministry of Education and Training, Vietnam International Education Development

Improving the efficiency of solar cells by upconverting sunlight using field enhancement from optimized nano structures (SunTune)

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Much of the energy from the Sun is lost in photovoltaic devices because of the spectral mismatch between the sunlight and the absorption region of the solar cell. In the present talk, I will report on recent activities within the SunTune project (suntune.au.dk) aimed at improving the efficiency of solar cells by upconverting the low-energy (long-wavelength) part of the sunlight. Upconversion requires merging the energy from two low-energy photons into one photon of higher energy and thus exhibits a non-linear dependence on intensity. Consequently, it typically occurs with fairly low probability at intensities corresponding to those of sunlight on the Earth. In the current project, the goal is to enhance the upconversion efficiency by employing nano-optical field enhancement. We recently demonstrated that a single layer of plasmonic gold nanodiscs on an Er³⁺ doped TiO₂ film could enhance the upconversion luminescence by a factor of 7 [1]. The current activities are directed towards optimizing such enhancement factors by employing so-called topological optimization of the design for the nano particles. Recently, simulations (in 2D) showed the capability of obtaining high field enhancements over a range of incidence angles and wavelengths (within the Er³⁺) absorption band [2]. Extensions to 3D are in progress and we hope to present new results at the conference. In parallel to the optimization of nano-particle design, we work on methods for constructing thick upconverter complexes, e.g. based on chemically synthesized upconverting coreshell nanoparticles. For use with organic solar cells, co-doped nanocrystals (e.g. Yb and Er) may be advantageous. For crystalline silicon solar cells, an appreciable contribution to the photocurrent from upconversion will have to rely on *downshifting* the light below the silicon band edge to the Er³⁺ absorption band; various solutions to this challenge will also be discussed. The SunTune project is funded by Innovation Fund Denmark.

- [1] H. Lakhotiya *et al.*, Appl. Phys. Lett. **109**, 263102 (2016); doi: 10.1063/1.4972785
- [2] J. Vester-Petersen *et al.*, submitted (2017).

Highly Efficient Hole and Electron Transporting Materials for Perovskite Solar Cells

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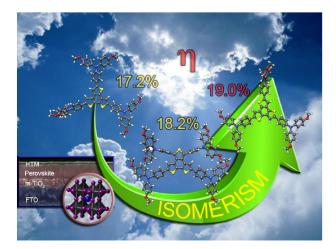
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Since the advent of organic–inorganic hybrid methylammonium (MA) lead halide MAPbX₃ perovskites as active materials for photovoltaic applications in 2009, [1] the PCE of perovskite-based solar cells (PSCs) has dramatically increased from the initial 3.8% to a recently certified 22.1%. [2] Emerging from this groundbreaking discovery, an unprecedented scientific research has sprouted in the field of photovoltaics due to their exceptional physical properties. Therefore, the development of cost-effective HTMs with high efficiency along with a good stability is an important task to address.

Planar and sulfur-rich polycyclic aromatic hydrocarbons bearing arylamine moieties have demonstrated to be a successful approach for designing new highly efficient HTMs for PSCs. [3] Conventionally, the π -extended conjugation associated with the planar and electron-rich structure of the fused heterocycles enable them to show strong stacking through intermolecular interactions (π – π , S···S), thereby bestowing enhanced hole-carrier mobilities. This behaviour is beatifully exemplified by sulfur-rich HTMs recently reported. [4]

The performance of the solar cells employing the novel HTMs were measured under simulated 1 sun irradiation and conversion efficiencies up to 19 % were observed.

On the other hand, electron transporting materials (ETMs) based on fullerenes has allowed to remove the TiO2 from the PSC and obtaining efficiency values around 14%. [5]



References

- [1] Kojima A., Teshima K., Shirai Y. and Miyasaka T., J. Am. Chem. Soc., 2009, 131, 17, 6050.
- [2] National Renewable Energy Laboratory, N.R.E.L.
- [3] Molina-Ontoria A., Zimmermann I., Garcia-Benito I., Gratia P, Roldán-Carmona C., Aghazada S., Graetzel M., Nazeeruddin M.K., and Martín, N. *Angew. Chem. Int. Ed.*, **2016**, *55*, 6270.
- [4] I. Zimmermann, J. Urieta-Mora, P. Gratia, J. Aragó, G. Grancini, A. Molina-Ontoria, E. Ortí, N. Martín, M. Khaja Nazeeruddin, Adv. Energy Mater. 2017, 7, 1601674.
- [5] M. Valles-Pelarda, B. Clasen Hames, I. García-Benito, O. Almora, A Molina-Ontoria, R. S. Sánchez, G. Garcia-Belmonte, N. Martín, I. Mora-Sero, *J. Phys. Chem. Lett*, **2016**, 7, 4622.



Photothermal Harnessing for Photocatalysis and Vaporization

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Using readily available renewable resources i.e. solar energy and seawater to secure sustainable fuel and freshwater for humanity is an impactful quest. Here, we have designed solar thermal collector composites that possess efficient photothermic properties for highly targeted interfacial phase transition reactions that are synergistically favorable for both catalysis and vaporization reactions. The photothermic effect arises from plasmonic metal nanoparticles or carbon broadband photoabsorption that exhibit localized interfacial heating which directly triggers surface-dominated catalysis and steam generation processes, with minimal heat losses, reduce thermal masses and optics implementation. The solar thermal collector nanocomposites are seawater and photo stable for practical solar conversion of seawater to simultaneously produce clean energy and water. Finally, a proof-of-concept all-in-one compact solar hydrogen and distillate production prototype demonstrates the viability of sustainable photothermic driven catalysis and desalination of seawater under natural sunlight. Importantly, this approach holds a great promise for enhancing energy and water productivity without considerable capital, infrastructure and environment ramifications.

Solar spectral conversion and structured illumination in photosynthesis and photochemical energy storage Lothar Wondraczek^{1,2}

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Solar energy harvesting is largely limited by the spectral sensitivity of the employed energy conversion system, where usually, large parts of the solar spectrum do not contribute to the harvesting scheme, and where, of the contributing fraction, not the full potential of each photon is efficiently used in the generation of electrical or chemical energy. Extrinsic sensitization through photoluminescent spectral conversion has been proposed as a route to at least partially overcome this issue in photovoltaics. Here, we will discuss a similar approach in the emerging context of photochemical energy harvesting and storage through natural or artificial photosynthesis. Clearly contrary to application in photovoltaic energy conversion, implementation of solar spectral conversion for extrinsic sensitization of a photosynthetic machinery is very straightforward, and less strict limitations with regard to quantum coherence are seen as compared to intrinsic sensitization. We now argue how and how not extrinsic sensitization through photoluminescent spectral conversion schemes and design strategies on system scale.



Multi-photon Phosphors

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Lanthanides have transformed the world of lighting in the past 40 years. Presently, almost all artificial light sources rely on emission of light by lanthanide ions. In many luminescent materials, also known as phosphors, one-to-one photon conversion downshifts one high energy photon to one lower energy photon in the desired spectral region. However, recently, there is a significant increase of attention for multi-photon phosphors relying on multi-photon conversion processes, either upconversion or downconversion. Insight in the multi-photon processes is not trivial but is needed to understand the mechanism and improve the efficiency of spectral conversion processes in multi-photon phosphors which is crucial for applications, including solar cells to reduce spectral mismatch losses.

In this presentation a short historical introduction to multi-photon conversion phosphors will be followed by an overview of recent developments of efficient up- and downconversion materials. Next it will be discussed how insight can be obtained in the mechanism and efficiency of up- and downconversion processes. An important aspect involves modelling of energy transfer and ligand quenching. For both up- and downconversion examples will be given on how modelling of luminescence decay curves can provide quantitative insight. A new ligand-quenching model will be presented and applied to understand multi-phonon vibrational quenching in NaYF₄:Er,Yb upconversion nanocrystals. Finally a new method will be presented that provides direct proof for downconversion. Correlated emission of photons in photon cutting materials can serve as a fingerprint for the occurrence of downconversion and can even be used to quantify the downconversion efficiency.

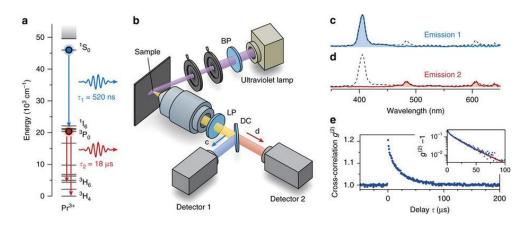


Figure 1 - Illustration correlated photon counting to demonstrate two-photon emission using $NaLaF_4:Pr^{3+}$ as model system. (a) Two-photon emission on Pr^{3+} . (b) Schematic set-up for correlated photon counting (c, d) Emission of Pr^{3+} in blue and red spectral region detected by separate detectors. (e) Correlated photon-counting signal.

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Nanoparticles for Luminescent Solar Concentrators

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Luminescent solar concentrators (LSC) are based on down shifting solar irradiance and concentrating red-shifted photons to solar cells attached to the sides of the LSC plate (Fig. 1). These have been developed in the 1970s using organic dye molecules, while in the past decade nanoparticles have been employed increasingly, as a result of their better stability, wider absorption range and tunability. With the present record device efficiency of 7%, material issues have hampered efficiency improvements, in particular re-absorption of light emitted by luminescent species due to small Stokes' shift. Several approaches have been followed to address this, such as type-II quantum dots, the use of plasmonic nanoparticles, as well as doped quantum dots and non-isotropic emission approaches. In this contribution, recent developments will be reviewed as well as potential application areas of LSCs as elements in Building Integrated photovoltaics (BIPV).

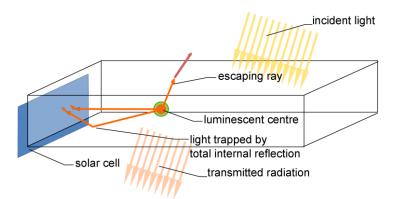


Figure 1. Schematic 3D view of a luminescent concentrator. AM1.5 light is incident at the top. The light is absorbed by luminescent species, and its luminescence is randomly emitted. Part of the emission falls within the escape cone and is lost from the luminescent concentrator at the surfaces. Another part is guided to the solar cell by total internal reflection. (Krumer, et al., Sol. Energy Mater. Sol. Cells 111 (2013) 57-65.

Shift2017 Spectral sHapIng For biomedical and energy applicaTions November, 13–17, 2017/Tenerife, Canary Islands, Spain.

Lanthanide-doped glasses as frequency converter for high-power LED applications

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Thermal management is one of the crucial concerns for mid- and high-power white light-emitting diodes (LEDs). Most of the white LEDs currently available on the market consist of a blue LED chip coated with a yellow phosphor-polymer composite. Besides the heat-induced degradation of the phosphor-polymer composite, also the decrease in light output upon increasing temperature, known as thermal quenching, is a pressing issue. Both result in a decrease in efficiency and changes in the color of the light emitted by the LED.

Lanthanide-doped glasses might represent an attractive alternative due to their higher thermal and chemical stability. The CIE color coordinates of double- and triple-doped glasses can be tuned over a broad spectral range by varying the lanthanide doping concentrations and ratios accordingly. Further, doping with two or more lanthanides allows for a change in CIE color coordinates by using different excitation wavelengths. Apart from the optical properties, the thermal conductivity of these glasses is of great importance for the practical use in high-power LED applications. Subsequent processing of the as-made glass to a glass ceramic enables an increase in thermal conductivity by at least one order of magnitude.

In this work, Eu³⁺, Tb³⁺, and Tm³⁺ single-, double- and triple-doped borate glasses are investigated for their photoluminescence (PL) and absolute PL quantum efficiency. The glasses are also characterized for their color stability up to temperatures of 400 °C. In addition, the thermal diffusivity is analyzed by means of infrared lock-in thermography. The thermal conductivity is calculated from the thermal diffusivity, the mass density, and the specific heat capacity.



Figure 1. Eu³⁺ and Tb³⁺ single- and double-doped borate glasses under ultraviolet excitation.

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Optofluidics for Energy and Environmental Applications

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The tight integration of microfluidics, nanofluidics and optics – optofluidics – has much to offer applications in energy and the environment. This talk will outline our groups work in this area. First in the area of renewable energy, I will describe our efforts in applying microsystems to better understand photosynthetic microorganisms, and engineer systems to encourage the production of bioproducts and subsequent processing. This topic will also include a highlight of an all-optical strategy to shift the wavelength from high- to low-absorbance to increase light distribution and overall effectiveness in a photobioreactor. Second I will outline our work in developing optofluidics approaches to understanding conventional and unconventional oil and gas operations as well as processing – with an eye to improve both the economic and environmental performance of these large scale operations. Lastly, I will outline our groups efforts in screening the effects of multiple stressors on ecosystems by employing massively parallel microcosms with individual light, and fluid control.

Challenges and Examples for Quantitative Fluorescence Measurements > 800 nm with Semiconductor and Lanthanide-Doped Nanocrystals

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There is an increasing interest in molecular and nanoscale with emission > 800 nm and recently also > 1000 nm for bioanalysis, medical diagnostics, bioimaging, and safety barcodes [1]. Mandatory for the comparison of different emitter classes and the rational design of the next generation of reporters for the short wavelength infrared (SWIR) region are reliable and quantitative photoluminescence measurements in this challenging wavelength region. This is of special relevance for nanocrystalline emitters like semiconductor quantum dots and rods as well as lanthanide-based upconversion and downconversion nanocrystals, where surface states and the accessibility of emissive states by quenchers largely control accomplishable photoluminescence quantum yields and hence, signal sizes and detection sensitivities from the reporter side. Such measurements are currently hampered by the lack of suitable methods and standards for instrument calibration and validation and quantum yield standards with emission > 800 nm and especially > 1000 nm [2-4].

In this respect, we present the design of integrating sphere setups for absolute and excitation power density-dependent measurements of emission spectra and photoluminescence quantum yields in the wavelength region of 650 to 1650 nm including calibration strategies and first candidates for potential fluorescence standards [3-5]. Subsequently, the photoluminescence properties of different types of nanocrystals are presented including the upconversion and downconversion emission of differently sized and surface functionalized lanthanide-doped nanoparticles and photoluminescence quenching effects are quantified.

Key words: NIR, IR fluorescence, quantum dot, upconversion nanocrystal, lanthanide em

References. [1] Hemmer E.; Benayas A.; Legare F., Vetrone F., *Nanoscale Horizons* **2016**; *1*, 168-84. [2] Semonin, O. E.; Johnson, J. C.; Luther, J. M.; Midgett, A. G.; Nozik, A. J.; Beard, M. C., *J. Phys. Chem. Lett.* **2010**, *1*, 2445-2450. [3] Hatami, S.; Wurth, C.; Kaiser, M.; Leubner, S.; Gabriel, S.; Bahrig, L.; Lesnyak, V.; Pauli, J.; Gaponik, N.; Eychmuller, A.; Resch-Genger, U., *Nanoscale* **2015**, *7*, 133-143. [4] Kaiser, M.; Würth, C.; Kraft, M.; Hyppänen, I.; Soukka, T; Resch-Genger, U., *Nanoscale* **2017**, in press (10.1039/C7NR02449E). [5] Würth C.; Kaiser, M.; Wilhelm, S.; Grauel B.; Hirsch T.; Resch-Genger U., *Nanoscale* **2017**, *9*, 4283-94.

Low fluence multiphoton imaging with alloyed lanthanide nanocrystals

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Multiphoton imaging techniques that convert low energy excitation to higher energy emission are widely used in complex systems to improve signal over background, reduce scatter in subsurface imaging, and limit photodamage. Multiphoton imaging relies on luminescent probes able to efficiently sum the energies of 2 or more incident photons, as well as lasers powerful enough to generate necessarily high fluences. Lanthanide-doped upconverting nanoparticles (UCNPs) have proven to be among the most efficient multiphoton probes, but even UCNPs with optimized Ln dopant levels require laser intensities that may be problematic for living systems. Here we develop fully alloyed UCNPs (aUCNPs) that can be imaged at the single particle level at laser fluences below 300 W/cm², ~9 orders of magnitude lower than required for standard single molecule 2-photon fluorescence imaging. These fluences are lower even than those required for single-photon single molecule techniques, multiphoton imaging of ensembles of fluorophores, and certain superresolution techniques. Using single UCNP characterization and kinetic models of lanthanide energy transfer to minimize energy loss, we find that addition of inert epitaxial shells radically changes optimal lanthanide compositions from Ln-doped NaYF₄ to fully alloyed NaEr_xYb_(1-x)F₄ nanocrystals.</sub> Core-shell alloyed aUCNPs are brighter than doped core-shell UCNPs at all laser fluences tested, and ensembles of NaEr_{0.2}Yb_{0.8}F₄ core/shell nanocrystals can be imaged at fluences as low as 2 W/cm². These aUCNPs open up the possibility of using low-energy and benign NIR excitation wavelengths without the need for the ultra-high peak powers that can damage samples.



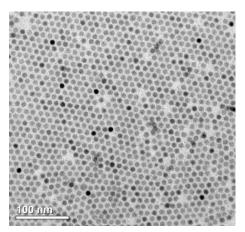
Control of Growth, Nucleation and Size of Monodisperse Core/Shell Upconversion Nanocrystals for Bioimaging

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TEM image of 10 nm NaYF₄:Yb,Er/NaYF₄ core/ shell particles (6 nm core, 2 nm thick shell)

Upconversion nanocrystals are currently investigated for a variety of applications including biological labelling, sensing and imaging and spectral conversion in solar cells. While solar energy conversion benefits from particles with high upconversion efficiency at low photon flux, biological imaging requires particles with small size, narrow size distributions and high light output at medium to high excitation densities. The dopant concentrations, core/shell structures and the particle size must therefore be optimized for each application. By making use of distinct optical and magnetic properties of the rare-earth ions, we have investigated in detail the growth mechanism of monodisperse core and core/shell particles of the sodium rare-earth fluorides (NaREF₄).^{1,2} The key feature of these materials is

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the simultaneous presence of particles of the cubic α -phase and the hexagonal β -phase of NaREF₄ during the synthesis, resulting in focusing of the particle size distribution during Ostwald ripening.²⁻⁵ The mean size of the particles can be varied over a wide range by adjusting the ratio of sodium to rare-earth ions in the synthesis, indicating that this parameter affects the nucleating of β -phase seeds.^{5,6} Controlling the nucleation is also important in the synthesis of core/shell particles in order to avoid the formation of additional particles of pure shell material. Moreover, the intermixing of core and shell should be weak during deposition of the shell.^{7,8} Particles with optimized core/shell structure and dopant concentration have been used as biolabels to unravel protein interactions inside living cells.⁹

- 1. Komban R. et al., Angew. Chem. 51:6506-6510, 2012
- 2. Voss B. et al., Nanoscale 5: 806-812, 2013
- 3. Raj A.N. et al., Chem. Mater. 26:5689-5694, 2014
- 4. Voss B. ACS Nano, 7:11242-11254, 2013
- 5. Rinkel T. et al., Nanoscale, 6:14523 14530, 2014
- 6. Dühnen S. et al., Chem. Mater. 27:4033-4039, 2015
- 7. Rinkel T. et al., Angew. Chem., 55:1164-1167, 2016
- 8. Dühnen S. et al., Chem. Mater. 27:8375–8386, 2015
- 9. Drees C. et al., Angew. Chem., 55: 11668-11672, 2016



Shifting Eu²⁺ Emission Bands to low Energies

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Recently, the development of red phosphors became very important for future LEDs of high light quality. In this context initially a blue light emitting GaN-Chip was coated with a yellow phosphor (YAG:Ce³⁺), yielded rather cold white light. Another approach with a more satisfying CRI is to coat near UV emitting LEDs with red, green and blue phosphors. For this so called phosphor converted LEDs in particular the development of red emitting phosphors is necessary. This is a real challenge due to the recommendations of its air and temperature long time stability, excitability at low energies and high emission efficiency.

The current aim is to find host lattices with Eu^{2+} doping where its d-f-transition can be excited by a blue or near UV Ga/InN-Chip followed by low energy emission. Here we present for the first time the Eu^{2+} doped perovskites MZrO₃ and MHfO₃ (M = Ca, Sr), which are extremely advantageous for applications, because they are air and long-time stability even at high temperatures. Most remarkably, these phosphors show extremely low energy with wavelength higher than 600 nm. The excitation bands depicts stringently low energy maxima at 530 and 490 nm for CaZrO₃:Eu²⁺ and SrZrO₃:Eu²⁺, respectively (Fig. 1).

Moreover, these materials are also very promising for biomedical applications due to their low lying emission and excitation bands, their low toxicity and high stability [1,2]. For this purpose, however, the materials must exist in nanosized form, which are available using novel preparation techniques using ionic liquids as solvents, which stabilize Eu²⁺ ions.

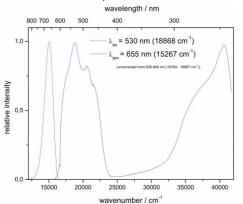




Fig. 1. Left: Emission and excitation spectra of CaZrO₃:Eu²⁺ at 10K. Right: photo of CaZrO₃:Eu²⁺ emission.

- [1] H. Cerqueira Streit, J. Kramer, M. Suta, C. Wickleder, Materials 2013, 6, 3079.
- [2] H. Terraschke, C. Wickleder, Chem. Rev., 2015, 115, 11352.

Shift2017Spectral sHapIng For biomedical and energy applications
November, 13–17, 2017/Tenerife, Canary Islands, Spain.

Upconverting nanoparticles (UCNPs): A platform for multiplexed 3D and super-resolution imaging

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Lanthanide ion-doped upconverting nanoparticles (UCNPs), which emit photons in the visible range upon absorption of NIR photons, have attracted great interest in the area of biological imaging owing to their numerous advantages. First, two-photon upconversion of NIR to the emission of a visible photon is so efficient that a tiny CW laser with the output of tens of milliwatts is sufficient as the excitation source even for single-particle detection. Therefore, "inexpensive" "wide-field" two-photon imaging can easily be achieved with UCNPs, which is not feasible with organic fluorophores and femtosecond laser systems used in conventional two-photon microscopy. Second, by employing NIR excitation, one can suppress cellular autofluorescence, hardly induce photo-damage to cells, and achieve deep penetration into tissues. In addition, UCNPs are extremely photo-stable without photoblinking and photobleaching, and finally, their cytotoxicity turns out to be very low. All these aspects are combined to produce a platform for wide-field two-photon microscopy, which is capable of high-speed, high-contrast, biocompatible, uninterrupted, longterm, live-cell imaging. Recently, we developed a method for fast and background-free multiplexed 3D imaging, which track multiple particles at the same time and with highly accurate coordinate determination. The multiplexed version enabled tracking of all the particles discovered in the cell in principle. We also developed super-resolution imaging techniques with sub-diffraction resolution using UCNPs. It is noteworthy that the 3D and the super-resolution imaging techniques do not sacrifice any advantages of UCNP-platform described above.

References

- [1] K. Shin, T. Jung, E. Lee, G. Lee, Y. Goh, J. Heo, M. J., E.-J. Jo, H. Lee, M.-G. Kim, and K. T. Lee, *Phys. Chem. Chem. Phys*, **2017**, *19*, 9739.
- [1] H. L. Jo, Y. H. Song, J. Park, E.-J. Jo, Y. Goh, K. Shin, M.-G. Kim and K. T. Lee, *Nanoscale* 2015, 7, 19397.
- [2] Y. I. Park, K. T. Lee, Y. D. Suh, T. Hyeon, Chem. Soc. Rev., 2015, 44, 1302.
- [3] Y. I. Park, S. H. Nam, J. H. Kim, Y. M. Bae, B. Yoo, H. M. Kim, K.-S. Jeon, J. S. Choi, K. T. Lee, Y. D. Suh, T. Hyeon, J. Phys. Chem. C, 2013, 117, 2239.
- [4] Y. M. Bae, Y. I. Park, S. H. Nam, J. H. Kim, K. Lee, H. M. Kim, B. Yoo, J. S. Choi, K. T. Lee, T. Hyeon, Y. D. Suh, *Biomaterials*, 2012, 33, 9080.
- [5] S. H. Nam, Y. M. Bae, Y. I. Park, J. H. Kim, H. M. Kim, J. S. Choi, K. T. Lee, T. Hyeon, Y. D. Suh, Angew. Chem. Int. Ed., 2011, 50, 6093.

Shaping nanoparticles for enhanced cardiovascular imaging

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Optical techniques are gaining a considerable attention for cardiovascular imaging. In particular optical coherence tomography (OCT) imaging is nowadays used as a minimally invasive technique for *in vivo* identification and assessment of unstable plaques as well as for the guidance of interventional procedures such as atherectomy and stent placements. Cardiovascular OCT imaging is based on the detection of the backscattered signal at tissue interfaces of near infrared light emitted by a broad band laser diode peaking at about 1.3µm. An innovative strategy to improve the OCT contrast up to the molecular level consists in the of use nanoparticles that enhance the OCT contrast and, at the same time, can be properly functionalized with antibodies to target specific proteins overexpressed by the tissue/cells. In this talk, it will be shown that a number of gold nanoparticles can be individually visualized under both static and dynamical conditions by means of a typical OCT system used in cardiovascular interventional surgery. Silica (core)/ Gold(Shell) shaped nanoparticles, commonly denoted as Golds Nanoshells (GNSs), are particularly suitable for cardiovascular OCT imaging due to their large backscattering cross section at the OCT laser wavelength. It will be shown how these nanoparticles produce enhanced OCT contrast in cells and tissues.

Novel nanoparticles for cardiovascular imaging include those that display luminescence together with OCT contrast. In this sense, we will show how PbS quantum dots are capable to simultaneously produce luminescence in the third biomedical window (1.6 μ m) and back-scattering contrast just under single laser excitation with the cardiovascular OCT laser (1.3 μ m). This opens a new avenue for future cardiovascular dual (Fluorescence +OCT) optical imaging at molecular level with great potential for future clinical applications.

Technological Progress, a Gate to a New Era: the 4th Space

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In the last decades, the technological development has been including new capacities and applications in medicine. Consider, for example, the progress in minimally invasive surgery and the new diagnosis techniques.

This contribution of technology to the biomedicine area is due to the work and research of the non-health professionals (engineers, physicist, etc.), and their approaches for resolving biomedical challenges from their technical point of view and respecting the clinical constraints.

In addition, today, information is increasingly accessible, patients consult the internet and can know all medical advances with a click in their computer. They easily accept all new health techniques that arise and assume their responsibility for caring their own health. Also, in the occidental countries, life expectancy is growing due to the reasons suggested above; the improvement of the medical procedures and the feed. Then, we are in an scenario where the now aged less than 18 years old are going to reach more than 100 years old, and consequently, our occidental society should review our professional retirement model, in order to preserve our health system and its sustainability.

We call the 4th-space to the slot of time where people now aged less than 18 years old, will reach more than 100 years old. Then, we have to teach to this people to manage their lifetime, their health, their economy, etc. They are going to be health services users for a long time, and the retirement should be re-planned for the sustainability of the health service.

This people will need to change their activities during the life, not only the physical activity but also their culture of use of the health system. They will be familiarized to have automatic aided devices in the houses, no just in the hospital.

Optical temperature sensing using upconversion emission of erbiumdoped lanthanum oxysulfide powders

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Upconversion processes in rare-earth doped materials have led to a wide range of applications including thermal sensing at bulk or micro-nano scales. One of the requirements for the optical sensors based on upconversion is that the radiative probabilities of the emitting levels must be high enough to show relatively large emission intensities. Rare-earth oxysulfides (R_2O_2S) with relatively low phonon energy (~400-500 cm⁻¹), good chemical and thermal stabilities, and low toxicity are promising materials for upconversion applications.

In this work we report a detailed spectroscopic study of the near-infrared to visible upconversion luminescence in $La_2O_2S:Er^{3+}$ nanocrystalline phosphors following excitation into the ${}^{4}I_{9/2}$ level. The analysis of the upconversion emission and excitation spectra as well as the decay curves indicates that energy transfer upconversion is the main mechanism responsible for the green (${}^{4}S_{3/2}$) and red (${}^{4}F_{9/2}$) upconversion luminescence. The fluorescence intensity ratio of the green upconverted emission from the two thermally coupled ${}^{2}H_{11/2}$ and ${}^{4}S_{3/2}$ levels and the temperature sensitivity have been evaluated between 230 K and 300 K for different Er^{3+} concentrations in order to determine the suitability of this material as a temperature sensor. A proof of concept which has been worked out by the authors demonstrates the feasibility of localized cooling by anti-Stokes IR pumping of this erbium-doped nanocrystalline powders.

A performance study of Nd-based stoichiometric random lasers

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Rare earth stoichiometric powder hosts have received the most attention for random laser (RL) action^{1,2}. In contrast to other laser hosts where the active ion is dispersed as a dopant in a crystalline matrix, stoichiometric hosts are pure chemical compounds of rare earth (RE) ions. In principle, the main variable that controls the quenching of the desired luminescence is the non-radiative energy transfer process between RE ions. In a microsecond time scale the high concentration of Nd³⁺ ions might give rise to short-range spatial energy transfer in the metastable level, as well as to long-range spatial energy migration among Nd³⁺ ions and thus, huge losses might be expected which would affect the threshold and slope efficiency for laser action. However, the fast build up of the random laser pulse makes the nonradiative losses produced by quenching concentration much less important than in a conventional laser.

This work presents a comparative study of the random lasing performance of several Nd based stoichiometric compounds, together with a discussion about the fundamental parameters which control their random laser operation.

On the other hand, we demonstrate that Nd-based crystal powder random laser provides Speckle-free transmission and reflection infrared images with higher values of contrast to noise ratio (CNR) than those obtained with the narrowband laser. These results open up new possibilities to enhance the field of high resolution imaging for optoelectronic and biomedical applications

(1)J. Azkargorta, I. Iparraguirre, M. Bettinelli, E. Cavalli, M. Barredo-Zuriarrain, S. García-Revilla, R. Balda, and J. Fernandez, Effects of pumping wavelength and pump density on the random laser performance of stoichiometric Nd crystal powders, Optics Express 22 (2014) 27365-27372.

(2) I. Iparraguirre, J. Azkargorta, K. Kamada, A. Yoshikawa, U. R. Rodríguez-Mendoza, V. Lavín, M. Barredo-Zuriarrain, R. Balda, J. Fernández, Random laser action in stoichiometric Nd₃Ga₅O₁₂ garnet crystal powder, Laser Physics Letters 13 (2016) 035402 (5pp).

Nanomaterials containing rare earths ions: chosen luminophores, coreshell surface functionalized nanoparticles and multifunctional hybrids; from synthesis to applications

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Results of investigations concerning selected nanomaterials based on inorganic matrices, e.g.: fluorides, borates, phosphates and vanadates, as hosts for luminescent lanthanide (Ln³⁺) ions, are presented. The nanosized materials synthesized using various methods were well-defined nanopowders and showed pure phase, high crystallinity and homogeneity, with the small and narrow particle size distribution and non-agglomeration. Obtained nanoluminophores (NL) and upconvering luminophores (UCNL) [1-4], core-shell surface functionalized (with amino or carboxylic groups) nanoparticles (NP) [4,6] and multifunctional hybrids [6] were structurally and spectroscopically characterized. Excitation and emission spectra, lifetimes, intensity parameters, chromaticity diagrams, lifetime measurements and quantum efficiencies of the materials are shown. Emission effectiveness of NL and UCNL, together with energy transfer and charge transfer schemes, quenching phenomena, and color purity with chromaticity coordinates, are discussed in relation to their composition, structure, size and morphology. NPs of exceptional luminescent properties having nanosized dimensions, good chemical and photochemical stabilities are considered as promising materials for many applications. We have successfully used chosen intense NL as labels modifying microcellulose fibers for documents security against counterfeiting [5]. Biocompatible, luminescent-plasmonic nanomaterials based on lanthanide and gold (e.g. CeF₃:Tb³⁺/SiO₂-NH₂/Au) or lanthanide and silver (e.g. GdPO₄:Eu³⁺/SiO₂/NH₂/Ag) nanoparticles for application in multimodal luminescence and/or SERS imaging are also discussed [6].

- [1] T. Grzyb, A. Gruszeczka, R. J. Wiglusz, S. Lis, J. Mater. Chem. C, 1 (2013) 5410-5418
- [2] A. Szczeszak, T. Grzyb, B. Barszcz, V. Nagirnyi, A. Kotlov, S. Lis, Inorg. Chem., 52 (2013) 4934–4940
- [3] T. Grzyb, K. Kubasiewicz, A. Szczeszak, S. Lis, Dalton Trans. 44 (2015) 4063-4069
- [4] M. Runowski, S. Lis, J. Luminescence, 170 (2016) 484-490
- [5] A. Erdman, P. Kulpinski, T. Grzyb, S. Lis, J. Luminescence, 169 (2016) 520-527
- [6] M. Runowski, S. Goderski, J. Paczesny, M. Księżopolska-Gocalska, A. Ekner-Grzyb, T. Grzyb, J. D. Rybka, M. Giersig, S. Lis, J. Phys. Chem. C, 120 (2016) 23788–23798

Solution based synthesis of complex shape and composition nano-structures for energy applications

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Energy conversion and storage materials are rapidly being developed for increased efficiency which leads to more and more complex compositions and shapes in multi-phase multi-functional materials systems. For solar-cells and photo-catalysts for fuel generation the devices are often complex with one or more absorbers and ultra-thin coatings or nano-particles for control of corrosion, tunneling or band-bending, and may also be used for increased mobility of electrons into a neighboring particle to separate the hole and electron efficiently. Further, there are catalysts for oxidation and reduction attached to the particles for solar fuel catalysts. At the same time, to make any impact world-wide, the materials have to be abundant and efficiently used as well as be of low toxicity and low cost. To achieve the latter, efficient processes capable of making high quality, multi-phase complex materials in one or few steps are required, which calls for increased understanding of materials synthesis processes from precursor to target materials.

Here we describe solution based synthesis routes using metal alkoxides and organically coordinated metal salts to achieve complex oxides and nano-composites with a focus on materials for photon to electricity or fuel synthesis. Oxides of varying complexities including doped and non-doped Fe₂O₃, TiO₂, Ln₂O₃ and ZnO in the forms of nano-particles, nano-sponges and thin- and ultrathin films. Special attention is paid to Ln-doped materials for photonic energy up-conversion devices.

The influence of the precursor, reaction kinetics and thermal treatment will be discussed in relation to the structures and properties obtained, as well as the possible synthesis of oxides with extended, metastable doping-levels. The syntheses and products were studied with a wide array of analytical techniques including; SEM, TEM, XRD, TGA, DSC/DTA, IR and Raman spectroscopy.

IE1

Fast single-site molecular water oxidation catalysts: one site is still enough

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The generation of solar fuels via artificial photosynthesis is a sustainable approach to address many of the challenges of our energy present and future. It requires the development of integrated systems that combine many features including light absorption, charge separation, water oxidation and water/CO2 reduction catalysis. Local and bulk proton management, in combination with

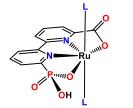


Figure 1. "Hybrid" bpcH catalysts.

product separation, are also key requirements for efficient and safe operation. We will discuss our progress towards these efforts with a major focus on water oxidation. This reaction has received considerable attention in the last decade due to its relevance in energy conversion and storage and as a way to gain insight into water oxidation in natural photosynthesis. We will present a new family of single-site water oxidation catalysts that outperforms all previously reported molecular

catalysts. This is the result of careful catalyst design to enhance fundamental aspects in the water oxidation mechanism from catalyst activation to the key O-O bond formation and O2 evolution steps. Our catalysts are "hybrid" systems that combine important features from bda-based catalysts1-3 and multifunctional bpa-catalysts,4 Figure 1. The carboxylate group from the bda systems is the "gatekeeper" and allows water coordination at the Ru(III) state, Figure 2. This provides access to proton-coupled electron transfer (PCET) processes in the following catalyst activation steps resulting in lower overpotentials and faster rates for these steps. The multifunctional phosphonate group from the bpa systems is the "enforcer" and facilitates O-O bond formation by significantly lowering the activation energy for this step via intramolecular atomproton transfer (i-APT). In addition, the phosphonate group also provides low energy pathways for oxidative activation steps and oxidation steps preceding O2 evolution via intramolecular PCET (i-PCET). The results that will be presented demonstrate that single-site water oxidation catalysis is a viable approach for reaching the required rates for practical applications in solar energy conversion. It also provides support for the potential role of this pathway in the oxygen evolving complex in photosystem II.

(1) Mechanism of water oxidation by [Ru(bda)(L)2]: the return of the "blue dimer", Concepcion, J. J.; Zhong, D. K.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. Chem. Commun. 2015, 51, 4105.

(2) A molecular ruthenium catalyst with water-oxidation activity comparable to that of photosystem II, Duan, L.; Bozoglian, F.; Mandal, S.; Stewart, B.; Privalov, T.; Llobet, A.; Sun, L. Nat. Chem. 2012, 4, 418.

(3) Manipulating the Rate-Limiting Step in Water Oxidation Catalysis by Ruthenium Bipyridine-Dicarboxylate Complexes, Shaffer, D. W.; Xie, Y.; Szalda, D. J.; Concepcion, J. J. Inorg. Chem. 2016, 55, 12024.

(4) Water Oxidation by Ruthenium Complexes Incorporating Multifunctional Bipyridyl Diphosphonate Ligands, Xie, Y.; Shaffer, D. W.; Lewandowska-Andralojc, A.; Szalda, D. J.; Concepcion, J. J. Angew. Chem., Int. Ed. 2016, 55, 8067.

Application of Up-Conversion Materials for Plastic Recycling

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There is an ever-increasing demand for the developing of more efficient and higher-yield sorting techniques for plastic waste. While traditional solutions are typically based on spectroscopic techniques, another possible solution is based on fluorescent labelling. This presentation reviews both down-shifting (DS) as well as up-conversion (UC) systems based on both inorganic- and organic-based materials as shown in **Table 1** [1]. The classical DS (or Stokes) process occurs when a photon with lower energy is emitted after the absorption of a higher energy photon, with a photoluminescent quantum yield (PLQY) of less than unity. In contrast, UC is a nonlinear, anti-Stokes process of combining two or more low energy near-infrared (NIR) photons to obtain the emission of a single higher energy photon. A key focus of this review is on the potential of UC labels based on trivalent lanthanides (Ln³⁺) as a promising technological solution for plastic recycling. While Ln³⁺ based UC materials possess two key disadvantages – low quantum yield and requiring high-power excitation -they also exhibit many unique features, such as high signal/noise ratio, the ability to tailor the colour of emitted light, long photoluminescent lifetimes, and low toxicity. The bulk of the review, focuses on recent advances in the Ln³⁺ activated inorganic nano- and micro-sized UC materials from the perspective of tailoring UC emission colour and intensity (see Figure 1) and how the plastic recycling industry could capitalise on this powerful materials system.

[1] Gao, G., Turshatov, A., Howard, I. A., Busko, D., Joseph, R., Hudry, D., & Richards, B. S. (2017). Up-Conversion Fluorescent Labels for Plastic Recycling: A Review. Advanced Sustainable Systems, doi: 10.1002/adsu.201600033.

Table 1. Figures-of-merit of fluorescent labelsfor plastic recycling (adapted from [1]).

Figure-of-merit	Inorganic		Organic	
	UC	DS	UC	DS
	vis-NIR	UV-vis	vis	UV-vis
Em. wavelength	UV-vis-NIR	vis-NIR	vis	vis
Stokes shift	large	large	medium	small
	weak	average	strong	strong
Sharp emission	yes		no	no
PLQY	low	average	low	high
S/N ratio	high	low	high	low
PL lifetime	μs – ms	µs – ms	μs	ns
Biocompatibility	good	good	?	?
Stability	excellent	excellent	poor	poor
Cost	low	low	mid	mid
Conc. required	high	high	low	low

Figure 1. UC fluorescent labels developed by the authors demonstrating a wide range of possible emission colours when excited at 980nm (0.2 W/cm²) (adapted from [1]).

Universidad de La Laguna



IE3



Luminescent solar concentrators: from BIPV to mobile electronics

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The interest in photovoltaic solar energy has grown exponentially in this century. More solar energy strikes the earth in one hour than is consumed by humankind in a whole year. Solar energy is, therefore, an underused resource. However, the high cost is still a limiting factor for massive uses. Luminescent solar concentrators [1,2] provide a promising solution for cheaper photovoltaic energy.

A luminescent solar concentrator (LSC) consists of a piece of glass or plastic plate coated with luminescent centers that absorb sunlight and emit it at a longer wavelength. A substantial part of the longer-wavelength light is trapped by total internal reflection and guided to the edges of the LSC plate, where it is absorbed by small area photovoltaic cells. LSCs provide an exciting new approach to harvest solar energy in buildings and mobile electronics. By converting windows and displays into LSC waveguides, it is possible to transform these passive surfaces into energy harvesting devices.

Efforts to translate this technology to the building envelope and electronic displays have been limited due to the performance and visual impact. Several strategies, such as FRET multichromophore systems [2-4] and vertical aligned dyes [3] have been proposed to increase the performance of LSCs. The colour and degree of transparency of an LSC, which are determined by the type and density of chromophores, can be chosen to meet specific building and display requirements and/or aesthetic criteria.

Photoluminescent polarizes have also been considered to replace conventional polarizers in electronic displays [4]. Displays absorb incident light and the unwanted polarization component of the backlight in LCDs. Instead of wasting the absorbed light, photoluminescent polarizers guide it to the frame of the display where it can be harvested by solar cells, extending the battery life of portable devices.

[1] W. H. Weber & J. Lambe, Appl. Opt. 15 (10), 2299–2300 (1976)

[2] M. J. Currie, J. K. Mapel, T. D. Heidel, S. Goffri & M. A. Baldo, *Science* 321 (5886), 226–228 (2008).

[3] C. L. Mulder, P. D. Reusswig, A. M. Velázquez, H. Kim, C. Rotschild & M. A. Baldo, *Optics Express*, Vol. 18, No. S1, A79-A90 (2010)

[4] A. Menéndez-Velázquez, C. L. Mulder, N. J. Thompson,

T. L. Andrew, P. D. Reusswig, C. Rotschild and M. A. Baldo, *Energy & Environmental Science.*, 2013, 6, 72-75 (2013)



Upconversion Material and its Application in Solar cells

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The minimization of transmission loss of solar photons is highly desirable for solar cells by extending the spectral absorption from visible to near-infrared (NIR) range. Herein, uniform NaYF₄:Yb/Er upconversion nanoparticles (UCNPs) were synthesized using a hydrothermal method, and the effects of the reaction time, solvents and the ethylenediaminetetraacetic (EDTA) acid concentrations on the upconverting optical properties were systematically investigated. Applying these materials at the back of amorphous silicon (a-Si) single junction solar cells, a 0.8 mA/cm² short circuit current density (J_{sc}) appeared under 980 nm infrared laser excitation when the solar cells with up-converting materials was placed in dark room. In addition, the Li⁺ co-doping and the plasmonic were employed for enhancing NaYF₄:Yb/Er upconversion luminescence intensity. Based the above optimization, NaYF₄:Yb,Er/Li-Ag@SiO₂ composites were created, the green and red emissions of NaYF₄:Yb,Er/Li-Ag@SiO₂ composites were doped into spiro-OMeTAD-based hole-transfer layer (HTM) of perovskite solar cells to enhance NIR absorption. The device made with 12 mg mL⁻¹ UCNPs in HTM exhibits a better photocurrent output of 20 μ A cm⁻² under 980 nm infrared laser excitation.

IE5

"Metal-oxide semiconductor photoanodes for sunlight-driven water splitting"

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Please indicate preference: ___Poster ___Oral __X_ Invited Speaker Specify Technical Area: ___Biomedical __X_ Energy

Implementation of a semiconductor material in photoelectrochemical water splitting device relies on the combination of effective solar light absorption, suitable band energetics and long-term stability of the photomaterial. In the case of semiconductors intended to operate as oxygen evolution photoanodes, for the reasons of stability in aqueous solutions and visible light absorption, the actual choice is restricted to a few metal oxides. However, none of those photomaterials including tungsten trioxide (WO3), bismuth vanadate (BiVO4) or hematite ferric oxide (Fe2O3) have the positions of the conduction band edges more negative than the hydrogen evolution potential, a condition necessary to perform unassisted water splitting. Consequently, continuing efforts are devoted to minimize the bias voltage required to perform visible light-driven photooxidation of water in a tandem device combining the photoelectrolyser with connected in series photovoltaic cell. These efforts include, in particular, modification of the semiconductor oxides by doping, development of new water oxidation electrocatalysts and incorporation into photoanodes of plasmonic metal nanostructures to improve light capture and charge photogeneration. Recent advances regarding the largely investigated photoanode material WO3 (Eg = 2.5 eV) will be discussed.

Acknowledgment

J. A. gratefully acknowledges funding from the National Science Center through Maestro grant 2013/10/A/ST5/00245.

Upconversion nanoparticles modified by sol-gel methods for applications in UV-Vis light activated processes

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Upconversion nanoparticles (UCNP) have been widely used since the 60's of the last century in several different applications. Near Infrared (NIR) pumping and emission spanning the UV-Vis region up to the IR is very attractive from the technological point of view. In this presentation we will show 3 main examples where light activated processes like photodynamic therapy (PDT), temperature and UV sensing and photocatalysis can benefit from the spectral properties of UCNP [1-3]. In the first case YVO₄:Yb³⁺:Ho³⁺ NP were incorporated in biocelllulose membranes. The overlap between the red upconversion emission and absorption of the well known PDT active chlroaluminum phthalocyanine (CIAIPc) allowed us to propose a composite membrane system where NIR activated production of reactive Oxygen species could be observed [1]. The second example involves a dual sensor of UV light and temperature [NaGdF₄:Yb³⁺:Er³⁺@SiO₂-Eu(tta)₃]. The dual nanothermometer was obtained from the NIR to visible upconversion signal of Er³⁺ together with the UV-excited downshifting emission from the Eu³⁺ complex. The UV degradation of the Eu³⁺ complex with the consequent emission quenching was taken in advantage to sensor the UV dose [2]. And finally, in the third example we will show that coupling of TiO₂ with UCNP is a promising strategy to develop NIR driven TiO₂-based photocatalysts. А rapid, efficient and reproducible coprecipitation/microwave assisted hydrothermal method was developed for the preparation of NaYF₄:Yb³⁺:Tm³⁺. The upconversion microrods were coated with anatase-TiO₂ and good photocatalytic activity was observed under both UV and NIR light [3].

Acknowledgments- Brazilian agencies FAPESP, CNPq and CAPES are acknowledged for financial support.

- [1]- K.Nigoghossian et al, Coll. and Interf. Sci. Comm. 2014, 2, 6.
- [2]- K.Nigoghossian et al, ACS Omega 2017, 2, 2065.
- [3]- S.Ullah et al, CrystEngComm 2017, 19, 3465.



Photonic crystal assisted rare-earth doped frequency conversion in solar energy applications

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In order to increase the efficiency of photovoltaic solar cells, photon absorption in an extended range of the solar spectrum is necessary, for example by means of up-conversion (UC) of sub-bandgap photons and down-conversion (DC) of above bandgap photons to minimize thermalization losses. In the latter case, quantum cutting (QC) of a photon of energy > 2 E_G into two photons of energy slightly higher than E_G can lead to enhanced quantum efficiencies.

While lanthanide-doped luminescent layers may be deposited on solar cell materials to achieve spectral conversion effects by methods like CVD or PVD, sol-gel (SG) processing is a low-cost technology which can be a good alternative for this purpose. The SG technique has the added advantage that it can be coupled with the deposition of multilayered 1-D photonic crystal structures like Bragg Mirrors (BMs) and micro-cavities (MCs) in order to integrate the spectral conversion function into an even more efficient structure.

In this work, lanthanide-doped SG-derived active layers have been deposited by spin-coating onto c-Si or silica glass substrates for frequency conversion, with particular emphasis on DC, involving host matrices like aluminosilicate glass and titania ceramics for the sensitizer/acceptor pair Tb/Yb. Selected active layers were also covered with suitable BMs, or embedded within MC structures modelled with Transfer Matrix Method software. The different materials and structures have been characterized by XRD, SEM, Ellipsometry, Raman and photoluminescence (PL) spectroscopies. PL lifetimes have been measured in selected cases and the energy transfer efficiencies between Tb³⁺ and Yb³⁺ ions have been determined.

Second order co-operative DC is clearly observed for the Tb/Yb pair following excitation at ~ 484 nm, but also at 330 and 377 nm. With the help of 1-D photonic crystal structures, namely MCs with a defect at ~ 1000 nm, the Yb³⁺ PL intensity is clearly enhanced.



Advanced materials for luminescent photovoltaic systems

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Abstract:

Luminescent solar devices have been investigated since the 1970's [1,2]. This paper presents how re cent material advances has led to plasmonic enhancement of these luminescent devices. Plasmonic Luminescent Down-Shifting (pLDS) and Plasmonic Luminescent Solar Concentrators (pLSC) are new optical approaches to increasing PV device efficiency by using plasmonic coupling between luminesc ent materials and advanced materials such as Ag or Au metal nanoparticles (MNP) [3, 4]. Using Ag o r Au nanomaterials the optical properties of fluorescent species can exhibit dramatic spectral chang es in their presence. This work exploits plasmonic coupling phenomena to enhance absorption/emi ssion in luminescent devices. The optical response of metal nanoparticles and their interaction with luminescent species has been investigated by optical measurement of absorption and emission. Mo st recent results will be presented in this paper.

References:

[1] Goetzberger & Greubel, 1977. Appl. Phys., 14 (1977), pp. 123–129.

[2] Hovel, H.J, Hodgson, R.T. and Woodall, J.M. (1979), "The effect of fluorescent wavelength shifting on solar cell spectral response", Solar Energy Materials., 2(1), 19-29.

[3] Ahmed, 2015. Materials Characterization and Plasmonic Interaction in Enhanced Luminescent D own-Shifting Layers for Photovoltaic Devices. PhD thesis, Dublin Institute of Technology, Ireland.

[4] Chandra, S., Doran, J., McCormack, S. J., Kennedy, M., Chatten, A. J., (2012). Enhanced quantum dot emission for luminescent solar concentrators using plasmonic interaction, Solar Energy Material s and Solar Cells, Volume 98, March 2012, Pages 385-390

Acknowledgements

The authors would like to acknowledge funding from the European Research Council for supporting the research at the Solar Energy Applications Group at Trinity College Dublin through the ERC Starter Grant: PEDAL 639760. They also acknowledge support from Science Foundation Ireland and scientific input from COST Action PEARL: CA16235.

IE9

Complex Fluorides of Yttrium and Alkali Elements as Efficient Upand Down-Conversion Materials for Versatile Applications

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Crystals of monoclinic LiKYF₅, orthorhombic K₂YF₅ and cubic Cs₂NaYF₆ fluorides containing different concentrations of Er³⁺ and/or Yb³⁺ ions up to 100 at% have been synthesized under hydrothermal conditions and their crystal structures have been refined with the Rietveld method. In the crystal structures of these fluorides there are layers of [YF₈] and chains of [YF₇] polyhedra connected by alkali ions as well as [YF₆] polyhedra isolated from each other by alkali ions, respectively. The Raman spectra, Fig. 1(a), confirm that these fluorides are low-phonon-energy materials.

Spectroscopic properties of Er³⁺ ions have been studied and absorption and stimulated-emission (SE) cross-sections have been obtained. The probabilities of radiative transitions have been determined within the Judd-Ofelt theory whereas luminescence decay studies have provided the quantification of non-radiative (NR) relaxation rates. The structure features of LiKYF₅, K₂YF₅ and Cs₂NaYF₆ result in exceptionally long excited-state lifetimes, weak concentration-quenching and NR relaxation, which makes these crystals very suitable for developing up- and down-conversion (UC and DC) materials.

Intense color-tunable (green-to-yellow) UC luminescence is observed for singly Er^{3+} -doped crystals, Fig. 1(b), and their color properties have been described in the CIE 1931 frame. For Yb³⁺, Er^{3+} codoped samples, visible UC luminescence in the blue, green and yellow regions is detected under near-IR excitation. The Yb³⁺ $\rightarrow Er^{3+}$ energy-transfer efficiency has been determined. Under UV excitation of Er^{3+} :K₂YbF₅, DC featuring a quantum efficiency of >160% is observed, Fig. 1(c). The developed materials are promising for spectral shifting (near-IR \leftrightarrow visible) for bio-imaging, labeling and solar cells.

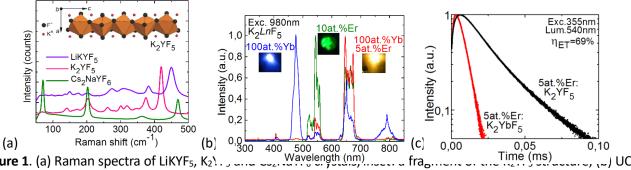


Figure 1. (a) Raman spectra of LiKYF₅, K_2 \., L_2 ..., Wavelength(nm)..., fra_{3} ..., L_1 fragment (ms) and (ms) but (ms) b





Spectral conversion under high solar concentration

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Spectral conversion via up-conversion, down-conversion and down-shifting, is one of the promising approaches for energy applications and 3rd generation photovoltaics. To enable significant power conversion efficiencies, very high irradiance is required especially in non-linear processes. In solar energy applications this irradiance translates to high solar concentrations. Currently the utilized range for concentrating photovoltaics is between 100 and 2,000 suns, however, for significant gains much higher solar concentrations are required, while the upper limit is on earth 46,000 suns. Here, the effect of solar concentration on the spectral conversion processes is reviewed in the basis of reported and demonstrated solar cells at multiple thousand suns.

Structural dynamics of large conductance calcium-and voltage-gated potassium channels revealed by Patch-Clamp Fluorometry

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In neurons, sites of Ca²⁺ influx and Ca²⁺ sensors are located within 20-50 nm, in subcellular "Ca²⁺ nanodomains". Such tight coupling is crucial for the functional properties of synapses and neuronal excitability. Two key players act together in nanodomains, coupling Ca2+ signal to membrane potential: the voltage-dependent Ca^{2+} channels (Cav) and the large conductance Ca^{2+} and voltagegated K⁺ channels (BK, hslo or KCa1.1). BK channels are characterized by synergistic activation by Ca²⁺ and membrane depolarization, but the complex molecular mechanism underlying channel function is not adequately understood. Information about the pore region, voltage sensing domain or isolated intracellular domains has been obtained separately using electrophysiology, biochemistry and crystallography. In our laboratory we use a combination of genetics, biochemistry, electrophysiology and spectroscopy, which we correlate with protein structural analysis, to investigate the real time structural dynamics underlying the molecular coupling of Ca²⁺, voltage and activation of the whole protein complex forming the BK channels in the membrane environment, its regulation by accessory subunits and channel effectors (Miranda et al., 2013; Miranda et al., 2016). BK subcellular localization and role in Ca^{2+} neuronal nanodomains make these channels perfect candidates as reporters of local changes in [Ca²⁺] restricted to specific subcellular regions close to the neuronal membrane. We have created fluorescent variants of the channel that report BK activity induced by Ca²⁺ binding, or Ca²⁺ binding and voltage (Giraldez et al., 2005). We aim to optimize and deploy these novel optoelectrical reporters to study physiologically relevant Ca²⁺-induced processes both in cellular and animal models. Overall, optically-active BK channels with spectrally-separate photoactivation and FRET modules offer many possibilities for the study of activation in mammalian cells.

References: Giraldez et al., JGP (2005) 126(5), 429; Miranda et al., PNAS (2013) 110(13), 5217; Miranda et al., PNAS (2016) 113(49), 14055.

Funding: European Research Council ERC-CoG-2014-648936 (NANOPDICS).

Control of laser induced temperature increase in bacteria through Green Fluorescent Protein nanothermometers

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Thermal therapy is frequently used in combination with other forms of cancer therapy to kill cancer cells and damage proteins and structures within the cell. Lasers can be used as the external energy source to produce heat in the tumor areas. Therefore, it is extremely important to control the laser induced temperature increase to reduce damage in nearby healthy tissues. In this paper, we use the fluorescence signal of Green Fluorescent Protein (GFP) over-expressed in an E. coli bacterial culture to detect laser induced temperature changes. For that purpose, the E. coli culture transfected with GFP is injected in a Fabry-Perot (FP) optofluidic planar microcavity. The GFP fluorescent resonant modes are detected. Shifts in the wavelengths of the resonant modes are used to determine the temperature increase as a function of the IR heating laser pump power. The combined use of GFP expressing bacterial culture and an optofluidic FP microcavity shows the advantages of non-toxicity and easy detection as the temperature detection is based on a simple emission spectrum of the efficient GFP molecules.

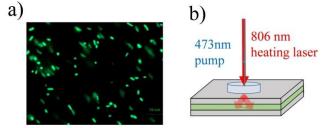


Figure 1 a) Fluorescence microscope image of the E. coli culture expressing GFP; b) Experimental set-up of the laser induced heating scheme.

Acknowlegments: This research was supported by European Regional Development Funds program (EU-FEDER) and MINECO (MAT2016-79866-R), (MAT2016-75586-C4-4-P), (SAF2016-80626-R), (SAF2014-61644-EXP).



Quantum Dots emitting in the third bio-window as potential contrast agents for bimodal intracoronary imaging

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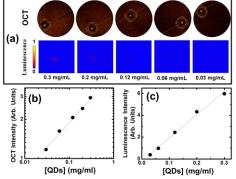
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Optical coherence tomography (OCT) has gained a considerable attention in interventional cardiovascular medicine and it is nowadays used at clinical level for the assessment of atherosclerotic lesions as well as for optimizing stent placement. The design and development of contrast agents for OCT are needed if it has to be used for molecular imaging [1, 2]. In this work, we have evaluated the potential use of PbS Infrared emitting Quantum Dots (IR-QDs) as OCT and photo luminescence multimodal intracoronary imaging contrast agents under single line laser excitation. The OCT contrast and scattering cross section of QDs have been compared to those of Gold Nano Particles. The simultaneous capacity of IR-QDs for back scattering of 1.3 μ m light and fluorescence generation under this excitation wavelength has been evaluated as function of dot concentration in aqueous suspensions by using an OCT clinical equipment, as shown in Figure 1. Thus, the ability of IR-QDs for simultaneous OCT and fluorescence imaging inside tissues is demonstrated with a tissue

penetration capability larger than 1mm. This new multimodal imaging capacity appears of special relevance in cardiovascular imaging as it could allow for unequivocal identification of inner lesions beyond the artery contour by using adequate functionalized IR-QDs.

Acknowledgements: Work supported by the Spanish Ministry of Economy and Competitiveness under Project Nr.MAT2016-75362-C3-1-R and by Instituto de Salud Carlos III under Project Nr. PI16/00812. Jie Hu acknowledges the scholarship from the China Scholarship Council (CSC, No. 201506650003). Dirk H. Ortgies is grateful to the Spanish Ministry of Economy and Competitiveness for a Juan de la Cierva scholarship (FJCI-2014-21101).

References: [1] Hu, Jie, et al. "Dynamic single gold nanoparticle visualization by clinical intracoronary optical coherence tomography." Journal of biophotonics, 2016, 10(5): 674-682. [2] Yoo, Hongki, et al. "Intra-arterial catheter for simultaneous microstructural and molecular imaging in vivo." Nature medicine, 2011, 17(12): 1680-1684.



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Figure 1 (a). Cross sectional OCT and infrared as obtained for different concentrations of QDs in the tubing. (b). Integrated OCT intensity as a function of the concentration of QDs. (c). Integrated infrared luminescence intensity as a function of the concentration of QDs. In (b) and (c) dots are experimental data and solid line is a guide for the eyes.

Upconversion nanoparticles for monitoring of enzymatic reactions in human serum

Universidad de La Laguna

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Upconversion luminescent nanoparticles (UCNPs) are characterized by their large anti-stokes emission, which makes them attractive candidates for bioassays as well as for bioimaging [1]. Excitation in the near infrared region of these lanthanide-doped nanoparticles avoid auto-fluorescence of biomolecules. Compared to other nanomaterials like quantum dots they exhibit low cytotoxicity, high photostability, no blinking and chemical inertness [2]. In the approach shown here, 808-nm excitable bright, monodisperse NaYF₄:Nd,Yb,Tm particles of diameters smaller than 40 nm for monitoring enzymatic reactions based on oxidases and dehydrogenases, were synthesized and fully characterized.

Furthermore, we demonstrate an application of those core-shell $NaYF_4$ nanoparticles with tandem sensitation $(Nd^{3+}/Yb^{3+} and Yb^{3+}/Tm^{3+})$ in self-referenced, continuous and simultaneous sensing of L lactate and D-glucose via enzymatic related reactions in serum. This is enabled by the spectral match of the luminescence emission of these luminescent nanomaterials with the absorption of the co-enzymes NADH and FAD. This concept can easy be adapted to many other enzymes and due to the colloidal stability and the biocompatibility of these particles they can be used for imaging of intracellular lactate concentrations.

References:

- [1] G. Chen, H. Qiu, P.N. Prasad, X. Chen, Chemical Reviews 114 (2014) 5161-5214
- [2] M. González-Béjar, J. Pérez-Prieto, Methods and Applications in Fluorescence 3.4 (2015) 042002.

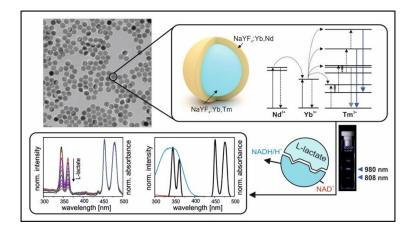


Fig. 1: Monodisperse core-shell UCNPs for monitoring enzymatic reactions at 808 nm excitation.

OB4

Nanocrystalline alkaline and rare earth M₂REF₇ fluorides (where M = Ca, Sr, Ba and RE = Y, La, Gd, Lu) for upconversion and bioapplications

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Oral

Biomedical

In recent years, the properties of upconverting nanoparticles (UCNPs) were investigated very intensively because of their potential applications. Particularly interesting are UCNPs which properties base on lanthanide ions (Ln³⁺) [1,2]. The knowledge of mechanisms responsible for the efficient upconversion process is increasing dynamically [3,4]. Also methods of NPs production are continuously developed as the demand for small and advanced NPs is growing [5,6]. One of the most popular and commonly used inorganic host materials for upconversion are fluorides. They have low phonon energy, high chemical stability and are a good electron acceptors. Nanomaterials based on fluorides are characterized by the relatively high value of quantum yield (QY) of luminescence [7,8]. Due to their properties, fluorides can be used in the production of efficient phosphors, new light sources or lasers. Also important are their potential biomedical applications [9].

The M₂REF₇ fluorides as well as their Yb³⁺/Ho³⁺, Yb³⁺/Er³⁺ or Yb³⁺/Tm³⁺-doped counterparts were synthesized by hydrothermal method. Three different M²⁺ ions: Ca²⁺, Sr²⁺, Ba²⁺, and four RE³⁺ ions: Y³⁺, La³⁺, Gd³⁺ and Lu³⁺ were used in order to obtain upconverting materials. The mechanism of materials formation was studied, indicating the influence of metal ions EDTA complexes stability on the final product composition. TEM images, revealed sizes of nanocrystals in the range of 9 – 37 nm. The obtained particles exhibited emission of light in the visible spectra, under excitation by 976 nm laser radiation. Excitation and emission spectra, luminescence decays, laser energy dependencies and upconversion quantum yields were measured to determine spectroscopic properties of prepared materials. Also temperature dependencies of luminescence were analyzed. The most intense emission under 976 nm excitation was observed for Sr₂LuF₇, Ba₂LuF₇ and Ba₂GdF₇-based samples. Nanoparticles based on Sr₂LuF₇ host compounds were used for cytotoxicity studies and their potential applications for bioimaging were determined by confocal microscopy.

References

- [1] X. Chuai, X. Guo, X. Liu, G. He, K. Zheng, C. He, W. Qin, Opt. Mater. (Amst). 44 (2015) 13–17.
- [2] L. Rao, W. Lu, T. Zeng, Z. Yi, H. Wang, H. Liu, S. Zeng, Dalton Trans. 43 (2014) 13343–8.
- [3] H. Dong, L.-D. Sun, C.-H. Yan, Chem. Soc. Rev. 44 (2015) 1608–1634.
- [4] G. Liu, Chem. Soc. Rev. 44 (2015) 1635–1652.
- [5] X. Li, S. Gai, C. Li, D. Wang, N. Niu, F. He, P. Yang, Inorg. Chem. 51 (2012) 3963–71.
- [6] F. Wang, D. Banerjee, Y. Liu, X. Chen, X. Liu, Analyst 135 (2010) 1839–54.
- [7] N. Jiang, S. Zhou, D. Su, J. Qiu, Phys. Status Solidi Rapid Res. Lett. 6 (2012) 487–489.
- [8] C.D.S. Brites, X. Xie, M.L. Debasu, X. Qin, R. Chen, W. Huang, J. Rocha, X. Liu, L.D. Carlos, Nat. Nanotechnol. (2016) 1–7.
- P.P. Fedorov, M.N. Mayakova, S. V. Kuznetsov, V. V. Voronov, R.P. Ermakov, K.S. Samarina, A.I. Popov, V. V. Osiko, Mater. Res. Bull. 47 (2012) 1794–1799.

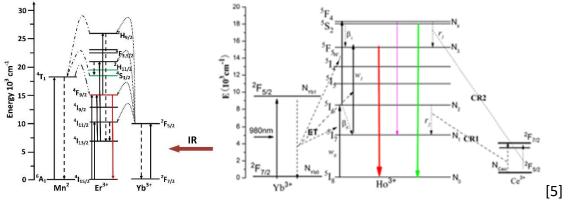
Tunable upconversion emission in inorganic nanomaterials based on rare earth fluorides and borates

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Oral

Biomedical

These days many attention is attracted to health and cancer therapy. Therefore, many studies are related to the biomedicine, including biosensors and bioimaging. One of the most desired compounds applied in biomedicine field are inorganic nanomaterials doped with lanthanide ions, which exhibit visible emission under infrared radiation. Especially nanophosphors, NPs, showing sharp and intense single-band of red upconversion emission are needed. These features are required due to lack of autofluorescence, deep penetration depth and low photobleaching. It is commonly known, that fluoride matrices exhibit low phonon energy, which decreases the probability of the radiationless relaxation [1]. On the other hand, NPs based on orthoborates exhibit good chemical and thermal stability [2,3]. For this reason luminescent materials doped with Yb³⁺/Er³⁺ and Mn²⁺ or Yb³⁺/Ho³⁺ and Ce³⁺ ions were synthesized under hydrothermal conditions. Introducing the Mn²⁺ or Ce³⁺ ions into the NPs structure enable to tune color of the emission from green to orange-red luminescence [4,5].



Funding for the research was provide by the Ministry of Science and Higher Education, Grant No.0145/IP2/2015/73 (2014-2016) and National Science Centre, Grant No. DEC-2016/21/B/ST5/00110 (2017-2019)

References:

- [1] T. Grzyb, A. Szczeszak, Z. Śniadecki, B. Idzikowski, S. Lis, J. Alloy. Comp. 686 (2016) 489–495.
- [2] A. Szczeszak, T. Grzyb, S. Lis, R.J. Wiglusz, Dalt. Trans. 41 (2012) 5824–5831.
- [3] W. Gao, J. Dong, J. Liu, X. Yan, Mater. Res. Bull. 80 (2016) 256–262.
- [4] D. Tian, D. Gao, B. Chong, X. Liu, Dalt. Trans. 44 (2015) 4133–4140.
- [5] W. Gao, R. Wang, Q. Han, J. Dong, L. Yan, H. Zheng, J. Phys. Chem. C (2015) 2349-2355.

OB6

Multifunctional Upconverting Nanoparticles for the Activation of Organic Photocatalysts

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Upconverting nanoparticles (UCNPs), i.e. nanoparticles that convert infrared excitation into visible emission, have removed the necessity to excite fluorophores in the UV or visible region of the electromagnetic spectrum. Particularly efficient are the upconversion processes in rare-earth-doped nanoparticles (RENPs) whose dopants not only are responsible for upconversion of infrared into visible light but also add additional diagnostic (multimodal bioimaging, thermometry) or therapeutic functionality (e.g. photothermal and/or photodynamic therapy) to the UCNPs. This opens up a range of *in vivo* applications because excitation can occur in the infrared, especially in the 1st biological window between 650 – 950 nm, where subcutaneous penetration by infrared light of biological tissues is possible, thereby greatly increasing potential *in vivo* targets of light-based techniques.^[1]

In modern organic chemistry, photocatalysis has gained a renewed interest. Typically, organic photocatalysts need UV-visible light for their activation, limiting their *in vivo* application. Recently, to avoid this limitation and expand their applicability towards *in vivo* reactions, different combinations with UCNPs have been described.^[2] In our research groups we set out to combine RENPs with various organic photocatalysts via their surface functionalization to obtain multifunctional nanoparticles that can not only activate the photocatalysts for classic organic reactions but display also multifunctionalty (imaging, thermometry, therapy) and thereby create synergistic effects.

We will present the synthesis, characterization and decoration with photocatalysts of NaGdF₄:Nd,Yb,Tm UCNPs and their application towards sensing and therapy combined with photocatalysis.

[1] Reviews on the topic: a) Zhou, B.; Shi, B.; Jin, D.; Liu, X. *Nat. Nanotechnol.* **2015**, *10*, 924. b) Reineck, P.; Gibson, B. C. *Adv. Opt. Mater.* **2017**, *5*, 1600446.

[2] a) Boyer, J. C.; Carling, C. J.; Chua, S. Y.; Wilson, D.; Johnsen, B.; Baillie, D.; Branda, N. R. *Chem. Eur. J.* 2012, *18*, 3122.
b) Lederhose, P.; Chen, Z.; Müller, R.; Blinco, J. P.; Wu, S.; Barner-Kowollik, C. *Angew. Chem. Int. Ed.* 2016, *55*, 12195. c)
Liu, X.; Que, I.; Kong, X.; Zhang, Y.; Tu, L.; Chang, Y.; Wang, T. T.; Chan, A.; Löwik, C. W. G. M.; Zhang, H. *Nanoscale* 2015, *7*, 14914. d) Ai, X.; Lyu, L.; Zhang, Y.; Tang, Y.; Mu, J.; Liu, F.; Zhou, Y.; Zuo, Z.; Liu, G.; Xing, B. *Angew. Chem. Int. Ed.* 2017, *56*, 3031.

Design, Synthesis, and Theranostic Application of Upconversion Nanoparticles with Tandem Sensitization

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Small, bright and colloidally stable upconversion nanoparticles (UCNPs) are desired for many theranostic applications. NaYF₄ doped by Yb³⁺ and Er³⁺ are the most common systems used so far, but these materials suffer from excitation at 980 nm, which causes sample heating by absorption of this wavelength by water. Here, we show the design and synthesis of core/multi-shell monodisperse, pure hexagonal nanoparticles with high upconversion efficiency excitable at 808 nm by tandem sensitation of Nd³⁺ to Yb³⁺. These particles are surface engineered to warrant colloidal stability as well as biocompatibility.

For Tm^{3+} doped particles with diameters in the range of 30 nm a systematic study of the upconversion efficiency influenced by doping ratios of lanthanide ions as well as by the relation of the core- to the shell-thickness allows a better understanding of the energy transfer. Architectures consisting of a core of ~24 nm NaYF₄(20%Yb,0.3%Tm) with a 4 nm thick NaYF₄(10%Nd,10%Yb) shell revealed maximum brightest at low power excitation. A growth of a thin inert shell of NaYF₄ enhanced the intensity these particles with tandem sensitation even more.

Tm³⁺ doped UCNPs with tandem sensitation have been applied for the NIR light triggered release of a drug for neural stem cell differentiation. The polymer coating changes its conformation upon excitation at 808 nm and a release of the drug provides the expression of stem cells in neurones. The advantages of this system are minimized sample heating, improved penetration depth and higher upconversion efficiency for enabling a complete release of the drug for stem cells differentiation.

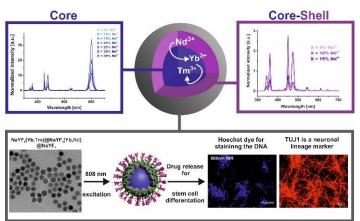


Fig. 1: Core/multi-shell monodisperse UCNPs for theranostic applications at 808 nm excitation. **OB8**

Ion exchange between luminescent nanoparticles evidences temperature-induced crossover in water molecules behavior

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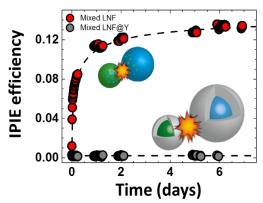
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Luminescent Nanofluids (LNFs) (colloidal suspensions of luminescent nanoparticles in a fluid) constitute a unique scenario to get a further insight into unexplored physical-chemical effects at the nanoscale by using the colloidal luminescent nanoparticles as local sensors. In this work we have studied the interparticle ion exchange (IPIE) between luminescent nanoparticles dispersed in liquid water.¹ These nanoparticles have the majority of its constituent ions at their surface and so that they act as supersensitive local probes at the nanoscale capable, as demonstrated in this work, to assess and monitor a temperature-induced water singularity at molecular scale. This change in the

behavior of water molecules with temperatures affects to many of its properties and it also plays a major role in the denaturation of proteins, for instance.^{2,3} The obtained results have unveiled that declustering of water above 45 °C leads to an enhancement of interparticle ion exchange as a result of collisions between nanoparticles. This is confirmed by comparing the results with those obtained growing a non-doped shell over the nanoparticles, which makes impossible the exchange of the luminescent ions in the LNF, as shown in the figure.

Acknowledgements: This work was supported by the Spanish Ministerio de Educación y Ciencia (MAT2013-47395-C4-1-R and MAT2016-75362-C3-1-R) and by COST Action CM1403. L.L.P. thanks the Universidad Autónoma de Madrid for the Formación de Personal Investigador program. P.H.G. thanks the Spanish Ministerio de Economia y Competitividad for the Juan de la Cierva program. K.S. thanks the Latvian National Research Program IMIS2 (302/2012).



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Figure. Long-term evolution of the IPIE efficiency of the normal mixed LNF (red dots) and the mixed LNF consisting of core/shell luminescent nanoparticles (grey dots) at 50 °C. Black dashed lines are guides to the eye. Insets: schematic diagrams of the collision between nanoparticles.

References: ¹ Han, S. *et al.* Multicolour synthesis in lanthanide-doped nanocrystals through cation exchange in water. *Nature Communications* **7** (2016). ² Maestro, L. *et al.* On the existence of two states in liquid water: impact on biological and nanoscopic systems. *International Journal of Nanotechnology* **13** (2016). ³ Davis, J. G. *et al.* Water structural transformation at molecular hydrophobic interfaces. *Nature* **491** (2012).

Tethering Luminescent Thermometry and Plasmonics to Assess Real-Time Thermal Flow in Nanoarchitectures

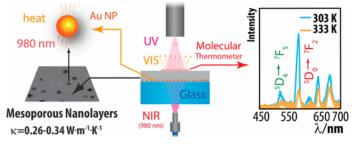
<u>Carlos D.S. Brites</u>^{1*}, Maria Cecilia Fuertes^{2,3}, Paula C. Angelomé², Eduardo D. Martínez², Galo J. A. A. Soler-Illia⁴, Luís D. Carlos¹

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The past decade has seen significant progresses in the ability to fabricate new mesoporous thin films with highly controlled pore systems and emerging applications in sensing, electrical and thermal isolation, microfluidics, solar cells engineering, energy storage and catalysis. Heat management at the micro and nanoscale is a key issue in most of these applications, requiring a complete thermal characterization of the films that is commonly performed using electrical methods. Here, plasmonic-induced heating (through Au NPs) is combined with Tb³⁺/Eu³⁺

luminescence thermometry [1] to measure the thermal conductivity of silica and titania mesoporous nanolayers. This communication will describe this innovative method [2] that yields to values in excelent accord with those measured by the evasive and destructive conventional 3ω -electrical method, simultaneously overcoming their main limitations.



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References

[1] L. D. Carlos, F. Palacio, Thermometry at the nanoscale: Techniques and selected applications, Royal Society of Chemistry, Oxfordshire 2016

[2] C. D. S. Brites, M. C. Fuertes, P. C. Angelomé, E. D. Martínez, P. P. Lima, G. J. A. A. Soler-Illia, L. D. Carlos, Tethering Luminescent Thermometry and Plasmonics: Light Manipulation to Assess Real-Time Thermal Flow in Nanoarchitectures, 2017, Nano Letters, DOI: 10.1021/acs.nanolett.7b01433

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Lanthanide(III)-Based Metallacrowns: Photophysical Properties and Biological Applications

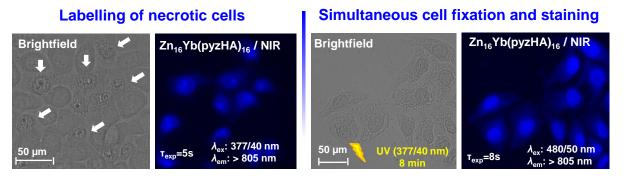
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> Please indicate preference: __Poster _X_ Oral __ Invited Speaker Specify Technical Area: _X_Biomedical __ Energy

Zn₁₆Ln metallacrowns (MCs) with an 'encapsulated sandwich' structure have demonstrated a high efficiency of sensitization of characteristic near-infrared (NIR) emission of Yb, Nd and Er ions as well as high photostability.^{1,2}

In this work we explore how photophysical properties (absorption spectra, luminescence lifetimes, quantum yields and sensitization efficiencies) of NIR-emitting Zn₁₆Ln MCs can be tuned by varying the nature of hydroxamic acids. In addition, we demonstrate that Zn₁₆Ln MCs assembled from pyrazinehydroxamic acid (pyzHA) can be used for exciting biological applications, i.e. as specific agents for labelling of cell necrosis³ or as simultaneous cell fixating and counter staining probes.⁴



This research has received funding from the European Community's Seventh Framework Program (FP7/2007-2013) (n° 611488 and n° 316906), the National Science Foundation (CHE-1361799), la Ligue Contre le Cancer, la Région Centre, le Canéropôle Grand Ouest, l'Agence Nationale de la Recherche (ANR-12-BS07-0012 and ANR-13-BS08-0011).

1 J. Jankolovits, C.M. Andolina, J.W. Kampf, K.N. Raymond, V.L. Pecoraro, *Angew. Chem.*, **2011**, *50*, 9660. 2 E.R. Trivedi, S.V. Eliseeva, J. Jankolovits, M. Olmstead, S. Petoud, V.L. Pecoraro, *J. Amer. Chem. Soc.* **2014**, *136*, 1526.

3. I. Martinic, S.V. Eliseeva, T.N. Nguyen, V.L. Pecoraro, S. Petoud, *J. Amer. Chem. Soc.*, **2017**, 139, 8388. 4. I. Martinic, S.V. Eliseeva, T.N. Nguyen, F. Foucher, F. Westall, V.L. Pecoraro, S. Petoud, *Chem. Sci.* **2017**, **DOI**: 10.1039/c7sc01872j



Increasing optical trapping forces by means of photonic nanojets

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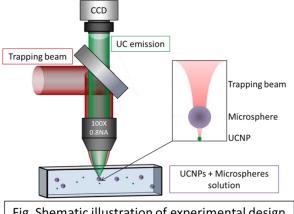
During the last decade fluorescent nanoparticles, and, in particular, upconverting nanoparticles (UCNPs), have become fundamental tools in both bioimaging and nanophotonics. Furthermore, the continuous development of synthesis routes has made possible the production of UCNPs with tailored optical properties so that, for example, it is possible nowadays to produce UCNPs which allow to perform bioimaging and sensing simultaneously. The next challenge in biosensing is the achievement of remote three-dimensional control over a single UCNP. It is required, for instance, for single particle intracelullar dynamic studies, as well as for fundamental single particle investigations. Nevertheless, attaining remote three-dimensional control over a single UCNP is not an easy task.

It could be accomplished by using optical tweezers (OT). Typically, the optical forces exerted by the OT radiation on a single UCNP are in the range of femtonewtons. Such small forces limit the

applications of OT for single UCNP manipulation.

In this work, we have faced this problem demonstrating that OT forces acting on a single UCNP can be substantially increased using as OT the photonic nanojet generated by an optically trapped silica microsphere.

Under certain conditions, a microsphere illuminated by a laser beam can produce a narrow beam with a beam waist under the Abbe diffraction limit known as photonic nanojet. Silica microspheres ($\sim 2 \mu m$) were used as focusing microlenses because of their relatively high refractive index and low optical



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Fig. Shematic illustration of experimental design

absorption. They can give rise to a focal spot of \sim 300 nm that can be used to trap and detect UCNPs. In this experiment, a microsphere is trapped by the trapping laser beam (980 nm) and the generated photonic nanojet is used as optical trap for the UCNP. This approach increases the optical force acting on the UCNPs, making them comparable to those exerted over metallic nanoparticles.

Acknowledgements: This work was supported by the Spanish Ministerio de Educación y Ciencia (MAT2016-75362-C3-1-R) and by COST Action CM1403. L.L.P. thanks the Universidad Autónoma de Madrid for the Formación de Personal Investigador program. P.H.G. thanks the Spanish Ministerio de Economia y Competitividad for the Juan de la Cierva program. P.R.S. thanks MINECO and the Fondo Social Europeo (FSE) for the "Promoción del talento y su Empleabilidad en I+D+i" statal program (BES-2014-069410).



In Vivo Application of Upconverting Force Sensors to Elucidate Neuromuscular Pump Action in *C. elegans*

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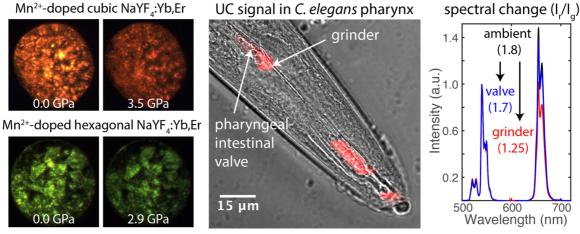
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The pump action in C. elegans is a neuron-regulated contraction and relaxation of muscles in the pharynx that allows the worms to feed^{1,2}. Abnormalities in feeding behavior can therefore indicate neurodegenerative diseases. Here, we combine electropharyngeograms (EPGs) with optical force measurements from upconverting nanoparticles (UCNPs) to understand how motor neurons influence the magnitude of forces exerted by pharyngeal muscles. Sub-25 nm Mn²⁺-doped NaYF₄:Yb,Er UCNPs with nano- to micro-Newton sensitivity provide a photostable color response to stress stimuli³. The energetic coupling between the crystal field sensitive *d*-metal and upconverting lanthanides is force-tunable, yielding a positive ("redder") or negative ("greener") change in the red to green Er³⁺ emission ratio for cubic- or hexagonal-phase NaYF₄ nanoparticles, respectively. We demonstrate the first in vivo application of these UCNPs to image and quantify forces along the pharynx. The worms are first incubated with water-soluble UCNPs (5 mg/mL) overnight, and then loaded in a microfluidic device for collection of upconversion spectra at key anatomical features. Based on ratiometric differences in emission, we find that forces exerted in the grinder (~10 µN) are nearly an order of magnitude higher than those exerted at the pharyngeal-intestinal value ($\sim 1 \mu N$). Furthermore, we correlate optical force measurements to voltage spikes in EPGs, which signal specific muscle contraction and relaxation events. Using optical and electrical readouts, we compare pump action duration, frequency, amplitude, and forces in wild-type, neurotransmitter-treated (5 mM serotonin), and mutant worms. From these results, we can provide the first in vivo determination of forces required for healthy function in *C. elegans*.

- 1. Raizen, D.M. and Avery, L. Neuron 1994, 12, 483-495.
- 2. Trojanowski, N.F.; Raizen, D.M.; Fang-Yen, C. Scientific reports 2016, 6.
- 3. Lay, A. et al. *Nano Letters* **2017**, DOI: 10.1021/acs.nanolett.7b00963.



Electric field sensitive upconverting nanoparticles for in vivo action potential imaging

Universidad de La Laguna

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It is crucial to record brain activity from the individual neuron scale to neural networks to fully understand the pathology of neurological diseases and develop new treatments. Optical techniques show great promise for imaging over these length scales; however, current methods generally require genetic encoding, rely on fluorophores that blink and bleach over time, or render the brains fixed or dead. Here, we have designed voltage-sensitive upconverting nanoparticles that overcome these limitations of current technology and thus facilitate live neural network imaging with nanometer spatial and sub-millisecond temporal resolution. These voltage responsive upconverting nanoprobes are sub-10 nm in size, with a heavily Yb³⁺-doped NaGdF₄ core and emitter-doped NaYF₄ shell. The small size ensures that the nanoparticles are readily integrated biologically, specifically into plasma membranes. The cores are doped with 60% Yb³⁺ to facilitate large absorption cross section at 980 nm. The optically excited Yb³⁺ transfer energy to emitters (e.g. Er³⁺ or Tm³⁺) in the shell. To prepare voltage sensitive upconverters, we replace the oleate ligand with a voltage sensitive dye (Di-3-ANEPPDHQ). In an electric field, the electronic states of Di-3-ANEPPDHQ shift and the its emission intensity decreases. This shift in the electronic states will change the coupling between the upconverters and the dye which we predict will lead to spectral and intensity changes in the upconverter emission when an electric field is applied. We have measured a decrease in the upconversion intensity of ~0.005% under an electric field of ~100 V/cm, comparable to the ~1-10% emission intensity change the dye undergoes in electric fields of 100 kV/cm, highlighting the sensitivity of these nanoparticles as electric field sensors.

Shift2017 Spectral sHapIng For biomedical and energy applications November, 13–17, 2017/Tenerife, Canary Islands, Spain.

Cancer drug control by UCNPs-based intracellular microrheometry.

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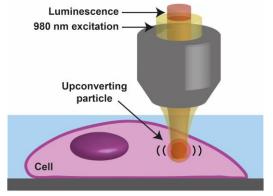
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Rheological parameters (viscosity, creep compliance and elasticity) play an important role in cell function and viability. For this reason, cancer drugs, such as Taxol and Colchicine, are aimed to alter the viscosity of the cells in order to abolish their division and, thus, cancer cell proliferation. Recently, an upconversion-based microrheology technique have been developed (*Nano Letters, 2016.*

16(12): p. 8005) for the determination of the intracellular viscosity (see Fig. 1). It is based on the analysis of the thermal fluctuation of upconverting particles. It takes advantage of the fact that disc-like upconverting particles present polarized emission which allows to track their angular orientation when optically excited. Since the magnitude of the thermal fluctuations of the upconverting particle depends on the viscosity of the surrounding medium, this last parameter could be measured from the analysis of the upconverting particle luminescence.

In this work, HeLa cancer cells have been incubated with upconverting particles. The uptake of the particles by



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Figure 1. Schematic representation of the upconversion-based microrheometry technique.

the cells allows to measure the intracellular viscosity by means of the named microrheology technique. The effect of Taxol and Colchicine on the intracellular viscosity of HeLa cells have been quantify and compared.

Studies such the here presented are mandatory in order to determine the changes that take place inside the intracellular environment due to an external stimulus. This could lead to, for example, the understanding and diagnose of diseases which effects are evidenced by the intracellular viscosity.

Acknowledgements: Paloma Rodríguez-Sevilla thanks MINECO and the Fondo Social Europeo (FSE) for the "Promoción del talento y su Empleabilidad en I+D+i" statal program (BES-2014-069410).



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Systematic Investigation of P-dependent Quantum Yields, Excited State Lifetimes and Emission Spectra of Yb³⁺, Er³⁺ doped ß-NaYF₄ Nanoparticles: Influence of Size, Microenvironment, Surface-Chemistry and Resonance Energy Transfer

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Solid state multi-band emitters like lanthanide doped up-conversion nanoparticles (UCNPs) are promising materials for energy and biotechnologies. These materials are excitable in the near infrared (NIR) and show emission bands from UV to SWIR with excellent photostability, and long luminescence lifetimes in the μ s range. The efficiency of these materials, i.e. the multiphoton absorption processes, the excitation power dependent population, and deactivation dynamics are strongly influenced by the particle size, structure, doping concentration, surface chemistry, and microenvironment.^[1,2,3] For applications UCNPs have to be optimized to meet the application relevant optical properties like the upconversion quantum yield (Φ_{UC}) and downshifting quantum yield (Φ_{PL}), luminescence lifetime and emission spectra.

We investigated β -NaYF₄ NPs co-doped with Yb³⁺ and Er³⁺ in aqueous and organic media and as powder. For the later, bulk and nanomaterial is compared. For dispersed particles the influence of surface chemistry (ligands), microenvironment (solvent) and size (10 to 43 nm) was studied. Especially for bioapplications the Förster-Resonance-Energy-Transfer (FRET) efficiency from UCNPs to organic dye molecules (rose bengal and sulforhodamine B) was optimized with respect to the UCNP size.

<u>References</u>

(1) Power-dependent upconversion quantum yield of NaYF₄:Yb³⁺, Er³⁺ nano- and micrometersized particles – measurements and simulations, *Nanoscale* (2017), DOI: 10.1039/C7NR02449E.

(2) Water dispersible upconverting nanoparticles: effects of surface modification on their luminescence and colloidal stability, *Nanoscale* Vol. 7 Issue 4 (2015) 1403-1410.

(3) Excitation power dependent population pathways and absolute quantum yields of upconversion nanoparticles in different solvents, *Nanoscale* Vol. 9 Issue 12 (2017) 4283-4294.

(4) Particle-size Dependent Förster Resonance Energy Transfer from Upconversion Nanoparticles to Organic Dyes, *Analytical Chemistry*, 2017, 89 (9), pp. 4868-4874.

Phosphonate-Functionalized Upconverting Nanoparticles As Multimodal Imaging Probes

Universidad de La Laguna

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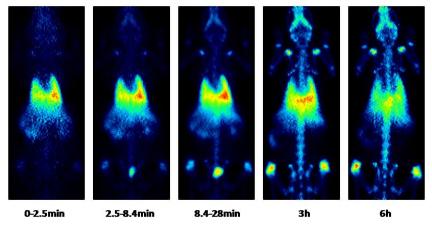
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Upconverting nanoparticles (UCNPs) are attracting much attention due to their unique optical properties. UCNPs efficiently convert near infrared light (NIR) into higher-energy UV and visible light (anti-Stokes) by multiphotonic processes.¹ For such reason, UCNPs are intensively investigated as phototriggers for the activation of prodrugs, including transition metal complexes (Ru, Pt)of biological relevance.² Besides their luminescence, these nanoparticles can be sensitive to magnetic fields and act as probes for MRI imaging, or can be labelled with radionuclides such as ¹⁸F and be detected by PET.^{1,3}

In this contribution, we will discuss our latest efforts in the development of UCNP-based multimodal (MRI/PET) imaging agents for bone targeting. Using ligand exchange procedures, we have prepared a series of phosphonate-functionalized NaGdF₄:Yb/Er UCNPs which show promising MRI properties and remarkable affinity for hydroxyapatite (inorganic constituent of bones). We also report on the *in vivo* biodistribution of ¹⁸F-labelled NaGdF₄:Yb/Er UCNPs in rats and on their capacity to accumulate in bones over time.

We thank the Spanish Ministry of Economy and Competitiveness (grant CTQ2012-39315 and CTQ2016-80844-R) and the COST Action CM 1403 for fruitful discussions.



1. J. Zhou, Q. Liu, W. Feng, Y. Sun, F. Li, Chem. Soc. Rev., 2015, 115, 395.

- 2. E.Ruggiero, S. Alonso-de Castro A. Habtemariam, L. Salassa, Dalton Trans., 2016, 45, 13012.
- 3. N. J. J. Johnson, W. Oakden, G. J. Stanisz, R. S. Prosser, F. C. J. M. van Veggel, Chem. Mater., 2011, 23, 3714.



Synthesis and Characterization of Rare Earth-doped ZrO₂ Nanoparticles

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The interest in rare earth materials increased steadily in the past years. Especially optical technologies like LEDs are in the focus but due to their broad optical properties also other applications are possible. Semiconductor nanoparticles like quantum dots provide many advantages for biological imaging due to their tunable optical properties. They are also superior compared to organic fluorophores in terms of photobleaching. Since they often contain toxic metals like cadmium, rare earth doped nanoparticles could be an alternative as luminescent nanomaterials. Because the luminescence of these nanoparticles is caused by 4f transitions the emission bands are very narrow and therefore easy to distinguish. It is also possible to cover an optical spectrum between the visible and the near infra-red range of the electromagnetic spectrum.

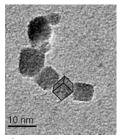


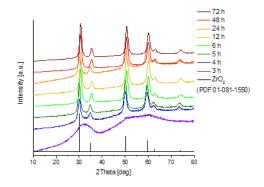
Fig. 1: ZrO₂ NPs

Cubic zirconium dioxide nanoparticles $(ZrO_2 NPs)$ with an edge length of 8 nm were synthesized by using a hydrothermal method. The nanocrystals were doped with different rare earth metals to cover a wide range of the

electromagnetic spectrum with their luminescence. Different concentrations of the rare earth elements were incorporated to investigate the influence on the emission properties. The particles

were characterized with TEM, EDX, powder diffraction and emission measurements.

For an application for example in biological system the nanoparticles have to be dispersible in water. Furthermore it is necessary to provide a possibility for specific functionalization. For this propose the ZrO₂ NPs were coated with a shell of silicon dioxide made form tetraethoxysilane



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Fig. 2: XRD pattern of ZrO_2 depending on the reaction time

and (3-aminopropyl)triethoxysilane. This shell provides free amine moieties on the surface which can be coupled with a carboxylic group to form amide bonds. With this method different epitopes can be introduced and the particles can be functionalized for a specific target.



Structural Peculiarities of the Polymer- DNA Assembles

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The goal of our work is that attempting to obtain a controlled structure and then improving the properties by adding small amounts of DNA or chromophores. The idea for using these partners it`s getting from desired applications which regard the biophotonic /NLO field. This can provide a way to obtain novel stimuli-responsive materials.

The used chromophores were synthesized starting from NLO sequences and contains both azobenzenes and carbazole groups in order to induce a response to an external and/or internal stimulus. DNA is also used in NLO application but has another important property and that is targeting specific molecules/cells/tissues.

This study was made to understand the perfect combination between the monomers (amides) and DNA/chromophores. The importance of this work is to highlight the best conditions and the mechanism to obtain new polymers with induced properties in order to be applied in specific fields. Moreover, we pursue to prove the possibility to control the structure and properties through the reaction parameters.

The molecular interaction and the surrounding media play an important role in changing of the fundamental properties of materials. So the electronically behaviors at molecular level are principally determined by the concentration of the NLO constitutive sequences. Demonstrating how such materials respond to a sensitive stimulus which affects the polar ordering is given by the solvatochromic, VCD, FT-IR and Raman studies.

The physical - chemical characterization of novel compounds, proposed by us, foreshadows the potential applications of polymer materials, with such sequences, in the biophotonic and NLO field.

Key words: nonlinear optic polymers, azo- polymers, carbazole, hyperpolarizability

REFERENCES

[1] J. B. Lee, A. S. Shai, M. J. Campolongo, N. Park, D. Luo, *Chem. Phys. Chem.*, **11**, 2081 (2010)

[2] Shiao-Wei Kuo, Ren-Shin Cheng, Polymer 50, 177 (2009).

[3] A. Rodriguez-Pulido, A. I. Kondrachuk, D. K. Prusty, J. Gao, M. A. Loi, A. Herrmann, *Angew. Chem. Int. Ed.*, **52**, 1008 (2013)

- [4] R. M. Zadegan , and M. L. Norton, Int. J. Mol. Sci., 13, 7149 (2012)
- [5] A. Czogalla, H. G. Franquelim, P. Schwille, , Biophysical Journal, 110, 1698 (2016)

[6] A.-M. Albu, Rev. Chim., **60**, 38, (2009)

[7] J. V.Grazulevicius, P. Strohriegl, J. Pielichowski, K. Pielichowski, Prog. Polym. Sci., 2, 1297 (2003)

- [8] G. S. He, L.-S. Tan, Q. Zheng., P. N. Prasad, Chem. Rev. 108, 1245 (2008)
- [9] A. Aldea, A.-M Albu, I. Rau, Optical Materials, 56, 90 (2016)

Long-luminescence-lifetime nanoparticles for time-gated autofluorescence-free bioimaging

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Fluorescence is nowadays a widely employed tool in the biomedical field for both in vitro and in vivo imaging. However, its applicability for in vivo imaging is hampered by the existence of strong autofluorescence signals especially in the ultraviolet and visible parts of the spectrum. Another limitation is the short penetration wavelength of visible light, which restricts the application of fluorescent imaging to in vitro and topical applications. Therefore, new fluorophores were developed that present emissions in the spectral regions known as biological windows (regions where light can penetrate deeper in biological tissue). The first one lies between wavelengths from 650 to 950 nm, it has been profusely studied although the penetration of light in this region is limited to a few millimeters. The second biological window (1000-1350 nm) is gaining increasing interest because light penetration over 1 cm can be obtained. However, the existence of autofluorescence in this region associated with pigmentation and diet limits the useful wavelengths to 1200-1350 nm.

In this talk, we present the elimination of autofluorescence signals in in vivo imaging, which takes advantage of the long luminescent lifetimes of trivalent rare earth ions (from 100 μ s to 1 ms) compared with the lifetime of the biomolecules causing this autofluorescence (<<1 ns). The combination of the optimization of the nanoparticles' composition (dopant selection and concentration) together with their emissions in the second biological window has allowed us to obtain deep tissue in vivo autofluorescence free images by developing a simple time-gated set up.

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Opto-Chemical and Laser Properties of a Novel Fluorescent Antiestrogen Derivative and its Potential Applications in Breast Cancer Photodynamic Chemotherapy

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Tamoxifen is the most common antiestrogen used in the chronic treatment of breast cancer. In these cells, it mainly binds to intracellular receptors (estrogen receptor alpha, ER) and antagonizes the binding of its cognate ligand, 17β -estradiol, thereby preventing uncontrolled hormonedependent cellular proliferation and growth. In the last decade, in our laboratories we have developed and characterized different tamoxifen derivatives, including a novel fluorescent tamoxifen conjugate: FLTX1. FLTX1 is formed by the covalent binding of tamoxifen to a common fluorescent biomarker NBD. This new prodrug was originally designed as a fluorescent biomarker to localize intracellular targets, which not only keeps the pharmacological activity of tamoxifen but also adds a luminescent functionality. Strikingly, the quantum efficiency of FLTX1 is so high that laser emission has been obtained as an emerging property. In this presentation, we will show its laser properties under three different configurations. First, as amplified spontaneous emission or mirrorless laser; second, through the evanescent field of WGMs of a ring resonator around an optical fiber; and finally as random laser in uterine tissues impregnated with the prodrug. In consideration of these properties, we have moved a step forward, under the hypothesis that in combination with a photosensitizer, such Rose Bengal (RB), FLTX1 might be used for photodynamic therapy. Under this paradigm, the new complex would act as a sensitizer in ER overexpressing cells (which feature the most prevalent form of hormone-dependent breast cancer). Thus, when optically excited, FLTX1 would transfer its energy to RB, which, in turn, would relax producing reactive oxygen species (ROS) that eventually would induce cell death. The advantage of using FLTX1 to activate RB is the selectivity exhibited by FLTX1 to target cells overexpressing ER, i.e. estrogen-dependent breast cancer cells. This approach would reduce the damage of other non-cancer (healthy) cells or surrounding tissues. We show here the results that confirm efficient energy transfer (FRET) between FLTX1 and RB, and demonstrate the subsequent generation of ROS. Moreover, we have designed a new FLTX1-RB complex covalently bound through a short linker and explored its opto-chemical properties. This is an original cancer therapy strategy that combines the pharmacological properties of tamoxifen and its laser dye features with a highly selective photodynamic therapy.

Acknowledgements. Supported by Research grant SAF2014-61644-EXP from MINECO (Spain).

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Polymetallic Lanthanide Near-infrared Emitting Compounds for Optical Microscopy: Dendrimer Complexes and Metal Organic Frameworks

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Luminescence-based detection possess important advantages for bioanalytical applications and imaging: high sensitivity, versatility and low costs of instrumentation. A common characteristic of biologic analytes is their presence in small quantities among complex matrices, that emit a significant background fluorescence (autofluorescence), limiting detection sensitivity.

The luminescence of lanthanide cations has several complementary advantages over the fluorescence of organic fluorophores and semiconductor nanocrystals, such as sharp emission bands, long luminescence lifetimes and strong resistance to photobleaching. In addition, several lanthanides emit near-infrared (NIR) photons that can cross deeply tissues for non-invasive investigations and that result in improved detection sensitivity.

The main requirement to generate lanthanide emission is to sensitize them with an appropriate chromophore ("antenna effect"). The choice of this antenna allows the tuning of the excitation wavelength of the resulting complexes.

An innovative concept for sensitization of NIR-emitting lanthanides is proposed herein; the current limitation of low quantum yields is compensated by using a large number of lanthanides and by maximizing the absorption of each discrete molecule, thereby increasing the number of emitted photons per unit of volume and the overall sensitivity. We have created several metal-organic frameworks and dendrimer macromolecular complexes and will discuss their designs, synthesis, structures, photophysical properties and applications for NIR biological imaging.

This research is supported through grants from the European Community's Seventh Framework Programmes (ITN Luminet, IEF Dendrimage), l'Agence National de la Recherche, La Ligue Contre le Cancer.

- 1) I. Martinic, S. V. Eliseeva, S. Petoud, J. Lumin. 2017, 189, 19.
- 2) A. Foucault-Collet, K. A. Gogick, K. A. White, S. Villette, A. Pallier, G. Collet, C. Kieda, T. Li, S. J. Geib, N. L. Rosi, S. Petoud, Proc. Natl. Acad. Sci. USA, 2013, 110, 17199.
- 3) A. Foucault-Collet, C. M. Shade, I. Nazarenko, S. Petoud, S. V. Eliseeva, Angew. Chem., 2014, 53, 2927.



Enhanced NIR-I Emission from Water Dispersible NIR-II Dye-Sensitized Core/Active Shell Upconverting Nanoparticles

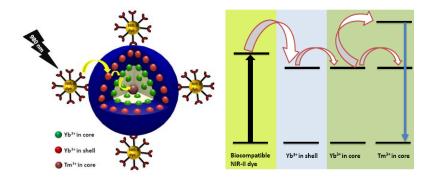
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Recently, there is a surge in the research interest towards near-infrared (NIR) dye-sensitized upconverting nanoparticles (UCNPs) as they can broaden the absorption range as well as enhance the upconversion efficiency of UCNPs [1-3]. Unfortunately, the UCNPs conjugated with the native form of NIR dye limited their scope for biological imaging (in vivo) in the NIR-I or NIR-II window. To overcome this shortcoming, it is essential to employ biocompatible NIR dye (water dispersible) for their use in optogenetic analysis in the NIR tissue optical window. In our work, we achieved a significant enhancement in NIR-I emission (i.e. 800 nm emission of Tm^{3+} ion) from water dispersible NIR-II dye-sensitized core/active shell UCNPs via the doping of ytterbium ions (Yb³⁺) in the UCNP shell, which bridged the energy transfer from the dye to the UCNP core. Practically, in comparison to native form, water dispersible dye along with their biocompatibility, can efficiently harvest irradiation energy, which is nonradiatively transferred to the Yb³⁺ ions in the shell and subsequently Yb³⁺ ions in the core that sensitize Tm^{3+} ions present in the core to generate upconversion luminescence from UCNPs. We envision that our water dispersible NIR-II dye-sensitized core/active shell UCNPs will not only have implications for a broad spectrum of photonic applications but also will pave the way for several biological applications.



[1] W. Q. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov and J. C. Hummelen, Nat. Photonics. 6, 560-564 (2012).

[2] G. Chen, J. Damasco, H. Qiu, W. Shao, T. Y. Ohulchanskyy, R. R. Valiev, X. Wu, G. Han, Y. Ang, C. Yang, H. Årgen and P. N. Prasad, Nano Lett. 15, 7400-7407 (2015).

[3] X. Wu, Y. Zhang, K. Takle, O. Bilsel, Z. Li, H. Lee, Z. Zhang, D. Li, W. Fan, C. Duan, E. M. Chan, C. Lois, Y. Xiang and G. Han, ACS Nano. 10, 1060-1066 (2016).



Trapping in the LiGa₅O₈:Cr infrared emitting persistent phosphor

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In recent years, interest in transition metal-doped persistent phosphors has increased significantly because of their potential for biomedical imaging. Chromium-doped gallates especially, have been studied intensively because of their near-infrared emission, situated in the first tissue-transparency window (between 650 and 950 nm), and long afterglow times¹. Research on Cr-doped nanophosphors has shown that these materials have good chemical stability and low toxicity. However, the mechanism behind the persistent luminescence is still unclear for many of these materials. A better understanding of the trap system should lead to a more targeted tuning of the host to increase the trapping capacity of these phosphors and thus improve their utility for imaging applications.

In this work, we focus on the phosphor LiGa₅O₈:Cr³⁺ (LGO) with emission around 720 nm and outstanding afterglow properties. The afterglow profile of LGO shows an approximate linear t⁻¹ behavior, which has been linked to either a tunneling mechanism or a thermally activated detrapping process from a broad distribution of traps in the host. Via a combination of temperature-dependent charging, afterglow and thermoluminescence measurements, we study the trap distribution and show how this distribution is influenced by the addition of either Si⁴⁺ and Ge⁴⁺ in the host. Both these ions significantly enhance the afterglow time of the LGO phosphor to over 8 hours, before intensity drops below 10^{-3} mW sr⁻¹ m⁻².

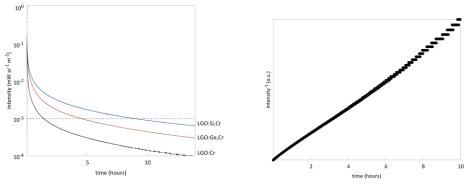


Figure 1: Afterglow curves of $LiGa_5O_8$:Cr, codoped with Si and Ge (left). The t^{-1} behavior of the LGO afterglow, indicating the presence of a broad trap distribution (right).

Zhuang et al., Optical Materials **36** (11), 1907 (2014).

1

Durability analysis of polymeric Eu³⁺ down-shifter on Si-based solar modules under outdoor conditions.

Universidad de La Laguna

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During the last decade, the cost reduction and the improvement on the fabrication technology have risen the importance of the photovoltaic (PV) energy inside of the electrical grids. Therefore, PV has a major acceptance in the society, positioning this industry as one of the lowest-cost options for future electricity generation.

However, the predominant technology, silicon front single junction, is limited by the Shockley– Queisser limits to values below 30% of efficiency. To continue the PV worldwide expansion, the industry needs to forward beyond the standard single-junction solar cells, and offer new cost-effective alternatives.

Different techniques to enhance the External Quantum Efficiency (EQE) in the UV range have been developed during the last years, as down conversion and down-shifting (DS) of UV photons to longer wavelengths in the visible range , where the EQE is closer to 100%, are the most profitable routes to improve the EQE in commercial solar cells.

The outdoor conditions, where the commercial PV module are installed, are a key issue on the reliability and efficiency of DS layer and the total energy conversion processes. Therefore, it is necessary to establish a measurement control in order to obtain accurate solar parameters, their relation with the components, a degradation analysis of the DS layer, and the influence on the behavior of a PV module under outdoor conditions.

In this work, first efficiency results for PV minimodules covered by Eu3+-based DS and tested under extreme outdoor conditions are presented.

OE1

Lanthanide decorated semiconductor quantum dots for use as broadly absorbing downshifters

Universidad de La Laguna

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Feel free to include figures, tables, acknowledgements and references, but please adjust to one page limit. The abstract should be up to a maximum of 300 words. (Font: Calibri, 12pt)

Luminophores with sharp emissions coupled to broad absorptions have many applications including solar energy harvesting and multichannel bioimaging. Lanthanide ions have very sharp, typically ~10 meV FWHM, emissions that are largely insensitive to temperature or surrounding environment. However, lanthanides do not absorb well outside of these transitions, so their ability to act as luminophores is limited. Doping semiconductors with lanthanides has been pursued in thin films, but these systems typically only show luminescence at cryogenic temperatures. Using lanthanide fluorides, it is seen that one can grow an optically active shell around a nanocrystal, and that the nanocrystal will transfer energy to the dopant species. Specifically, Yb is placed around InP, and a narrow emission line at 980 nm is observed with efficiencies as high as 0.5% absolute. This system is explored using optical techniques, electron microscopy, and x-ray characterization methods to show a system with rare earth dopants optically interfaced with semiconductor quantum dots.

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Downconversion enhancement by Ag nanoaggregates in Tb³⁺/Yb³⁺ doped sol-gel glass and glass-ceramic films for solar cell applications

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Please indicate preference: ___Poster _X_ Oral ___ Invited Speaker Specify Technical Area: ___Biomedical _X_ Energy

The frequency conversion properties of rare earth ions may be enhanced by the presence of metal nanoaggregates/nanoparticles. In this presentation, we report the study of down-converting silicazirconia glass and glass-ceramic thin films doped by Tb³⁺/Yb³⁺ ions and Ag nanoaggregates, which combine the spectral properties of rare-earth-doped materials with the optical sensitizing effects of the metal nanostructures. The preparation of sodium-containing silica-zirconia layers was carried out by sol-gel synthesis, followed by thermal treatments at 700°C (glass) or 1000°C (glass-ceramics). Ag introduction was then obtained by ion-exchange in a molten salt bath and the samples were subsequently annealed in air to induce the migration and aggregation of the metal ions. Results of structural, compositional and optical characterization are given, providing evidence for UV-VIS to NIR down-conversion, which could find potential applications to increase the efficiency of Si-based PV solar cells.

Large area tunable visible-to-NIR luminescent solar concentrators based on organic-inorganic hybrids

Universidad de La Laguna

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Please indicate preference: ___Poster x Oral ___ Invited Speaker Specify Technical Area: ___Biomedical __X_ Energy

Luminescent solar concentrators (LSCs) appear as an interesting way to cope with the limitations of commercial photovoltaic (PV) devices, namely the mismatch between its response and the solar spectrum, with the additional advantage of facilitating the integration of PV into the urban environment.^[1-3] Here, it is presented a new geometry for LSCs based on triangular hollow-core plastic optical fibers (POF), filled with organic-inorganic hybrid materials doped with Rhodamine 6G, an Eu³⁺-beta diketonate complex and Rhodamine 800, with ability to absorb the UV and visible components of the solar spectrum and conferring visible and NIR emission to the active layers. The LSCs were coupled to a Si-based commercial photodiode and characterized in terms of the optical conversion efficiency (η_{opt}) and external quantum efficiency (EQE) yielding η_{opt} values up to 1.5 % and an effective relative increase in the EQE of Si-based PV devices exceeding 60 % (for Rhodamine 6G-based LSC). Due to the absence of comparable values reported in the literature for LSCs, we compared it to down-shifting (DS) layers deposited on PV cells surface. The EQE relative increase here reported corresponds to an absolute EQE increase of ~80 % in the 300-400 nm range, which is higher than the ~40 % record value reported for DS layers based on Lumogen 300^[4] and Lumogen yellow^[5] organic dyes dispersed in PMMA deposited on Si and dye-sensitized solar cells, respectively.

References

- [1] W. H. Weber, J. Lambe, *Appl. Optics* **1976**, 15, 2299.
- [2] R. Reisfeld, S. Neuman, *Nature* **1978**, 274, 144.
- [3] M. G. Debije, P. P. C. Verbunt, Adv. Energ. Mater. 2012, 2, 12.
- [4] K. R. McIntosh, G. Lau, J. N. Cotsell, K. Hanton, D. L. Batzner, F. Bettiol, B. S. Richards, *Prog. Photovolt: Res. Appl.* 2009, 17, 191.
- [5] H. Ahmed, S. J. McCormack, J. Doran, Int. J. Spectrosc. **2016**, 2016, 8543475.

OE4

Universidad de La Laguna

Spectral shifts in waxes

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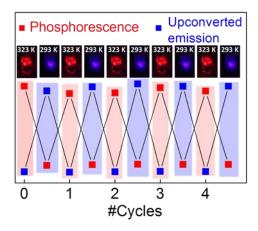
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Phase change materials (PCMs) and waxes are mainly known for their capacity to store and release a large amount of heat during their melting and recrystallization processes.¹ This property, combined with the fact that the phase transition can be reversibly performed several times without inducing chemical degradation, make PCMs promising materials for energy saving insulating coatings in smart buildings. However, the solid-liquid transition of PCMs could be further exploited to modify the absorption or luminescence properties of a dispersed dye, thus providing thermally switchable optical systems. So far, the only well-established example of PCM-based optical switch is given by commercial dye-based thermochromic pigments, in which the solid-liquid transition of an encapsulated acidic PCM induces the reversible development of the color of the pH-sensitive dye dissolved in.²

In this presentation I will overview novel, straightforward and versatile strategies we developed in our group to achieve thermally tunable optical properties based on paraffin waxes. In particular, it will be showed how the solid-liquid transition of these materials was successfully exploited to obtain switchable upconverted and downconverted emission properties of organic molecular dyes.³



- [1] A. Sharma, V. Tyagi, C.R. Chen, D. Buddhi, *En. Rev.* **2009**, *13*, 318–345.
- [2] S. M. Burkinshaw, J. Griffiths, A. D. Towns, J. Mater. Chem. 1998, 8, 2677–2683.

[3] G. Massaro, J. Hernando, D. Ruiz-Molina, C. Roscini, L. Latterini, Chem. Mater. 2016, 28, 738–745.



Highly Luminescent Films as Enhancer of Photovoltaic Devices

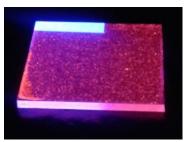
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The most extended Si based conventional photovoltaic cells show low efficiency in the UV region, however this low efficiency can be enhanced by the use of suitable down-shifters or downconverters which transform the wavelength of the incoming radiation into a wavelength for which the Si based cells have high efficiency. In this sense some metal-organic europium(III) luminescent complexes are good candidates for such purposes since they can exhibit large absorption at wavelengths below 400 nm and significant emissions at the VIS range. A simplified version of the sensitized luminescence process of the lanthanideorganic hybrid materials comprises the following steps: i) the



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Fig. 1. Down-shifter layer under 356 nm UV radiation.

transition from the ground singlet state (S_0) to excited singlet states (S_n^*) of the complex molecule which involves the organic ligands, ii) the succeeding intersystem crossing (ISC) to one of its lower energy triplet states iii) the energy transfer to the emissive states of the Ln³⁺ ions and finally iv) the Ln³⁺ emission. One of the key points for the good performance of the Eu(III) complexes resides in the right selection of the organic ligands and in this presentation we will describe the ligands, their features and the synthesis of the complexes for the construction of effective complex species. In particular, phenanthroline and their derivatives are good candidates for such purposes.

In addition to the active species a suitable device for an effective transmission of the converted radiation needs to be developed. In this sense, poly(methylmethacrylate) films doped with the active species have been proved to reach high levels of conversion of the UV radiation and the EQE is increased respect to the photovoltaic device without the active species. In the presentation we will also describe the construction and the performance of the device covered with the downshifter film.

OE6

Shift2017 Spectral sHapIng For biomedical and energy applications November, 13–17, 2017/Tenerife, Canary Islands, Spain.

Up-conversion Thresholds: Describing the Power Dependence of Up-Conversion from Triplet Annihilation Systems to Lanthanide Core-Shell Nanoparticles

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> > Specify Technical Area: Energy

Describing how the up-conversion (UC) emission intensity (and efficiency) varies with the optical power of the excitation is important for understanding and comparing UC materials. To this end, a useful parameter is theUC threshold; it expresses the input optical power required in order for the UC efficiency to approache its maximal value. In this contribution, we discuss the theoretical underpinnings of UC thresholds based on rate equation models and present our recent work on the determination of thresholds via a variety of experimental techniques. We demonstrate how moving beyond the standard steady-state characterization of the power-dependence to time-resolved measurements using square-wave excitation cycles can reveal more information about the UC system and allow a more accurate determination of the UC threshold value. We apply these techniques to a variety of UC systems:

- i) organic triplet-triplet annihilation up-conversion (TTA-UC) solutions,
- ii) lanthanide up-conversion phosphors,
- iii) lanthanide core-shell nanoparticles.

In this way we exemplify how the UC threshold can be a useful figure-of-merit to compare materials not only within a single family but also between different families of materials.

Figure 1. Intensity dependence curves for different emission bands of Yb³⁺, Er³⁺ doped upconverting material

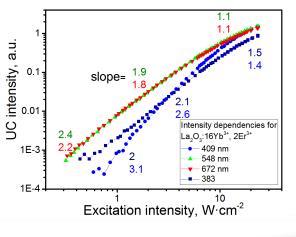
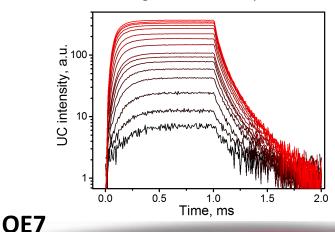


Figure 2. Power dependent temporal profiles of TTA-UC used for estimation of UC threshold based on fitting with the rate equations

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Near-infra-red plasmonic nano structures for upconversion enhancement

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Upconversion is a process by which low-energy photons are converted into high-energy photons. Since a decade, the progress in this field is commendable and significant plasmonically enhanced upconversion of light at wavelengths of 980 and 808 nm have been reported. However, upconversion enhancement of 1500 nm light in rare earth metals using plasmonics is less explored.

Recently we observed a 7 fold enhancement in upconversion of 1500 nm light into 980 nm light in Er³⁺ doped TiO₂ thin-films with geometrically optimized Au nano-discs [1]. A finite-element numerical approach was employed for designing the plasmonic structures [1]. The present paper reports the extension to Au nano-discs buried inside Er^{3+} doped TiO₂ thin films, where even higher upconversion efficiency is expected. In addition, plasmonically enhanced upconversion of 1500 nm light in Er³⁺ doped NaYF₄ nanoparticle-based thin films is investigated. We fabricate thin films of commercial Er³⁺ doped NaYF₄ nanoparticles via drop-cast-assisted spin-coating techniques and are investigating random arrays of Au nanodiscs produced on top via Electron Beam Lithography (EBL). EBL defined nanodiscs of \sim 400 nm diameter and \sim 50 nm height show a surface plasmon resonance (SPR) at the desired 1500 nm wavelength which also validates the numerical outcomes. We have studied the SPR spectral peak position on the layer as a function of the nano-disc size and it exhibits the well-known spectral red shift with increasing nano-disc size. Presently, we are chemically synthesizing our own Er³⁺ doped NaYF₄ nanoparticles and optimizing the structures for efficient upconversion luminescence by introducing appropriate inert-shell thicknesses around the particles by an Ostwald ripening method [2,3]. Therefore, future studies of upconversion enhancement may be carried out on highly efficient home-grown Er³⁺ doped NaYF₄ thin films.

[1] H. Lakhotiya et al., Appl. Phys. Lett. 109, 263102 (2016).

[2] H.-X. Mai et al. J. Phys. Chem. C 111, 13730 (2007).

[3] N. J. J. Johnson et al. J. Am. Chem. Soc. 134, 11068 (2012).

OE8

Shift2017 Spectral sHapIng For biomedical and energy applications November, 13–17, 2017/Tenerife, Canary Islands, Spain.

Universidad de La Laguna

Exploration of REE-bearing mineral resources at the Canary Island Volcanic Province: Gran Canaria Island and neighboring seamounts of Amanay, Banquete, and Conception Bank

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Please indicate preference: ___Poster X Oral ___ Invited Speaker Specify Technical Area: ___Biomedical X Energy

Rare-Earth Elements (REE) show an increasing interest for high-tech industries and interdisciplinary research teams to take advantage of their physical-chemical properties, and thus resulting in a wide variety of new applications, as for instance, in biomedical and energy sciences. In this sense, REEenriched, mineral-based resources can be found at particular locations under specific geological settings. Hence, we explore both subaerial (i.e.: Gran Canaria Island) and submarine (i.e.: Amanay, Banquete, and Conception Bank) materials as potential REE mineral sources from the Canary Island Volcanic Province (CIVP) based on prior literature¹. A set of silica-undersaturated and felsic, alkaline rocks and related soils and paleosols from the Mio-Pliocene, intraplate volcanic island of Gran Canaria was analyzed for geochemical studies, as well as igneous rocks, sedimentary rocks and deep-sea sediments from nearby seamounts. As a result, REE total contents were constrained, in ascending order, as follows: (i) submarine sediments (<60 ppm); (ii) alkaline picrites, basalts, basanite-tephrites of seamounts (<400 ppm); (iii) subaerial Mio-Pliocene, per-alkaline syenites, trachytes, rhyolites, haüyne-phonolites (400-600 ppm) and phonolite-nephelinites (<1000 ppm); (iv) B-horizon and saprolites (1300-1600 ppm); and (v) ferromanganese crusts (1500-2500 ppm). In general, LREEs abundances are higher than HREEs. REE-enrichment is significant for deep-sea ferromanganese crusts and subaerial soils. Positive correlations between REE and Mn-oxides are inferred, thus involving REE mobility by Mn leaching and precipitation as Mn-oxides, but also Caphosphates (e.g.: fluorapatite, brytholite) with granular habits and dendritic textures in soils; as well as by ionic substitutions of Fe-Mn-oxyhydroxides (e.g.: todorokite, goethite) in crusts. This work is financially supported by the Spanish Ministry of Economy and Competitiveness projects ENE2013-47826-C4-1-R and ENE2016-74889-C4-2R.

^{1.} Mangas, J., et al., "Rare earth minerals in carbonatite of Basal Complex of Fuerteventura (Canary Islands, Spain)", in Mineral Deposits: Research and exploration - where do they meet?. Papunen, H. (Ed.), Balkema, Rotterdam, 475-478 (1997).



A bridge over troubled gaps: evidences of up-conversion driven photocatalysis for H₂ generation and organic dye degradation

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The efficient use of energy from the Sun is probably the basic pylon of the necessary and challenging paradigm shift to face the climate change, by means of artificial photosynthesis and solar fuels generation.¹ In this context there is a great interest in harvesting renewable energy from the large near-infrared (NIR) range of the solar spectrum (approx. 50% of the total incoming sun's radiation) for energy and environmental applications, by shifting NIR photons into UV-VIS ones using up-conversion (UC) photonic mechanisms to bridge large gaps of efficient photocatalysts.²

In this work we present peculiarities of high intense UC UV-blue emissions in K₂YbF₅:Tm³⁺ hydrothermal crystals under 980 nm laser excitation, successfully applied to photocatalytic experiments, firstly, aimed at Methylene Blue (MB) degradation activity with TiO₂, and secondly, at hydrogen and oxygen evolution via water-splitting employing Rh-Cr loaded SrTiO₃:Al catalysts.³ We have carried out exhaustive control dark experiments and adsorption measurements, to isolate and assure the real role of UC effect on the activation of photocatalysts by using NIR radiation, as a clear evidence of a pure photonic approach. These results lead the way to promising photocatalytic applications using commercial low-power and cost-effective laser diodes, and moreover, put us one step closer to use the NIR part of the solar spectrum for enhancing solar-driven photocatalytic decontamination and sustainable hydrogen production.

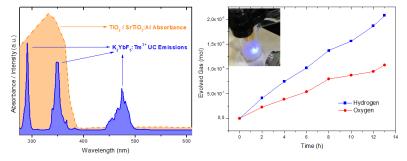


Figure: (Left) High intensity UC emissions clearly above the absorbance range of TiO_2 or Rh-Cr loaded SrTiO₃:Al catalysts; (Right) H₂ – O₂ evolution in water-splitting reactor under NIR-to UV-blue UC emissions from a K₂YbF₅:Tm³⁺ hydrothermal crystals

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Acknowledgements: Authors thank to Spanish Ministry of Economy and Competitiveness under projects ENE2013-47826-C4-1-R and ENE2016-74889-C4-2-R for the support. P. Acosta Mora also thanks to "The University of Tokyo" and "Consejería de Economía, Industria, Comercio y Conocimiento para el apoyo a la actividad de I+D+I, Campus de Excelencia Internacional CEI Canarias-ULL" for the support.

References:

¹ Wondraczek, L., Tyystjärvi, E., Méndez-Ramos, J., Müller, F. A. and Zhang, Q., Adv. Science, 2015, vol 2, Issue 2;

² M.E. Borges, M Sierra, J Méndez-Ramos, P Acosta-Mora, J.C. Ruiz-Morales, P Esparza. Solar Energy Mat. and Solar Cells, 2016, 155, pp.194 - 201;

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³ Y. Ham, T. Hisatomi, Y. Goto, Y. Moriya, Y. Sakata, A. Yamakata, J. Kubota, K. Domen, J. Mater. Chem. A, 2016, 4, 3027-3033.

NIR to Visible Upconversion of composite polymeric aerogels

Universidad de La Laguna

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Please indicate preference: __Poster _x_Oral __ Invited Speaker Specify Technical Area: __Biomedical _x_Energy

Polymeric aerogels have very high porosity that make them interesting for many technological fields, such as thermal and acoustic insulation, catalyst supports, water/air purification and airborne particle filtration.¹ In the present investigation, CaF_2 or SrF_2 nanomaterials doped with lanthanide ions (as Yb³⁺, Er^{3+} or Tm³⁺ ions) with typical particle size around 15-20nm are prepared by an environmental friendly solvothermal technique, using oleate group as capping agent². The obtained nanoparticles (NPs) are incorporated in syndiotactic polystyrene (s-PS) aerogels polymer. The monolithic s-PS/NPs composite aerogels are prepared with a sol-gel process followed by solvent extraction with supercritical CO₂. These NP/s-PS composite aerogels (NPs concentration around 50% wt) have an apparent porosity up to 98% and surface area up to 300 m²/g. The aerogels show a fibrillar morphology with a good dispersion of the NPs within the aerogel macropores. Upconversion properties of the aerogel have been investigated with a NIR infrared laser at 980 nm as the excitation and emission of Er^{3+} ions in the visible (green and red) and near infrared regions has been observed and investigated.

References

1. Daniel, C.; Longo, S.; Ricciardi, R.; Reverchon, E.; Guerra, G., Monolithic nanoporous crystalline aerogels. *Macromol. Rapid Commun.* **2013**, *34* (15), 1194-207.

2. Pedroni, M.; Piccinelli, F.; Passuello, T.; Giarola, M.; Mariotto, G.; Polizzi, S.; Bettinelli, M.; Speghini, A., Lanthanide doped upconverting colloidal CaF_2 nanoparticles prepared by a single-step hydrothermal method: toward efficient materials with near infrared-to-near infrared upconversion emission. *Nanoscale* **2011**, *3* (4), 1456-1460.

OE12

Crystal structure and chemical interfaces in core@shell upconverting nanocrystals: there is still plenty of room.

Universidad de La Laguna

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Please indicate preference: Oral Specify Technical Area: Energy

Core@shell design represents an important class of upconverting architectures because of its capability to dramatically increase the absolute upconversion quantum yield (UCQY) of upconverting nanocrystals (UCNCs) but also to tune energy migration pathways. Despite that, very little is known regarding the chemical and structural characteristics of lanthanide-doped core@shell (single- or multi-shell) UCNCs. Indeed, the formation of core@shell nanoarchitectures with sharp chemical interfaces grown by epitaxy is still considered as being obvious. Nevertheless, recent publications on the correlation between absolute UCQY and the thickness of the protecting shell on one hand [Nano Lett. 2016, 16, 7241] and the absence of concentration quenching in heavily "doped" core@shell UCNCs on the other hand [J. Am. Chem. Soc. 2017, 139, 3275] question the whole core@shell decoupling theory that has been proposed until now. In this presentation, we will discuss our investigations based on local chemical analyses and in depth structural characterizations that led to a new crystallochemical model to describe core@shell UCNCs (Fig. 1). The model considerably digresses from the commonly accepted epitaxial growth concept with sharp chemical interfaces. Indeed, the formation of a non-homogeneous solid solution characterized by both chemical concentration gradients (Fig. 1b) and the continuous modification of cell parameters (Fig. 1c) must be considered instead. The optical consequences of the newly proposed crystallochemical model of core@shell UCNCs will be discussed based on recently published data. The UC community is facing a major challenge regarding the "structure – property" relationship and the rational design of complex upconverting nanoarchitectures. Our results pave the way towards the comprehensive understanding of upconversion properties in core@shell UCNCs. Because of their massive use both in the biomedical and energy fields, the presentation will be of major interest to the whole upconversion community.

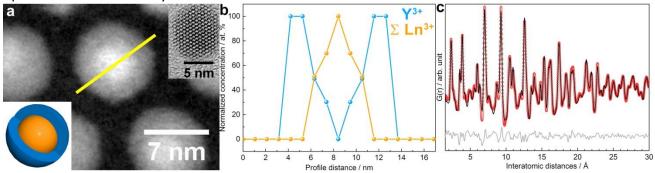


Figure 1. a) NaGdF₄:Yb:Er@NaYF₄ core-shell upconverting nanocrystals, b) space-dependent chemical analysis (yellow line in Fig. 1a) with Σ Ln=Gd+Yb+Er, and c) the corresponding structural characterization from which a new crystallochemical model was extracted to describe core@shell upconverting nanocrystals.



Room temperature synthesis and luminescence of β -NaGdF₄: Eu³⁺, Er³⁺, and Yb³⁺, Er³⁺ nanocrystals

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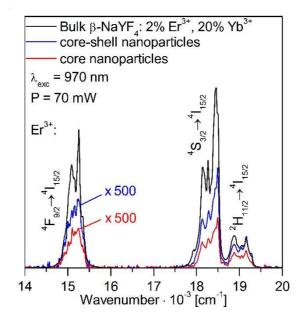
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Please indicate preference: ___Poster X Oral ___ Invited Speaker Specify Technical Area: ___Biomedical X Energy

Phase pure hexagonal β -NaGdF₄: Eu³⁺, Er³⁺ samples of less than 10 nm particle size were synthesized in ethylene glycol within 24 hours at room temperature. The materials were characterized by powder X-ray diffraction, electron microscopy, and luminescence spectroscopy. The luminescence and energy transfer between Gd³⁺, Eu³⁺, and Er³⁺ ions were investigated upon UV excitation.

 β -NaGdF₄: Yb³⁺, Er³⁺ nanoparticles were prepared by microwave heating in ethylene glycol and ionic liquid mixtures. The synthesis was optimized for green Er³⁺ upconversion emission under 970 nm excitation. Solvent composition, water content, core/shell structure, and reaction temperature were identified as key parameters for material synthesis. 10 nm core/shell particles achieved more than 1/1000 of bulk material upconversion intensity, see the Figure.



OE14

Enhanced Ln³⁺ Ions Luminescence from Ln³⁺-Doped Nanocrystals via Sensitization and Its Application in Silicon Solar Cell

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Specify Technical Area: Energy

Lanthanides (Ln³⁺) ions-doped materials have unique properties like sharp luminescence arising from downconversion/upconversion, longer lifetimes, large Stokes shift, etc. These properties of Ln³⁺-doped materials find various applications such as developing optoelectronic devices, lasers, bio imaging, solar cell, etc. However, one of the limitations of the Ln³⁺ ions is their low absorption coefficient resulting in low luminescence quantum yield (QY). Our strategy is to improve QY of Ln³⁺doped materials via sensitization.¹ Our first approach is to utilize suitable organic ligands as capping agent and sensitizer. This is achieved by attaching 4,4,4-trifluoro-1-phenyl-1,3 butanedione (TPB) to the surface of Eu³⁺-doped LiYF₄ nanocrystals (NCs). The strong absorbance and energy level overlap of TPB ligands with Eu³⁺ ions resulted in efficient energy transfer from TBP ligands to Eu³⁺ ions. The broadband ultraviolet excitation and intense red emission of Eu³⁺ ions have been explored for the enhancement of solar cell efficiency.² A ~9 % relative enahncement of photocurrent is noted upon UV excitation. In another approach, Eu³⁺ ions were sensitized using carbon dots (C-dots) in Eu³⁺doped LaF₃-C dots nanocomposites.³ This C-dots have high absorbance in ultraviolet (UV) region. Upon UV excitation, C-dots emit in the range of 370 nm to 500 nm and efficiently transfer energy to Eu³⁺ ions. This energy transfer via C-dots leads to the broadband excitation of Eu³⁺ ions can have potential use in phosphor based LEDs or solar cell.

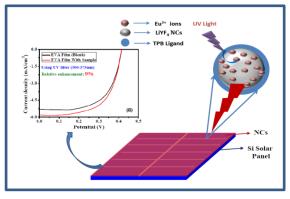


Fig. Schematic representation of enhancement of the Si solar cell photocurrent of using TPB capped Eu³⁺ doped LiYF₄ NCs.

[1] J. C. G. Buenzli and C. Piguet, Chem. Soc. Rev., 2005, 34, 1048.

[2] Carlos, L. D.; Sá Ferreira, R. A.; Rainho, J. P.; Bermudez, V. de Zea, Adv. Func. Mater., 2002, 12, 819.

[3] T. Samanta, C. Hazra, V. Mahalingam, New J. Chem., 2015, 39, 106.



Universidad de La Laguna

UV and temperature-sensing based on NaGdF₄:Yb³⁺:Er³⁺@SiO₂-Eu(tta)₃ nanoparticles

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A multifunctional nanosystem was synthesized to be applied as a dual-sensor of UV-light and temperature NaGdF₄:Yb³⁺:Er³⁺ upconverting nanoparticles (UCNPs) were synthesized and coated with a silica shell to which a europium(III) complex was incorporated. The synthesis of NaGdF₄ UCNPs was performed via thermal decomposition of lanthanide ion fluoride precursors in the presence of oleic acid. In order to achieve sufficient water dispersibility, the surface of hydrophobic oleate-capped UCNPs in the hexagonal phase was modified by a silica coating through a modified Stöber process by a reverse micro-emulsion method. Eu(tta)₃ (tta-thenoyltrifluoroacetonate) complex was prepared in situ at the silica shell. A dual-mode nanothermometer was obtained from a NIR to visible upconversion fluorescence signal of Er³⁺ ions together with UV excited down-shifting emission from Eu³⁺ complex. Measurements were performed near the physiological temperature range (293-323 K) revealing excellent linearity ($R^2 > 0.99$) and relatively high thermal sensitivities $(\geq 1.5 \% \cdot K^{-1})$. The Eu(tta)₃ complex present in the silica shell was tested as UV sensor due to the Eu³⁺ luminescence dependence on UV-light exposure time with no influence on the thermometer operation based on the upconversion emission. The material shows potential for application in lightactivated therapies, such as photodynamic therapy (PDT) and photothermal therapy (PTT) to control the light and thermal doses.

Reference: K. Nigoghossian, Y. Messaddeq, D. Boudreau, S. J. L. Ribeiro, ACS Omega, 2, 2065–2071, (2017).

Acknowledgements

This study was supported by the Brazilians agencies Fapesp, CAPES and CNPq (process numbers 99999.010867/2014-07 and 141253/2014-2); Natural Sciences and Engineering Research Council of Canada; and Fonds de recherche du Québec - Nature et Technologies.



Spectroscopic properties of YAG:Mn,Nd nanocrystals as a new luminescent thermometer

Universidad de La Laguna

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Luminescent thermometers have found a lot of interest due to application in integrated photonic devices, micro/nano-electronics and potential application in biomedical field¹ ^[1]. So far, several approaches for temperature sensing, exploiting different optically active ions, have been presented but their main drawback was unsatisfying sensitivity. Recently new generation of thermometers based on lanthanides and transition metals have gained attention^{2,3}. Luminescent thermometer based on highly temperature dependent d-d Cr³⁺ transitions being normalized to barely temperature dependent f-f Nd³⁺ transitions allowed to get sensitivity as high as 4.89%/°C in the physiological temperature range. Here, a new type of luminescent thermometer based on manganese and neodymium ions is proposed. A series of Y_{3-x}Nd_xAl_{5-y}Mn_yO₁₂ (where x=0.01 and y=0.001, 0.005, 0.01 and 0.02) nanocrystals was synthesized using modified Pechini's method. Their suitability for non-contact temperature sensing was investigated as a function of Mn and Nd concentrations as well as grain size.

Acknowledgements

The "High sensitive thermal imaging for biomedical and microelectronic application" project is carried out within the First Team programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.

References

- 1. D. Jaque, F. Vetrone, Nanoscale 4 (2012) 4301-4326
- 2. L. Marciniak, A. Bednarkiewicz, D. Kowalska, W. Strek, J Mater Chem C, 4 (2016) 5559-5563.
- 3. L. Marciniak, A. Bednarkiewicz, J. Drabik, K. Trejgis, W. Strek, Phys Chem Chem Phys 19 (2017) 7343-7351.

PB2



The influence of grain size and dopant concentration on the spectroscopic properties of YAG: V³⁺, Eu³⁺ nanocrystalline luminescent thermometers

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As it was recently shown, that transition metal ions, due to their strongly temperature-dependent optical properties, can be interesting alternative to lanthanide ions in temperature sensing applications¹. Luminescence thermometry exploits the relationship between temperature and luminescence properties, which gives thermal representation of light generating objects². Based on the first promising results of luminescent YAG:Cr³⁺,Nd³⁺ thermometer ³, new luminescent nanomaterial YAG:V³⁺,Eu³⁺ was successfully obtained and evaluated. This is the first study where vanadium was applied for luminescent thermometry. As it is well known thermal stability of emission intensity of transition metal ions is strongly dependent on the dopant concentration, grain size of nanocrystals as well as local ion's chemical environment. Therefore detailed analysis of the impact of these parameters on the sensitivity of YAG:V³⁺,Eu³⁺ nanocrystalline luminescent thermometers will be investigated.

Acknowledgements

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References

- 1. L. Marciniak, A. Bednarkiewicz, D. Kowalska, W. Strek, J Mater Chem C, 4 (2016) 5559-5563.
- 2. D. Jaque, F. Vetrone, Nanoscale 4 (2012) 4301-4326
- 3. L. Marciniak, A. Bednarkiewicz, J. Drabik, K. Trejgis, W. Strek, *Phys Chem Chem Phys* 19 (2017) 7343-7351.





The influence of structural changes in Y₃Al_{5-x}Ga_xO₁₂ on the sensitivity of Cr³⁺ based luminescent nanothermometers

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Poster Biomedical

Luminescent nanothermometers are promising research tool in some scientific disciplines like biomedical engineering, micro/nano-electronics or photonics¹. Among aforementioned applications one of the most significant importance is biomedical, because luminescent thermometry can be a powerful tool for remote analysis of cellular metabolism or can be a source of feedback information for hyperthermia of cancers²⁻⁴. To be useful, such luminescent thermometers must assure sufficient sensitivity, high brightness and should operate in optical transparency window of biological tissues. Up to now a few luminescent thermometers which fulfill these requirements were proposed, mainly based on lanthanide ions' emission⁵⁻⁹. Recently a new approach for temperature sensing based on temperature dependent luminescence intensity of transition metal ions was demonstrated, which can be especially attractive for biomedical applications due to its high sensitivity, spectral compatibility with tissues and high brigtness¹⁰. It is known that changes in host matrix structure of optical active ions could affect thermal stability of emission intensity. Therefore, the purpose of this work is to optimize the sensitivity of Y₃Al_{5-x}Ga_xO₁₂: Cr³⁺ nanocrystalline luminescent thermometer through local ion's chemical environment modification.

Acknowledgements

The "High sensitive thermal imaging for biomedical and microelectronic application" project is carried out within the First Team programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.

References

1 D.Jaque ; Vetrone, F., Nanoscale, 4 (2012) 4301-4326

2 H. Huang, S. Delikanli, H. Zeng, D. M. Ferkey and A. Pralle, Nature Nanotechnology, 5 (2010) 602-606

3 D. Jaque, L. Martinez Maestro, B. del Rosal, P. Haro-Gonzalez, A. Benayas, J. L. Plaza, E. Martin Rodriguez and J. Garcia Sole, Nanoscale, 6 (2014) 9494-9530

4 C. F. Chapman, Y. Liu, G. J. Sonek and B. J. Tromberg, Photochemistry and Photobiology, 65 (1995) 416-425

5 D. Wawrzynczyk, A. Bednarkiewicz, M. Nyk, W. Strek and M. Samoc, Nanoscale, 4 (2012) 6959-6961

6 A. Benayas, B. del Rosal, A. Pérez-Delgado, K. Santacruz-Gómez, D. Jaque, G. A. Hirata and F. Vetrone, Advanced Optical Materials, 3 (2015) 687-694

7 S. Balabhadra, M. L. Debasu, C. D. S. Brites, L. A. O. Nunes, O. L. Malta, J. Rocha, M. Bettinelli and L. D. Carlos, *Nanoscale*, 7 (2015) 17261-17267

8 L. Marciniak, K. Prorok, L. Frances-Soriano, J. Perez-Prieto and A. Bednarkiewicz, Nanoscale, 8 (2016) 5037-5042

9 E. C. Ximendes, W. Q. Santos, U. Rocha, U. K. Kagola, F. Sanz-Rodríguez, N. Fernández, A. d. S. Gouveia-Neto, D. Bravo, A. M. Domingo, B. del Rosal, C. D. S. Brites, L. D. Carlos, D. Jaque and C. Jacinto, *Nano Letters*, 16 (2016) 1695-1703

10 L. Marciniak, A. Bednarkiewicz, D. Kowalska, W. Strek, J Mater Chem C, 4 (2016) 5559-5563





LaAlO₃: Mn⁴⁺ as near-infrared emitting persistent luminescent phosphor for medical imaging

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The applications of persistent phosphors have traditionally been limited to toys, emergency illumination and security signs. However, the development of near-infrared emitting persistent phosphors with bright luminescence and long afterglow properties has attracted much attention for application to in vivo bio-imaging systems or medical imaging^{[1][2]}.

In the present work, manganese doped perovskite lanthanide aluminates (LaAlO₃) were synthesized and the persistent luminescent behavior was optimized. In order to improve the near-infrared intensities of persistent luminescence from LaAlO₃: Mn⁴⁺ phosphors, a series of samples were prepared by solid state reaction in air through doping with a variety of ions with different valence states at 1550 °C. The doping effects and their possible mechanisms were investigated. The afterglow of this material is strongly improved by co-doping with ions with a lower valence state, leading to charge compensation.

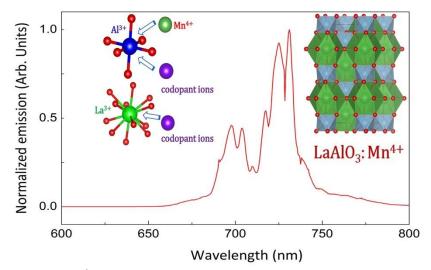


Figure 1. LaAlO₃: Mn⁴⁺ as near-infrared emitting persistent luminescent phosphor

Reference

de Chermont, Q. I. M. *et al.* Nanoprobes with near-infrared persistent luminescence for in vivo imaging. *Proceedings of the National Academy of Sciences* **104**, 9266-9271 (2007).
 Pan, Z., Lu, Y.-Y. & Liu, F. Sunlight-activated long-persistent luminescence in the near-infrared

from Cr³⁺-doped zinc gallogermanates. Nature materials **11**, 58-63 (2012).



Technological Challenges for the Optical Physics in the Diabetes-Related Lower Extremity Disease

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Diabetes is a chronic disease in which the body does not manage well the insulin and elevated levels of glucose in the blood and urine are produced. This is one of the diseases that most affects the developed countries and that first appears in the countries that are growing economically. The diabetes-related lower extremity disease is a well-known complication of long-standing diabetes, and it is the leading cause of non-traumatic limb amputations worldwide [1].

In this work we propose, from the optical physics and signal processing point of view, new technological challenging methods that contribute to the medical treatment of this disease; one of the most frequent disorders in Canary Islands.

We approach the whole problem, presenting proposals for both: diagnosis, with home and hospital service applications for patients; and therapy, focused on endovascular surgery for avoiding amputations. Then, for the early detection of the disease, we are working on a non-invasive device for acquiring and processing the thermographic images, using the appropriate sensors and algorithms. This device will allow to measure the gradient of temperature in the foot and will detect the disease before skin complications appear. A low cost solution is proposed using a smartphone device, and a more sophisticated and powerful device is proposed, under the same physical idea, for the hospital service.

On the other hand, in case that the disease appears, we propose a new model for the typical implant used in endovascular surgery: a stent. Our proposal tries to define some features that could be added to this implant in order to have a more customized and physician-controlled therapy. In our model/idea of this stent, the optical physics and nanotechnologies approaches could be used. It would include an external control of the implant, based on the response of the material to changes of temperature or any other physical property, for managing the drugs release or reloading it. Also, an induced current could be used to produce an electrolytic effect that avoids the hyperplasia. In case the stent should be removed, it would be useful to have a design that take into account the properties of the material used for its manufacturing, to allow fold and magnetic retrieval on a wire-based tool.

[1] J. Aragón-Sánchez, A. García-Rojas, J.L. Lázaro-Martinez, Y. Quintana-Marrero, M. Maynar, M. Rabellino, M.J. Hernández-Herrero, J.J. Cabrera-Galván. Epidemiology of diabetes-related lower extremity amputations in Gran Canaria, Canary Islands (Spain), Diabetes Research and Clinical Practice, Volume 86, Issue 1, October 2009, Pages e6-e8.

Heterogeneously Nd³⁺ Doped Single Nanoparticles for NIR-induced Heat Conversion, Luminescence, and Thermometry

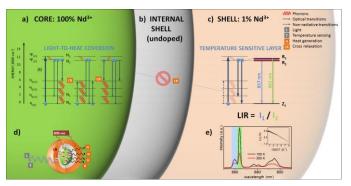
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Intentional design and fabrication of nanoparticles with desirable morphology and composition, with multiple functionalities have emerged over the last couple of years as a very active field of research. This can be achieved by synthesis core–(multi)shell heterogeneous nanoparticles. This approach provides new opportunities in searching for new properties and broadening functionalities, which are neither present or available in bulk materials or homogenous nanoparticle counterparts. Proper design and selection of composition allows to obtain multifunctional tools e.g. ones combining magnetic and optical properties^[1,2], displaying multicolor volumetric images^[3] or broadened a remote temperature range readout with two thermometers within single nanoparticle^[4].

In this work we show that the coreshell design of Nd³⁺ doped heterogeneous nanoparticles already allows three optical functions, namely efficient (η >72%) light-toheat conversion, bright NIR emission, and sensitive (S_R>0.1 %/K) localized temperature quantification, to be built within a single c.a. 25 nm nanoparticle^[5]. In order to understand how core-shell architecture affects optical properties of NaYF₄:Nd³⁺ structures, the following four monodispersed samples have been synthesized: NaNdF₄, NaYF₄:1%Nd @ NaYF₄, NaNdF₄ @ NaYF₄:1%Nd and NaNdF₄@



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Figure 1. Schematic design of 100Nd@Y@1Nd as single nanoparticles (d) combing all antithetical features of high efficiency in light-to-heat conversion (H), high luminescence efficiency (L) and high sensitivity in temperature sensing (T)^[5].

 $NaYF_4 @ 1\%Nd^{3+}:NaYF_4$, and fully structurally (XRD) morphologically (TEM, maps of compositions) and spectroscopically (emission spectra, decay curves, quantum efficiencies) analyzed. Moreover with the aid of thermovision camera, we quantified the amount of light-converted heats in chloroform colloidal solutions of different designs of nanoparticles (20 mg/ml) and estimate the efficiency of this conversion.

[5] L. Marciniak, A. Pilch, S. Arabasz, D. Jin, A. Bednarkiewicz, Nanoscale 2017, 9, 8288-8297.



^[1] Z. C. Xu, Y. L. Hou and S. H. Sun, Journal of the American Chemical Society, 2007, 129, 8698-8699

^[2] V. Salgueirino-Maceira, M. A. Correa-Duarte, M. Spasova, L. M. Liz-Marzan and M. Farle, Advanced Functional Materials, 2006, 16, 509-514.

^[3] R. R. Deng, F. Qin, R. F. Chen, W. Huang, M. H. Hong and X. G. Liu, *Nature Nanotechnology*, 2015, **10**, 237-242

^[4] L. Marciniak, K. Prorok, L. Frances-Soriano, J. Perez-Prieto and A. Bednarkiewicz, *Nanoscale*, 2016, **8**, 5037-5042.



Upconversion nanoparticle labeling of EGFR using click chemistry and three-dimensional live-cell imaging

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Please indicate preference: _O_Poster __ Oral __ Invited Speaker

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Fluorescence imaging enables visualization of the biomolecules in living cells and is widely applied to basic biological research, diagnosis and therapy. Lanthanide-doped upconversion nanoparticles (UCNPs) exhibit superior performance to conventional fluorescent dyes for long-term living cell imaging due to minimized autofluorescence and good photostability such as non-photobleaching and non-photoblinking nature. As for the usage of UCNPs for targeting and delivery, it remains challenging to achieve high selectivity. We report on a click labeling technique for better targeting ability of UCNPs to the extracellular domains of epidermal growth factor receptor (EGFR). The alkyne conjugated UCNPs were used to target the azide group present in the unnatural amino acids (UAAs) in EGFR. This approach enables precise targeting and long-term real-time imaging in living cells. It is expected that this technique will be useful for imaging the delivery of the drug and their interaction with organelles at the cellular level.



Cooperative bidirectional motion of motor proteins revealed at the single particle level

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Specify Technical Area: _O_Biomedical __ Energy

The motor proteins (kinesins and dyneins) transport the internalized material along the microtubule (MT). While endosomes transports undergo both anterograde and retrograde motions, the detailed transport mechanisms in the living cells are yet to be known. Here we report our finding that the MT-mediated transports by kinesins and dyneins are achieved cooperatively in SH-SY5Y neuroblastoma cells. We performed multiplexed long-term particle tracking by using upconverting nanoparticles (UCNPs) by covering 500 nm along Z-axis. The inhibition of cytoplasmic dyneins by erythro-9-[3-(2-hydroxynonyl)] adenine (EHNA) deactivates intracellular transport in both directions, which cannot be explained by the tug of war mechanism. Furthermore, we demonstrated that the transports were composed of four modes with different speeds. The speed modes exhibited a symmetrical distribution with respect to two opposite directions. In addition, the transitions between distinct modes were observed during the transports.



Distinct Mechanisms for The Upconversion of NaYF4:Yb³⁺,Er³⁺ Nanoparticles Revealed by Stimulated Emission Depletion

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Lanthanide-doped upconversion nanoparticles (UCNPs) have been regarded as the nanomaterials for various applications such as biosensing probe, drug delivery system (DDS), and solar cells due to their intrinsic optical properties and photostability. Especially, upconversion process in UCNP (NaYF₄:Yb³⁺,Er³⁺/NaYF₄), which emits in the visible range under NIR irradiation, provides biomedical imaging field with a lot of advantages. Additionally, the development of super-resolution microscopy enabled to overcome diffraction limit, which is the fundamental optical property. We found that the red emission (655 nm) in UCNPs was depleted by 1540-nm emission depletion(ED) beam, while the green emission (525 and 545 nm) was affected rarely in both single particle level and colloidal solution. In our research, we report the distinct depletion behavior between the green and the red emission originate from different photophysical pathways. Moreover, this photoswitching effect by ED beam for red emission can lead to possibility of UCNPs as imaging probe in stimulated emission depletion (STED) microscope.

Multiplexed 3D Tracking of Single Upconversion Nanoparticles (UCNPs) in Living Cells

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Lanthanide-doped upconversion nanoparticles (UCNPs) are useful probes for three-dimensional (3D) single-particle tracking in living cells because of a number of advantages such as photo-stability (no photoblinking and no photobleaching), minimized cellular autofluorescence and low level of photo-damage to cells by the near-infrared excitation. Recently, we took the advantages of UCNPs for 3D real-time imaging (Jo et al, Nanoscale 2015, 7, 19397). In our previous research, all section images were acquired by wide-field epi-fluorescence microscopy, and then ~15 section images were piled up to make one 3D image which illustrates the distribution of single UCNPs in the living cell. One 3D image took ~1 second to be obtained and sets of such images were combined and analyzed as a function of time to produce a movie. The drawbacks of our previous approach were: (1) the software allowed tracking only one trajectory where there are tens of trajectories, and (2) the zpositions of the particles determined by Gaussian fitting exhibited artifacts due to the backlash of the stepping motor used for scanning the objective positions. Here, we will report the advanced methods for 3D live cell imaging and novel biological findings that have not been observable by previous methods. In doing so, we were able to (1) obtain section images with accurate z-positions by introducing piezo-electric mount for the objective, and (2) analyze multiplexed trajectories for ~10 particles transported simultaneously in HeLa cells. For drug deliveries, gene deliveries, and others, cellular uptake and nucleus uptake of nanoparticles are important factors. Through the three types of UCNPs, we will discuss the relationships among the surface charges of UCNPs, uptake rates, and their motions.

Lanthanide doped Upconversion Nanoparticles for Biological Applications Suman Devi^{1, 2}, M. Niraj Luwang^{1, 2*}

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Non-linear phenomenon of luminescent upconversion via lanthanides doped fluoride host matrix have gained tremendous research interest in past decades due to its fascinating photo-physical properties like absorption in biological window(i.e., 700-1000 nm), anti-stroke shift, non-invasive to biological tissues, reduced auto-fluorescence and deep penetration depth. Hence, makes their wide application in biomedical like bioimaging, biodetection, theranostics and immunological assay etc. When lanthanide doped nanoparticles are prepared, with decrease in particle size upconversion emission decreases and possess low quantum efficiency, concentration quenching. Defects and ligands acts as quenchers in excited rare earth ions resulting in low upconversion efficiency which in turn hinders their real time application. Thus enhanced upconversion emission without hindering other properties is challenging. Enhancement in upconversion efficiency can be attained by engineered nanoparticles in few ways i) tailoring the local symmetry of luminescence center ii) Surface passivation by core shell iii) plasmonic enhancement by coating with noble metals.

In this present work we report detailed investigation of structural and optical properties of alkali metal doped BaYF₅: $Ln^{3+}(Ln^{3+} = Yb^{3+}, Er^{3+}/Tm^{3+}/Ho^{3+})$ upconversion nanoparticles synthesized by coprecipitation method. Upconversion photoluminescence have been examined by exciting at 980 nm laser. As shown in Figure 1 doping of alkali earth at cationic site has no impact on crystal structure as no impurity peaks were observed but plays crucial role in crystalline size and upconversion emission as shown in Figure 2. With increasing alkali doping enhancement in upconversion efficiency has been observed which may be ascribed to distortion of local symmetry of luminescence centre. The enhanced upconversion efficiency can find its real time biological application.

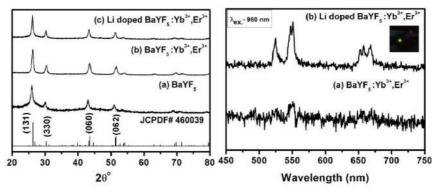


Fig. 1 shows powder XRD pattern of with and without alkali metal doped $BaYF_5{:}Yb^{3+}, Er^{3+}$

Fig.2 Shows upconversion with and without alkali metal doped $BaYF_{5}$: $Yb^{3\ast}, Er^{3\ast}$

Reference:

1. Chen et al., Chemical reviews 2014, 114(10), 5161-5214.

2. Zhao et al., Nanoscale 2013, 5(17), 8084-8089.

Acknowledgement: Grateful to CSIR, India, for providing Senior Research Fellowship

Nd³⁺-sensitized up-conversion emission in GdVO₄:Er³⁺ and GdVO₄:Ho³⁺ nanoparticles

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Considerable efforts have been made to prepare up-converting nanoparticles (UCNPs) which absorb radiation in the near infrared region (NIR). Until recently, diode lasers at 980 nm have been commonly applied as optical pump sources in the NIR. However, these light sources show serious deficiencies in biomedical applications. Light penetration into a biological tissue is low, while water strongly absorbs at about 1000 nm and quickly heats up. It is therefore essential to overcome the tissue overheating and the limited tissue penetration depth. Hence, the latest trend in the UCNPs research is to employ sources at 808 nm. At this wavelength, light penetrates deeper and water slightly absorbs and slowly heats up. In order to enable absorption at 808 nm, Yb³⁺ ions have been first replaced by suitable organic colors; nowadays, Nd³⁺ ions, showing main absorption maximum at 808 nm, have been utilized. Herein, Nd³⁺ ions were used to serve as a primary sensitizer, taking over the role of Yb³⁺ ions in a typical sensitizer/activator UCNPs system. The Nd³⁺-sensitized GdVO₄:Er³⁺ and GdVO₄:Ho³⁺ UCNPs were synthesized using a high temperature solid-state reaction technique. The amount of Ho³⁺, Er³⁺ and Nd³⁺ ions was optimized to be 1 mol%. The excitation wavelength was successfully tuned at 808 nm. The two strong characteristic fluorescence bands as well as one weaker band correspond to transitions of Er^{3+} ions; respectively, they are centered at 523 nm ($^{2}H_{11/2}$ \rightarrow ⁴I₁₅), 552 nm (⁴S_{3/2} \rightarrow ⁴I_{15/2}) and 658 nm (⁴F_{9/2} \rightarrow ⁴I_{15/2}). The fluorescence bands centered at 649 and 543 nm correspond to ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ and ${}^{5}F_{4}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ transitions of Ho³⁺ ions. It is important to point out that the fluorescence intensity is bright enough in both samples.

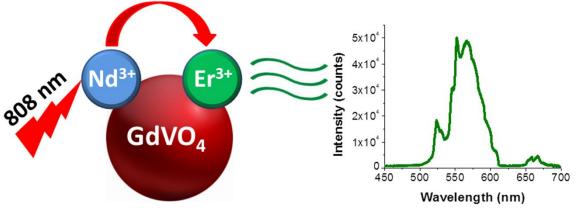


Figure 1. UC mechanism and a spectrum of $GdVO_4$: Er^{3+}/Nd^{3+} UCNPs excited at 808 nm.

Acknowledgments I gratefully acknowledge the COST conference grant (Action CM1403) partially supporting my attendce at this conference. This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects no 45020 and 172056).

Rare Earth doped Nanostructured Apatites for Theranostic Applications

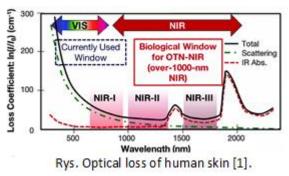
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Recently, nanomaterials doped with lanthanide (Ln³⁺) ions have been gained attention of many areas, including biology and medicine because of their unique spectroscopic properties, such as narrow emission bands, large anti-Stokes shifts and resistance to photobleaching. If the appropriate

Ln³⁺ dopants (e.g. Yb³⁺/Er³⁺) are selected, it is possible to convert of near infrared (NIR) radiation to visible light, what makes such doped nanocrystals a good alternative both for quantum dots and organic fluorescent dyes. Moreover, the emission and excitation of the up-converting nanoparticles is held in the optical window of biological tissues to minimize the overheating effect from the excitation irradiation at 980 nm the biological markers (Rys.)[1].



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The apatites- calcium phosphate based bioceramics have been used as a matrix for upconverting Ln³⁺ ions for possible theranostic applications (therapy and diagnosis). The nanosized apatites are the most efficient materials for being used in bone repair processes in comparison with the microsized compounds. They can stimulate the tissue regeneration process at the bone or implant interface due to high biocompatibility with hard tissues [2]. Thanks to the properties of incorporation the up-converting ions, the apatites could be additionally used for a real-time monitoring of treatment effect after bone surgery [3].

The nanoapatites doped with the up-converting rare earth ions have been prepared using wet chemistry method. The structural properties and morphology of the particles have been studied by means of XRD, TEM and SEM techniques. The spectroscopic properties of obtained materials have been investigated in detail using emission spectra, power dependence and emission kinetics. The achieved results open the possibilities of application the proposed materials in theranostic.

References:

[1] F. Vetrone et al., Nanoscale Horiz., 1 (2016) 168-184

[2] R. J. Wiglusz et al., Mater. Sci. Eng.C, 69 (2016) 17-26

[3] R. J. Wiglusz et al., RSC Advances, 7 (2017) 30086-30095



Upconversion ratiometric thermometer based on Nd³⁺ excited state absorption

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Temperature is a fundamental physical quantity, the measure of which is of great interest in many scientific and technology fields. Most of the sensors used nowadays need direct contact to properly measure the temperature, therefore are ineffective for sub-micrometric measurements needed in fields of nanomedicine or semiconductor industry. To overcome this intrinsic limit of traditional thermometry, great effort is spent in development of luminescent thermometers.

In this contribution, we report a new ratiometric method to measure temperature from the Tm^{3+} upconversion in core-shell KY₃F₁₀ based nanoparticles. The Tm^{3+} ion is excited by a cascade of energy transfer processes from an active core codoped with Nd³⁺ and Yb³⁺ and an active shell codoped with Yb³⁺ and Tm³⁺. The thermometric parameter is defined as the ratio between emission intensities of Tm³⁺ ions for different excitation energies, exploiting the Stark levels of Nd³⁺ ions. The same system can be useful as nanothermometer exploiting the Stokes emissions of Yb³⁺. Preliminary results indicate that nanothermometry on the upconversion emission is interesting for its high sensitivity.





Phosphate doped with lanthanide ions embedded into polylactic acid composite – spectroscopic properties

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Regenerative medicine comes in many forms promising to develop new biomedical treatments for the people that suffering due to burden of trauma, congenital defects and degenerative diseases. Recently, the biggest effort has been put in seeking materials that could help and accelerate the regenerative process by stimulating the body's own repair mechanisms to functionally heal previously irreparable tissues or organs. Nowadays, the materials broadly using in medicine with great biological properties are calcium phosphates and polylactic acids.

The calcium phosphates occur into the human bodies, among others they are biocompatible, bioactive and are able to form a chemical bond with the living tissue¹. L-lactic acid is presented in the metabolism of all animals and microorganisms, and hence, it is non-toxic for the human beings. The biocompatible and biodegrable poly(L-lactic) acid (PLA) can enhance the adhesion and elasticity of the composite materials, therefore is broadly used to surgical suture, implants, screws and as carriers in drug delivery systems. Among the fillers, the phosphates are particularly important because are the main component of the vertebrate bones. Moreover, it is relatively simple to obtain and modify. During degradation of the PLA in the human body the phosphates are gradually released and transformed into the natural bone tissue that can raise the osseointegration of the composite calcium phosphate bioceramics².

Nanomaterials based on the lanthanide compounds are great candidates for biofluorescence probes due to the narrow emission bands, long lifetimes, low photobleaching and relativly low toxicity in comparison with the conventional organic dyes. Their long emission lifetimes enable using the time-resolved spectroscopy for elimination of the fluorescence of tissue³.

Acknowlegements for financial support within the Project no. UMO-2015/19/B/ST5/01330 to the National Science Centre in Poland (NCN).

References:

¹ M. Sadat-Shojai, M. T. Khorasani, E. Dinpanah-Khoshdargi and A. Jamshidi Mehdi "Synthesis methods for nanosized hydroxyapatite with diverse structures" **Acta Biomater.**, 2013, **9**, 7591–7621.

² Q. Yuan, J. Wu, C. Qin, A. Xu, Z. Zhang, S. Lin, X. Ren and P. Zhang "Spin-coating synthesis and characterization of Zn-doped hydroxyapatite/ polylactic acid composite coatings" Surf. Coat. Technol., 2016, **307**, 461–469.

³ S. S. Syamchand and G. Sony "Europium enabled luminescent nanoparticles for biomedical applications" J. Lumin., 2015, 165, 190–215.





New advances in 3D-technology applied to Biomedicine

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In many techniques, 3D images are captured using a lens array, in which every lens captures angular distribution of the light rays at its principal point, enabling direct capture of the light ray field at a single shooting. However, the definitive spatial resolution is much lower compared to the native image sensor. In despite of the fact that several 3D Image methods have been recently developed, they are usually laborious, computationally intensive and they do not allow the correction of the optical aberration of the full scene, yielding to final blurred images. We show here a new method to capture 3D scene in real time without any additional hardware needed. Furthermore, the technique has been computationally optimized in real time to provide best images, generating the desired points of view.

This optimized method results especially suitable for 3D microscopy imaging in biology. More specifically, technology is fitted for samples embedded in a medium with a variation of the refraction index, as occurred with the majority of biological samples currently employed in research. The possibility to obtain real-time 3d observations is crucial to understand the development of macromolecular/cellular structures, and also to decipher the developing of brain structures in living organisms. In addition, this method is extremely useful to analyse "time lapse" experiments in subcellular compartments, cells and also living organisms, not only on fluorescent material but also in untreated natural conditions. In this Congress we show several examples of biological samples using this 3D microscopy imaging technique.

Fundings: This work has been funded by the DPI2015-66458-C2-2-R project (MINECO) to JMRR and AA.

X-ray and Near-Infrared Excitation of Luminescence in Ln doped Nanoparticles for Bio-imaging Applications

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We present some recent results of our group regarding the X-ray and near infrared (NIR) to NIR up-conversion luminescence properties of lanthanide (Ln) doped nanoparticles (NPs). The investigated nanoparticles are composed of CeO₂ and Y_2O_3/Lu_2O_3 as hosts and Er and Tm Ln as luminescence activators [1-3].

It is suggested in the literature that CeO_2 NPs selectively protect from radiation damage normal but not cancer cells, acting thus as both radio-protecting and radio-sensitizing agent. Conversely, Ln doped Y₂O₃ (Lu₂O₃) are widely used for phosphor/scintillation applications, due to their facile synthesis in the nanometer regime and favorable physical properties.

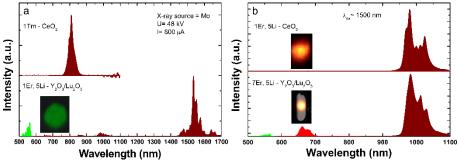


Fig. 1 (a) Emission spectra of Tm – CeO₂ and Er – Y₂O₃/Lu₂O₃ NPs under X-ray irradiation (Mo source with maximum debit dose of 2 Gy/s); (b) Up-conversion emission spectra of Er – CeO₂ and Er – Y₂O₃/Lu₂O₃ NPs under 1500 nm excitation. Digital photos of the emitted light from Er – CeO₂ and Er – Y₂O₃/Lu₂O₃ NPs under X-ray and 1500 nm excitations are also included.

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Under X-ray excitation, Tm-CeO₂ NPs display monochromatic emission at 800 nm, while for the Er--Y₂O₃/Lu₂O₃ NPs, the 1500 nm emission represents 80% of the total emission (Fig. 1a). Under 1500 nm up-conversion excitation of Er-CeO₂ and Er- Y₂O₃/Lu₂O₃ NPs, almost 98 and 90% of the total emission is concentrated in NIR at 980 nm, respectively (Fig. 1b). In all, the optical properties suggest that the Ln doped CeO₂ and Y₂O₃/Lu₂O₃ NPs have a good potential for therapy and bioimaging applications.

[1] M. Florea, D. Avram, B. Cojocaru, I. Tiseanu, V. Parvulescu, C. Tiseanu, *Phys. Chem. Chem. Phys.* (2016) 18, 182668 – 18277;

[2] D. Avram, A. Urda, B. Cojocaru, I. Tiseanu, M. Florea, C. Tiseanu, *Phys. Chem. Chem. Phys.Commun.* (**2015**) 17, 30988 – 30992;

[3] D. Avram, B. Cojocaru, I. Tiseanu, M. Florea, C. Tiseanu, J. Phys. Chem. C (**2017**) 121 (26), 14274 – 14284

Acknowledgements: The authors acknowledge CNCS-UEFISCDI, project number PN-III-P4-ID-PCE-2016-0305 and program NUCLEU, contract 4N/2016 for the financial support.



Nanothermometry and nanoheating applied to biomedicine. Near-infrared emitting rare-earth doped nano-garnets

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In order to assure light penetration into tissues efficiently, luminescence nanoparticles used in biophotonic applications have to be excited and emit in the near-infrared biological windows (NIR-BW), since visible light cannot carry out such penetration because of the combination of light scattering and light absorption caused by different compounds in tissues. Furthermore, by means of NIR-BW excitation not only efficient penetration is reached but lower damage of the tissue as well. Rare-earth ions have the advantage of having multiple absorption and emission bands in the BWs. Besides, they show low cytotoxicity and do not need any functionalization to enter the cell. The excitation has been carried out with a laser at around 800 nm, within the first NIR-BW, in order to analyze the NIR emissions in the three NIR-BWs of trivalent neodymium, erbium and thulium in Gd₃Ga₅O₁₂, Y₃Ga₅O₁₂ and Lu₃Ga₅O₁₂ nano-garnets, and study their potential use as optical nano-thermometers and nano-heaters in biomedicine.





Nanoperovskites doped with RE³⁺ ions as optical temperature sensors working in the near infrared region

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Recently, many studies have been carried out in order to optimize the luminescence properties of trivalent rare-earth (RE³⁺)-doped nanocrystals due to their size, shape, phase and concentration dependency. The main feature of the nanocrystals is the capacity to keep the luminescence properties compared to bulk counterparts, making them useful as optical temperature sensor or in the bio-imaging field. Ions such as Nd³⁺ and Tm³⁺ can be excited and emit in the near infrared range or the well-known biological windows, which are those regions in which the infrared radiation through the human skin is optimal. In this sense, doping nanoperovskites with these ions would be very interesting due to the sharpness nature of the emission peaks in the near infrared range, allowing to check with high resolution any changes of these peaks with the temperature (shifts, full width at half maximum,..). This feature suggests the potential application of yttrium orthoaluminate nanoperovskites doped with these ions as optical temperature sensors working in the near infrared region with high thermal sensitivities.

Nanoperovskite doped with Yb³⁺ and Tm³⁺ ions used as optical upconversion temperature sensor

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Under 975 nm excitation, the temperature dependence of the infrared upconverted emission bands of the $YAlO_3$: $2\%Yb^{3+}$, $2\%Tm^{3+}$ nano-perovskites was studied to test their thermal sensing capability. The emission bands, originating from ${}^3F_3 \rightarrow {}^3H_6$ and ${}^3H_4 \rightarrow {}^3H_6$ transitions, are located at 690 and 800 nm respectively (first biological window of the human tissue), and were measured from RT to 470 K. The calibration of the optical sensor has been made by two different methods. In the first one, based in the fluorescence intensity ratio technique (FIR), the areas under the two emission bands were used. In the second procedure the ratio of two different wavelengths is estimated. The results showed a higher sensitivity in the biophysical temperature range for the FIR method, while a better sensitivity was obtained with the second method for temperatures above 340 K.

Once the calibration was made, it was possible to control the temperature of the nanoperovskite from RT until 470 K while heating the sample with the laser excitation.

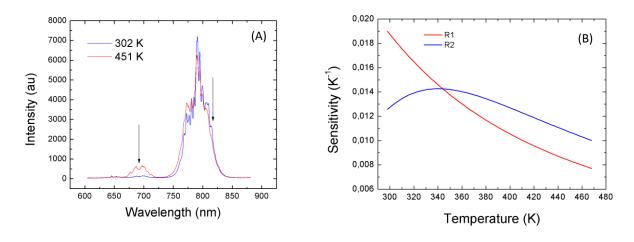


Figure 1. (A) Emission spectra obtained at two different temperatures under 980 nm diode laser excitation. The arrows show the peaks used in the second calibration method (R2): 690 and 815 nm. (B) Sensitivity of the FIR technique, where R1 belongs to the first method (FIR) and R2 belongs to the second one.

Acknowledgments

This research was partially supported by MINECO (MAT2013-46649-C4-4-P, MAT2015-71070-REDC, and MAT2016-75586-C4-4-P), and by the EU-FEDER funds. M. A. Hernández-Rodríguez thanks MINECO for FPI grant (BES-2014-068666).

Whispering Gallery Modes in a holmium doped glass microsphere: temperature sensor in the second biological window

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The shift of the Whispering Gallery Modes wavelengths with the temperature of three emission bands (660 nm, 760 nm and 1200 nm) of Ho³⁺ doped yttrium aluminosilicate microspheres were analysed, in order to study their viability as thermal sensors. A 532 nm continuous laser was used to excite and heat the microspheres, paying special attention to the emission band at 1200 nm due to its interesting applications. The average displacement rates of the WGM peaks with the laser power were estimated, obtaining values of 17.6 pm/mW, 20.85 pm/mW and 35.16 pm/mW for the emission bands centred at 660 nm, 760 nm and 1200 nm, respectively. It was found that the temperature resolution of this method is 0.18 K for the band centred in 660 nm, 0.16 K for the 760 nm band and 0.06 K for the 1200 nm band.

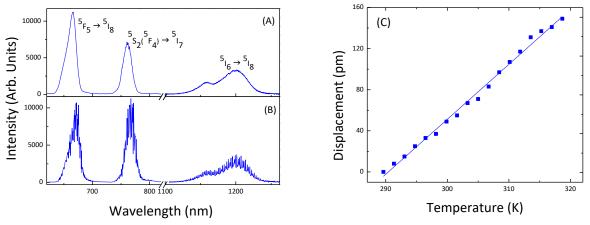


Figure 1. (A) Emission spectrum of a Ho³⁺ doped YAS microsphere obtained under excitation at 532 nm at room temperature, placing the detection at its centre (showing the corresponding transitions). (B) Emission spectrum of a Ho³⁺ doped YAS microsphere showing the WGM under excitation at 532 nm at room temperature, placing the detection at the border of the microsphere. (C) Displacement of the WGM peaks at the 660 nm emission of a Ho³⁺ doped YAS microsphere as a function of temperature.

Acknowledgments

This research was partially supported by MINECO (MAT2013-46649-C4-4-P, MAT2015-71070-REDC, and MAT2016-75586-C4-4-P), and by the EU-FEDER funds. M. A. Hernández-Rodríguez thanks MINECO for FPI grant (BES-2014-068666).

Visible-Light-Responsive Azopolymers for Photopatterning and Solar Energy Storage

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Please indicate preference: <u>x</u> Poster <u>Oral</u> Invited Speaker Specify Technical Area: <u>Biomedical</u> <u>x</u> Energy

Photoswitchable polymers are promising candidates for information storage and solar energy storage. However, two general problems for photoswitchable polymers used in rewritable optical storage are photobleaching and inefficient switching processes in solid state. To overcome both of these obstacles, we demonstrate the synthesis of a new visible-light-switchable azobenzene-containing polymer (azopolymer) with nonstackable azo chromophores for reversible and stable information storage. The new azopolymer (PmAzo) contains orthomethoxy-substituted azobenzene (mAzo) groups on the polymer side chains and shows reversible trans-to-cis isomerization by using distinct wavelengths of visible light. PmAzo is better suited for reversible optical storage than conventional UV-responsive azopolymers because visible light avoids the photodamage caused by UV light and mAzo groups do not π - π stack in solid state, making photopatterning of PmAzo fully reversible. Moreover, photoinduced patterns on PmAzo can be stored for more than half a year. These properties distinguish PmAzo as a promising candidate for rewritable and stable information storage.

Additionally we implemented a UV-sensitive azopolymer (PAzo) and the visible-light-sensitive azopolymer (PmAzo), combined with a fluorescent dye and a filter, to create a four-layer solar thermal cell. While most azopolymers discharge under visible irradiation, our device can use a true solar spectrum to store energy. This cell achieves a record solar efficiency (0.4%) amongst azobenzene polymer-based solar thermal fuels.

- [1] P. Weis, D. Wang, S. Wu, *Macromolecules* **2016**, *49*, 6368-6373.
- [2] A. K. Saydjari, P. Weis, S. Wu, *Advanced Energy Materials* **2017**, *7*, 1601622.

Yb,Er up-conversion luminescence from molecular hybrid thin films prepared by ALD/MLD

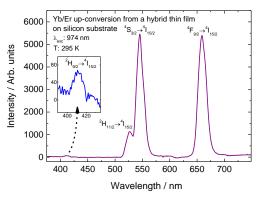
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The ability to convert low-energy infrared radiation into a higher energy emission of visible light has made the lanthanide ion based up-conversion luminescence highly studied in medical diagnostics and microscopy [1,2]. Another potential application of up-conversion luminescence materials is in photovoltaics [3], where the combination of organic molecules and lanthanides (e.g. Yb³⁺ and Er³⁺) can offer enhanced absorption in the NIR spectral range.

Atomic/molecular layer deposition (ALD/MLD) thinfilm technique offers a new way to prepare hybrid materials [4]. The technique enables the atomic/molecular layer-by-layer growth of inorganicorganic thin films with precise thickness and composition control. In this work, inorganic-organic thin films were prepared on silicon substrate using pyrazine as the ligand for the Yb/Er complex. The film showed green, red and even blue up-conversion emissions due to the ${}^{2}H_{11/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$; ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$; ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions of Er³⁺, respectively (Fig.). The blue Yb, Er up-conversion has not been reported for nanocrystalline or amorphous materials before.



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Fig. Up-conversion luminescence from a hybrid thin film prepared from Yb/Er and pyrazine complex.

References

- 1. F. Auzel, Chem. Rev. (2004) 104, 139-174.
- 2. I. Hyppänen et al., Terrae Rarae (2009) 16, 1-6.
- 3. J. C. Goldschmidt and S. Fischer, Adv. Opt. Mater. (2015) 3, 510-535.
- 4. P. Sundberg and M. Karppinen, Beilstein J. Nanotechnol. (2014) 5, 1104-1136.

Universidad de La Laguna

Photoluminescent polymer aerogels based on poly(N-Isopropylacrylamide) - rare earth complexes

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Please indicate preference: Poster Specify Technical Area: Applications in energy and photochemistry

Highly luminescent polymer aerogels used as photonic conversion mediums could be potentially interesting for applications in electronic devices¹, especially for new approaches in energy efficient lighting sources. Our research team successfully prepared highly luminescent polymer aerogels based on poly(N-Isopropylacrylamide) - Eu³⁺, Tb³⁺ and Y³⁺ cations. Initially, we took advantage by the favorable molecular configuration of N-Isopropylacrylamide as a ligand for the previously mentioned cations. Therefore in the first step, 1/3 metal to ligand ratio complexes were prepared in aqueous medium. Further on, the resulted complex aqueous solution is mixed with N,N'-methylene bisacrylamide used as a crosslinker and polymerized in the presence of 2-Hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone as photoinitiator. The polymerization process undergoes at 240K in the presence of 310 nm UV radiation. The resulted cryogels were further freeze dried to obtain the photoluminescent polymer aerogels (Fig.1a,b). By simply varying the water content in the first preparation step, it is possible to obtain aerogels with controlled pore size. Our method permits the preparation of aerogels with any required shape and densities lower then 0.01 g/cm³. The morpho-structural investigation of the prepared photoluminescent aerogels were performed through FT-IR, TGA, SEM (Fig.1.c) and Fluorescence spectroscopy.



Figure 1. The prepared poly(N-Isopropylacrylamide)-Tb³⁺ aerogel (a) under UV excitation, (b) in ambient lighting conditions, (c) SEM image of the aerogel

References

[1] C. S. Stan, P. Horlescu, M. Popa, A. Coroaba, L. E. Ursu, Photoluminescent polymer composites with R, G, B emission and their potential applications in LCD displays, New J. of Chemistry 40, pp.6505 – 6512, 2016.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS–UEFISCDI, Project Number PNIII-77PED/2017.

The use of synthetic hackmanites in storing UV radiation and X-rays

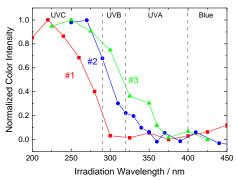
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Hackmanite is a mineral with the general formula $Na_8Al_6Si_6O_{24}(Cl,S)_2$. When it is prepared synthetically, the composition can be altered and different elements added to the formula. The general properties of hackmanites are tenebrescence, luminescence and persistent luminescence [1]. The properties depend on the composition of the hackmanite. Luminescence properties can be optimized by replacing some of the sodium with lithium [2]. On the other side, by doing other compositional tailoring we can alter the tenebrescence properties.

Changing the composition in synthetic hackmanites changes the tenebrescence excitation spectrum of the material (Figure 1). In tenebrescence, a material changes color when exposed to radiation with a high enough energy (usually UV radiation). The energy of the radiation is stored in the material when color centers are created [3]. The energy can be released from the color center thermally or by visible light. If the material is stored at room temperature in darkness, the material will stay in the colored state and store the energy until the energy is released.



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Figure 1 Tenebrescence excitation spectra for three different compositions of synthetic hackmanite.

Our new research has shown that synthetic hackmanites can also store X-rays by inducing tenebrescence in the material. Also in this case the colored state can be maintained in darkness and the energy will stay stored.

[1] Norrbo, I. *et al.*, Persistent Luminescence of Tenebrescent Na₈Al₆Si₆O₂₄(Cl,S)₂: Multifunctional Optical Markers, *Inorg. Chem.*, **54**, (2015), 7717 7724.

[2] Norrbo, I. *et al.*, Lanthanide and Heavy Metal Free Long White Persistent Luminescence from Ti Doped Li-Hackmanite: A Versatile, Low-Cost Material, *Adv. Funct. Mater.*, **27**, (2017), 1606547.

[3] Medved, D. B., Hackmanite and its tenebrescent properties, Am. Mineral., **39**, (1953), 615–629.



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Reliable supply of clean and affordable energies is a crucial challenge of the 21st century. This implies an increase in the use of renewable energies, preferentially those involving primary sources such as, for instance, photovoltaic (PV) [1]. The recent developments of PV cells manufacture pushed the efficiency of c-Si solar cells to values approaching the theoretical limit of 29%. One way to increase the efficiency of PV cells is using luminescent solar concentrators (LSCs) that are devices comprising a transparent matrix embedding optically active centres that absorb the incident radiation, which is re-emitted at a specific wavelength and transferred by total internal reflection to PV cells located at the edges of the matrix [2]. In this work, we demonstrate bio-LSCs based on chlorophyll molecules, extracted from *Spirulina maxima* which is an abundant cyanobacteria, incorporated in organicinorganic hybrids (tri/di-ureasils). The photophysical properties of the chlorophyll molecules after incorporation into the hybrids closely resemble those in an ethanolic solution (an absolute emission quantum yield of ~0.16 and a fluorescence lifetime of ~8 ns). The LSCs were coupled to a Si-based commercial photodiode revealing an optical conversion efficiency (η_{opt}) and the external quantum efficiency (EQE) gain around 40% and 23%, respectively, illustrating the potential of this approach for the development of bio-LSCs.

^{1.} Debije, M.G. and P.P.C. Verbunt, *Thirty Years of Luminescent Solar Concentrator Research: Solar Energy for the Built Environment*. Advanced Energy Materials, 2012. **2**(1): p. 12-35.

^{2.} Correia, S.F.H., et al., *Luminescent solar concentrators: challenges for lanthanide-based organic-inorganic hybrid materials.* Journal of Materials Chemistry A, 2014. **2**(16): p. 5580-5596.



Characterisation of Upconversion Materials by Spectral and Time-Resolved Luminescence

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Up-conversion luminescence by lanthanide-doped materials is typically characterized using NIR laser excitation. The emitted spectrum and associated photoluminescence lifetimes are a function of the crystal composition, the lanthanide ions present, the laser excitation density, and the phase (solution/solid/film). In order to reliably study these effects, a highly sensitive, precise instrument is needed to appropriately record accurate and reproducible data. The narrowband structure of the lanthanide emission requires high spectral resolution.

The steady-state and time-resolved luminescence of lanthanide-based upconversion materials has been studied with commercial photoluminescence spectrometers. A pulsed laser source allows studying the growth and decay kinetics of each different transition, providing an insight into the dynamics of the process. The time-resolved decay curves allow distinguishing between excited state absorption (ESA) and energy transfer upconversion (ETU) processes, as well as associated rates and efficiencies of the up-conversion mechanisms. The results from two separate studies will be presented and compared.



Design and Preparation of Luminescent Films Applied to Photovoltaic Technologies

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There is a rising interest in enhancing the activity of Si photovoltaic cells due to show low efficient in the UV and IR region. Spectral converters can be used to convert solar photons into wavelengths that are more effectively captured by the photovoltaic device through a photoluminescence process. Two methods based on photoluminescence are considered: the use of **down-shifters** which transform one absorbed high-energy photon into one of lower energy that can be harvested more efficiently by photovoltaic cells and the use of **up-converters** which convert photons from the near infrared range into the UV-visible through multi-photon and energy transfer mechanisms.

In the present work, we prepared different polymethylmethacrylate (PMMA) luminescent films to be applied in PV technology. We mixed down-shifter and up-converter materials with the PMMA to prepare by tape casting or spin-coating the luminescent films which are placed on top of the PV cell. We analysed chemical, optical and photoelectrical properties of the optically active film and the PV device.

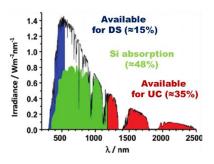


Fig.1. Solar irradiation standard spectrum (AM 1.5G) (black), the main absorption regions of down-shifters (blue), up-converters (red) and Si solar cell (green).

Shift2017 Spectral sHapIng For biomedical and energy applications November, 13–17, 2017/Tenerife, Canary Islands, Spain.

Universidad de La Laguna

Optical characterization of perovskite thin layers produced by one-step deposition method for solar light harvesting

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Organometal halide perovskite thin films for harvesting solar energy have been produced using a one-step deposition method assisted with non polar washing treatment. Spectroscopic ellipsometry allows controlling the film thickness and homogeneity of methylammonium lead iodide (CH3NH3PbI3) perovskites layers deposited on glass substrates. Spectral mapping on the surface of active layers confirms that highly reproducible thin films have been successfully deposited with an average thickness of approximately 400 nm with a corresponding refraction index of 2.5. Analyses of optical transmittance and spectral reflectance have been performed. Moreover, X-Rays Diffraction (XRD) and Atomic Forces Microscopy (AFM) measurements have been also carried out. Therefore, a simple and relatively cost effective process to fabricate perovskite solar cells has been created controlling the optoelectronic properties of the deposited layers.

Optical analysis of PAN/TiO2, PAN/Bi2O3, and PAN/SbSI electrospun composite fibrous mats

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The aim of study was prepare the PAN nanofibers reinforced by TiO2/Bi2O3 nanoparticles and SbSI nanowires and investigation of their morphology and optical properties. The polymer and composites nanofibers were obtained using electrospinning method from PAN/DMF solutions doped by nanofillers. The investigations of influence of process parameters on the morphology obtained fibrous mats were carried out on the basis of their images of surface topography obtained using a scanning electron microscopy (SEM). The incorporation of semiconductor nanofillers on the surfaces and in volume of PAN nanofibers were confirmed by energy dispersive X-ray (EDX). Spectral investigations of diffusive reflectance and transmittance have been used to determine absorption as well as scattering coefficients of the PAN, PAN/TiO₂, PAN/Bi₂O₃, and PAN/SbSI nanofibers. Mechanisms of absorption and energy gaps of the investigated materials have been determined.

Keywords: Composite nanofibers; PAN/TiO₂; PAN/Bi₂O₃; PAN/SbSI; Optical properties

Acknowledgements

The research presented in this article was financed by the National Science Centre, Poland based on the decision number 2014/15/B/ST8/04767.

This publication was financed by the Ministry of Science and Higher Education of Poland as the statutory financial grant of the Faculty of Mechanical Engineering SUT in 2017.

Polymeric nanofibers filled by TiO₂ NWs – synthesis, structural and optical investigation of the novel type of nanocomposite material

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The aim of study was prepare the polivinylopirolidone (PVP) nanofibers filled by titanium oxides (TiO₂) nanowires and investigation of their morphology, structure and optical properties. The polymer and composites nanofibers were obtained using electrospinning method from PVP/EtOH solutions doped by nanofillers. The investigations of influence of process parameters on the morphology obtained fibrous mats were carried out on the basis of their images of surface topography obtained using a scanning electron microscopy (SEM). The incorporation of used TiO₂ nanowires in the volume of PVP nanofibers were confirmed by energy dispersive X-ray (EDX). A high-resolution transmission electron microscope (TEM) was used along with X-ray diffraction analysis (XRD) in order to analyze the structure of obtained materials. The analysis of the optical properties and the energy gap of the prepared PVP/ TiO₂ NWs composite nanofibers were determined by spectral analysis of the absorbance in the function of the energy of radiation carry out using a UV-Vis spectrophotometer.

Keywords: Composite nanofibers; Electrospinning method; Titanium oxides nanowires; Optical properties

Acknowledgements

The research presented in this article was financed by the National Science Centre, Poland based on the decision number 2014/15/B/ST8/04767.

This publication was financed by the Ministry of Science and Higher Education of Poland as the statutory financial grant of the Faculty of Mechanical Engineering SUT in 2017.

Luminescent 70SiO₂-30HfO₂ layers doped rare earth ions for enhanced silicon solar cell performance by using Down-Conversion process.

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Abstract

A down-converting (DC) layer placed on the front side of a silicon solar cell has the potential to generate more than one low-energy photon for every incident high-energy photon. The aim of this work is to study the possibility to improve the efficiency of solar cells by using down-conversion glass and glass-ceramic layers based on 70SiO₂-30HfO₂ doped Tb³⁺/Yb³⁺. The down-conversion process is based on a cooperative energy transfer mechanism between one Tb³⁺ and two Yb³⁺ ions Yb³⁺ has only one excited level (${}^{2}F_{5/2}$). The relaxation ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ between the excited state and the fundamental level produces a near infra-red (NIR) photon at 980 nm wavelength, which is close to the edge of silicon band gap. On the other hand Tb³⁺ is used as sensitizer, with absorption in the blue at 488 nm through the ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ energy levels and cooperative transfer to Yb³⁺ ions.

Previous studies on $70SiO_2-30HfO_2$ down-converting waveguides [1] showed transfer efficiency as high as 54.6% for glass-ceramic films activated by the maximum rare earth amount: [Tb + Yb] = 9%. These studies reported also that for a given concentration of donors (Tb³⁺), increasing the number of acceptors (Yb³⁺) located close to the Tb³⁺ ion can have detrimental effects due to concentration quenching. Therefore the optimal concentration rate resulted in [Yb]/[Tb] = 4.

In the current study we compare two series of $70SiO_2-30HfO_2$ samples glass (G) and glass-ceramic (GC) activated by different molar concentrations of rare earths [Tb + Yb]/[Si + Hf] = 12%, 15%, 17%, 19% and 21% prepared by sol–gel route using the dip-coating technique.

[1] A. Bouajaj et al; "Tb³⁺/Yb³⁺ codoped silica–hafnia glass and glass–ceramic waveguides to improve the efficiency of photovoltaic solar cells"; Optical Materials 52 (2016) 62–68.

The impact of nanoparticles size on luminescent properties of LaPO₄: Eu³⁺ systems

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Rare-earth doped LaPO₄ systems represent a significant class of luminescent nanomaterials with an orthophosphate host material that has been proven to be suitable host matrix as a highly powerful emitter of light and broadly used in production of the luminescent and up-conversion materials. This work provides detailed studies of the nanoparticles size effect on structure and luminescent properties of LaPO₄:Eu³⁺ nanoparticles synthesized by four different methods: high temperature solid-state, co-precipitation, reverse micelle and colloidal route. These methods provided spherical particles of 2, 5 and 100 nm and short nanorods of 2-4 nm in diameter and 15-20 nm in length. All particles crystallized in a single monoclinic monazite phase of LaPO₄. Analysis of emission intensities vs Eu³⁺ concentration showed that this host material could be heavily doped with Eu³⁺, exclusively in case of colloidal nanoparticles, i.e. no quenching of emission occurred up to stoichiometric compound (EuPO₄). Emission quenching of other samples occurred at 10mol% Eu³⁺ (with respect to Y^{3+} ions). With the increase of Eu³⁺ concentration, the unit-cell parameter slightly increases to accommodate larger Eu³⁺ at sites of smaller La³⁺ ions. The photoluminescent emission spectra show four characteristic bands in red region: at 592 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$), at 612 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$), at 652 nm $({}^{5}D_{0} \rightarrow {}^{7}F_{3})$ and at 684 nm $({}^{5}D_{0} \rightarrow {}^{7}F_{4})$. The position and intensity ratio of these transitions are affected by the symmetry and the strength of the crystal field at the europium site.

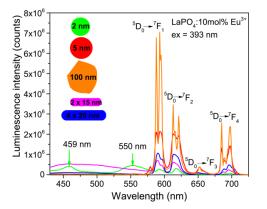


Figure 1. Size effect on the luminescence spectra of LaPO₄:10mol% Eu^{3+} nanoparticles obtained by different synthesis methods: colloidal, reverse micelle, co-precipitation, co-precipitation (annealed at 600°C) and solid-state recorded at 393 nm excitation wavelength.

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Acknowledgments

The authors acknowledge the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project no 45020 and 172056). The work of K. Smits was supported by Latvian National Research Programme IMIS2 (Grant No. 302/2012). The work of T. Gavrilović was supported by postdoctoral Latvian national research programme.

Ultraviolet and visible up-conversion in SiO₂-BaY_{0.78-x}Yb_{0.2}Tm_{0.02}Gd_xF₅ doped glass-ceramics under 980 nm excitation

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Rare-earth (RE) doped nanostructured oxyfluoride glass-ceramics, obtained from controlled crystallization of precursor glasses by adequate heat treatments, have received increasing attention in last decades due to their potential applications in optical communication, laser action, solar cells, etc...[1,2]. These materials combine besides transparency with mechanical and chemical resistance of the oxide glasses, the low phonon energy and good solubility for RE ions of the fluoride crystals. On the other hand, sol-gel synthesis is a room temperature glass preparation method, with the advantages of its low cost, easiness, controlled concentration and size, excellent purity and dispersion, alternative to conventional high-temperature melting techniques.

 $Ba(YGd)F_5$ is very attractive host for RE ions for providing high intensity UV and visible upconversion emissions, under IR excitation, due to its very low phonon energy environment which enhances luminescence. Among RE ions, Tm^{3^+} is well known for its IR to UV and blue up-conversion emissions. Frequently, by co-doping with Yb³⁺, the emissions can be intensified remarkably due to larger absorption cross-section of Yb³⁺ and the high efficient energy transfer to Tm³⁺ ions.

We have successfully obtained, sol-gel derived nano-glass-ceramics containing Yb³⁺-Tm³⁺ doped BaY_{0.78-x}Yb_{0.2}Tm_{0.02}Gd_xF₅ nanocrystals, where x = 0, 0.2, 0.4, 0.6 and 0.78 (mol%), after adequate heat treatment of precursor glasses. X-ray diffraction and high-resolution transmission electron microscope images confirmed the precipitation and distribution of nanocrystals, with controlled size dispersed, in an amorphous silica network. Typical blue and red up-conversion emissions of Tm³⁺ ions, seen by naked eye, were observed. Moreover, high efficient infrared to UV up-conversion emissions, corresponding to ¹I₆ and ¹D₂ levels of Tm³⁺ ions, ascribed to 5 and 4-photon processes, were observed respectively, along with deep-UV Gd³⁺ up-conversion emission, where Yb³⁺ and Tm³⁺ ions act as sensitizers, opening the way to developing short-wavelength solid-state lasers with applications in integrated photonics devices.

[1] P.P. Fedorov, A.A. Luginina, A.I. Popov, J. Fluo. Chem. 172 (2015) 22-50.

[2] D. Chen, W. Xiang, X. Liang, J. Zhong, H. Yu, M. Ding, H. Lu, Z. Ji, J. Europ. Chem. Soc. 35 (2015) 859-869.

[3] A.C. Yanes, A. Santana-Alonso, J. Méndez-Ramos, J. del-Castillo, V.D. Rodríguez, Adv. Funct. Mater. 21 (2011) 3136-3142.

Investigation of quantum cutting process followed by energy transfer in Mn²⁺, Pr³⁺ co-doped SrF₂ and CaF₂ nanoparticles

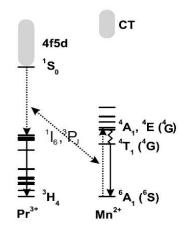
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The quantum cutting process is observed in some Pr^{3+} doped materials, in which the lowest state of a 4f5d electronic configuration does not overlap the ${}^{1}S_{0}$ electronic level. In such materials, the radiative emission of two lower-energy photons can take place (${}^{1}S_{0} \rightarrow {}^{1}I_{6}$ and ${}^{3}P_{0} \rightarrow {}^{3}H_{4}$) as a result of one high-energy photon absorption. From ${}^{1}S_{0}$ level, the first emitted photon has a wavelength of 405 nm, which is not very useful in the practical applications of energy converters. Hence, the energy transfer to neighboring co-dopant ions capable of absorbing that photon is desirable. One of the promising ion, that can play a role as an energy acceptor, is Mn^{2+} [1,2]. It not only possesses the absorption transitions corresponding to Pr^{3+} emission, but also it is able to shift the emission energy to visible range from green to red color, which can be used in displays or imaging applications.



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Figure 1. The scheme of quantum cutting process followed by energy transfer between Pr^{3+} and Mn^{2+} ions, from [2].

In this work an investigation of quantum cutting followed by energy transfer process in alkaline earth fluoride nanoparticles (MF₂, where M=Sr, Ca) co-doped with Pr³⁺ and Mn²⁺ ions will be presented. The samples have been synthesized by modified hydrothermal route, which allowed to obtain narrow size distribution of single phase nanoparticles. The incorporation of both dopants into the structure has been confirmed by diffuse-reflectance measurements and their concentration by inductively coupled plasma optical emission spectrometry (ICP-OES) technique. The crystalline structure has been confirmed by X-Ray Powder Diffraction measurements. The ability to photon cutting by Pr³⁺ ions is determined in both crystalline SrF₂ and CaF₂ hosts. Absorption and emission spectra of singly doped (with Mn²⁺ ions) and co-doped (Mn²⁺ and Pr³⁺ ions) nanofluorides in the visible and near UV range will be presented. The concentration dependency of the luminescence properties is also investigated.

E. van der Kolk, P. Dorenbos, C. W. E. van Eijk, J. Appl. Phys. 95 (2004) 7867
 A. Kuzmanoski, V. Pankratov, C. Feldmann, Journal of Luminescence 179 (2016) 555





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