COLLOID CHEMISTRY GROUP

Universidade Vigo

Annual Research Report
2017

From left to right :Jorge Pérez-Juste, Laura Valencia Matarranz, Pablo Hervés Beloso, Gustavo Bodelón González, Sarah De Marchi Lourenço, Daniel García Lojo, Alba Vazquez Arias, Maria José Cordero Ferradás, Sergio Rodal Cedeira, Paulo Pérez Lourido, Emilia Garcia Martínez, Veronica Montes García, José A. Cuadrado Martín, Isabel Pastoriza Santos

RESEARCH PROGRAM

The research activity of the Colloid Chemistry Group is focused on the synthesis and formation mechanisms of metal, semiconductor, magnetic and hybrid nanoparticles with controlled composition, size and morphology; the creation of colloidal composites, including functionalized carbon nanotubes; nanostructured thin films and nanoparticle ordered arrays in two and three dimensions; the optical characterization of nanoparticles and their assemblies; and the use of metal nanoparticles as biosensors.

Extenal Collaborators

Fabrice Vallée (CNRS, Lyon)
Sara Bals (U. Antwerp)
Salvo Sortino (U. Catania, Italy)
Andrés Guerrero (U. Complutense, Madrid)
Manfred Stamm (Technische Universität Dresden)
Hossein Tavakol (Isfahan University of Technology)
Patricia Taladriz (Technische U. Braunschweig)
Sergio Gómez Graña (U.Complutense,Madrid)
Natalia del Fatti (U. Lyon, France)
Niek Buurma (Cardiff U., UK)
Jacques Leng (Université Bordeaux)
José M. Taboada (U. Extremadura)
Rafael Contreras (U. Málaga)
Sara Abalde (INL-Braga)
Lakshminarayana Polavarapu (L-M Universt. München)

Collaborators at Universidade de Vigo

Ángel Rodríguez de Lera (Organic Chemistry)
Africa Gónzalez (Inmunology)
Elisa González (Analytical Chemistry)
Pío Gonzalez (Applied Physics)
Fernando Obelleiro (Teoría de la Señal)

Staff Members

Pablo Hervés-Beloso
Jorge Pérez-Juste
Laura M. Valencia Matarraz
Luis M. Liz-Marzán **(on leave CIC Biomagune, San Sebastián)**
Isabel Pastoriza-Santos
Paulo Pérez-Lourido
Emilia García Martínez

Postdoctoral Researchers

Gustavo Bodelón González
Sara Núñez Sánchez
Lorena Vázquez Iglesias

Ph. D. Students

Verónica Montes García
Sergio Rodal Cedeira
Sarah de Marchi Lourenço
M. Goretti Castro Justo (march 2017)
Daniel García Lojo
Alba Vázquez Arias
María Ángeles Fernández Muiños
Anxo Casais Carreira

Master Students

Carlos Fernández Lodeiro

Lab. Tecnhnicians
M. José Cordero Ferradas

Administration
José Antonio Cuadrado Martín

Visiting students to conduct experiments or extend collaboration
Florent Rodriguez, visiting student from Paris Diderot University (03/04/2017-28/05/2017)
Vadim Becquer, visiting student from Paris Diderot University (05/06/2017-04/08/2017)
Vito de Bellis, visiting student from University of Bari Aldo Moro (11/09/2017-09/11/2017

Research Visitors/ Seminars
Marek Grzelczak (CIC BiomaGUNE)
Pablo Ferreria (University of Texas at Austin-USA)
Alexander Castro Grijalba, visiting research from University of Mendoza-Argentina (04/09/2017-02/03/2018)

Research Funding
ERC (*Plasmaquo*)
Ministerio de Economía y Competitividad
Xunta de Galicia
Universidade de Vigo
Agencia Española de Cooperación Internacional
Fundación Ramón Areces

Awards

Luis M. Liz Marzán

- 2017 Blaise Pascal Medal in Materials Science
- JCIS – Darsh Wasan Award

PhD Thesis

Goretti Castro Justo
New Lanthanide Complexes with Macrocyclic Ligands as Potencial PARACEST Contrast Agents
University of Vigo, march 2017
Supervisors: Paulo Pérez Lourido and Laura Valencia Matarranz

Verónica Montes García
Synthesis and characterization of New Hybrid Materials Based on Metal Nanoparticles for SERS Detection
University of Vigo, december 2017
Supervisors: Isabel Pastoriza Santos and Jorge Pérez Juste

Editorial Activity

Jorge Pérez Juste
Editorial Board of Nanomaterials (MDPI)
Editorial Board of Journal of nanomaterials (Wiley-Hindawi)

Invited Lectures at Conferences, Courses and Workshops

Isabel Pastoriza-Santos

Plasmonic nanostructures as biomedical tools
17th Congress of the European Society for Photobiology
4 - 8, Setember 2017 Pisa (Italy)

Pd. The new plasmonic material
Nanoscience with Nanocrystals – Nanax8
3-7, July 2017 Braga (Portugal)

Au and Ag nanostructures: Synthesis and apllications
II Workshop on Chemistry of Group 11 Elements
26-27, January 2017, Barcelona (Spain)

Plasmonic PP nanorods: Synthesis, sensing and catalytic capabilities
5th International Conference on Multifunctional Hybrid and Nanomaterials – HYMA2017
6-10, March 2017 Lisboa (Portugal)

Plataformas nanoplasmónicas en catálisis, imagen y detección
VII Jornada de Química CISQ – Universidad de La Rioja
16, June 2017 Logroño (Spain)

Jorge Pérez Juste

Au@Ag@ZIF-8 manoparticles as universal SERS-tags for the robust immobilization of functional proteins
31st Conference of the European Colloid and Interface Society - ECIS2017
3-8, September 2017 Madrid (Spain)

Designing SERRS tags for Biosensing and Bioimaging
Nanoscience with Nanocrystals - Nanax8
3-7, July 2017 Braga (Portugal)

Presentations and Conferences by Group Members

Gustavo Bodelón González

Detection and imaging of quorum sensing in Pseudomonas aeruginosa biofilm communities by surfaces enhanced resonance RAMAN spectroscopy
NanoWordl Conference 2017
3-5, April 2017, Boston (USA)

Imaging bacterial inter-species chemical interactions by SERS
Nanoscience with Nanocrystals – Nanax8
3-7, July 2017 Braga (Portugal)

Designing of 3D nanocrystal assemblies induced by microfluidics for advanced applications in SERS detection
2nd Workshop on Biomaterials and Applications – BioMAPP2017
27 – 28, April 2017 Santiago de Compostela (Spain)

Application of surface-enhanced Raman scattering (SERS) spectroscopy far uftrasensitive detection and imaging microbial metabolites
International Conference on Environmental, Industrial and Applied Microbiology - BioMicroWorld 2017
18-20, October 2017 Barcelona (Spain)

Verónica Montes Garcia

Imaging bacterial interspecies chemical interactions by surface-enhanced Raman scattering
International Conference on Enhanced Spectroscopies - ICES2017
4-7, September 2017 Munich (Germany)

Au@Ag SERRS tags coupled to a lateral flow immunoassay for the sensitive detection of Pneumolysin
International Conference on Enhanced Spectroscopies -ICES2017
4-7, September 2017 Munich (Germany) - **Best Poster Award**

Au@Ag SERRS tags coupled to a lateral flow immunoassay for the sensitive detection of Pneumolysin)
Nanoscience with Nanocrystals – Nanax8
3-7, July 2017 Braga (Portugal) **(Poster)**

Supramolecular mediated plasmonic thin films for ultrasensitive and multiplex SERS bases PAH detection
5th International Conference on Multifunctional, Hybrid and Nanomaterials – HYMA2017
6-10, March 2017 Lisboa (Portugal)

A SERRS-based lateral flow inmunoassay for ultrasensitive detection of biomolecules
2nd Workshop on Biomaterials and Applications – BioMAPP2017
27-28, April 2017 Santiago de Compostela (Spain) **Best Oral Presentation Award**

Lateral Flow Immunoasay compled to Au@Ag SERS tags for Ultrasensitive detection of Pneumolysin
I IBEROS Network meeting
5 July 2017 Porto (Portugal) **(Poster)**

Sarah de Marchi Lourenço

SERS-plasmonic biosensors based on Au@Ag@ZIF-8 nanocrystals for multiplex detection
Nanoscience with Nanocrystals – Nanax8
3-7 July 2017 Braga (Portugal) **(Poster)**

Synthesis and characterization of novel SERS tags based on Au@Ag@ZIF-8 nanocrystals for bioapplications
2nd Workshop on Biomaterials and Applications – BioMAPP2017
27-28 April 2017 Santiago de Compostela (Spain)

Metal Nanoparticles@ZIF-8 Nanocomposites aas SERS tags for Multiplex biodetection
5th International Conference on Multifunctional, Hybrid and Nanomaterials – HYMA2017
6-10, March 2017 Lisboa (Portugal)

Sergio Rodal Cedeira

Shape-controlled syntheis of plasmonic nanorattles via galvanic replacement-seeded growth method
Nanoscience with Nanocrystals – Nanax8
3-7 July 2017 Braga (Portugal)

New plasmonic Au@Pd nanoparticles from synthesis to applications
2nd Workshop on Biomaterials and Applications – BioMAPP2017
27-28 April 2017 Santiago de Compostela (Spain) **(Poster)**

Galvanic replacement coupled to seeded growth as a route for shape controlled synthesis of plasmonic nanorattles
5th International Conference on Multifunctional, Hybrid and Nanomaterials – HYMA2017
6-10, March 2017 Lisboa (Portugal) **(Poster)**

Synthesis of SERS encoded NPs via galvanic replacement seeded growth method
Nanomaterials Apllied to Life Science International Conference - NALS2017
13-15, December 2017 Gijón (Spain)

Daniel Garcia Lojo

3D Assembly of nanocrystals induced by microfluidic platforms for advanced applications in SERS detection.
Nanoscience with Nanocrystals – Nanax8
3-7 July 2017 Braga (Portugal)

Design of 3D assembly of nanocrystals induced by microfluidic for advanced applications in SERS detection
2nd Workshop on Biomaterials and Applications – BioMAPP2017
27-28 April 2017 Santiago de Compostela (Spain) **(Poster)**

Sara Nuñez Sanchez

Exploring Colloidal Chemsitry Routes for nanoparticle Synthesis of a Novel Molecular Plasmon-Like Material
Nanomaterials Apllied to Life Science International Conference - NALS2017
13-15, December 2017 Gijón (Spain)

Outreach Activities

Participation of predoctoral students in “Days of approach to chemistry” for secondary school students.
Galician Nanomedicine Network. December 2017.

Participation of predoctoral students in “CINBIO science week” for elementary school students.
December 2017 .

Research Publications

1.Gold Nanoparticles for Regulation of Cell Function and Behaviour
G. Bodelón, C. Costas, I. Pastoriza.Santos, J. Pérez-Juste, L.M. Liz-Marzán
Nano Today, 2017, 13, 40-60

2.Au@Ag SERRS tags coupled to a lateral flow immunoassay for the sensitive detection of Pneumolysin
L. Blanco-Covián, V. Montes-García, A. Girard, M. T. Fernández-Abedul, J. Perez-Juste, I.Pastoriza-Santos, K. Faulds, D. Graham and M. C. Blanco-López
Nanoscale, 2017, 9, 2051–2058

3.Screen-printed carbon electrodes doped with TiO2-Au nanocomposites with improved electrocatalytic performance
R. Gusmão, V. López-Puente, L. Yate, I. Pastoriza-Santos, J. Pérez-Juste, E. González-Romero
Materials Today Communications, 2017, 11, 11–17

4.Developing the family of picolinate ligands for Mn2+complexation
Forgács, R. Pujales-Paradela, M. Regueiro-Figueroa, L. Valencia, D. Esteban-Gómez, M. Botta, C. Platas-Iglesias
Dalton Trans, 2017, 46, 1546-1558

5.Plasmonic/magnetic Nanocomposites: Gold Nanorods-functionalized Silica coated Magnetic Nanoparticles
E. Redolfi Riva, I. Pastoriza Santos, A. Lak, T. Pellegrino, J. Pérez Juste, V. Mattoli
Journal of Colloid and Interface Science, 2017, 502, 201-209

6.Imaging Bacterial Inter-Species Chemical Interactions by Surface Enhanced Raman Scattering
G. Bodelon, V. Montes-García, C. Costas, I. Pérez-Juste, J. Pérez-Juste, I. Pastoriza-Santos, L. Liz-Marzán
ACS Nano, 2017, 11, 4631-4640

7.Biogenic Synthesis of Metal NPs using a Biosurfactant Extracted from Corn and their Antimicrobial Properties
S. Gómez-Graña, M. Pérez-Ameneiro, X. Vecino, I. Pastoriza-Santos, J. Pérez-Juste, J. M. Cruz, A. B. Moldes
Nanomaterials, 2017, 7, 139

8.Nanoplasmonically-engineered Random Lasing in Organic Semiconductor Thin Films
E. Heydari, I. Pastoriza-Santos, L. M. Liz-Marzán, J. Stumpe
Nanoscale Horizons, 2017, 2, 261-266

9.Pillar[5]arene-Based Supramolecular Plasmonic Thin Films for Label-free, Quantitative and Multiplex SERS Detection
V. Montes García, B. Gómez-González, D. Solís, J. Taboada, N. Jiménez Otero, J. de Uña- Álvarez, F. Obelleiro, L. García-Río, J. Perez-Juste, I. Pastoriza-Santos
ACS Appl. Mater. Interfaces, 2017, 9 (31), 26372–26382

10.Shape control in ZIF-8 nanocrystals and metal nanoparticles@ZIF-8 heterostructures
G. Zheng, Z. Chen, K. Sentosun, I.Pérez-Juste, S. Bals, L. M. Liz-Marzán, I. Pastoriza- Santos, J. Pérez-Juste, M. Hong
Nanoscale, 2017, 9, 16645-16651

11.Osteogenic effects of simvastatin-loaded mesoporous titania thin films
M. Lopez-Alvarez, V. López-Puente, C. Rodriguez-Valencia, P. Angelomé, L.M. Liz-Marzan, J. Serra, I. Pastoriza-Santos, P. Gonzalez
Biomed. Mater., 2017, in press

12.Structure and Vacancy Distribution in Copper Telluride Nanoparticles Determine Plasmon Activity in the Near IR
T. Willhammar, K. Sentosun, S. Mourdikoudis, B. Goris, M. Kurttepelia, M. Bercx, D. Lamoen, B. Partoens, I. Pastoriza-Santos, J. Pérez-Juste, L.M. Liz-Marzán, S. Bals, G. van Tendeloo
Nature Communications, 2017, 8, 14925

Abstracts of Selected Publications

Nanoscale, 2017, **9,** 16645-16651 D.O.I.: 10.1039/C7NR03739B

Shape control in ZIF-8 nanocrystals and metal nanoparticles@ZIF-8 heterostructures

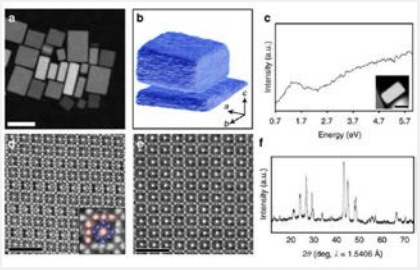
G. Zheng, Z. Chen, K. Sentosun, I.Pérez-Juste, S. Bals, L. M. Liz-Marzán, I. Pastoriza-Santos, J. Pérez-Juste, M. Hong

Shape control in metal–organic frameworks still remains a challenge. We propose a strategy based on the capping agent modulator method to control the shape of ZIF-8 nanocrystals. This approach requires the use of a surfactant, cetyltrimethylammonium bromide (CTAB), and a second capping agent, tris(hydroxymethyl)aminomethane (TRIS), to obtain ZIF-8 nanocrystals with morphology control in aqueous media. Semiempirical computational simulations suggest that both shape-inducing agents adsorb onto different surface facets of ZIF-8, thereby slowing down their crystal growth rates. While CTAB molecules preferentially adsorb onto the {100} facets, leading to ZIF-8 particles with cubic morphology, TRIS preferentially stabilizes the {111} facets, inducing the formation of octahedral crystals. Interestingly, the presence of both capping agents leads to nanocrystals with irregular shapes and higher index facets, such as hexapods and burr puzzles. Additionally, the combination of ZIF-8 nanocrystals with other materials is expected to impart additional properties due to the hybrid nature of the resulting nanocomposites. In the present case, the presence of CTAB and TRIS molecules as capping agents facilitates the synthesis of metal nanoparticle@ZIF-8 nanocomposites, due to synergistic effects which could be of use in a number of applications such as catalysis, gas sensing and storage.

Nature Communications, 2017**, 8**, 14925 D.O.I.: 10.1038/ncomms 14925

Structure and vacancy distribution in copper telluride nanoparticles influence plasmonic activity in the near-infrared

Tom Willhammar, Kadir Sentosun, Stefanos Mourdikoudis, Bart Goris, Mert Kurttepeli, Marnik Bercx, Dirk Lamoen, Bart Partoens, Isabel Pastoriza-Santos, Jorge Pérez-Juste, Luis M. Liz-Marzán, Sara Bals, Gustaaf Van Tendeloo

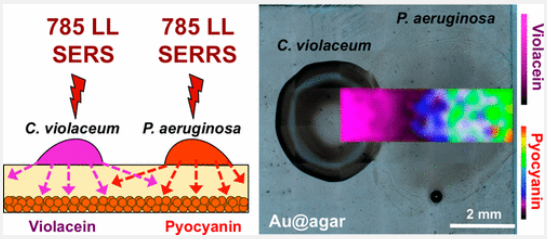


Copper chalcogenides find applications in different domains including photonics, photothermal therapy and photovoltaics. CuTe nanocrystals have been proposed as an alternative to noble metal particles for plasmonics. Although it is known that deviations from stoichiometry are a prerequisite for plasmonic activity in the near-infrared, an accurate description of the material and its (optical) properties is hindered by an insufficient understanding of the atomic structure and the influence of defects, especially for materials in their nanocrystalline form. We demonstrate that the structure of Cu1.5±xTe nanocrystals can be determined using electron diffraction tomography. Real-space high-resolution electron tomography directly reveals the three-dimensional distribution of vacancies in the structure. Through first-principles density functional theory, we furthermore demonstrate that the influence of these vacancies on the optical properties of the nanocrystals is determined. Since our methodology is applicable to a variety of crystalline nanostructured materials, it is expected to provide unique insights concerning structure–property correlations.

ACS Nano, 2017**, 11**, 4631-4640 D.O.I.: 10.1021/acsnano.7b00258

Imaging Bacterial Inter-Species Chemical Interactions by Surface Enhanced Raman Scattering

G. Bodelon, V. Montes-García, C. Costas, I. Pérez-Juste, J. Pérez-Juste, I. Pastoriza-Santos, L. Liz-Marzán

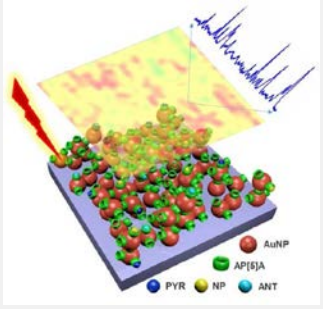


Microbes produce bioactive chemical compounds to influence the physiology and growth of their neighbors, and our understanding of their biological activities may be enhanced by our ability to visualize such molecules in vivo. We demonstrate here the application of surface-enhanced Raman scattering spectroscopy for simultaneous detection of quorum-sensing-regulated pyocyanin and violacein, produced respectively by Pseudomonas aeruginosa and Chromobacterium violaceum bacterial colonies, grown as a coculture on agar-based plasmonic substrates. Our plasmonic approach allowed us to visualize the expression and spatial distribution of the microbial metabolites in the coculture taking place as a result of interspecies chemical interactions. By combining surface-enhanced Raman scattering spectroscopy with analysis of gene expression we provide insight into the chemical interplay occurring between the interacting bacterial species. This highly sensitive, cost-effective, and easy to implement approach allows spatiotemporal imaging of cellular metabolites in live microbial colonies grown on agar with no need for sample preparation, thereby providing a powerful tool for the analysis of microbial chemotypes.

ACS Appl. Mater. Interfaces, 2017**, 9 (31**), 26372–26382 D.O.I: 10.1021/acsami.7b08297

Pillar[5]arene-Based Supramolecular Plasmonic Thin Films for Label-free, Quantitative and Multiplex SERS Detection

V. Montes García, B. Gómez-González, D. Solís, J. Taboada, N. Jiménez Otero, J. de Uña-Álvarez, F. Obelleiro, L. García-Río, J. Perez-Juste, I. Pastoriza-Santos



Novel plasmonic thin films based on electrostatic layer-by-layer (LbL) deposition of citrate-stabilized Au nanoparticles (NPs) and ammonium pillar[5]arene (AP[5]A) have been developed. The supramolecular-induced LbL assembly of the plasmonic nanoparticles yields the formation of controlled hot spots with uniform interparticle distances. At the same time, this strategy allows modulating the density and dimensions of the Au aggregates, and therefore the optical response, on the thin film with the number of AuNP-AP[5]A deposition cycles. Characterization of the AuNP-AP[5]A hybrid platforms as a function of the deposition cycles was performed by means of visible–NIR absorption spectroscopy, and scanning electron and atomic force microscopies, showing larger aggregates with the number of cycles. Additionally, the surface enhanced Raman scattering efficiency of the resulting AuNP-AP[5]A thin films has been investigated for three different laser excitations (633, 785, and 830 nm) and using pyrene as Raman probe. The best performance was shown by the AuNP-AP[5]A film obtained with two deposition cycles ((AuNP-AP[5]A)2) when excited with a 785 laser line. The optical response and SERS efficiency of the thin films were also simulated using the M3 solver and employing computer aided design models built based on SEM images of the different films. The use of host molecules as building blocks to fabricate (AuNP-AP[5]A)2) films has enabled the ultradetection, in liquid and gas phase, of low molecular weight polyaromatic hydrocarbons, PAHs, with no affinity for gold but toward the hydrophobic AP[5]A cavity. Besides, these plasmonic platforms allowed achieving quantitative detection within certain concentration regimes. Finally, the multiplex sensing capabilities of the AuNP-AP[5]A)2 were evaluated for their ability to detect in liquid and gas phase three different PAHs.