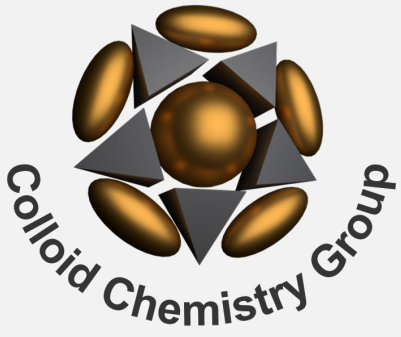
COLLOID CHEMISTRY GROUP



Universidade Vigo

Annual Research Report

2018

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)
Jacques Leng (Université Bordeaux)
Andrés Guerrero (U. Complutense, Madrid)
Manfred Stamm (Technische Universität Dresden)
Hossein Tavakol (Isfahan University of Technology)
Patricia Taladriz (Technische U. Braunschweig)
Lakshminarayana Polavarapu (L-M Universt. München)
Guangchao Zheng (Hong Kong Polytechnic University)
Luis M. Liz-Marzán (CICBiomaGUNE)
José M. Taboada (U. Extremadura)
Rafael Contreras-Cáceres (U. Málaga)
Sara Abalde (INL-Braga)
Teko Napporn (Université Poitiers)

Collaborators at Universidade de Vigo

Ángel Rodríguez de Lera / Esther Vazquez (Organic Chemistry)
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
Sergio Gómez Graña
Veronica Montes García (september 2018)

Ph. D. Students

Sergio Rodal Cedeira
Sarah de Marchi Lourenço
Daniel García Lojo
Alba Vázquez Arias
Anxo Casais Carreira
Carlos Fernández Lodeiro

Master Students

Carlos Fernández Lodeiro (july 2018)
Carla Estévez Varela

Lab. Tecnhnicians

M. José Cordero Ferradas

Administration

José Antonio Cuadrado Martín

Visiting students to conduct experiments or extend collaboration

Naiara Vieira Godoy, visiting student from Universidade Estadual de Campinas (01/02/2018-31/07/2018)

Research Visitors/ Seminars

Sara Skrabalak (Indiana University)
Maria Fernanda Cardinal (Universidad Nacional de Sanmartin - Argentina
Paula C. Angelomé (Instituto de Nanociencia y Naotecnología – Argentina)
Alexander Castro Grijalba, visiting research from University of Mendoza-Argentina (04/09/2017-02/03/2018)

Research Funding

Ministerio de Economía y Competitividad
Xunta de Galicia
Universidade de Vigo
Agencia Española de Cooperación Internacional
Fundación Ramón Areces
UE - Feder

Editorial Activity

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

Isabel Pastoriza Santos
Editorial Board of Nanomaterials (MDPI)

Invited Lectures at Conferences, Courses and Workshops

Isabel Pastoriza-Santos

Nanoplasmonic for imaging and sensing based on surface enhanced RAMAN scattering
3th International Caparica Conference Nanoparticles/Nanomaterials and Applications 2018 ISN2A2018
22-25 January 2018, Caparica (Portugal) **(Plenary)**

Plasmonic nanorattles via galvanic replacement-seeded growth method: Towards a Universal SERS Tag
GOLD 2018 8Th International Conference
15-18 July 2018, Paris (France)

Plasmonic nanostructures: synthesis and applications
Let's talk about science, The interdisciplinarity of light – University of Porto
5 July 2018, Porto (Portugal) **(Invited)**

Fabrication of plasmonic nanostructures for SERS sensing
Seminarios Instituto de Investigación en nanociencia – Universidad de Zaragoza
13 April 2018, Zaragoza (Spain)

Plasmonic nanorattles via galvanic replacement-seeded growth method: Towards a Universal SERS Tag
ICORS2018 The 26Th International Conference on RAMAN Spectroscopy
26-31 August 2018 Jeju (Korea)

Plasmonic nanostructures for sensing and imaging
Materials.it 2018
22-26 October 2018, Bolonia (Italia) **(Invited)**

Noble metal nanostructures and their plasmonic effects
CEN 2018, Spanish Conference on Nanophotonics
3-5 October 2018, Donostia-San Sebastián (Spain) **(Keynote)**

Fabrication of Plasmonic Nanostructures for Surface-enhanced Raman Scattering sensing
Seminario en la Facultad de Ciencias de la Universidad de Porto, Portugal
11 December 2018

Jorge Pérez Juste

Microfluidic induced supercrystals for on-chip ultrasensitive SERS detection
GOLD 2018 8Th International Conference
15-18 July 2018, Paris (France)

Au@Ag@ZIF-8 nanocrystals as SERS tags for the immobilization of proteins and multiplex Immunophenotyping
ICORS2018 The 26Th International Conference on RAMAN Spectroscopy
26-31 August 2018, Jeju (Korea) **(Invited)**

Plasmonic nanorattles via galvanic replacement-seeded growth method: towards universal SERS tags
Nano Day 2018
9 october 2018, Lisboa (Portugal)

Presentations and Conferences by Group Members

Gustavo Bodelón González

Application of surface-enhanced Raman scattering (SERS) spectroscopy for ultrasensitive detection and imaging microbio/ metabolites
3th International Caparica Conference Nanoparticles/Nanomaterials and Applications 2018 ISN2A2018,
22-25 January 2018, Caparica (Portugal)

Filaments, Membranes, Cells-and their Interactions
SoftComp Topical Workshop 2018
28-31 January 2018, Jülich (Germany) **(Invited)**

Surface-enhanced Raman scattering (SERS) imaging of bioactive metabolites in mixed bacterial populations
NanoBio&Med 2018
20-22 November, Barcelona (Spain)

Verónica Montes Garcia

Molecularly imprinted plasmonic nanosensor for highly sensitive SERS detection of PAHs
III Jornada Científica IBEROS
19 march 2018, Porto (Portugal)

Au@Ag SERRS tags coupled to a lateral flow immunoassay for the sensitive detection of Pneumolysin
II Annual Meeting CINBIO
25-26 June 2018, Vigo (Spain) **(Poster)**

Sergio Gómez Graña

Selective melanoma treatment using a targeted chemo-photothermal therapy
II Annual Meeting CINBIO
25-26 June 2018, Vigo (Spain)

Gold-Silica nanohybrids for light assisted therapy for melanoma
IV Jornada Científica IBEROS
20 November 2018, Vigo (Spain)

Nanotecnología: Un mundo por descubrir
Jornada "Tecnoloxías emerxentes e materiais innovadores no sector da construcción" – Kreactive Habitat
27 November 2018 CTAG-Porriño (Spain)

Sarah de Marchi Lourenço

Metal nanoparticles @MOF nanocomposites as SERS tags for biodetection
II Annual Meeting CINBIO
25-26 June 2018, Vigo (Spain)

Sergio Rodal Cedeira

Quantum plexcitonic nanoprobes for ultrasensitive SERS biosensing
ESR 2018 Workshop. COST Action Nanoscale Quatum optics
6-7 September 2018, Braga (Portugal)

Closed-hollow Au SERRS tags for bioimaging
II Annual Meeting CINBIO
25-26 June 2018, Vigo (Spain) **(Poster)**

Daniel Garcia Lojo

Plasmonic Microfluidic platforms based Au nanoactahedra assemblies for ultrasensitive SERS detection
3th International Caparica Conference Nanoparticles/Nanomaterials and Applications 2018 ISN2A2018
22-25 January 2018, Caparica (Portugal) **(Poster)**

Microfluidic induced supercrystals for on-chip ultrasensitive SERS detection (POSTER)
II Annual Meeting CINBIO
25-26 June 2018, Vigo (Spain) **(Poster)**

Microfluidic-Induced 3D Assembly of Nanocrystals for SERS Ultradetection in-Chip
International Workshop on Self-assembly and Hierarchical Materials in Biomedicine (SAHMB)
8-10 October 2018 Donosti (Spain)

Sara Nuñez Sanchez

J-Aggregates as building blocks for photonic materials: excitonic and plexcitonic nanostructures
Photonic and Optoelectronic Materials 2018
9-10 April 2018 Exeter (Reino Unido) **(Invited)**

Molecular Excitonic Materials for a Fully Plastic Nanophotonics
ECIO2018 20th European Conference on Integrated Optics
30 May – 1 June 2018, Valencia (Spain) **(Poster)**

Using Optical Amplifiers Materials to Design Bio-activators at Nanoscale.
ECIO2018 20th European Conference on Integrated Optics
30 May – 1 June 2018, Valencia (Spain) **(Poster)**

Molecular materials as novel building block for nanophotonics:excitonic and plexcitonic nanostructures
E-MRS Fall Meeting 2018
17-20 September 2018 Warsaw (Polonia) **(Invited)**

Subwavelength confinement with J-agregates. A novel quantum material for nanophotonics
ESR 2018 Workshop. COST Action Nanoscale Quatum Optics
6-7 September 2018, Braga (Portugal)

J-Aggregates: an active supramolecular building block for nanophotonics
SNAIA2018, Smart Nanomaterials 2018
10-13 December 2018, (Francia) **(Invited)**

Nanoscale light-confinement using J-aggregates
PHOTON 2018 Aston University
3-6 September 2018, Birmingham (United Kigdom)

Alba Vazquez Arias
Closed-hollow Au SERRS tag for Bioimaging
3th International Caparica Conference Nanoparticles/Nanomaterials and Applications 2018 ISN2A2018
22-25 January 2018, Caparica (Portugal) **(Oral and Poster) Best Oral Presentation Award**

Immunophenotype detection using closed-hollow AU SERRs tags
III Jornada Científica IBEROS
19 March 2018, Porto (Portugal)

Nanolamps for ligth-induced modulation of cell function
A. Vázquez-Arias, S. Nuñez-Sánchez, M. J. Cordero-Ferradás, G. Bodelón, J. Pérez-Juste, I. PastorizaSantos.
II Annual Meeting CINBIO
25-26 June 2018, Vigo (Spain) **(Oral Best Presentation)**

Upconverting nanoparticles for optogenetic applications
IV Jornada Científica IBEROS
11 July 2018, Lugo (Spain)

Carlos Fernández Lodeiro
Iron (II) as a promising reducing agent in the synthesis of metal nanoparticles
Nano Day 2018
9 October 2018, Lisboa (Portugal)

Outreach Activities

- Participation in “They do Science” for university students, February 11, 2018
- Participation in “Pint of Science”, May 15, 2018 Vigo
- Participation in “Open Day of CINBIO”, October 26, 2018
- Participation in “Days of approach to nanomedicine” for secondary school students. Galician Nanomedicine Network, November 6-8, 2018.
- Participation in Outreach activities organized by the Department of Chemistry for highschool students

Research Publications

1. On the consequences of the stereochemical activity of the BI(iii) lone pai rin cyclen-based complexes. The [Bi(DO·A)] case
R. Pujales-Paradela, A. Rodriguez-Rodriguez, A. Gayoso-Padula, I. Brandariz, L. Valencia, D. Esteban-Gomez, C. Platas-Iglesias
Dalton Transaction, 2018, 47, 39, 13830-13842

2. Osteogenic effects of simvastatin-loaded mesoporous titania thin films
M. López-Alvarez, V. López-Puente, C. Rodríguez-Valencia, P. Angelomé, L.M. Liz-Marzán, J. Serra, I. Pastoriza-Santos, P. González
Biomed. Mater., 2018, 13, 025017

3. Seeded growth synthesis of gold nanotriangles: Size control, SAXS analysis, and SERS performance
C. Kuttner, M. Mayer, M. Dulle, A. I. Moscoso, J. M. López-Romero, S. Förster, A. Fery, J. Perez-Juste, R. Contreras-Caceres
ACS Appl. Mater. Interfaces, 2018, 10 (13), 11152–11163

4. Surface-enhanced Raman scattering spectroscopy for label-free analysis of P. aeruginosa quorum sensing
G. Bodelón, V. Montes-García, J. Pérez-Juste, I. Pastoriza-Santos
Front. Cell. Infect. Microbiol., 2018, 8, 143

5. Nitric oxide release from a cucurbituril encapsulated NO-Donor
A. Acuña, N. Basilio, M. Parajó, J. C. C Mejuto, J. Pérez-Juste, P. Taladriz-Blanco, L. García-Río
Org. Biomol. Chem., 2018, 16, 4272-4278

6. Light scattering vs. plasmon effects: Optical transitions in molecular oxygen near a metal nanoparticle
M. Bregnhøj, S. Rodal-Cedeira, I. Pastoriza-Santos, P. R. Ogilby
J. Phys. Chem. C., 2018, 122 (27), 15625–15634

7. Pillar[5]arene-stabilized plasmonic nanoparticles as selective SERS sensors
V. Montes-García, S. Rodal-Cedeira, M. J. Cordero-Ferradás, B. Gómez, L. García-Río, I. Pastoriza-Santos, J. Pérez-Juste
Isr.J.Chem. C., 2018, 58, 11, 1215-1224

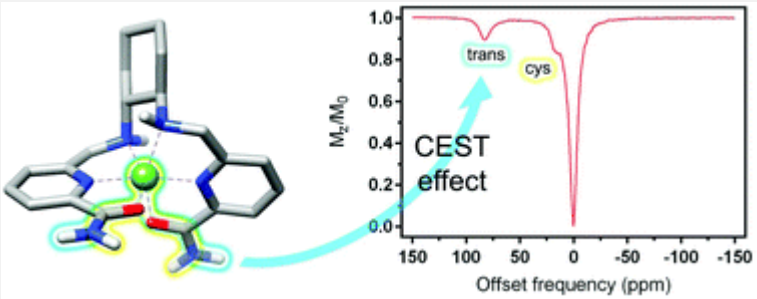
8. Plasmonic polymer nanocomposites
I. Pastoriza-Santos, C. Kinnear, J. Pérez-Juste, P. Mulvaney, L. M. Liz-Marzán
Nature Reviews Materials, 2018, 3, 375-391

9. Tuning the morphology and chiroptical properties of discrete gold nanorods with amino acids
G. Zheng, Z. Bao, J. Pérez Juste, R. Du, W. Liu, J. Dai, W. Zhang, L. Yoon Suk Lee, K.-Yin Wong
Angew. Chem. Int. Ed., 2018, 57, 1-7

Dalton Transaction, 2018, 47, 39, 13830-13842

On the consequences of the stereochemical activity of the BI(iii) lone pai rin cyclen-based complexes. The [Bi(DO·A)] case

R. Pujales-Paradela, A. Rodríguez-Rodríguez, A. Gayoso-Padula, I. Brandariz, L. Valencia, D. Esteban-Gómez, C. Platas-Iglesias

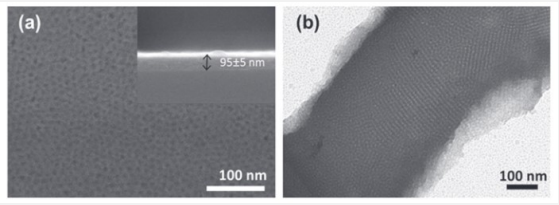


The Ni^{2+} complexes with hexadentate ligands containing two 6-methylpicolinamide groups linked by ethane-1,2-diamine (dedpam) or cyclohexane-1,2-diamine (chxdedpam) spacers were investigated as potential contrast agents in magnetic resonance imaging (MRI). The properties of the complexes were compared to that of the analogues containing 6-methylpicolinate units ($dedpa^{2-}$ and $chxdedpa^{2-}$). The X-ray structure of the $[Ni(dedpam)]^{2+}$ complex reveals a six-coordinated metal ion with a distorted octahedral environment. The protonation constants of the $dedpa^{2-}$ and dedpam ligands and the stability constants of their Ni^{2+} complexes were determined using pH-potentiometry and spectrophotometric titrations (25 °C, 0.15 M NaCl). The [Ni(dedpa)] complex ($\log K_{NiL}$ = 20.88(1)) was found to be considerably more stable than the corresponding amide derivative $[Ni(dedpam)]^{2+}$ ($\log K_{NiL}$ = 14.29(2)). However, the amide derivative $[Ni(chxdedpam)]^{2+}$ was found to be considerably more inert with respect to proton-assisted dissociation than the carboxylate derivative [Ni(chxdedpa)]. A detailed 1H NMR and DFT study was conducted to assign the ^1H NMR spectra of the [Ni(chxdedpa)] and $[Ni(chxdedpam)]^{2+}$ complexes. The observed ^1H NMR paramagnetic shifts were found to be dominated by the Fermi contact contribution. The amide resonances of $[Ni(chxdedpam)]^{2+}$ at 91.5 and 22.2 ppm were found to provide a sizeable chemical exchange saturation transfer effect, paving the way for the development of NiCEST agents based on these rigid non-macrocyclic platforms.

Biomed. Mater., 2018, 13, 025017

Osteogenic effects of simvastatin-loaded mesoporous titania thin films

M. López-Alvarez, V. López-Puente, C. Rodríguez-Valencia, P. Angelomé, L.M. Liz-Marzán, J. Serra, I. Pastoriza-Santos, P. González



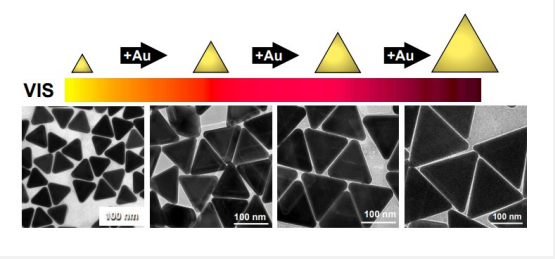
The use of statins in the field of bone regeneration is under current investigation due to the existing demand for non-toxic anabolic agents capable of enhancing bone formation in cases of substantial loss. Simvastatin, a coenzyme currently prescribed in clinics to inhibit cholesterol biosynthesis, has been proven to promote

osteogenic differentiation by stimulating bone formation and inhibiting osteoclasts activity. We present the loading of simvastatin in mesoporous TiO2 thin films toward combining the pro-osteogenic properties of this molecule with the demonstrated bioactivity of titania. TiO2 thin films processing and characterization were carried out, as well as evaluation of MC3T3-E1 pre-osteoblasts viability when directly incubated with different concentrations of simvastatin, followed by the analysis of osteogenic activity promoted by simvastatin upon loading in the thin films. The accessible porosity of 36% quantified on the 95 ± 5 nm thick mesoporous thin films, together with pore diameters of 5.5 nm, necks between pores of 2.8 nm and interpore distances of 12 ± 2 nm allow the loading of the simvastatin molecule, as confirmed by FTIR spectroscopy. Simvastatin was found to promote MC3T3-E1 pre-osteoblasts viability at concentrations ≤0.01 g L^{-1}, with a cytotoxicity threshold of 0.05 g L^{-1}. We additionally found that film loadings with 0.001 g L^{-1} simvastatin promotes statistically higher MC3T3-E1 pre-osteoblast proliferation whereas a higher concentration of 0.01 g L^{-1} leads to statistically higher osteogenic activity (ALP synthesis), after 21 days of incubation, as compared to unloaded films. These results demonstrate the potential of simvastatin local administration based on bioactive mesoporous thin films to promote pro-osteogenic properties. By focusing this strategy on the coating of metallic prostheses, the supply of simvastatin to the target tissue can be favored and risks of systemic side effects will be reduced while enhancing the osteointegration of the implants.

ACS Appl. Mater. Interfaces, 2018, 10 (13), 11152–11163

Seeded growth synthesis of gold nanotriangles: Size control, SAXS analysis, and SERS performance

C. Kuttner, M. Mayer, M. Dulle, A. I. Moscoso, J. M. López-Romero, S. Förster, A. Fery, J. Pérez-Juste, R. Contreras-Caceres

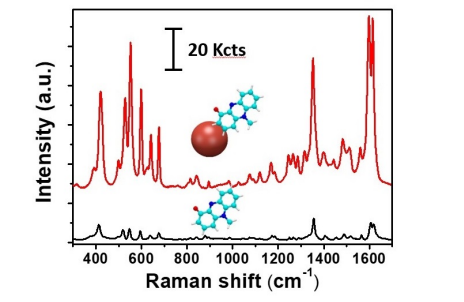


We studied the controlled growth of triangular prismatic Au nanoparticles with different beveled sides for surface-enhanced Raman spectroscopy (SERS) applications. First, in a seedless synthesis using 3-butenoic acid (3BA) and benzyldimethylammonium chloride (BDAC), gold nanotriangles (AuNTs) were synthesized in a mixture with gold nanooctahedra (AuNOCs) and separated by depletion-induced flocculation. Here, the influence of temperature, pH, and reducing agent on the reaction kinetics was initially investigated by UV–vis and correlated to the size and yield of AuNT seeds. In a second step, the AuNT size was increased by seed-mediated overgrowth with Au. We show for the first time that preformed 3BA-synthesized AuNT seeds can be overgrown up to a final edge length of 175 nm and a thickness of 80 nm while maintaining their triangular shape and tip sharpness. The NT morphology, including edge length, thickness, and tip rounding, was precisely characterized in dispersion by small-angle X-ray scattering and in dry state by transmission electron microscopy and field-emission scanning electron microscopy. For sensor purposes, we studied the size-dependent SERS performance of AuNTs yielding analytical enhancement factors between 0.9 × 10^4 and 5.6 × 10^4 and nanomolar limit of detection (10^{-8}–10^{-9} M) for 4-mercaptobenzoic acid and BDAC. These results confirm that the 3BA approach allows the fabrication of AuNTs in a whole range of sizes maintaining the NT morphology. This enables tailoring of localized surface plasmon resonances between 590 and 740 nm, even in the near-infrared window of a biological tissue, for use as colloidal SERS sensing agents or for optoelectronic applications.

Front. Cell. Infect. Microbiol., 2018, 8, 143

Surface-enhanced Raman scattering spectroscopy for label-free analysis of P. aeruginosa quorum sensing

G. Bodelón, V. Montes-García, J. Pérez-Juste, I. Pastoriza-Santos

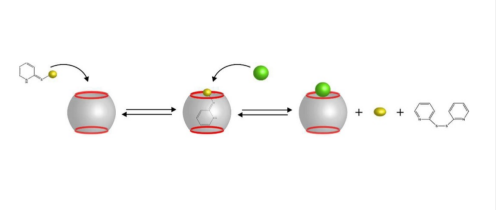


Bacterial quorum sensing systems regulate the production of an ample variety of bioactive extracellular compounds that are involved in interspecies microbial interactions and in the interplay between the microbes and their hosts. The development of new approaches for enabling chemical detection of such cellular activities is important in order to gain new insight into their function and biological significance. In recent years, surface-enhanced Raman scattering (SERS) spectroscopy has emerged as an ultrasensitive analytical tool employing rationally designed plasmonic nanostructured substrates. This review highlights recent advances of SERS spectroscopy for label-free detection and imaging of quorum sensing-regulated processes in the human opportunistic pathogen Pseudomonas aeruginosa. We also briefly describe the challenges and limitations of the technique and conclude with a summary of future prospects for the field.

Org. Biomol. Chem., 2018, 16, 4272-4278

Nitric oxide release from a cucurbituril encapsulated NO-Donor

A. Acuña, N. Basilio, M. Parajo, J. C. C Mejuto, J. Perez-Juste, P. Taladriz-Blanco, L. Garcia Rio

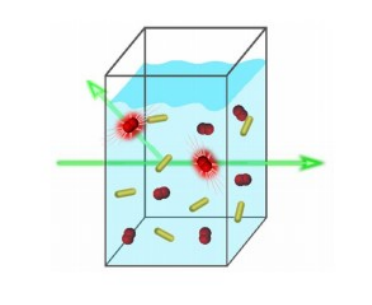


Controlling *S*-nitrosothiol decomposition, with the consequent release of nitric oxide, is a topic of great research interest. The incorporation of nitrosomercaptopyridine (SNO^+) into the cucurbit[7]uril cavity results in a large increase of its nitrosation equilibrium constant. This effect being a consequence of the preferential stabilization of organic cations by the formation of host : guest complexes with CB7 results in a drastic reduction of the SNO^+ denitrosation rate constant. Moreover, SNO^+ encapsulation also prevents its decomposition yielding disulfide and nitric oxide. The expulsion of SNO^+ from the cucurbituril cavity through the application of a chemical stimulus (competitive binding) results in controlled nitric oxide release as was confirmed by using a NO selective electrode

J. Phys. Chem. C., 2018, 122 (27), 15625–15634

M. Bregnhøj, S. Rodal-Cedeira, I. Pastoriza-Santos, P. R. Ogilby

Light scattering vs. plasmon effects: Optical transitions in molecular oxygen near a metal nanoparticle

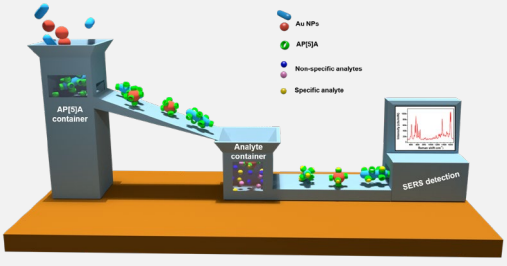


The localized surface plasmon of a metal nanoparticle can influence the optical properties of a molecule in the plasmon field. In a previous study of molecular oxygen adjacent to nanodisks on a flat substrate, we showed that a plasmon field can increase the probability of the $O_2(a^1\,\Delta_g) \rightarrow O_2(X^3\,\Sigma_g^-)$ radiative transition at 1275 nm. For the present study, we set out to ascertain if metal nanoparticles suspended in a liquid solvent could likewise induce measurable plasmonic effects on optical transitions in oxygen. Metal nanoparticles were prepared with the intent of selectively perturbing the 765 nm $O_2(X^3\,\Sigma_g^-) \rightarrow O_2(b^1\,\Sigma_g^+)$ absorption transition. Because $O_2(b^1\,\Sigma_g^+)$ efficiently decays to O2(a1 Δg), we used the spectrally distinct $O_2(a^1\,\Delta_g) \rightarrow O_2(X^3\,\Sigma_g^-)$ phosphorescent transition at 1275 nm to probe the potential plasmon effects at 765 nm. Although we indeed observed nanoparticle-mediated effects on the $O_2(X^3\,\Sigma_g^-) \rightarrow O_2(b^1\,\Sigma_g^+)$ transition, our present data are readily explained in terms of a nanoparticledependent change in the path length of light propagation through the sample. We modeled the latter using features of radiative transfer theory. As such, we cannot claim to observe a plasmonic effect on oxygen from these nanoparticles suspended in solution. Instead, our results point to the general importance of considering the effects of light scattering, certainly for experiments on suspended metal nanoparticles. Indeed, the extent to which light scattering can influence such optical experiments leads us to infer that many claims of a plasmonic effect could be misassigned

Isr.J.Chem. C., 2018, 58, 11, 1215-1224

Pillar[5]arene-stabilized plasmonic nanoparticles as selective SERS sensors

V. Montes-García, S. Rodal-Cedeira, M. J. Cordero-Ferradás, B. Gómez, L. García-Río, I. Pastoriza-Santos, J. Pérez-Juste



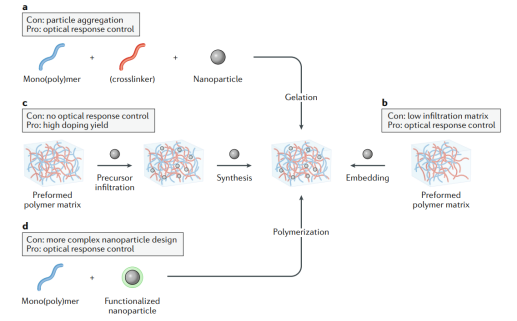
We present here a simple procedure for the surface modification of plasmonic nanoparticles (NPs) with a cationic water-soluble ammonium pillar[5]arene (AP[5]A) in order to create selective surface-enhanced Raman scattering (SERS) spectroscopy based sensors. The strategy is based on a ligand exchange reaction between the AP[5]A and the stabilizing agent of the as-prepared plasmonic NPs. The approach could be applied to plasmonic nanoparticles either negatively charged, stabilized by citrate ions (Au spheres) or positively charged, stabilized by cetyltrimethylammonium bromide (Au and Au@Ag nanorods). The SERS

performance of all systems was studied as a function of NP size and excitation laser line by using an analyte with no affinity towards the metal surface such as pyrene. The analytical enhancement factor (AEF) for the different systems was estimated between 0.55×104 and 1.49×105. Finally the synergistic effect of combining supramolecular chemistry and plasmonic NPs is demonstrated through SERS-based detection, in aqueous media, of molecules with no affinity towards a bare plasmonic substrate such as the contaminant pyrene or the biomolecule pyocyanin with nanomolar limit of detection.

Nature Reviews Materials, 2018, 3, 375-391

Plasmonic polymer nanocomposites

I. Pastoriza-Santos, C. Kinnear, J. Pérez-Juste, P. Mulvaney, L. M. Liz-Marzán



The optical properties of metal nanoparticles, particularly their localized surface plasmon effects, are well established. These plasmonic nanoparticles can respond to their surroundings or even influence the optical processes (for example, absorption, fluorescence and Raman scattering) of molecules located at their surface. As a result, plasmonic nanoparticles have been developed for multiple purposes, ranging from the detection of chemicals and biological molecules to light-harvesting enhancement in solar cells. By dispersing the nanoparticles in polymers and creating a hybrid material, the robustness, responsiveness and flexibility of the system are enhanced while preserving the intrinsic properties of the nanoparticles. In this Review, we discuss the fabrication and applications of plasmonic polymer nanocomposites, focusing on applications in optical data storage, sensing and imaging and photothermal gels for in vivo therapy. Within the nanocomposites, the nanoporosity of the matrix, the overall mechanical stability and the dispersion of the nanoparticles are important parameters for achieving the best performance. In the future, translation of these materials into commercial products rests on the ability to scale up the production of plasmonic polymer nanocomposites with tailored optical features.

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Tuning the morphology and chiroptical properties of discrete gold nanorods with amino acids

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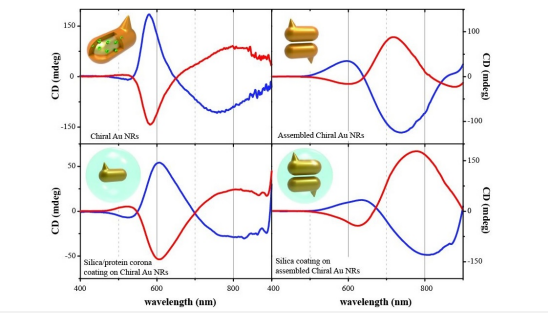

The synthesis of discrete nanostructures with a strong, persistent, stable plasmonic circular dichroism (PCD) signal is challenging. We report a seed-mediated growth approach to obtain discrete Au nanorods with high and stable chiroptical responses (c-Au NRs) in the visible to near-IR region. The morphology of the c-Au NRs was governed by the concentration of l- or d-cysteine used. The amino acids encapsulated within the discrete gold nanostructure enhance their PCD signal, attributed to coupling of dipoles of chiral molecules with the near-field induced optical activity at the hot spots inside the c-Au NRs. The stability of the PCD signal and biocompatibility of c-Au NRs was improved by coating with silica or protein corona. Discrete c-Au NR@SiO_2 with Janus or core–shell configurations retained their PCD signal even in organic solvents. A side-by-side assembly of c-Au NRs induced by l-glutathione led to further PCD signal enhancement, with anisotropic g factors as high as 0.048