

2014

# BioNanoPlasmonics Laboratory Activity Report







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# **OVERVIEW**

#### Overview

#### **RESEARCH PROGRAMME**

The research activity of the BioNanoPlasmonics Lab is focused on the synthesis and formation mechanisms of 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. The group is closely linked to the Colloid Chemistry Group at the University of Vigo, where it was located until recently.

#### SCIENTIFIC OUTPUTS

The scientific activity of BioNanoPlasmonics Laboratory in 2014 can be summarized as follows: 36 publications in high impact scientific journals, 8 ongoing PhD theses, 27 invited lectures and seminars and 3 awards.

#### **GROUP MEMBERS**

During 2014 the group led by Prof. Luis M. Liz-Marzán has been composed by 22 researchers (13 postdoctoral research associates, 7 Ph.D. students and 2 research assistants) and a project manager.



### **Current Group Members**

Prof. Luis M. Liz-Marzán Ikerbasque Professor



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Dr. Judith Langer
Postdoctoral Research Associate



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# **GROUP MEMBERS**

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Dr. Anna Llanes-Pallàs **Project Manager** 



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#### FORMER GROUP MEMBERS

- **Dr. Lakshminarayana Polavarapu** Sept 2012-Mar 2014
- Dr. Amane Shiohara Sept 2012- May 2014
- **Dr. Marta Ibisate** Jul 2013- Jul 2014
- Dr. Sergey Novikov Oct 2012- Oct 2014

# **GROUP MEMBERS**

#### **VISITING RESEARCHERS**

- Martin Mayer (University of Bayreuth) 07/01/2014 to 28/03/2014
- Jakub Ostapko (IPC PAS, Poland) 20/01/2014 to 14/02/2014
- **Fabrice Laye** (Karlsruhe Institute of Technology, Germany) 28/04/2014 to 30/05/2014
- **Ahmet Bekdemir** (EPFL, Switzerland) 28/04/2014 to 30/05/2014
- Clara Fabregat (Visiting Student under the Programme "Joves i Ciència" from Fundació La Pedrera) 01/07/2014 to 18/07/2014
- Brendan Darby (Victoria University Wellington, New Zeland) 25/08/2014 to 12/09/2014
- Svetlana Avvakumova (Università Milano Bicocca, Italy) 06/10/2014 to 02/11/2014
- Anna Li Volsi (Università degli Studi di Palermo, Italy) 15/09/2014 to 15/12/2014
- Prof. Lluís Marsal (Universitat Rovira i Virgili, Tarragona, Spain) 01/10/2014 to 31/12/2014
- Ana Percebom (Universidade Estadual de Campinas, Brasil) 04/05/2014 to 03/05/2015

### Scientific Output

#### **AWARDS**

#### **Highly Cited Researcher**

Luis Liz-Marzán was included in the new lists of *Highly Cited Researchers (Thomson Reuters)*, in two fields: Chemistry and Materials Science.

#### 2014 Medal of the Royal Spanish Society of Chemistry

Awarded to Luis Liz-Marzán by the *Royal Spanish Society of Chemistry (RSEQ)* as recognition for his scientific career. This is the most prestigious award granted by the institution that represents the chemistry scientific community of Spain.

#### 2014 Francqui Chair

Awarded to Luis Liz-Marzán by the Catholic University of Leuven. The "Francqui Chairs" are awarded to renowned Belgian or non-Belgian scientists for stays at Belgian universities, where they should participate in the scientific life and provide specialized teaching.

#### **BBVA Foundation Research Grant**

Marek Grzelczak has been awarded with one of the Grants to Researchers from *Fundación BBVA*. These grants are aimed at young researchers with a high scientific production who are in an intermediate stage of his career.

#### **EDITORIAL ACTIVITY**

#### **Editorial Boards (LL-M)**

- Senior Editor of Langmuir (*American Chemical Society*).
- International Editorial Advisory Board of **Journal of Materials Chemistry B** (*Royal Society of Chemistry*).
- Advisory Board of Nano Today (*Elsevier*).
- *Editorial Board* of Theranostics (*Ivyspring*).
- *International Advisory Board* of ChemistryOpen (*Wiley-VCH*).
- Editorial Advisory Board of Chemistry of Materials (American Chemical Society).
- International Advisory Board of Advanced Optical Materials (Wiley-VCH).
- Executive Editorial Board of Particle & Particle Systems Characterization (Wiley-VCH).
- Editorial Advisory Board of Hybrid Materials (Versita).
- *Board of Reviewing Editors* of Science (AAAS).
- Editorial Advisory Board of ACS Nano (American Chemical Society).
- Editorial Board of Chemistry A European Journal (Wiley-VCH).
- *International Advisory Board* of ChemNanoMat (*Wiley-VCH*).

#### **Guest Editor**

Luis Liz-Marzán served as guest editor of the first issue of volume 31 of Particle & Particle Systems Characterization is dedicated to particle research in the Basque Country. All the articles in this issue are offered for free (open access).

Luis Liz-Marzán served as co-guest editor (with Catherine J. Murphy and Jianfang Wang) of a special issue of Chemical Society Reviews on "Nanoplasmonics" (May 2014).

#### **MASTER THESIS**

#### María San Román

Nanoparticle aggregates as chemical amplifiers

Date: 24/09/2014 Supervisors: Marek Grzelczak and Luis Liz-Marzán

#### INVITED LECTURES AT CONFERENCES, COURSES AND WORKSHOPS

Plasmonic Nanoparticles. From Synthesis to Applications (Plenary)

1st International Symposium on Nanoparticles/Nanomaterials and Applications, Lisbon (Portugal) 20-22 January 2014

2. Self-Assembly of Plasmonic Nanoparticles

The Third International Conference on Frontiers of Plasmonics (FOP3), Xiamen (China) 26 March – 1 April 2014

3. *Understanding Synthesis and Assembly of Metal Nanoparticles* (**Plenary**)

Symposium on Chemistry, a Crossway toward Interdisciplinary: A Symposium for the dissemination of chemical development, Namur (Belgium) 3-4 June 2014

*Metal Nanoparticles for Plasmonic Sensing* (**Opening Plenary**)

Workshop on "New Materials for a Better Life"

Bilbao (Spain) 12 June 2014

Assembly of Noble Metal Nanoparticles (Discussion Leader)

Gordon Research Conference on Noble Metal Nanoparticles, South Hadley (USA) 15-20 June 2014

6. Metal Particles with Unusual Morphologies

Workshop on "Trends in (Nano)photonics: a few summer tales on Photonics", San Sebastian (Spain) 24 July 2014

7. Understanding and Directing Nanocrystal Growth and Assembly (Plenary)

ISACS 15, Challenges in Nanoscience, San Diego (USA) 17-20 August 2014

The Role of Ligands and Additives in Metal Nanocrystal Growth (Plenary)

EuChemS 2014, Istanbul (Turkey) 31 August-4 September 2014

9. Directed Self-Assembly of Plasmonic Colloids (Plenary)

6th Szeged International Workshop on Advances in Nanoscience (SIWAN 2014), Szeged (Hungary) 15-18 October 2014

10. Gold Nanorods and Nanostars as Biosensing Transductors

Seminar on Advanced Nanomaterials for Bioapplications, Vigo (Spain) 24 October 2014

11. Engineering nanoplasmonic colloids (Plenary)

Inorganic and Hybrid Materials Forum, Ludwigshafen (Germany) 18 November 2014

#### **INVITED SEMINARS**

- Morphology control and directed assembly of colloidal plasmonic nanoparticles 1. FUNSOM, Soochow University, China (April 2014)
- 2. Anisotropic and Janus nanoparticles SINANO, Chinese Academy of Science (April 2014)

- 3. Hybrid Nanomaterials for Plasmonic (Bio)Sensing Queen Mary University of London (April 2014)
- 4. Mecanismos de Crecimiento y Ensamblaje de Nanopartículas Master de Ciencia y Tecnología Química, Vigo (April 2014)
- 5. Nanopartículas: Mecanismos de Crecimiento y Autoensamblaje Universidad Complutense de Madrid (May 2014)
- 6. Directed Synthesis and Assembly of Nanoparticles King Saud University, Riad (May 2014)
- Engineering Nanoplasmonic Colloids into Sensing Devices 7. King Saud University, Riad (May 2014)
- Engineering nanoplasmonic colloids into sensing devices 8. Katholieke Universiteit Leuven (June 2014)
- Nanotechnology as a Tool in Biotechnology 9. Centro Nacional de Biotecnología (CNB-CSIC), Madrid (June 2014)
- Anisotropic and Janus Metal Nanoparticles 10. Nanochemistry Seminar, University of Toronto (June 2014)
- Directed Self-Assembly of Nanoparticles 11. California Nanosystems Institute, UCLA (August 2014)
- 12. Tailoring Metal Nanoparticle Synthesis and Assembly for SERS Rice University, Houston (August 2014)
- Nanoingeniería Basada en Química Coloidal 13. Universidad de Sevilla (October 2014)
- 14. Engineering Nanoplasmonic Colloids into Sensing Devices University of Hamburg (November 2014)
- 15. Nanoengineering from single to multiparticle systems XIV Jornada Científica del ICMOL, Valencia (December 2014)
- 16. Usando Nanopartículas para Biotecnología Reunión de Jóvenes Investigadores en el Extranjero, A Coruña (December 2014)

#### PRESENTATIONS AT CONFERENCES FROM GROUP MEMBERS

#### Dr. Marek Grzelczak

Glycan-stabilized Plasmonic nanoparticles: An attractive nanomaterial for bio-application (oral), 247th American Chemical Society National Meeting, Dallas (USA), 16 March 2014.

Integration of cobalt oxide with molecular and polymeric photocatalyst for efficient storage of solar energy in chemical bond (oral), 247th American Chemical Society National Meeting, Dallas (USA), 19 March 2014.

The Use of Plasmonic Nanoparticles for Self-Assembly and Photochemistry (oral), PANIC nanoconference, Wroclaw (Poland), 28 April 2014.

Hydrophobic Interactions Modulate Self-assembly of Gold Nanoparticles (oral), Soft Comp Annual Meeting, Heraklion (Greece), 29 May 2014.

Application of Gold Nanoparticles in Biosensing (oral), Summer Symposium on Nanomaterials and their application to Biology and Medicine, Poznan (Poland), 16 June 2014.

#### Dr. Judith Langer

Flexible nanostar substrates for SERS (poster)

Surface-enhanced Spectroscopies (SES), Chemnitz (Germany), 07-10 August 2014.

#### Dr. Marta Ibisate

Photoluminescence properties of dye-doped silica coated gold nanoparticles (oral)

SoftComp Annual Meeting, Heraklion (Greece), 27 May 2014

#### Leonardo Scarabelli

Synthesis and Overgrowth of Au Nanotriangles and Nanorods: crystallographic evolution in the presence *of different surface-active species* (poster)

Gordon Research Seminar (USA) - 14 - 15 June, 2014

Synthesis and Overgrowth of Au Nanotriangles and Nanorods: crystallographic evolution in the presence *of different surface-active species* (poster)

Gordon Research Conference (USA) - 15 - 20 June, 2014

#### Andrea La Porta

*Gold Nanowires as SERS Substrate* (oral)

Jóvenes Investigadores en Coloides e Interfases II, Granada (Spain), 27 April 2014

Gold Nanowires as SERS Substrate (oral)

SoftComp Annual Meeting, Heraklion (Greece), 27 May 2014

#### María San Román

Nanopartículas de oro como amplificadores de señal (oral)

V Reunión Gallega de Jóvenes Investigadores en el Extranjero, A Coruña, Spain, 29/12/2014

#### Ana Sánchez-Iglesias

Steric Hindrance Induces Cross-like Self-assembly of Gold Nanodumbbells (poster)

PANIC 2014 PhoBiA Annual Nanophotonics International Conference, Wroclau, Poland, 27-30 April 2014

The importance of shape and surface chemistry in colloidal nanofabrication (oral)

SoftComp/ESMI Annual Meeting 2014, Heraklion, Crete, Grecia, 26-30 May 2014

#### CONFERENCE AND WORKSHOP ORGANIZATION (LL-M)

Co-Chair of Symposium "Interactions of Cells with Colloidal Particles" at 247th ACS National Meeting, Dallas (USA), 16-20 Mar 2014.

Scientific committee of the NaNaX6 conference, Bad Hofgastein (Austria), 18 – 23 May 2014.

Scientific committee of the **Surfactants in Solution 2014** conference, Coimbra, 22 – 27 June 2014.

Scientific committee of the 2nd international conference on Bioinspired and Biobased Chemistry **& Materials** conference, Nice (France), 15 – 17 Oct 2014.

Scientific committee of the EMN Fall Meeting, Energy Materials Nanotechnology, Orlando (USA), 22 - 25 November 2014.

#### RESEARCH PUBLICATIONS

- 1. C. Hamon, S. Novikov, L. Scarabelli, L. Basabe-Desmonts, L.M. Liz-Marzán, Hierarchical Self-Assembly of Gold Nanoparticles into Patterned Plasmonic Nanostructures *ACS Nano* **2014**, 8, 10694–10703. **DOI**: 10.1021/nn504407z
- 2. H. Xie, Y. Lin, M. Mazo, C. Chiappini, A. Sánchez-Iglesias, L.M. Liz-Marzán, M.M. Stevens, Identification of Intracellular Gold Nanoparticles Using Surface-enhanced Raman Scattering Nanoscale **2014**, 6, 12403-12407. **DOI**: 10.1039/C4NR04687K
- D.M. Solís, I.M. Taboada, F. Obelleiro, L.M. Liz-Marzán, F.J. García de Abajo, Towards Ultimate Nanoplasmonics Modeling ACS Nano 2014, 8, 7559-7570. DOI: 10.1021/nn5037703
- B. Goris, G. Guzzinati, C. Fernández-López, J. Pérez-Juste, L.M. Liz-Marzán, A. Trügler, U. Hohenester, J. Verbeeck, S. Bals, G. van Tendeloo, Plasmon Mapping in Au@Ag Nanocube Assemblies *J. Phys. Chem. C* **2014**, *118*, 15356–15362. **DOI**: 10.1021/jp502584t
- A. Shiohara, J. Langer, L. Polavarapu, L.M. Liz-Marzán, Solution Processed Polydimethylsiloxane/Gold Nanostar Flexible Substrates for Plasmonic Sensing Nanoscale **2014**, 6, 9817–9823. **DOI**: 10.1039/c4nr02648a
- A. La Porta, M. Grzelczak, L.M. Liz-Marzán, Gold Nanowire Forests for SERS Detection ChemistryOpen 2014, 3, 146–151 (Featured cover image). DOI: 10.1002/open.201402009R1
- M. Grzelczak, A. Sánchez-Iglesias, L.M. Liz-Marzán, A General Approach toward Polymer-Coated Plasmonic Nanostructures CrystEngComm 2014, 16, 9425-9429 (cover image). DOI: 10.1039/C4CE00724G
- Y. Wang, L. Polavarapu, L.M. Liz-Marzán, Reduced Graphene Oxide-Supported Gold Nanostars for SERS Sensing and Drug Delivery ACS Appl. Mater. Interf., in press. (cover image). DOI: 10.1021/am501382y
- L. Polavarapu, A. La Porta, S.M. Novikov, M. Coronado-Puchau, L.M. Liz-Marzán, Pen-on-paper Approach Toward the Design of Universal Surface Enhanced Raman Scattering Substrates Small 2014, 10, 3065–3071 (Frontispiece, highlighted in Materials Views). **DOI**: 10.1002/smll.201400438
- 10. G. Bodelón, S. Mourdikoudis, L. Yate, I. Pastoriza-Santos, J. Pérez-Juste, L.M. Liz-Marzán, Nickel Nanoparticle-Doped Paper as a Bioactive Scaffold for Targeted and Robust Immobilization of Functional Proteins ACS Nano 2014, 8, 6221-6231. DOI: 10.1021/nn5016665
- 11. L. Scarabelli, M. Coronado-Puchau, J.J. Giner-Casares, J. Langer, L.M. Liz-Marzán, Monodisperse Gold Nanotriangles: Size Control, Large-Scale Self-Assembly and Performance in Surface Enhanced Raman Scattering ACS Nano 2014, 8, 5833-5842. DOI: 10.1021/nn500727w
- 12. L. Saa, M. Coronado-Puchau, V. Pavlov, L.M. Liz-Marzán, Enzymatic Etching of Gold Nanorods by Horseradish Peroxidase and Application to Blood Glucose Detection Nanoscale, 2014, 6, 7405-7409. DOI: 10.1039/C4NR01323A
- 13. B. Goris, L. Polavarapu, S. Bals, G. Van Tendeloo, L.M. Liz-Marzán, Monitoring Galvanic Replacement Through Three-Dimensional Morphological and Chemical Mappina Nano Lett. 2014, 14, 3220–3226 (Science Editor's Choice). DOI: 10.1021/nl500593j

- 14. V. Montes-García, C. Fernández-López, B. Gómez, I. Pérez-Juste, L. García-Río, L.M. Liz-Marzán, J. Pérez-Juste, I. Pastoriza-Santos, *Pillar[5]arene mediated synthesis of gold nanoparticles: Size control* and sensing capabilities Chem. Eur. J. 2014, 20, 8404-8409. DOI: 10.1002/chem.201402073
- 15. J. E. Galván-Moya, T. Altantzis, K. Nelissen, F.M. Peeters, M. Grzelczak, L.M. Liz-Marzán, S. Bals, G. Van Tendeloo, Self-organisation of highly symmetric nanoassemblies: a matter of competition ACS Nano 2014, 8, 3869-3875. DOI: 10.1021/nn500715d
- 16. L. M. Maestro, P. Haro-González, A. Sánchez-Iglesias, L.M. Liz-Marzán, J.G. Solé, D. Jaque, Quantum dot thermometry evaluation of geometry dependent heating efficiency in gold nanoparticles Langmuir **2014**, *30*, 1650–1658. **DOI**: 10.1021/la403435v
- 17. N. Almora-Barrios, G. Novell-Leruth, P. Whiting, L.M. Liz-Marzán, N. López, Theoretical description of the role of halides, silver, and surfactants on the structure of gold nanorods Nano Lett. 2014, 14, 871-875. DOI: 10.1021/nl404661u
- 18. S. Hormeño, P. Gregorio-Godoy, J. Pérez-Juste, L.M. Liz-Marzán, B.H. Juárez, J.R. Arias-Gonzalez, Laser Heating Tunability by Off-resonant Irradiation of Gold Nanoparticles Small **2014**, 10, 376–384. **DOI**: 10.1002/smll.201301912.
- 19. P. Quaresma, I. Osório, G. Dória, P.A. Carvalho, A. Pereira, J. Langer, J.P. Araújo, I. Pastoriza-Santos, L.M. Liz-Marzán, R. Franco, P. Baptista, E. Pereira, Star-shaped magnetite@gold nanoparticles for protein magnetic separation and SERS detection RSC Adv. **2014**, 4, 3659–3667. **DOI**: 10.1039/c3ra46762g
- 20. D. Rodríguez-Fernández, T. Altantzis, H. Heidari, S. Bals, L.M. Liz-Marzán, A Protecting Group Approach toward Au-Silica Janus Nanostars Chem. Commun. 2014, 50, 79-81. (Highlighted in Oxford Univ. Press, ScienceDaily, NanoWerk, Nanotech-Now, Quantum Times, etc.). DOI: 10.1039/C3CC47531J
- 21. S. Abalde-Cela, C. Abell, R.A. Alvarez-Puebla, L.M. Liz-Marzán, Real-Time Dual-Channel Multiplex SERS Ultradetection *J. Phys. Chem. Lett.* **2014**, *5*, 73–79. **DOI**: 10.1021/jz402419k
- 22. M. Grzelczak, N. Kulisic, M. Prato, A. Mateo-Alonso, The Influence of Molecular Structure on the Self-Assembly of Phenanthroline Derivatives Into Crystalline Nanowires Part. Part. Syst. Charact., **2014**, 31, 121-125. **DOI**: 10.1002/ppsc.201300289
- 23. S.M. Novikov, A. Sánchez-Iglesias, M.K. Schmidt, A. Chuvilin, J. Aizpurua, M. Grzelczak, L.M. Liz-Marzán, Gold Spiky Nanodumbbells. Anisotropy in Gold Nanostars Part. Part. Syst. Charact., 2014, 26, 77-80 (Frontispiece). DOI: 10.1002/ppsc.201300257

#### **EDITORIALS**

- L.M. Liz-Marzán, The Basque Country Special Issue Part. Part. Syst. Charact., **2014**, 26, 9-10. **DOI**: 10.1002/ppsc.201300374
- L.M. Liz-Marzán, C.J. Murphy, J. Wang, Nanoplasmonics Chem. Soc. Rev. 2014, 43, 3820-3822. (Editorial). DOI: 10.1039/c4cs90026i

#### **REVIEWS**

- 1. L. Polavarapu, J. Pérez-Juste, Q.-H. Xu, L.M. Liz-Marzán, Optical Sensing of Biological, Chemical and Ionic Species Through Aggregation of Plasmonic Nanoparticles J. Mater. Chem. C 2014, 2, 7460-7476. DOI: 10.1039/C4TC01142B
- A. Shiohara, Y. Wang, L.M. Liz-Marzán, Recent Approaches Toward Creation of Hot Spots for SERS Detection *I. Photochem. Photobiol. C* **2014**, *21*, 2–25. **DOI**: 10.1016/j.jphotochemrev.2014.09.001
- 3. B.H.Juarez, L.M. Liz-Marzán, Nanomateriales a la Carta *Investigación y Ciencia* **2014**, 459, 62–70 (in Spanish)
- B.H.Juarez, L.M. Liz-Marzán, Microgels and Nanoparticles: Where Micro and Nano Go Hand in Hand Z. Phys. Chem., in press. **DOI**: 10.1515/zpch-2014-0578
- M. Grzelczak, L.M. Liz-Marzán, Exploiting Hydrophobic Interactions at the Nanoscale J. Phys. Chem. Lett. **2014**, *5*, 2455–2463. (cover image). **DOI**: 10.1021/jz500984w
- S. Bals, B. Goris, L.M. Liz-Marzán, G. Van Tendeloo, Three-Dimensional Characterization of Metal Nanoparticles and their Assemblies by Electron Tomography Angew. Chem. Int. Ed. **2014**, 53, 10600–10610 (frontispiece). **DOI**: 10.1002/anie.201401059
- I.J. Giner-Casares, L.M. Liz-Marzán, Plasmonic Nanoparticles in 2D for Biological Applications: Towards Active Multipurpose Platforms Nano Today **2014**, 9, 365–377. **DOI**: 10.1016/j.nantod.2014.05.004
- V. Montes-García, J. Pérez-Juste, I. Pastoriza-Santos, L.M. Liz-Marzán, Metal Nanoparticles and Supramolecular Macrocycles: A Tale of Synergy Chem. Eur. J. 2014, 20, 10874-10883 (Frontispiece, highlighted in CEJ Facebook and Angewandte Spotlight). DOI: 10.1002/chem.201403107
- 9. P.C. Angelome, L.M. Liz-Marzán, Synthesis and Applications of Mesoporous Nanocomposites Containing Metal Nanoparticles *J. Sol-Gel Sci. Technol.* **2014**, *70*, 180–190. **DOI**: 10.1007/s10971-013-3238-8
- 10. R. Cao-Milán, L. M. Liz-Marzán, Gold nanoparticle conjugates: recent advances toward clinical applications Exp. Op. Drug. Del. 2014, 11, 741-752. DOI: 10.1517/17425247.2014.891582
- 11. M. Grzelczak, L.M. Liz-Marzán, The relevance of light in the formation of colloidal metal nanoparticles Chem. Soc. Rev. 2014, 43, 2089–2097. DOI: 10.1039/C3CS60256G
- 12. S.E. Lohse, N.D. Burrows, L. Scarabelli, L.M. Liz-Marzán, C.J. Murphy, Anisotropic Noble Metal Nanocrystal Growth: The Role of Halides Chem. Mater., 2014, 26, 34-43. (Chem. Mater. 25 Anniv. Issue). DOI: 10.1021/cm402384j

#### ABSTRACTS OF SELECTED PUBLICATIONS

CrystEngComm 2014, 16, 9425-9429

A General Approach toward Polymer-Coated Plasmonic Nanostructures

M. Grzelczak, A. Sánchez-Iglesias, L.M. Liz-Marzán



We report a generic method for the preparation of polymer-coated plasmonic nanostructures with tunable thickness of the hydrophobic polymer spacer. By simply changing the order of addition of a block copolymer and water, encapsulation of either individual or assembled nanoparticles within copolymer micelles can be selected, thus providing wide versatility to the method.

#### ChemistryOpen 2014, 3, 146-151 Gold Nanowire Forests for SERS Detection A. La Porta, M. Grzelczak, L.M. Liz-Marzán



Simple wet chemistry has been applied to control the vertical growth of gold nanowires on a glass substrate. As a consequence, the longitudinal localized surface plasmon band position can be tuned from 656 to 1477 nm in a few minutes by simply controlling the growth rate and time. This allowed us to select the optimum conditions for maximum electromagnetic enhancement and performance in surface enhanced Raman scattering (SERS) detection. SERS measurements confirmed the uniform and reproducible distribution of the nanowires on the substrate, with the subsequent high reproducibility of hot spot formation. Detection of malachite green in water and of 1naphthalenethiol from the gas phase are demonstrated as proof-of-concept applications of these three-dimensional SERS substrates.

Featured Cover Image.

Small 2014. 10. 3065-3071

Pen-on-paper Approach Toward the Design of Universal Surface Enhanced Raman Scattering Substrates L. Polavarapu, A. La Porta, S.M. Novikov, M. Coronado-Puchau, L.M. Liz-Marzán

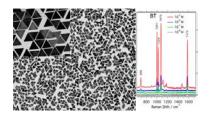


The translation of a technology from the laboratory into the real world should meet the demand of economic viability and operational simplicity. Inspired by recent advances in conductive ink pens for electronic devices on paper, we present a "pen-on-paper" approach for making surface enhanced Raman scattering (SERS) substrates. Through this approach, no professional training is required to create SERS arrays on paper using an ordinary fountain pen filled with plasmonic inks comprising metal nanoparticles of arbitrary shape and size. We demonstrate the use of plasmonic inks made of gold nanospheres, silver nanospheres and gold nanorods, to write SERS arrays that can be used with various excitation wavelengths. The strong SERS activity of these features allowed us to reach detection limits down to 10 attomoles of dye molecules in a sample volume of 10 µL, depending on the excitation wavelength, dye molecule and type of nanoparticles. Furthermore, such simple substrates were applied to pesticide detection down to 20 ppb. This universal approach offers portable, cost effective fabrication of efficient SERS substrates at the point of care. This approach should bring SERS closer to the real world through ink cartridges to be fixed to a pen to create plasmonic sensors at will. Highlighted in Materials Views.

ACS Nano., 2014, 8, 5833 - 5842

Monodisperse Gold Nanotriangles: Size Control, Large-Scale Self-Assembly, and Performance in Surface-**Enhanced Raman Scattering** 

L. Scarabelli, M. Coronado-Puchau, J.J. Giner-Casares, J. Langer, L.M. Liz-Marzán

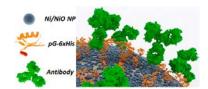


Au nanotriangles display interesting nanoplasmonic features with potential application in various fields. However, such applications have been hindered by the lack of efficient synthetic methods yielding sufficient size and shape monodispersity, as well as by insufficient morphological stability. We present here a synthesis and purification protocol that efficiently addresses these issues. The size of the nanotriangles can be tuned within a wide range by simply changing the experimental parameters. The obtained monodispersity leads to extended self-assembly, not only on electron microscopy grids but also at the air-liquid interface, allowing transfer onto centimeter-size substrates. These extended monolayers show promising performance as surface-enhanced Raman scattering substrates, as demonstrated for thiophenol detection.

#### ACS Nano, 2014, 8, 6221-6231

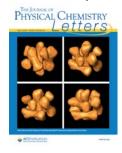
Nickel Nanoparticle-Doped Paper as a Bioactive Scaffold for Targeted and Robust Immobilization of **Functional Proteins** 

G. Bodelón, S. Mourdikoudis, L. Yate, I. Pastoriza-Santos, J. Pérez-Juste, L.M. Liz-Marzán



Cellulose-based materials are widely used in analytical chemistry as platforms for chromatographic and immunodiagnostic techniques. Due to its countless advantages (e.g., mechanical properties, three-dimensional structure, large surface to volume area, biocompatibility and biodegradability, and high industrial availability), paper has been rediscovered as a valuable substrate for sensors. Polymeric materials such as cellulosic paper present high protein capture ability, resulting in a large increase of detection signal and improved assay sensitivity. However, cellulose is a rather nonreactive material for direct chemical coupling. Aiming at developing an efficient method for controlled conjugation of cellulose-based materials with proteins, we devised and fabricated a hybrid scaffold based on the adsorption and *in situ* self-assembly of surface-oxidized Ni nanoparticles on filter paper, which serve as "docking sites" for the selective immobilization of proteins containing polyhistidine tags (His-tag). We demonstrate that the interaction between the nickel substrate and the His-tagged protein G is remarkably resilient toward chemicals at concentrations that quickly disrupt standard Ni-NTA and Ni-IDA complexes, so that this system can be used for applications in which a robust attachment is desired. The bioconjugation with His-tagged protein G allowed the binding of anti-Salmonella antibodies that mediated the immuno-capture of live and motile Salmonella bacteria. The versatility and biocompatibility of the nickel substrate were further demonstrated by enzymatic reactions.

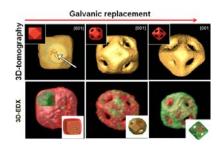
J. Phys. Chem. Lett., 2014, 5, 2455-2463. Exploiting Hydrophobic Interactions at the Nanoscale M. Grzelczak, L.M. Liz-Marzán



Hydrophobic effects are ubiquitous and manifest themselves in everyday processes such as solubilizing oil, precipitating molecules, and formation of particles or foam. Although this phenomenon is often intuitively recognized, it is not straightforward to predict it and, in particular, to control it experimentally. Hydrophobic effects are however progressively gaining recognition as an important tool providing control at the nanoscale, which may ultimately lead to the design of responsive metamaterials with unprecedented functionalities under non-equilibrium conditions.

#### Nano Lett. 2014, 14, 3220-3226

Monitoring Galvanic Replacement Through Three-Dimensional Morphological and Chemical Mapping B. Goris, L. Polavarapu, S. Bals, G. Van Tendeloo, L.M. Liz-Marzán



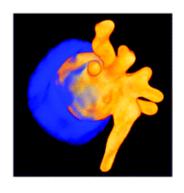
Galvanic replacement reactions on metal nanoparticles are often used for the preparation of hollow nanostructures with tunable porosity and chemical composition, leading to tailored optical and catalytic properties. However, the precise interplay between the three-dimensional (3D) morphology and chemical composition of nanostructures during galvanic replacement is not always well understood as the 3D chemical imaging of nanoscale materials is still challenging. It is especially far from straightforward to obtain detailed information from the inside of hollow nanostructures using electron microscopy techniques such as SEM or TEM. We demonstrate here that a combination of state-of-the-art EDX mapping with electron tomography results in the unambiguous determination of both morphology transformation and elemental composition of nanostructures in 3D, during galvanic replacement of Ag nanocubes. This work provides direct and unambiguous experimental evidence toward understanding the galvanic replacement reaction. In addition, the powerful approach presented here can be applied to a wide range of nanoscale transformation processes, which will undoubtedly guide the development of novel nanostructures.

Highlighted in Science.

#### **Chem Commun.,** 2014, *50*, 79-81

A Protecting Group Approach toward Au-Silica Janus Nanostars

D. Rodríguez-Fernández, T. Altantzis, H. Heidari, S. Bals, L.M. Liz-Marzán



The concept of protecting groups, widely used in organic chemistry, has been applied for the synthesis of Au-silica Janus stars, in which gold branches protrude from one half of Au-silica Janus spheres. This configuration opens up new possibilities to apply the plasmonic properties of gold nanostars, as well as a variety of chemical functionalizations on the silica component.

(Highlighted in Oxford Univ. Press, ScienceDaily, NanoWerk, Nanotech-Now, Quantum Times, etc.).

Part. Part. Syst. Charact., 2014, 26, 77-80

Gold Spiky Nanodumbbells. Anisotropy in Gold Nanostars

S.M. Novikov, A. Sánchez-Iglesias, M.K. Schmidt, A. Chuvilin, J. Aizpurua, M. Grzelczak, L.M. Liz-Marzán



A new type of gold nanoparticle—called "spiky nanodumbbells"—is introduced. These particles combine the anisotropy of nanorods with sharp nanoscale features of nanostars, which are important for SERS applications. Both the morphology and the optical response of the particles are characterized in detail, and the experimental results are compared with FDTD simulations, showing good agreement.

# **SCIENTIFIC COLLABORATIONS**

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# **RESEARCH FUNDING**

# Research Funding

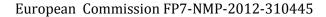
Ikerbasque Basque Foundation for Science

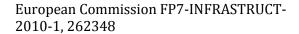


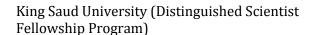
ERC Advanced Grant 267867

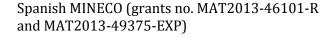


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