Macroscale Construction of Plasmonic 3D Supercrystals *via* Templated Assembly of Monodisperse Gold Nanospheres

Christoph Hanske,[a] Guillermo González-Rubio,[a,b] Cyrille Hamon,[a] Pilar Formentín,[c] Evgeny Modin,[d] Andrey Chuvilin,[d] Andrés Guerrero-Martínez,[b] Lluis F. Marsal,[c] and Luis M. Liz-Marzán.[a,e,f]

[a] BioNanoPlasmonics Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20014 Donostia - San Sebastián, Spain
[b] Departamento de Química Física I, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain
[c] Department of Electronic Engineering, Universitat Rovira i Virgili, Av. Països Catalans, 26, 43007 Tarragona, Spain
[d] Electron Microscopy Laboratory, CIC nanoGUNE, Tolosa Hiribidea, 76, 20019 Donostia-San Sebastian, Spain
[e] Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain
[f] Biomedical Research Networking Center in Bioengineering, Biomaterials, and Nanomedicine, CIBER-BBN, 20014 Donostia - San Sebastián, Spain
cmhanske@cicbiomagune.es

Ordered arrangements of plasmonic nanoparticles are crucial for a plethora of intriguing technologies such as optical metamaterials, subwavelength light management, or ultrasensitive molecular detection.[1,2] For three-dimensional assemblies, the most common building blocks are gold nanospheres, which can form supercrystals with face-centered cubic (fcc) or hexagonal close-packed (hcp) lattices in dense packing. Hereby, despite much progress in the assembly of small mesostructures, preserving ordered packing in large supercrystals remains a major challenge demanding both exceptionally regular particles as well as reliable assembly techniques.[3,4]

In this contribution, we present solutions for these two important aspects. First, a facile protocol is introduced yielding gold nanoparticles that are not only monodisperse in size but also remarkably spherical and rounded: hereby, growing the particles quickly to the desired size and removing surface roughness subsequently by an efficient etching procedure enabled the synthesis of large quantities of well-defined nanospheres with diameters up to 110 nm. Second, we discuss the arrangement of nanospheres into pyramid-shaped supercrystals by template-assisted self-assembly: after PEGylation and partial removal of the stabilizing surfactant these gold nanospheres could be utilized to build arrays of separated pyramids by simple drying of highly concentrated dispersions between a topographically structured, hydrophobic stamp and a flat hydrophilic target substrate. Thereby, uniform pyramid assemblies were obtained over mm^2 areas. Investigation by high magnification SEM and focused ion beam cutting through individual square base pyramids showed that the nanospheres assembled into an fcc lattice forming high-quality, micron-sized supercrystals.

Our results represent a facile pathway enabling the large-scale assembly of highly organized plasmonic supercrystals, which is of special importance for functional materials with applications, for instance, in light harvesting and sensing.

References

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