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Communication

Dissymmetric silica nanospheres: a first step to difunctionalized nanomaterials

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This communication reports the synthesis of silica nanoparticles dissymmetrically decorated by gold nanoclusters, using a gas–liquid interface as a dissymmetrization tool. The effective dissymmetrization of the nanoparticles was clearly observed using transmission electron microscopy. These results suggest that each hemisphere of these nanostructures can be further specifically functionalized, leading to promising nanomaterials with specific properties.

One of the current major challenges in materials chemistry is the synthesis of complex nanoscale structures, whose properties can be tuned by manipulating the arrangement of their constituents. To date, both covalent and non-covalent strategies have been used to assemble building units into various structures.[1] Simultaneously, the air–water interface has been shown to be a powerful tool for the organization of nanoparticles into 2D arrays.[2] Similar behavior is seen along a liquid–solid interface in the case of self-assembly on a solid substrate.[3] This property of interfaces which forces the chemical entities to organize themselves has been therefore frequently used to build new materials,[4] or to control the epitaxial growth of crystals[5] or the formation of a mesoscopically organized medium[6] along a structured interface.

Outside this organizing effect, the interface between two media may also induce or be used to induce a dissymmetry in an initially symmetric object adsorbed along this interface. Indeed, let us suppose that isotropic particles are organized along the gas–water interface (see Fig. 1). Each particle presents two sides, one in contact with the gas phase, the other one in contact with the aqueous subphase. Therefore, these two sides are no longer identical and may react differently. This difference in the reacting behavior may be simply due to a difference in the accessibility of the two sides. For example, if the reacting entity is water soluble, it may reach the side in contact with water and not the other one, leading to dissymmetrized particles (see Fig. 1). This theoretical idea has very recently been tested successfully by Fujimoto *et al.*,[7] who synthesized unsymmetric microspheres at liquid–solid or air–liquid interfaces.

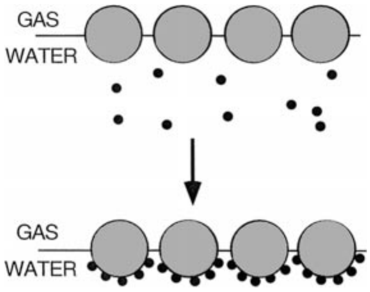

Fig. 1 Schematic procedure used in this paper to elaborate dissymmetric nanoparticles. In gray: silica nanoparticles; in black: gold nanoparticles.

The object of this communication is to report the dissymmetrization of objects in the size range from tens to hundreds of nanometers, using the air–liquid interface as a dissymmetrization tool. NH_2 functionalized silica nanospheres have been selected as models for initially symmetric entities which will be spread at the gas–water interface. They are indeed of particular interest for the following reasons. Firstly, their synthesis is easily achieved through the base-catalyzed hydrolysis of tetraethylorthosilicate, as described by Stober *et al.*,[8] and their average size is easily controlled. Secondly, their surface composition can be tailor-made by *in situ* grafting of a heterofunctional alkoxysilane.[9] In our case, the grafting of the amine functions onto the silica nanospheres was achieved using 3-aminopropyltrimethoxysilane as a reagent. Transmission electron microscopy (TEM; JEOL 2000 FX) shows that the shape and size of the synthesized silica nanoparticles are highly regular. Their diameter is close to 90–120 nm.

To react with such spherical models, we have selected negatively charged gold nanoparticles.[10] Indeed, Westcott *et al.* have shown that such gold nanoparticles can be readily adsorbed on NH_2 functionalized silica spheres leading to new symmetrical nanostructures.[9] Furthermore, the elaboration of these gold–silica entities may be of particular interest in the fields of biology and medicine, as the final products may support various functionalities.

A dispersion of the amino functionalized silica particles in chloroform was spread along a solution of gold nanoparticles[11] contained in a KSV 5000 trough. The Langmuir film was then compressed slowly (*ca.* 1 $cm^2\ min^{-1}$) until the surface pressure reached 10 $mN\ m^{-1}$.[12] The film was partially recovered onto carbon coated copper grids (size 200 mesh), by touching the face of the grid to the liquid surface, in order to be analysed by TEM. For comparison, the same solution of gold nanoparticles was mixed with an aqueous dispersion of the amino functionalized silica particles. In that case and as previously reported,[9] the gold nanoparticles were adsorbed all along the surface of the silica particles. The surface coverage was isotropic and less than 20%. In contrast, the particles spread at the gas–water interface clearly present a dissymmetry, as shown in Fig. 2 and 3. The gold nanoparticles are generally bound to one particular part of the silica sphere, forming a sort of cap on the top of it. It should be noted that if the silica sphere does not rotate during deposition, the gold nanoparticles will be found theoretically on the top of the silica particle deposited onto the grid and the particle dissymmetry can not be clearly shown by TEM (see the large particle at the bottom left of Fig. 3). Nevertheless, in such a case, all the gold nanoparticles fixed on a silica sphere have generally a similar contrast in the TEM picture, suggesting that they are indeed on the same

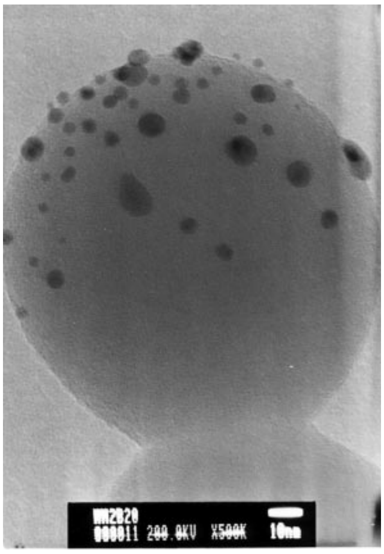

Fig. 2 TEM image (160×110 nm^2) showing a typical dissymmetric particle.

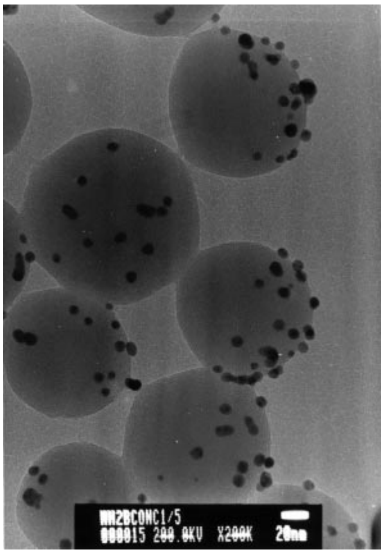

Fig. 3 Typical TEM image showing various dissymmetric nanostructures (scale bar = 20 nm).

moiety of the silica sphere. This demonstrates that the gas–water interface can indeed be used as a tool to dissymmetrize nanoparticles. No correlation was found between the size of the gold nanoparticle cap and the radius of the silica particles. This is a clear indication that, because of their size polydispersity, the silica particles in the Langmuir film may be more or less in contact with the aqueous subphase, leading to a varying and uncorrelated size of the gold adsorbed area. Preliminary experiments show that changing the size of the silica particles (up to 300 nm) or of the gold nanoparticles (up to 20 nm) does not appear to modify the process of dissymmetrization at the gas–water interface.

The experiments described above demonstrate that the elaboration of dissymmetrized nanoparticles can be easily performed using the gas–water interface as a tool for the dissymmetrization. We are currently extending our work to other reacting entities and particles, using also liquid–solid or solid–gas interfaces as dissymmetrization tools. We have therefore the opportunity to develop new inorganic or hybrid organic–inorganic nanomaterials presenting spatial as well as chemical dissymmetry. Indeed, each hemisphere of the dissymmetric nanospheres can be further specifically functionalized, leading to systems which could be highly useful in particular for biological applications or for the elaboration of new display devices.

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Notes and references

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10 Aqueous dispersions of gold nanoparticles (diameter close to 8–10 nm) were prepared by reduction of chloroauric acid according to the procedure already published: A. Meier and D. Meissner, in *Nanoparticles in Solids and Solutions*, ed. J. H. Fendler and I. Dekany, Kluwer Academic Publishers, Dordrecht, 1996, pp. 421–449. Experimentally, to a 0.08 mM $HAuCl_4$ solution (100 mL) cooled at 5 °C and purged with argon, 0.5 mL of a 0.1 M trisodium citrate solution is added. Then, a freshly prepared aqueous solution of $NaBH_4$ is added dropwise until the solution turns to red-purple.

11 The chloroform dispersion has an average concentration of *ca.* 2 mg of silica per ml. The subphase is a five-fold diluted solution of the pristine dispersion of gold nanoparticles obtained following the procedure described in ref. 10.

12 The obtained Langmuir film was stable at 10 mN m^{-1} as no variation of the surface pressure greater than 0.5 mN m^{-1} was registered over a time period of 12 hours.

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