

Towards large amounts of *Janus* nanoparticles through a protection–deprotection route†

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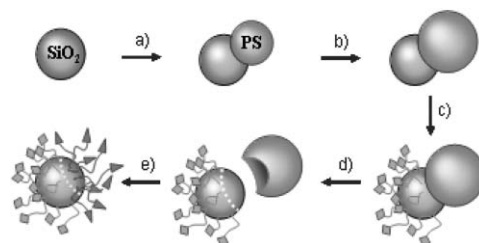
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Janus silica nanoparticles, regioselectively functionalized by two different chemical groups, were synthesized through a multistep procedure based on the use of a polystyrene nodule as a protecting mask.

Since the original work of Casagrande and Veyssié in the late eighties,¹ several methods for fabricating surface-dissymmetrical particles, firstly called “Janus” particles by de Gennes² with reference to the double-faced god of the Doors (literally “Janus” in Latin), have been reported. Most of these techniques are based on the use of an interface between two media³ or the exposure to a directional flux⁴ as dissymmetrization tool. For instance, micrometric “Janus” polystyrene latexes have been obtained recently by replication of particle monolayers at liquid surfaces⁵ or by micro-contact printing techniques.⁶ Nevertheless, there are only few reports on the synthesis of large amounts of “Janus” structures that are smaller than one micron.⁷ Here we report a new method to create Janus nanoparticles in batch, at the gram scale. On the basis of the concept that a removable mask can temporarily protect a part of an object in a reactive medium, a polymer nodule is grown onto the surface of silica particles to yield silica/polymer dissymmetrical colloids. The unprotected mineral part of the resulting snowman-like particles is selectively functionalized and the protecting polymer mask is removed in a subsequent step (Scheme 1).

To demonstrate the regioselectivity of the surface modification reaction, we used gold nanocolloids as markers, and we also grew a gold cap on a single side of the mineral spheres. Besides demonstrating the efficiency of using a polymer latex as a protective mask, this work offers a convenient methodology to fabricate large amounts of surface-dissymmetrical functional nanoparticles. These



Scheme 1 Schematic representation of the consecutive stages for the fabrication of the “Janus” nanoparticles.

nanostructures may be useful for biomedical applications such as cells or proteins binding, biosensors, or may act as particulate surfactants in the stabilization of complex media.

The synthetic route for making the “Janus” nanoparticles first consists in the emulsion polymerization of styrene in the presence of silica particles (with diameters ranging from 50 to 150 nm), which have been surface-modified by polymerizable groups (see Supplementary Information†). In such conditions, the formation of polystyrene nodules is highly favored at the silica surface.⁸ Then, in the case when the ratio between the number of silica seeds and the number of growing nodules is close to one, snowman-like hybrid nanostructures are obtained^{9,10} with a high yield, *ca.* 85% (see stage a) on Scheme 1 and Fig. 1). Lone silica particles or hybrid particles made of two polystyrene nodules attached to one silica sphere are in fact rarely observed. The affinity of the polystyrene nodule for the mineral sphere and the morphology of the resulting hybrid nanostructures can be tuned by varying the density of polymerizable groups at the surface of the mineral precursors and the reaction time (stage b)).¹⁰ The formation of the snowman-like particles is based on the copolymerization of oligomers with the double bonds which are present at the silica surface. Chemisorbed polymer chains are thus generated. As the density of polymerizable groups at the surface of the silica particles is low, these polymer chains form one single nodule at the surface

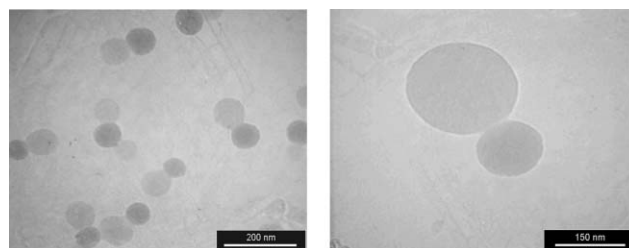


Fig. 1 Transmission electron microscopy (TEM) images of snowman-like particles. Diameter of the silica seeds: 80 nm (left) and 150 nm (right).

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† Electronic supplementary information (ESI) available: experimental procedure to synthesize the snowman-like hybrid particles. TEM image of latex particles isolated by centrifugation from the “Janus” silica particles after their separation. TEM images of silica nanoparticles functionalized with amine or methyl-groups on the whole surface after reaction with gold nanocolloids. TEM image of a “Janus” nanoparticle regioselectively coated by a gold cap. See DOI: 10.1039/b507486j

of the silica particle, as the high interfacial energy (due to the presence of unreacted silanol groups) does not promote their spreading on the surface.

The specific functionalization of the unprotected silica surface with a trialkoxysilane derivative is then carried out (stage c)). For example, the grafting of methyl groups can be easily achieved by adding methyltriethoxysilane (typically, in a quantity corresponding to 15 functions per nm^2 of nanoparticles surface) in a slightly basic water–ethanol (50 : 50 v/v) suspension of the snowman-like particles. After three dialysis stages *versus* water which aim to remove the unreacted species, the separation of the organic and mineral components is realized under ultra-sonication (350 W) in pure water for 45 minutes, or by ultra-centrifugation in an aqueous solution of sodium dodecyl sulfate (0.04 mol L^{-1}) at 50 000 rpm during 15 minutes (stage d)). The surfactant favors the separation of the two parts by decreasing the surface energy of the created interfaces. TEM images (Fig. 2) of the resulting suspension confirm the presence of latex particles exhibiting a circular notch (indicated by arrows) as a trace of their previous anchoring at the silica surface, and deprotected “Janus” silica particles. The organic and mineral species can be isolated by centrifugation at 4000 rpm in an ethanol–water (50 : 50 v/v) mixture, the silica particles sedimenting whereas the latex particles remain in the supernatant (see Supplementary Information Fig. 1†). Typically, one gram of “Janus” particles can be obtained within two days.

Possibly, the deprotected zone of the silica surface can be functionalized in a similar way as previously, with a second trialkoxysilane derivative (stage e)). For instance, the grafting of amine groups can be achieved by using aminopropyltriethoxysilane. The efficiency of this functionalization can be evidenced by mixing the hybrid colloids with an aqueous suspension of citrate-stabilized 18 nm gold nanoparticles,¹¹ which specifically adsorb onto the amine-grafted mineral surface.¹² Indeed, TEM images shown in Fig. 3 clearly demonstrate that the gold nanocolloids are adsorbed onto a specific zone of the silica particles, suggesting their dissymmetrical “Janus” character. As a comparison, similar experiments with silica particles functionalized with amine or methyl groups on the whole surface were also carried out. The first ones exhibited heavy isotropic coverage of gold nanocolloids whereas no adsorption was observed on the second ones (see Supplementary Information Fig. 2†). We have also taken benefit of this regioselective functionalization of the silica spheres with amine groups to synthesize a gold cap onto one side of the silica particles, following the procedure reported by Graf and van Blaaderen¹³ (see Supplementary Information Fig. 3†). Such heterostructures can be rendered sensitive to the gradient of their

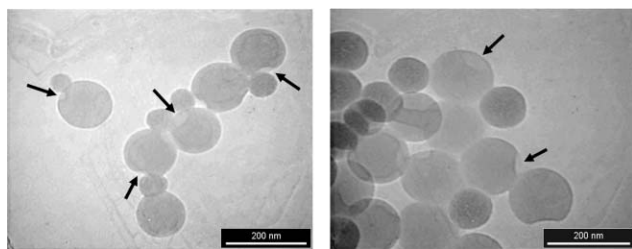


Fig. 2 TEM images of the latex and silica particles partially (left) and fully separated (right). Diameter of the silica seeds : 80 nm (left) and 100 nm (right).

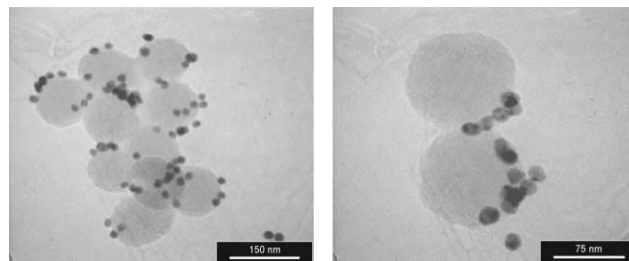


Fig. 3 TEM images of “Janus” silica nanoparticles (diameter : 100 nm) in which the amine grafted area is decorated by gold nanocolloids, the remaining area being functionalized by methyl groups.

physicochemical microenvironment through a subsequent functionalization of the metallic cap by thiols with ionizable groups.^{4a}

In summary, we have demonstrated an efficient strategy to form large amounts of “Janus” nanoparticles based on the use of a polymer nodule as a mask. This method offers easy access to nanostructures that can be amphiphilic, bifluorescent, responsive to an electric field (with both hemispheres of opposite charges) or simply functional for subsequent regioselective surface chemistry. We believe that such materials will be useful as biological and chemical sensors,¹⁴ stabilizers of complex media,¹⁵ and nanocomponents in smart displays.¹⁵

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