Supplementary Material for Chemical Communications

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

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Supplementary Material (ESI)
(4 pages)

Experimental

Fabrication of silica particles

500 mL of absolute ethanol (J.T. Baker) and 37.5 mL of an aqueous solution of ammonia (25% in water, SDS) were introduced in a three-neck round flask of 1 L equipped with a refrigerating system. The mixture was stirred at 300 rpm to homogenize and heated at different temperatures, depending on the desired final particle diameter (50 nm at 70°C; 80 nm at 65°C; 100 nm at 50°C; 150 nm at 35°C). After stabilization, 15 mL of tetraethoxysilane (TEOS, Fluka) was added quickly and reaction occurred at the chosen temperature under permanent stirring. Silica size was determined statistically while analyzing TEM pictures.

To promote the growth of the polystyrene nodules at the surface of the silica particles, this one must be modified with polymerizable groups. Two routes have been used :

Silica surface modification by polymerizable groups via the adsorption of poly(ethylene glycol) methacrylate macromonomer

A stock solution of poly(ethylene glycol) methacrylate macromonomer (Polysciences) was added to the silica suspension in deionized water obtained with a MilliQ system (Millipore). Adsorption was performed at 25°C and allowed to equilibrate for at least 3 hours. The chosen concentration was taken equal to 1,5 µmoles of methacrylate groups per nm^2 of inorganic surface.

Silica surface modification by polymerizable groups via the grafting of methacryloxymethyltriethoxysilane

To graft polymerizable groups onto the silica surface, a given volume of methacryloxymethyltriethoxysilane (MMS, Gelest-ABCR) was added directly into the silica particles suspension at the end of their synthesis. After stirring for 3 hours at ambient temperature, the reaction medium was heated to 90°C during 1 hour to promote covalent bonding. When the synthesis was completed, the main part of ethanol and ammonia was removed through evaporation under reduced pressure.

All the silica suspensions were then dialyzed against water until neutral pH in order to remove the remaining reactants and replace ethanol with water.

Synthesis of snowman-like particles

Emulsion polymerization of styrene (Sigma) was performed in the presence of silica particles which had been surface-modified by polymerizable groups, via one of the two above methods. The suspension of silica particles was transferred into a thermostated reactor and the monomer was introduced. To stabilize the emulsion, a surfactant is usually added which can also tune the size of the latex particles. In our case, we used a nonylphenol poly(oxyethylenic) non-ionic surfactant (Synperonic NP30, Fluka) and its concentration (3 $g.L^{-1}$ in all the cases) was chosen such as we got latexes with diameters around 100 nm and 200 nm after 1 and 3 hours of reaction, respectively. Then, the suspension was purged with nitrogen and heated up at 70°C before adding sodium persulfate as initiator (Aldrich, 0.5% by weight relative to monomer) to start polymerization. Samples were taken from the batch at different times to study the kinetics of the reaction and its consequences on the particles morphology.

Grafting methyl groups on the snowman-like particles or amine groups on the "Janus" particles

A similar procedure as above was carried out with methyltriethoxysilane (Aldrich) or aminopropyltriethoxysilane (Aldrich) to graft methyl or amine groups at the surface of the snowman-like or "Janus" particles, respectively. A given volume of the trialkoxysilane was added into the suspension of the particles. After stirring for 3 hours at ambient temperature, the reaction medium was heated to 70°C during 1 hour to promote covalent bonding.

Transmission Electron Microscopy

TEM experiments were performed with a JEOL 2000 FX microscope (accelerating voltage of 200 kV). The samples were prepared as follows: the particles were dispersed in water and one drop of the dilute suspension was deposited on a copper grid coated with a carbon membrane.

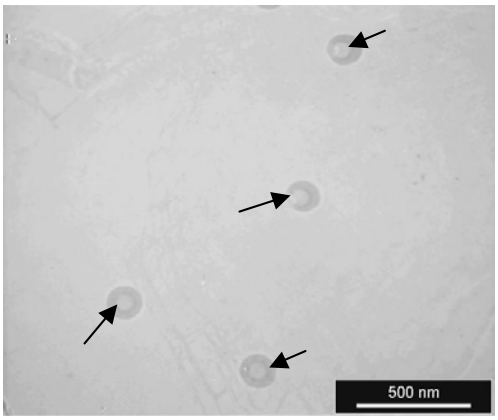

Fig. 1 TEM image of latex particles isolated by centrifugation from the "Janus" silica particles after their separation. One can clearly see the circular notch (pointed by arrows) as a trace of their previous anchoring at the silica surface.

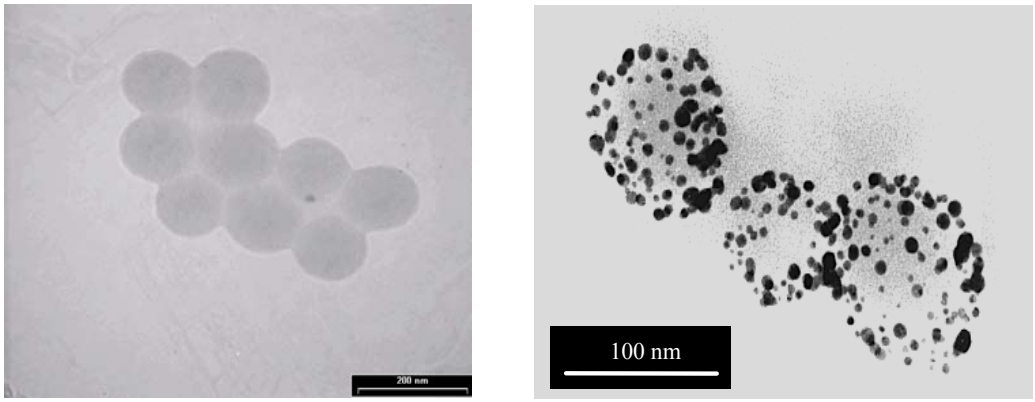

Fig. 2 TEM images of silica nanoparticles functionalized with methyl (left) and amine groups (right) on the whole surface after reaction with gold nanocolloids.

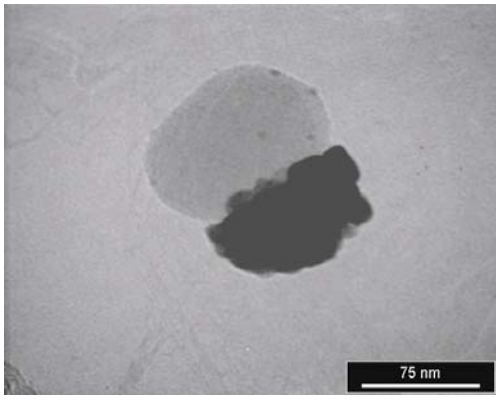

Fig. 3 TEM image of a "Janus" silica nanoparticle regioselectively coated by a gold cap.