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Regioselective Coating of Tetrapod-like Clusters with Silica

ANTHONY DÉSERT,[1,4] CÉLINE HUBERT,[2] ANTOINE THILL,[3] OLIVIER SPALLA,[3] JEAN-CHRISTOPHE TAVEAU,[4] OLIVIER LAMBERT,[4] MURIEL LANSALOT,[5] ELODIE BOURGEAT-LAMI,[5] ETIENNE DUGUET,[1] AND SERGE RAVAINE[2,*]

[1]CNRS, Univ. Bordeaux, ICMCB, Pessac, France
[2]CNRS, Univ. Bordeaux, CRPP, Pessac, France
[3]Commissariat à l'Energie Atomique, Gif-sur-Yvette, France
[4]Univ. Bordeaux, CNRS, CBMN, Pessac, France
[5]Université de Lyon, CPE Lyon, CNRS, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, Villeurbanne, France

We describe an easy procedure to regioselectively coat binary tetrapod-like silica/polystyrene clusters with silica. First we show that the addition of tetraethoxysilane into a basic hydroalcoholic suspension of binary tetrapods induces the preferential growth of their silica core, which conforms to the shape of the polystyrene nodules while growing. On the contrary, we show that the formation of a continuous silica shell around the clusters is promoted if silanol groups have been incorporated at the surface of the polystyrene nodules before the addition of tetraethoxysilane. The thickness and the roughness of the silica coating can be tuned by varying several experimental parameters.

Keywords Surface modification; colloidal molecules; silica

1. Introduction

Many different strategies have been developed during the last decade to produce non-spherical colloidal particles with precisely defined morphologies and surface properties, often called "colloidal molecules" [1–5]. One approach is to start with preformed spherical particles and to control their aggregation into polyhedral clusters. Examples of this approach include colloidal aggregation on micro-patterned substrates [6] or on evaporating emulsions droplets [7]. If the particles are made up of different components, they

*Address correspondence to Serge Ravaine, Centre de Recherche Paul Pascal, 115, avenue du Dr. A. Schweitzer 33600 Pessac, France. E-mail: ravaine@crpp-bordeaux.cnrs.fr

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have patterned surfaces as well as anisotropic compositions. Such hybrids can open unprecedented opportunities that cannot be provided by simple mixtures of their individual constituents. Among hybrid particles, multipod-like particles, *i.e*. colloids made of a central core bearing on their surface a small number (typically from 2 to 12) of particles of a different chemical nature, have emerged into a promising class in itself in recent years. We have recently reported the high-yield synthesis of binary polystyrene (PS)/silica multipods with a controlled morphology by a seeded-growth emulsion polymerization of styrene [8–9]. These multipod-like particles can be used as endotemplates to produce multivalent silica particles, favoring the growth of the silica core of the binary clusters by carefully adjusting the experimental conditions [10]. It has also been shown that the multipods can be encapsulated by a silica shell through the incorporation of silanol groups (SiOH) on the surface of the PS nodules using 3-(trimethoxysilyl)propyl methacrylate (MPS) as a functional (co)monomer during the emulsion polymerization, followed by the hydrolysis/condensation of tetraethoxysilane (TEOS) [11]. In this paper, we clearly evidence the role of the MPS as promoting agent of the silica shell formation. We also discuss the influence of several experimental parameters such as the concentration of tetrapods, the amount of TEOS, or the water content in the reaction medium on the formation of the silica shell. Silica-coated tetrapod-like particles can be used as elementary building blocks for the elaboration of novel materials with new properties, such as photonic crystal with a full 'band gap' that can inhibit the propagation of light and modify the spontaneous emission of photons at visible wavelengths.

2. Experimental Section

2.1. Materials

Tetraethoxysilane (TEOS, 98%, Aldrich) and 3-(trimethoxysilyl)propyl methacrylate (MPS, Aldrich, 98%) were all used as received. Absolute ethanol was purchased from Scharlau (99.9%), and ammonia solution (25–30%) was from J.T. Baker. Water was Milli-Q grade (Millipore).

2.2. Methods

Synthesis of tetrapods. Aqueous suspensions of tetrapods (yield ∼70%) made of a central silica core (D_{Si} = 44 nm) and four polystyrene satellite nodules (D_{PS} = 140 nm) were prepared by seeded emulsion polymerization of styrene using a mixture of surfactants (sodium dodecylsulfate SDS and Synperonic® NP30, wt. ratio 5/95), according to an already published procedure [8–9].

Silica shell formation. 100 μL of MPS were added to the medium at the end of the polymerization reaction and the mixture was stirred at 70°C for 2 h. A certain volume V_{TEOS} (see text) of TEOS was diluted ten times in absolute ethanol. The resulting solution was introduced continuously in a mixture of a certain volume V_{tetra} of an aqueous suspension of MPS-modified tetrapods (at $\sim 1.8^{*}10^{16}$ particles L^{-1}), 23.1 mL of absolute ethanol and ammonia solution at 0.5 mL h^{-1} thanks to a single-syringe pump. The mixture was stirred at room temperature during 12 h.

The addition of TEOS under similar conditions to a suspension of tetrapods which have not been modified with MPS led to the growth of the silica core only.

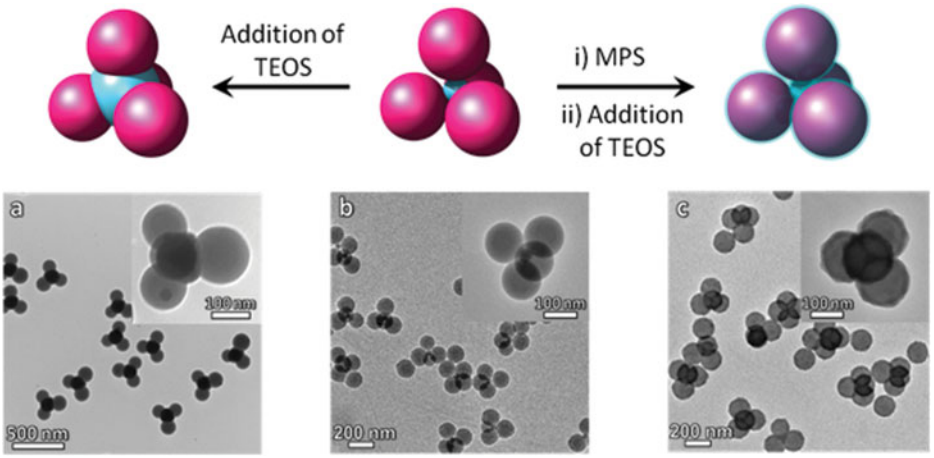

Figure 1. TEM views of tetrapods before (b) and after the growth of their silica core (a) or their coating with a silica shell (c). $V_{TEOS} = 200\ \mu L$; $V_{tetra} = 1$ mL; $[NH_3] = 0.5$ mol L^{-1}; $[H_2O] = 3.6$ mol L^{-1}.

TEM characterization. TEM images were obtained with a FEI CM120 microscope operating at an accelerating voltage of 120 kV. The samples were prepared as follows: colloids were diluted in ethanol and one drop of the diluted suspension was deposited on a copper grid coated with a carbon membrane.

3. Results

3.1. Importance of the MPS Modification

In a first series of experiments, we slowly added a dilute solution of tetraethoxysilane in ethanol into a hydroalcoholic suspension of tetrapods obtained by the seeded emulsion polymerization of styrene, in presence of ammonia. Figure 1 shows that a preferential polycondensation of TEOS molecules onto the surface of the silica core of the binary particles occurs, leading to its growth. While growing, the silica surface conforms to the shape of the PS nodules. We took benefit of this conformational growth by subsequently dissolving the PS nodules in THF during 4 h. After three cycles of centrifugation/redispersion in THF to remove the dissolved polymer, tetravalent silica particles with four concave notches were obtained [8].

In order to favour the formation of a silica shell around the tetrapod-like clusters, we thus adopted a strategy initially proposed to incorporate silanol groups (SiOH) on the surface of polystyrene latex particles [12, 13]. 3-(trimethoxysilyl)propyl methacrylate (MPS) was added as a functional (co)monomer just before the completion of the emulsion polymerization and the mixture was let to react during 2 h at 70°C. By reacting MPS at the polymer particle surface, we aimed to produce tetrapods whose polystyrene nodules exhibit surface properties similar to those of silica microspheres. The slow addition of 200 μL of TEOS to a basic hydroalcoholic suspension of modified tetrapods induced their encapsulation by a thin silica shell, as shown in Figure 1c. A shell thickness of 12 ± 2 nm was determined by analysis of TEM images.

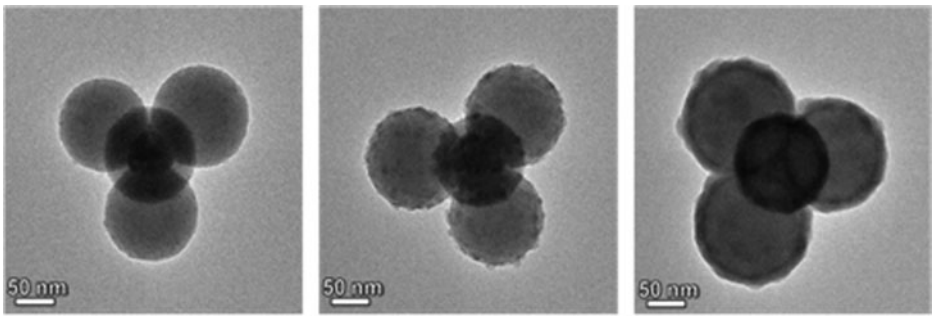

Figure 2. TEM images of tetrapods coated by a silica shell. From left to right, $V_{TEOS} = 25\ \mu L$, 100 μL and 300 μL. $V_{tetra} = 1$ mL; $[NH_3] = 0.5$ mol L^{-1}; $[H_2O] = 3.6$ mol L^{-1}.

3.2. Influence of TEOS Quantity

Working with MPS-modified tetrapods, we studied the influence of the quantity of silica precursor by running a series of experiments during which 25 μL, 100 μL or 300 μL of TEOS were added. Figure 2 shows that the larger the volume of TEOS, the thicker the resulting silica shell, as expected. For a volume of 300 μL, the objects obtained are quite similar to those obtained with $V_{TEOS} = 200\ \mu L$, with a slightly thicker shell ($\approx$15 nm). For $V_{TEOS} = 100\ \mu L$, the PS nodules are coated by a very thin shell, mainly revealed by its irregularities. For $V_{TEOS} = 25\ \mu L$, it is difficult to discern any silica layer (just a greater roughness).

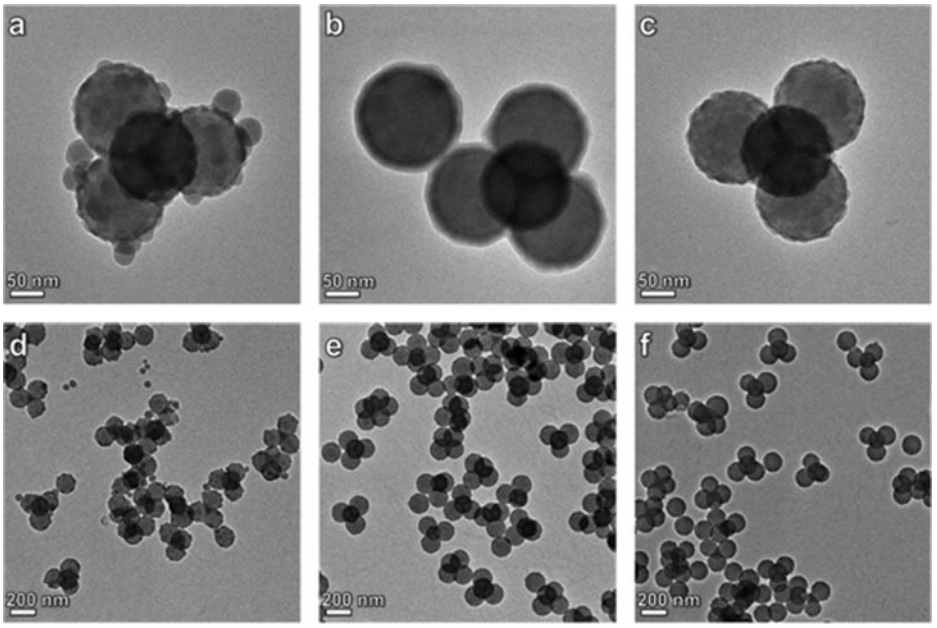

Figure 3. TEM images of tetrapods coated by a silica shell. (a–d) $V_{tetra} = 0.5$ mL, (b–e) $V_{tetra} =$ 1 mL, (c–f) $V_{tetra} = 2$ mL. $V_{TEOS} = 200\ \mu L$; $[NH_3] = 0.5$ mol L^{-1}.

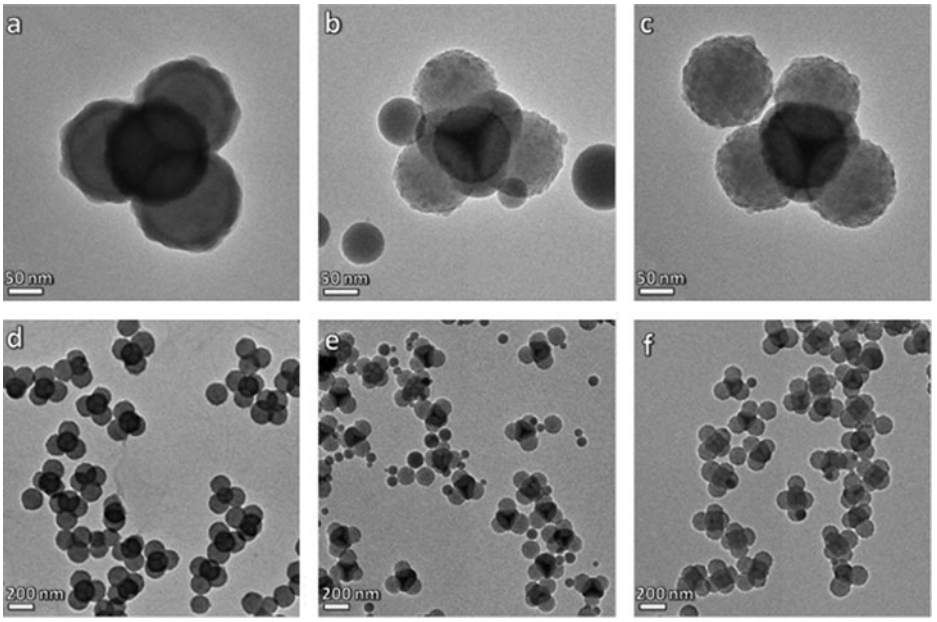

Figure 4. TEM images of tetrapods coated by a silica shell. (a–d) $V_{tetra} = 1$ mL, $[H_2O] = 3.6$ mol L^{-1}, $V_{TEOS} = 100$ μL; $[NH_3] = 0.5$ mol L^{-1}; (b–e) $V_{tetra} = 1$ mL, $[H_2O] = 14.7$ mol L^{-1}. $V_{TEOS} = 100$ μL; $[NH_3] = 0.5$ mol L^{-1}; (c–f) $V_{tetra} = 2$ mL, $[H_2O] = 14.2$ mol L^{-1}, $V_{TEOS} = 200$ μL; $[NH_3] = 0.3$ mol L^{-1}.

3.3. Influence of Tetrapod-like Clusters' Concentration

We have also conducted experiments by varying the quantity of MPS-modified tetrapods during the incorporation of TEOS. Dividing by two the amount of tetrapods leads to homogeneous nucleation of silica particles, as shown in Figures 3a and 3d. The surface developed by the tetrapods appears to be insufficient to accommodate all the intermediate reaction species before any nucleation. Silica particles resulting from the nucleation are stuck to the surface of the nodules where they may continue to grow. When the concentration of colloids is doubled, the thickness of the silica shell is reduced (≈5 nm) (see Figures 3c and 3f), as expected.

3.4. Influence of Water Content

We have also checked the influence of the water content in the reaction medium on the growth of the silica shell. Figure 4 shows that multiplying the concentration of water by 4 induces a drastic modification of the morphology of the resulting tetrapods. Water strongly promotes the growth of the silica core and homogeneous nucleation to the detriment of the encapsulation of the PS nodules, which are covered only by a thin crust of irregular silica. A similar result was obtained when the quantity of tetrapods was doubled (Figures 4c and f).

4. Conclusion

We have shown that the incorporation of silanol groups at the surface of the PS nodules of tetrapod-like clusters through the addition of MPS at the end of their synthesis favours their encapsulation by a thin silica shell. The thickness and the roughness of the shell can be finely tuned by controlling the quantities of silica precursor and of binary tetrapods. When the tetrapods are not modified with MPS, the addition of TEOS results in the preferential growth of their silica core. Very interesting tetravalent silica particles can thus be formed by the subsequent dissolution of the polymer nodules. We are currently assembling the silica-coated tetrapods in the form of colloidal crystals, which may have a diamond-like structure and thus lead to the formation of a full photonic band gap [14]. Moreover, the silica surface of the encapsulated tetrapod-like structures can be easily functionalized with organosilane derivatives that makes them useful for a number of applications.

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