Colloidal Chemistry

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Synthesis and Site-Specific Functionalization of Tetravalent, Hexavalent, and Dodecavalent Silica Particles**

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The past decade has been witness to the development of new chemical and physical methods allowing the synthesis of colloidal particles of different shapes with a good size and shape selectivity. Colloidal triangles,[1] ellipsoids,[2] cubes,[3,4] spheroids,[4] tripods,[5] tetrapods,[6] rods,[7] dumbbells,[8] or prisms[9] have been produced. Owing to their shape anisotropy, these colloidal entities allow the construction of structures that differ from those of simple symmetry that have been commonly obtained from isotropic spherical particles. The self-organization of colloidal rods into nematic or smectic phases has often been reported.[10] More recently, Rossi et al. have prepared crystals with a simple cubic symmetry from micron-sized cubic particles.[11] The bottom-up construction of novel functional materials and devices with more complex and predictable architectures requires the engineering of colloidal building blocks with not only a good size and shape selectivity but also with a control over the location of their surface functions. It would be thus possible to get colloidal particles with directional interactions and predetermined "instructions" for assembly, making them similar to atoms which have valences. Nelson has theoretically initiated the concept of giving valences to colloids and thus using them to direct particle self-assembly.[12] Zhang and Glotzer[13] have developed a simple model of empirical pair potentials between patch and core particle atoms to gain a general understanding of self-assembly. Since then, many other models have been developed to describe patchy particle interactions.[14] From the experimental point of view, the selective functionalization of faces of silver nanocubes by using a poly(dimethylsiloxane) stamp was performed by Rycenga et al.[15] Definite assembly patterns were obtained, which were dictated by the number of functionalized faces. Li et al. have reported the synthesis of tetrapodal particles that mimic hybrid orbitals with tetrapodal (sp^3) configurations, using close-packed colloidal crystals as templates.[16] The podal ends of the particles were selectively tethered with functional groups, thereby granting them the capability of site-specific directional bonding, leading to the formation of colloidal molecules. Chen et al. have synthesized "triblock Janus" particles through decoration of spheres with two hydrophobic poles of tunable area, separated by an electrically charged middle band.[17] After overnight sedimentation, the triblock Janus particles self-assemble into a two-dimensional kagome lattice, as the consequence of the attraction of neighboring particles at their poles in a geometrical arrangement limited by their size. The major limitation of these three approaches is that the quantity of regioselectively modified particles that are produced is very low, owing to the use of either a planar substrate or a colloidal crystal as templates.

We have reported the high-yield synthesis of binary polystyrene (PS)/silica multipods with a controlled morphology by a seeded-growth emulsion polymerization of styrene,[18] which was recently optimized by taking advantage of the complementary roles of nonionic and ionic surfactants.[19] Here, we report a high-yield batch synthesis of concave tetravalent, hexavalent, and dodecavalent silica particles by using binary tetrapods, hexapods, and dodecapods as endo-templates, respectively. We demonstrate that the growth of the silica core of the binary clusters can be favored by carefully adjusting the experimental conditions. While growing, the silica surface conforms to the shape of the PS nodules, leading to concave multivalent silica particles after dissolution of the polymer (Scheme 1). Following a strategy that we developed for the production of Janus silica particles,[20] we used the polymer nodules as temporary protecting masks to: 1) regioselectively modify the silica surface with amine functional groups and 2) grow a titanium dioxide layer over the unprotected surface of tetravalent silica particles.

The initial ingredients of our fabrication route are binary tetra-, hexa-, or dodecapods made of a central silica core and four, six, or twelve PS satellite nodules (see Figure S1 in the Supporting Information). The synthesis starts with the slow addition (ca. 5 mL h^{-1}) of a dilute solution of tetraethoxysilane (TEOS; 100 μL) in ethanol into a hydroalcoholic suspension of multipods, in presence of ammonia. The preferential polycondensation of TEOS molecules onto the surface of the silica core of the binary particles leads to its growth. While growing, the silica surface conforms to the shape of the PS nodules (Figure 1).

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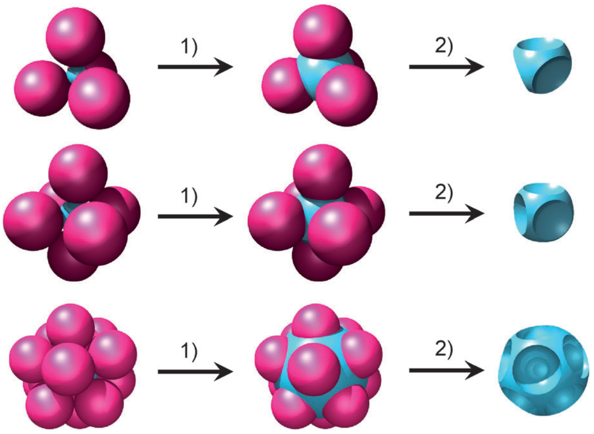


Scheme 1. Diagram showing the synthetic steps involved in the preparation of tetra-, hexa-, and dodecavalent silica particles: 1) silica growth; 2) dissolution of the PS nodules.

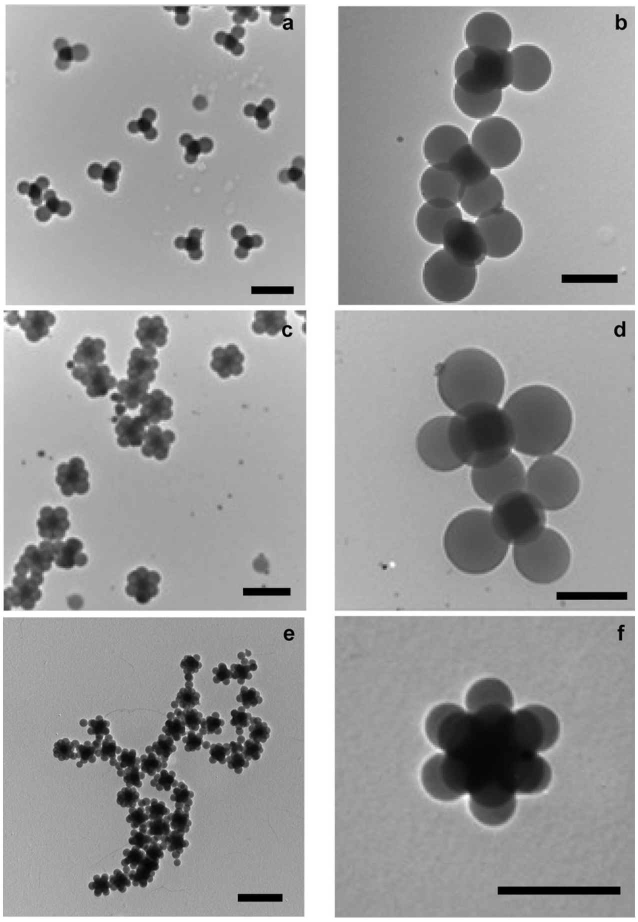


Figure 1. Low- and high-magnification TEM images of tetrapods (a, b), hexapods (c, d), and dodecapods (e, f) after the growth of the silica core. Scale bar: 500 nm (a, c, and e); 200 nm (b, d, and f).

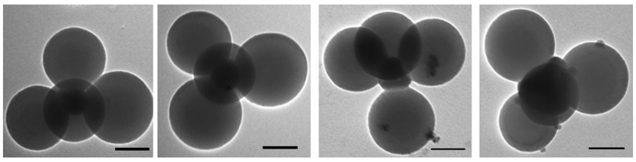


Figure 2. A time series of TEM images showing the growth of the silica core of tetrapods. From left to right, time after the beginning of the addition of 100 μL of TEOS is: 0 min, 30 min, 60 min, and 240 min. Scale bar: 100 nm.

Table 1: Time variation of the edge-length values of the tetrahedral silica cores for various volumes of TEOS, V_{TEOS}, injected into the reactive medium at 5 mL h^{-1}.

	Edge length[b] [nm]		
Time[a] [min]	$V_{TEOS} = 100\ \mu L$	$V_{TEOS} = 200\ \mu L$	$V_{TEOS} = 500\ \mu L$
30	87 ± 2	88 ± 2	88 ± 2
60	96 ± 3	129 ± 4	130 ± 4
120	125 ± 5	150 ± 5	187 ± 5
240	137 ± 5	160 ± 7	200 ± 7
360	155 ± 8	175 ± 10	205 ± 10

[a] Time after the beginning of the addition of TEOS. [b] Measured by statistical analysis of TEM images over ca. 20 particles.

The growth kinetics were studied by measuring the edge length of the growing silica tetrahedra, obtained when tetrapods were used as seeds (Figure 2). The growth continues until six hours after the beginning of the addition of TEOS (Table 1), in agreement with the kinetics of the sol–gel reactions of this silica precursor under basic conditions.[21] The final silica tetrahedral particles have an edge length of (155 ± 8) nm, while the initial diameter of the silica core of the tetrapods was 85 nm. To further increase the size of the silica tetrahedra, the volume of the alcoholic solution of TEOS injected into the tetrapod suspension was multiplied by two and five. Larger silica tetrahedra were effectively produced (Table 1), but the formation of silica protuberances at the surface of the PS nodules was also observed (see Figure S2 in the Supporting Information). A possible formation mechanism of these silica bumps may consist in the adsorption of silane oligomers at the surface of the PS nodules and the resulting formation of silica domains on several locations. These domains preferentially adsorb TEOS oligomers over bare PS nodule surface, which would preferentially enlarge the silica domains. The addition rate of the TEOS solution had no influence on the formation of the silica bumps, as they could still be observed when injecting a large volume of the silica precursor as slow as 0.5 mL h^{-1} (see Figure S3 in the Supporting Information). To avoid the formation of these protuberances, which induces the presence of impurities among the multivalent silica particles (evidence for this is reported in the next paragraph), we thus favored the addition of a low volume of TEOS (ca. 100 μL) into the suspension of multipods.

The second step of the synthesis corresponds to the dissolution of the PS nodules in tetrahydrofuran (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 (Figure 3 a, b). Similarly, hexavalent particles with a dice-like morphology (Figure 3 c, d) and dodecavalent particles (Figure 3 e, f) were produced through the growth of the silica core

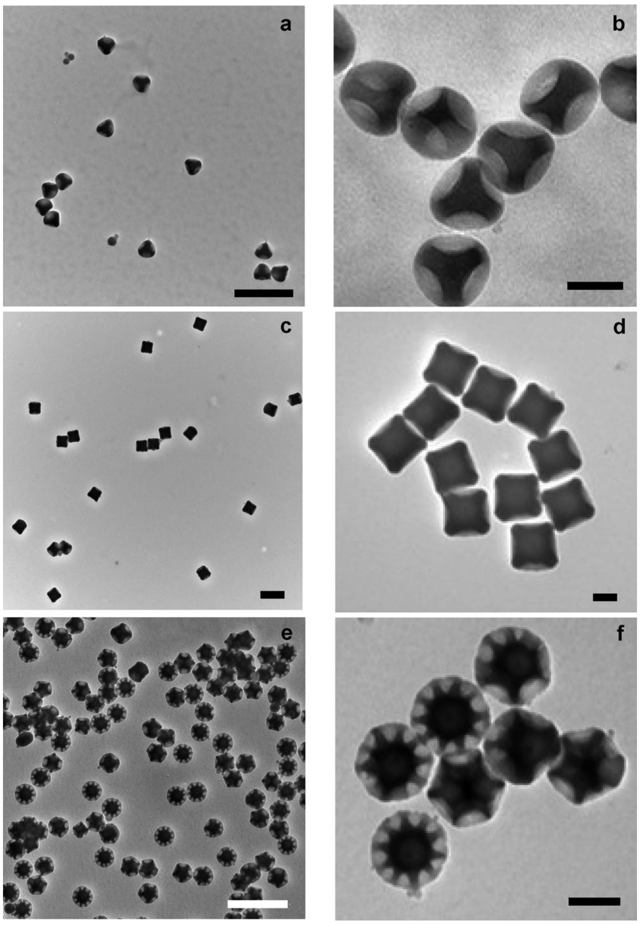


Figure 3. Low- and high-magnification TEM images of tetravalent (a, b), hexavalent (c, d), and dodecavalent (e, f) silica particles. Scale bar: 500 nm (a, c, and e); 100 nm (b, d, and f).

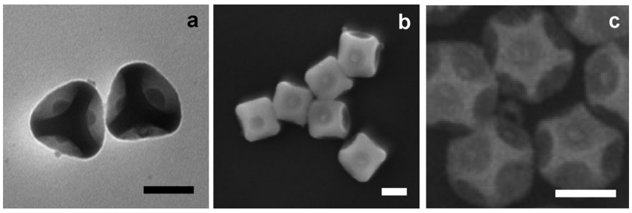


Figure 4. TEM image of tetravalent (a) and SEM images of hexavalent (b) and dodecavalent (c) silica particles showing the remaining bumps after the incomplete dissolution of the PS nodules. Scale bar: 100 nm.

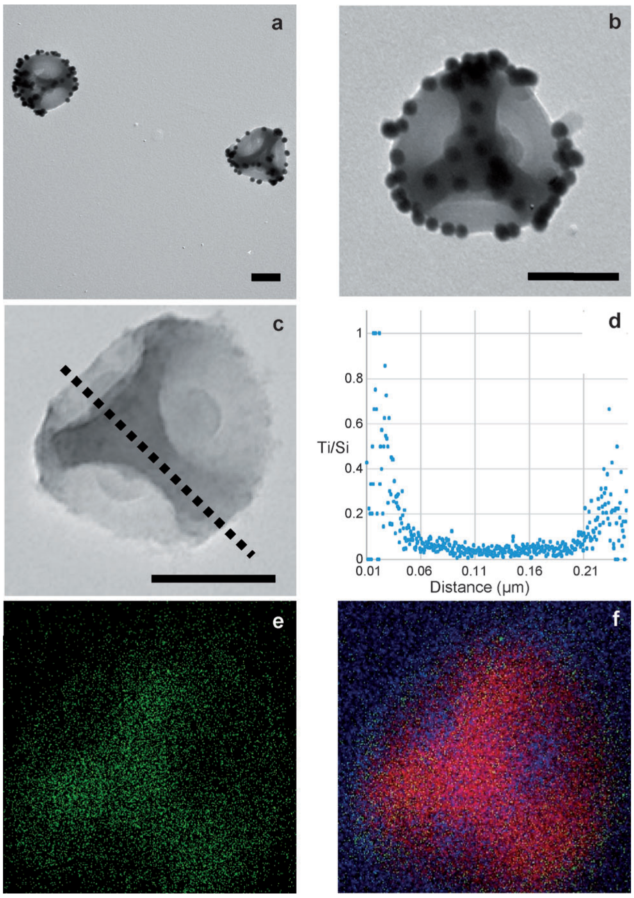
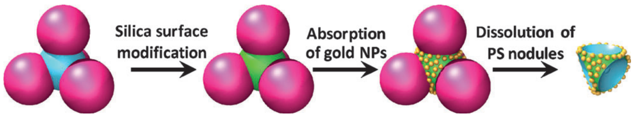


Figure 5. a,b) TEM images of tetravalent silica nanoparticles in which the amine-grafted area is decorated by gold nanocolloids; c) STEM image of a titania-coated tetravalent particle after partial dissolution of the PS nodules; d) plot of the Ti/Si ratio along the dotted line drawn in (c); e) STEM EDX mapping of Ti; f) STEM EDX mapping with C (blue), Si (red), and Ti (green) signals. Scale bar: 100 nm.

of hexapods and dodecapods, respectively. The morphology of the particles can be better appreciated by looking at three-dimensional schematic views, which were created using the real experimental values of the diameters of PS nodules and silica cores and of the contact angle between PS nodules and silica core (see Movies S1, S2 and S3 in the Supporting Information). Yields were equal to 88 %, 84 %, and 82 % for tetravalent, hexavalent, and dodecavalent particles, respectively, as determined by statistical analysis of TEM images over about 80 clusters.

Interestingly, by decreasing the time of the THF treatment to one hour, it was possible to not totally dissolve the PS nodules and to leave small bumps in the center of each concave notch (Figure 4). The organic nature of these bumps was confirmed by using energy-dispersive X-ray spectroscopy (EDX) analyses coupled with scanning transmission electron microscopy (STEM), which clearly show that they contain carbon (Figure 5 f). This feature could be useful for a further selective chemical modification of these bumps with bifunctional molecular linkers to guide the silica particles assembly. In the case of dissolving the PS nodules of the particles shown in Figure S2 in the Supporting Information, polydisperse silica spheres were also observed among the multivalent particles, as a reminiscence of the silica protuberances, which were located at the surface of the organic lobes (see Figure S4 in the Supporting Information).

Furthermore, we have reported that the PS nodules can serve as temporary protecting masks to specifically modify the unprotected silica surface with functional groups.[20] Following this strategy, the grafting of amine groups was easily achieved by adding (3-aminopropyl)triethoxysilane (typically, in a quantity corresponding to 10 functions per nm^2 of silica surface) in a suspension of tetrapods, after the growth of their silica core (Scheme 2). The efficiency of this



Scheme 2. Diagram of the site-specific functionalization of the tetravalent silica particles with amine groups.

functionalization can be evidenced by mixing the hybrid colloids with an aqueous suspension of citrate-stabilized 15 nm gold nanoparticles, which specifically adsorb onto the amine-grafted mineral surface.[22]

After the dissolution of the PS nodules, the gold nanoparticles packed densely on the amine-modified silica surface, whereas no gold nanoparticle was visible on the nonmodified surface of the concave faces of the silica particles (Figure 5 a,b), thus indicating highly selective functionalization. The use of the PS nodules as temporary masks was further demonstrated by the addition of titanium tetraisopropoxide after the growth of the silica core of the binary particles. After the partial dissolution of the PS nodules, TEM characterization (Figure 5 c) and the plot of the variation of the Ti/Si ratio across the particle (Figure 5 d) extracted from STEM EDX mapping show that a thin TiO_2 layer has grown at the silica surface. The EDX mapping shown in Figure 5 e confirms that the titania layer only grew over the unprotected zones of the silica surface.

In summary, a high-yield chemical route for the preparation of tetra-, hexa-, and dodecavalent silica particles was developed on the basis of the growth of the silica core of the corresponding binary PS/silica multipods. The successful functionalization of the nonprotected surface of the grown silica core was also demonstrated, thereby providing the possibility of having particles with anisotropic geometry and chemistry. A large panel of multivalent particles presenting various sizes, shapes, and concavities, can be easily designed by using other multipod-like binary particles[18] and by tuning the growth of the silica core. These new colloidal particles represent a general class of building blocks for experimental studies of self- and directed-assembly processes. Indeed, the scalability of the synthesis approach allows the preparation of colloids in amounts sufficient for studying their interactions in water. Moreover, the combination of these "lock" particles with "key" particles with a size that matches the radius of their spherical cavities in the presence of a depletant would lead to the formation of new supracolloids with a well-defined morphology.[23] The formation of a diamond-like lattice from the tetravalent particles can also be envisaged.[24]

Experimental Section

Tetrapods, hexapods, and dodecapods made of a central silica core and four, six, or twelve polystyrene satellite nodules were prepared by seeded emulsion polymerization of styrene, according to a published procedure.[18,19]

The synthesis of multivalent silica particles was performed in the following conditions: a certain volume of TEOS ($\geq 99\,\%$, Fluka), V_{TEOS}, was diluted ten times in absolute ethanol. The resulting solution was introduced continuously in a mixture of 1 mL of an aqueous suspension of multipods (at ca. 10^{16} particles L^{-1}), 45.5 mL of absolute ethanol and 3.2 mL of ammonia (25 % in water, SDS) at a precise rate thanks to a single-syringe pump (one should note that the one-shot addition of the TEOS solution must be avoided, as it induces the formation of small silica nanoparticles in the bulk). The mixture was stirred at room temperature during 12 h. To graft amine groups onto the unprotected silica surface, a given volume of (3-aminopropyl)triethoxysilane (APTES, Aldrich) corresponding to a nominal surface density of 10 functions nm^{-2} was added directly into the particle suspension. The mixture was stirred at 40 °C for 2 h to promote covalent bonding. The particle dispersion was purified by 3 cycles of centrifugation/redispersion in absolute ethanol. 15 nm citrate-stabilized gold nanoparticles, which were synthesized as previously described,[25] were added into 20 mL of the functionalized binary particles dispersion. The mixture was stirred at room temperature overnight, and then the particle assemblies were collected by centrifugation and washed three times with absolute ethanol.

To coat the unprotected silica surface with a titania layer, 450 µL of titanium tetraisopropoxide (Aldrich) solution (28 mM in ethanol) were added into 100 µL of a binary particle suspension in absolute ethanol.

The dissolution of the PS nodules was done in 100 mL of tetrahydrofuran (Sigma–Aldrich) at room temperature during 4 h. After three cycles of centrifugation/redispersion in THF to remove the dissolved polymer, the multivalent silica particles were finally redispersed in absolute ethanol.

TEM experiments were performed with a Hitachi H600 microscope operating at 75 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. SEM characterizations were performed with a JEOL JSM-6700F microscope.

Chemical analyses carried out by STEM coupled to EDX were acquired with a JEOL 2200 FS equipped with a field emissive gun, operating at 200 kV and with a point resolution of 0.23 nm.

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