Binary Colloids

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A Chemical Synthetic Route towards "Colloidal Molecules"**

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A non-exhaustive list of fields in which extensive research has been dedicated to colloidal particles during the past century includes condensed matter physics, biology, optics, materials science, and chemistry. Both our current understanding of various physical phenomena and our capability to fabricate new functional materials have been considerably enriched by the development of synthetic strategies that are capable of generating copious quantities of colloidal entities of good size uniformity. Nevertheless, most of the available monodisperse colloidal materials are spherical, as the minimization of the interfacial free energy strongly drives a particle to adopt such a shape.[1] This strongly limits the number of new structures which can be engineered by using these colloids as building blocks. For instance, the crystallization of spherical colloids into three-dimensional periodic lattices has recently allowed the emergence of a very active field of research—photonic colloidal crystals, known as artificial opals. Nevertheless, the light diffraction properties of these crystals are rather limited because of their face-centered cubic lattice, which results from the packing of spheres. It has been predicted that crystals with a lower degree of symmetry, such as the diamond lattice, can exhibit a full photonic bandgap. To build such photonic crystals, well-defined colloids with nonspherical shapes are required. Van Blaaderen recently introduced the elegant term of "colloidal molecules",[2] which takes into account that spherical colloids can be treated as if they were atoms and that molecules can form more complex materials than can atoms. Therefore, the reproducible fabrication of large amounts of colloids that have a good uniformity in chemical composition, surface properties, size, and shape is a huge challenge.[3] Intensive efforts during the last decade have led to the development of nonspherical colloids of various shapes (such as rods,[4–6] wires,[7] triangles,[8] prisms,[9] cubes,[10] ellipsoids,[11] octahedra,[12] tetrapods,[13]), but few of these samples combined the requirements of a true monodispersity in size and shape and the production of sufficiently large quantities. A promising synthetic procedure involves the use of a physical template to better control these two parameters. Micropatterned charged monolayers[14–17] or relief structures[18–23] on two-dimensional substrates were used to fabricate mono or binary clusters of colloids with high-arrangement accuracies, but in very small quantities. Three-dimensional templates such as liquid[24] or emulsion droplets[25,26] were also exploited to form complex colloidal assemblies with well-controlled sizes and morphologies. For example, a clever approach based on the generation of oil-in-water emulsions containing polymer microspheres and the subsequent controlled oil evaporation was first developed by Manoharan et al.,[27–29] and led to aggregates that contain a precise number of polymer microspheres. This procedure was extended by Cho et al. to the production of colloids with different morphologies[30] and of binary clusters[31] by using water-in-oil emulsions. We have recently reported a facile chemical route for producing biphasic colloids made of polystyrene (PS) latex particles bound to a silica core by adjusting the ratio between the number of silica seeds and the number of PS latex particles. In particular, we have observed the formation of snowmanlike[32] and octopod-like colloids[33] when the ratios are close to 1 and 8, respectively. We noticed that a slight polydispersity in size of the silica seeds was the principal cause of the formation of colloids with a variable number of PS latex particles. This observation might suggest that this number could be simply modulated by controlling the silica size and size polydispersity. In order to verify this assumption, we have carried out a series of experiments with silica seeds which are highly monodisperse in size.

We show herein that a full set of new binary colloids with regular morphology can be obtained in a high yield. Moreover, we demonstrate that the amount of PS latex per binary cluster can be calculated from the size of the silica seed by solving an equation which results from the minimization of a two-term energy. The first term is an attraction towards the center and the contribution of the second term produces two-body particle repulsions, which can balance the attractive central force. A key feature of our approach is that, for a given size of silica seed, the synthetic process is reproducible, fast, and may yield grams of binary colloids.

The main components of our fabrication process are uniformly sized silica beads (5% polydispersity), which were

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synthesized according to a procedure adapted from the methods of Stöber[34] and Kang.[35] Their surface is activated through the covalent grafting of methacryloxymethyltriethoxysilane (MMS) prior to use as seeds in a reactor where styrene is polymerized in water (emulsion conditions). Treatment with MMS is required to drive the polymerization and promote the subsequent growth of polymer nodules at the silica surface.[33] In all experiments, the polymerization conditions (that is, the concentrations of styrene, initiator, and surfactant) remained unchanged. Only the diameter of the silica seeds (D_{Si}) and concentration were varied in order to keep the number of silica seeds (N_{Si}) much lower than the number of PS particles (N_{PS}), which means that free latex particles were also produced in the reactor. We first carried out two series of experiments with 125 nm and 170 nm silica seeds that have a narrower size distribution than those used in our previous study.[33] A thorough analysis of the transmission electron microscopy (TEM) images revealed that a large amount of hexapod-like ($N_{PS/Si}=6$) and octopod-like ($N_{PS/Si}=8$) clusters were obtained after a polymerization time of two hours (which corresponds to a monomer conversion of about 30%). The cluster yields were up to 60%, as determined by statistical analysis of TEM images over about 75 clusters. In order to confirm that these morphologies were present in the reaction medium and did not result from a possible rearrangement or distortion during the drying step on the TEM grid, cryo-electron microscopy experiments were performed on samples directly collected from the polymerization reactor. More interestingly, electron tomography experiments were performed for the first time on such frozen collected samples. Therefore, tilt-series were collected automatically from $-60°$ to $+60°$ at 2° intervals along the tilt axis. These projections were realigned and used to reconstruct some colloids in three dimensions. Subsequently, the reconstructed clusters were manipulated by free rotation in order to observe them in numerous directions and to reveal their 3D morphology. For example, the cryo-TEM pictures of hexapods and octopods are shown in Figure 1 a–c (top). The 3D reconstructions of these binary clusters (Figure 1 d–f) reveal they are octahedra and square antiprisms, respectively. Therefore, these regular morphologies pre-existed in the aqueous solution of the reacting medium and were generated during the polymerization stage.

The formation of these regular polyhedra was assumed to correspond to optimal arrangements of the PS nodules around the central silica seed. Thus, the criterion governing these optima had to be considered. We assumed that the synthesis of the clusters was the result of the competition between two forces—a repulsive force between the polymer nodules that could account for the presence of negative charges at their surface as they are partially immersed into the aqueous reactive medium, and an attractive force towards the silica seeds, which could account for the presence of the coupling agent. Interestingly, Atiyah and Sutcliffe have recently studied the minimization of the energy of n points whose positions are unconstrained on the surface of a sphere [Eq. (1)]:[36]

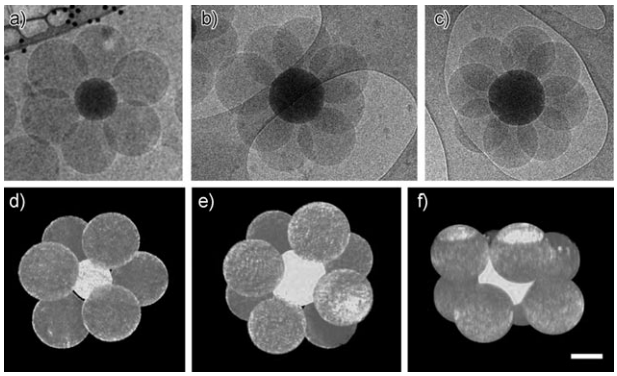

Figure 1. Top: hexapod-like and octopod-like silica/PS clusters as observed by cryo-TEM after 2 h of polymerization from silica seeds with $D_{Si}=125$ nm (a) and $D_{Si}=170$ nm (b and c). 3D tomographic reconstructions of the same silica/PS clusters revealing they are octahedra (d) and square antiprisms (e and f), respectively. Scale bar: 100 nm.

$$E_P=\sum_i^n \frac{1}{2}x_i^2+\sum_i^n \sum_{j<i} \frac{1}{|x_i-x_j|} \tag{1}$$

where the first term is an attraction towards the origin and the second term is the Coulombic energy, which can balance the attractive central force. It was shown that the minimal energy configurations for $n=6$ and $n=8$ are similar to those that we observed experimentally. However, they also showed that when n is greater than 13, all the points do not lie on the surface of a sphere and multishell structures are formed. This statement is in contradiction with the structure of the raspberry-like clusters which were obtained when using 500 nm and 1 μm silica seeds.[37] We therefore considered another model developed by Battye et al.,[38] in which the Coulombic energy is replaced by a term that produces two-body particle repulsions, but keeps the same first term for the attraction. Under such conditions, the minimization of the energy of n points, which are constrained to lie on a sphere of a given radius ρ, led to Equation (2):

$$\rho=\frac{2n}{3}-\frac{1}{2n} \tag{2}$$

which indicates that all n points lie on the surface of a sphere whose radius grows linearly with n. If this model revealed the formation of the binary clusters to be consistent, we could expect a similar dependence between the silica-seed diameter and the number of PS nodules per silica seed, $N_{PS/Si}$. The formation of hexapods and octopods from 125 nm and 170 nm silica seeds, respectively, allowed us to verify this equation on the condition that introducing a multiplicative constant K (ca. 16.2), which would involve various factors such as the size of the PS nodule [Eq (3)]:

$$\frac{D_{Si}}{2}=K\left(\frac{2N_{PS/Si}}{3}-\frac{1}{2N_{PS/Si}}\right) \tag{3}$$

We then used Equation (3) to calculate the D_{Si} values that are likely to lead to new morphologies corresponding to $N_{PS/Si}$ values lower than 6 and larger than 8. Subsequently, silica

particles with average diameters as close as possible to the calculated values were synthesized and used as seeds (Table 1).

Table 1: Experimental synthesis conditions and main results concerning the silica/PS clusters prepared in this work.

Expected $N_{PS/Si}$	2	3	4	6	8	10	12
calculated D_{Si} [nm]	35	59	82	127	171	214	258
synthesized D_{Si} [nm]	42	64	85	125	170	212	255
C_{si} [g L^{-1}]	0.2	0.5	1.2	3.2	4.7	4.7	4.7
N_{Si}[a] [$\times 10^{15}$ L^{-1}]	2.26	1.68	1.70	1.34	0.83	0.43	0.25
N_{PS}[b] [$\times 10^{15}$ L^{-1}]	8.93	9.24	9.85	10.92	11.17	10.63	10.27
N_{PS}/N_{Si}	≈ 4	≈ 5	≈ 6	≈ 8	≈ 13	≈ 25	≈ 41
$N_{PS/Si}$[c]	2	3	4	6	8	10	12

[a] N_{Si} = number of silica seeds introduced in the reactive medium. [b] N_{PS} = number of PS particles calculated from the weight of dried extracts and PS nodule size as observed on TEM and SEM images. [c] Directly observed in TEM and SEM images (see Figure 2).

Figure 2 shows SEM and TEM images of the silica/PS clusters generated after 2 h of polymerization from silica beads with diameters that range from 42 nm to 255 nm. If we consider the center of each PS nodule as a vertex of a polyhedron, new regular figures may be recognized, that is, a line segment for bipods (number of latex per silica bead, $N_{PS/Si} = 2$), a triangle for tripods ($N_{PS/Si} = 3$), a tetrahedron for tetrapods ($N_{PS/Si} = 4$), which continue up to an icosahedron for dodecapods ($N_{PS/Si} = 12$). All the observed morphologies for $2 \leq N_{PS/Si} \leq 12$ are identical to the minimal-energy configurations for the corresponding values of n obtained by Battye et al.[38] Therefore, their model based on two competing forces was successfully applied to the formation of our polyhedral binary clusters and allowed us to design and synthesize new morphologies. The attractive force results from the surface modification of the silica seeds with MMS. The origin of the repulsive force is very probably correlated to the presence of the non ionic surfactant which hinders the coalescence of the growing PS nodules. Yields of the cluster synthesis were up to 90% for bipods (see Figure 3), around 75% for tripods, around 70% for tetrapods (see Figure 3), around 60% for hexapods and for octopods, and around 40% for decapods and for dodecapods, as determined by statistical analysis of TEM and SEM images. Impurities include clusters with missing or extra PS nodules (mainly because of the remaining slight polydispersity in size of the silica seeds) and clusters that present an imperfect morphology because of the fact that all the attached nodules are not correctly positioned.

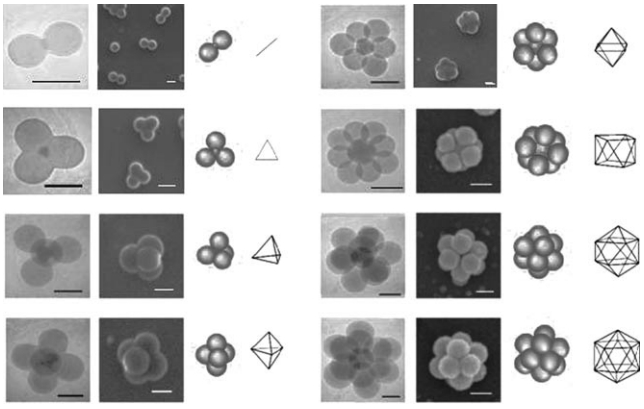

Figure 2. Transmission and scanning electron micrographs of the binary clusters obtained after 2 h with silica seeds of different diameters (left columns, scale bar: 200 nm). Schematic drawings of the sphere configurations (center columns). Polyhedra formed by drawing lines from the center of each PS nodule to its neighbours (right columns).

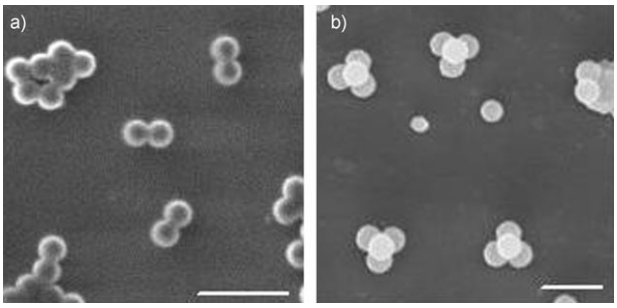

Figure 3. SEM views of a) bipods and b) tetrapods obtained after 2 h from 42 nm and 85 nm silica seeds, respectively. Scale bar: 600 nm.

In summary, a facile chemical route for preparing well-defined binary colloidal clusters was proposed on the basis of a seeded emulsion polymerization. The binary clusters may be considered as another example of "complex colloids".[39] They display polyhedral arrangements, which result from the minimization of a two-term energy. This minimization principle provides not only some insights into the mechanism of the constrained growth of polymer nodules onto the surface of seeds, but it also can be viewed as an analogue at the mesoscopic scale of the valence shell electron pair repulsion (VSEPR) model allowing to predict the molecular geometry. Indeed, the regular bipods, tripods, and tetrapods may be compared to the space-filling models of simple binuclear molecules such as $BeCl_2$, BF_3, and CH_4.

An exciting prospect of this work is to extend this synthetic route to mimic all the molecules that have a single central atom: not only incomplete morphologies such as bent geometries (H_2O or $SnCl_2$), trigonal pyramids (NH_3), but also multinuclear molecules whose the central atom is combined with more than two atom types. Indeed, the experimental parameters, which can be easily varied, are the nodule-to-seed ratio, the seed nature, the polymerization time (for adjusting the nodule size to the seed size) and the successive addition of monomers of different natures. The scalability of this technique would allow the preparation of colloids in amounts sufficient for studying their interactions in water and their packing to create original materials.[40–42]

Experimental Section

Silica seeds were synthesized by following the well-known Stöber procedure.[34] This technique, based on the hydrolysis–condensation of tetraethoxysilane (TEOS, 99%, Fluka) in a water/ethanol medium,

allowed the nucleation and growth of well-defined particles that have a spherical shape and a diameter that varies between 30 nm to 200 nm, depending on the temperature of the reaction, with smaller particles produced at higher temperatures. A typical procedure is as follows: absolute ethanol (91% vol, J. T. Baker), ammonia (6% vol, 25% in water, Carlo Erba), TEOS (3% vol) were mixed at the chosen temperature and stirred at 300 rpm during 24 h. For instance, 212 nm and 85 nm particles were obtained at 20°C and 40°C, respectively. In many cases the Stöber technique yields a standard deviation of the particle diameter of around 15%. In order to control the size of the particles within a range of few nanometers, a procedure developed by Kang et al.[35] was used in a second step. This method consists of adding a solution of the silica initiator dropwise into a mixture of methanol, water, and ammonium hydroxide. In contrast, Stöber et al. mixed all the reagents together at the beginning in a batch process. In this second stage, the above suspension was used as a seed for the growth of silica in order to obtain particles with good control over the size and size polydispersity (ca. 5%). The surface of the silica seeds was functionalized through the chemical grafting of methacryloxymethyltriethoxysilane (MMS, ABCR; corresponding to 1.66 $\mu mol\,m^{-2}$). The calculated amount of MMS was added into a stock silica suspension (100 mL) and reacted for 3 h at ambient temperature and for 1 h at 90°C under continuous stirring (300 rpm). The particles were subsequently purified by dialysis against water until neutral pH was reached in order to remove the remaining reactants and replace ethanol with water. Silica suspensions were concentrated and their final concentration was determined by measuring the mass of a dried extract.

The synthesis of binary clusters was performed under the following conditions: Styrene (100 $g\,L^{-1}$) and nonylphenol poly(oxyethylenic) nonionic surfactant (Synperonic NP30, Fluka, 3 $g\,L^{-1}$), were poured into a thermoregulated reactor under a nitrogen atmosphere and the aqueous suspension of functionalized silica particles was added. The concentration of silica particles was adjusted in order to keep the number of silica seeds much lower than the number of polystyrene particles, which meant that free latex particles were also produced in the reactor. The temperature was fixed at 70°C. Sodium persulfate (0.5 wt% relative to the monomer, Aldrich) was added to the reaction mixture under continuous stirring (300 rpm) to initiate the polymerization.

TEM experiments were performed with a JEOL 2000 FX microscope (accelerating voltage of 200 kV). The samples were prepared as follows: Colloids, as directly collected from the reactor, were diluted in ethanol and one drop of the diluted suspension was deposited on a copper grid that was coated with a carbon membrane. Clusters in the dried state were also examined by using a Scanning Electron Microscopy (SEM) after sputter coating with gold. These images were performed with a JEOLJSM-840 A scanning electron microscope operating at 10 kV.

Cryo-electron microscopy: A sample of the aqueous dispersion (5 μL) of the clusters was deposited onto a holey carbon-coated copper grid. The excess liquid was blotted with a filter paper and the grid was plunged into a liquid ethane bath cooled with liquid nitrogen (Leica EM CPC). Specimens were maintained at a temperature of approximately −170°C, using a cryo holder (Gatan), and were observed with a FEI Tecnai F20 electron microscope operating at 200 kV and at a nominal magnification of 19000X under low-dose conditions. Images were recorded with a 2 K × 2 K low scan CCD camera (Gatan). During cryo-electron tomography experiments, tilt series were collected automatically from −60° to +60° at 2° intervals along the tilt axis by using the FEI tomography software. The defocus was approximately 10 μm and the magnification was set such that each CCD pixel corresponded to 1.08 nm at the specimen level. For image processing using colloidal gold particles as fiducial markers, the 2D projection images, binned twofold, were aligned with the IMOD software package images and then tomographic reconstructions were calculated by weighted back-projection using the Priism package.

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