TEMPLATING NANOCRYSTALS WITH DENDRIMERS: A MESOSCOPIC MODEL SYSTEM

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Introduction

Organic-inorganic hybrid nanostructures have generated great interest due to a variety of potential applications as electrical, optical, medical and information storage materials. Biological nanocomposites produced in nature have excellent properties. The method of polymer nanotemplating, i.e. using a polymeric matrix to control the growth of an inorganic crystal, has been shown to be an effective synthetic route for producing polymer/inorganic composites[1]. However, in order to understand the mechanisms involved, a model system is needed.

Dendrimers have been characterized as having a very low polydispersity[2] and a size range from (1 to 15) nm. This spans the characteristic sizes of low molecular mass molecules, polymers and colloids, thereby offering an unique mesoscopic system.

Organic-inorganic hybrid materials based on dendrimers have been recently reported by several authors[3-8]. It has been shown that dendrimers are able to stabilize metal clusters in solution. Although several studies propose that dendrimers can act as "nanotemplates", none of the studies show if the colloid is formed inside the dendrimer or if the colloids formed can be influenced by varying the so-called "template". In this study, we investigate poly(amidoamine) (PAMAM) dendrimers of generation 2 to 10 (G2 to G10) as potential nanotemplates in aqueous solution.

Experimental

Synthesis. PAMAM dendrimers of G2 to G4 were purchased from Aldrich Chemical Company and G5 to G10 were supplied by Dendritech (Michigan Molecular Institute)[9]. For gold colloids, dilute aqueous solutions of PAMAM dendrimers (mass fraction of 0.1 %) were mixed with aqueous solutions of $HAuCl_4$ at controlled stoichiometries. After stirring the solutions for 1 h, sodium borohydride in basic aqueous solution (0.1 M $NaOH^{[10]}$) was added. For CdS colloids, dendrimer solutions were mixed with aqueous solutions of $Cd(NO_3)_2$, and then aqueous solutions of Na_2S were added.

Transmission Electron Microscopy (TEM). Carbon coated copper grids, 300-mesh formvar-free, were treated for (2 to 5) s in a glow-discharge tube to impart hydrophilic character to the carbon substrate. Stained specimens were prepared by depositing the sample solutions on the grid and inverting the grid on a drop of aqueous phosphotungstic acid solution (mass fraction of 2 %) that had been neutralized with NaOH. The grid was then blotted on filter paper and air dried. TEM images were obtained at 120 kV with a Phillips 400T at a magnification of 46000 X and 100000 X.

Small Angle X-ray Scattering (SAXS). SAXS data were collected at the Advanced Polymer Beamline at Brookhaven National Laboratory, X27C[11] using a 2D image plate detector (BAS2000, Fuji). The span of scattering vector magnitudes ($q = (4\pi/\lambda)\sin(\theta)$, 2θ scattering angle) was in the range $0.2 \text{ nm}^{-1} < q < 4.4 \text{ nm}^{-1}$. Experimental intensities were corrected for incident intensity and for background scattering. The scattering curves presented here were obtained by averaging three individual measurements. The uncertainties are the standard deviations of the mean intensity. All scattering intensities were corrected for solvent scattering. The scattering curve I(q) was Fourier transformed into the pair distance distribution function P(r) using the program ITP (*Indirect Transformation for the Calculation of P(r)*) by O. Glatter[12,13,14].

Results and Discussion

Gold-dendrimer hybrid particles. Our approach that is shown schematically in Figure 1 relies on the attraction between charged dendrimers and oppositely charged metal ions. Chemical reactions can be performed on the inorganic precursors attached to the dendrimer, producing colloid structures that are controlled by the dendrimer. The concept of using charged, solvent-penetrable nano-polymer-particles as templates in aqueous solution was first applied to polyelectrolyte microgels[15].

The stabilization of gold colloids in aqueous solution by the PAMAM dendrimers is possible over a wide range of reaction conditions. In order to control the size of the particles, one needs to optimize the ratio of the added gold ions to dendrimer, the dendrimer concentration in solution, and the reduction rate. Results reported here correspond to a loading ratio of dendrimer end groups to gold ions of 1:1, solutions with a dendrimer mass fraction of 0.12 % and a slow reduction rate.
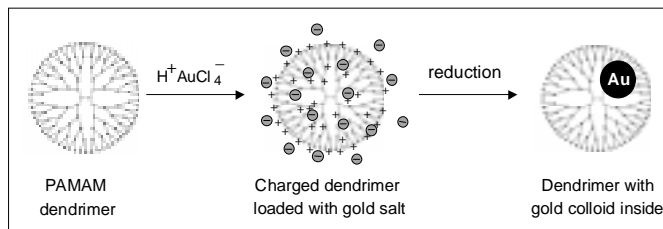

Figure 1. Dendrimer nanotemplating in aqueous solution.

Characterization. TEM on G9-dendrimer-gold hybrid particles in Figure 2 indicates that the colloid particles are formed inside the dendrimer. One gold particle per dendrimer is predominantly formed. The sizes estimated for the dendrimer and gold are 13 nm and 4 nm, respectively. The measured dendrimer size agrees with previous reports of the size of unmodified PAMAM dendrimer[2,16].

SAXS provides more detailed information about the colloid structures. Figure 3 shows data for an unmodified G9 dendrimer, Figure 4 for dendrimer-gold hybrid-particles. The different particle characteristics can be measured by Fourier transformation of the scattering curve I(q) into into real space, i.e. the pair distance distribution functions P(r). The shape of P(r) for the unmodified dendrimer shown in Figure 3b corresponds to a homogenous sphere of 13 nm diameter. In contrast, P(r) for the hybrid particle in Figure 4b is typical of a layered sphere with a maximum dimension of 13 nm. This result proves that the gold is indeed formed inside of the dendrimer. Furthermore, modeling of the P(r) reveals that the gold particle is located inside the dendrimer with an offset from the center. TEM and SAXS measurements of the diameter of the gold particle are in agreement.

The G9 dendrimer was loaded with gold corresponding to a gold-ion to end-group ratio of 1:1, i.e. 2048 gold atoms per one dendrimer. If one gold colloid is formed per dendrimer, the diameter would be 4 nm. Thus, the postulate that the gold ions from one dendrimer form one particle is reasonable. The gold-colloid formation is indeed templated by the dendrimer.
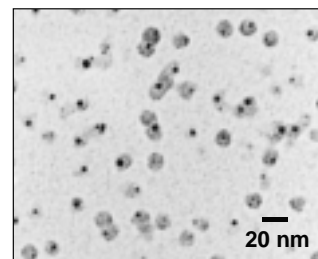

Figure 2. TEM of G9 PAMAM dendrimers containing gold colloids. The black dots are the gold and the 13 nm gray areas are the dendrimer with phosphotungstic acid.

Effect of dendrimer generation. The effect of the dendrimer generation on the colloid size is not simple, i.e. for G2, the colloids formed are larger than those obtained with G4. For G6 to G9 the gold diameter increases with increasing generation number. For G10, multiple smaller gold particles per dendrimer are formed. In this context, one has to consider how the dendrimer structure itself changes with generation: G2 is a star-like molecule with 16 end groups, G3 to G5 have star-like as well as sphere-like features, and higher generation dendrimers show a spherical structure[17].

For G2 and G4 dendrimers, gold colloids of 4 nm and 2 nm diameter, respectively, are detected by TEM as well as by SAXS. We also observe larger dendrimer aggregates. Thus our results for low generation dendrimers are in agreement with results of other authors[4,18]. For the smallest dendrimers, a single dendrimer does not provide enough material to stabilize the surface of

one gold colloid. In addition, very small metal clusters are less stable than large ones and therefore tend to form larger clusters containing the amount of gold from more than one dendrimer. This results in a hybrid structure of a metal colloid surrounded by several dendrimers. The colloid-formation mechanism for these low generation dendrimers is different than for high generation dendrimers. The gold colloids are not formed inside a "pre-existing container", but the nanostructure organizes only when the colloid is produced chemically. The colloid stabilization can be considered as an analogue to the classical stabilization mechanism with low molar mass molecules like citric acid [19]. The molecules can become attached to the colloid surface and act as stabilizers, but they do not template the colloid.

For G7 to G9, individual dendrimer molecules containing single gold colloid particles are formed. The structure of the hybrid particles corresponds to the G9 sample discussed before. The colloid diameters of 2.5 nm, 3.2 nm and 4 nm (within a range of ± 0.2 nm) agree well with the expected sizes for 512, 1024 and 2048 atoms. The mid-generation dendrimers obviously offer the best conditions in terms of a "host-guest nanoscale" synthesis. Their structure provides sufficient polymer to stabilize the surface of the forming colloidal particle, along with enough flexibility for the growth of only one particle from all of the gold ions loaded in the dendrimer. Therefore, the number of gold atoms that build one colloid can precisely be controlled with these dendrimers.

For G10, multiple smaller gold particles inside one dendrimer are observed. As the generation number increases, the internal dendrimer segment density increases slightly[17]. The volume of a single gold nanocluster would double with each generation, yet the space available for its formation would decrease. In general, the growth of a colloid is determined by the free energy of the crystal formation and surface tension. When the colloid grows inside a polymeric matrix, the elastic forces of the surrounding polymer become important and the growth of a nucleated colloid is limited by the finite extension of neighboring polymer chains. For the G10 dendrimer, it may be that the chain flexibility is not sufficiently high to allow for the growth of one colloidal particle. On the other hand, the increased surface to be stabilized for multiple smaller particles is likely to be provided by the G10 dendrimer. About four 3 nm-gold colloids inside one G10 dendrimer are formed, which is in good agreement with the expected amount of 4096 atoms, i.e. the "fixed-loading law" remains valid. Thus the G10 dendrimer realizes a host-guest nanotemplating, and the different dendrimer structure results in a different colloid morphology.
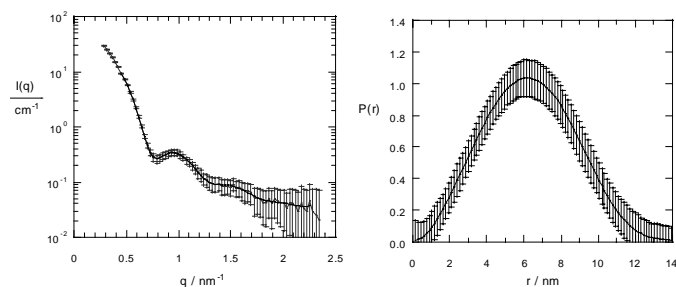
Figure 3. a) Small angle x-ray scattering curve I(q) for the unmodified G9 PAMAM-dendrimer. Error bars are the measured standard deviation in I(q) and b) pair distribution function P(r) obtained by indirect Fourier transformation of the scattering data I(q).
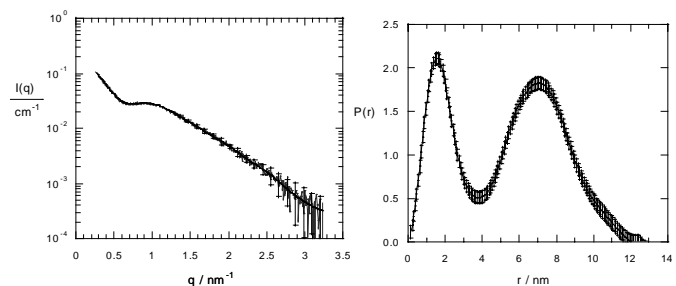
Figure 4. a) Small angle x-ray scattering curve I(q) for the gold containing G9 PAMAM-dendrimer and b) pair distribution function P(r)

Cadmium sulfide-dendrimer hybrid particles. Cadmium sulfide-dendrimer nanocomposites were synthesized by first loading the dendrimer with cadmium ions via coordination to its amine end groups. In a second step, sodium sulfide is added, which results in the formation of cadmium sulfide nanocrystals. These semiconductor quantum dots show a strong fluorescence when excited with UV light. The color of the fluorescent light varies with dendrimer generation, e.g. lower generation dendrimers emit yellow, while blue fluorescence is found for G9. This indicates that the smaller dendrimers form larger CdS nanoclusters than larger ones, in agreement with the change of stabilizing mechanism that was found for gold colloids. Again, for G9 colloids are completely formed inside the dendrimer as evident from the unchanged total particle diameter determined by small angle scattering. Thus the mechanisms of dendrimer nanotemplating are not restricted to a specific chemistry. The fundamental concept can be widely applied.

Conclusions

PAMAM dendrimers are shown to be effective as nanotemplates for inorganic nanocrystals. They not only stabilize the inorganic colloid in aqueous solution, but also determine the architecture of the nanostructures formed. G2 to G4 dendrimers behave like low molecular mass colloid stabilizers, i. e. several dendrimers become attached to the surface of the particle colloid. G6 to G10 dendrimers act as effective "polymeric" templates. One colloid particle is formed inside one dendrimer, demonstrating a template mechanism known as "host-guest nanoscale synthesis". To our knowledge, this is the first time such a transition has been shown from colloid "stabilization" by low molecular mass molecules to "polymer nanotemplating" with increase of molecular mass but constant chemistry of the stabilizing species.

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