Communication

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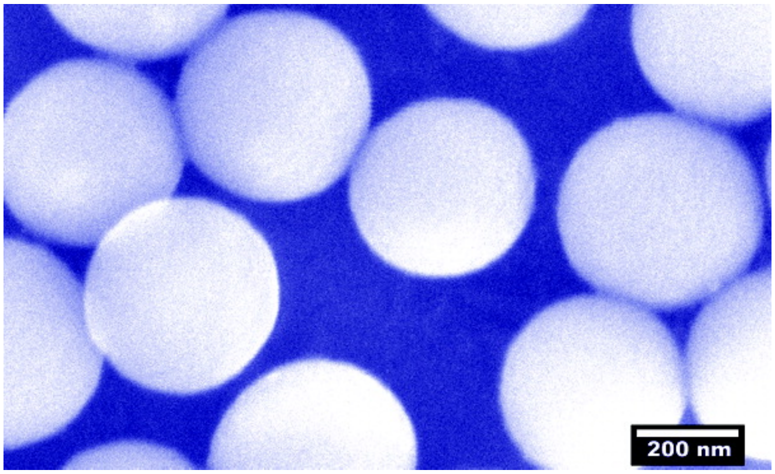

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Coordination-Induced Formation of Submicrometer-Scale, Monodisperse, Spherical Colloids of Organic−Inorganic Hybrid Materials at Room Temperature

Xuping Sun, Shaojun Dong,* and Erkang Wang*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate School of the Chinese Academy of Sciences, Changchun 130022, Jilin, PR China

Received May 27, 2005; E-mail: dongsj@ciac.jl.cn; ekwang@ciac.jl.cn

Colloids are essential in a variety of applications, such as in pigments, recording materials, ceramics, electronics, catalysis, medical diagnostics, and drug delivery system, etc.[1] Among them, monodisperse colloidal particles have attracted increasing attention because they hold promise as materials used in biosensors,[2] photonic crystals,[3] colloidal lithography,[4] porous membranes,[5] nanostamp for soft lithography,[6] microlenses,[7] and seed particles for the core−shell and hollow spheres,[8] etc. Therefore, considerable attention has been paid to strategies for fabricating monodisperse colloidal particles, and a wealth of preparative methods are reported.[1,9] Coordination polymers are a new class of organic−inorganic hybrid materials, in which metal ions are linked together by organic bridging ligands, and have developed extremely rapidly during the past years.[10] Up to now, although a few studies on the formation of particles of coordination polymers, including nanoparticles[11] and gels,[12] have been reported, no attention has been paid to the production of submicrometer-scale, monodisperse colloids of such organic−inorganic hybrid materials. In this communication, we present the first preparation of submicrometer-scale, monodisperse, spherical colloids of coordination polymers, involving the mixture of H_2PtCl_6 and *p*-phenylenediamine (PPD) aqueous solutions at room temperature. The influence of molar ratio and concentration of reactants on such colloids are investigated, and the optimum experimental parameters for the formation of monodisperse products are also given.

Sample 1 was prepared as following: In a typical experiment, 14 μL of 0.15 M PPD aqueous solution was introduced into 4 mL of water first, and then 55 μL of 0.038 M H_2PtCl_6 aqueous solution with 1:1 molar ratio of PPD to Pt was added into the resulting solution under vigorous stirring at room temperature. A gradual color change was observed, and a large amount of precipitate occurred within several hours. The precipitate thus formed was collected by centrifugation, washed several times with absolute ethanol and water, and then suspended in water. The suspension thus formed was used for further characterization.

Figure 1a shows low magnification SEM image of as-prepared precipitate, which clearly indicates that the precipitate consists of a large quantity of submicrometer-scale particles. Inset shows the size distribution histogram of such particles, demonstrating that these particles are monodisperse colloids about 420 nm in diameter. We further examined the particle size of such colloids by dynamic light scattering (DLS) characterization. The DSL results for the suspension reveal that the mean particle size of such colloids is about 415 nm with narrow size distribution, which is in good agreement with the data obtained from SEM image. Higher magnification SEM image shown in Figure 1b reveals that these particles are spherical in shape and well-separated from each other, which can be further confirmed by corresponding TEM image, as shown in Figure 1c. A local magnification of a single colloidal sphere by TEM indicates that the resulting particles have electron-microscopically perfectly smooth surface (Figure 1d). The chemical composition of the resulting colloids was determined by energy-dispersed spectrum (EDS) (Figure S1) of the resulting colloids coated on an indium tin oxide (ITO) glass slide. The peaks of Pt, Cl, C, and N are found (other peaks originated from the ITO substrate), indicating that the colloids are products of PPD and H_2PtCl_6.

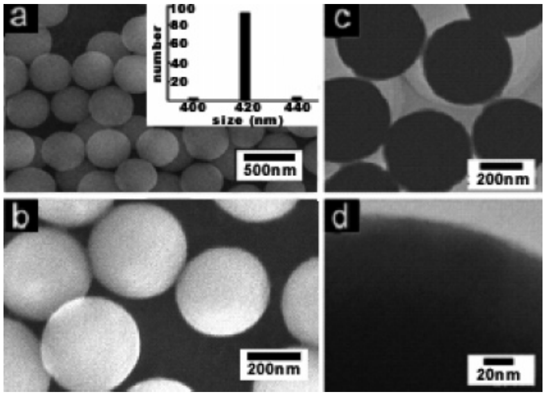

Figure 1. (a) Low magnification SEM image and corresponding size distribution histogram (inset), (b) high magnification SEM image, and (c) TEM image of the resulting particles; (d) local magnification of a single colloid.

It is well-documented that nitrogen ligand can coordinate with Pt(II) or Pt(IV) cation.[13] Although the nitrogen ligand of phenylenediamine can coordinate with many metal cations, the ligands derived from PPD can only coordinate one nitrogen atom to any one metal cation due to its strong steric effect.[10c] Please note the following experiment facts: (1) Both mixing H_2PtCl_6 and PPD in basic condition and mixing K_2PtCl_6 and PPD also give colloidal particles. (2) Mixing H_2PtCl_6 and *o*-phenylenediamine or *m*-phenylenediamine cannot produce colloidal particles. These observations indicate that only coordination interactions contribute to colloid formation, and the critical parameter is the use of bridging ligands. Therefore, we can suggest that the formation of such submicrometer-scale colloids in our present study is attributed to coordination-induced assembly from $PtCl_6^{2-}$ and PPD. A plausible formation process is briefly presented as following: When $PtCl_6^{2-}$ and PPD are mixed together, the two nitrogen atoms on the para positions of one PPD aromatic ring can coordinate to two different Pt(IV) cations, resulting in PPD-bridged structure,[10d] and the Pt species contained in as-formed structure can further capture other PPD molecules by coordination interactions along different directions. This coordination-induced assembly process can proceed repeatedly until the depletion of reactants in the solution, resulting in the formation of large coordination polymers, finally. However, the detailed formation mechanism of such submicrometer-scale, monodisperse colloidal spheres of coordination polymers is not clear at present time and needs further investigation. Please note that

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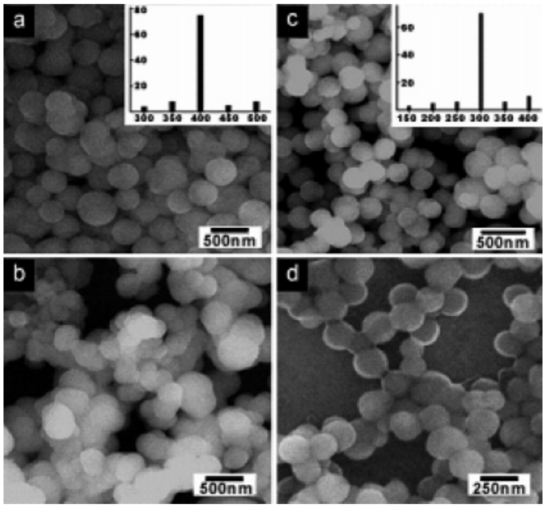

Figure 2. SEM images of particles obtained at a molar ratio of (a) 2:1, (b) 4:1, (c) 1:2, and (d) 1:4 of PPD to Pt. Inset: size distribution histogram.

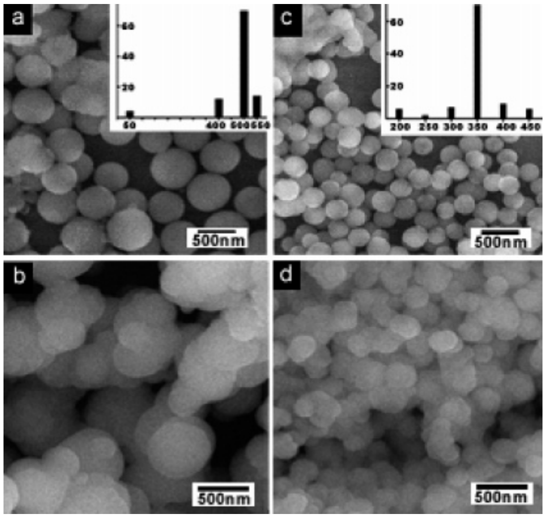

Figure 3. SEM images of colloids obtained with (a) 4-fold, (b) 10-fold, (c) $^1/_2$, and (d) $^1/_4$ concentration of reactants. Inset: size distribution histogram.

the XPS spectrum of the colloids shows two binding energy peaks of Pt 4f region at 72.4 and 75.5 eV (Figure S2), which can be assigned to Pt(II) species.[14] It can be attributed to the following two reasons: (1) Pt(IV) undergoes a partial reduction to give Pt(II) during the formation of coordination polymers;[15] (2) the photoredox reaction for Pt(IV) coordination polymers by X-ray irradiation during the collection of XPS spectrum will reduce Pt(IV) to Pt(II).[13b] It is worthwhile mentioning that the mixture of PPD and other complexes, including $PtCl_4^{2-}$ and $PdCl_4^{2-}$, also produces colloidal spheres, indicating this preparative route is general to colloids of coordination polymers.

We examined the influence of the molar ratio of PPD to Pt on the colloids thus formed by varying the amount of PPD used, under otherwise identical conditions used for preparing sample 1. At 2:1 molar ratio, we obtained products consisting of isolated colloidal spheres with a mean diameter of 400 nm and a fraction of fused particles (Figure 2a). A 4:1 molar ratio gave products mainly containing a large quantity of fused particles (Figure 2b). When the molar ratio was 1:2, isolated colloidal spheres mainly containing products with a mean diameter of 300 nm were produced (Figure 2c). However, 1:4 molar ratio gave products mainly consisting of fused, chainlike particles, as shown in Figure 2d.

Figure 3 shows SEM images of particles obtained at different concentration of reactants, under otherwise identical conditions used for preparing sample 1. When the concentration was increased 4-fold, we obtained products mainly consisting of isolated colloidal spheres with a mean diameter of 500 nm (Figure 3a). When the concentration was further increased 10-fold, we observed a large quantity of fused particles (Figure 3b). On the other hand, decreasing the concentration down to $^1/_2$ and $^1/_4$ produced isolated particles with a mean diameter of 350 (Figure 3c) and fused particles (Figure 3d), respectively.

In conclusion, coordination-based assembly in solution has been proven to be an effective strategy for the facile preparation of submicrometer-scale, monodisperse, spherical colloids of organic−inorganic hybrid materials at room temperature. The particle size and polydispersity can be controlled by the molar ratio and concentration of reactants, and the monodisperse products are obtained at 1:1 molar ratio and moderate concentration. Our observations are significant for the following reasons. (1) It provides a mild, room temperature route to fine colloids, avoiding the use of high temperature, which is crucial to the formation of fine colloids of inorganic materials.[9b] (2) Such colloids are new hybrid materials with versatile properties provoked by combining the merits of two sources and may find applications in many fields.[10] (3) Such colloids are easily broken up by a strong reducing reagent, such as $NaBH_4$, because of the reduction of the Pt cations contained therein, and therefore, they hold promise as easily decomposable colloidal templates for the fabrication of hollow spheres for a variety of applications.[8]

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Supporting Information Available: Energy-dispersed spectrum (EDS) and XPS spectrum of the Pt 4f region of the colloids of sample 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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