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Synthesis and Size Control of Gold Nanoparticles Stabilized by Poly(methylphenylphosphazene)

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Since the development of simple solution-phase methods for the synthesis and stabilization of gold nanoparticles,[1] research in this field has undergone a rapid expansion. Applications of gold nanoparticles now include biological markers,[2] DNA sensors,[3] molecular recognition systems,[4] and nanoscale electronics.[5] The use of polymer systems interacting with colloidal metal nanoparticles has been explored as a means of particle size control, stabilization, and organization,[6−8] but stabilization has typically been through pendant groups attached to the polymer backbone (e.g., 2-pyrrolidone, cyano, thiol,[7] or pyridine groups[8]). The only reported stabilization of metal nanoparticles by a polymer backbone involved chemical vapor deposition rather than chemistry in solution.[9] We report here the first solution-phase synthesis of gold nanoparticles[10] stabilized by the nitrogen lone pair electrons on the *backbone* of the *inorganic* polymer, poly(methylphenylphosphazene) (PMPP), $[Me(Ph)PN]_n$.[11] The gold nanoparticle−PMPP system resists aggregation in solution and shows no aggregation below the glass transition temperature (T_g) of PMPP as a solid. Varying the ratio of PMPP to Au prior to reduction allows control of gold nanoparticle size.

The synthesis of gold nanoparticles was accomplished using a room-temperature, two-phase, one-pot reaction involving the reduction of gold in the presence of PMPP.[12] The $HAuCl_4$ was dissolved in H_2O and a phase-transfer reagent (tetraoctylammonium bromide) was employed to move the salt into toluene over a period of 3 h.[13] PMPP was then added to the organic solution,[14] and the solution was stirred for 1 h. Reduction of the gold in the $AuCl_4^-$ was accomplished by adding $NaBH_4$ in H_2O, which produced an immediate dark-purple-colored organic layer. The mixture was stirred for 24 h after the addition of $NaBH_4$. The dark-purple polymer−Au nanoparticle composites were precipitated into hexane, dried under vacuum at room temperature, and redissolved for further studies. The molar ratio of PMPP monomer unit to $HAuCl_4$ was between 4 and 40 for all studies.

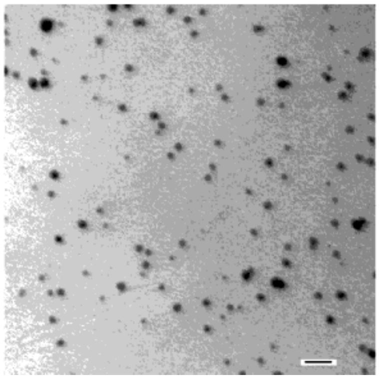

Figure 1. TEM image of 40:1 PMPP-Au nanoparticle composite. The scale bar is 20 nm.

Transmission electron microscopy (TEM) images of typical PMPP−Au nanoparticle composites (Figure 1) show that the gold nanoparticles are uniformly distributed throughout the polymer and the relative density of nanoparticles decreases as the ratio of polymer to gold increases. Varying the ratio of PMPP to $HAuCl_4$ controls the average size of gold nanoparticles within the PMPP matrix. Analysis of the TEM data[15] indicates that the average particle size for the 4:1, 8:1, and 40:1 PMPP−Au nanoparticle composites are 7.4, 6.8, and 5.1 nm, respectively.[16] Thus, as the amount of stabilizing PMPP is increased, the average size of the nanoparticles decreases. The stabilization is believed to result from the interaction of gold with the unusually basic nitrogen centers in the polymer backbone.[17]

The UV−visible absorption spectra for freshly prepared PMPP−Au nanoparticle composites dissolved in THF (Figure 2) show a broad absorption centered at 540 nm. This absorption is characteristic for gold nanocrystals in a size regime below 10 nm and is due to a localized surface plasmon oscillation.[18]

The PMPP−Au nanoparticle composites are relatively stable, showing no change in the nanoparticle density, size distribution, or absorption spectra after at least 6 months at temperatures below the T_g of PMPP (37 °C).

In solution, or at temperatures above the T_g, the gold nanoparticles are free to move and exhibit clustering over time. Figure 3 shows the TEM images of a PMPP−Au nanoparticle composite after heating at 45 °C for 1 and 24 h. Qualitatively, the gold

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[13] A typical synthesis employed 30.5 mg of $HAuCl_4$, dissolved in 4.0 mL of deionized H_2O, and 220 mg of tetraoctylammonium bromide.

[14] PMPP was dissolved in 0.5 mL of toluene and added to the toluene solution containing the tetraoctylammonium−gold complex. Masses of PMPP ranged from 0.05 to 0.5 g.

[15] Digital TEM images were analyzed to determine particle sizes using NIH Image.

[16] The standard deviations were 0.96, 1.33, and 0.25, respectively. These represent differences of 14, 20, and 5% relative to the average particle sizes. Comparable percent variations have been observed for gold nanoparticles stabilized by pendant thiol, cyano, and pyrrolidone groups on polymers. See ref 7a.

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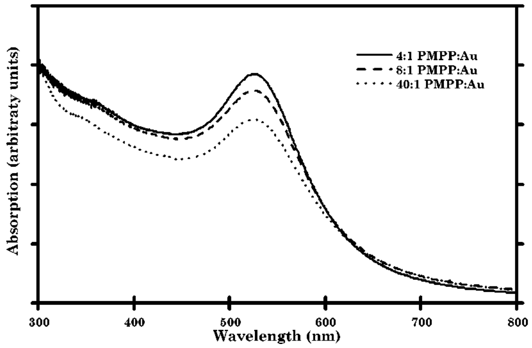

Figure 2. UV−visible absorption spectra for freshly prepared solutions of PMPP−Au composites.

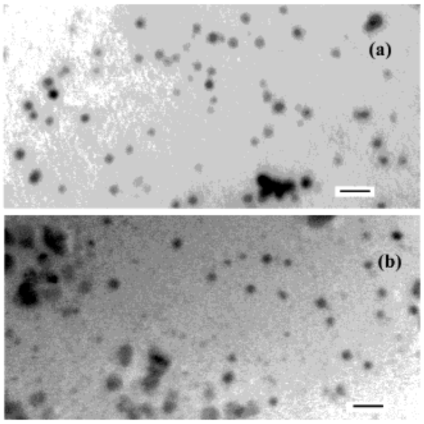

Figure 3. TEM of the 40:1 PMPP−Au composite after heating at 45 °C for (a) 1 h and (b) 24 h. Scale bars are 20 nm.

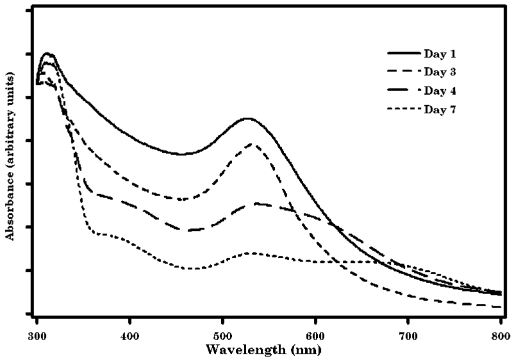

Figure 4. UV−visible absorption spectra of a solution of 40:1 PMPP−Au nanoparticle composite over time.

nanoparticles exhibit clustering in the TEM images after heating when compared with the original composites in Figure 1.

This clustering phenomenon is also manifested in the UV−visible absorption plots of solutions of PMPP−Au composites over time (Figure 4). The absorption spectra show a decrease in the intensity of the surface plasmon absorption resonance at 540 nm.

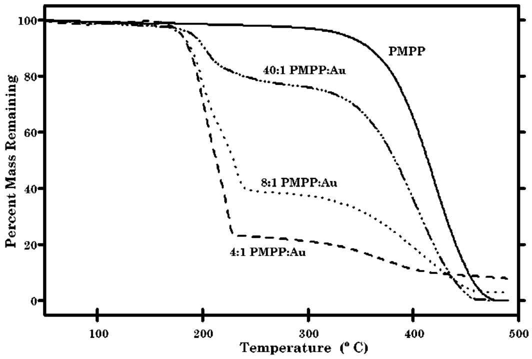

Figure 5. TGA plots of PMPP and PMPP:Au nanocomposites.

The thermal gravimetric analyses (TGA) data shown in Figure 5 indicate that the Au nanoparticles promote the decomposition of PMPP. Pure PMPP has an onset of decomposition at ~350 °C, which is attributed to the formation and subsequent sublimation of cyclic phosphazenes, the latter of which accounts for the low residual weight after thermolysis.[19] The gold nanocomposites, however, all show an earlier decomposition at ~185 °C as well as that at 350 °C. The composites with the greater proportion of gold not only show greater weight losses at 185 °C, but also have a larger remaining mass upon complete thermolysis, presumably due to nonvolatile metallic gold. The second weight loss at 350 °C is likely due to decomposition of segments of PMPP that are not complexed to the gold nanoparticles. The lowering of decomposition temperature is consistent with earlier observations of PMPP in the presence of transition metals and protons.[17,20]

In summary, PMPP has been used as a stabilizing medium in the synthesis of gold nanoparticles. The PMPP−Au nanoparticle composites are stable and resist aggregation at room temperature. The size of the nanoparticles can be controlled by varying the PMPP−Au ratio, with increased concentrations of PMPP favoring smaller particle size. TGA indicates that the presence of gold nanoparticles lowers the decomposition temperature of PMPP. Some aggregation of the particles occurs above the T_g of PMPP or when the composites are dissolved in solution. The use of PMPP to stabilize gold nanoparticles suggests that related poly(alkyl/arylphosphazenes) will also stabilize gold and other metal nanoparticles. The ease of modification of these polymers, the wide range of properties achieved by modification (e.g., water solubility), and the current understanding of the structure−property relationships will facilitate the optimization and control of particle size, shape, and aggregation.

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Supporting Information Available: TEM micrographs of 4:1 and 8:1 PMPP−Au nanoparticle composites and histogram plots showing gold nanoparticle size distributions (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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