

Synthesis and Characterization of Monodispersed Core–Shell Spherical Colloids with Movable Cores

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Spherical colloids with hollow interiors have received considerable attention due to their niche application as small containers for microencapsulation.¹ Templating against various types of colloidal particles has been intensively explored as an effective route to the generation of hollow spheres from materials as diverse as inorganic ceramics, organic polymers, and their hybrids.^{1–4} Most work in this area has, however, been focused on the development of synthetic methodologies. Very little attention has been directed toward the functionalization of the interiors of these hollow particles.⁵ In addition, there are only a limited set of reports that address the diffusion of chemical reagents across the shells of hollow particles.⁶ Here we describe the synthesis of polymer hollow spheres whose interiors were functionalized with movable gold nanoparticles. The incorporation of gold particles as movable cores into these polymer shells has allowed us to measure their shell thickness by SEM without fracturing the particles. The encapsulated gold nanoparticles also provide an optical probe for monitoring the diffusion of chemical reagents into and out of the polymer shells.

The schematic procedure consisting of three major steps was shown in Figure 1. The first step involved the conformal coating of gold nanoparticles (~50 nm in diameter) with uniform shells of amorphous silica derived from the tetraethyl orthosilicate (TEOS) precursor.^{5b} A submonolayer of ((chloromethyl)phenylethyl)-trichlorosilane (CMTS) – the initiator for atom transfer radical polymerization (ATRP)⁷ – was then attached to the surface of each Au@SiO₂ particle using the siloxane linkage.⁸ In the next step, uniform polymer shells with controllable thickness were formed on the CMTS-terminated surfaces via ATRP of a monomer such as benzyl methacrylate (BzMA).⁷ Finally, the silica shell sandwiched between the gold core and the polymer shell was selectively dissolved using aqueous HF to generate poly(benzyl methacrylate) (PBzMA) hollow particles containing movable gold cores. Depending on whether the interiors of these polymer shells were filled with water or air, we specify them as Au@Air@PBzMA or Au@Water@PBzMA, respectively.

Figure 2A shows a backscattering SEM image of the double-shelled, spherical colloids of Au@SiO₂@PBzMA, indicating that the gold core was located in the center of each particle and the spherical shape was maintained after polymer coating. The thickness of PBzMA shells was calculated as ~20 nm by comparing the mean sizes of Au@SiO₂ and Au@SiO₂@PBzMA particles. Figure 2B shows a backscattering SEM image of Au@Air@PBzMA particles obtained by selectively dissolving the silica layers in aqueous HF. The size and shape of these colloids were essentially unchanged after HF etching, and the polymer shells did not collapse when liquid was evaporated from their interiors during SEM sample preparation. Note that most gold cores (as marked by arrows) were not located in the centers of these particles. It is believed that the encapsulated gold nanoparticle was free to move within each PBzMA shell if it was filled with liquid. When the liquid was completely evaporated, the gold core tended to stick to the wall as

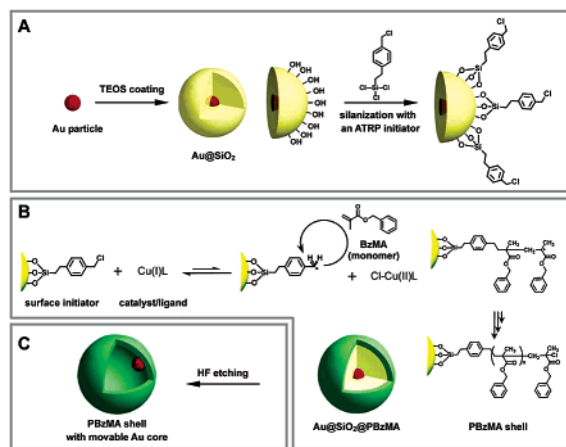


Figure 1. Schematic procedure used to generate PBzMA hollow beads containing movable gold cores.

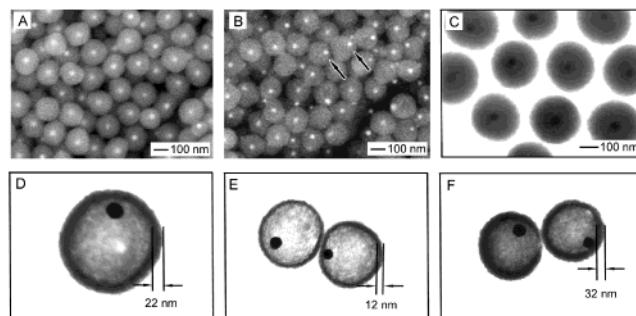


Figure 2. (A, B) Backscattering SEM and (C, D) TEM images of Au@SiO₂@PBzMA particles before (A, C) and after (B, D) HF etching. The polymerization time was 4 h, and the polymer shell was ~22 nm thick. (E, F) TEM images of Au@Air@PBzMA particles synthesized using different polymerization times: (E) 3 h and (F) 6 h. The polymer shells were ~12 and ~32 nm in thickness, respectively.

a result of the attractive capillary force between their surfaces. Depending on where the gold core was located relative to the electron beam, the separation between the gold core and the exterior surface of the shell was expected to vary over a range of values limited by two numbers: the thickness of the shell and the radius of the hollow colloids (Figure S1). A shell thickness of ~20 nm was estimated from the minimum separation (between the gold core and the exterior surface of the shell); this value was in good agreement with the value obtained using other methods. In this regard, backscattering SEM may provide a useful tool for directly determining the thickness of a closed shell, which might be difficult to measure using TEM when the shell is too thick or the contrast is too low. We further characterize these core–shell colloids with TEM; Figure 2C and D shows TEM images of a sample (the same batch as in Figure 2A) before and after SiO₂ etching with HF. In Figure 2C, both SiO₂ and PBzMA shells could be observed as

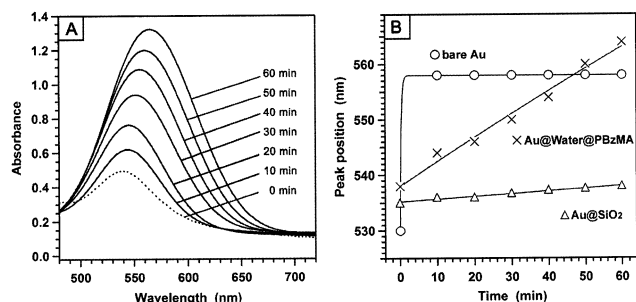


Figure 3. (A) UV-vis absorption spectra of Au@Water@PBzMA particles after they had been added into quinoline for different periods of time. (B) Dependence of plasmon peak position observed for the same gold nanoparticles encapsulated with different configurations: as-received Au, Au@SiO₂ core-shell, and Au@Water@PBzMA colloids.

uniform, conformal coatings (with a slight difference in contrast) on the surfaces of Au nanoparticles. The thickness of PBzMA shells determined from the TEM image (Figure 2D, ~22 nm) was consistent with the SEM measurements. Figure 2E and F shows TEM images of two other samples of Au@Air@PBzMA particles where the polymerization was allowed to proceed for 3 and 6 h, respectively. The thickness of PBzMA shells was changed from 22 to 12 and 32 nm. Thicker polymer shells (~80 nm) have also been synthesized by further extending the polymerization time up to 18 h. These demonstrations suggest that it is possible to generate Au@Air@PBzMA and other related core-shell colloids with a controllable size and shell thickness.

The colloids containing movable gold cores provide a unique system for investigating the diffusion of chemicals across the polymer shells. Figure 3A shows UV-vis absorption spectra of Au@Water@PBzMA (obtained from an aqueous suspension through centrifugation, with the interiors of the shells still filled with water) after they had been redispersed in quinoline for different periods of time. Because quinoline has a refractive index higher than that of water (1.62 vs 1.33), the surface plasmon resonance peak of gold cores was shifted to longer wavelengths as quinoline diffused into and water diffused out of the polymer shells.⁹ This observation was consistent with calculations based on the Mie scattering theory (as shown in Figure S2). The dependence of plasmon peak position on time is plotted in Figure 3B, together with similar measurements on bare Au colloids and Au@SiO₂ colloids. As expected, the plasmon peak of bare Au colloids immediately jumped from 530 to 558 nm when quinoline was added, and the plasmon peak of Au cores embedded in Au@SiO₂ particles was essentially unchanged at 535 nm after quinoline had been added for 1 h. These two cases correspond to extremely quick and infinitely slow diffusion of quinoline to the surfaces of gold nanoparticles. For the outflow of water across the PBzMA shells into quinoline, a diffusion coefficient of $\sim 4.76 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$ was estimated by fitting the time-dependence of the refractive index inside the shell (Figure S3).¹⁰ In comparison, the diffusion coefficient of water across a water/liquid interface is $\sim 4.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

In summary, we have demonstrated a practical route to the facial synthesis of spherical hollow colloids of PBzMA that contained movable cores of Au nanoparticles. This procedure should be extendable to many other systems that involve the use of different combinations of materials for the core and the shell.

These core-shell colloids may also find use as building blocks to form colloidal crystals with photonic band gap properties different from those of conventional core-shell or hollow particles.¹²

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Supporting Information Available: Computed extinction spectra and diffusion coefficients (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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