Laser-Assisted Synthesis of Superparamagnetic Fe@Au Core-Shell Nanoparticles

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Received: October 24, 2005; In Final Form: February 14, 2006

A novel method combining wet chemistry for synthesis of an Fe core, 532 nm laser irradiation of Fe nanoparticles and Au powder in liquid medium for deposition of an Au shell, and sequential magnetic extraction/ acid washing for purification has been developed to fabricate oxidation-resistant Fe@Au magnetic core— shell nanoparticles. The nanoparticles have been extensively characterized at various stages during and up to several months after completion of the synthesis by a suite of electron microscopy techniques (HRTEM, HAADF STEM, EDX), X-ray diffraction (XRD), UV—vis spectroscopy, inductively coupled plasma atomic emission spectroscopy, and magnetometry. The surface plasmon resonance of the Fe@Au nanoparticles is red shifted and much broadened as compared with that of pure colloidal nano-gold, which is explained to be predominantly a shell-thickness effect. The Au shell consists of partially fused ~3-nm-diameter fcc Au nanoparticles (lattice interplanar distance, d = 2.36 Å). The 18-nm-diameter magnetic core is bcc Fe single domain (d = 2.03 Å). The nanoparticles are superparamagnetic at room temperature (300 K) with a blocking temperature, $T_{\rm b}$, of \approx 170 K. After 4 months of shelf storage in normal laboratory conditions, their mass magnetization per Fe content was measured to be 210 emu/g, ~96% of the Fe bulk value.

Introduction

The recent surge in research on core—shell nanoparticles is driven by their multiple potential applications as well as interest in their fundamental properties. Shell addition can enhance stability and dispersibility of naked core particles and modify or enhance their properties.^{1,2} To date, gold has been the preferred coating material because of its well-known optical properties and chemical functionability.^{3,4}

Magnetic-core gold-shell nanoparticles are of particular importance because of their potential biodiagnostic applications, such as rapid magnetic separation and concentration of biomaterials.⁵ Recently, gold-coated Fe₃O₄ magnetic core nanoparticles (MNP) have been synthesized through wet chemical methods.⁶ However, pure Fe core nanoparticles are expected to be superior for such applications because of the high saturation magnetization of iron, $M_s = 218$ emu/g at 300 K, which is a factor of >2 larger than that of Fe₃O₄ (93 emu/g). Unprotected Fe nanoparticles are highly reactive in aqueous environment; thus, for biomedical applications they have to be coated with a protective layer such as a Au shell. Unfortunately, successful preparation of Fe@Au nanoparticles has been an enduring scientific challenge. There have been several reports of the synthesis of gold/iron/gold and iron/gold (Fe@Au) MNPs.7-9 However, detailed characterization of such nanoparticles has indicated rather fast oxidation of the Fe core.¹⁰⁻¹⁴ Recently, Ban et al. reported¹⁵ the synthesis of Fe@Au nanoparticles by partial replacement reaction. Although the authors measured high mass magnetization per pure Fe content of their nanoparticles (170 emu/g), long-term oxidation resistance of the Fe core was not addressed.

The main objective of the present project was to produce oxidation-resistant Fe@Au nanoparticles employing a laser ablation method. Laser ablation of solvent-suspended metal powders has previously been used in our group for synthesis of Au–Ag alloy nanoparticles of predetermined composition.¹⁶ Two general routes for synthesis of the Fe@Au nanoparticles have been explored. The first one consists of making both the Fe core and the Au shell using the laser ablation method. The second one, which is reported here, consists of preparing the Fe core by wet chemistry and subsequently coating the core with Au by laser ablation of Au powder. Magnetic extraction and acid washing of nanoparticles constitute the third step in both routes. The main advantages of the second route are a higher overall yield and better control of the size of the magnetic core.

Experimental Section

Homogeneous Nucleation Synthesis of Fe Nanoparticles. Monodispersed Fe nanoparticles were prepared under nitrogen atmosphere via thermal decomposition of iron pentacarbonyl, Fe(CO)₅.¹⁷ In a typical homogeneous nucleation synthesis of ~8-nm-diameter particles, 2.28 g of oleic acid (OA) was stirred in 20 mL of octyl ether, the solution was heated to 40 °C, and 0.3 mL of Fe(CO)₅ was injected in a 1:3 molar ratio to the OA. Following the injection, the reaction mixture became orangeyellow. After 30 min of refluxing, the mixture became black. The mixture was stirred for an additional 2 h under reflux and then cooled to room temperature. The particles were precipitated by addition of a large amount of ethanol and subsequent centrifugation. The precipitate was washed with ethanol or methanol. The solid residue was then extracted with 45 mL of hexane to form a black homogeneous solution.

Au Coating Process. In the coating process, 0.067 g of Fe nanoparticles in 25 mL of hexane was added to a three-neck

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Figure 1. Schematic diagram of the experimental process for fabrication of Fe@Au magnetic core-shell nanoparticles.

round-bottom flask containing 0.30 g of fine Au powder (Nanophase, 80-nm nominal diameter), 25 mL of water, and 15 mL of octane. Cationic surfactant cetyltrimethylammonium bromide (CTAB) was used as a stabilizing agent in aqueous phase (0.02 M). As a cosurfactant, 10 mL of 1-butanol was used. Nitrogen gas was flowed over the mixture to provide an inert nonreactive atmosphere. The mixture was vigorously stirred and irradiated with a pulsed 532-nm laser beam (Coherent, Infinity; 20 Hz, 65 mJ/pulse). The laser beam was unfocused and had a diameter of \sim 3.5 mm at the surface of the mixture. Gold nanoparticles, with surface plasmon resonance (SPR) located in the visible, absorbed 532-nm radiation more efficiently than the Fe NPs,18 which do not have SPR in the visible. During a single laser pulse, gold particles consecutively absorbed several photons, which led to their intense heating and subsequent decomposition.^{19,20} Because the melting temperature of a Au NP decreases with decreasing size, the decomposition process intensified during the irradiation. Nanoparticle charging followed by Coulomb disintegration might also have played a role.²¹ Au atoms, clusters, and nanoparticles condensed on Fe NPs, forming shells. Further interaction with the laser beam resulted in fusion of the shell particles and formation of a complete Au shell protecting the Fe core from oxidation. During the coating process the Fe nanoparticles were protected from oxidation by free radicals created by photodecomposition of a solvent and a cosurfactant (e.g., propanol or 1-butanol).²² After 2 h of laser irradiation, the mixture was centrifuged for 10-15 min to separate the oil phase from the aqueous solution.

Extraction and Purification of Fe@Au Nanoparticles. Following the laser irradiation, the mixture contained pure Au NPs, uncoated or partially Au-coated Fe NPs, and fully Au-coated Fe NPs (Fe@Au core—shell NPs). The Fe-containing nanoparticles were extracted with a rare earth magnet, redispersed in water, magnetically extracted again, and washed with a methanol/chloroform solution (1:1 volume ratio) to remove CTAB surfactant. Next, the nanoparticles were acid washed (HCl, 11.9%) to remove the uncoated and incompletely Au-coated Fe nanoparticles. The magnetic extraction/acid washing procedure was repeated until the acid wash contained no iron. Finally, the acid-resistant Fe@Au NPs were magnetically extracted and redispersed in water/CTAB solution. The Au coating and purification steps of the procedure are illustrated in Figure 1.

Characterization. The NPs were thoroughly characterized at various stages of the project, during and up to several months after completion of the synthesis, by a suite of transmission electron microscopy (TEM) techniques (HRTEM, HAADF STEM, EDX), X-ray diffractometry (XRD), UV-vis spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-AES), and magnetometry. Bright field TEM (Philips, CM20) was employed to determine the size distribution of the nanoparticles. To avoid the nonmonotonic contrast, such as that generated by diffraction or Fresnel fringes, Z-contrast imaging, generated by high-angle annular dark field (HAADF) scanning TEM (STEM), was used for investigation of structure and morphology of the Fe@Au core-shell NPs. Details of the coreshell structure were also studied by high-resolution TEM (HRTEM). XRD of the Fe@Au core-shell NPs dried in a vacuum was also performed. A Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda = 1.54056$ Å) was scanned in the $25^{\circ} \le 2\theta \le 100^{\circ}$ range with a step size of 0.02° . Atomic composition of nanoparticle samples was analyzed by global and single-particle EDX spectroscopy and ICP-AES. The optical response of NP solutions was monitored by UV-vis spectroscopy (Varian, Cary 3). Functionalization of the Au shell was investigated by FT-Raman spectroscopy. Finally, magnetization of the nanoparticles was measured with a Quantum Design Physical Property Measurement System (PPMS) using the extraction method with sensitivities of 2 \times 10⁻⁵ and 1 \times 10^{-8} emu for DC and AC magnetization, respectively. For the Fe@Au core-shell nanoparticles, DC magnetization was measured at 10 and 300 K; also, ZFC and FC curves were recorded at 50 Oe in the 2-300 K temperature range. In the measurements, a sample of dried Fe@Au nanoparticles (6.08 mg) was immobilized in a plastic capsule with zero magnetic contribution.

Results and Discussion

Thorough characterization of the nanoparticles synthesized in this project has shown that upon completion of the threestep procedure presented above, oxidation-resistant Fe@Au core-shell magnetic nanoparticles have been successfully synthesized.



Figure 2. TEM micrograph and corresponding diameter distribution histogram of Fe nanoparticles produced by thermodecomposition.

The magnetic Fe core of the Fe@Au nanoparticles is a single domain; its average size is significantly larger (see below) than that of the original Fe nanoparticles produced through thermal decomposition of Fe(CO)5, which was determined by electron microscopy to be equal to 7.8 nm (Figure 2). Panels a and b of Figure 3 show TEM micrographs and corresponding particle diameter histograms for the magnetically extracted Fe-containing nanoparticles before and after acid treatment, respectively. Because Fe has a lower electron density than Au, the dark contrast in the magnified TEM image in Figure 3a (inset) corresponds to gold, whereas the bright one to iron. The magnified image in Figure 3a (inset) shows that the gold shell consists of incompletely fused nanoparticles. The average particle size is about 10.9 nm before (Figure 3a) and 22.6 nm after acid washing (Figure 3b), which indicates that nanoparticles with the Au shell thicker than 3-4 nm are more likely to survive the acid treatment.

The structure of the Fe@Au nanoparticles was further studied by HRTEM (Figure 4). The image in Figure 4a was recorded with the electron beam focused at the surface of a particle. Multidomain structure with a regular lattice interplanar distance (d = 2.36 Å), which corresponds to fcc Au (111), was observed. The size of Au crystallites ranged from ~ 2 to 4 nm. With the electron beam focused inside the particle, a ~18-nm-diameter crystallite with the lattice interplanar distance of d = 2.03 Å corresponding to bcc Fe (100) was observed (Figure 4b). By focusing the e-beam at the bottom of the nanoparticle, multiple domains with a size and a lattice interplanar distance similar to those at the top surface were observed, which indicated that the bottom part of the core-shell NPs was also made of gold crystallites. Analyzing HRTEM micrographs, we estimated the average Fe core diameter and the Au shell thickness to be equal to ~ 18 and ~ 4 nm, respectively. More precise evaluation of the size distributions was done using HAADF STEM micrographs (Figure 5). Electrons collected with an HAADF detector were not Bragg scattered; hence, HAADF images showed little or no diffraction effects. The size of the shell-building Au particles and the average total diameter of the core-shell nanoparticles were estimated to be $\sim 3-4$ and 22.6 nm, respectively, in good agreement with the HRTEM estimates.

The average diameter of the Fe core in Fe@Au, equal to ~ 18 nm as estimated by HRTEM or ~ 18.6 nm as estimated by HAADF, is significantly larger than the initial average size of the Fe nanoparticles (7.8 nm). A mechanism of the Fe core



Figure 3. Bright field TEM micrographs and corresponding diameter distribution histograms of Fe-containing nanoparticles (a) before and (b) after acid treatment.

growth during the laser irradiation is likely similar to that of the Au shell formation outlined above. Despite weak absorption of Fe nanoparticles in the visible, prolonged 532-nm laser irradiation leads to their heating and, consequently, decomposition. The Fe atoms and small clusters condense on a surface of larger particles. Coalescence of stabilizing agent decorated metal nanoparticles has been demonstrated for thiolate-stabilized nanogold.²³ The photodecomposition is more efficient for the small particles, because of a melting temperature depression with decreasing nanoparticle diameter; this leads to a shift of nanoparticle size distribution toward larger diameters. The melting temperature of an 8-nm-diameter Fe particle was predicted to be as low as 570 °C, down from 1538 °C for bulk iron.²⁴

The presence of a highly crystalline Au shell in our Fe@Au nanoparticles was confirmed by observation of a well-developed fcc Au XRD pattern (Figure 6). It should be noted that X-ray diffraction is inconclusive with respect to determination of the structure and chemical composition of an Fe-containing core coated by a heavy atom (Au) shell, because the shell precludes observation of diffraction peaks corresponding to either pure iron or iron oxide core.²⁵

Pure colloidal nano-Fe in aqueous media exhibits only a weak continuous absorption spectrum in the visible range,¹⁸ whereas Au NPs show a size-dependent absorption due to strong SPR. Thus, the color of the colloidal solutions studied in this project



Figure 4. HRTEM micrographs of Fe@Au core-shell nanoparticles recorded with the focal plane of the objective lens set inside (a) the shell and (b) the core of the nanoparticle.



Figure 5. HAADF micrograph of Fe@Au nanoparticles.

was predominantly determined by optical response of the gold fraction. Following the laser irradiation and prior to the magnetic extraction of the Fe-containing nanoparticles, the solution appeared ruby red and the SPR absorption peak was observed at 528 nm (Figure 7a). The residual solution after magnetic confinement of nanoparticles displayed red color. The optical response of that solution with the SPR maximum observed at 516 nm was largely determined by pure Au nanoparticles (Figure 7b). The solution containing magnetically extracted and redispersed nanoparticles prior to acid treatment was dark red; the SPR band was significantly broader, as compared with the two solutions discussed above, and red shifted to \sim 546 nm (Figure 7c). Finally, the solution containing the Fe@Au nanoparticles, magnetically extracted following acid washing and redispersed in H₂O with 0.02 M CTAB, showed purple color with the SPR



Figure 6. XRD pattern of Fe@Au nanoparticles.



Figure 7. Colloidal solutions and their corresponding UV-vis absorption spectra at various stages of the Fe@Au production process: (a) after laser-assisted Au coating of Fe nanoparticles; (b) residual solution after magnetic confinement of Fe-containing nanoparticles, which are visible as a dark cluster near the bottom of the sample bottle; (c) solution of redispersed Fe-containing nanoparticles prior to acid washing; (d) magnetically extracted Fe@Au nanoparticles redispersed in H₂O with CTAB.

band even broader and shifted further to the red (Figure 7d) as compared with the solution shown in Figure 7c.

The spectrum of the Fe@Au colloid has been modeled using complex dielectric functions of bulk Fe²⁶ and Au²⁷ and the geometric parameters of the nanoparticles determined by electron microscopy. Details of the method have previously been described by Mulvaney.²⁸

The core and the shell dielectric constant functions were approximated from the bulk functions by scaling the bulk damping frequency, Γ , by R_b/R_e factor, where R_b and R_e are the bulk and effective mean free paths, respectively. This



Figure 8. UV-vis absorption spectrum of Fe@Au core-shell nanoparticles in water with CTAB observed (solid line) and calculated using bulk dielectric constant functions of Fe and Au and geometric parameters determined by TEM (dotted line).



Figure 9. ZFC and FC curves of Fe@Au core-shell nanoparticles measured 4 months after synthesis of the nanoparticles.

approach takes into account nanoparticle size effects, but neglects all other effects.

The spectrum was initially simulated in the 400–700 nm range for typical acid-treated Fe@Au nanoparticles (see Figures 5b and 7) with the shell diameter $R_s = 22$ nm and the core diameter $R_c = 18$ nm immersed in water ($\epsilon_m = 1.77$) using the scaled complex dielectric constant functions and taking $R_b = 50$ nm for the bulk electron mean free path for both Fe and Au. Taking into account the fact that the observed spectrum was heterogeneously broadened due to the distribution of nanoparticle core and shell sizes in the sample, the agreement between the observed and the simulated spectrum was remarkably good. With just slightly adjusted (effective) values of the simulation parameters, $R_s = 22.8$ nm, $R_c = 18.4$ nm, and $R_b = 52$ nm, well within the acceptable experimental range, the simulated spectrum was brought into near perfect agreement with the observed one (see Figure 8).

Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of the Fe@Au nanoparticles are shown in Figure 9. The field-dependent blocking temperature, $T_b = 170$ K, was estimated as the average value of the temperatures corresponding to the onset of irreversibility between the FC and ZFC curves (225 K) and the maximum of the ZFC curve (115 K). Assuming that the energy barriers are correctly described by the anisotropy energy *KV*, where *K* is the total anisotropy constant of the particles and *V* is the volume of the magnetic core, the average diameter (*D*) of the magnetic core can be estimated²⁹ from the $KV \approx 25k_{\rm B}T_{\rm b}$ relationship with $V = \pi D^3/6$, where $k_{\rm B}$ is the



Figure 10. Hysteresis loops of Fe@Au core-shell nanoparticles at 10 K (dotted lines, \bigcirc) and 300 K (solid line, \bullet) measured 4 months after synthesis of the nanoparticles.

Boltzman constant. Using the value of the anisotropy constant determined at liquid-He temperatures for pure Fe, $K = 5.4 \times 10^4$ J m⁻³, the average diameter of 12.6 nm is obtained, which is significantly smaller than the HRTEM estimate of 18 nm. However, it should be pointed out that at 170 K the Fe anisotropy constant, assuming a temperature dependence similar to that of magnetite,³⁰ could be as much as 50% smaller, leading, in turn, to the noticeably larger core diameter estimate of 15.2 nm.

Figure 10 shows the 10 and 300 K hysteresis loops recorded for the Fe@Au nanoparticles. Prior to the magnetic measurements the sample was shelf stored in normal laboratory conditions for 4 months. The room temperature (300 K) saturation magnetization, $M_{\rm s}$, was estimated by extrapolation to be 0.3 emu. With the Fe mass fraction in the Fe@Au sample measured by ICP-AES to be 23.5% and the total mass of the sample to be 6.08 mg, the Fe@Au saturation magnetization per pure Fe is calculated as 210 emu/g, which is only slightly smaller than the bulk Fe value of 218 emu/g. The Fe mass fraction was alternatively estimated at 29.4% using the average sizes of the Fe core and the Fe@Au nanoparticle equal to 18 and 22.6 nm, as discussed above, and bulk densities of Au and Fe equal to 19300 and 7874 kg/m3, respectively, yielding the saturation magnetization per Fe content equal to 179 emu/g. Given the approximate nature of the second calculation (average particle sizes used, residual content of CTAB in the dry sample neglected, etc.), the agreement of both estimates with the bulk Fe value is very good. The magnetization measurements support our claim of the core being highly crystalline Fe. The second saturation magnetization estimate, the smaller and less precise of the two, is still almost twice as large as the saturation magnetization of Fe₃O₄. Cho et al.¹⁴ determined, using the average values of the core and the shell sizes, the saturation magnetization per Fe contents of their sample to be 152 emu/g. The somewhat smaller value as compared with our estimates may result form the partial Fe core oxidation, which is evident from the temperature dependence of resistance and Mössbauer spectra of their sample. More recently, Cho et al.¹² reported a saturation magnetization per Fe content of Fe@Au nanoparticles equal to 162 emu/g with the Fe fraction determined by ICP-AES. Their sample had a poor oxidation resistance, which resulted in the saturation magnetization decreasing to 50% of the initial value after just 5 days of storage. Most recently, Ban et al.15 reported the synthesis of Fe@Au nanoparticles with saturation magnetization per Fe content equal to 170 emu/g, which suggests a high content of pure Fe in the core. The authors



Figure 11. FT-Raman spectrum of $Fe@Au-S(CH_2)_{11}OH$ in CH_2Cl_2 (red trace), $HS(CH_2)_{11}OH$ in CH_2Cl_2 (blue trace), and pure CH_2Cl_2 (black trace). Downward-pointing arrows indicate SH stretch peaks.



Figure 12. EDX spectra of (a) Fe@Au and (b) Fe nanoparticles stored in normal laboratory conditions for 2 weeks.

claimed that no oxygen was present in the core, but some of their arguments were unconvincing. As mentioned above, XRD is inconclusive with respect to the core structure and chemical composition when a heavy atom (Au) shell is present. Also, in the EDX spectrum they omitted the energies below 1 keV, where the oxygen peak would appear if oxygen was present in the core. It should also be pointed out that they did not discuss long-term oxidation resistance of their nanoparticles.

At room temperature (300 K) our Fe@Au nanoparticles are superparamagnetic. The coercivity, H_c , is approximately 12 Oe, and the remanent magnetization, M_r , is 0.0019 emu. As expected for the superparamagnetic material, the M_r/M_s ratio is very small, 0.006. At 10 K, coercivity equals 200 Oe. For comparison, Cho et al.¹⁴ measured for their Fe@Au nanoparticles coercivity equal to 240 Oe at 5 K. A close examination of the 10 K curve reveals a slope change with the field approaching zero value, which can be attributed to the presence of a small fraction of agglomerated and interacting nanoparticles in the sample.

Excellent stability of our Fe@Au nanoparticles against core oxidation was verified by EDX spectroscopy. Figure 12 shows EDX spectra of (a) Fe@Au and (b) unprotected Fe nanoparticles after 2 weeks of shelf storage in normal laboratory conditions. Although a strong oxygen peak is present in the spectrum of unprotected Fe nanoparticles (b), no oxygen is observed in the



Figure 13. EDX spectra of a single Fe@Au nanoparticle with the electron beam traversing the particle (a) at the center through both the shell and the core and (b) away from the center through the shell only.

spectrum of Fe@Au nanoparticles (a). Figure 13 shows EDX spectra of an isolated Fe@Au nanoparticle recorded with the electron beam traversing the particle (a) through the center, and thus through both the shell and the core, and (b) away from the center through the shell only. In addition to the C and Cu peaks originating from the sample support, trace b shows only Au peaks, whereas trace a shows both Au and Fe peaks, as expected for a core/shell nanoparticle. The reader should note that no oxygen peak is present in either trace.

The Fe@Au nanoparticles synthesized in this project are stabilized with the cationic surfactant CTAB. Various applications of the Fe@Au magnetic nanoparticles may require use of different surfactants or surface functionalization. Due to the strong chemical affinity of Au and -SH, CTAB can be readily displaced by dodecanethiol, N-mercaptoundecanoic acid (MUA), and similar derivatives. To test the Au shell functionability, the Fe@Au NPs were redispersed in dichloromethane (CH₂Cl₂) and capped with 11-mercapto-1-undecanol (HSC₁₁H₂₂OH). It has been reported that 11-mercaptoundecanate immobilized on the surface of Au nanoparticles was used as a template for peptide elongation.³¹ The S-H and C-S stretches were observed by FT-Raman spectroscopy for pure 11-mercapto-1-undecanol at 1380 and 2700 cm⁻¹, respectively (Figure 11, middle trace). Both stretches were, however, absent from the spectra when 11-mercapto-1-undecanol was added to the solution of Fe@Au in CH₂Cl₂, indicating attachment of the 11-mercapto-1-undecanol to the Au surface (Figure 11, top trace).

Conclusions

A novel method for the synthesis of oxidation-resistant Fe@Au core-shell magnetic nanoparticles has been developed. It combines wet chemistry for the Fe core synthesis with laser irradiation for the Au shell formation and magnetic extraction/ acid washing for sample purification. The effect of irradiation is complex, but it most likely involves the fragmentation of Au particles into small clusters, which through repeated heating and melting tightly coat the iron core. Magnetic extraction separates from the laser-irradiated mixture Fe-containing nanoparticles, whereas acid washing removes those nanoparticles that are uncoated or incompletely Au-coated. The purified product contains Fe@Au core-shell nanoparticles; the nanoparticles are superparamagnetic at room temperature (300 K) and exhibit an

excellent long-term oxidation resistance. After 4 months of shelf storage in normal laboratory conditions, they showed high saturation magnetization per Fe content, 210 emu/g, which is comparable (96%) to that of pure bulk iron. The high saturation magnetization, as compared with iron oxide and other magnetic material containing nanoparticles, makes the Fe@Au structure very attractive for theranostic applications where, in addition to surface functionability, efficient and rapid magnetic manipulation is required. The Fe@Au nanoparticles can be prepared in either aqueous or organic medium, and well-known gold chemistry can be applied readily.

Acknowledgment. We thank Prof. G. A. Botton and N. Braidy from McMaster University for HAADF STEM measurements. J.Z. thanks the National Research Council and the Natural Sciences and Engineering Research Council (NSERC) for the support of a NSERC visiting fellowship.

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