Controlled Fabrication of Gold/Polymer Nanocomposites with a Highly Structured Poly(*N*-acylethylenimine) Shell

Mariana Rusa, James K. Whitesell, and Marye Anne Fox*

Department of Chemistry, North Carolina State University, Campus Box 8204, Raleigh, North Carolina 27695

Received July 16, 2003; Revised Manuscript Received February 3, 2004

ABSTRACT: Two families of well-defined organic—inorganic nanocomposites have been synthesized either by attachment of an initiator as a capping self-assembled monolayer on a gold cluster onto which a macromolecule is grown in situ or by preformation of a defined polymer, followed by covalent or adsorptive attachment to a surface-capped metal cluster. The characteristics of these composites are compared in size and local organization. Possessing nanometer-sized gold clusters at the core and poly(*N*-acylethylenimine) chains radially or tangentially connected to the core, the resulting materials were characterized by TEM, GPC, UV, IR, NMR, and XPS spectroscopies. Larger particles with narrower polydispersity were obtained by in situ growth of the polymer on a preformed metal cluster, with best results being attained with a mixture of brominated and nonbrominated thiols in which steric accessibility to the initiator sites is varied.

Introduction

Nanostructured materials have attracted much attention because of their applications in several fields such as optical and magnetic devices, catalysts, or biological sensors.¹ Nanocomposites that include metallic particles within a protective organic shell of polymer² (i.e., polystyrene, poly(dimethylsiloxane), poly(ethylene oxide), poly(carbodiimides), poly(vinylpyridine), etc.) have been shown to be suitable for hierarchical selforganization into nanoassemblies.³ The organic shell determines the chemical properties of such materials and regulates chemical interactions with their environment, whereas many of the physical properties of these composites are determined by the size and shape of the metal core as well as the surrounding organic layer.⁴

Thus, because precise control of the size of a contained metal nanoparticle and the chemical behavior of a composite (stability and reactivity) are important, directed synthesis is an important goal. Advances in nanotechnology will require a more complete understanding of intriguing new properties that depend on particle size, and synthetic routes that permit structural variation are crucial. These experiments can therefore serve to bridge the gap of chemical and physical properties as structure changes from individual molecules to bulk materials.⁵

The choice of shell and core materials for such composites is generally predicated on their independent properties. Gold clusters can be prepared chemically homogeneous, easy to clean, and virtually free of contamination. In addition, gold clusters of nanometer size absorb light strongly in the visible region and can be characterized spectroscopicaly at relatively low concentrations.⁶ Poly(*N*-acylethylenimine) (PNAI) possesses several special characteristics: high hydrophilicity and water solubility as required for most biological applications; good miscibility with a wide range of organic polymers; extremely low toxicity; desirable biocompatibility; easy preparation by living cationic polymerization, enabling effective control of molecular parameters and introduction of functional end groups that can moderate surface properties; and sufficient chemical

versatility to permit a range of subsequent chemical reactions that allow them to fill various structural and/ or functional roles within the final composite. In addition, to achieve complete control of the properties of the resulting nanocomposites, it is desirable to prepare monodisperse particles with respect to size, shape, and internal structure. Although significant advances have been made in the assembly of such structures,⁷ the challenge to design and prepare three-dimensional objects of precisely controlled geometry remains an important goal.

We have chosen to investigate nanocomposites comprised of a gold cluster as core capped by organic polymers. Living cationic ring-opening polymerization of 2-substituted 2-oxazolines was chosen as a synthetic route to a defined, flexible hydrophilic/hydrophobic (depending on substituent) polymer (Scheme 1). This method also produces controlled chain length and narrow polydispersity, while retaining appropriate functionalities for organization and chemical anchoring at either terminal end.⁸⁻¹⁰ When a surface-functionalized gold cluster was used to initiate the polymerization, covalent anchoring of the synthetic polymer was easily achieved.

Seeking new synthetic methodologies for polymerencased colloidal nanoparticles, we report here an evaluation of materials prepared via four synthetic sequences to narrowly dispersed nanocomposites with a gold core and highly structured poly(N-acylethylenimine) shell. These involve either preformation of a gold cluster capped with initiator, which subsequently acts as a multisite seed for the polymerization of the monomer (2-ethyl-2-oxazoline), or, as an alternative, the in situ capping of prepared gold nanoparticles with a preformed poly(*N*-acylethylenimine). For each of these routes, two variants are presented: (a) attachment of an ω -functionalized thiol as a self-assembled monolayer (SAM) which needs further chemical transformation to be converted to an initiator group; (b) attachment of an active initiator as a SAM onto which a macromolecule is grown in situ (for the first route); or stabilization of gold nanoparticles by preformed PNAI such that the



polymer is either chemically bound or physisorbed onto the core metal cluster (for the second route). The size distribution and long-term stability against aggregation of each of the resulting composites are then described.

Experimental Section

Chemicals. Dry tetrahydrofuran (THF), chloroform, methanol (MeOH), and ethanol were distilled under dry N_2 and stored over molecular sieves (4 Å). 2-Ethyl-2-oxazoline (EOZO) was purified by heating to reflux for 2 h over KOH and subsequently distilling under dry N_2 before being stored over molecular sieves. Other reagents (a THF solution of lithium triethylborohydride (1.0 M), hydrogen tetrachloroaureate(III) trihydrate, 11-hydroxyundecanethiolate (HUT), *n*-undecanethiol (UT), trifluoromethanesulfonic anhydride, 4-phenylazoaniline, sodium cyanide (NaCN), 1,10-diododecane, 1,11-dibromoundecane, 1,10-dibromodecane, acetic acid, thiourea, NaOH, dilute HCl, hexamethyldisilathiane, tetrabutylammonium fluoride (TBAF), ammonium chloride, and NaBH₄) were used as received.

Thiol Synthesis. For the synthesis of 10-bromodecanethiol and 11-bromoundecanethiol, a modification of the previous route to 10-iododecanethiol was employed.¹¹ Thus, the $1,\omega$ -dibromoalkane was treated with 1 equiv of thiourea, heated to reflux for 1 h in 95% ethanol, treated with a slight excess of NaOH under N₂ for 20 min, and then neutralized with dilute HCl. The ethanol was removed under reduced pressure, and the product was extracted from the aqueous phase using chloroform. The crude product was purified by column chromatography (silica, hexane).

Preparation of 1,@-Bromoalkanethiol (BrAT)-Functionalized Gold Nanoparticles. Thiol-stabilized gold nanoparticles were synthesized using a modified literature method.¹² A color-free solution of 1 mM BrAT in 10 mL of THF was added under vigorous stirring to a pale yellow solution of hydrogen tetrachloroaureate(III) (0.5 mM) trihydrate in MeOH in a 100 mL jacketed flask. The solution became orange-brown within 1 min. Acetic acid (5 mL) was added to the mixture. After further stirring at room temperature for 20 min, 5 mL of NaBH₄ solution (1 M) was added dropwise under efficient cooling. The mixture turned dark immediately, and the solution was stirred for 3 h. The solvents were then removed by evaporation under N₂. The product was washed three times with diethyl ether and water. The resulting solution was poured into centrifuge tubes filled with anhydrous ethanol (2:1 (v/v) ethanol:solution mixture). The nanoparticles were precipitated, and the supernatant was discarded. The process was repeated twice after the solution was briefly sonicated. The purified nanoparticles were dried in a vacuum desiccator overnight. The products are soluble in THF, toluene, hexane, chloroform, and ethyl ether and can be repeatedly precipitated and redissolved, forming pink to dark red solutions, depending on the concentration of the final product.

Surface-Initiated Polymerization of 2-Ethyl-2-oxazoline. Freshly prepared and vacuum-dried BrAT-functionalized nanoparticles (0.1 g) were transferred into a 50 mL reaction vessel equipped with a condenser and a three-way stopcock. Under dry N₂, and using airtight syringes and septa, 5 mL of dry CHCl₃ and 1 mL of freshly distilled 2-ethyl-2-oxazoline were added at 0 °C under vigorous stirring. The reaction mixture was then heated on an oil bath and allowed to react under reflux for 3 days. The polymerization was terminated by adding a solution of 0.1 g of 4-phenylazoaniline in 1 mL of dry CHCl₃ at 0 °C. After stirring for 1 day at room temperature, the crude product was isolated (precipitation CHCl₃/ ether), filtered, and vacuum-dried overnight. AH - nucleophilic agent

Synthesis of Poly(*N*-acylethylenimine). Poly(*N*-acylethylenimine) (PNAI) samples were prepared according to a published procedure.^{7,9} Under dry N₂, 0.02 mol of 2-ethyl-2-oxazoline was added to a solution of 0.001 mol of initiator (1-iodoodecane (ID) or 1,10-iododecanethiol (IDT)) in 4 mL of CHCl₃ at 0 °C using syringes. The reaction vessel was sealed and allowed to react under reflux. A terminal-OH group was introduced by adding a slight excess of aqueous K₂CO₃. *M_w* was 3225 as determined by GPC using polystyrene standards.

Preparation of Gold Nanoparticles Stabilized by PNAI. A color-free solution of 0.2 g of poly(*N*-acylethylenimine) with or without a thiol-terminal group in 6 mL of MeOH was added under vigorous stirring to a pale yellow solution of 0.1 g of hydrogen tetrachloroaureate(III) trihydrate (0.1 equiv to the N-acylethylenimine unit) in 6 mL of MeOH in a 100 mL jacketed flask. The solution became orange within 1 min. After further stirring at room temperature for 10 min, 3 mL of NaBH₄ solution (1 M) was added dropwise under efficient cooling. The mixture turned dark red immediately. The solution was stirred for 12 h before solvent was removed under a stream of N2. The product was dissolved in CHCl3 and washed three times with water. The resulting solution was briefly dried with anhydrous Na₂SO₄, the solvent was removed under reduced pressure, and the purified particles were dried in a vacuum desiccator. The particles are soluble in chloroform and can be repeatedly precipitated and redissolved, forming pink to dark red solutions, depending on the concentration of the final product.

Spectral Characterization. a. Transmission Electron Microscopy (TEM). High-resolution TEM images of the particles were obtained with a side-entry Phillips CM12 electron microscope operating at 120 keV. The samples were prepared by drop-casting 1 drop of a ~10 mg/mL nanoparticle solution in CH₂Cl₂ onto standard carbon-coated Formvar films on copper grids (300 mesh) and drying in air for 30 min. For each sample, two typical regions were scanned. The average cluster diameters were obtained using Scion Image software.

b. Absorption Spectroscopy. UV/vis spectra were obtained on a Shimadzu UV-3101 PC/UV-vis-NIR scanning spectrophotometer. Solution spectra were obtained by measuring the absorption of dilute solutions in a quartz cell with a 1 cm path length referenced to a CHCl₃ blank.

c. Fourier Transform Infrared Spectroscopy. Transmission FTIR spectra were recorded using a Nicolet 510P FT-IR spectrometer as thin transparent pellets of the composite in a KBr matrix. Spectra were obtained by collecting and averaging 200 scans at a resolution of 2 cm⁻¹. External reflection infrared spectra (ER-FTIR) were recorded using a Magna 550 spectrometer (Nicolet) equipped with a grazing angle setup (fixed angle of 80°); reported spectra were averaged from 500 scans accumulated at 2 cm⁻¹ resolution.

d. Gel Permeation Chromatography (GPC) (Size Exclusion). Molecular weight and molecular weight distribution were measured via GPC using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector at a flow rate of 1 mL/ min at room temperature on two PL-Gel mixed C columns. Chloroform was the mobile phase. Molecular weights are reported relative to narrow molecular weight polystyrene standards (Pressure Chemical, Inc.).

e. Nuclear Magnetic Resonance Spectroscopy. NMR spectra were recorded on a Mercury 300 spectrometer in $CDCl_3$.

f. X-ray Photoelectron Spectroscopy (XPS). Spectra were obtained on a Riber LAS-3000 X-ray photoelectron spectrometer using an Mg K α (1254 eV). Element levels were recorded at an electron takeoff angle of ~75°. Samples of the



Figure 1. Illustrative representation of the "grafting from" method used for the preparation of shell–core nanocomposites from monolayers bearing different terminal functionality: (a) attachment of an ω -hydroxyl-functionalized thiol to a gold surface as a self-assembled monolayer, which needs further chemical transformation (e.g., treatment with trifluoromethane-sulfonic anhydride) to be converted to an initiator group as a site from which polymer is grown; (b) direct attachment of an initiator (e.g., an ω -bromo-functionalized thiol) as a SAM onto which a macromolecule is grown in situ.

solid-state nanoparticles were prepared by placing a drop of the nanoparticle solution onto a silicon wafer and allowing the solvent (CH_2Cl_2) to evaporate. The samples of particles obtained by surface-initiated polymerization were collected before the addition of the terminating agent.

Results and Discussion

One of the principal aims of nanotechnology is to control the size and morphology of nanoparticles and nanostructured materials by fabricating them as ordered structures.¹³ The preparation of stabilized metal nanoparticles of controlled size can be achieved by multiple methods, the most frequently used being the reduction of metal salts in the presence of capping agents such as alkanethiols.¹⁴ The unique features of PNAI prompted us to examine its possible use in the controlled syntheses of capped nanoparticles and nanoparticle/polymer composites.

Our initial synthetic approach was to prepare highly monodisperse capped nanoparticles by a procedure developed by Ulman et al.⁵ for gold nanoparticles functionalized by short aliphatic thiols. Single-phase synthesis of alkanethiol-functionalized gold is especially suitable for the preparation of uncontaminated nanoparticles because of the surfactant-free conditions employed (Figure 1a, X = OH). However, in our hands, this method failed to produce nanoparticles with precisely controlled geometry and functionality and with a very narrow size distribution. Likely, this difficulty may be related to monolayer surfaces containing high concentrations of OH groups on mobile organic chains.¹⁵ Such systems are not stable and may aggregate over time as



Figure 2. Schematic representation of the "grafting onto" method used for preparation of shell–core nanocomposites: preformation of polymer, followed by (a) covalent binding of an end-functionalized polymer (when X is a thiol anchoring group) or (b) adsorption of preformed polymer (when X = H) to the gold surface.

influenced by surface reorganization and the adsorption of contaminants. On the basis of our observations, we conclude that synthesis of nanoparticles with a range of surface OH concentrations gives a broad distribution of particles of highly variable stability. In the next step, OH groups on the surface were transformed into triflate initiator groups for the polymerization of EOZO.^{7a,8}

The work of Jordan and co-workers would seem to provide direct precedent for the polymerization route outlined in Figure 1a. However, this route was not successful for our attempt to obtain particles with different sizes and grafting densities because it failed in the synthesis of the core particles with a range of OH surface concentrations and because a substantial quantity of dispersed, unanchored polymer is always present (Figure 1a), having been produced concurrently by this method. This is likely due to the presence of unbound initiator (trifluoromethanesulfonic acid) which cannot be avoided, as this reagent is an unavoidable side product in the transformation of OH into an active initiator.

To avoid these problems while retaining our focus on the ability to predict confidently the structure of a nanocomposite material, we have developed here two alternative methods which are reported for the first time for this polymer: (1) direct preparation of gold clusters which contain the desired amount of initiating groups on the surface, followed by in situ growth of the polymer coat (Figure 1b), or (2) stabilization of gold clusters with a preformed polymer (Figure 2), by covalent bonding (pathway a) or by physical adsorption of polymer lacking end functionality (pathway b).

Better results were obtained by attaching the polymerizable groups at the periphery of the metal nanoparticles (Figure 1b). The second method is nonetheless a very simple way to obtain gold/PNAI nanocomposite with a reasonably narrow size dispersity and remarkable stability.

Direct Preparation of Gold Clusters with Initiating Groups on the Surface and in Situ Growth of Nanoparticles. We chose a thiol-anchored alkyl halide as the initiating group on the basis of previous work and on its ability to initiate the polymerization of 2-oxazolines (Scheme 1). We could therefore access



routes to anchorable macromolecules with a considerable range of molecular weights and backbone characteristics.¹⁶ For this purpose, we synthesized 10-iododecanethiol (IDT), 10-bromodecanethiol (BrDT), and 11bromoundecanethiol (BrUT) as capping agents to obtain a capped self-assembled monolayer (SAM) on gold bearing terminal functionality that could initiate polymerization. The choice of the initiator was based on its stability in the next steps of the synthesis and in the purification of the thiol-capped gold nanoparticles.

For the synthesis of the iodo- or bromoalkanethiols required for capping, two adapted methods were used (trimethylsilylthioxy dehalogenation or thiourea displacement on diiodo or dibromoalkane), producing pure product in relatively low yield (\sim 30%) in both cases. For the synthesis of the functionalized gold particles, the recently reported in situ reduction of the appropiate gold salt with superhydride (developed by Ulman and Jordan)⁵ proved to be unsuitable when ω -halogenated alkanethiols are used. As observed in other analogous experiments in our group,¹⁷ CH₂X terminal groups were converted to CH₃ groups under these reductive reaction conditions. Therefore, we developed another route for the facile preparation of metal nanoparticles bearing CH₂-Br groups at the periphery (Scheme 2). Even though we successfully obtained SAMs of IDT on planar gold, competing degradation of the iodo group¹⁸ under these conditions gave a worse yield than did the analogous bromide. With iodoalkanethiols, we obtained particles that tend to agglomerate slowly, eventually flocculating. With bromoalkanethiols, this behavior was not observed, and we successfully obtained stable and characterizable particles from this latter route (Scheme 2).

The synthesis of thiol-capped gold nanoparticles was achieved in a MeOH-THF mixture in which the gold salt, the bromothiols, and the reducing agent are soluble. We synthesized a series of surface-brominated gold nanoparticles where brominated thiols of two lengths (BrDT and BrUT) were used alone or in combination with the *n*-undecanethiol (UT) (Scheme 2). Successful preparation of the capped nanoparticles was confirmed by FTIR and ¹H NMR spectroscopy. Thus, strong IR stretches for the CH₂ v_s and CH₂ v_{as} bands were observed at 2848 and 2918 \pm 2 cm^{-1} , respectively, in the capped gold clusters. The proton signals in the ¹H NMR spectra of the bromo-functionalized nanoparticles, though significantly broadened, appeared at chemical shifts almost identical to those of the free thiols. It is known that NMR line broadening for proteins and polymers is caused by their slow rotation in solution; the alkanethiolate-protected clusters behave analogously.

As shown in Figure 3, no significant differences in size or dispersity could be observed when either the functionalized thiol (BrUT) alone or mixtures of BrUT and UT were used for capping.

Water-soluble, stable, and relatively monodisperse nanocomposites were prepared by surface-initiated cationic polymerizations of 2-oxazolines by the Br-functionalized gold nanoparticles (Scheme 3). Termination of the polymerization was accomplished by treatment with 4-phenylazoaniline (PAA; Scheme 3), but many



^a The shaded ball represents a gold cluster and one thiol surface group is shown, as representative of densely packed thiols.

other nucleophiles with the desired chemical or physical properties could also be used. PAA was chosen because it is photosensitive, and the structural stability of the nanoparticle can be enhanced by photodimerization of the azo groups.¹⁹

The analysis of these composite particles, as well as previously reported theoretical considerations,²⁰ lead us to believe that the polymeric shell thus obtained is highly structured. As in proteins, the poly(*N*-acyleth-ylenimine) backbone can fold into a helical conformation. Even if the amido side chain results in partial tacticity, each three atom repeat unit causes the polymer to organize so that the side chains alternate along the main chain. This natural conformation of PNAI makes this composite polymer a good candidate for a highly organized structure. Furthermore, the polymer can be synthesized with a very narrow molecular weight distribution and with a variety of terminal functional groups.

The successful preparation of nanocomposites by the route shown in Scheme 3 was confirmed by FTIR and ¹H NMR spectroscopy. Spectral features characteristic of the polymer are the appearance of the strong amide band (1640 cm⁻¹), the characteristic stretching vibrational modes of the methylene groups in the polymer backbone, and the propionyl side chain around 2979 and 2941 cm⁻¹. In the ¹H NMR spectra, the characteristic peaks appear at 3.46 ppm (N–CH₂–CH₂–, 4H), 2.3 ppm (CO–CH₂–CH₃, 2H), and 1.1 ppm (CH₂–CH₃, 3H).

Surface crowding causes significant irregularity during initiation as well as during the growth of the polymer chains. The overcrowding of peripheral initiating groups must be avoided, especially when the goal is preparation of well-defined spherical aggregates as highly structured nanocomposites. The importance of free access to the terminal polymerizable groups was illustrated by the synthesis of nanoparticles stabilized with a mixture of unbrominated thiol (UT) and a brominated thiol with different length (BrDT or BrUT). Patterning the surface with thiols with different lengths in order to achieve a better exposure of the initiating groups is reported here for the first time. For the particles with a sterically hindered initiator site (e.g., BrDT/UT-stabilized nanoparticles, Figure 4, left), no significant polymerization could be observed upon treatment with EOZO. The best results were obtained instead with particles capped with a BrUT/UT mixture (Figure 4, right) where the initiating end group is more exposed than when the nanoparticles are capped only with a monolayer of BrUT. A similar sensitivity to local steric influence was observed by Murray and co-workers in the reactivity of functionalized monolayer-protected clusters (MPC).21

The main advantage proposed here in route 1b is the fact that the formation of unbounded polymer is largely



Figure 3. TEM images of gold nanoparticles functionalized with a SAM of BrUT (upper image + chart) and a mixed monolayer of BrUT/UT (lower image + chart) and their respective TEM-derived nanoparticle size distributions.



Figure 4. A cartoon illustrating steric accessibility of the active groups in a SAM on gold obtained from a mixture of undecanethiol (UT) and 10-bromodecanethiol (BrDT) (left) and a mixture of UT and 11-bromoundecanethiol (BrUT) (right).

avoided. In this case, the initiator is already linked to the surface, and the particles used as supports for the subsequent polymerization were previously purified. Consequently, we can avoid free initiating centers in the polymerization step. In route 1a, in contrast, the transformation of the active centers by the initiating

groups is done on the particles themselves, and a concomitant purification is not possible. Because of the sensitivity of the triflate groups, the presence of freely dispersed, unbound initiating groups cannot be avoided.

These stabilized shell—core particles might be converted to hollow nanometer-sized polymer capsules by



decomposition of the metallic core. The resulting hollow polymer shells might then be filled with size-matched biological guests, providing the new applications of the complex organic—inorganic composite assemblies. Further studies introducing surface functionalization via the termination step—a versatile and simple way of facilitating polymer characterization and the design of unique properties—are being pursued.

Formation of Aqueous Dispersed Gold Nanoparticles Stabilized by Preformed Poly(N-acylethylenimine). Nanocomposite materials prepared by incorporation of metallic clusters into a preformed polymer matrix are of great interest in terms of their potential applications. For the formulation of nanocomposite materials as films or fibers, homogeneous blending of the nanoparticles into the matrix is highly desirable. For these applications, miscibility with the polymer matrix and maintenance of their structural stabilities are essential. We demonstrate here that poly-(*N*-acylethylenimine) can successfully stabilize gold nanoparticles over long periods of time, with no change in spectra being observable over several months. Attempts to chemically functionalize gold nanoparticles in aqueous media have usually failed as the particles aggregate.²² The use of water-soluble precursors to protect Au clusters in water may be desirable because it permits avoidance of harmful organic solvents that are often trapped in the composite during synthesis.

Some polymers may be effective stabilizers for preparing narrowly dispersed metal nanoparticles and for preventing flocculation of colloidal metal particles,²³ but to our knowledge the use of such water-soluble preformed polymer for direct attachment to the gold surface is unprecedented. Our approach is to produce shellcore nanocomposites by chemical reduction in aqueous solution containing terminal thiolated preformed polymer or the parent polymer. This step is then followed by covalent (Scheme 4) or by physical adsorption (Scheme 5) to the surface.

Apparently, in the presence of HAuCl₄ ion pairs are formed upon treatment with PNAI, as indicated by the color changes observed when the solutions are mixed. The addition of acetic acid (to adjust the solution pH) has little or no influence on color or consistency of the mixture.

The polymers used in this "grafting onto" route were obtained by polymerization of EOZO initiated by 1-iododecane or 1,10-iododecanethiol. As in our recent experiments, we obtained poly(*N*-acylethylenimine) (PNAI) or the thiol end-functionalized poly(*N*-acyleth-



Figure 5. XPS spectra showing the different N/C stoichiometries for particles stabilized with the two types of preformed polymers, with (a) and without (b) a thiol anchoring group.

ylenimine) (PNAI-SH) in high yields, with narrow molecular weight distribution and an absence of side products.¹⁶ A low concentration of monomer and a high initiator/monomer ratio leading to a low molecular weight for the resulting polymer were used in order to avoid the interference of the terminal thiols in the polymerization.

The preparation of polymer-coated nanoparticles can be done directly in water, but we have used methanol in order to derive comparative data for the physical properties of the shell-core clusters prepared by Scheme 2 or 4. By using a preformed polymer either with (PNAI-SH) or without (PNAI) an anchoring group, remarkably stable PNAI/gold nanoparticle composites were obtained. In the polymer/composites prepared by Scheme 4 or 5, FTIR spectra show an amide band at 1640 cm^{-1} unchanged after the NaBH₄ reduction, indicating that the poly(*N*-acylethylenimine) backbone survived the reduction conditions. The chemical behaviors of these two families were also quite similar, except for small differences in size and polydispersity. From the relative sharpness of the peaks in its IR spectrum and the presence in its UV-vis spectra of a plasmon band at 520 nm (which is the region characteristic of alkanethiolcapped gold nanoparticles of the reported size range), we conclude that a polymer with terminal SH group is







Figure 6. HRTEM micrographs of nanocomposites prepared from BrUT-stabilized nanoparticles (a) and BrUT/UT-stabilized nanoparticles (b).

attached preferentially radially to the gold surface. Also, a polymer with an SH end group linked to a hydrophobic aliphatic segment can favor this organization. A similar polymer-induced ordering of short hydrophobic chains has been observed also for lipopolymers associated with hydrophobic interfaces.²⁴ In the adsorbed polymer, in contrast, excellent stability arises from the known chelation of polyethylenimine with metals at amido coordination sites.²⁵

Like alkanethiolate-coated MPCs, these nanocomposites are very stable in solution or as a solvent-free powder. They can be repeatedly dissolved in common organic solvents and recovered without decomposition or aggregation. Absorption spectroscopy and TEM images reveal no spectral changes, and hence long-term stability against aggregation, for periods as long as 2 months.

XPS. Analyses of SAMs by X-ray photoelectron spectroscopy (XPS) provides information regarding the chemical composition of the layered organic film and its underlying substrate.²⁶ This technique has specifically been used to characterize thiol-derived SAMs on gold nanoparticles,²⁷ and we expected that XPS might reveal the origin of the observed differences between the particles obtained by routes described by Schemes 3–5. Indeed, by measuring the peak intensity specific for the amido N (binding energy 400.8 eV) in these composites



Figure 7. HRTEM micrographs of nanocomposites prepared by stabilization with a preformed polymer containing (a) or not (b) an anchoring SH group.

(relative to the binding energy of C 1s at 284.6 eV, Figure 5), we find a higher N content for those composites obtained with the preformed polymer (Scheme 4) containing a thiol anchoring group than with those obtained by the same method but without a terminal SH group (Scheme 5). This observation suggests that in the thiolated polymer attachment is Au–S covalent and radial to the surface. The higher N content is consistent with thicker layering, and the intensities observed in the IR spectrum for composite attained through Scheme 4 are comparable with those obtained by the in situ growth method (Scheme 3), indicative in both cases of a more highly structured polymeric shell.

Transmission Electron Microscopy. TEM has provided extensive information about the sizes and, to a much lesser extent, the shapes of metal nanoparticles.²⁸ Figure 6 illustrates high-resolution TEM images of the particles obtained by in situ growth of particles capped with brominated thiols (cf. Figure 3). As previously discussed, the particles prepared from gold nanoparticles in which a covalently bound initiator is highly exposed are more uniform, relatively large (10–12 nm), and exhibit a surprisingly narrow size distribution.

In contrast, TEM images of particles obtained by Scheme 4 or 5 (metal cluster formation in the presence of a preformed poly(N-acylethylenimine)) show that the particles are relatively small (about 2–3 nm in diameter) and possess a size distribution comparable with other polymer-stabilized gold particles reported in the literature²³ (Figure 7). The significantly smaller size of



Figure 8. FTIR spectra of the particles obtained by surface-initiated polymerization ((a), BrUT/UT-functionalized starting nanoparticles; (b), BrUT-functionalized starting nanoparticles) and by stabilization with preformed polymer (containing (c) or not (d) anchoring SH groups).

these particles (Figure 7) compared with those obtained by the first method (Figure 6) is expected, given that sterically bulky ligands tend to produce smaller Au core sizes. These observations thus suggest a connection between the rate of core growth and the dynamics of surface passivation.^{17,29}

The average diameters of the populations of nanoparticles produced by the latter method are around 3 nm for the composites obtained by stabilization with PNAI-SH (Figure 7a) and 2.5 nm for those obtained by stabilization with PNAI (Figure 7b) (cf. Figure 2). Although core sizes of MPCs depend sensitively on reaction conditions,³⁰ these composites have been prepared under the same reaction conditions. It is quite conceivable that different size distribution patterns might result if reaction conditions are varied. In any case, we do not obtain large composites or narrow polydispersity by Scheme 4 or 5, as in the case for particles obtained by the first method, Scheme 3. Thus, we obtain much larger particles when the surfacefunctionalized metal cluster was used as a nucleation point and as an initiator for subsequent growth of the polymeric shell. Others routes allowing us to define the scale over which structural organization is maintained are under investigation in our laboratory.

FTIR. As in alkanethiolate-coated MPCs, 30,31 infrared spectroscopy has provided valuable information regarding the conformation and ordering of the polymeric chains on the metal surface. Changes in the frequency and bandwidth in the C-H, C-C stretching regions and in the amide band are considered indicative of order in the composite shell. These results were consistent with the observations made by analyzing TEM images and XPS spectra, supporting a better organization of the encapsulating polymeric shell in those composites obtained by living cationic surface-initiated polymerization on the monolayer-capped gold cluster (Scheme 3) than in the in situ production of metal cluster in the presence of preformed polymer (Schemes 4 and 5). The FTIR spectra of the first nanocomposites showed narrower (width at half-maximum) methylene, propionyl, and amide bands (Figure 8), indicative of enhanced packing of the PNAI chains.³² By comparing the composites obtained by surface-initiated polymerization on gold clusters capped with different thiols, we observed that

in composites in which the initiator was more exposed (Figure 4, right) more ordered packing is encountered (Figure 8a). The highest level of disorder observed for the composites was obtained by in situ formation of the gold particles in the presence of preformed polymer without a terminal thiol anchoring group. Likely, these observations may be indicative of a different packing mode—tangential to the surface (Figure 8d).

All these analyses confirm that the proposed routes successfully lead to gold/polymer nanocomposites with different, but highly ordered, structures. Nevertheless, further investigation is necessary in order to identify the different grafting densities and the specific molecular weights of the appended polymer chains.

Conclusions

Our studies have shown that PNAI is an effective polymer for dispersing and stabilizing gold nanoparticles. Two synthetic routes give gold/PNAI composites in high yield: direct preparation of thiol-linked alkyl halide capped gold clusters, in which the surface-bound bromide initiates growth of an EOZO polymeric shell, or the production of gold colloid in the presence of preformed polymer, with or without a covalent thiol linker. These routes yield narrow size-dispersed nanocomposites with highly structured polymeric shells. The resulting composites in which polymer was grown from the bound bromide initiator are approximately 10-12 nm in diameter, a size range which contrasts with remarkably stable small (2-4 nm) polymer-encased composites obtained when the gold cluster is produced in the presence of preformed polymer.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, Chemistry Division, Fundamental Interactions Branch, Grant DE-FG02-01ER15280.

References and Notes

- Fendler, J. H., Ed.; Nanoparticles and Nanostructured Films, Wiley-VCH: Weinheim, 1998.
- (2) Jordan, R.; Ulman, A.; Kang, J. F.; Rafailovich, M. H.; Sokolov, J. J. Am. Chem. Soc. 1999, 121, 1016. (b) Fan, X.
 W.; Xia, C. J.; Fulghum, T.; Park, M. K.; Locklin, J.; Advincula, R. C. Langmuir 2003, 19, 916. (c) Beecroft, L. L.;

Ober, C. K. Chem. Mater. 1997, 9, 1302. (d) Corbierre, M. K.; Cameron, N. S.; Sutton, M.; Mochrie, S. G. J.; Lurio, L. B.; Ruhm, A.; Lennox, R. B. J. Am. Chem. Soc. 2001, 123, 10411. (e) Hashimoto, T.; Harada, M.; Sakamoto, N. Macromolecules 1999, 32, 6867. (f) Hicks, J. F.; Seok-Shon, Y.; Murray, R. W. Langmuir 2002, 18, 2288.

- Fox, M. A. Acc. Chem. Res. 1999, 32, 201. (b) Whitesell, J. (3)K.; Chang, H. K.; Fox, M. A.; Galoppini, E.; Watkins, D. M.; Fox, H.; Hong, B. Pure Appl. Chem. 1996, 68, 1469.
- Leff, D. V.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. J. Phys. (4) Chem. 1995, 99, 7036.
- Yee, C. K.; Jordan, R.; Ulman, A.; White, H.; King, A.; (5)Rafailovich, M.; Sokolov, J. Langmuir 1999, 15, 3486. (b) Chanel, K. Y.; Scotti, M.; Ulman, A.; White, H.; Rafailovich, M.; Sokolov, J. *Langmuir* **1999**, *15*, 4314.
 (6) Yguerabide, J.; Yguerabide, E. E. *Anal. Biochem.* **1998**, *262*,
- 137
- (7) Jordan, R.; West, N.; Ulman, A.; Chou, Y. M.; Nuyken, O. Macromolecules 2001, 34, 1606. (b) Jordan, R.; Martin, K.; Rader, H. J.; Unger, K. K. *Macromolecules* **2001**, *34*, 8858. (c) Jordan, R.; Graf, K.; Riegler, H.; Unger, K. K. *Chem.* Commun. 1996, 1025. (d) Chance, J. J.; Purdy, W. C. Langmuir 1997, 13, 4487.

- (8) Jordan, R.; Ulman, A. J. Am. Chem. Soc. 1998, 120, 243.
 (9) Kobayashi, S. Prog. Polym. Sci. 1990, 15, 752.
 (10) Aoi, K.; Okada, M. Prog. Polym. Sci. 1996, 21, 151.
 (11) Cheng, J.; Miller, C. J. Phys. Chem. B 1997, 101, 1058. (b)
- Hu, J.; Fox, M. A. J. Org. Chem. 1999, 64, 4959.
 Johnson, S. R.; Evans, S. D.; Brydson, R. Langmuir 1998, 14, 6639. (b) Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. J. Chem. Soc., Chem. Commun. 1995, 1655.
- (13) Takagi, K.; Ishiwatari, T. Chem. Lett. 2002, 990. (14) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman,
- (15) Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers,
- J. E. Adv. Colloid Interface Sci. 1992, 39, 175.
- (16) M. Rusa, Ph.D. Thesis, Iassy-Montpellier, 2001.
 (17) Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. J. Am. Chem. Soc. 2003, 125, 6491.
- (18) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. J. Am. Chem. Soc. 1989, 111, 321
- (19) Zhang, J.; Whitesell, J. K.; Fox, M. A. Chem. Mater. 2001, 13, 2323.
 (b) Hu, J.; Zhang, J.; Liu, F.; Kittredge, K.; Whitesell, J. K.; Fox, M. A. J. Am. Chem. Soc. 2001, 123, 1464.
- (20) Litt, M.; Rahl, F.; Roldan, L. G. J. Polym. Sci., Polym. Phys. Ed. 1969, 7, 463.
- (21) Templeton, A. C.; Hostetler, M. J.; Kraft, C. T.; Murray, R. W. J. Am. Chem. Soc. 1998, 120, 1906.

- (22) Kamat, P. V. J. Phys. Chem. B 2002, 106, 7729.
- (23) Liu, Y.; Cheng, S. Z.; Wen, X.; Hu, J. Langmuir 2002, 18, 10500. (b) Manners, I. Science **2001**, 294, 1664. (c) Moller, M.; Spatz, J. P. Curr. Opin. Colloid Interface Sci. 1997, 2, 177. (d) Groehn, F.; Chim, G.; Bauer, B. J.; Amis, E. J. Macromolecules 2001, 34, 2179. (e) Teranishi, T.; Kiyokowa, I.; Miyake, M. Adv. Mater. 1998, 10, 596.
- (24) Wurlitzer, A.; Politsch, E.; Huebner, S.; Kruger, P.; Weygand, M.; Kjaer, K.; Hommes, P.; Nuyken, O.; Cevc, G.; Loshe, M. Macromolecules 2001, 34, 1334.
- (25) Park, C.; McAlvin, J. E.; Fraser, C. L.; Thomas, E. L. Chem. Mater. 2002, 14, 1225. (b) McAlvin, J. E.; Fraser, C. L. Macromolecules 1999, 32, 1341.
- (26) Ulman, A.; Elman, J. F. In Characterization of Organic Thin Films; Ulman, A., Ed.; Butterworth-Heinemann: Boston, 1995.
- (27) Bourg, M. C.; Badia, A.; Lennox, R. B. J. Phys. Chem. B 2000, 104, 6562. (b) Johnson, S. R.; Evans, S. D.; Mahon, S. W.; Ulman, A. Langmuir 1996, 12, 51. (c) Porter, Jr., L. A.; Ji, D.; Westcott, S. L.; Graupe, M.; Czernuszewicz, R. S.; Halas, N. J.; Lee, T. R. Langmuir 1998, 14, 7378.
- (28) Green, S. J.; Stokes, J. J.; Hostetler, M. J.; Pietron, J.; Murray, R. W. J. Phys. Chem. B **1997**, 101, 2663. (b) Hostetler, M. J.; Zhong, C.-J.; Yen, B. K. H.; Anderegg, J.; Gross, S. M.; Evans, N. D.; Porter, M.; Murray, R. W. J. Am. Chem. Soc. **1998**, 120, 9396. (c) Ingram, R. S.; Murray, R. W. Langmuir 1998, 14, 4115. (d) Porter, L. A.; Ji, D.; Westcott, S. L.; Graupe, M.; Czernuszewicz, R. S.; Halas, N. J.; Lee, T. R. *Langmuir* **1998**, *14*, 7378. (e) Cliffel, D. E.; Zamborini, F. P.; Gross, S. M.; Murray, R. W. Langmuir 2000, *16*, 9699. (f) Hu, J.; Zhang, J.; Liu, F.; Kittredge, K.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 1464. (g) Fang, H.; Du, C.; Qu, S.; Li, Y.; Song, Y.; Li, H.; Liu, H.; Zhu, D. Chem. Phys. Lett. 2002, 364, 290. (h) Yang, W.; Chen, M.; Knoll, W.; Deng, H. Langmuir 2002, 18, 4124.
- (29) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. Acc. Chem. Res. 2000, 33, 27.
- (30) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignal, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. Langmuir 1998, 14, 17.
- (31) Hostetler, M. J.; Stokes, J. J.; Murray, R. W. Langmuir 1996, 12, 3604. (b) Templeton, A. C.; Hostetler, M. J.; Draft, C. T.; Murray, R. W. J. Am. Chem. Soc. 1998, 120, 1906.
- (32) Bain, C. D.; Whitesides, G. M. Science 1988, 240, 62.

MA035008I