Articles

Surface Modification of Gold Nanorods with Polymers Synthesized by Reversible Addition−Fragmentation Chain Transfer Polymerization

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Herein we describe the surface modification of gold nanorods via the postpolymerization immobilization of polymers prepared by reversible addition−fragmentation chain transfer (RAFT). Gold nanorods have been synthesized via a three-step seed-mediated process and then subsequently modified with RAFT-preformed poly(2-(dimethylamino)ethyl methacrylate), poly(acrylic acid), and polystyrene homopolymers, with and without the use of reducing agents. Transmission electron microscopy has been used to visually monitor nanorod formations and UV−visible spectroscopy has been used to observe the absorption properties of nanorod formations. Both techniques monitored nanorods with and without surface modifications. This research provides a general and versatile technique for the surface modification of gold nanorods utilizing a wide range of polymers. Polymer modification of nanorods will potentially aid in nanorod self-assembly and ordering processes.

Introduction

Nanometer-scale structures have generated a great deal of interest as potential building blocks for nanostructured materials, composites,[1] nanoscale electronic devices,[1,2] ultra-high-density magnetic recording systems,[3] and optical devices.[4] Gold nanoparticles are of particular interest, as they are one of the most stable metal nanoparticles and possess fascinating properties, including their ability to assemble in multiple shapes, and size-related electronic, magnetic, and optical properties, leading to a wide range of applications, including catalysis and biology.[5] Recently, interest in gold nanorods has increased due to their effectiveness as 1D semiconductors, their efficiency in electron transport, and their potential use in other nanoelectronic devices.[2] Gold nanorods also possess such properties as strong surface-enhanced Raman scattering (SERS), fluorescence, and anisotropic chemical reactivity.[6,7] The potential usefulness of gold nanoparticles in these fields, as well as the bottom-up approach of nanotechnology, is considered key in the preparation of novel materials and building blocks for the 21st century.[5]

Many of the targeted applications for gold nanoparticles require their incorporation into a thin film.[8−10] Currently, films containing nanoparticles are made by spin-coating, spraying, painting of nanoparticle−matrix mixtures, or layer-by-layer (LbL) assemblies.[8−11] Recently, there has been considerable interest in developing techniques facilitating the self-assembly of nanostructures, such as nanorods, into ordered arrays.[12] Microphase separation of a diblock copolymer could help to promote ordering of nanoparticles, creating highly organized hybrid materials.[13−16] One of the crucial steps in preparing these systems is modification of

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the surface of the nanoparticles with suitable materials, such as polymers.

The first attempt to modify the surface of gold nanorods using polymers was reported by Gole and co-workers,[17,18] who utilized a LbL approach to modify the gold nanorod surface via alternating layers of poly(sodium 4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC). The LbL technique establishes a simple method to construct polymer films of a controlled thickness through absorption of cationic and anionic polymers in dilute solution.[19] This method generally produces highly interpenetrating layers of polymer that do not give a well-defined interface between the two layers, and the bonding between the polymer and the nanorod surface is noncovalent, which can lead to instabilities.[20,21] The limitation of this technique is that anionic and cationic polyelectrolytes are required to modify the nanorods, which limits the types of functionalities available and the types of systems the nanorods can be incorporated into.[19] As such, stronger bonding to the substrate surface, control over the thickness of the polymer layer, and the ability to utilize more than just polyelectrolyte materials would be highly beneficial. Polymers prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization offers each of these benefits.

RAFT is an exceptionally versatile controlled/“living” free radical polymerization (CLRP) technique that operates via a degenerative chain transfer mechanism in which thiocarbonylthio compounds act as chain transfer agents (CTAs).[22−31] Many different compounds, such as dithioesters, trithiocarbonates, xanthates, and dithiocarbamates have been utilized as RAFT CTAs. Cumyl dithiobenzoate (CDTB) and *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DATC) are two of the most widely used RAFT CTAs chosen to polymerize a variety of monomers.[32−34] RAFT is arguably the most adaptable of all the CLRP techniques, due to the ability of polymerizations to be conducted under a variety of conditions; it is the most flexible technique with respect to monomer choice and functional group tolerance and allows for the preparation of materials with complex/advanced architectures. Reduction of the RAFT thiocarbonylthio compound into thiol end groups allows for the surface modification of gold nanorods with RAFT-prepared polymers. The thiol end groups are what provide covalent attachment of the RAFT-prepared polymers to gold surfaces.[35] Recently, the surface modification of gold surfaces and nanospheres using well-defined homopolymers and (co)-polymers prepared via RAFT polymerization has been reported.[35−37] In this work, RAFT-prepared polymers were reduced using sodium borohydride ($NaBH_4$) either in the presence of a gold surface or in-situ with gold salt, to produce polymer-coated surfaces or polymer-stabilized nanospheres.

Herein we report a general procedure employing polymers prepared by RAFT polymerization for the surface modification of gold nanorods. To the best of our knowledge, this is the first report of the use of RAFT-prepared polymers for the modification of gold nanorods and also the first report of surface modification of gold nanorods with hydrophobic polymers. This procedure involves a two-step process: first gold nanorods are prepared via a seed-mediated route,[6] followed by reduction of various RAFT-prepared polymers using either $NaBH_4$ or lithium aluminum hydride ($LiAlH_4$) to enable covalent attachment of the polymers to the surface of the nanorods.[35] As an alternative to this procedure, nonreduced RAFT-prepared polymers have also been immobilized on the surface of nanorods via attachment of the CTA end group.[38] Using these techniques, we have modified the surface of gold nanorods with both hydrophilic polymers poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) and poly(acrylic acid) (PAA) and the hydrophobic polymer polystyrene (PS).

Experimental Section

Materials. Chloroauric acid ($HAuCl_4{\cdot}3H_2O$), trisodium citrate, sodium borohydride ($NaBH_4$), lithium aluminum hydride ($LiAlH_4$), ascorbic acid, dimethylformamide (DMF), and CTAB were all purchased from Sigma-Aldrich and used as received. Sodium hydroxide (NaOH) from Mallinckrodt, deionized ultrafiltered water (DIUF) from Fisher, and 4,4′-azobis(4-cyanopentanoic acid) (ACVA) from Aldrich were purchased from the respective suppliers and used as received. Acrylic acid and styrene were passed through a column of activated basic alumina (Acros, 50−200 μm) before use. PDMAEMA with M_n 9600 and PDI 1.13 was provided by ABL, and PAA with M_n 11 200 and PDI 1.13 and PS with M_n 9700 and

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PDI 1.06 were synthesized in our lab. The DATC CTA was synthesized according to the procedure by Lai et al.[32]

Preparation of 3.5-nm Citrate-Stabilized Gold Nanoparticle Seeds.[6,39] Negatively charged gold nanoparticle seeds were synthesized via a 20-mL aqueous solution of 2.5×10^{-4} M $HAuCl_4$ and 2.5×10^{-4} M trisodium citrate to which 0.6 mL of ice cold 0.1 M $NaBH_4$ was added with stirring. Upon addition of $NaBH_4$, the solution begins to turn orange-red in color, which indicates the formation of gold nanoparticles. This solution was stored at 25 °C for at least 3 h prior to use.

Preparation of Growth Solution.[6,39] In a 250-mL flask, 100 mL of deionized water was added to 2.5×10^{-4} M $HAuCl_4$ and 3 g of solid CTAB. This solution was heated using a hot plate stirrer until the CTAB was fully dissolved and the mixture is a golden-yellow color. Once this growth solution was cooled to room temperature, it was utilized in the synthesis of gold nanorods.

Synthesis of Gold Nanorods.[6,39] A three-step seeding protocol was used for the synthesis of gold nanorods. Two 20-mL scintillation vials and one 250-mL flask were labeled A, B, and C, respectively. A 9-mL volume of growth solution containing 2.5×10^{-4} M $HAuCl_4$ and 0.1 M CTAB was added to scintillation vials A and B, while 45 mL was added to flask C. A 50-μL volume of freshly prepared 0.1 M ascorbic acid and 0.1 M NaOH was then added to vials A and B, and 250 μL of each were added to flask C. Once added and stirred, the golden-yellow color of the growth solution turns clear. At this time, 1.0 mL of the 3.5-nm seed solution was added to vial A, and the mixture stirred for 30 s, which yields a red-purple color change. Next, 1.0 mL of solution from vial A was mixed into vial B and stirred for 1 min, yielding a color change to purple. Upon this color change, 5.0 mL of the solution in vial B was mixed into flask C and stirred to homogenize the solution. Flask C was then placed in a 28 °C oil bath for 16 h to promote synthesis of gold nanorods.

After the 16 h time period it was necessary to purify the solution to obtain the gold nanorods. A pipet was used to slowly remove the red-brown solution within the flask until a faint gold-brown residue was left at the bottom. A 5.0-mL sample of DIUF water was added to the bottom of the flask and was stirred vigorously, yielding a gold-brown colored liquid. Mixtures of shapes (triangles, hexagons, and rods) are contained within this solution and all are utilized for subsequent coating. The excess CTAB was removed from this solution by centrifugation in a test tube three times and rinsing with DIUF water, yielding purified gold nanorods. In order to increase the signal strength of the nanorods throughout the various characterization techniques, five of the single batches are combined into one large batch upon the completion of centrifugation.

Synthesis of PDMAEMA. To a round-bottomed flask (100.0 mL capacity) equipped with a magnetic stir bar were added CDTB (259 mg, 9.50×10^{-4} mol), DMAEMA (19.01 g, 0.121 mol), and AIBN (31.0 mg, 1.90×10^{-4} mol). Then 0.2-mL aliquots were transferred from this stock solution to eight separate vials (10.0-mL capacity). Each vial and the round bottomed flask were sealed with a septum. Each vial was then purged with nitrogen for 5−10 min. The main solution was purged for 20 min. Subsequently, all reaction flasks were immersed in a preheated oil bath at 70 °C. Vials were removed at various time intervals, and a small aliquot from each vial was removed, diluted with DMF, and analyzed by SEC. Additionally, an aliquot was taken from each vial, diluted with deuterated chloroform, and analyzed by NMR spectroscopy. For the remaining bulk solution, PDMAEMA homopolymer was isolated by precipitation into cold hexane and redissolved in THF followed by reprecipitation in cold hexane. The hexane was decanted and the polymer dried at 40 °C in vacuo overnight to yield the final PDMAMEA (M_n 9600 and PDI 1.13).

Synthesis of PAA. A 100-mL Schlenk flask was charged with acrylic acid and DMF, sealed with a rubber septum, placed in an ice bath, and degassed with nitrogen for 1 h. The ACVA and DATC were added to a separate 100-mL Schlenk flask containing a stir bar, sealed with rubber stopper, degassed, back-filled with nitrogen three times, and finally left under nitrogen. The acrylic acid solution was transferred to the flask containing the ACVA and DATC via cannula and placed in a 70 °C oil bath for 9 h. After this time, the polymer solution was placed in small crystallization dish at 50 °C in a vacuum oven overnight to remove any unreacted monomer and solvent to yield the final PAA (M_n 11 200 and a PDI 1.13).

Synthesis of PS. A 100-mL Schlenk flask was charged with styrene and DATC, sealed with a rubber septum, placed in an ice bath, and degassed with nitrogen for 1 h. The Schlenk line to the flask was then degassed, back-filled with nitrogen three times, and finally left under nitrogen and opened to the flask. The styrene and DATC solution was then placed in a 140 °C oil bath for 9 h. After this time, the polymer solution was placed in small crystallization dish at 50 °C in a vacuum oven overnight to remove any unreacted monomer to yield the final PS (M_n 9700 and a PDI 1.06).

Grafting of PDMAEMA, PAA, and PS to Gold Nanorods. An array of weights (0.02−0.15 g) of PDMAEMA and PAA was added to separate vials containing approximately 5 mL of DIUF water, and the solids were allowed to completely dissolve before use. The polymer solution was then added to a mixture of nanorods and degassed under nitrogen for 30 min. A 1.0 M $NaBH_4$ solution, with varying volumes (0.15−0.5 mL), was added to these polymer/nanorod mixtures under nitrogen in a dropwise fashion, at which time bubbling occurs. A variety of weights (0.02−0.15 g) of PS was added to a vial containing approximately 5 mL of DMF and allowed to completely dissolve before use. A solution of gold nanorods in DIUF water was centrifuged three times, with the DIUF water being replaced with DMF until all of the DIUF water was removed. This polymer solution was added to a mixture of gold nanorods in DMF and degassed under nitrogen for 30 min. To the PS/nanorod mixture was added $LiAlH_4$ in DMF of varying concentrations under nitrogen in a dropwise fashion, at which time bubbling occurs. Stir bars were added to all of the polymer/nanorod mixtures in vials and allowed to stir under nitrogen for 24 h. This same procedure was followed for all polymers with the exception of not adding the reducing agent to the solutions before stirring for 24 h.

Instrumentation. Molecular weights and molecular weight distributions of the PDAMEMA were determined by size exclusion chromatography (SEC) in DMF at a flow rate of 1.0 mL min^{-1} and 40 °C. The system was comprised of a Waters 515 HPLC pump, Waters 2410 RI detector, Waters 2457 Dual l absorbance detector, column oven, and a PolymerLabs PLgel 5 mm MIXED-C 300 × 7.5 mm column. The column was calibrated with a series of narrow molecular weight distribution PAA standards (PolymerLabs). Molecular weights and weight distribution of PAA were determined by aqueous size exclusion chromatography (ASEC) at 25 °C using Super AW 3000 and 4000 columns utilizing the Wyatt ASTRA SEC/LS software package. The mobile phase consisted of 20% acetonitrile/80% 0.05 M Na_2SO_4. The flow rate was maintained at 0.35 mL/min with an Agilent 1100 series isocratic pump. The detectors included a Wyatt Optilab DSP interferometric refractometer, a Wyatt DAWN EOS multiangle laser light scattering (MALLS) detector operating at $\lambda = 690$ nm, and a Polymer Labs LC1200 UV−vis detector.

The molecular weight of the PS was determined by gel permeation chromatography (GPC) at 30 °C. A Hewlett-Packard

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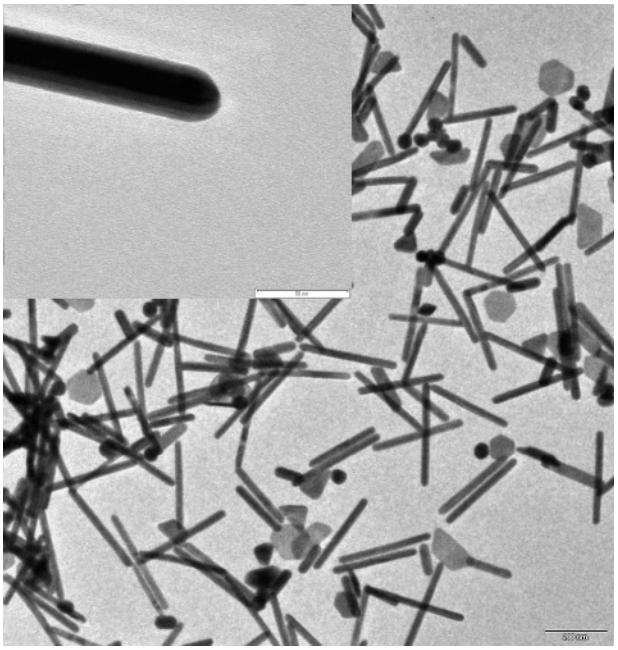

Figure 1. Gold nanorods synthesized from 3.5-nm citrate-stabilized gold nanoparticle seeds. Inset shows close up of nanorod without polymer coating or CTAB (scale bar = 200 nm, inset scale bar = 50 nm).

1084B liquid chromatograph coupled to a Waters R401 differential refractometer and a Wyatt Technology miniDAWN multiangle laser light scattering (MALLS) detector. Two Hewlett-Packard Plgel 5 μm mixed-D columns with a linear range of molecular weights from 200 to 400 000 g/mol in series with THF as the eluent at a flow rate of 1.0 mL/min were used. Astra 4.90.07 software supplied by Wyatt Technology was used to determine the molecular weights of the PS via light scattering.

UV−vis was performed on a Thermo Electron Corp., Nicolet Evolution 300 BB spectrophotometer with a xenon lamp and utilized standard 10 mm quartz cuvets. The TEM was performed on a Philips CM200 with an accelerating voltage of 200 kV and utilized a Keen View Soft Imaging System coupled to iTEM Universal TEM Imaging Platform Software.

Results and Discussion

The use of a seed-mediated approach for the preparation of gold nanorods has been well-documented.[6,17,18,39−41] This approach initially involves the reduction of gold salts with a strong reducing agent, in water, to produce gold nanospheres or seed particles. Following this, more gold salt is reduced with a weak reducing agent in the presence of a surface-directing agent, leading to the controlled formation of gold nanorods of defined aspect ratio.[40,41] In this study, the same approach was utilized for the synthesis of all gold nanorod samples. As previously reported, this synthetic approach typically yields a variety of shapes and sizes of gold nanoparticles, but usually provides a good concentration (>90% yield) of nanorods. Similar results were seen in the preparation of gold nanorods for this study, with the presence of triangular, hexagonal, and spherical nanoparticles detected by TEM (Figure 1). After a 16-h synthesis time, TEM images indicated a high yield of nanorod structures with an average length of 250 nm and average diameter of 25 nm (aspect ratio of 10) formed from a 3.5-nm gold seed. Following synthesis of the nanorods, excess CTAB was removed from the system by repeatedly washing with DIUF water or DMF, centrifuging, and then removing supernatant. This process was repeated at least three times, and TEM images confirm that very little, if any, free CTAB is left in the system. The excess CTAB can be ascertained from TEM images due to its nature of aggregating around the rods or the excess CTAB crystallizing on the TEM grid. These aggregations of CTAB are void in the TEM images after subsequent washings of the nanorods, and therefore it is concluded that the CTAB does is not remain in the solution. While it is a relatively simple procedure to remove excess CTAB from the system, there is not an efficient way of separating shapes such as spheres and triangles from the nanorod system. As such, the prepared nanorod samples, containing small percentages of other shapes, were used for the subsequent polymer-coating process without any further purification. In conjunction with TEM analysis, UV−visible spectroscopy was also used to characterize the uncoated gold nanorods. In order to obtain a relatively strong UV−vis absorption spectra, five individual gold nanorod batches, prepared under identical conditions using the three-step seed-mediated synthesis, were combined together into one batch. The UV−vis absorption spectra of the uncoated gold nanorods show two main absorption maxima (Figures 3, 5, 7). The first absorption maxima is located around 520−530 nm and is attributed to the transverse surface plasmon resonance absorption band.[12,17,40] The second absorption maxima is a longitudinal surface plasmon resonance band and is red-shifted toward the near-IR region. This absorption band is particularly sensitive to changes in the aspect ratio of the nanorods.[12,17,40]

Following synthesis and purification, the gold nanorods were coated with various polymers prepared via RAFT polymerization (Schemes 1 and 2). To test the versatility of the proposed coating method, two functional hydrophilic polymers, PDMAEMA and PAA, and one nonfunctional hydrophobic polymer, PS, were chosen. Each of the polymers was synthesized using standard air-free techniques, resulting in polymers with narrow molecular weight distributions and experimental molecular weights that were close to theoretical. The PS and PAA were synthesized using DATC CTA, resulting in a trithiocarbonate end group on each of these polymers. Due to the use of cumyl dithiobenzoate for its synthesis, the PDMAEMA contained a dithioester end group. These CTAs were chosen for preparation of these polymers based on procedures reported in literature.[32−34] Each of the polymers were isolated by removal of solvent and any unreacted monomer under vacuum, or by precipitation, and used without further purification.

The RAFT-generated polymers were immobilized onto the surface of the gold nanorods using two different techniques. The first technique involved dissolution of the polymer in a suitable solvent, followed by the addition of the gold nanorods, and finally a reducing agent was added to reduce either the trithiocarbonate or dithioester end groups on the polymers to thiols.[35] The second technique was essentially the same as the first, except reducing agent was not added

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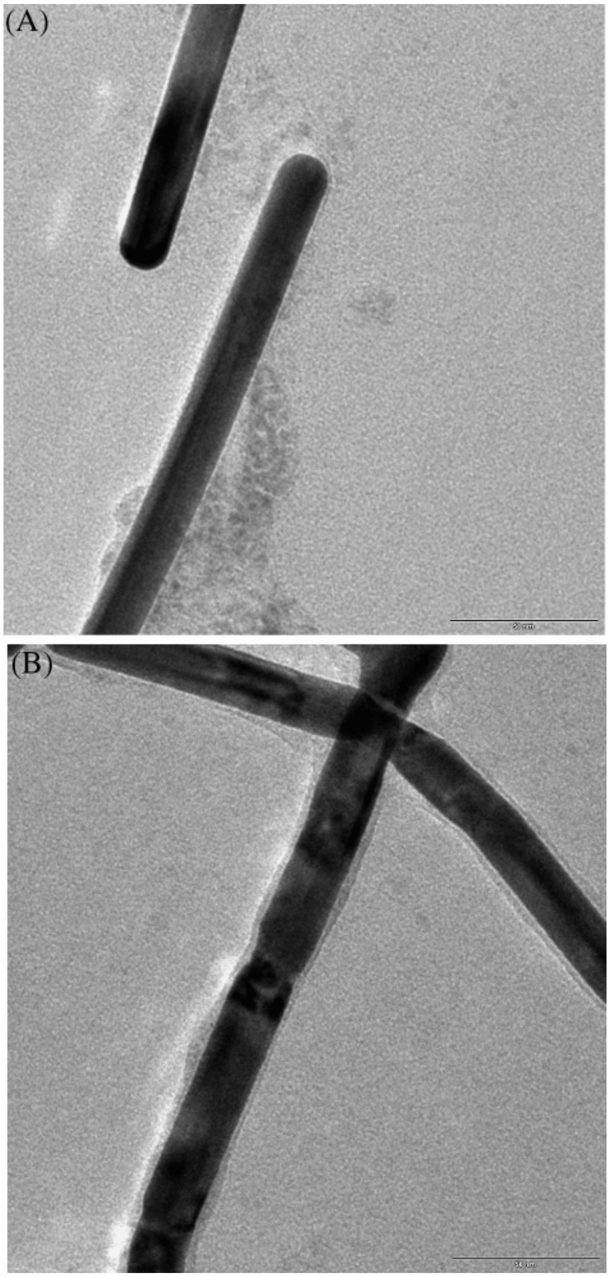

Figure 2. (A) PDMAEMA with $NaBH_4$ and (B) PDMAEMA without $NaBH_4$ (scale bar = 50 nm)

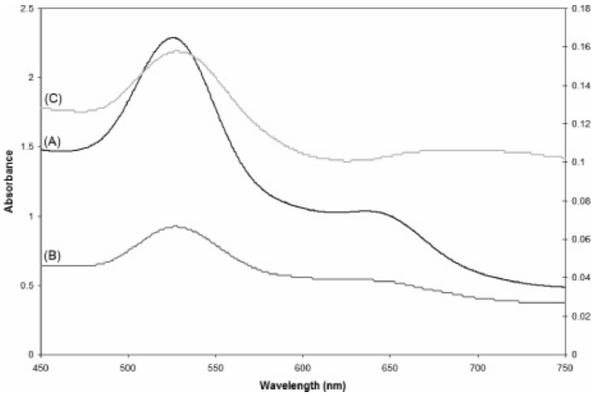

Figure 3. UV−vis spectra of (A) Au nanorods, (B) Au nanorods with PDMAEMA and $NaBH_4$, and (C) Au nanorods with PDMAEMA and without $NaBH_4$

to the system. Recent reports have demonstrated that RAFT CTAs containing either dithioester or trithiocarbonate groups are capable of forming self-assembled monolayers on gold surfaces via adsorption through the sulfur atoms.[35−37,42] While this study did not investigate the adsorption of polymeric materials, the CTA end groups on RAFT polymers should behave in a similar manner. The first step in each of these techniques involves dissolving the polymers in a suitable solvent. Both the PDMAEMA and the PAA were dissolved in DIUF water, while the PS was dissolved in DMF. The next step involves addition of the plain gold nanorods to the dissolved polymers. In the case of PDMAEMA and PAA, an aqueous solution of the gold nanorods was added under an inert atmosphere. In the case of the PS, a batch of gold nanorods in DIUF water was centrifuged and the water was replaced with DMF over the course of three repeated

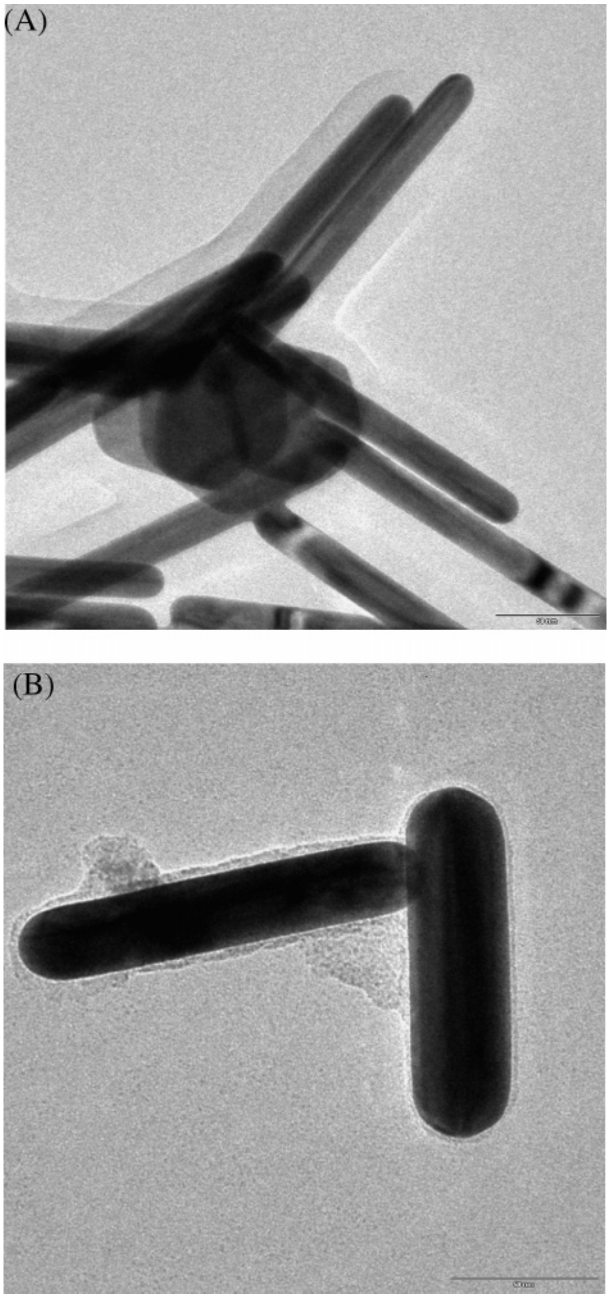

Figure 4. (A) PAA with $NaBH_4$ and (B) PAA without $NaBH_4$ (scale bar = 50 nm)

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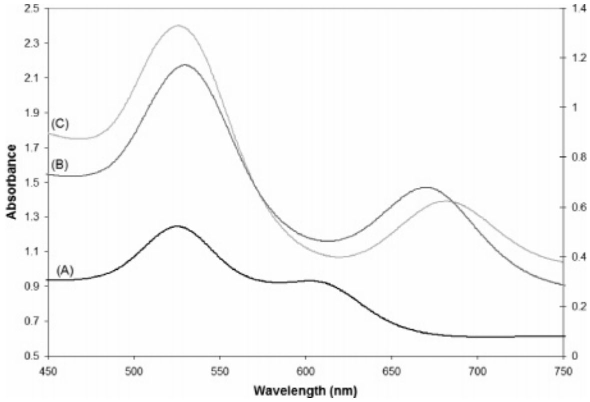


Figure 5. UV−vis spectra of (A) Au nanorods, (B) Au nanorods with PAA and $NaBH_4$, and (C) Au nanorods with PAA and without $NaBH_4$

centrifugations and washings to ensure full removal of the water. The DMF nanorod solution was then added to the dissolved PS under an inert atmosphere. For the second immobilization technique, involving no reducing agent, the samples were then stirred under an inert atmosphere for 24 h. In the case of the first immobilization technique, reducing agent was added to each system. For the PDMAEMA and PAA samples, an aqueous solution of $NaBH_4$ was used as the reducing agent, and for the PS sample, a solution of DMF and $LiAlH_4$ was used. In each system the reducing agent was added dropwise and the samples were then left to stir for 24 h under inert conditions. After immobilization of the polymers to the gold nanorod surfaces, the samples are centrifuged in order to isolate the nanorods with polymer grafted to them in the solution and remove any ungrafted polymer, which should remain in the supernatant. This washing process was repeated three times with the corresponding solvent to remove any residual free polymer found in the solution. Each of these techniques provides samples containing gold nanorods with PDMAEMA, PAA, or PS attached to their surface.

Verification of grafting the RAFT-generated polymers to the surface of the gold nanorods was performed via TEM and UV−vis spectroscopy. The TEM images of PDMAEMA immobilized upon the surface of nanorods using each of the techniques outlined above can be seen in Figure 2. Figure 2A shows the gold nanorods treated with PDMAEMA utilizing $NaBH_4$ as a reducing agent. As can be seen, the gold nanorods appear to be completely coated with the PDMAEMA. The PDMAEMA coating seems to be relatively uniform for both the sides and ends of the nanorods, with the TEM images indicating an approximate thickness of 3 nm of PDMAEMA. Figure 2B shows the gold nanorods treated with PDMAEMA without the addition of a reducing agent. Once again, an approximately uniform layer of PDMAEMA, with an average thickness of 3 nm, surrounds the gold nanorods. UV−vis spectroscopy was also used to help verify grafting of the RAFT-prepared polymers to the surface of the gold nanorods. It has been previously shown that UV−vis spectroscopy is a powerful tool to monitor coating of gold nanorods with polyelectrolyte multilayers.[17,18] This work demonstrated that the adsorption maxima due to the transverse surface plasmon band of the gold nanorods undergo a small red-shift upon grafting of the polyelectrolyte to the surface of the nanorods. This shift in adsorption maxima was attributed to changes in the local refractive index at the surface of the rods, due to the presence of the polyelectrolyte, resulting in an increase in the local dielectric function. It was also shown that the shift in the peak wavelength for the transverse surface plasmon band is highly sensitive to the amount of material adsorbed to the particle surface. Figure 3 shows the UV−vis absorption spectra for PDMAEMA grafted to gold nanorods with and without reducing agent, in comparison to the ungrafted gold nanorods. The absorption maximum for the transverse surface plasmon band of the ungrafted nanorods occurs at a wavelength of 526 nm. Upon coating the gold nanorods with PDMAEMA, there is a small red shift in the transverse surface plasmon band of 528 nm when reducing agent was used and 529 nm when it was not used. The increase in

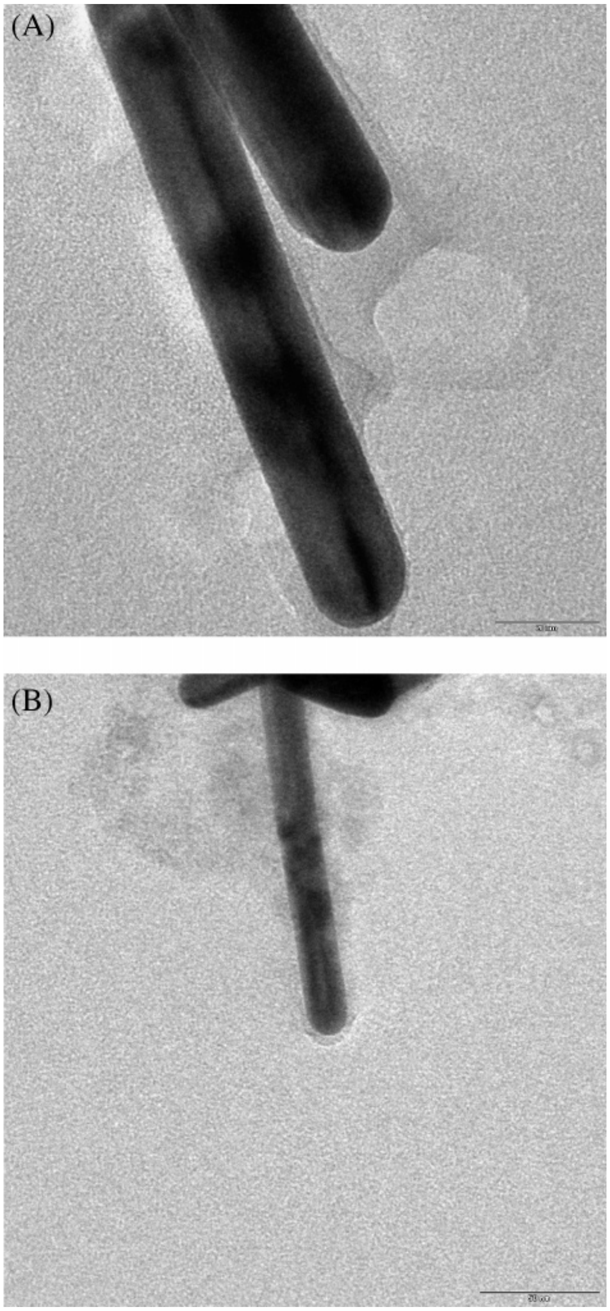


Figure 6. (A) PS with $LiAlH_4$ (scale bar = 20 nm) and (B) PS without $LiAlH_4$ (scale bar = 50 nm)

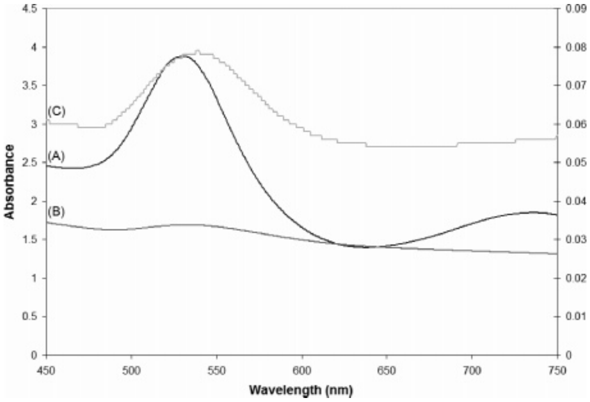
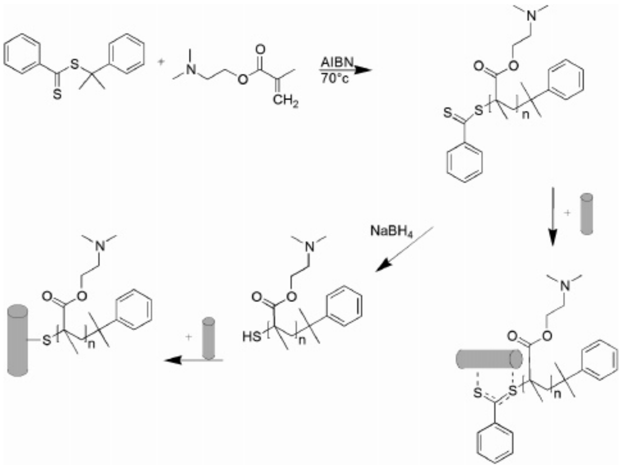
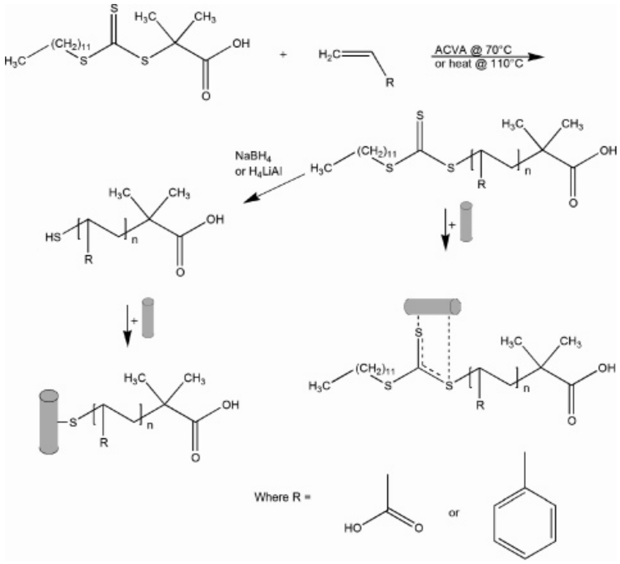


Figure 7. UV−vis spectra of (A) Au nanorods, (B) Au nanorods with PS and $LiAlH_4$, and (C) Au nanorods with PS and without $LiAlH_4$

Scheme 1. Proposed Mechanism Describing Synthesis, Reduction, and Immobilization of RAFT-Prepared PDMAEMA on a Gold Surface



Scheme 2. Proposed Mechanism Describing Synthesis, Reduction, and Immobilization of RAFT-Prepared PAA and PS on a Gold Surface



wavelength seen upon coating the nanorods with the PDMAEMA relates closely to the average thickness of the PDMAEMA surrounding the nanorods, which is 3 nm, as determined by TEM. This corresponds well with the observations of Gole and Murphy,[12] who demonstrated that the nanometer increase in the wavelength of the transverse surface plasmon band matched the nanometer thickness of polyelectrolyte adsorbed to the surface of gold nanorods. It should also be mentioned that there appears to be little, if any, broadening of the surface plasmon band peak, which indicates that aggregation upon grafting of the polymer to the surface of the nanorods does not occur. It should be noted that immobilization of the polymers onto the surface of the gold nanorods constitutes a “grafting to” technique. As such it is expected that the grafting density will be low, resulting in the immobilized polymer chains adopting a “mushroom” type conformation on the surface. While the scaling relationship for immobilized polymers occupying a mushroom conformation demonstrates that the thickness of the polymer coating is proportional to the average degree of polymerization of the polymer chains, in this case, a correlation between the molecular weight of the polymers and the resulting thickness on the surface of the nanorods is difficult to obtain.

Figure 4 shows the TEM images for RAFT-generated PAA polymer grafted to the surface of gold nanorods both with and without the use of a reducing agent. An average thickness of 14 nm of PAA surrounds nanorods that were grafted with $NaBH_4$ as a reducing agent (Figure 4A). However, in the case when no reducing agent was used during the grafting process, the average thickness of the PAA coating the gold nanorods is only 3 nm (Figure 4B). UV−vis spectra for the PAA grafted nanorods (Figure 5) once again show that there is a red-shift in the absorption maxima of the transverse surface plasmon band for both of the grafting techniques. In this case, the uncoated, purified nanorods yield a 526-nm wavelength absorption maximum. When PAA is grafted to the surface using $NaBH_4$ as the reducing agent, there is a shift in the absorption maximum to 531 nm, and when PAA is grafted to the nanorods with no reducing agent, there is an upward shift in absorption maximum to 527 nm. For the grafting of PAA to the surface of the gold nanorods, in each case the red-shift in the transverse surface plasmon band maxima does not correspond well with the observed thickness obtained from TEM images. This is attributed to the fact that significant broadening is seen in the transverse surface plasmon band when PAA is attached to the surface of the nanorods, which suggests that aggregation is occurring in solution, possibly due to hydrogen bonding between the PAA chains. This appears to have a significant effect upon the correlation between the thickness of the PAA attached to the surface of the nanorods and the red-shift seen in the UV−vis spectra. Further studies are currently being conducted to investigate this phenomenon.

The final RAFT-generated polymer to be utilized in this study was PS. Once again, TEM micrographs demonstrate that PS is grafted to the surface of the gold nanorods regardless of whether reducing agent is used or not (Figure 6). Figure 6A indicates an average PS thickness of 3 nm surrounding the nanorod when $LiAlH_4$ reducing agent is used versus an 8-nm thickness found in Figure 6B when it is not used. Again, UV−vis spectroscopy was used to verify a red-shift in the transverse surface plasmon band maxima for the samples (Figure 7). The uncoated purified gold nanorods show an absorption maximum of 530 nm and when RAFT-generated PS is grafted to the surface. The absorption maxima shift upward to 534 nm when the $LiAlH_4$ reducing agent was used and to 540 nm when no reducing agent was used. The shifts in the absorption maxima for the transverse surface plasmon band correspond closely to the nanometer thicknesses seen in the TEM images. There also appears to be little if any peak broadening of the surface absorption maxima, suggesting that aggregation is not occurring. It should be noted that the absorption intensity for the PS-coated samples was very weak in the UV−visible spectra and as such it was difficult to obtain intense spectra even when using five individual batches of coated nanorods combined into one.

TEM and UV−vis spectroscopy results also provide indirect evidence that the RAFT-generated polymers are covalently attached to the nanorods. To demonstrate that the presence of the RAFT CTA end group on the polymers is vital for attachment to the gold nanorods, both coating procedures outlined above (with and without reducing agent) were conducted with PDMAEMA, PAA, and PS prepared via conventional free radical polymerization. In this case, the polymers did not contain either a dithioester or trithiocarbonate end group and, as such, in each of the experiments TEM micrographs indicated that there was no polymer attached to the surface of the nanorods. This was also confirmed by UV−vis spectroscopy, as there was no change in the position of the transverse surface plasmon band maxima. Another indication that the RAFT-generated polymers are covalently attached to the surface of the gold nanorods is that after coating of the nanorods using RAFT-generated polymers, the samples are repeatedly washed in a suitable solvent for the polymer (DIUF water for the PDMAEMA and PAA and DMF for the PS). After numerous washing and centrifugation cycles, TEM images show that the polymer is still attached to the surface of the nanorods and UV−vis spectroscopy still shows a red-shift in the absorption maxima of the transverse surface plasmon band. It has been previously shown that there is a blue-shift in the transverse surface plasmon band of nanoparticles if polymer unwrapping occurs.[17] As there is no change in the red-shift seen in the coated gold nanorods, even after repeated washing with a good solvent for the polymer, it appears as though polymer unwrapping from the surface of the nanorods does not occur.

Conclusion

A versatile procedure for surface modification of gold nanorods using RAFT-generated polymers has been developed. This procedure initially involves synthesis of gold nanorods utilizing a three-step seed-mediated process to generate nanorods in high yield and with controllable aspect ratios. Next, PDMAEMA, PAA, and PS were prepared using RAFT polymerization and were grafted to the surface of the gold nanorods. Two grafting procedures were tested, one involving the use of a reducing agent to convert the RAFT CTA end group on the polymers to a thiol and one where no reducing agent was used and grafting was assumed to occur via coordination of the RAFT CTA to the surface of the gold nanorods. In each case, TEM images both before and after grafting indicates that the nanorods are completely surrounded by a relatively uniform polymer layer, regardless of the grafting technique used. The thickness of the polymer attached to the surface of the nanorods varied from 3 to 14 nm, depending on the polymer and grafting conditions used. UV−vis spectroscopy also provided evidence of the grafting of RAFT-generated polymers to the surface of the nanorods due to consistent red-shifts in the absorption maximum of the transverse surface plasmon band for each sample. For both the PDMAEMA and PS, the shifts in the surface absorption maxima corresponded well with the TEM-observed thicknesses. For the PAA sample, aggregation appears to occur in solution, resulting in a difference between the observed thicknesses and the absorption maxima.

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