Polyelectrolyte-Coated Gold Nanorods: Synthesis, Characterization and Immobilization

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The versatile layer-by-layer (LbL) approach has been used for the synthesis of polyelectrolyte-coated gold nanorods. The simple process first involves the synthesis of gold nanorods by our previously published three-step seed-mediated protocol. The presence of a bilayer of the surfactant cetyltrimethylammonium bromide (CTAB) on the gold nanorod surface imparts a net positive charge to the nanorods. Alternate adsorption of anionic and cationic polyelectrolytes on these positively charged gold nanorods leads to the formation of polyelectrolyte multilayers around the nanorods. These coated gold nanorods have been characterized by UV−vis spectroscopy, zeta potential measurements, and transmission electron microscopy (TEM). Depending on the surface chemical functionality of the coated gold nanorods, they have been selectively immobilized onto either cationic or anionic surfaces. Scanning electron microscopy (SEM) has been used to visualize the immobilized nanorods and to determine the nanorod density on flat surfaces.
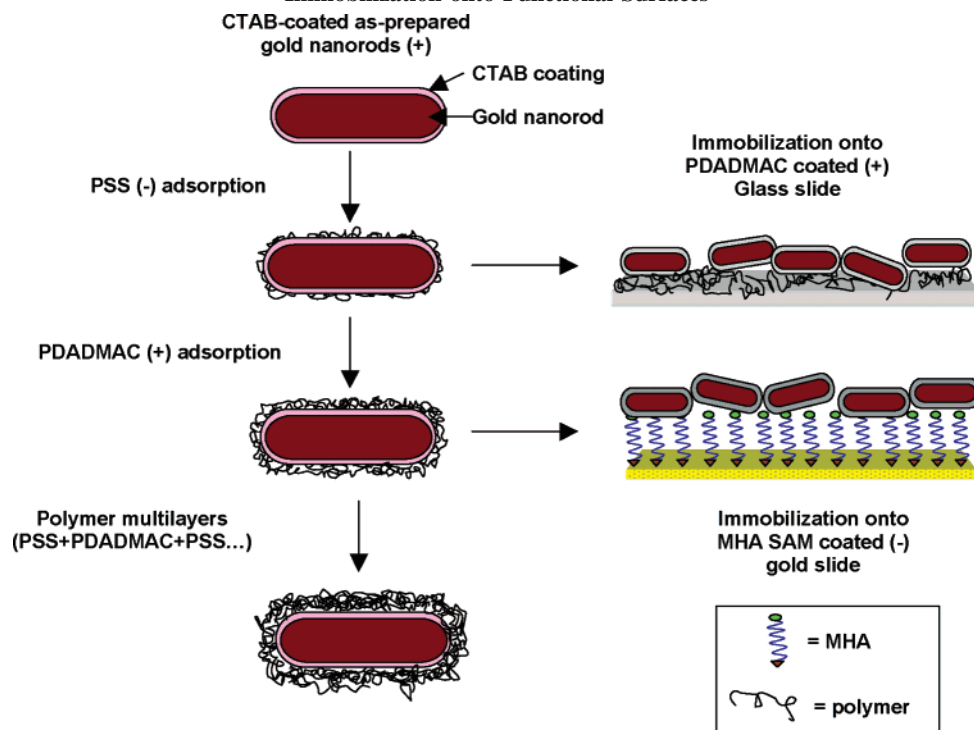
Introduction

Interest in 1-D inorganic nanomaterials such as nanorods and nanowires stems from their shape-dependent optoelectronic and surface properties.[1] These properties hold immense potential for electronics,[2a−c] sensing,[2d−h] use as barcodes for biological imaging,[2i,j] and so forth. Several routes for the synthesis of nanorods and nanowires are available.[1c] Most of the routes commonly employ a template, rigid or soft, which induces anisotropic growth. Rigid templates such as porous polymer films and alumina membranes[3a−c] and mesoporous silica such as MCM-41[3d,e] and carbon nanotubes[3f,g] have been used to synthesize a variety of metal and semiconductor 1-D nanomaterials. The colloidal route generally uses a soft template or a surfactant as the directing agent, wherein the nanorod growth is initiated by a photochemical,[4a,b] an electrochemical,[4c] or a seed-mediated method.[5] We believe

that among the several routes available for the synthesis of 1-D metallic nanostructures,[1c,3−5] the colloidal route offers great synthetic flexibility and the ability to vary numerous parameters.[5] Studies pertaining to the role of different parameters in metal nanorod synthesis, such as size and nature of the seed,[5h] surfactant tail length,[5f] additive ions,[5b,d] solution pH,[5e] and so forth, have been studied by us in great detail.

The important role of the nanocrystal capping agent is brought out in several different research areas such as chemical reactions on nanosurfaces,[6a] construction of nanoparticle thin films,[6b,c] sensing, and biomedical applications.[6d,e] Complex organic molecules, functional thiols, and biomolecules such as DNA can be coupled to the nanoparticles for many useful applications.[6] Hence, surface modification of nanoentities after their synthesis is an important step to realize nanomaterial applications. The first step involved in the surface modification of 1-D nanostructures requires

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(1) (a) El-Sayed, M. *Acc. Chem. Res.* **2001**, *34*, 257. (b) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. (c) Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, Y. Q. *Adv. Mater.* **2003**, *15*, 353.
(2) (a) van Houten, H.; Beenakker, C. *Phys. Today* **1996**, *7*, 22. (b) Chung, S. W.; Yu, Y.; Heath, J. R. *Appl. Phys. Lett.* **2000**, *76*, 2068. (c) Huang, Y.; Duan, X.; Wei, Q.; Lieber, C. M. *Science* **2001** *291*, 630. (d) Favier, F.; Walter, E. C.; Zach, M. P.; Benter, T.; Penner, R. M. *Science* **2001**, *293*, 2227. (e) Cui, Y.; Wei, Q.; Park, H.; Lieber, C. M. *Science* **2001** *293*, 1289. (f) Mohamed, M. B.; Volkov, V.; Link, S.; El-Sayed, M. A. *Chem. Phys. Lett.* **2000**, *317*, 517. (g) Tang, Z.; Kotov, N. A.; Giersig, M. *Science* **2002**, *297*, 237. (h) Nikoobakht, B.; Wang, J.; El-Sayed, M. A. *Chem. Phys. Lett.* **2002**, *366*, 17. (i) Nicewarner-Peña, S. R.; Freeman, R. G.; Reiss, B. D.; He, L.; Peña, D. J.; Walton, I. D.; Cromer, R.; Keating, C. D.; Natan, M. J. *Science* **2001**, *294*, 137. (j) Nicewarner-Peña, S. R.; Carado, A. J.; Shale, K. E.; Keating, C. D. *J. Phys. Chem. B* **2003**, *107*, 7360.
(3) (a) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739. (b) Martin, C. R. *Acc. Chem. Res.* **1995**, *28*, 61. (c) Martin, B. R.; Dermody, D. J.; Reiss, B. D.; Fang, M. L.; Lyon, A.; Natan, M. J.; Mallouk, T. E. *Adv. Mater.* **1999**, *11*, 1021. (d) Hong, B. H.; Bae, S. C.; Lee, C.; Jeong, S.; Kim, K. S. *Science* **2001**, *294*, 348. (e) Bhattacharyya, S.; Saha, S. K.; Chakravorty, D. *Appl. Phys. Lett.* **2000**, *77*, 3770. (f) Ajayan, P. M.; Iijima, S. *Nature* **1993**, *361*, 333. (g) Govindaraj, A.; Satishkumar, B. C.; Nath, M.; Rao, C. N. R. *Chem. Mater.* **2000**, *12*, 202.

(4) (a) Esumi, K.; Matsuhisa, K.; Torigoe, K. *Langmuir* **1995**, *11*, 3285. (b) Kim, F.; Song, J. H.; Yang, P. *J. Am. Chem. Soc.* **2002**, *124*, 14316. (c) Ying, Y.; Chang, S. S.; Lee, C. L.; Wang, C. R. C. *J. Phys. Chem. B* **1997**, *101*, 6661.
(5) (a) Jana, N. R.; Gearheart, L.; Murphy, C. J. *J. Phys. Chem. B* **2001**, *105*, 4065. (b) Jana, N. R.; Gearheart, L.; Murphy, C. J *Chem. Commun*. **2001**, 617. (c) Caswell, K. K.; Bender, C. M.; Murphy, C. J. *Nano Lett.* **2003**, *3*, 667. (d) Murphy, C. J.; Jana, N. R. *Adv. Mater.* **2002**, *14*, 80. (e) Busbee, B. D.; Obare, S. O.; Murphy, C. J. *Adv. Mater.* **2003**, *15*, 414. (f) Gao, J.; Bender, C. M.; Murphy, C. J. *Langmuir* **2003**, *19*, 9065. (g) Sau, T. K.; Murphy, C. J. *Langmuir* **2004**, *20*, 6414. (h) Gole, A.; Murphy, C. J. *Chem. Mater.* **2004**, *16*, 3633. (i) Johnson, C. J.; Dujardin, E.; Davis, S. A.; Murphy, C. J.; Mann, S. *J. Mater. Chem.* **2002**, *12*, 17654. (j) Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, *15*, 1957. (k) Perez-Juste, J.; Liz-Marzan, L. M.; Carnie, S.; Chan, D. Y. C.; Mulvaney, P. *Adv. Funct. Mater.* **2004**, *14*, 571.
(6) (a) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res*. **2000**, *33*, 27. (b) Fendler, J. H. *Chem. Mater.* **1996**, *8*, 1616. (c) Sastry, M. In *Handbook of Surfaces and Interfaces of Materials*, Vol. 3; Nalwa, H. S., Ed.; Academic Press: San Diego, CA, 2001; p 87. (d) Mirkin, C. A. *Inorg. Chem.* **2000**, *39*, 2258. (e) Nam, J.-M.; Stoeva, S. I.; Mirkin, C. A. *J. Am. Chem. Soc.* **2004**, *126*, 5932.

Scheme 1. Schematic Diagram Illustrating the Layer-by-Layer (LbL) Coating Process of Gold Nanorods and Their Subsequent Immobilization onto Functional Surfaces

CTAB-coated as-prepared
gold nanorods (+)

CTAB coating

Gold nanorod

Immobilization onto
PDADMAC coated (+)
Glass slide

PSS (−) adsorption

PDADMAC (+) adsorption

Immobilization onto
MHA SAM coated (−)
gold slide

Polymer multilayers
(PSS+PDADMAC+PSS...)

= MHA

= polymer

selective removal of the template (used for its synthesis) followed by surface modification. The groups of Mallouk, Keating, and others use different functional molecules, biomolecules, and polyelectrolytes to functionalize nanowire surfaces, preceded by the removal of the rigid template.[7] In our case, the presence of the positively charged cetyltrimethylammonium bromide (CTAB) molecules on the gold nanorod surface functions as a stabilizing agent in addition to its initial use as a directing agent for nanorod synthesis. We have recently demonstrated that these CTAB-coated gold nanorods can be used "as is" for their organization onto planar surfaces via electrostatic interactions.[8] To further enhance the versatility of the gold nanorods, one could either replace the CTAB coating or overcoat on top of the existing coating. Surface modification by thiols to nanorod edges has been previously demonstrated.[9] It would be desirable to modify the entire nanorod surface for different applications.

The quest for achieving nanorod surface modification led us to consider the versatile layer-by-layer (LbL) approach developed by the groups of Decher,[10] Mohwald,[11] and Caruso[12] and used extensively to coat different 2-D and 3-D surfaces. This approach involves sequential deposition of anionic and cationic polyelectrolytes onto oppositely charged surfaces through electrostatic self-assembly. In our case, the as-prepared gold nanorods are positively charged because of the presence of a bilayer of CTAB.[13] In this paper, we show that CTAB facilitates electrostatic adsorption of an anionic polyelectrolyte, poly(sodium-4-styrenesulfonate), PSS. Charge reversal is further utilized for the subsequent adsorption of a cationic polyelectrolyte, poly(diallyldimethylammonium chloride), PDADMAC, and the process is continued to deposit polyelectrolyte multilayers. These coated gold nanorods have been characterized by UV−vis spectroscopy, zeta potential measurements, and transmission electron microscopy (TEM). The coated gold nanorods have been preferentially organized onto either cationic (PDADMAC-coated) glass slides or anionic (16-mercaptohexadocanoic acid (MHA) coated self-assembled monolayer, (SAM) surfaces. These immobilized rods were visualized by scanning electron microscopy (SEM). The entire process

(7) (a) Cai, L. T.; Skulason, H.; Kushmerick, J. G.; Pollack, S. K.; Naciri, J.; Shashidhar, R.; Allara, D. L.; Mallouk, T. E.; Mayer, T. S. *J. Phys. Chem. B* **2004**, *108*, 2827. (b) Hernandez, R. M.; Richter, L.; Semancik, S.; Stranick, S.; Mallouk, T. E. *Chem. Mater.* **2004**, *16*, 3431. (c) Keating, C. D.; Natan, M. J. *Adv. Mater.* **2003**, *15*, 451. (d) Mbindyo, J. K. N.; Reiss, B. D.; Martin, B. R.; Keating, C. D.; Natan, M. J.; Mallouk, T. E. *Adv. Mater.* **2001**, *13*, 249. (e) Yu, J.-S.; Kim, J. Y.; Lee, S.; Mbindyo, J. K. N.; Martin, B. R.; Mallouk, T. E. *Chem. Commun.* **2000**, 2445. (f) Guo, Y.-G.; Wan, L.-J.; Bai, C.-L. *J. Phys. Chem. B* **2003**, *107*, 5441.

(8) Gole, A.; Orendorff, C. J.; Murphy, C. J. *Langmuir* **2004**, *20*, 7117.

(9) (a) Caswell, K. K.; Wilson, J. N.; Bunz, U. H. F.; Murphy, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 13914. (b) Thomas, K. G.; Barazzouk, S.; Ipe B. I.; Joseph, S. T. S.; Kamat, P. V. *J. Phys. Chem. B* **2004**, *108*, 13066.

(10) (a) Decher, G.; *Science* **1997**, *277*, 1232. (b) Lvov, Y.; Decher, G.; Sukhorukov, G. *Macromolecules* **1993**, *26*, 5396. (c) Ruths, J.; Essler, F.; Decher, G.; Riegler, H.; *Langmuir* **2000**, *16*, 8871. (d) Lavalle, Ph.; Gergely, C.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C.; Picart, C. *Macromolecules* **2002**, *35*, 4458.

(11) (a) Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282*, 1111. (b) Antipov, A. A.; Sukhorukov, G. B.; Mohwald, H. *Langmuir* **2003**, *19*, 2444. (c) Caruso, F.; Lichtenfeld, H.; Donath, E.; Mohwald, H. *Macromolecules* **1999**, *32*, 2317. (d) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S. A.; Mohwald, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2202.

(12) (a) Caruso, F. *Adv. Mater.* **2001**, *13*, 11. (b) Cho, J.; Quinn, J. F.; Caruso, F. *J. Am. Chem. Soc.* **2004**, *126*, 2270. (c) Blomberg, E.; Poptoshev, E.; Claesson, P. M.; Caruso, F. *Langmuir* **2004**, *20*, 5432. (d) Salgueirino-Maceira, V.; Caruso, F.; Liz-Marzan, L. M. *J. Phys. Chem. B* **2003**, *107*, 10990. (e) Mayya, K. S.; Gittins, D. I.; Dibaj, A. M.; Caruso, F. *Nano Lett.* **2001**, *1*, 727. (f) Gittins, D. I.; Caruso, F. *J. Phys. Chem. B* **2001**, *105*, 6846. (g) Mayya, K. S.; Schoeler, B.; Caruso, F. *Adv. Funct. Mater.* **2003**, *13*, 183.

(13) (a) Nikoobakht, B.; El-Sayed, M. A. *Langmuir* **2001**, *17*, 6368.

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is shown in Scheme 1. The LbL strategy utilized in this report is an important step toward surface functionalization of gold nanorods. These coated gold nanorods hold promise as building blocks for the synthesis of nano/superstructures, complex films, and for different sensing applications.

Experimental Section

Materials. Chloroauric acid ($HAuCl_4 \cdot 3H_2O$), trisodium citrate, sodium borohydride ($NaBH_4$), ascorbic acid, and 16-mercaptohexadecanoic acid (16-MHA) were obtained from Aldrich and used as received. The polyelectrolytes, poly(sodium-4-styrenesulfonate) (PSS), $M_w \sim 70\,000$ g/mol and poly(diallyldimethylammonium chloride) (PDADMAC), $M_w \sim 15\,000$ g/mol, were obtained from Aldrich and used without further purification. Cetyltrimethylammonium bromide (CTAB) was obtained from Sigma and used as received. Sodium chloride (NaCl) was purchased from Fisher chemicals. All the glassware was cleaned by aqua regia and rinsed with deionized water prior to experiments.

Synthesis of Gold Nanorods. Gold nanorods were synthesized by the seed-mediated template-assisted protocol as has been described elaborately in our earlier publications[5a,h] This protocol gives fairly monodisperse, stable gold nanorods (stabilized by a bilayer of CTAB)[13] that have lengths ~500−600 nm and diameters ~25−30 nm. This protocol produces a high percentage of gold nanorods although small rods and other shapes (triangles and spheres) are also present.[5h]

Polyelectrolyte Coating of Gold Nanorods (LbL Deposition). Aliquots of as-prepared (unpurified, containing excess CTAB) gold nanorods were taken in 1.5-mL microcentrifuge tubes and centrifuged once at 8000 rpm for 6 min. A pellet of gold nanorods was formed at the bottom of the microcentrifuge tubes. The supernatant colorless solution (containing excess CTAB) was slowly removed without disturbing the pellet. For polyelectrolyte coating experiments, two pellets were combined to double the nanorod concentration.

Stock solutions of PSS and PDADMAC, both at 10 mg/mL concentration, were prepared in 1 mM aqueous NaCl solution. To the microcentrifuge tubes containing the gold nanorod pellets, 1 mL of 1 mM NaCl was added simultaneously with 200 μL of PSS stock solution. After 30-min adsorption time, the excess polymer in the supernatant fraction was removed by centrifugation (8000 rpm, 6 min), and the pellet was redispersed in 1 mL of 1mM NaCl solution. Successive repetition of this step was used to form polyelectrolyte multilayers. After a desired number of coatings was reached (1, 2, or 4 polyelectrolyte layers), the nanorod solution was centrifuged twice and redispersed in deionized water. The gold nanorods were also redispersed in 1 mM aqueous NaCl solutions for salt-dependent immobilization studies (see below). The coated nanorods were stable for weeks as judged by the absence of any color changes over time.

Instrumentation. UV−vis spectroscopy was performed on a Varian model Cary 500 Scan UV−vis spectrophotometer. Zeta potential measurements were performed on a Brookhaven Zeta-PALS instrument. Transmission electron microscopy (TEM) measurements were performed on a Hitachi H-8000 TEM instrument operating at an accelerating voltage of 200 kV. For TEM, samples were prepared by placing a 3-μL drop of the purified gold nanorod solutions on carbon-coated copper grids and drying for 1 h. Scanning electron microscopy (SEM) measurements of the gold nanorods immobilized onto different functional surfaces (see below) was performed using a Philips XL 30 ESEM instrument. Images were recorded at various magnifications. SEM measurements were also used to determine the density of immobilized nanorods by counting individual nanorods in the image.

Formation of Monolayer-Coated Slides. Glass slides (dimensions: 3 × 1 in. surface area) used for immobilization were cleaned thoroughly using piranha solution ($H_2SO_4:H_2O_2 = 3:1$), rinsing in deionized water, and drying in flowing nitrogen.

(a) Formation of Cationic Surfaces. 1 cm^2 pieces of these clean glass slides were cut and further rinsed in deionized water and immersed for ca. 1 h in PDADMAC solution (10 mg/mL in 1 mM NaCl (aq)), washed in deionized water, and dried in flowing nitrogen.

(b) Formation of Anionic Surfaces. Two-hundred-nanometer-thick gold films were sputtercoated onto the cleaned glass slides after initially depositing a layer (10 nm) of chromium. 1 cm^2 pieces of these slides were cut and were immersed into 10^{-3} M ethanolic solution of 16-MHA for 24 h and thereafter rinsed with ethanol and dried in flowing nitrogen.

Immobilization of Gold Nanorods. The cationic and anionic surfaces formed as mentioned above were immersed into the as-prepared and polyelectrolyte-coated gold nanorod solutions held at pH 6.5 for a period of 4 h. The choice of pH comes from our earlier studies of nanorod immobilization, wherein the as-prepared pH ~ 6.5 is optimum for gold nanorod immobilization for MHA (the pK_a of MHA ~5.2).[8] Thereafter, the films were rinsed in deionized water (to remove unbound gold nanorods) and dried in flowing nitrogen.

Controls and Reproducibility Checks. Each experiment of polyelectrolyte coating of gold nanorods, TEM, zeta potential, and UV−vis measurements were repeated at least thrice to confirm reproducibility of the data. Appropriate control experiments for immobilization were carried out such as immobilization of polyelectrolyte-coated gold nanorods on both cationic and anionic surfaces.

Results and Discussion

Polyelectrolyte coating of gold nanocrystals has been studied in detail previously by Caruso and co-workers.[12f,g] Their coating studies address parameters such as the polymer type, concentration, chain length, particle diameter, and total salt concentration. To achieve polyelectrolyte coating of oppositely charged nanoparticles, the polymers should be flexible and have a chain length comparable to the dimensions of the nanoparticle. Higher molecular weight polymers correspond to larger polymer chain lengths. Hence, larger colloidal particles would require higher molecular weight polymers and vice versa for optimal coating. It is well-known that a certain amount of salt is required to allow charged polymer chains to be in an extended configuration. Shorter polymer chains need higher salt concentrations, compared to longer polymer chains, to effectively wrap around an oppositely charged nanoparticle. However, a high salt concentration would uncontrollably aggregate the nanoparticles. Furthermore, a high molecular weight polymer induces aggregation of nanoparticles through bridging.[12,14] Considering all these factors, a delicate balance of these parameters is essential to prevent flocculation, insufficient coating due to the polymer rigidity, and salt-induced alteration in the screening length.[12,14] Gittins et al. demonstrate that a low salt concentration (1 mM) and a polymer range of 15−20 kDa are ideal for coating nanoparticles of sizes ~30 nm.[12f]

(14) (a) Kunze, K.-K.; Netz, R. R. *Phys. Rev. Lett.* **2000**, *85*, 4389. (b) Netz, R. R.; Joanny, J.-F. *Macromolecules* **1999**, *32*, 9026. (c) Chodanowski, P.; Stoll, S. *J. Chem. Phys.* **2001**, *115*, 4951.
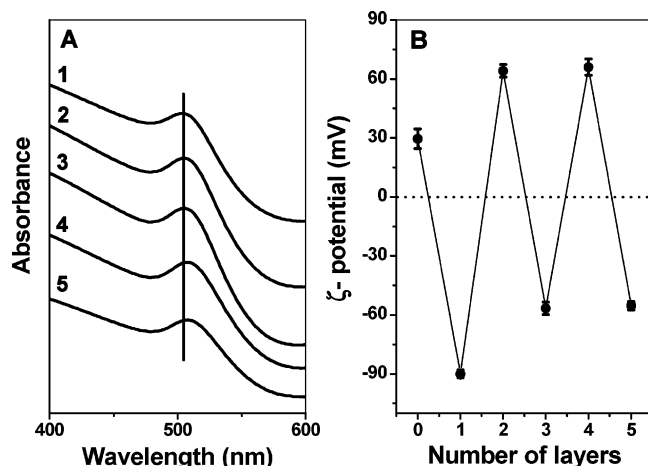
Figure 1. (A) UV−vis spectra of gold nanorods as a function of polymer coatings: curve 1: uncoated as-prepared gold nanorods; curve 2: one layer of PSS; curve 3: two layers of polymer (PSS + PDADMAC); curve 4: three layers of polymer (PSS + PDADMAC + PSS); curve 5: four layers of polymer (PSS + PDADMAC + PSS + PDADMAC). Curves are offset for clarity. (B) Zeta potential (ζ) data for gold nanorods as a function of polymer coatings.

As the gold nanorod dimensions in our case are 500−600 nm in length and 25−30-nm thickness, we have chosen our polymers with these characteristics ($M_w \sim$ 15000−70000 g/mol and salt concentration = 1 mM).

As mentioned in the Experimental Section, the as-prepared positively charged gold nanorods were first coated with a layer of anionic polymer PSS. Subsequently, multilayers of oppositely charged polymers were formed (PDADMAC−PSS−PDADMAC...). The UV−vis spectra of the gold nanorods as a function of different polymer coatings are shown in Figure 1 A. The absorption peak around 500 nm is due to the transverse surface plasmon band of the gold nanocrystals.[15] It can be seen that there is a small red-shift (∼6 nm) in the plasmon band maxima as a function of the number of polymer coatings (502 nm for as-prepared gold nanorods, curve 1; 505 nm after first layer of polymer, curve 2; and finally to 508 nm for four layers of the polymer, curve 5). It is well-known that as the local dielectric function increases, it results in a red-shift of the nanocrystal plasmon band.[15] The small shift observed by us is consistent with the changes in the local refractive index from that of water (*n* = 1.33) to that of polyelectrolyte (*n* ∼ 1.5) upon polymer adsorption. Furthermore, the peak wavelength shift is highly sensitive to the amount of material adsorbed to the particle surface.[15] Thus, UV−vis spectroscopy can be used as a tool to monitor the deposition of polyelectrolyte multilayers. The plasmon band does not show any broadening, thus ruling out any possible aggregation of the nanorods upon polymer adsorption. Gittins et al. observe a blue-shift in their nanoparticle plasmon band because of polymer unwrapping.[12f] The absence of such a plasmon band blue-shift in our case suggests that the polymer does not unwrap from the coated nanorods. These small red-shifts in plasmon band maxima are consistent with the work of Caruso and co-workers

wherein they demonstrate the polyelectrolyte multilayer coating of spherical gold nanoparticles.[12f,g] The red-shift is indicative of a higher refractive index surrounding the nanorods (organic polyelectrolyte compared to water). Gold nanorods exhibit transverse as well as longitudinal surface plasmon bands.[1a,5a] As explained in the Experimental Section, along with high aspect ratio gold nanorods, the synthetic protocol yields a small number of lower aspect ratio rods and other shapes such as triangles and spheres.[5h] These other shapes gave rise to additional bands at ca. 800 and 1200 nm.[5h] Hence, to simplify the analysis process, we have chosen to study only the shifts in the transverse plasmon band as a function of polymer adsorption.

One of the prerequisites for the sequential deposition of oppositely charged polyelectrolytes onto surfaces is charge reversal after each step of polymer deposition.[10] The most efficient way to determine this is by zeta potential measurements at each stage of polymer coating (Figure 1B). The zeta potential of as-prepared gold nanorods (purified) is ca. +30 mV because of the presence of a bilayer of CTAB on the nanorod surface. It can be clearly seen that there is charge reversal upon sequential polymer adsorption.

Direct visualization of polymer coating of the gold nanorods can be achieved by TEM measurements. Figure 2 A−D shows the high-magnification TEM micrographs of the gold nanorods coated by different layers of polyelectrolytes. It can be clearly seen that the gold nanorods are uniformly coated by the polymer (a faint layer surrounding the darker rods). A rough estimate of the thickness of the polymer coating of gold nanorods can be made from the TEM images. After one layer of polymer coating (PSS), a diffuse polymer layer can be seen that has a thickness of ∼3 nm. This thickness increases to ∼6 nm after four layers of polymer coating. Caruso et al. observe similar small increases in the size of the polymer-coated nanoparticles that were characterized using analytical ultracentrifugation.[12g] The nanorods are individually coated by the polymer and are not coated as aggregates. Such aggregate coating was observed for high molecular PDADMAC ($M_w \sim$ 10 0000−20 0000 g/mol) (Supplementary Information Figure S1).

The main advantage of polymer-coated rods is their ability to be utilized as either cationic or anionic functional entities, possibly with variable charge densities. Recently, we have demonstrated the use of the intrinsic charge on the as-prepared gold nanorods (because of the presence of CTAB) to electrostatically organize them onto acid-terminated self-assembled monolayer (SAM) films.[8] Polymer coating of cationic gold nanorods makes possible the selective immobilization onto both cationic (PDADMAC-coated glass slide) or anionic (MHA-SAM) surfaces. Furthermore, the ability to organize the coated rods onto either conducting surfaces such as gold and nonconducting surfaces such as glass strengthens the utility of such coated nanorods. As explained in the Experimental Section, functional surfaces were formed by coating the glass slides by a layer of PDADMAC (cationic surface) or by formation of an MHA SAM on the gold-coated glass slides. These slides were further immersed into aqueous solutions of uncoated and coated gold nanorods held at pH ∼ 6.5 for a period of 4 h.

(15) (a) Mulvaney, P. *Langmuir* **1996**, *12*, 788. (b) Alvarez, M. M.; Khoury, J. T.; Schaaf, T. G.; Shafigullin, M. N.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **1997**, *101*, 3706. (c) Underwood, S.; Mulvaney, P. *Langmuir* **1994**, *10*, 3427. (d) Henglein, A.; Mulvaney, P.; Linnert, T.; Holzwarth, A. *J. Phys. Chem.* **1992**, *96*, 2411.
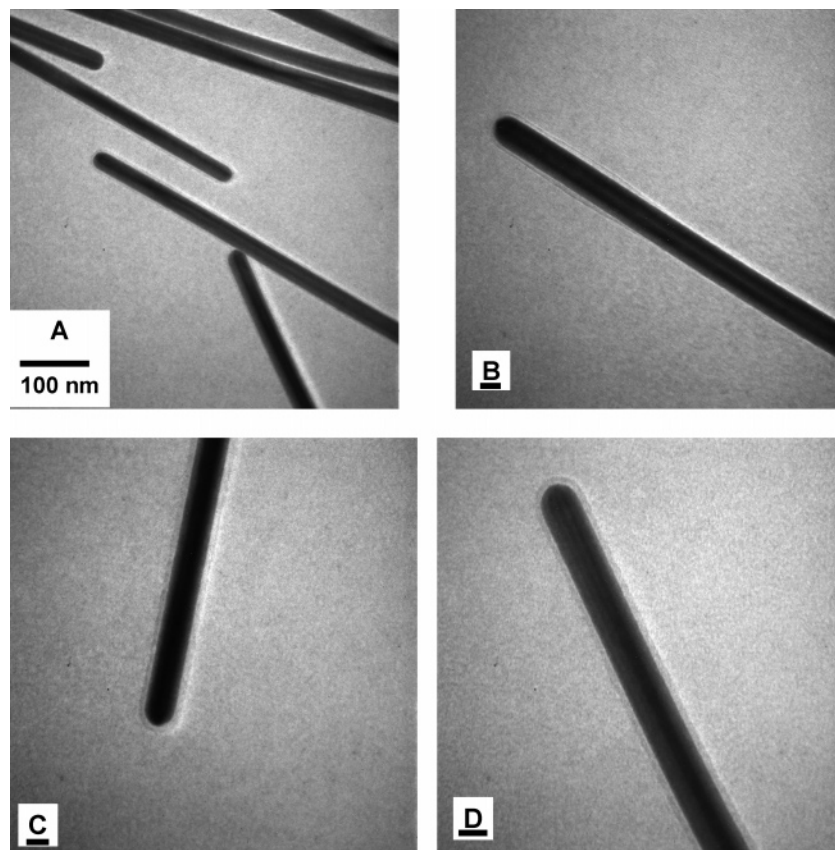
Figure 2. TEM micrographs of gold nanorods as a function of number of polymer layers. (A) One layer of polymer (PSS); (B) two layers of polymer (PSS + PDADMAC); (C) three layers of polymer (PSS + PDADMAC + PSS); (D) four layers of polymer (PSS + PDADMAC + PSS + PDADMAC). The scale bar in B−D is 20 nm.

In our earlier report, we had observed the immobilization of gold nanorods to be pH dependent and found that the as-prepared gold nanorod pH of 6.5 was ideal for immobilization onto MHA SAM surfaces.[8] Hence, we have maintained this immobilization condition.

Figure 3 shows the SEM micrographs of the as-prepared, cationic gold nanorods immobilized onto the anionic MHA SAM (Figure 3A), one layer of polymer (PSS) coated gold nanorods immobilized onto PDADMAC-coated glass slide (Figure 3B), and two layers of polymer (PSS + PDADMAC) coated gold nanorods immobilized onto MHA SAM (Figure 3C). Attractive electrostatic interaction between CTAB-coated nanorods and the anionic surface (Figure 3A), PSS-coated nanorods and the PDADMAC-coated slide (Figure 3B), and PDADMAC-coated nanorods and the anionic SAM surface (Figure 3C) is responsible for immobilization. By inspection, the images clearly show an increased density of immobilization of polyelectrolyte-coated gold nanorods (Figure 3B, C) compared to the as-prepared gold nanorods (Figure 3A). The density increases from ca. 11.9 rods/μm^2 (Figure 3A) to ca. 15.3 rods/μm^2 (Figure 3B) and 15.03 rods/μm^2 (Figure 3C), respectively. Furthermore, the absence of clumping/aggregation of the nanorods upon immobilization further increase the utility of these nanorod-coated surfaces for different sensing applications that require uniformly coated surfaces. The comparison of the type of gold nanorods, their overall zeta potential, and their immobilization density has been outlined in Table 1. The variation in the density of nanorod immobilization is possibly correlated

with the overall charge on the nanorods as evidenced by their zeta potential measurement (Table 1).

Immobilization of gold nanorods was also carried out in the presence of salt. Salt should screen electrostatic interactions and therefore reduce the amount of nanorods immobilized. As explained in the Experimental Section, the gold nanorods after the coating stage are centrifuged and rinsed twice. To study the salt effect, the purified rods were redispersed in aqueous 1 mM NaCl solutions instead of deionized water. The cationic and anionic functional surfaces (PDADMAC-coated glass slide and MHA SAM surface) were further immersed in these gold nanorod solutions. After 4-h immobilization, the slides were rinsed in deionized water and dried in flowing nitrogen and further studied by SEM measurements (data not shown for brevity). Nanorod density was calculated by counting individual nanorods. The results indicate that the density of immobilized gold nanorods in the presence of salt was less than that in the absence of the salt, further supporting the electrostatic nature of the immobilization process (Table 1).

Appropriate control experiments were carried out to compare electrostatic immobilization versus nonspecific adsorption. For this purpose, a cationic functional surface (PDADMAC-coated glass slide) was immersed in an aqueous solution of gold nanorods coated with two layers of the polymer (PSS + PDADMAC). Electrostatic repulsion between the similarly charged substrate and the coated nanorods resulted in a low-density surface coverage of aggregated nanorods. A representative SEM image is shown in supple-
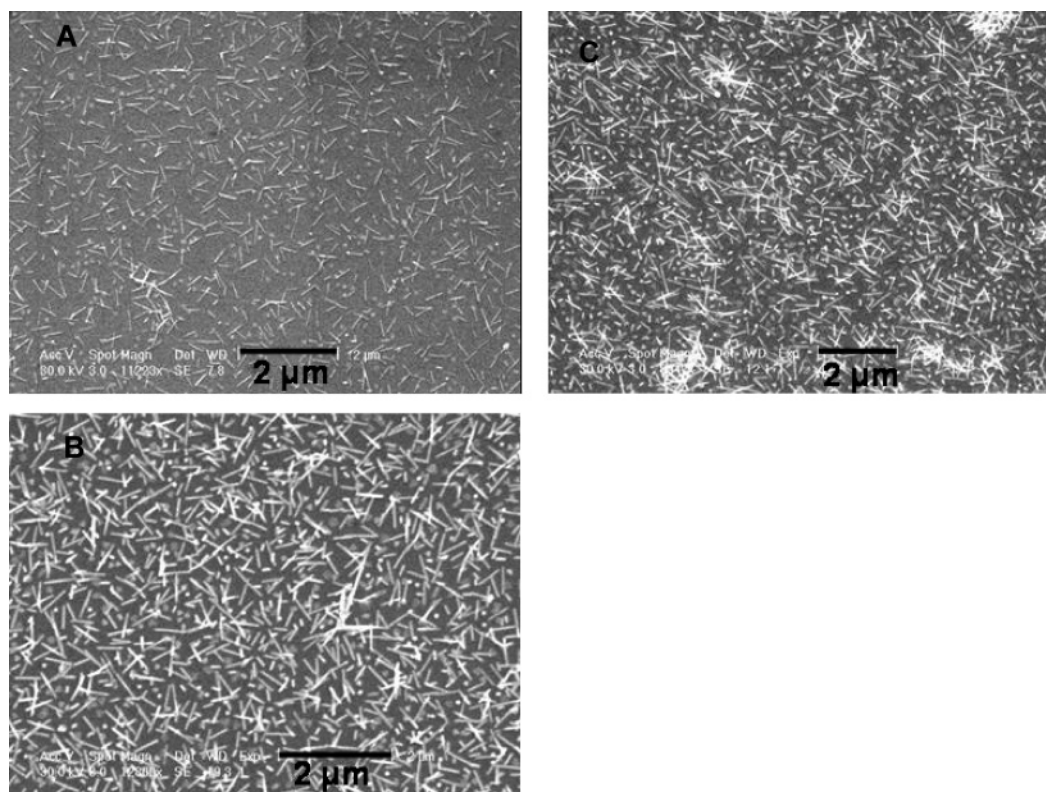
Figure 3. SEM micrographs of gold nanorods immobilized onto functional surfaces. (A) As-prepared (CTAB-coated) gold nanorods immobilized on MHA SAM-coated gold film; (B) one-layer PSS-coated gold nanorods immobilized onto PDADMAC-modified glass slide; (C) two layers of polymer (PSS + PDADMAC) coated gold nanorods immobilized onto MHA SAM-coated gold slide.

Table 1. Parameters Obtained for Polyelectrolyte-Coated Gold Nanorods and Their Immobilization onto Planar Functional Surfaces

surface group on gold nanorods	zeta potential (ζ) mV	immobilization surface	density of immobilized rods (rods/μm^2)
CTAB (nanorods suspended in deionized water)	+29.5 ± 5	MHA SAM	11.94 ± 1.25
one polymer layer (PSS) (nanorods suspended in deionized water)	−90 ± 2	PDADMAC-coated glass slide	15.3 ± 1.7
one polymer layer (PSS) (nanorods suspended in 1 mM NaCl)	−59.15 ± 5.38	PDADMAC-coated glass slide	13.3 ± 0.9
two polymer layers (PSS + PDADMAC) (nanorods suspended in deionized water)	+64.11 ± 3.23	MHA SAM	15.03 ± 1.07
two polymer layers (PSS + PDADMAC) (nanorods suspended in 1 mM NaCl)	+55.32 ± 2.1	MHA SAM	13.05 ± 0.55

mentary information Figure S2. A similar experiment with anionic surface (MHA SAM surface) and PSS-coated nanorods gave an analogous result.

Conclusion

A simple process for altering the surface properties of gold nanorods has been achieved by the layer-by-layer (LbL) assembly of polyelectrolytes. The polymer coating of the gold nanorods has been monitored by the surface plasmon red-shifts observed in the UV−vis measurements. Absence of any blue-shift in the visible spectra at any polymer adsorption stage rules out any unwrapping of the polymer. A charge reversal at each polymer adsorption stage, as observed by zeta potential measurements, suggests successful polymer multilayer coating of the gold nanorods. The thickness of the polymer coating increases as a function of polymer coating cycles as evidenced by TEM measurements. These coated gold nanorods were selectively organized onto conducting (gold-coated glass slides) and nonconducting (polymer-coated glass slides) anionic/cationic surfaces. The density of gold nanorod immobilization can be controlled by simple salt addition. The LbL strategy for surface modification greatly broadens the applicability of the gold nanorods. This study opens up an entire new series of applications such as synthesis of nanorod superstructures, complex films, and use of coated nanorods for different sensing applications.

Supporting Information Available: TEM image of one layer of high molecular weight PDADMAC ($M_w \sim 10\,0000-20\,0000$) on PSS-coated gold nanorods (S1). SEM image of nonspecific adsorption of gold nanorods onto similarly charged surface (S2). This material is available free of charge via the Internet at http://pubs.acs.org.