Polyelectrolyte Coating Provides a Facile Route to Suspend Gold Nanorods in Polar Organic Solvents and Hydrophobic Polymers

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ABSTRACT The widely used and versatile polyelectrolyte layer-by-layer (LbL) nanoparticle coating strategy allows for gold nanorods to be transferred from aqueous media into a broad range of polar organic solvents without aggregation. The uniform dispersity and stability of the nanorods in organic solvents allows for uniform incorporation of nanorods into a variety of hydrophobic polymers.

KEYWORDS: gold nanorods • polyelectrolytes • layer-by-layer coating • organic solvents • nanocomposite

INTRODUCTION

Gold nanorods have unique optical properties and promising chemical and biological applications (1−5). The most common synthetic routes to gold nanorods are in aqueous solution, and the final nanorods bear a bilayer of the shape-directing surfactant cetyltrimethylammonium bromide (CTAB) on their surfaces (4, 6, 7). The CTAB bilayer provides surface charge that prevents particle aggregation in water. However, CTAB molecules tend to desorb in organic solvents resulting in nanoparticle aggregation (8, 9). The synthesis of gold nanorods directly in organic solvents is not yet reported, although there are methods to transfer gold nanorods into organic solvents that use surface modification with alkylthiols or surfactant-assisted phase transfer (10−16). However, these approaches suffer from different limitations; modification with alkylthiols is difficult because of the need to displace surface-bound CTAB and can result in nanorod aggregation; moreover, the exact composition of the nanorod surface is generally unknown in these mixed systems. The use of phase transfer agents is limited to organic solvents that are immiscible with water. Herein, we report the successful transfer of polyelectrolyte-coated gold nanorods into a wide range of polar organic solvents and the uniform incorporation of these nanoparticles in hydrophobic polymer matrices. Although LbL coating with polyelectrolytes is well-documented in the literature for a wide variety of nanoparticle systems, in order to flip the surface charge of colloids and to place reactive amines or acid groups toward the solvent (17−19), we have found no reports that discuss the dispersion of polyelectrolyte-coated nanoparticles in nonaqueous solvents.

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EXPERIMENTAL SECTION

Gold nanorods were prepared using the wet chemical seed-mediated method (see the Supporting Information for details). Gold nanorods were coated with polyelectrolytes using layer-by-layer coating method as we reported previousely and detailed in the Supporting Information. Three polyelectrolytes were used: poly(allylamine hydrochloride), (PAH, MW ≈ 15 000 g/mol), poly(acrylic acid, sodium salt) (PAA, MW ≈ 15 000 g/mol), and poly(sodium 4-styrenesulfonate) (PSS, MW ≈ 70 000 g/mol). After coating, gold nanorod solutions were centrifuged at 11 000 rpm for 20 min to pellet the nanoparticles and remove the aqueous supernatant. The leftover pellets were then suspended in the polar organic solvent of choice. Nanocomposites were prepared by mixing PAA-coated gold nanorod in organic solvents with polymers and then the polymers were cured as detailed in the Supporting Information.

RESULTS AND DISCUSSION

CTAB-capped gold nanorods (zeta potential +57.62 ± 1.02), (CTAB-NRs) were synthesized with excellent shape and size monodispersity using the seed mediated wet chemical approach (see Figure S1 in the Supporting Information) (20). Gold nanorods were purified and then overcoated with sodium polyacrylate (PAA, anionic polyelectrolyte) or polystyrenesulfonate (PSS, anionic polyelectolyte). With PAA or PSS overcoating the nanorods, the measured zeta potentials are −30.29 ± 1.07 mV and −46.99 ± 1.35 mV respectively. Another round of polyelectrolyte coating on top of the PAA coated rods with polyallylamine hydrochloride (PAH, cationinc polyelectrolyte) yields a positive zeta potential of +42.22 ± 2.42 mV. Each layer of polyelectrolyte that is added to the gold nanorods adds ∼1.5 nm of thickness to the polymeric layer (21). The stability of PAA-coated rods (PAA-NRs) against aggregation in different polar organic solvents was evaluated using ultraviolet-visible (UV-vis) spectroscopy and dynamic light scattering (DLS). Figure 1 illustrates the stability of PAA-NRs compared to the original CTAB-NRs in polar organic solvents. The spectra show severe broadening and changes in the shape of the longitudinal plasmon band of CTAB-NRs in organic solvents, indicating nanorod aggregation (22, 23). However, PAA-NRs in most polar organic solvents do not
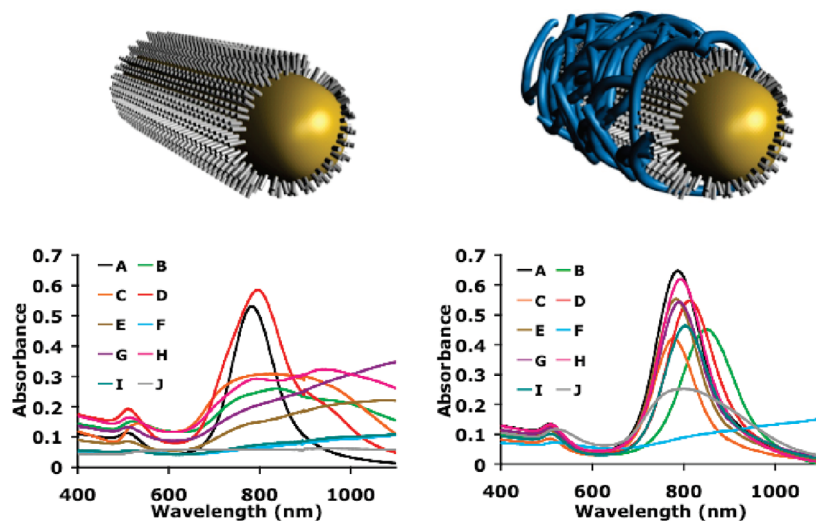
FIGURE 1. Schematic of CTAB-capped gold nanorods (left top) and PAA-coated gold nanorods (right top) UV−vis spectra of CTAB-capped (left) and PAA-coated (right) gold nanorods suspended in water and polar organic solvents. (A) water; (B) dimethylsulfoxide, DMSO; (C) acetonitrile; (D) dimethylformamide, DMF; (E) methanol; (F) diethyleneglycol, DEG; (G) ethanol; (H) acetone; (I) 1-propanol; (J) tetrahydrofuran, THF.
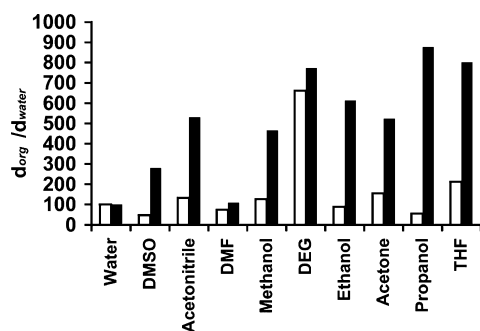

FIGURE 2. Relative dynamic light scattering of aspect ratio 4 PAA-coated GNRs (white bars) and CTAB-capped (black bars) in different polar organic solvents.

FIGURE 3. Peak maxima (λ_{max}) versus refractive index (n) for PAA-coated nanorods in the solvents where no aggregation was observed.

experience the same plasmon band broadening; spectral shapes are similar to the control spectrum in aqueous media (although at slightly different final concentrations), with slight red shifts and minimal broadening that corresponds to a change in refractive index of the solvents.

Dynamic light scattering measurements of gold nanorods in organic solvents agree with the UV-Vis spectra and indicate that PAA-NRs have increased stability against aggregation in most polar organic solvents compared to CTAB-NRs (Figure 2). Values for hydrodynamic diameters in organic solvents (d_{org}) were corrected for the viscosity and refractive index of the solvents and normalized to the control value in water (d_{water}); see the Supporting Information for details (24).

The position of the gold nanorod longitudinal plasmon peak (λ_{max}) depends on aspect ratio (length/width), plasmon coupling of the nanorods, and refractive index of the surrounding dielectric (22, 23). Plots of λ_{max} against the refractive index of the solvents (n_D) were linear with an R^2 value of 0.97 (Figure 3), in good agreement with the limited previous literature from phase transfer methods (9) or from dipping of immobilized gold nanorod chips into different solvents (25).
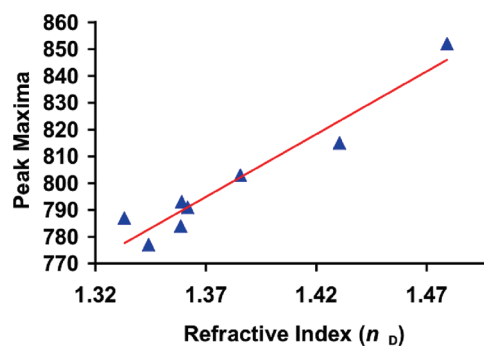
Table 1. Compiled Data Showing the Stability against Aggregation of Polyelectrolyte-Coated Gold Nanorods in Various Polar Organic Solvents (28)[a]

solvent	dielectric constant	CTAB-NRs	PAA-NRs	PSS-NRs	PAH-NRs
water	80.1	√	√	√	√
DMSO	46.7	×	√	√	√
acetonitrile	37.5	×	√	√	√
DMF	36.7	×	√	√	√
methanol	32.7	×	√	√	√
diethyleneglycol	31.69	×	×	√	√
ethanol	24.5	×	√	√	√
acetone	20.7	×	√	√	√
1-propanol	20	×	√	√	√
THF	7.58	×	×	×	×
1, 4-dioxane	2.25	×	√	×	×

[a] The stability was determined from UV−vis spectroscopy and DLS results. (√) indicates stable against aggregation and (×) indicates aggregation.

The transfer of polyelectrolyte-coated gold nanorods to so many organic solvents is remarkable considering that the polyelectrolytes provide a highly charged surface upon coating. We believe that this polyelectrolyte-coating acts as both stabilizer and solubilizer for the gold nanorods in that it captures the CTAB bilayer and prevents its
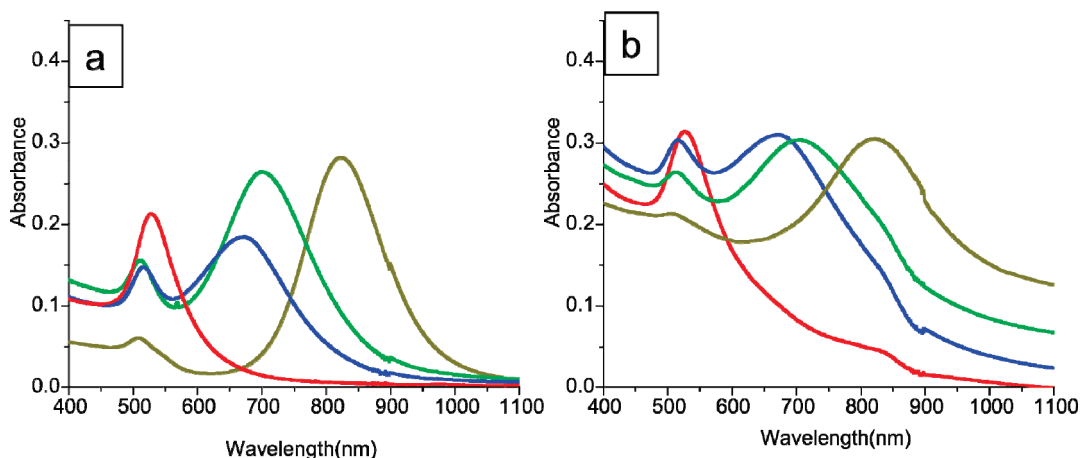
FIGURE 4. UV−vis spectra of gold nanorods with different aspect ratios (a) in solution of DMF and (b) in cured PDMS films (∼1000 μm thick). In both UV−vis spectra the curves correspond to the following aspect ratios: red = 1, blue = 2.3, green = 3.2, and gold = 4.
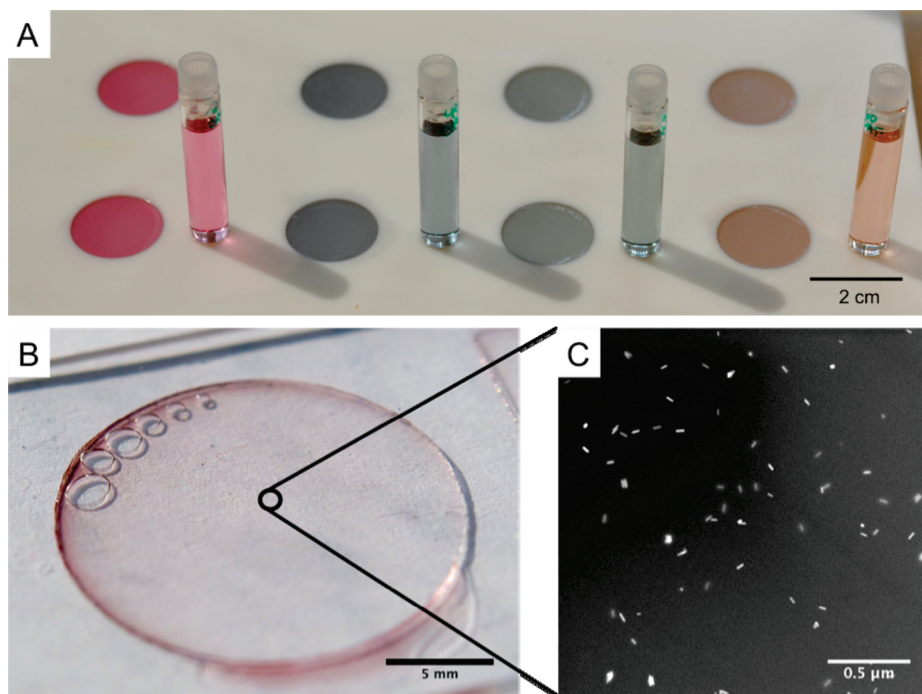

FIGURE 5. (a) Photograph shows prepared PDMS films and the solutions used to prepare the PDMS films. (b) Photograph of a ∼60 μm PMMA film containing gold nanorods sandwiched between a glass slide and a coverslip. (c) Dark-field STEM image of PMMA-gold nanorod composite thin film showing well-dispersed rods in the polymer matrix.

desorption into the organic bulk and at the same time provides surface charge, and thus stability against aggregation, via ionization in the polar organic solvents (26, 27). To test this hypothesis, we measured zeta potential measurements for PAA-NRs in water, methanol, and ethanol (we could not test all solvents due to incompatibilities with the DLS instrument). We found that the PAA-NRs have negative effective surface charges in all the solvents tested: water (−30.29 ± 1.07 mV), methanol (−20.22 ± 2.20 mV), ethanol (−15.32 ± 1.6 mV). The zeta potential values provide evidence that polyelectrolytes do in fact dissociate in polar organic solvents and qualitatively behave in a manner that is similar to aqueous solutions (26, 27). Furthermore, our findings are in accord with the dispersibility of carbon nanotubes, in polar organic solvents, that have

been reduced with alkali metals to form polyelectrolyte salts on the surface (27).

The successful transfer of PAA-NRs into organic solvents motivated us to investigate other types of polyelectrolytes with different structure/charge properties by testing the stability of anionic PSS-coated and cationic PAH-coated gold nanorods in organic solvents. As summarized in Table 1, we found that all tested polyelectrolyte (PAA, PSS, and PAH) allow for enhanced stability in most of the tested solvents compared to the CTAB-capped nanorods (see Figures S2−S3 in the Supporting Information). These results illustrate that the polyelectrolyte LbL coating of nanoparticles provides a generalized route for transfer of nanoparticles into polar organic solvents regardless of the structure/charge of the polyelectrolyte, at least for the poly-

electrolytes tested here. Experiments to understand the solvation, ionization, and other factors that contribute to the nanoparticle—polyelectrolyte—solvent interactions and promote stability are in progress.

Nanoparticle—polymer mixtures (nanocomposites) are of interest for advanced applications that need improved mechanical, optical, or electrical properties of the composite material (8, 29). Gold nanoparticles are excellent light absorbers/scatterers in the visible and near-infrared, which should open potential uses in applications such as plasmonic light concentrators, antennas, lenses, and resonators (30). However, many polymers are hydrophobic and thus the aqueous media is not ideal for preparing nanocomposites with uniform dispersion of nanoparticles within the polymer matrix (31—34). Using polyelectrolyte-coated gold nanorods in organic solvents, we demonstrate the uniform incorporation of gold nanorods into three types of polymers: poly-dimethylsiloxane (PDMS), a photocurable polyurethane adhesive (Norland Optical Adhesive 61(NOA)), and poly(methyl methacrylate) (PMMA). Figure 4 shows PDMS films that have been prepared using different aspect ratios of PAA-NRs with similar spectral features of gold nanorods in solution that support the uniform dispersion of the nanorods in the films (see the Supporting Information for preparation details). High-quality PMMA and NOA films that show retention of gold nanorod spectral features were also fabricated from polyelectrolyte-coated gold nanorods in organic solvents (Figure S4 in the Supporting Information). Dark-field STEM images of PAA-coated rods in a PMMA film show an even distribution of gold nanorods within the film, which agrees with the UV—vis spectra of thin polymer films (Figure 5).

In addition to being able to produce polymer-nanorod composites in a variety of hydrophobic polymers, we were also able to easily control the loading of gold nanorods into the polymer films. We were able to concentrate polyelectrolyte-coated gold nanorods in organic solvents to extremely high concentration (>50 nM in rods, 100× that in water) and use these concentrated solution to prepare thin composite films. For example, we have fabricated 200 μm thick NOA films with an optical density of over 2 at the longitudinal plasmon band maximum, containing 0.02 % gold nanorods by weight (see Figure S5 in the Supporting Information). Based on their extremely large extinction coefficients (~5 × 10^9 cm^{-1} M^{-1}), gold nanorods provide high optical densities from low loadings in thin films. This result is important for possible applications in thin films devices such as solar cells, where thin films with high optical absorption is desired.

CONCLUSION

In conclusion, we have demonstrated that the ubiquitous LbL strategy of coating gold nanorods with polyelectrolytes allows coated nanoparticles to be uniformly suspended in both wide range of polar organic solvents and hydrophobic polymer films. This approach could be expanded to other nanoparticle systems because LbL polyelectrolyte coating of nanoparticles is used for many types of nanomaterials (17, 18, 31—34). We believe that

this facile route for transferring nanoparticles into organic solvents from the aqueous phase will enable a wide variety of applications for these materials.

Supporting Information Available: Gold nanorod synthesis and coating, λ_{max} vs refractive indexes plots, films preparation and characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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