Large-Scale Silica Overcoating of Gold Nanorods with Tunable Shell Thicknesses

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Supporting Information

ABSTRACT: Gold nanorods (GNRs) overcoated with SiO$_2$ are of interest for enhancing the shape stability of GNRs during photothermal heating, for further functionalization with silanes, and for biomedical applications. While methods have recently been developed for synthesizing GNRs on a large scale, SiO$_2$ overcoating of GNRs is still conducted on a small reaction scale. Here, we report a method for large-scale synthesis of SiO$_2$-overcoated GNRs (SiO$_2$-GNRs), which gives ~190 mg of SiO$_2$-GNRs. SiO$_2$ is deposited onto and encapsulates the cetyltrimethylammonium bromide (CTAB) coatings that stabilize GNRs by adding tetraethoxysilane (TEOS) via syringe pump. Control over the CTAB concentration is critically important for obtaining uniform overcoatings. Optical absorbance spectra of SiO$_2$-GNRs closely resemble those of uncoated GNRs, which indicates overcoating of single rather than multiple GNRs and confirms that they remain well dispersed. By adjusting the reaction conditions, shells as thick as ~20 nm can be obtained. For thin shells (<10 nm), addition of poly(ethylene glycol) silane (PEG-silane) at different times during the overcoating reaction allows facile control over the shell thickness, giving shells as thin as ~2 nm. The bulky PEG chain terminates further cross-linking and deposition of SiO$_2$.

INTRODUCTION

Encapsulating gold nanorods (GNRs) in SiO$_2$ shells enhances their thermal stability, which is important for preserving their rod shape and longitudinal surface plasmon resonance (LSPR) during photothermal heating.\cite{1-5} SiO$_2$ shells are also biocompatible, reduce toxicity because they no longer require a minimum concentration of cetyltrimethylammonium bromide (CTAB) for dispersion in solution,\cite{6-8} and facilitate functionalization with silanes, which can be used for further chemical modification, including click chemistry.\cite{9-11} SiO$_2$-overcoated GNRs (SiO$_2$-GNRs) are of particular interest for biomedical applications, including photothermal therapy,\cite{5,12,13} photoacoustic imaging,\cite{2,14-16} biosensing,\cite{17,18} drug delivery,\cite{19,20} and cancer cell imaging.\cite{21-24} SiO$_2$-GNRs may also be used for catalysis, where the SiO$_2$ coating makes nanoparticles (NPs) more durable and tolerant of harsh environments.\cite{25-27}

SiO$_2$ is usually deposited onto Au surfaces after modifying the surface using polymer templates\cite{18,28-33} because of the weak affinity between SiO$_2$ and Au. The Stöber method,\cite{34} which has been widely used for synthesizing spherical SiO$_2$ particles, has been adapted for overcoating GNRs with SiO$_2$. Gorelikov and Matsuura first reported a single-step procedure for overcoating GNRs with SiO$_2$ using the CTAB coatings as a template for deposition of a mesoporous SiO$_2$ shell.\cite{35} In their method, the number of consecutive injections of tetraethoxysilane (TEOS) into a solution of CTAB-stabilized GNRs at 30 min intervals and the reaction time both gave control over the SiO$_2$ shell thickness. In a recent modification of this method, the CTAB concentration was used to control the SiO$_2$ shell thickness.\cite{10} CTAB coatings have also been used to template deposition of SiO$_2$ onto other kinds of NPs, including CdSe/ZnS quantum dots and CuO, Cu$_2$N, Fe$_3$O$_4$, and Ag NPs.\cite{35-38}

Poly(ethylene glycol) (PEG) coatings are commonly employed on SiO$_2$ NPs (or films) to reduce the coverage of exposed silanol groups and to improve biocompatibility by preventing nonspecific adsorption of proteins and allowing better dispersion in electrolyte solutions, such as those found in biological environments.\cite{39-45} Poly(ethylene glycol) silane (PEG-silane) has been shown to quench deposition of SiO$_2$ from TEOS and can thus be used to terminate deposition of SiO$_2$ coatings.\cite{36} Surface modification with PEG-silane has also been shown to enhance the long-term colloidal stability of Au NPs.\cite{47}

Current procedures for synthesizing SiO$_2$-GNRs produce only small amounts of material (<10 mg). Here, we report an increase in the scale of SiO$_2$-GNR synthesis to ~190 mg with excellent control over the SiO$_2$ shell thickness (3–20 nm). When PEG-silane is added prior to completion of SiO$_2$ shell growth, shells as thin as 2 nm can be obtained. Addition of PEG-silane also gives insights into the kinetics of SiO$_2$ shell growth. In the process of optimizing the reaction conditions, we have also discovered other growth regimes that may be useful for obtaining asymmetrical SiO$_2$ shells or cross-linked SiO$_2$-GNR networks.

Received: December 26, 2014
Revised: February 18, 2015
Published: February 26, 2015

DOI: 10.1021/cm504764v
Chem. Mater. 2015, 27, 2888–2894

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SiO₂ shells deposited onto NPs are often porous, where the porosity depends on the use of surfactants and silicate reactants. Some studies have reported control over the pore size by modifying the polymer or surfactant coating used to template SiO₂ growth.48–50 The method of Gorelikov and Matsuura, on which our synthesis is based, yields porous SiO₂ shells, which are similarly reported here. Future work may include controlling the pore size to control access of molecules to the surface of the Au core, such as for surface-enhanced Raman spectroscopy (SERS)51 and drug delivery, including cancer therapeutics.43,44 In addition, combining the porosity of SiO₂ overcoatings with photothermal heating of GNRs may allow for efficient triggering of drug release.54

**EXPERIMENTAL SECTION**

**Chemicals.** CTAB (Sigma-Aldrich, 99%, H6269), KBr (Alfa Aesar, ACS, 99% min), AgNO₃ (Alfa Aesar, 99.9995%), HAuCl₄·xH₂O (Alfa Aesar, 99.9999%, where x was estimated as 3), deionized water (Ricca, ACS Reagent grade, ASTM Type I, ASTM Type II), acetic acid (AA, J.T. Baker, 99.5%), and NaBH₄ (Sigma-Aldrich, 99%, 213462) were used in the GNR synthesis. TEOS (Alfa Aesar, 99.9%), NaOH (Sigma-Aldrich 98%), 2-[methoxy(polyethyleneoxy)]₄,₃,propyltrimethoxysilane (PEG-silane, Gelest, 90%), and anhydrous methanol (EMD, DriSolv) were used for the SiO₂ overcoating. Methanol (Macron, UltimAR) was used for purification of SiO₂-GNRs and PEG-functionalized SiO₂-GNRs (PEG-SiO₂-GNRs).

**Gold Nanorod Synthesis and Purification.** CTAB-stabilized GNRs were synthesized according to a method that we recently reported, resulting in a 1 L aqueous solution containing ~190 mg of GNRs with average dimensions of 77 × 21 nm, which have an LSPR of ~800 nm.45 Obtaining an optimal concentration of CTAB after purification is critical not only for stabilizing GNRs against aggregation before SiO₂ overcoating but also for depositing uniform SiO₂ coatings, while avoiding formation of spherical SiO₂ NPs that do not encapsulate GNRs. The GNR stock solution has a CTAB concentration of 0.1 M. Two cycles of centrifugation (Thermo Scientific Sorvall Legend XIR with Fiberlite F15-6 × 100 fixed-angle rotor), each at 10000 g for 20 min, were performed at 30 °C to avoid crystallization of CTAB while concentrating the GNRs and removing excess CTAB. The GNR stock solution was fractionated into volumes of 60 mL for each centrifuge tube. After the first centrifugation cycle, ~58 mL of the nearly colorless supernatant was removed by pipetting from each tube. Deionized water was added to bring the volume of solution in each centrifuge tube to 60 mL. Therefore, this 30X dilution step gives a final CTAB concentration of 3.3 mM, while the GNRs have the same concentration as in the stock solution. After centrifuging a second time, ~58 mL of the supernatant containing CTAB was removed, and the remaining 2 mL of GNR solution was collected from each tube. The 2 mL product was then diluted to 6 mL by adding 4 mL of deionized water, giving a final CTAB concentration of 1.1 mM and an effective 10X increase in the concentration of GNRs as compared with the stock solution before purification. Fractions of this purified GNR solution from multiple centrifuge tubes were combined as needed to provide more material for SiO₂ overcoating.

**Silica Overcoating Reaction on Standard 10 mL Scale.** All reactions were conducted in a temperature-controlled water bath at 30 °C. A solution of 0.1 M NaOH was prepared in deionized water, and TEOS was diluted in anhydrous methanol, giving a 20% v/v TEOS solution. Unless noted otherwise, reactions were conducted on the following 10 mL, standard scale. For the synthesis of SiO₂-GNRs (or PEG-SiO₂-GNRs), 0.1 M NaOH was added dropwise to 10 mL of the purified GNR solution (containing ~19 mg of GNRs and 1.1 mM CTAB) in 20 mL scintillation vials, while quickly stirring with a magnetic stir bar (octagonal with pivot ring, 5/16″ diameter, 1/2″ long). The pH was adjusted to 10–10.4. A variable amount (31.3–500 μL) of the TEOS solution (20% v/v) was loaded into a syringe and injected into the pH-adjusted aqueous solution of GNRs by syringe pump over a period of 5 min. The solution was gently stirred (70 rpm) for 30 min and was then kept unstirred in the water bath for another 20 h. The product contained SiO₂-GNRs with uniform SiO₂ shells, whose thickness could be adjusted between 3 and 20 nm by varying the volume of TEOS solution. For improved control of ultrathin SiO₂ overcoatings (<10 nm thick), 40 μL of neat PEG-silane was added at different times (30 min to 2 h) after completing injection of TEOS solution, which caused early termination of the shell growth reaction. (It should be noted that the 30 min of gentle stirring immediately after injection of the TEOS solution is included in counting the time at which PEG-silane was added, which is why 30 min was the shortest time at which PEG-silane could be added.) For all PEG-silane addition times, the reaction mixture was stirred for 30 min after adding the PEG-silane and was then allowed to sit in the water bath for 20 h without stirring.

**Large-Scale Synthesis of SiO₂-GNRs and PEG-SiO₂-GNRs.** The overcoating reaction can scale up 10-fold to a 100 mL, large scale using ~190 mg of GNRs, which were obtained from 1 L (before purification and concentration) of the CTAB-stabilized GNR solution. The reactant concentrations, pH, temperature, and timing were kept the same as for the standard scale. The amounts of TEOS solution (20% v/v) and PEG-silane were multiplied by a factor of 10, and the TEOS solution was injected over a period of 5 min. For the large-scale synthesis, the PEG-silane was added dropwise, and the reaction was conducted in 125 mL Erlenmeyer flasks using a longer magnetic stir bar (octagonal with pivot ring, 5/16″ diameter, 2″ long).

**Purification.** In each centrifuge tube, 2 mL of the as-synthesized SiO₂-GNR (or PEG-SiO₂-GNR) solution was diluted with methanol to a total volume of 40 mL. Five centrifugation cycles (IEC Centra-MP4 with IEC 854 4 × 50 fixed-angle rotor), each at 8500g for 10 min and at room temperature, were required to remove reaction byproducts. After each cycle, the supernatant was removed, leaving ~1 mL of SiO₂-GNR (or PEG-SiO₂-GNR) solution, which was then diluted with methanol to a total volume of 40 mL before starting the next cycle. After the last cycle, the ~1 mL of the product in each centrifuge tube was combined with the other fractions for storage without further dilution.

**Characterization.** Transmission electron microscopy (TEM) was performed using a JEOL 2000FX microscope operated at 200 kV to examine the GNR core and SiO₂ shell morphologies and to measure the average SiO₂ shell thickness from samples of 100 NPs. Optical absorbance spectra were acquired using an Ocean Optics CHEM-USB4-VIS-NIR spectrophotometer. Absorbance spectra for SiO₂-GNRs and PEG-SiO₂-GNRs were normalized to the spectrum for the uncoated GNRs at 400 nm.

**RESULTS AND DISCUSSION**

**SiO₂-GNR Synthesis.** Use of a syringe pump automates addition of TEOS and allows for improved control over the reaction, as compared with adding the TEOS solution all at once or in smaller increments. Under properly optimized conditions, the CTAB coatings template deposition of porous SiO₂ shells onto the GNRs (Figure 1b–f and histograms of the SiO₂ shell thickness in the Supporting Information, Figure S2). The porous structure of the SiO₂ shells is apparent in the TEM images. A more detailed study to characterize and control the porosity of the SiO₂ shells would be informative and useful for some applications but is beyond the scope of this paper. The SiO₂ shell thickness was adjusted (3.3–17.3 nm) by varying the volume of TEOS solution added (31.3–500 μL), while maintaining the same reaction time and conditions (Figure 1g). The CTAB coatings remain between the GNR cores and SiO₂ shells but do not appear as lighter corona in TEM images, because TEM images include contrast from segments of the SiO₂ shell that cover the CTAB layer in the out-of-plane direction above and below the widest part of the GNR.
For the samples prepared using 31.3–250 μL of the 20% TEOS solution with shell thicknesses of 3.3–16.0 nm (Figure 1b–e), the SiO₂ shell volume (\(V_{\text{SiO₂}}\)) has a linear dependence on the volume of 20% TEOS solution (\(V_{\text{TEOS}}\)): 
\[V_{\text{SiO₂}} = aV_{\text{TEOS}} + b,\]
where \(a = 0.84 \times 10^3 \text{ nm}^3/\mu\text{L}\) and \(b = 5.7 \times 10^3 \text{ nm}^3\) (Figure 1h). The intercept term, \(b\), is quite close to zero and corresponds to a shell thickness of 0.9 nm. The linear trend among these data points indicates that the yield of the reaction for the conversion of TEOS into SiO₂ is similar for these samples. In contrast, the data point for the sample that used 500 μL of the 20% TEOS solution with a shell thickness of 17.3 nm (Figure 1f) lies far below the trendline (Figure 1h), which indicates a significantly lower yield. When using this larger amount of TEOS, a reaction time of 20 h may not be long enough to complete the reaction.

The following calculations suggest that most of the TEOS solution is consumed and deposited onto the GNRs during the reaction. Based on the size of the GNRs, their concentration, and the SiO₂ shell volume (calculated from TEM measurements of the shell thickness and treating the GNRs and SiO₂-GNRs as concentric cylinders), the density of the SiO₂ shells can be calculated, assuming 100% yield. If the actual yield is close to 100%, then the calculated value will agree with known values for the density of porous SiO₂ (1.3–2.1 g/cm³).⁵⁶ Furthermore, the density of fused SiO₂ (2.2 g/cm³) is a reasonable upper limit because it is amorphous and nonporous; porosity would cause a decrease in the density. Since a substantially lower actual yield would give thinner shells, the resulting calculated density would exceed the maximum reference value of the density for porous SiO₂.

The sample prepared using 125 μL of the 20% TEOS solution had a SiO₂ shell thickness of 10.3 nm (Figure 1d). Dividing this amount of TEOS by the number of GNRs in the solution gives \(1.9 \times 10^6\) molecules of TEOS per GNR. If each TEOS molecule is converted into one unit of SiO₂ in the shell, the mass of SiO₂ units (\(1.9 \times 10^{-16}\) g) divided by the volume of the shell (\(1.1 \times 10^5\) nm³) gives a density of 1.7 g/cm³, which is in the range of values for porous SiO₂. Therefore, the reaction goes at least mostly and possibly entirely to completion. The wide range of reference values for the density of porous SiO₂ does not allow us to unambiguously conclude that the reaction goes entirely to completion. Similar densities are also calculated for the other samples that used 31.3 μL (2.0 g/cm³), 62.5 μL (1.3 g/cm³), or 250 μL (1.7 g/cm³) of the 20% TEOS solution (Figure 1b,c,e). For the sample prepared using 500 μL of the 20% TEOS solution with a SiO₂ shell thickness of 17.3 nm, however, a density of 3.0 g/cm³ was calculated, but the TEM image (Figure 1f) shows a porous shell structure. This suggests (in agreement with the discussion of the SiO₂ shell volume) the reaction did not go as far to completion as for the other samples.

**Effect and Importance of CTAB Concentration.** The CTAB coating on GNRs templates deposition of SiO₂. A large excess of CTAB is used in the synthesis of GNRs. For example, in our method, the CTAB:HAuCl₄ molar ratio is 98:1.⁵⁵ After purifying the GNRs, the final CTAB concentration is 1.1 mM, which is close to the critical micelle concentration (CMC) of CTAB in water (0.9 mM).⁵⁷ The absence of additional, spherical SiO₂ NPs that do not encapsulate GNRs is consistent with removal of most of the excess CTAB that was used in the GNR synthesis (Figure 1b–f). If a substantial excess of CTAB would be present, empty CTAB micelles would also template deposition of SiO₂ (Figure 5a). A CTAB concentration slightly exceeding the CMC was chosen because a concentration below the CMC would likely alter the structure of the CTAB layer on GNRs and destabilize them in solution or cause formation of nonuniform SiO₂ shells.⁵⁸

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**Figure 1.** TEM images of uncoated GNRs and SiO₂-GNRs synthesized on the 10 mL scale using different volumes of 20% TEOS solution and measurements of the SiO₂ shell thickness: (a) no TEOS, uncoated GNRs, (b) 31.3 μL, 3.3 nm, (c) 62.5 μL, 7.7 nm, (d) 125 μL, 10.3 nm, (e) 250 μL, 16.0 nm, and (f) 500 μL, 17.3 nm. Plots of the SiO₂ shell (g) thickness and (h) volume (calculated for concentric cylinders) as a function of the volume of TEOS solution.

DOI: 10.1021/cm504764v
Chem. Mater. 2015, 27, 2888–2894
In a recent study by Murphy and co-workers, which also extended earlier work by Gorelikov and Matsuura, the amount of free CTAB in the reaction solution was used to control the SiO$_2$ shell thickness. When more CTAB was added, thinner SiO$_2$ shells resulted. Adding more CTAB may alter partitioning of the TEOS deposition onto GNRs and empty CTAB micelles. When there is a greater proportion of empty CTAB micelles, more TEOS may be deposited onto them, leaving thinner SiO$_2$ shells on the GNRs. Centrifugation was performed after the overcoating reaction to remove the excess SiO$_2$ particles. In contrast, here, the free CTAB was reduced to minimize the number of empty CTAB micelles in the solution, while still having enough CTAB to stabilize the GNRs in the solution. The methanol in which the TEOS is diluted may also perturb the CTAB layer on the GNRs, giving nonuniform SiO$_2$ overcoatings, as described later.

**PEG-SiO$_2$-GNR Synthesis.** As an alternative to adding less TEOS, SiO$_2$ shells thinner than 10 nm could also be obtained with more precise thickness control by adding PEG-silane to terminate SiO$_2$ shell growth. The timing of the PEG-silane injection determined the extent of shell growth prior to terminating the reaction. Our method for obtaining $\sim$10 nm thick shells using 125 μL of the 20% TEOS solution was extended by adding 40 μL of PEG-silane at variable times after adding the TEOS solution. For example, injection of PEG-silane 30 min after adding the TEOS solution gave a final shell thickness of 5.0 nm (Figure 2a). This method also provides insights into the early stage of SiO$_2$ shell growth from TEOS. When PEG-silane was added after 45, 60, or 120 min, respective shell thicknesses of 7.5, 8.9, and 9.2 nm were obtained (Figure 2b–d and histograms of the SiO$_2$ shell thickness in the Supporting Information, Figure S3). Therefore, SiO$_2$ shell growth is rapid over the first hour but slows significantly during the second hour of growth (Figure 2e).

Termination with PEG-silane also appears to alter the outer surface of the SiO$_2$ shell (Figure 2f). In the absence of PEG-silane, pores in the SiO$_2$ are exposed on the outer surface of SiO$_2$-GNRs. Termination with PEG-silane results in a smoother surface on PEG-SiO$_2$-GNRs, which could be especially important for thin SiO$_2$ shells, where the size of the pores may approach the thickness of the SiO$_2$ shell. While the mechanism for smoothing the surface is not known, this result suggests that PEG-silane is disproportionately deposited into or on top of the exposed pores on the surface of SiO$_2$-GNRs. Apart from the large steric size of the PEG chain, each PEG-silane molecule can form only three Si–O bonds to the SiO$_2$ shell rather than four for TEOS. This difference might also be significant for understanding smoothing when adding PEG-silane.

**Optical Absorbance Spectroscopy.** Absorbance spectra of SiO$_2$-GNRs were acquired immediately after completing the overcoating reactions and before purification by diluting the samples with deionized water (Figure 3a). As the SiO$_2$ shell thickness increased, the LSPR absorbance band redshifted. This effect has also been observed by others and has been attributed to the higher refractive index of SiO$_2$ than water (1.33). Experiment and theory have shown that the LSPR redshifts when GNRs are dispersed in different solvents, where the magnitude of the redshift scales with the refractive index of the solvent. Reported values for the index of refraction of porous SiO$_2$ range between 1.28 and 1.45, whereas quartz has an index of refraction of 1.46. It is well known that the index of refraction of SiO$_2$ scales with its density. The redshift for SiO$_2$-GNRs in water indicates that the index of refraction for the SiO$_2$ shells is greater than 1.33, but a value below 1.45 is anticipated due to the porosity of the SiO$_2$ shells. The width of the LSPR absorbance band does not substantially change after depositing SiO$_2$, which indicates that the SiO$_2$-GNRs are well dispersed in solution rather than agglomerated, since agglomeration would cause significant broadening. Unlike CTAB-stabilized GNRs, which disperse well only in water (or in mixtures with water as the major component), SiO$_2$-GNRs and PEG-SiO$_2$-GNRs readily disperse in water, methanol, and ethanol.

Absorbance spectra of PEG-SiO$_2$-GNRs after purification and dispersion in methanol exhibit no shift in the LSPR maximum.
A reduced redshift for PEG-SiO₂-GNRs compared with SiO₂-GNRs has been reported by others.63 The absence of a redshift in the LSPR for our PEG-SiO₂-GNRs can be partially explained by the thinner SiO₂ shells than for SiO₂-GNRs, where thinner shells are not redshifted as greatly as thicker shells. Nevertheless, a redshift would be expected, since the refractive index of methanol (1.33) is close to that of water (1.33). The PEG coating might also affect the optical properties, since the refractive index of PEG-silane (1.45) is likely greater than that of the porous SiO₂ shells. While the refractive index of water and methanol is less than that of SiO₂, resulting in a redshift for SiO₂-GNRs, the refractive index of PEG-silane that is greater than that of SiO₂ may reduce the magnitude of the redshift for PEG-SiO₂-GNRs.

**Large-Scale Synthesis of SiO₂-GNRs and PEG-SiO₂-GNRs.** The SiO₂-GNR and PEG-SiO₂-GNR syntheses have both been scaled to the 100 mL, large scale. We do not anticipate an immediate problem in further increasing the scale. Slow mixing when adding reagents into the solution is a potential problem for larger volumes, but we do not know at what scale this could arise. TEM images and optical absorbance spectra for large-scale syntheses of PEG-SiO₂-GNRs (using 625 μL of the 20% TEOS solution) with ultrathin SiO₂ shells (2.2 ± 0.5 nm thick shells) are presented in Figure 4 and in the Supporting Information, Figure S1, respectively. Histograms of the SiO₂ shell thicknesses are provided in the Supporting Information, Figures S4−S5. For the PEG-SiO₂-GNRs, the proportional amount of TEOS was reduced (in comparison with the 10 mL scale) to facilitate formation of thinner SiO₂ shells. Dropwise addition of 400 μL of PEG-silane while stirring 30 min after completing addition of the TEOS solution was followed by stirring for another 30 min and then allowing the reaction to continue for 20 h without stirring. Combining reduction of the amount of TEOS and addition of PEG-silane allows for growth of ultrathin SiO₂ shells.

**SiO₂ Overcoating under Non-Optimal Conditions.** While developing our optimized procedure for depositing uniform SiO₂ shells, several other morphologies were obtained under different conditions (10 mL scale), some of which are of interest for further exploration.

Since the CTAB coatings on GNRs template deposition of SiO₂, the presence of excess CTAB micelles allows for undesired growth of SiO₂ NPs that do not encapsulate GNRs. Instead of using our optimized two-step, high-speed centrifugation procedure, a slower centrifugation process (1700 g for 45 s) was performed to remove crystallized CTAB while the sample was still cold after refrigeration. This milder purification process still leaves a significant amount of CTAB in solution, which causes formation of SiO₂ NPs that do not encapsulate GNRs, along with SiO₂-GNRs (Figure 5a).

When a larger amount (1000 μL) of 20% TEOS solution is introduced into the GNR solution during the 5 min injection (conducted in the same manner as the optimized method, only adding a larger amount of TEOS solution), irregular SiO₂ shells result, where one end of the GNR often protrudes out through the SiO₂ shell (Figure 5b). The nonuniformity might be explained by the larger amount of methanol in which the TEOS is diluted. When the methanol:water ratio exceeds a threshold value, CTAB may begin dissolving from the surface of the GNRs. Curvature at the ends of the GNRs also makes the CTAB layer less stable and more easily removed from the ends than along the sides of the GNRs. Removing the CTAB coatings that template SiO₂ deposition on some regions of the GNRs could prevent coating of those regions with SiO₂.58 The asymmetric SiO₂ overcoating of GNRs makes them patchy (or Janus) particles, which are of interest for electronic devices.

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**Figure 4.** Large-scale (100 mL) synthesis of PEG-SiO₂-GNRs with 2.2 ± 0.5 nm thick shells: (a) TEM image and (b) optical absorbance spectrum with inset of a TEM image at higher magnification.
thickness of 14.2 μm shorter reaction time (10 h, rather than the standard 20 h) when 500 cores remain protected by the SiO2 shells and do not coalesce reduced steric blockage, as compared with the sides. The GNR might be attributed to the higher surface energy of the tips and reaction time may also be used to control the SiO2 shell identical reaction conditions (Figure 1f). Therefore, the 14.2 nm were obtained (Figure 5d), in comparison with 17.3 ± 2.6 nm.

Figure 5. TEM images of SiO2-GNRs synthesized on the 10 mL scale under non-optimal conditions: (a) containing additional spherical SiO2 NPs when excess CTAB is present in the solution, (b) irregular shells when a large volume (1000 μL) of 20% v/v TEOS solution is used, (c) cross-linking, when the duration of the reaction is too long (5 days, after injecting 500 μL of 20% v/v TEOS solution), and (d) for a shorter reaction time (10 h, rather than the standard 20 h) when 500 μL of 20% v/v TEOS solution was injected, which gave a reduced shell thickness of 14.2 ± 2.0 nm rather than 17.3 ± 2.6 nm.

biosensing, drug delivery, and catalysis. Patchy SiO2 overcoatings may also be used for the selective growth of other kinds of materials.58,65

Extending the reaction time (e.g., to 5 days) without stirring results in a cross-linked network of SiO2-GNRs (Figure 5c). Cross-linking is most favorable at the tips of SiO2-GNRs, which might be attributed to the higher surface energy of the tips and reduced steric blockage, as compared with the sides. The GNR cores remain protected by the SiO2 shells and do not coalesce together. Optical absorbance spectra of the cross-linked network (Supporting Information, Figure S6) exhibit a redshift and broadening in the LSPR. It may be possible to further control the degree of cross-linking by varying the reaction conditions. Supercritical drying of a dispersion of cross-linked SiO2-GNRs might give aerogels.66 The large number of junctions between SiO2-GNRs may also make these materials attractive for use as SERS substrates.67

Cross-linking at long reaction times highlights the importance of the reaction time as a parameter for controlling the SiO2 shell thickness. The reaction time for obtaining “optimal”, uniform overcoatings without cross-linking is coupled to other parameters, such as the concentrations and amounts of TEOS and GNRs. Termination with PEG-silane shows that, under optimal conditions, the SiO2 shell grows quickly during the first hour and then more gradually (Figure 2e). When a reaction using 500 μL of the TEOS solution was stopped after 10 h, uniform SiO2 coatings with a thickness of 14.2 nm were obtained (Figure 5d), in comparison with 17.3 nm when the reaction was run for 20 h under otherwise identical reaction conditions (Figure 1f). Therefore, the reaction time may also be used to control the SiO2 shell thickness, but we favor 20 h reaction times to allow the reaction to proceed further toward completion and to use the amount of TEOS and addition of PEG-silane to control the shell thickness.

CONCLUSIONS
SiO2-GNRs have been synthesized on a large scale with tunable shell thicknesses by either varying the amount of TEOS or adding PEG-silane to terminate shell growth. By optimizing the CTAB concentration, uniform SiO2 coatings have been obtained, while avoiding formation of SiO2 NPs that do not encapsulate GNRs. The minimal change in the optical absorbance spectrum during the overcoating reaction indicates that cross-linking between (PEG-)SiO2-GNRs is also avoided. This method may be extended to other kinds of NP core materials coated with CTAB to template SiO2 deposition. Large-scale synthesis of (PEG-)SiO2-GNRs will facilitate applications that require large amounts of material, and PEG-SiO2-GNRs may be especially well-suited for biomedical applications.

ASSOCIATED CONTENT
Supporting Information
Additional TEM images and optical absorbance spectrum for a large-scale synthesis of SiO2-GNRs. Histograms of SiO2 shell thickness on SiO2-GNRs and PEG-SiO2-GNRs. Optical absorbance spectra of uncoated and cross-linked SiO2-GNRs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This research was supported by the National Science Foundation (DMR-1056653 and the Research Triangle MRSEC, DMR-1121107) and the National Institutes for Health Grant 1R21HL111968-01A1. The authors acknowledge T.H. LaBean for use of his high-speed centrifuge and the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.

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