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Single-Step Coating of Mesoporous Silica on Cetyltrimethyl Ammonium Bromide-Capped Nanoparticles

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ABSTRACT

A generalized, single-step synthesis procedure to coat individual cetyltrimethyl ammonium bromide- (CTAB) capped nanoparticles with a thin layer of mesoporous silica is outlined. This coating method was demonstrated on CTAB-capped Au nanorods and CTAB-transferred CdSe/ZnS quantum dots with silica coatings ∼15 nm thick containing pores ∼4 nm in diameter. This porous silica coating can serve as a platform for further surface modification to facilitate the rapid translation of nanoparticles to a wide range of end applications.

The development of a general and simple method to coat as-synthesized nanoparticles such that their surfaces can be easily modified would assist in translating promising new nanoparticles into novel and niche applications.[1,2] Effective wet chemical synthesis methods for nanoparticles of different shapes, sizes, and materials have been extensively reviewed in the literature.[3] However, the successful integration of as-synthesized nanoparticles into useful devices is not trivial because these nanoparticles often require application-specific coatings to passivate and/or fuse the nanoparticle to target molecules or surfaces.[2] Such interfacial coatings are usually synthesized as a continuation of the nanoparticle fabrication process, using a synthetic route that is often nanoparticle- or laboratory-specific, and not easily transferable between materials, structures, and applications. The development of a common platform coating that can be synthesized in a separate, successive step can decouple issues related to the chemistry of nanoparticle fabrication from user-dependent, application-specific optimization. For maximum adaptability, the ideal common platform coating should be potentially multifunctional, allowing both a surface for simple conjugation to target molecules and the ability to adjust its morphology to control the degree to which the encapsulated nanoparticle interacts with its surrounding environment. If end-users themselves can independently tailor as-synthesized nanoparticles for their specific applications through the adoption of a simple and generalized coating technology, the full range of available nanoparticles can be made widely accessible to the scientific community.

Silica is an excellent candidate for such a generalized platform coating as it is an extensively studied biomaterial with a surface that can be chemically modified with other ligands for conjugation to molecular targets. Smooth, uniform silica shells have been successfully deposited on a variety of colloidal particles of metals,[4−10] metal oxides,[11−13] and semiconductors[14] based on the well-known Stöber method.[15] However, the syntheses of these silica coatings typically require their own intermediate coatings and/or are material specific, relying on the existing surface coating of the as-synthesized colloid (e.g., poly(vinylpyrrolidone) on silver nanowires,[8] citrate-stabilized silver nanoparticles,[6] Daxad 19-stabilized silver nanoparticles),[5] or are exclusive to the material itself (e.g., iron oxide's strong native affinity toward silica).[12] Although the use of intermediate coatings can arguably form the basis of a common silica-coating procedure, these themselves are generally multistep procedures that require several additional functionalization steps to form an intermediate coating layer for the deposition of silica (e.g., adsorbed polymer poly(vinylpyrrolidone),[1] a silane coupling agent,[9,10] or polyelectrolytes[4]). Finally, although the thickness of the smooth, uniform silica coatings that typically result from these syntheses can be tightly controlled, the morphology of the coatings is often fixed and generally does not allow for the exposed surface area or degree to which the encapsulated nanoparticle interacts with its environment to be adjusted over a wide range.

Cationic surfactant−silicate systems have long been used to synthesize bulk, film, and particle silicate mesoporous structures,[16] and from this basis mesoporous silica shells have been successfully deposited on solid cores using CTAB (cetyltrimethyl ammonium bromide) cationic surfactant molecules as the structure-directing agent.[17−20] In previous studies, the mesoporous coatings were developed by simple stoichiometric mixing of the silicate and organic components,

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with the nanoparticles acting as nucleation sites for the growth of the mesoporous shell. In these methods, the deposition of a thin intermediate layer on the nanoparticles (e.g., microporous silica[18−20] or poly(vinylpyrrolidone)[17]) prior to mesoporous silica growth was found to be necessary to result in high mesoporous silica-coating yields for single nanoparticles.

In this report, we outline a simple method for the direct coating of single nanoparticles with thin, highly porous silica shells without an intermediary coating step. We hypothesized that CTAB molecules strongly localized on individual nanoparticles can be used as the template for the three-dimensional polymerization of a common alkoxide-based silica precursor, tetraethyl orthosilicate (TEOS), for high-yield coating of nanoparticles with mesoporous silica. CTAB molecules, which can serve not only as the stabilizing surfactant for the nanoparticles in the aqueous phase, can also serve as the organic template for the formation of the mesoporous silica coating via base-catalyzed hydrolysis of TEOS and subsequent condensation of silica onto the surface of the CTAB molecules.

This procedure presents an atypical approach to the coating of CTAB-capped nanoparticles with silica, as previous studies suggested that exposed CTAB does not lead to the controlled hydrolysis and condensation of TEOS on the nanoparticle surface and that the deposition of intermediate coatings on CTAB-capped nanoparticles prior to silica coating is required.[4,10] To obtain the smooth surface desired for certain applications, we propose that the mesoporous silica coating can be used as a scaffold for the deposition of more TEOS to alter the morphology of the silica shell. Furthermore, the silica surface can additionally allow the attachment of other targeting agents tailored for different applications. As CTAB is a common surfactant used in the synthesis of nanoparticles using microemulsions,[3b] as a shape-inducing agent for metal (e.g., Au nanorods (NRs))[21] and metal oxide (e.g., Cu_2O whiskers)[11] nanoparticles, and has also been used as a secondary surfactant to transfer hydrophobic ligand-capped nanocrystals from their organic growth medium to the aqueous phase,[22] the CTAB-terminated nanoparticle system may thus provide a common foundation for mesoporous silica coatings. To demonstrate that the same coating methodology may be employed independent of the existing surfactants/capping ligands on as-synthesized nanoparticles fabricated in organic versus aqueous media, this method was directly demonstrated on as-grown CTAB-stabilized Au NRs and on octadecylamine-capped quantum dots (QDs) after phase transfer to water using CTAB.

In the case of covering Au NRs with porous silica, the coating synthesis is a straightforward, single-step procedure. Au NRs (with lengths of ~35 nm and diameters of ~10 nm) were synthesized in aqueous media using CTAB as the shape-inducing surfactant according to a previously published method.[21] After the removal of excess CTAB surfactant by centrifugation, the as-synthesized Au NRs were redispersed in Milli-Q water (Au NR concentration of ~10^{15} particles/L). Porous silica coatings were formed by injecting TEOS ($Si(OEt)_4$) to create a concentration of ~8 mM in the CTAB-coated Au NRs solution (pH adjusted to 10~11) and then stirring for several days. Surprisingly, without any intermediate coating or pretreatment of the Au NRs, mesoporous silica coatings were consistently and uniformly deposited on the Au NRs. The coatings were ~15 nm thick with disordered pores ~4 nm in diameter separated by silica walls ~2 nm thick (Figure 1). The disordered nature and pore size of these silica coatings are consistent with previous work in which very large mesoporous silica spheres (~150 nm in size) were used to encapsulate multiple CTAB-transferred nanoparticles clustered together.[13] Previous studies of mesoporous silica shell growth on nanoparticle surfaces suggest a three-stage mechanism for the formation of the mesoporous shell: silica oligomerization, formation of silica/CTAB primary particles, and the aggregation of the primary particles.[19] In this system, the CTAB surfactant molecules were strongly localized on the nanoparticle surfaces compared to in solution (~0.0015 M), causing silica/CTAB primary particles to form and aggregate directly on the nanoparticle surfaces, which may have promoted mesoporous shell growth compared to free mesoporous silica particle formation.

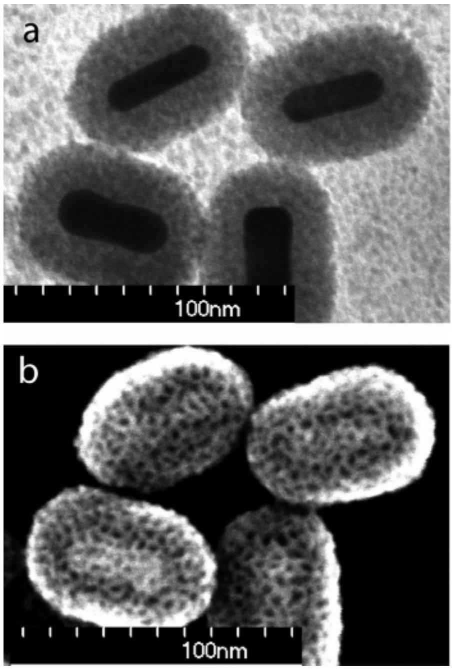

Figure 1. Scanning transmission electron spectroscopy (STEM) images of mesoporous silica-coated Au nanorods. (a) TEM image and (b) SEM image.

From transmission electron microscopy, it was found that the formation of the mesoporous silica coating occurred within 1 h of the final injection of the TEOS (Figure 2a). However, there appeared to be nonuniform development of the mesoporous coating on the Au NRs, particularly at their ends. The silica coating partially detached from the Au NRs after 1 h of reaction, which may indicate incomplete polymerization or poor mechanical stability exacerbated by centrifugation. After 10 h of reaction time, although the morphology of the coating did not appear to change appreciably, the mesoporous coating appeared to be slightly thicker than at earlier time periods with more complete coating of the ends of the NRs (Figure 2b). The completed

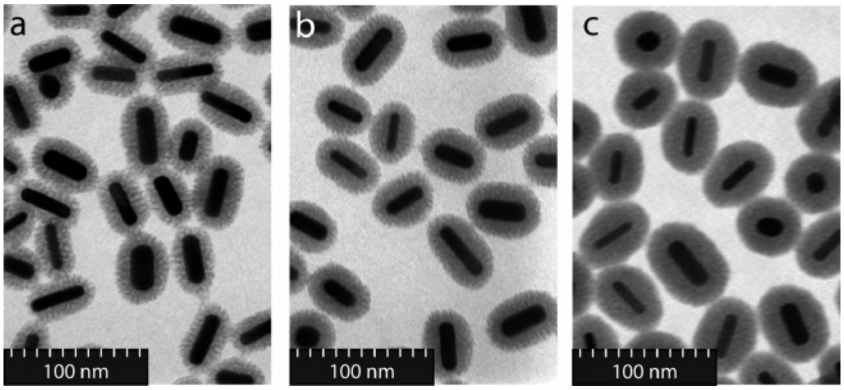

Figure 2. TEM images of mesoporous silica-coated Au NRs after (a) 1 h, (b) 10 h, and (c) 500 h.

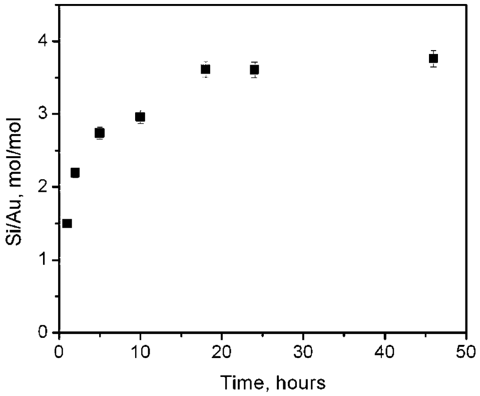

Figure 3. Ratio of Si/Au as a function of TEOS reaction time for mesoporous silica deposition on Au NRs. Time zero is taken to be after the final injection of TEOS to the Au NR solution.

reaction that resulted in the ~15 nm thick mesoporous silica coating on the Au NRs can be observed in Figure 2c, taken after 500 h of reaction time. Corresponding measurements of the Si/Au ratio taken by inductively coupled plasma atomic emission spectroscopy of the Au NRs were used to further investigate the development of the mesoporous silica coating as a function of reaction time (Figure 3). Consistent with the electron microscopy images, the Si/Au ratio increased in the initial ~18 h of the reaction after which the Si/Au ratio became stable. The Si/Au ratios were stable for a minimum of 3 weeks after the initiation of the reaction.

CdSe/ZnS core/shell QDs synthesized in octadecylamine were used to investigate whether the same silica-coating procedure could be applied to nanoparticles synthesized in organic solvents without a native CTAB coating. Monodisperse CdSe/ZnS core/shell QDs capped with octadecylamine were synthesized according to a previous method[23] and were transferred to water using CTAB.[22] The transfer of the QDs to water using CTAB was determined to be a key step for successful growth of silica coatings on individual QDs. Suboptimal transfer of QDs into water can result in the formation of QD clusters, which will lead to encapsulation of multiple QDs with the silica coating. After removal of excess CTAB from the water solution, the silica coating was grown on the QDs in a similar manner as in the case of the Au NRs. TEOS was injected into the pH-adjusted solution containing the CTAB-transferred QDs and stirred for several days. The morphology of the silica coating (shell thickness, pore size, and silica wall thickness) on the QDs was found to be similar to that on the Au NRs (Figure 4), although the QDs were significantly smaller and had higher curvatures than the Au NRs.

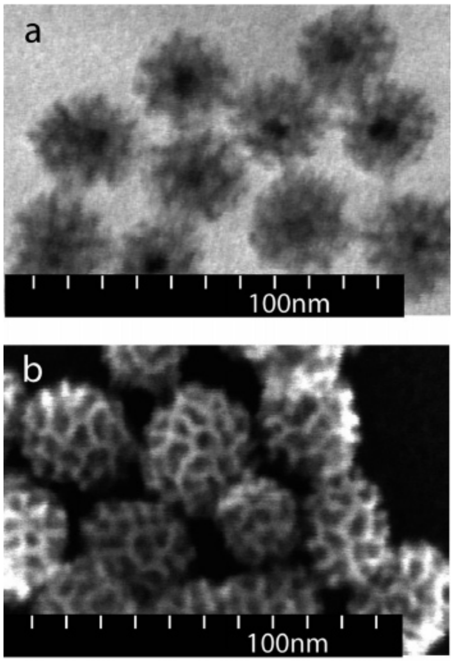

Figure 4. STEM images of mesoporous silica-coated CdSe/ZnS QDs. (a) TEM image and (b) SEM image.

To demonstrate that the morphology and the thickness of the mesoporous silica coating can be altered, additional silica layers were deposited using the Stöber method.[15] For controlled and homogeneous deposition of TEOS on the mesoporous silica layer without the nucleation of free silica particles, the CTAB surfactant must be completely removed from the surface of the mesoporous silica coating.[4,9] To do this, the silica-coated nanoparticles were washed a minimum of 5 times by centrifugation and redispersion in methanol. The removal of the adsorbed positively charged CTAB surfactant from the surface of mesoporous silica-coated Au NRs was confirmed using zeta potential measurements. With no washing, the adsorption of the cationic surfactant leads to a positively charged surface of ~ +50 mV. The gradual removal of the CTAB surfactant after 3−4 washings is

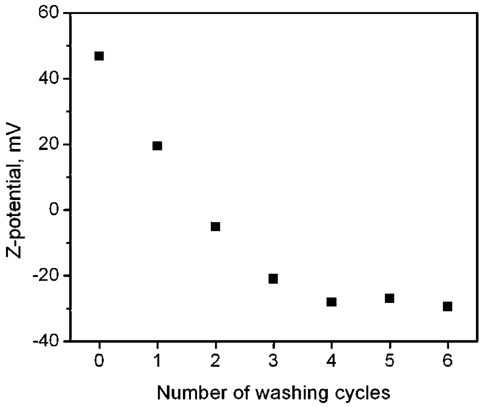

Figure 5. Zeta potential measurements of mesoporous silica-coated Au NRs as a function of washing cycles.

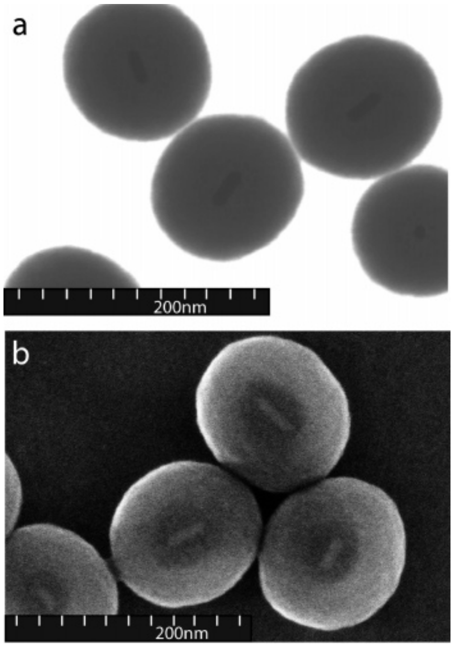

Figure 6. STEM images of very thick silica coating grown on top of mesoporous silica-coated Au nanorods. (a) TEM image and (b) SEM image.

reflected in the decrease of the zeta potential measurements, stabilizing to a negatively charged, CTAB-free surface of ~ -30 mV (Figure 5).

Typically, the washed silica-coated nanoparticles of concentration $\sim 10^{15}$ particles/L were dispersed in a mixture of methanol and an ammonia−water solution. Several consecutive injections of TEOS were conducted to achieve a desired thickness of silica coating.[8−10,12] The thickness of the silica coating increased with time, as long as there was sufficient TEOS in solution. An example of this growth can be seen in Figure 6, where a very thick (~60 nm) layer of silica was deposited on cleaned porous silica-coated Au NRs by injecting TEOS to a concentration of 45 mM. The growth of the additional silica layer smoothed out the surface of the porous silica and reduced the aspect ratio such that the overall structure became more spherical with silica growth. It is not yet clear if the further growth of silica can completely fill the mesoporous holes of the initial silica layer. It is anticipated that the degree to which the underlying pores are filled will be dependent on the deposition rate of the additional silica layers.[8−10,12]

In summary, we outline a simple, robust procedure to encapsulate CTAB-coated nanoparticles with mesoporous silica. The as-synthesized coating is highly porous and can allow interaction between the encapsulated nanoparticle and its surrounding environment. This porosity may facilitate the removal of the initial nanoparticle to make hollow silica mesoporous nanoshells[10,24] or allow the controlled release of drug molecules from the mesopores.[13] The mesoporous coating can also act as a scaffold for the growth of further layers of silica or for the conjugation of other molecules.[25] This technique can clearly be extended to other CTAB-coated nanostructures and to colloids of other dimensions and may be used as a platform for multicomponent, hierarchical hybrid systems.[2] This method represents a relevant and directed approach to the design of new and novel nanoparticles and promotes the adoption, modification, and translation of various as-synthesized nanoparticles to individualized applications at the discretion of the end-user.

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Supporting Information Available: Experimental and instrumental details, synthesis of Au NRs, mesoporous silica coating on Au NRs and CdSe/ZnS QDs, and deposition of additional layers of silica on mesoporous silica. This material is available free of charge via the Internet at http://pubs.acs.org.

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