Organic–Inorganic Hybrid Composites

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A Thin Silica–Polymer Shell for Functionalizing Colloidal Inorganic Nanoparticles**

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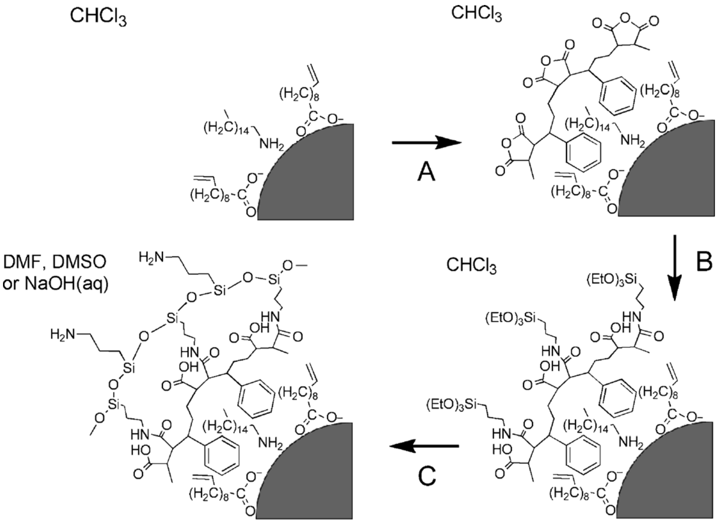
Universally applicable, thin, and reproducible coatings for colloidal nanoparticles are a prerequisite for almost any of the wide-ranging applications of these exciting materials. Many techniques developed for coating and functionalization of nanoparticles have restrictions toward future applications with regard to key properties, such as solubility, size, and colloidal stability.[1] The greatest weakness of current methods, such as ligand exchange,[2] silica shells of various thicknesses,[3–5] and organic shells,[6,7] is the strong dependence of the chemistry on the inorganic core surface. Herein, InP/ZnS and Fe_3O_4 colloidal inorganic nanoparticles that have different surface properties are coated with a thin, cross-linked and functionalized shell containing organic and inorganic layers. Although not shown in this report, the method has also been applied to other colloidal particles, such as Au, $CuInS_2$ (CIS), CdSe/ZnS, and InP. This work expands nanoparticle coating techniques to develop a completely new type of hybrid coating technique. Using silicon as a marker, we conclusively prove that the underlying amphiphilic polymer foundation[8–12] is arranged on the particle surface as predicted in past reports.



Scheme 1. Formation of the thin layer around the nanoparticle. A) The amphiphilic polymer, PSMA, wraps around the particle. B) The silica precursor, TEAPS, opens the anhydride ring on the polymer and attaches the silane to the polymer. C) Polymerization between the bound and free TEAPS to form a thin silica layer. The solvent used at each stage is noted above each structure.

The synthesis of the hybrid surface layer takes advantage of the adsorption of amphiphilic polymers to the hydrophobic stabilizing ligands on the colloidal nanoparticle surfaces. Commercial poly(styrene-*co*-maleic anhydride) (PSMA) was adsorbed as described by Mulvaney and coworkers (Scheme 1, step A).[8] The silica precursor, 3-aminopropyltriethoxysilane (TEAPS), was then reacted, resulting in a silane being tethered to the polymer (Scheme 1, step B). Generally, other methods for thin silica layers[3,4,13] use trimethoxysilanes as silica precursors. In an effort to separate the nucleophilic attack of the silica precursor to the polymer foundation and the polymerization to form silica the triethoxysilane equivalent was used, thus attempting to resolve steps B and C in Scheme 1. The temperature of the reaction mixture was also lowered to further aid this process. The polymerization of the tethered silica precursors occurs (Scheme 1, step C) resulting in particles that are soluble in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and 0.05 M NaOH (aq).

High-resolution transmission electron microscopy (HRTEM) and dynamic light scattering (DLS) measurements (Figure 1) both show that the particles were well-dispersed in solution. The DLS results show an increase in the hydrodynamic radius of the particles during the synthesis indicating that a layer has formed on the surface of the particles. The HRTEM image of a single hybrid-layer-coated particle (Figure 1b) showed no indication of a layer. This is unsurprising because the layer is amorphous and consists of elements that scatter electrons weakly. Once transferred to 0.05 M NaOH (aq) the zeta potential of the colloid was −37.1 mV indicating a good stability.

Retention of nanoparticle properties when coated with a hybrid layer is fundamental for their application. To investigate the retention of nanoparticle properties, the luminescence of InP/ZnS quantum dots was monitored during the formation of the layer. The luminescence decreased by approximately 33 % between polymer coating and growth of the silica component of the layer. Once transferred to DMF the luminescence was still present although approximately

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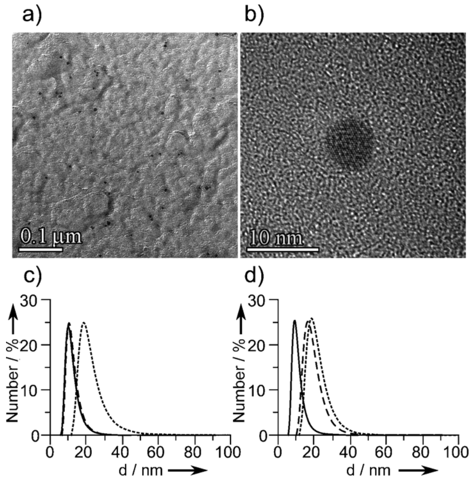

Figure 1. a) TEM image showing well-separated Fe_3O_4 particles coated with hybrid layer and b) HRTEM image of a single Fe_3O_4 particle coated with the hybrid layer. c) DLS size distribution showing InP/ZnS particles coated with the hybrid layer and transferred to 0.05 M NaOH (aq). d) DLS size distribution showing Fe_3O_4 particles coated with the hybrid layer, after transfer to DMF. In c) and d) the full lines represent the uncoated particles in $CHCl_3$, the dotted lines represent particles after coating in $CHCl_3$ and the dashed lines represent particles in the new respective solvent (*d* = particle size).

halved relative to the luminescence observed before the transfer to $CHCl_3$.

The IR spectrum of the hybrid-layer-coated particles was compared to that of the layer precursors (Figure 2). The hybrid layer contains many chemical functionalities (Scheme 1), which complicates the characterization, but the presence of an amide group (1556 and 1634 cm^{-1}; Figure 2, top), and the disappearance of the vibrational modes of acid anhydride from the original polymer (1775 and 1855 cm^{-1}, Figure 2, bottom), verify the successful reaction between silane and polymer on the particle surface. The hybrid layer IR spectrum shows a broad Si–O band (3500 cm^{-1}–2500 cm^{-1}; Figure 2, top), which is a characteristic feature of amorphous silica. The Si–O peak in the silane spectrum (1067 cm^{-1}) is still present in the hybrid layer spectrum but is widened (1068 cm^{-1}). Both signals indicate Si–O bonds from silica are present in the hybrid-layer-coated particle. Numerous bands from both silane and polymer can be seen superimposed on the coated particle spectrum, demonstrating retention of key functionalities. The weak amine peaks observed in the silane spectrum (1600 cm^{-1}, 3366 cm^{-1}) are masked by other features in the hybrid layer spectrum.

To confirm the presence of multiple nitrogen environments, X-ray photoelectron spectroscopy (XPS) was used. The spectrum for the N 1s electron from InP/ZnS with the hybrid layer (Figure 3) shows an asymmetric peak, not present in the XPS results of the untreated InP/ZnS and after addition of polymer. Fitting was achieved using a pair of Gaussian functions separated by 1.71 eV, which confirms two environments: an amine (lower energy) and an amide (higher energy) environment. Other peaks, such as the C 1s peak, contained too many potential environments for an accurate analysis and were not fitted.

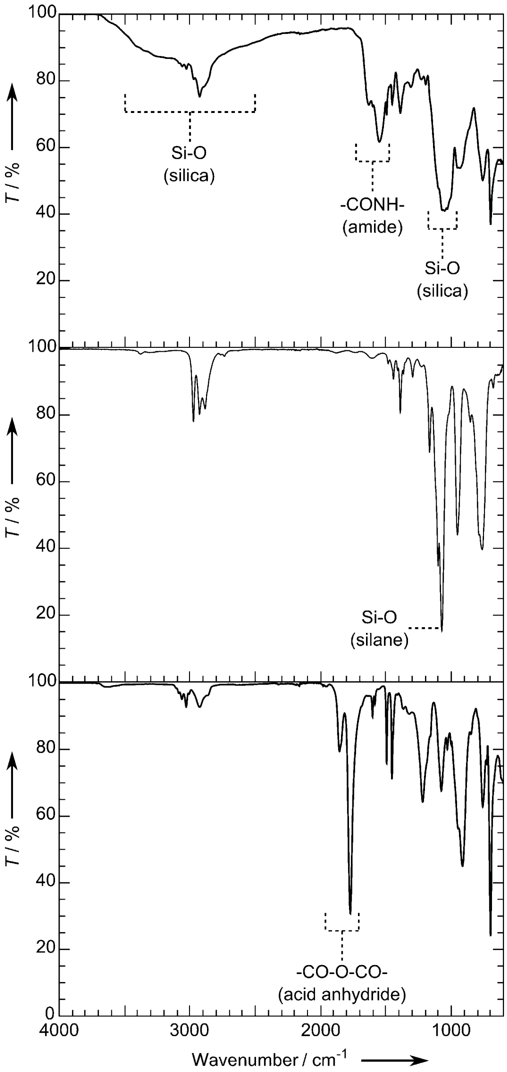

Figure 2. IR spectra (*T* = transmittance) with the key functionalities labeled for Fe_3O_4 coated with the hybrid layer (top), silane precursor (middle), and poly(styrene-*co*-maleic anhydride) (bottom).

Figure 3. XPS spectrum observing the N 1s electron of InP/ZnS coated with hybrid layer. XPS spectrum (dots), baseline (dashed line), Gaussian function for the amide group (dotted and dashed line), Gaussian function for the amine group (dotted and long dashed line) and envelope formed from both Gaussian functions (full line).

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Energy dispersive X-ray spectroscopy (EDXS) measurements were performed on individual Fe_3O_4 particles at the different stages of layer formation (Figure 4). As expected, polymer-coated particles showed no silicon signal. After reaction with silane and transfer to DMF a silicon peak was evident and the oxygen peak increased dramatically, confirming the presence of these elements in the outer coating. The large copper and carbon peaks originate from the TEM grid.

Electron energy loss spectroscopy (EELS) images were collected to locate electrons that had lost energy to selected elements. Figure 5 (left) shows the TEM image for Fe_3O_4 particles coated with the hybrid layer; as previously seen in Figure 1, the hybrid layer is not visible. The image was filtered to observe electrons that had lost energy to Fe and the particles are still visible (Figure 5, center). The image was again filtered to observe electrons interacting with Si (Figure 5, right). Si is clearly located on the surface of the Fe_3O_4 particles, which appear slightly larger in the Si-filtered image, indicating that the diameter of the hybrid-layer-coated particle is larger than the initial particle (consistent with the DLS data, Figure 1) and also that the coating is rather uniform.

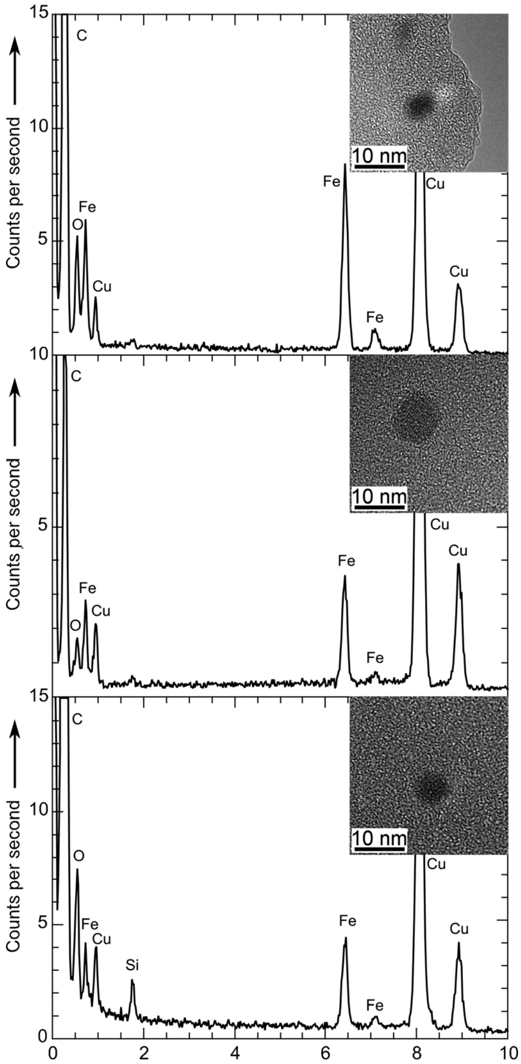

Figure 4. Energy dispersive X-ray spectroscopy (EDXS) measurements of Fe_3O_4 at each stage of hybrid layer formation with an inset TEM image depicting the region of the EDXS measurement. Top panel: Untreated Fe_3O_4 nanoparticles, middle panel: Fe_3O_4 particles coated with polymer foundation, and bottom panel: Fe_3O_4 with complete hybrid layer.

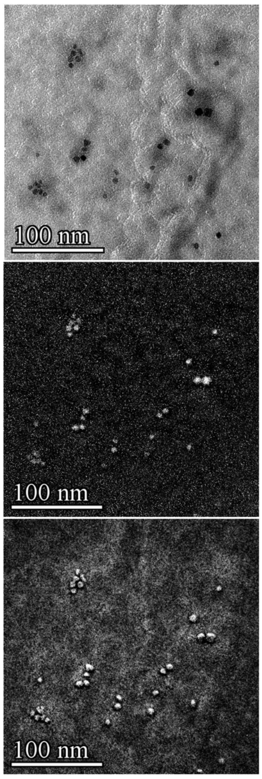

Figure 5. EELS images of Fe_3O_4 nanoparticles with hybrid layer. TEM image of Fe_3O_4 nanoparticles (top), EELS image showing Fe only (middle), and EELS image showing Si only (bottom).

The use of amphiphilic polymers with colloidal inorganic nanoparticles has become increasingly popular but little direct proof exists as to the location or uniformity of the layer. Silicon in the silica layer provides a marker to locate the amphiphilic polymer foundation using EELS measurements. Figure 5 serves to prove that the amphiphilic polymer is located on the surface of individual particles and the layer is uniform across the surface. The EDX measurements (Figure 4) also support this conclusion though not as elegantly as the EELS.

In summary, a novel hybrid material consisting of organic and inorganic polymers has been successfully synthesized around the surface of two distinct types of colloidal inorganic nanoparticles forming a thin layer which results in non-aggregated colloidally stable particles. The layer was characterized using IR spectroscopy and XPS, confirming that the reaction had taken place by the presence of amide and amine groups and silica. The location of the hybrid material was confirmed using EDXS and EELS showing that the layer was formed on the surface of the particles. As a consequence silicon acts as a marker proving that the amphiphilic polymers

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used are located on the surface of the colloidal inorganic particles thus supporting the work of Parak, Mulvaney, and others.[8,10,12] It is envisioned that this material can act as a foundation for further incorporation of colloidal inorganic particles into more complex materials.

Experimental Section

The procedure for the synthesis of InP/ZnS quantum dots was based on an earlier publication by Xu et al.[14] made up to 7 mL. The procedure for the synthesis of Fe_3O_4 particles used was described by Lattuada and Hatton[15] and the saturated particle in toluene solution was diluted 100-fold. An amount of 0.5 mL of this solution was used in a typical reaction.

To determine the quantity of poly(styrene-*co*-maleic anhydride) (Aldrich, $M_n = 1700$; PSMA) required, a series of water transfer experiments were undertaken where the amount of PSMA was varied using the method of Lees et al.[8] Typically, InP/ZnS (100 μL) redispersed in chloroform (1 mL) required 0.9 mg of PSMA in $CHCl_3$ to achieve a transfer when 0.5 mL of a 0.12 M aqueous solution of ethanolamine (Sigma–Aldrich, $\geq 99.9\,\%$) was added.

Coating of colloidal inorganic particles with a thin hybrid organic–inorganic layer was achieved as follows:

Using InP/ZnS as an example, InP/ZnS (100 μL) were redispersed in chloroform (1 mL) and were stirred with PSMA (0.9 mg) overnight. 3-Aminopropyltriethoxysilane (7 μL, Sigma–Aldrich, 99 %) was added and stirred at 18 °C for 24 h. Toluene was added to precipitate the particles. The resulting precipitate was redispersed in tetrahydrofuran (1 mL, Sigma–Aldrich, $\geq 99.5\,\%$), dimethylsulfoxide (1 mL, Sigma–Aldrich, $\geq 8.0\,\%$) or 1 mL of 0.05 M NaOH (aq) (Fisher Scientific, $\geq 98.0\,\%$).

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