Formation of Cobalt Oxide Nanotubes: Effect of Intermolecular Hydrogen Bonding between Co(III) Complex Precursors Incorporated onto Colloidal Templates

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ABSTRACT

Several water-soluble cobalt(III) complexes were employed as precursors to form cobalt oxide nanostructures. These complexes were incorporated into polyelectrolyte multilayers precoated onto colloidal particles, followed by calcination. Cobalt complexes with strong intermolecular hydrogen bonding form one-dimensional Co₃O₄ nanotube structures. Short Co₃O₄ nanotubes with defects and broken spheres are formed when cobalt complexes with weak or no intermolecular hydrogen bonding are used. The sites for disulfide bond formation present on some complexes were found to be unessential for the nanotube formation.

A great deal of effort has been directed toward the synthesis of one-dimensional (1-D) nanostructured materials with a high aspect ratio (e.g., nanotubes). The unique properties of these materials could find application in areas as diverse as electronics, optics, materials research, and medical science. Numerous papers have been published on the preparation and characterization of these new materials. These materials include, but are not limited to, carbon nanotubes, WS₂, MoS₂, BN, V₂O₅, TiO₂, Al₂O₃, SiO₂, and the recently reported bismuth nanotubes. Despite the tremendous amount of work on the development of synthetic methodologies for and the exploration of various applications of these materials, there has been limited work about the elucidation of the relationship between the chemical nature of the materials involved in the syntheses and the final nanostructures. Nevertheless, several recent papers addressing this issue indicate that it is important to understand the mechanism for the formation of these 1-D structures if optimizing the preparative procedures and tailoring the functionality of the final materials are desired.

We wish to report the effect of altering the functional groups of the precursors incorporated into polyelectrolyte (PE) multilayers predeposited onto colloidal particles on the final shapes of the nanomaterials. Recently, the treatment of precursors incorporated into the PE multilayers coated onto templates, such as nanosphere, nanorod, and planar surface, has been demonstrated by Caruso and co-workers to be a versatile technique for the synthesis of nanomaterials. Thus far, it appears that shapes of the as-prepared materials are generally dictated by those of the templates. We show here that fine-tuning the chemical structures of the precursors incorporated into the PE multilayers can have a profound influence on the shapes of the resultant nanomaterials.

In our approach, polystyrene (PS) colloidal particles (640 nm in diameter, measured by AFM) were precoated with PE multilayers via the layer-by-layer (LbL) method, followed by infiltration of a precursor (e.g., precursor 1, (cysteinato-N,S)bis(ethylenediamine)cobalt(III), shown in Figure 1). Broken hollow cobalt oxide nanospheres were initially expected from calcination of the template because the PE/precursor-coated colloidal templates are spherical (Route 1 in Figure 2). Surprisingly, exclusive formation of cobalt oxide nanotubes was observed. We found that the use of precursor 1 caused these colloidal particles to aggregate into a unique pearl necklace-like structure that we believe is the new template for the nanotube formation. This new procedure should complement other existing methods for the production of inorganic nanotubes. Thus, the chemical origin for threading the PE/precursor-coated PS nanospheres...
Precursor 1 is capable of forming both intermolecular hydrogen bonding (through the free acid group) and disulfide bonds (through the oxidation of the thiolato group). Because an attempt of using FTIR to detect any peaks associated with the S-S stretching of the putative disulfide bond was not successful (presumably due to the overwhelming background signals arising from the abundant PE and PS molecules), we decided to investigate the mechanism by varying the functional groups on the precursor to prohibit either the intermolecular H-bonding or disulfide bond formation.

In addition to precursor 1, three other cobalt complexes (structures shown in Figure 1) were employed as precursors. 25 In designing these precursors, several criteria were followed in order to keep the preparative parameters for the nanomaterials constant. First, all of these precursors are water soluble and contain a Co(III) center coordinated by ethylenediamine ligands. Second, the cations bear the same number of charges (2+). Finally, the functional groups on all the precursors have been systematically varied. Specifically, the sulfenato complex (precursor 2) can only form hydrogen bonding (disulfide bond formation is not possible because the thiolato group has been oxidized) and the coordinated water molecule in precursor 3 should form much weaker hydrogen bonds both for steric and electronic reasons. Precursor 4 cannot form H-bonds but might form a disulfide bond through linking unoxidized sulfide sites on two adjacent molecules.

We first employed a flow-injection quartz crystal microbalance (FI-QCM) 26 to study the infiltration behavior of the four precursors at crystals precoated with PE multilayers. The FI-QCM can monitor the incorporation of the precursors into the PE layers in situ and provide insight to the relationship between the precursor structure and the amount of precursor infiltration. Figure 3a shows the time-resolved QCM response to the precursor infiltration. It is clear that the amount of infiltration increased with the PE layer number. The linear dependence of the amount of precursor incorporated on the number of PE layers is shown in the inset ($R^2$ value = 0.995). As can be seen, the incorporation of a greater quantity of a given precursor into a thicker PE film suggests that the extent of precursor infiltration can be precisely controlled by varying the number of PE layers. When the outermost PE layer was changed to the positively charged PDADMAC, no precursor incorporation was observed. As shown in recent work by Caruso and co-workers, 22 the incorporation of a precursor into the PE layers should be driven by the electrostatic attraction between the positively charged precursor and the negatively charges on the outermost PE layer (i.e., the negatively charged PSS). We also compared the difference in the infiltration behavior among the different precursors. Figure 3b displays a series of FI-QCM responses showing the amounts of precursors infiltrated at films of the same number of PE layers. The fact that all precursors can be incorporated into the PE layers suggests that they are suitable candidates for the formation of either type of nanomaterials shown in Figure 2. The analogous QCM responses between precursors 1 and 2 could be ascribed to the similarities in their molecular weights and structures. The other two precursors exhibited different QCM responses with either a smaller (precursor 3) or a larger (precursor 4) mass change than that associated with precursors 1 and 2. The different QCM responses shown by the four precursors appear to be reflective of the difference among their chemical structures.

The colloidal particles incorporating different precursors were found to aggregate differently in solutions. Figure 4a is a representative TEM image showing the pearl necklace-like structure that interconnects colloidal particles containing PE/precursor 2, which is analogous to that derived from precursor 1. 23 However, the PS nanospheres incorporating precursor 3 or 4 were found to produce only randomly dispersed particles (Figure 4b). It is interesting to note that PS particles with PE coatings loaded with precursor 1 and 2...
did not yield 2- or 3-D structures. Although the exact reason for the preferential formation of the 1-D structure is not entirely clear, we believe that it is possible that adjoining two colloidal particles requires a relatively large number of H-bonds and the pearl necklace-like structure facilitates the formation of a greater number of intermolecular H-bonds between two adjacent colloidal particles. Because only one free acid group (the essential moiety for H-bond formation) is present on each octahedral Co(III) in precursor 1 or 2, the number of H-bonds between most colloidal particles would be reduced by the congested particle arrangement associated with the 2- or 3-D structure. Consequently, formation of the 1-D structure comprising interconnected particles is more stable than that of the 2- or 3-D structure.

We finally examined the shapes of the cobalt-containing nanomaterials calcined from precursors infiltrated into 5 bilayers of PDADMAC/PSS pre-deposited onto PS particles. We finally examined the shapes of the cobalt-containing nanomaterials calcined from precursors infiltrated into 5 bilayers of PDADMAC/PSS pre-deposited onto PS particles.

Figure 5 shows a SEM image of a cobalt oxide nanotube produced from calcination of the PS particles coated with PE layers containing precursor 1 or 2.

Figure 6 displays AFM and TEM micrographs of the cobalt oxide nanostructures. Bundles of cobalt oxide nanotubes were also observed by AFM. AFM images indicated that both precursors 1 and 2 yielded long nanotubes (Figure 6a and 6c). The tubular characteristics were further confirmed by the TEM image (Figure 6b). The length and diameter of the nanotubes were 3–4 \( \mu \text{m} \) and 200–400 nm, respectively. X-ray diffraction and selected area electron diffraction (SAED) patterns of nanotubes derived from both precursors all indicate that their compositions are of polycrystalline spinel \( \text{Co}_3 \text{O}_4 \). Energy-dispersive X-ray spectroscopy showed only signals associated with cobalt upon calcination, suggesting that all of the organic components from the precursor, the PE layers, and the PS cores had been removed. When precursor 3 was used, the resultant nanomaterials were found to be either shorter tubes and/or broken spheres with many defects (Figure 6d).
and 6e), whereas precursor 4 resulted in products that consisted of predominantly broken nanospheres. SAED and XRD analyses demonstrated that the formed nanostructures were also composed of spinel Co₃O₄ with polycrystalline phases.

As suggested above, the formation of Co₃O₄ nanotubes should originate from calcination of the pearl necklace-like structure. The PE shells separating the interconnected colloidal particles might have been ruptured by the gaseous species from the calcination step. Portions of the PE shells that were not between the colloidal particles experienced a smaller gas pressure and remained intact. With the increased calcination time, these shells further sinter and evolved into rigid nanotube structures of Co₃O₄. These processes are pictorially shown by Route 2 in Figure 2.

It appears that the prerequisite for the nanotube formation is the interconnection of several precursor/PE-coated nanospheres to form a new template, and the sole driving force for such an interconnection is the intermolecular H-bonding formation. This conclusion is supported by the observation that weaker H-bonding (precursor 3) or no H-bonding (precursor 4) can only give rise to much shorter nanotubes or broken nanospheres. In any case, it is apparent that disulfide bond formation (if any) is not an important factor for creating the nanotubes. Our conclusions are in agreement with several recent reports on the effect of H-bonding for the formation of linear tubular structures derived from cyclic polypeptides, for the synthesis of nanotubes originated from organic calix[4]hydroquinone, and for the production of tubular silica structures from organogel templates.

In summary, the mechanism for the formation of cobalt oxide nanotubes fabricated via a new route involving calcination of cobalt complex precursor/PE layers coated onto colloidal particles has been elucidated. This is accomplished by systematically varying the functional groups on the cobalt complex precursors. Although all precursors result in the formation of polycrystalline Co₃O₄, the shapes of the final products were found to be highly dependent on the functional groups on the precursors. When intermolecular H-bonding formation is favored, an interesting pearl necklace-like

Figure 6. AFM images of cobalt oxide nanostructures derived from the calcination of the various precursors incorporated into the PE layers precoated onto the PS particles. Images (a), (c), (d), and (f) represent the nanostructures from precursors 1, 2, 3, and 4, respectively. The TEM images in (b) and (e) show cobalt oxide nanostructures produced from calcination of precursors 1 and 3 incorporated into the PE coatings on the PS particles, respectively.
structure composed of several precursor/PE-coated colloidal particles can be formed in the solution and serves as the new template for the eventual nanotube formation. Our results demonstrate that shapes of nanomaterials produced through this scheme are related not only to the preparative parameters, but also to the presence of specific functional groups on the precursor molecules.

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References

(23) PDADMAC, Mw = 200 000–350 000, and PSS, Mw = 70 000 were acquired from Aldrich. 50 mL of a concentrated suspension of PS spheres (5.8 wt % solution, Interfacial Dynamics Corporation, Portland, OR) was diluted to 1 mL. 1 mL of a PDADMAC solution (containing 0.5 M NaCl) was added. After a 15-min PDADMAC adsorption, the excess PDADMAC was removed by three repeated centrifugation (3800 g, 10 min) and washing cycles. PSS (1 mg/mL, containing 0.5 M NaCl) was then added to the PDADMAC modified PS particle suspension. After the same deposition time, the adsorbed PSS was removed by three repeated centrifugation (3800 g, 10 min) and washing cycles. These steps were repeated to form a desired PE layer number. The subsequent step for incorporating the cobalt complex precursors (64 mM in water) followed the aforementioned procedure except that the time for the infiltration of cobalt complexes was 30 min. Finally the PS particles incorporating cobalt complexes were air-dried onto quartz substrates, and calcined at 385 °C (5 °C min⁻¹) for 2 h under N₂ and for 6 h under O₂.
(27) AFM images were collected in the contact mode with a Molecular Imaging (Phoenix, AZ) atomic force microscope. TEM measurements were performed on a JEOL JEM-2000 FX microscope operated at 200 kV. It is also capable of determining the electron diffraction pattern. SEM measurements were carried out with a Cambridge Stereoscan 250 instrument operated at 20 kV that is equipped with a Link energy-dispersive X-ray analyzer. The XRD measurements were carried out using a Rigaku X-ray diffractometer (Cu Ka radiation, 50 kV, 70 mA). PS particles incorporating cobalt complexes were placed onto silicon wafers, air-dried, and calcined for the XRD analysis.

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