Self-Assembled Gold Nanoshells on Biodegradable Chitosan Fibers

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Received April 7, 2006; Revised Manuscript Received May 11, 2006

A novel chitosan fiber core/gold shell structural organic−inorganic composite was presented via a facile and eco-friendly approach. The chitosan fiber and gold/chitosan composites were characterized with the assistance of scanning electron microscopy and transmission electron microscopy observations. The chitosan fibers used in this study were 50 nm to 5 μm in diameter and up to hundreds of micrometers in length. The gold shells were typically 20−50 nm in depth, and their lattice fringes obliquely intersecting at an angle of 60° were displayed. The formation mechanism of the as-fabricated chitosan fiber core with gold as the shell structural composites was also schematically discussed.

Chitosan, a linear (β-1,4)-linked biopolysaccharide, is an *N*-deacetylated derivative polyelectrolyte of chitin and the second-most abundant natural polysaccharide after cellulose, with excellent biodegradability, biocompatibility, and nontoxicity.[1] Enormous efforts have been made in its potential applications in biofabrication,[2] pharmaceutics,[3] biomedicine,[1−4] food,[5] textiles,[6] and so forth. Because of the unique cationic polyelectrolyte character of chitosan and its gel- and film-forming ability, one-dimensional (1-D) chitosan fibers in solution can provide scaffolds for the adsorption of metal ions with opposite charges. Various fabrication methods such as wet-spinning[7] and electrospinning[8] for 1-D chitosan fibers have been studied. With the assistance of chitosan solution, the synthesis of gold nanoparticles (NPs) has been extensively reported.[9−11] Thin films of chitosan/Au were prepared via irradiation at 253.7 nm under ambient conditions by Miyama et al.[9] Chitosan was also considered to be a stabilizing agent and catalyst in a study where self-sustained chitosan films embedded with gold NPs were applied for surface-enhanced Raman scattering by dos Santos, Jr., et al.[10] It was further suggested that gold salt could be reduced to zerovalent gold NPs by chitosan itself without any additional reducers or stabilizers by Yang's group.[11] The advantage of using chitosan for the reduction of auric ions and the stabilization of as-formed gold NPs is that the process is facile and will not induce any environmental toxicity or biological hazards. The fabrication of gold NP assemblies on linear chitosan fibers, however, still remains a great challenge, especially for chitosan/gold, core/shell structured fibers. Successful realization of this type of 1-D structure will furnish the possibility of building a new generation of fibrous biosensors and functional devices because of its high surface-to-volume ratios and potentially enhanced sensitivity. Other polymers such as poly(ethylene oxide) (PEO) were once employed as templates for the 1-D arrangement of gold NPs using electrospinning by Kim.[12] But no amino groups were present in PEO chains. These amino groups are significant sites for chemical immobilization.

In this study, the chitosan fiber core with gold as the shell structural organic−inorganic composite is presented through the formation of chitosan fibers, adsorption, then the in-situ reduction of chloroauric ions, and consequently the self-assembly of gold NPs on 1-D chitosan fibers. Prior to the self-assembly process, the 1-D chitosan fibers were fabricated using a freeze-drying method (temperature: −89 °C; pressure: 115 mP for 48 h) starting from chitosan NPs (degree of deacetylation: 95%; molecule weight: 500 kDa, Haidebei Ltd., China) in a surfactant-free aqueous suspension (~0.3% w/v) partially cross-linked with glutaraldehyde. The as-formed 1-D chitosan fibers were consequently dispersed into a 0.025 mol·L^{-1} aqueous tetrachloroauric (III) acid ($HAuCl_4$, International Laboratory) solution for further formation of gold NPs in an ambient environment under mild magnetic stirring for 6 days. The typical 1-D chitosan fibers and the forthcoming gold/chitosan composites were observed using a field emission scanning electronic microscope (FESEM; JSM-6335F at 3.0 kV, JEOL), and the images are displayed in Figure 1. The diameters of the 1-D chitosan fibers were mainly from 50 nm to 5 μm, and the lengths were up to hundreds of micrometers. The diameters and lengths can be tuned by varying the experimental conditions.

Figure 1A,B demonstrates examples of bundles of well-growing thin chitosan fibers formed linearly with diameters of around 100 nm at two different magnification rates. The thick chitosan fibers were around 2 μm in diameter, as presented in Figure 1C. At the beginning of the gold formation on chitosan fibers, the reaction cells on the chitosan surface can be morphologically observed/indexed using the rectangular frame (Figure 1D). The as-formed gold NPs were assumed to undergo an equilibrium status of surface and interface interaction, including the adsorption and formation of nuclei, crystal growth, dispersion, self-assembly, and agglomeration on chitosan surfaces. Large self-assembled flakes with a thickness of around 50 nm were observed, which partially proved the formation of gold shells on the fiber surface, as seen in Figure 1E. The size of gold flakes grew larger and larger with prolonged time, and a continuous layer gradually formed on the fiber surface, as

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10.1021/bm060340y CCC: $33.50
Published on Web 08/31/2006

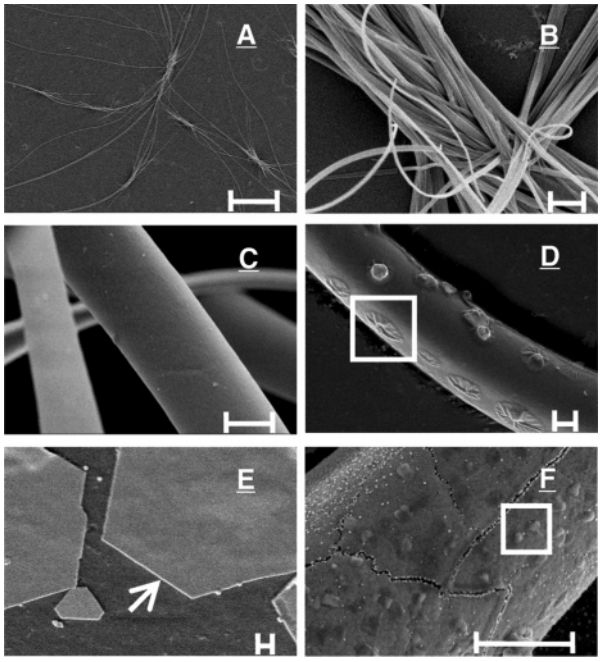

Figure 1. SEM images of (A,B) typical smaller 1-D chitosan fibers, (C) typical larger 1-D chitosan fibers, (D) typical surface status (indexed place) at the beginning of the formation of gold NPs, (E) typical gold shells formed on the surface of a 1-D chitosan fiber, and (F) the as-formed chitosan/gold fiber and the gold NPs in the solution (indexed with the frame). Scale bars: A, 20 μm; B, 500 nm; C, 1 μm; D, 1μm; E, 200 nm; F, 1 μm.

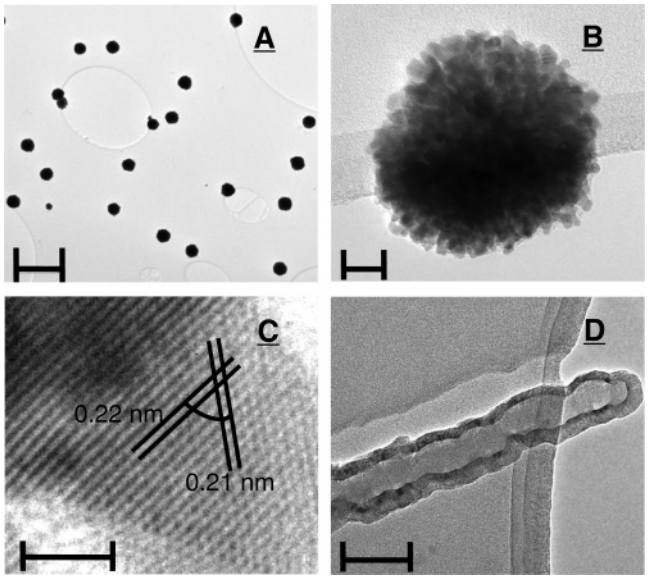

Figure 2. TEM observations of (A,B) gold NPs, (C) high-resolution display of the detailed lattice fringes obliquely intersecting at an angle of 60° of gold crystallites, and (D) typical core/shell structure of chitosan/gold. Scale bars: A, 1 μm; B, 20 nm; C, 2 nm; D, 100 nm.

shown in Figure 1F. The protrusions indexed in Figure 1F are examples of clustered gold NPs and were further determined using a transmission electron microscope (TEM; JEOL JEM 2010 operated at 200 kV). Thus, typical sphere clusters were 200 nm (Figure 2A). High-resolution observation (Figure 2B) showed that they were made up of 5 nm gold NPs. The dots in the images represented gold NPs and were not arranged regularly as in the face-centered cubic (fcc) lattice. Figure 2C displays the detailed lattice fringe oblique intersection at an angle of 60° of the gold crystallites. The core/shell structure was revealed by a typical example, shown in Figure 2D. It was evident that

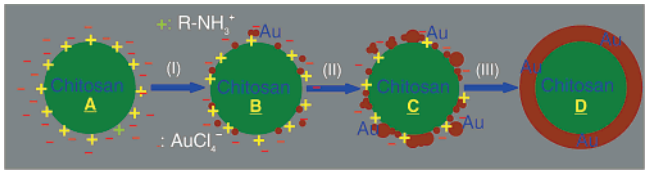

Figure 3. Schematic illustration of cross-sections displaying the formation mechanism of the chitosan fiber core with gold as the shell. (A) The anionic $AuCl_4^-$ ions were adsorbed onto the cationic surfaces of chitosan fibers. After reduction and nucleation process I, gold NPs were adsorbed on the fiber or dispersed in the solution (B). Process II shows the growth and aggregation of gold NPs (C), and, finally, via process III, the shell structure was formed by layers around the chitosan fiber by the layers of the gold NPs (D).

a 50 nm chitosan fiber core was surrounded by a 20 nm gold shell.

The mechanism of gold NP-modified chitosan fibers was schematically conjectured from the FESEM and TEM observations and is demonstrated in Figure 3. 1-D chitosan fibers in aqueous solution, with positive charges of $R-NH_3^+$ (R represents the chitosan main chain) on the surface, provided a scaffold for the absorption of oppositely charged $AuCl_4^-$ ions. As illustrated in Figure 3A, $AuCl_4^-$ anions were electrostatically adsorbed onto cationic chitosan main chains in aqueous solution. Thereafter, the ion-absorbed scaffolds transformed the $AuCl_4^-$ ions to metallic gold at the initial reaction stage by a reduction reaction. After being reduced by the chitosan chain (Figure 3B), the gold nuclei associated with as-formed gold NPs self-assembled onto the surface of the chitosan fiber as a result of both van der Waals force and the high affinity between the amino group and the gold particles (Figure 3C). After fully covering the chitosan surface, NPs dispersed in the solution were randomly moved by Brownian motion and approached neighboring particles, similar to that described in Pei's report.[13]

In summary, we demonstrated our original work of fabricating a chitosan fiber core with gold as the shell structural organic−inorganic composite through the formation of chitosan fibers, adsorption, then the in-situ reduction of chloroauric ions, and consequently the self-assembly of gold NPs on 1-D chitosan fibers. The chitosan fibers used in this study were 50 nm to 5 μm in diameter and up to hundreds of micrometers in length. Gold shells were typically 20−50 nm in depth, and their lattice fringes obliquely intersecting at an angle of 60° were revealed. On the basis of SEM and TEM evidences, the self-assembly activity of gold NPs on 1-D fibers was schematically described. Successful realization of this type of novel core−shell structural material would be significant for the fabrication of a new generation of fibrous biosensors and other functional devices because of the high surface-to-volume ratios and the potentially enhanced sensitivity of the materials.

Acknowledgment. R.H.W. and Z.G.H. gratefully acknowledge the Ph.D. fellowship and funding of this study by the The Hong Kong Polytechnic University (HKPolyU RGG3 and RGF8). The authors would like to thank the Research Grants Council (RGC Reference HKPolyU 5289/03E) and the Innovative and Technology Fund of the Hong Kong SAR Government (ZP0D).

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BM060340Y