Fabricating gold nanoparticle–oxide nanotube composite materials by a self-assembly method

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Abstract

Composition of nanostructured metal particles on oxide tubes (TiO 2 and ZrO 2 ) were fabricated and characterized. The composite materials were examined by transmission electron microscopy, scanning electron microscopy, FT-IR absorption, and UV–visible absorption spectra. The results of characterization showed that the composites indeed contained both oxide tubes and gold nanoparticles and that the gold nanoparticles were intimately associated with the nanotubes.

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1. Introduction

The development of practical strategies for the assembly of inorganic nanoparticles into well-defined arrays is thus an area of considerable current interest, because it offers opportunities to exploit their unique optical and electronic properties and possibilities to probe new, potentially collective phenomena [1,2]. Among the oxide nanotubes, TiO 2 is one of the most investigated oxide materials owing to its technological importance. Titanium dioxide is a wide-bandgap semiconductor and is well known to be a good oxidizing agent for photoexcited molecules or functional groups [3]. As such, it has been widely employed as a photocatalyst [4–6], as a sensor material [7,8], and as an electrode in a dye-based photovoltaic cell [9]. ZrO 2 is also an important functional material and the film deposited on the metal surface has been extensively used in the fields of catalysis [10], sensors [11], and transparent conductors [12]. Au colloidal nanoparticles have received much attention in recent years. Gold has become a favored coating material because of its simple synthetic procedure and chemical functionality [20]. For example, Au particles have been widely used for electronic and biological applications [13,14]. Self-assembly of nanoparticles becomes more and more important because novel collective properties will be produced in the ordered array of nanoparticles. Previous efforts to deposit metal nanoclusters as thin films using Langmuir–Blodgett (LB) films or the self-assembled monolayer approach provided the lower coverage of these particles [15–20]. Although these techniques using LB films or the self-assembled monolayer approach are quite effective for assembling gold nanoparticles as two-dimensional arrays on an electrode surface, their low surface area limits their use for further chemical modification. There are nearly no reports about the assembly of nanoparticles in oxide nanotubes to fabricate the new composite materials [21,22]. Some reports only involve the composite materials with carbon nanotubes [23–25].

Here we present a simple method of fabricating three-dimensional assemblies of gold nanoparticles on TiO 2 and ZrO 2 nanotubes. The modification of oxide tubes with gold colloids represents an effective approach in this regard. Results from characterizations using transmission electron microscope (TEM), scanning electron microscope (SEM), and UV–visible absorption spectra (UV–vis) showed that the composite indeed contained both tita-
nium tubes and gold nanoparticles and that the gold nanoparticles were intimately associated with the nanotubes.

2. Experimental

2.1. Preparation of TiO$_2$ sol–gel solution

TiO$_2$ nanotubes were prepared using the sol–gel method: 5 ml of butyl titanate was added to 25 ml of ethanol with stirring for 10 min in ice water bath. Then a mixed solution of 25 ml ethanol, 0.5 ml water, and 1.5 ml glacial acetic acid were added slowly and the solution was stirred for another 30 min.

2.2. Preparation of ZrO$_2$ sol–gel solution

ZrO$_2$ nanotubes were also prepared using the sol–gel method: 1.0 g of ZrOCl$_2$·8H$_2$O was dissolved in 20 ml of ethanol/water (volume ratio 4:1) with stirring for 10 min. Then 0.2 ml of HNO$_3$ (65%), followed by 5 ml of an ethano-lic solution of acetylacetone (0.15 g), were added and the solution was stirred for another 1 h. The solution was aged overnight to obtain the ZrO$_2$ sol.

2.3. Preparation of TiO$_2$ and ZrO$_2$ nanotubes

Alumina template membranes with a diameter of 100 nm (obtained from Whatman Company) were immersed into the TiO$_2$ and ZrO$_2$ sol for 15 and 30 min, respectively. After removal from the sol, the membrane was dried in air at room temperature and annealed. The annealed temperature was ramped up (100 °C/h) to 500 °C and maintained for 6 h; then the temperature was ramped back down (30 °C/h) to room temperature.

2.4. Preparation of gold colloids

Gold colloids were prepared according to Ref. [26]. All glassware used in the following procedures was cleaned in a bath of freshly prepared 3:1 HNO$_3$ and HCl, rinsed thoroughly in twice-distilled water, and dried in air. Then 7.5 ml (1%) of sodium citrate solution was added to a boiling 500-ml (0.01%) HAuCl$_4$ aqueous solution. Stirred for 70 s, the color of solution changes to claret red. The solution was heated and stirred for another 15 min. The products were stored in brown glass bottles at ca. 4 °C.

2.5. Assembling of Au–TiO$_2$ and Au–ZrO$_2$ composites

The composite of Au colloids and TiO$_2$ (ZrO$_2$) nanotubes was assembled via (3-aminopropyl)trimethoxysilane. TiO$_2$ (ZrO$_2$) samples were immersed in 3 M NaOH aqueous solution for 10 min to remove the alumina membrane. The sample was carefully washed with distilled water three times. Then TiO$_2$ (ZrO$_2$) nanotubes were added to the 1% (3-aminopropyl)trimethoxysilane (APS) solution and sonication was performed in a sonic bath for 0.5 h. The sample was washed with distilled water for twice and added to Au colloid solution for 12 h. Hybrid structures of gold nanoparticle–TiO$_2$ (ZrO$_2$) nanotubes were obtained.

2.6. Analytical methods

The diameters of the gold colloids were about 15 nm and were measured using transmission electron microscopy (TEM).

TEM images were performed using a JEOL-JEM 200CX transmission electron microscope (TEM) working at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) pictures were recorded on a JSM-5900 instrument.

UV-3100 photospectrometer (SHIMADZU) was used to record the UV–visible absorption spectra of the as-prepared particles. VECTOR 22 (Bruker Company, Germany) was used to record the FT-IR absorption spectra of the as-prepared particles.

3. Results and discussion

We used the solution of butyl titanate ((C$_4$H$_9$O)$_4$Ti) and ZrOCl$_2$·8H$_2$O as the precursor in the sol–gel process, and an AAO membrane was used as the template for the preparation of the TiO$_2$ and ZrO$_2$ nanotubes. Figs. 1a and 1b show the transmission electron microscopy (TEM) and ED images of TiO$_2$ nanotubes. Fig. 1c shows the TEM image of ZrO$_2$. They were prepared by immersing the AAO membrane into the sol of TiO$_2$ and ZrO$_2$ and calcined in a muffle at 500 °C for 6 h. The wall thickness of the TiO$_2$ and ZrO$_2$ tubes was varied by changing the immersion time of the AAO membrane in the TiO$_2$ and ZrO$_2$ sol. The TiO$_2$ and ZrO$_2$ nanotubes could grow to nanowires when the immersion time was longer than 30 min for TiO$_2$ and 2 h for ZrO$_2$. Electron diffraction pattern of the TiO$_2$ nanotubes shown in Fig. 1 indicates that the tubes are polycrystalline. The pattern can be indexed to the (101) (004) (200) (105) (204) indicating that TiO$_2$ belongs to anatase. The AAO membrane with TiO$_2$ and ZrO$_2$ nanotubes was dissolved in the 3 M NaOH aqueous solution to remove the template. The dissolving time is 15 min for TiO$_2$ and 20 min for ZrO$_2$. In the course of dissolving, the outer wall surface of TiO$_2$ and ZrO$_2$ nanotubes may produce a large quantity of hydroxyl. FT-IR studies for alkali-treated TiO$_2$ and ZrO$_2$ nanotubes, as shown in Fig. 2, indicated the existence of hydroxyl groups. The peak value of hydroxyl. FT-IR studies for alkali-treated TiO$_2$ and ZrO$_2$ nanotubes, as shown in Fig. 2, indicated the existence of hydroxyl groups. The peak value of hydroxyl. FT-IR studies for alkali-treated TiO$_2$ and ZrO$_2$ nanotubes, as shown in Fig. 2, indicated the existence of hydroxyl groups. The peak value of hydroxyl. FT-IR studies for alkali-treated TiO$_2$ and ZrO$_2$ nanotubes, as shown in Fig. 2, indicated the existence of hydroxyl groups. The peak value of hydroxyl.

Fig. 1. The transmission electron microscopy (TEM) and ED image of TiO$_2$ nanotubes. (a) Images of ED and single TiO$_2$ nanotube. (b) Images of TiO$_2$ nanotubes. (c) Image of ZrO$_2$ nanotubes.

Fig. 2. FT-IR spectra of alkali-dissolved TiO$_2$ (a) and ZrO$_2$ (b) nanotubes. (APS)/water (1:100 v/v) and were sonicated in a sonic bath for 0.5 h. After this treatment, the outer wall surface of the tubes was modified on APS because of the generation of –O–Si– between the –OH groups (from outer wall surface of TiO$_2$) and the CH$_3$O–Si– (from APS). The nanotubes were thorough washed with deionized water and centrifuged several times, then dispersed in water again. In this study, TiO$_2$ nanotubes are used as the beginning template material.

Au colloids were prepared by using sodium citrate method. The size of Au particles is ca. 15 nm. The TEM image of Au nanoparticles is shown in Fig. 3. Gold nanoparticles are assembled on TiO$_2$ nanotubes via APS on the outer wall surface of TiO$_2$ nanotubes under ambient conditions. After the TiO$_2$ nanotubes with APS modification, the solution of TiO$_2$ nanotubes was mixed with a gold colloid for 12 h. The negatively charged gold nanoparticles were attached to the surface of the nanotubes through the electrostatic interaction between the amino groups of nanotube and the nanoparticles. The complete scheme for the nanotube surface modification and the gold nanoparticle attached on the oxide nanotube surface is shown in Fig. 4. The TEM images were prepared by dispersing the nanotubes in ethanol. Nanostructured gold colloids on TiO$_2$ and ZrO$_2$ nanotubes observed in Fig. 5 suggest that these particles retain the identity of individual nanoparticles. Fig. 6a shows the SEM images of TiO$_2$ nanotubes after dissolving partial alumina membrane, in this image, highly ordered and a perfect array of TiO$_2$ nanotubes are observed. The length of the nanotubes corresponds to the thickness of the AAO membrane. The SEM image of gold nanoparticle–TiO$_2$ nanotubes is shown in Fig. 6b. Compared with the slippery and clean surface of TiO$_2$ nanotubes (in Fig. 6a), the rough surface is observed, which shows gold nanoparticles dispersed on the outer wall surface of TiO$_2$ tubes. To make a comparison, the experiment in the absence of APS has been carried out, and gold on the TiO$_2$ nanotubes could not be observed. Therefore, we can deduce that the structure of the APS plays an important role in the assembly of the gold–TiO$_2$ nanotubes composites.

Fig. 7 shows the UV absorption spectra of TiO$_2$ nanotubes (curve (a)), gold colloids (curve (b)), and nanostructured composite (curve (c)). There is no obvious absorption peak in the range of 400–800 nm in curve (a). The absorption peak is observed at 520 nm in curve (b) and attributed to the typical surface plasma response of the gold nanoparticles. However, the different absorption peaks are observed in composite material: there are two peaks appearing at 530 nm and 620 nm in curve (c). In order to find the reason for the different absorption, the APS is added into the Au colloid solution, and the spectrum is shown in curve (d). There are
two peaks appearing at 530 and 620 nm in curve (d). The amino group of the APS can couple with the surface of the Au nanoparticle with a negative charge to change the plasma character of the Au nanoparticle. So the peak at 530 nm can be attributed to the surface plasma absorption of the gold nanoparticles and the peak at 620 nm can be attributed to the new surface character of Au nanoparticles with APS. The similar absorption peaks in curve (c) can prove that the Au nanoparticle can assemble to the oxide nanotubes by the interaction with amino group of the nanotube surface.

4. Conclusion

In summary, gold nanoparticles can be effectively assembled to TiO$_2$ and ZrO$_2$ nanotubes via (3-aminopropyl)trimethoxysilane under ambient conditions. Results from the characterization of the composites show that the gold nanoparticles are intimately associated with the nanotubes surface. These nanoparticle-modified nanotube composites could be used in catalytic, electronic and optical applications.
Fig. 6. (a) SEM images of TiO$_2$ nanotubes and (b) hybrid structures of gold nanoparticle–TiO$_2$ nanotubes.

Fig. 7. The UV absorption spectra of TiO$_2$ nanotubes: (a) absorption spectrum of TiO$_2$ nanotubes, (b) absorption spectrum of Au colloid, (c) absorption spectra of Au–TiO$_2$ composites, and (d) absorption spectrum of Au–APS.

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