Preparation and characterization of silicon dioxide nanotubes with silver in inner wall

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A simple approach for the synthesis of large quantities of silicon dioxide nanotubes with silver in inner wall was developed via sol-gel process at room temperature. Silver nitrate acted simultaneously as a template precursor and silver source during the process. Scanning electron microscopy and transmission electron microscopy images show that the nanotubes are 0.5–10 μm in length, and 200 nm in width. Energy dispersive X-Ray spectroscopy analysis results revealed the existence of S, Si, O, C and Ag in silicon dioxide nanotube. UV-Vis spectroscopy further revealed the existence of Ag by exhibiting the typical surface plasmon absorption maximum at 405 nm. +

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1. Introduction

Since the initial discovery of carbon nanotubes by Iijima in 1991 [1], the synthesis of one-dimensional inorganic nanomaterials with tubular structures has attracted a tremendous interest because of their wide range of potential applications in catalysts supports [2], sensor [3], separations [4], magnetism [5], chromatography [6], drug/gene delivery carriers [7], and photoluminescence [8]. Numerous methods have been developed to synthesize tubular-structured inorganic materials, which can basically be separated into two parts: the synthesis with and without template. The templates being used to synthesize inorganic nanotubes included hard template [9-11] and soft template [12-14]. The syntheses of nanotubular-structured materials without templates involved high temperature process [15], hydrothermal methords [16-18] and other methods [19-21].

Among various tubular-structured inorganic nanomaterials, silica nanotubes have received significant attention due to their stable and strong luminescence characteristics in both solvent and the solid state, and potential applications in bioseparation [22], bioanalysis [23, 24], optical sensors and luminescence diodes [25]. Recently, many efforts have been paid to encapsulate foreign materials inside hollow cavities of silica nanotubes in order to create unique nanocomposite materials. For instance, Geng *et al.* [26] has synthesized CdSe-filled silica nanotubes by the reaction of silica, silicon, cadmium and selenium under a stream of high purity argon gas at 1200°C. Similar strategy has also been utilized to synthesize Ge-filled silicon dioxide nanotube [27], indium sulfide filled silica nanotube [28], ZnS-filled silica nanotube [29], and etc.

Silver has been one of the main materials investigated in many technologies. It displays the highest electrical and thermal conductivities among all kinds of metals. It has also been extensively exploited in a variety of applications that range from catalysis, through electronics, to photonics and photography [30, 31]. Therefore, it is of particular interest to synthesize and study silver-filled tubular materials. In 2002, Yin et al. [32] reported the synthesis of silver/silica nanocables, in which silver nanowire were first produced by using platinum nanoparticles as seeds for the heterogeneous nucleation and growth of silver that was produced via the reduction of silver nitrate in the presence of the poly (vinyl pyrrolidone) (PVP), and then coated with amorphous silica by sol-gel method. Despite these efforts, however, there is still a need to develop a more simple method.

In the present work, we reported the synthesis of novel silica nanotubes with silver in inner wall via sol-gel technique at room temperature, in which silver nitrate ($AgNO_3$) was used as silver precursors and a structural modifier under the assistant of 3-Mercaptopropyltrimethoxysilane (MPTMS). Silver nitrate ($AgNO_3$) and MPTMS were first dissolved in ethanol and stirred overnight, and the resulted gel was dropped into the solution prepared from water, ethanol, ammonia aqueous and tetraethyl orthosilicate (TEOS). The morphology of the product exhibits almost exclusively nanotubes, without the need for additional template removal steps. A self-template growing mechanism was proposed to explain the growth mechanism. The novelty of the approach described in this research relies on its fundamental simplicity.

2. Experimental section

2.1 Instrumental and reagents

TEOS and $AgNO_3$ were obtained from Kemiou Chemical Reagent (Tianjin, China). Ethanol and formaldehyde were purchased from North Medical

Chemical Reagent (Tianjin, China). 3-Mercaptopropyltrimethoxysilane (MPTMS) was obtained from Alfa Aesar (Tianjin, China). All the reagents were at least of analytical grade and used as received without further purification. Ammonium solution (28–30% NH_4OH) was purchased from North Medical Chemical Reagent (Tianjin, China). Deionized water (>18.2 MΩ cm) was obtained from a Millipore Milli-Q purification system.

2.2 Synthesis of silicon dioxide nanotubes adorned with silver in inner surface

MPTMS (0.15 mL) and $AgNO_3$ (106.17mg) were dissolved in 50.0 mL of ethanol. The homogenous mixtures were then stirred overnight at room temperature. The formed gel was referred as A.

TEOS (3.0 mL) was added dropwised into the solution prepared of ethanol (80.0 mL), aqueous solution of ammonia (25-28%, 5.0 mL) and water (5.0 mL) under magnetic stirring with a speed *ca.* 300 rpm. The solution was referred as B.

Subsequently, the solution A and 4.0 mL of TEOS was slowly added dropwise to the solution B in sequence. The mixtures were then stirred for 2 h at room temperature. At last, formaldehyde was added into the solution and stirred for 1h. The obtained precipitates were subjected to centrifugation to collect the silica nanotubes, which were washed three times with fresh alcohol and water, respectively, to remove residual NH_4OH and unreacted TEOS.

2.3 Characterization

Samples for field emission transmission electron microscopy (FETEM) were deposited onto carbon-coated copper electron microscope grids and dried in air. FETEM analysis was performed using Tecnai F20 G^2 (FEI Company, Netherland.). Energy dispersive X-Ray spectroscopy (EDS) analysis was performed using a system attached to the FETEM. Scanning electron microscopy (SEM) was performed using SU-1510. (HITACHI SU-1510, Japan). Fourier Transform Infrared (FTIR) spectra were obtained at a resolution of 1 cm^{-1} with a Bruker FT-IR spectrophotometer between 4,000 and 400 cm^{-1}. The IR measurements of the powder samples were performed in the form of KBr pellets.

3. Results and discussion

3.1 Morphology characterization

In this research, TEOS as silica precursors, silver nitrate as silver resources and a re-template, MPTMS as a chelator and formaldehyde as a reducing agent for silver were employed to synthesize silica nanotube with silver in inner wall in the absence of any additional template. A yellow product was obtained (Inset of Fig. 1a). The product was investigated by FETEM. As shown in Fig. 1a, the length of obtained nanotube is at least tens of micrometers. From Fig. 1b, it can be seen that the channel of the tube is open. We can observe that the inner and outer diameters of the tubes are about 78 nm and 200 nm respectively, and the thickness of nanotube wall is *ca.* 61 nm (Fig. 1c). The surface of obtained nanotube is coarse. We can also clearly observe that the formation of Ag nanoparticles was doped in silica nanotube inner wall. The morphology of nanotube has also observed by the low magnified SEM (Fig. 2 a). It is show that some nanoparticles are coexisted with the nanotube. In contrast, silica nanomaterials synthesized using a similar procedure but in the absence of $AgNO_3$ gave only sub-micrometer sized particles, indicating the particular effect of $AgNO_3$ in the formation of silver-filled nanotubes (Fig. 2 b). Moreover, MPTMS is another key factor to influence the morphologies of materials. When 3-aminopropyltriethoxysilane was used instead of MPTMS, the materials had the morphologies of the interconnected nanoparticles (Fig. 2 c).

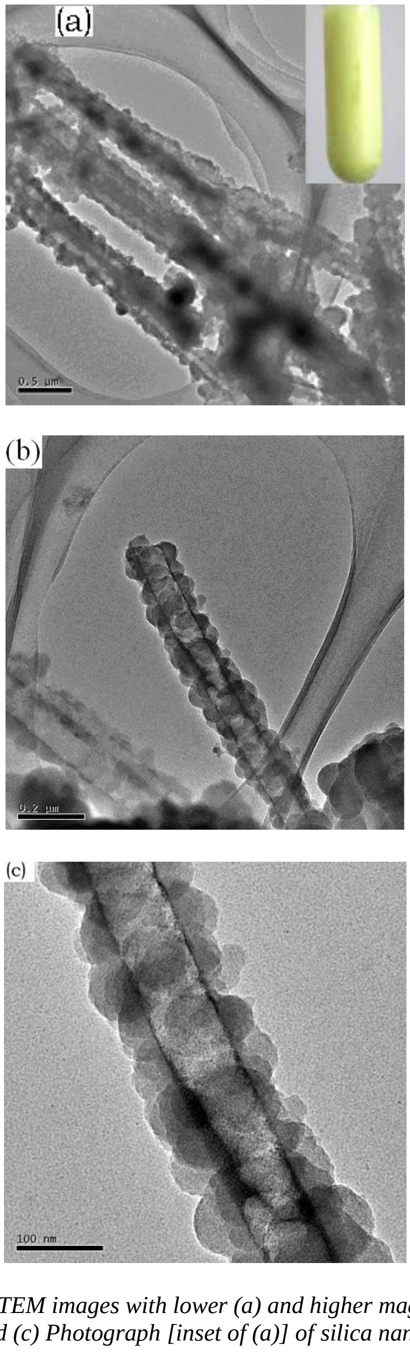

Fig. 1. FETEM images with lower (a) and higher magnification (b) and (c) Photograph [inset of (a)] of silica nanotube.

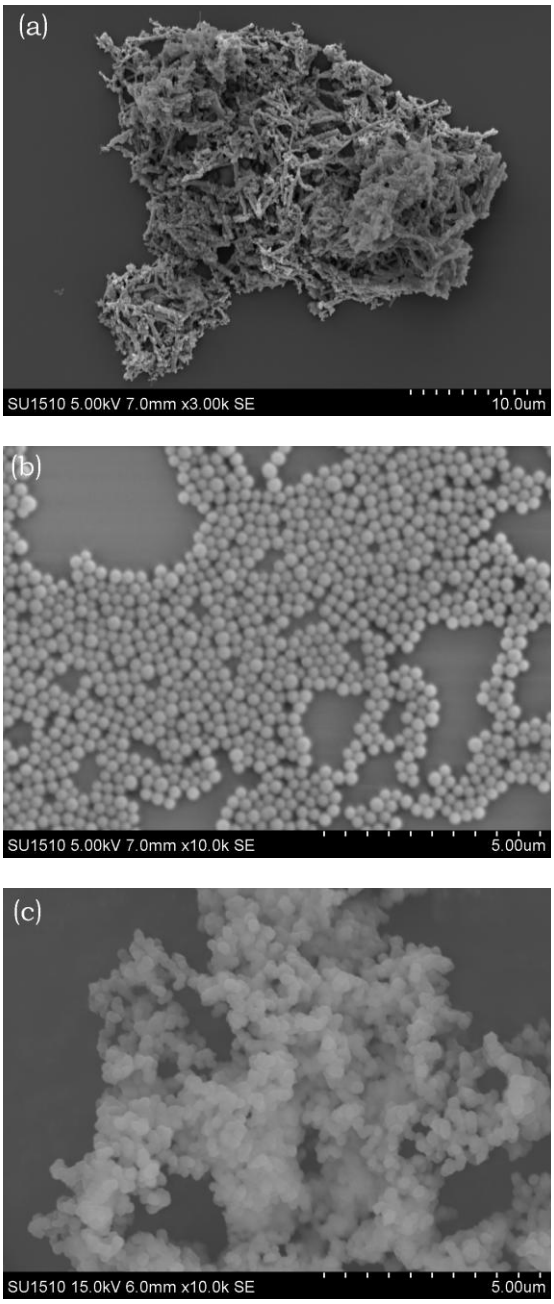

Fig. 2. SEM images: (a) the same silica nanotubes as in Fig 1; (b) silica nanomaterials synthesized in the absence of $AgNO_3$; (c) silica nanomaterials synthesized by using 3-aminopropyltriethoxysilane instead of MPTMS.

3.2 Energy dispersive X-Ray spectroscopy analysis

The elemental composition of the obtained silica nanotubes was performed using the EDS on the TEM. Figure 3 showed the EDS spectrum of the silica dioxide nanotubes. The peaks around 3.40 keV is correspond to silver. The peaks situated at binding energies of 0.25 KeV and 2.3 KeV belongs to carbon of the propyl hydrocarbon chains and sulfur of the thiol groups of MPTMS, respectively. The peak around 1.74 KeV belong to silicon of silica network is also detected. The copper peaks corresponding to TEM holding grid are observed at 8.06 and 8.94 KeV. The result indicated that Ag has been successful filled in silica nanotube. The quantitative results on the chemical composition analyses of silica nanotube were displayed in Table 1.

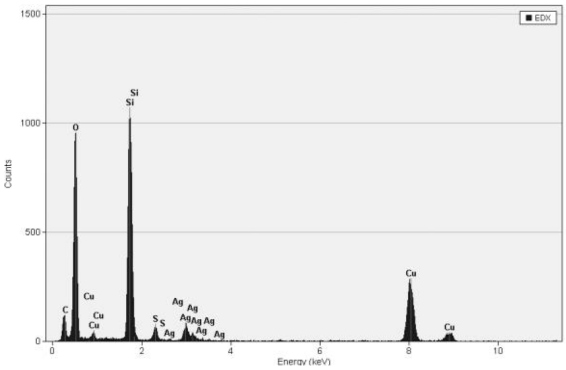

Fig. 3. EDS analysis of silica nanotubes.

Table 1. Percentage of elements presents in silica nanotubes coated with silver.

Element	Weight % in silica nanotube
C(K)	8.476
O(K)	53.371
Si(K)	34.913
S(K)	1.672
Ag(K)	1.566

Table 1 presented the average mass values (%), obtained by EDS ananlysis, to the nanotubes. In this case, the peaks of the copper from holding grid were excluded of the calculus.

3.3 Fourier transform infrared spectroscopy analysis

In order to qualitative identification of the organic functional groups, the resulted nanotubes were also been characterized by FTIR spectroscopy. Fig. 4 illustrated the FTIR spectra of the silver doped silica nanotubes. The bands at 1220, 1070, 791, and 470 cm^{-1} are assigned to the typical Si-O-Si bands of the condensed silica network. The weak bands at 1470 and 1390 cm^{-1} are attributed to bending vibrations of methylene groups, and the weak frequency bands at 2925 and 2960 cm^{-1} corresponding to the methylene stretching vibrations of the propyl chains of MPTMS. The absorbance at 960 cm^{-1} is associated with the noncondensed Si-OH groups. The broad band around 3424 cm^{-1} and the strong peak around 1630 cm^{-1} are due to the stretching and bending vibrations of adsorbed H_2O. Although EDX analysis showed sulfur elemental present, the peak associated with the S-H bond could not been observed in its IR spectrum. That may be attributed to the low absorption coefficient of the S-H stretching [33].

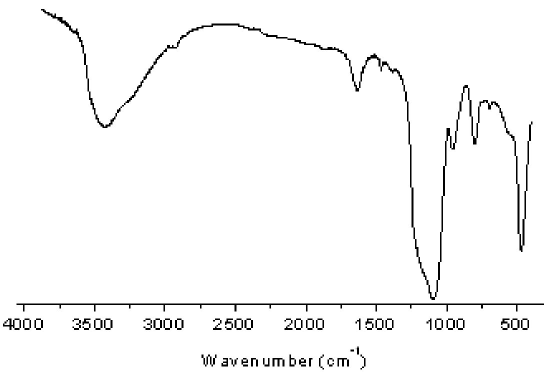

Fig. 4. FTIR spectra of silica nanotubs.

3.4 UV-Vis spectroscopy analysis

The silver doped silica nanotube was also monitored using UV-Vis extinction spectroscopy. Because of the strong light scattering from these nanotubes in water, the silver surface plasmon resonance absorption (curve a in Fig. 5) could not be observed. However, a DMSO-water mixture was used to match the refractive indices of the colloidal particles (curves b in Fig. 5), the UV-Vis spectroscopy revealed the existence of silver nanoparticles by exhibing the typical surface plasmon absorption maxima at 418-420 nm.

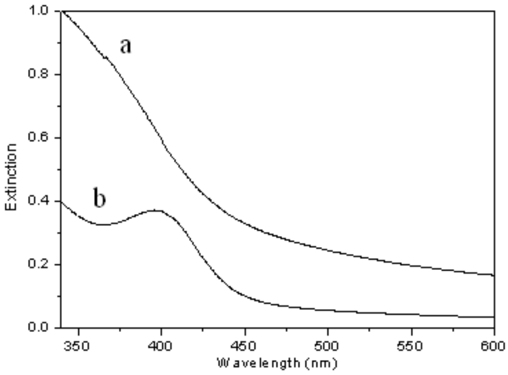

Fig. 5. UV-Vis extinction spectra of nanotubes (a) in water, n = 1.337; (b) in DMSO-Water mixtures, n=1.472.

3.5 Formation mechanism of silica nanotube

When MPTMS and silver nitrate was mixed in ethanol, the thiol groups of MPTMS tended to interact with metal ions by the cleavage of an S–H bond and the spontaneous formation of an S-metal bond. MPTMS also formed self-assembled long rows where molecules followed one by one [22]. In addition, Silver ions were reduced by ethanol, which has been used to reduce noble metals salts for the preparation of metal nanoparticles [23]. Thus, the following reactions should be taken into account.

$$Ag_n + Ag^+ + CH_3CH_2OH \rightarrow Ag_{n+1} + H^+ + CH_3CH_2O$$

In fact, the solution A indeed exhibited a yellow colour, which might come from nano sized silver. Nano sized silver might assembled in the form of the tubular structure under the assistant of MPTMS. When the solution A was added dropwise into the solution B, a silica dioxide shell was then formed on the surface of the tubular structure by hydrolysis and condensation of MPTMS with TEOS in an ethanolic ammonia suspension.

4. Conclusions

The novel nanostructures of silver coated silica nanotubes inner wall have been obtained through a simple sol-gel process at room temperature, in which $AgNO_3$ has been employed as a structural modifier to guide the formation of silver-filled silica nanotube under the assistant of MPTMS. This synthetic strategy might be extended to synthesize other similar nanostructures, which is potentially important for novel optoelectronic nanodevices. Further studies on the above system are underway and the results will be reported in near future.

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