Simple Synthesis for Hierarchical SiO$_2$ Tubes with Adjustable Mesoporous

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Abstract—**With the aid of cotton template and precursor solution of mesoporous silica, hierarchical mesoporous SiO$_2$ tubes with size–adjustable mesoporous in the tube–wall were synthesized through sol–gel method. The products are tubular silica that inherit the hierarchical structure of initial cotton and contain mesopores in their wall. The size of mesoporous in the wall can be adjusted by change the mixture ratio of mesoporous silica precursor solution. Noble metal particles, silver and gold, were introduced into the surface of mesoporous silica tubes respectively to obtain a uniform distribution of noble metal nanoparticles on the tube–wall. This method can be applied to many nature substance templates with different structures to prepare various structural SiO$_2$ materials.**

Keywords-natural substance template; SiO$_2$ tubes; size–adjustable; sol–gel chemistry

I. INTRODUCTION

One-dimensional silica-based nanostructural materials, such as nanotubes, have been vigorously investigated due to their specific mechanical, electrical, and chemical properties. These materials were generally synthesized by hydrolysis of TEOS on the surface of various templates, such as anodic aluminum oxide membranes,[1] crystalline fibers,[2] carbon nanotubes,[3] and silicon nanowires,[4] followed by removal of templates. Mesoporous silica materials, such as MCM-41/48, have found widespread application for industrial, technological and domestic purposes.[5,6] Combination of mesopores and tubular structure can obtain functional silica materials with complicated structures that can satisfy the demand for improved silica types with specific properties. Some researches indicated that tubular silica with a nanometer-sized hollow cavity have attracted increasing attention in natural science and materials science fields from the viewpoint of their potential applications and the continuing interest in fundamental phenomena specific to a confined nanospace.[7–9] Since the first report on the synthesis of silica tubes with mesopores in the wall by Mou's group,[10] a few mesostructured silica tubes have been prepared.[11–20] However, the simple morphology of these artificial template substrates mentioned above severely limits the variety of structures and morphologies of the products.

Here, we successfully synthesized mesoporous silica tubes through a simple and efficient method by using hierarchical cotton fibers as the hard template and cetyltrimethylammonium bromide (CTAB) micelles as the soft template This material inherits the .hierarchical morphology of cotton and the diameter of tubes range from tens nanometers to several microns. This hierarchical silica tubes with mesoporous wall was obtained by sol−gel process of tetraethyl silicate in the presence of cationic surfactant CTAB followed by the mixture covering on the cotton fibers. The size of mesopores in the wall was adjustable by varying the ratio of silica precursor. Then, we prepared Ag/silica and Au/silica composites through introduce silver and gold nanoparticles into the sample above, respectively.

II. EXPERIMENTAL

A. Materials

Cetyltrimethylammonium bromide (CTAB, 99.0%) and tetraethyl orthosilicate (TEOS, 28.4%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Hydrogen tetrachloroaurate trihydrate (HAuCl$_4 \cdot$3H$_2$O, 99.99%), silver nitrate (AgNO$_3$, 99.85%) and sodium borohydride (NaBH$_4$, 99%) were purchased from Acros Organics. Milli-Q water (resistivity, 18.2 MΩ cm^{-1}) was used in all related cases. All the chemicals were used as-received without any further purification.

B. Synthesis of Mesoporous Silica tubes

In our experiment, two different kinds of mesoporous silica tubes have been prepared. Both silica samples were synthesized as follows. In a large narrow–mouth bottle, 1 g of CTAB was dissolved in a mixture of 3.5 ml of NaOH aqueous solution (2 M) and 480 ml of deionized water. After addition of 5 ml of TEOS with vigorous stirring for 10 min at 80 ºC, the mixture was treated by two ways. One was directly filtered, washed with distilled water and dried at 90 ºC overnight followed by calcined at 600 ºC in air for 6 h. The obtained production was named MSP−1. The other method was adding the cotton in the mixture and then kept statically at the same temperature for another 10 min. Finally, the coated cotton was filtered, washed with distilled water and dried at 90 ºC overnight followed by calcined at 600 ºC in air for 6 h. The resulting silica product was typically in the form of tubes with mesopores in the wall, which was dominated as S−1. Sample MSP−2 and S−2 were made through the same process above. The only difference between two samples is the ratio of the initial silica precursors. The amounts of CTAB, NaOH (2 M), deionized water and TEOS were 2 g, 7 ml, 480 ml and 9 ml, respectively for S−2 sample that means the amounts of NaOH, CTAB and TEOS in the S−2 precursor were twice of those in S−1 precursor in the case of same amount of deionized water.

C. Preparation of Ag /S–1 and Au /S–1 Composites

The mesoporous silica tubes S–1 were immersed in 0.2 M AgNO$_3$ ethanol/water (1:1 v/v) solution for 2 h, followed by thorough washing with Milli–Q water and dried in air. Photoreduction of silver was achieved by subjecting the mesoporous silica tubes to UV irradiation (365 nm, 16 W) for 2 h. Then Ag /S–1 composite was obtained.

The mesoporous silica tubes S-1 were impregnating in 5 ml iced–cold 0.1 M NaBH$_4$ in ethanol/water (1:1 v/v) for 2 min, followed by washing thoroughly with deionized water and dried in air. Then, the sample was dipped in 5 ml iced-cold 2.5 × 10-4 M HAuCl$_4$ in ethanol/water (1:1 v/v) for another 2 min to obtain Au /S–1 composite

D. Characterizations

SEM observation was performed on a SIRON field emission scanning electron microscopy at an acceleration voltage of 25.0 kV. The TEM image were performed by a JEM-200CX transmission electron microscope (TEM) operating at an acceleration voltage of 160 kV, and a JEM-2010 transmission electron microscope operating at 200 kV. Adsorption and desorption isotherms of nitrogen were obtained at 77 K on a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer. The linear part of the Brunauer–Emmett–Teller (BET) equation was used for the specific surface area determination.
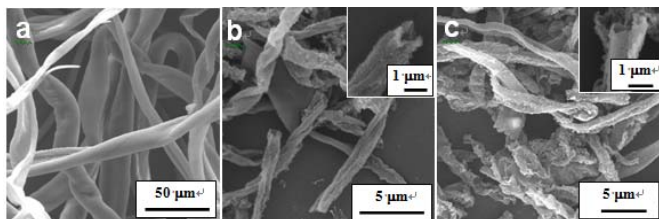
III. RESULTS AND DISCUSSION

FIGURE I. FE-SEM IMAGE OF (a) COTTON FIBERS, (b) S–1 SAMPLE AND (c) S–2 SAMPLE. THE INSETS IN PANEL B AND C ARE ENLARGEMENT OF TOP PART OF SILICA TUBE.

A. Hierarchical Mesoporous Silica tubes

Cotton has a randomly crossed network of microfibers that are composed of nanofibers, and each individual nanofiber is an assemble of β-D-glucose polymer chains through multiple hydrogen bonding. The existence of surface hydroxyl groups provides a suitable platform for the deposition of a silica gel layer on the surface of cellulose nanofibers, and removal of cotton template results in the final hierarchical silica nanotubes. Figure 1a shows that bare cotton possess a macro to nanoscopic random morphological hierarchy and each fiber of cotton has a smooth surface. Figure 1b and 1c are SEM images of S–1 and S–2 samples after complete removal of the cotton fiber component, respectively, which indicate the resultant silica samples possess overall morphological characteristics of the initial cotton though the surface of each fiber became rough. The overview FE-SEM images show both sample are consisted of randomly interconnected nanotube assemblies with high aspect ratios. The outer diameters of the nanotubes range from nanometers to microns. The highly magnified SEM image of individual mesoporous silica tube

exhibits the obvious open ends nanotubular structures (Insets in Figure 1b and 1c). These observations demonstrate that the original morphology of the initial natural cellulose fibers is faithfully replicated by nanotubular silica film at nano-precision and the products can be regarded as negatively replication of the original structure of the initial cotton substance.
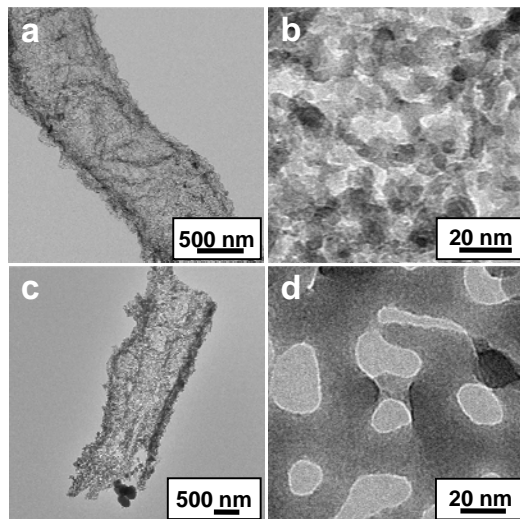

FIGURE II. (a) TEM AND (b) HRTEM IMAGES OF S–1 SAMPLE. (c) TEM AND (d) HRTEM IMAGES OF S–2 SAMPLE.

The TEM of individual tube of S–1 (Figure 2a) indicates that the tube wall of uniform thickness of 150–200 nm is clearly observed, which means the sample possesses tubular structure. HRTEM observation (Figure 2b) demonstrates more detail of the tube wall, which shows large number of mesopores with size of 10–20 nm randomly located in tube wall of the silica tube. TEM (Figure 2c) and HRTEM micrographs (Figure 2d) of S–2 indicate the S–2 is composed of silica tubes with a lot of irregular mesoporous of 15–30 nm in the wall. The difference on size of mesopores between S–1 and S–2 sample is most probably caused by the ratio variety of two initial MCM-41 precursor solutions. These results indicate that the whole samples prepared are hierarchical mesoporous silica tubes and the mesopores size can be altered by changing the initial precursor solution.
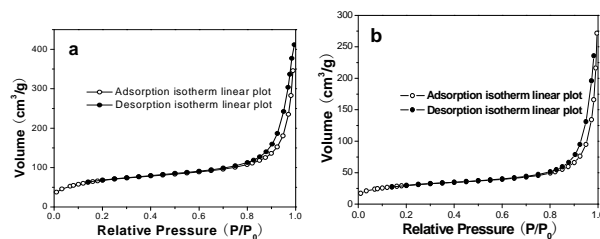

FIGURE III. N2 ADSORPTION/DESORPTION ISOTHERM OF (a) S–1 SAMPLE AND (b) S–2 SAMPLE.

Figure 3a and 3b shows the nitrogen adsorption-desorption isotherms for mesoporous silica nanotubes S–1 and S–2, respectively. The mesoporous silica nanotubes exhibit typical type IV adsorption isotherms with narrow hysteresis loops,

which indicate the existence of mesopores in the structure of samples. The obvious adsorptions of N_2 at high relative pressure (e.g., $P/P_0 > 0.8$) in both isotherms indicate the formation of relative large additional mesoporosity. The pore sizes obtained from the nitrogen physisorption isotherms are 16 nm for S−1 and 23 nm for S−2 samples respectively, which agrees with those from observations of TEM images of S-1 and S−2 samples in Fig2. The large values of BET surface area (about 231.9m^2/g for S−1 sample and 102.4m^2/g for S−2 sample) and pore volume (0.63 cm^3/g for S−1 and 0.42 cm^3/g S−2) of our productions possibly attributed to the formation of larger holes due to the removal of CTAB micelles/silica composite particles at the starting of synthesis process.

B. *Introduction of Ag or Au Nanoparticles in the Wall of Mesoporous Silica Tubes*

Due to the large specific surface area, the mesoporous silica nanotubes provide a practical platform for noble metal Ag or Au particles. Here, the Ag nanoparticles were introduced by means of photocatalytic reduction of AgNO$_3$ to Ag. The incorporation of Au nanoparticles was through reduction of HAuCl$_4$ by NaBH$_4$. Figure 4a and 4c respectively show the FE-SEM images of individual Ag/S-1 and Au/S-1 tube, in which the cotton structure preserved perfectly that was as same as the S−1 sample (Figure 1b). It indicates that the introduction process of noble metal nanoparticles did not destroy the structure of sample. As presented in the TEM image (Figure 4c and d), a large number of individual Ag and Au nanoparticles with spherical shape are decorated on the surface of mesoporous silica nanotube. The size of these nanoparticles are quite uniform, which are measured about 7 nm and 3 nm for Ag/S-1 and Au/S-1, respectively.
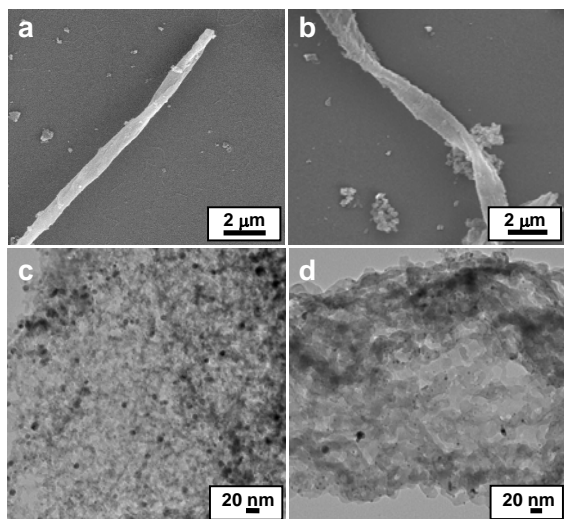

FIGURE IV. (a) SEM AND (b) TEM IMAGES OF AG/S−1 COMPOSITE. (c) SEM AND (d) TEM IMAGES OF AU/ S−1 COMPOSITE.

IV. CONCLUSIONS

Hierarchical mesoporous silica tubes have been fabricated through a simple route by employing cheap cotton cellulose fibers as hard template, which contributes to the formation of tubular structure, and mesoporous silica precursor as soft template that responsible for forming mesopores on the tube wall. The final sample is a composite of a tubular structure and mesopores in its wall that can be adjustable by varying the solution ratio of silica precursor. The introduction of mesopores into the silica tubes can not only improve the structure but also enlarge the BET surface area of this composite, which is favor of the widely application in many fields. The currently developed method can be readily applied to prepare a variety of mesoporous silica materials with tailored structures, properties and functions for specific practical applications, such as catalysis, adsorption, microreactor, sensors, delivery and so on. Then noble metal particles, Ag and Au, have introduced the mesoporous silica tubes and made Ag (Au)/mesoporous silica tubes composite with uniform distribution Ag or Au particles.

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