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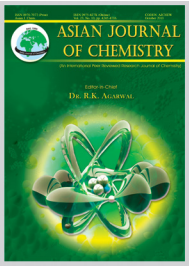

Synthesis of TiO_2/SnO_2 Composite Nanowire Arrays *via* Electrophoretic Deposition Method†

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Highly ordered TiO_2/SnO_2 composite nanowire arrays were synthesized by electrophoretic deposition method using anodic aluminium oxide as template. Careful structural characterization indicates that the prepared composite nanowires are composed of small nanocrystallines of rutile TiO_2 and tetragonal SnO_2 with amorphous grain boundaries. The mechanism of the electrophoretic deposition is discussed.

Key Words: TiO_2/SnO_2 composite nanowire arrays, Electrophoretic deposition, Anodic aluminium oxide template.

INTRODUCTION

TiO_2/SnO_2 composite have attracted great interests for its potential application in gas sensors, photocatalytic decontamination treatment and solar-cell photoelectrodes. Although TiO_2/SnO_2 composite nanoparticles and thin films have been successful fabricated and well investigated. Comparatively few work on 1-D TiO_2/SnO_2 composite have been reported for lacking of proper fabrication method[1-4]. Electrophoretic deposition, combined with sol-gel processing and template method has been reported to be one of the feasible methods to fabricate inorganic of orgnic 1-D nanomaterials[5-7]. In this way, charged sol particles are driven to certain electrode by external electric field and aggregated into anodic aluminium oxide template holes tightly, which finally leads to the formation of ordered solid nanowires. According to the mechanism of electrophoretic deposition, we suppose 1-D composite nanomaterials can be fabricated by this method.

In this work, uniform morphology, highly ordered TiO_2/SnO_2 composite nanowires arrays were fabricated *via* electrophoretic deposition method with the help of anodic aluminium oxide template. Their morphology, chemical composition and structure were characterized by scanning electron microscopy (SEM), (transmission electron microscopy) TEM, X-ray diffraction pattern (XRD) and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

SEM (JEOL JSM-5600LV) and TEM (JEOL 2010 with EDX) were used to investigate the morphology and chemical composition of the nanowires. The prepared samples were sputter-coated with a thin gold layer prior to observation in the SEM. XRD (Phillips X' Pert Pro MPD) was used to determine the crystal structure and XPS (KRATOS AXIS ULTR) was used to characterize the valence of the elements of the nanowires. The anodic aluminium oxide template used in this work was from Whatman Co., England, with pore diameter of 200 nm. All the reagents used in this experiment were of analytical grade, purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd. The water used in all process is tri-distilled water.

Fabrication of TiO_2/SnO_2 composite nanowire arrays. 10.2 mL $(C_4H_9O)_4Ti$ was dissolved in 40 mL dehydrated alcohol and certain nitric acid was dropwise added to ensure the pH at 3.5. The solution was stirred electromagnetically for 2 h and became transparent colourless colloidal. At the same time, 3.51 g $SnCl_4 \cdot 5H_2O$ and 3 mL hydrochloric acid added dropwise was dissolved in 40 mL dehydrated alcohol. The solution became a yellowish sol after 2 h of circumfluence in water bath (80 ºC). Then the two prepared colloids were mixed under magnetic stirring to form a stable light yellow composite sol. Electrophoretic deposition was performed in a bi-electrodes system. An anodic aluminium oxide template membrane, with a surface sputter-coated with gold, acted as working electrode (negative electrode) and a reeled platinum thread acted counter electrode. The electrodes paralleled to each other and were set *ca.* 3 cm apart. For electrophoretic deposition, a direct potential of 5 V was applied on the electrodes and sustained for 2 h. At the end of electrophoretic deposition, excess sol was blotted off the membrane with filter paper. Samples

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prepared in this manner were annealed at 400 ºC for 2 h and then 650 ºC for 6 h. Careful wet chemical etching with 1 mol/L NaOH was required to remove part of the alumina membrane before the structural characterization.

RESULTS AND DISCUSSION

As illustrated in the SEM patterns (Fig. 1), the obtained nanowires have unique morphology and orderly distribution. They are about 50 μ in length, which corresponds to the thickness of the anodic aluminium oxide template. It is shown that a few of the nanowire heads are hollow, which implies the electrophoretic deposition is a bottom up process. The filled length of the pores is determined by the electrophoretic deposition rate and the deposition time. The EDX spectrum suggests that the nanowire arrays are only composed of Ti, Sn and O. The Ti to Sn atomic ratio is measured as 21:8.1, very close to the nominal doping ratio of 3:1. The presence of the Au and Cu peaks in the EDX spectrum is due to the sputt-coated Au layer on the sample and copper fix-holder for SEM observation.

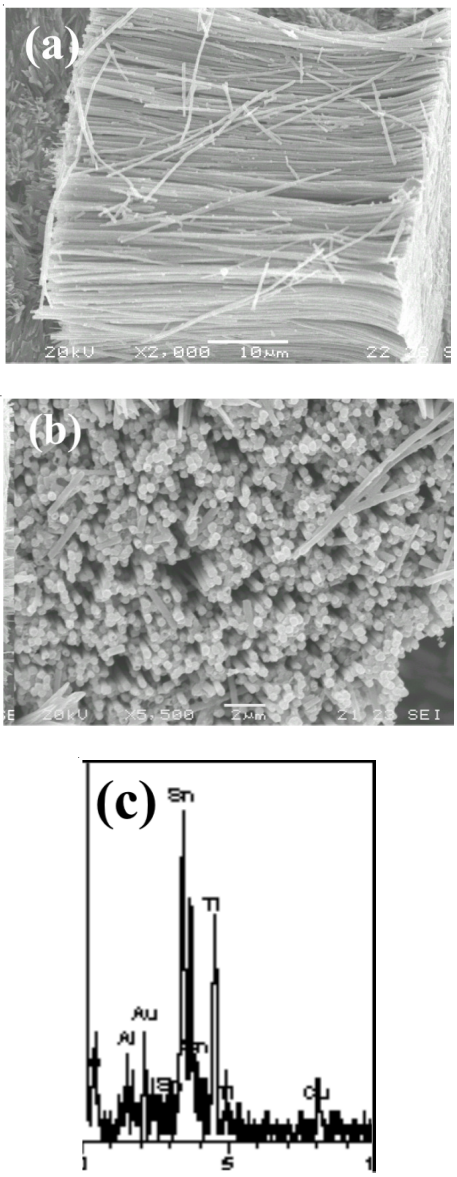

Fig. 1. SEM images of TiO_2/SnO_2 nanowire arrays: (a) side view, (b) top view and (c) corresponding EDX spectrum

The TEM and HRTEM (high resolution TEM) images of the composite nanowires are shown in Fig. 2. It is found that the diameter of the obtained nanowairs is around 190 nm, a little thinner than those of the anodic aluminium oxide template pores. This is because of the densification of the gel during annealing process[8]. The nanowires are composed of lots of small nano-crystallines with diameter of 10-20 nanometers. The electron diffraction pattern indicates the composite nanowire is of polycrystal. In the HRTEM pattern (Fig. 2(b)), the diffraction fringe distances at "a" and "b" area are 0.226 and 0.264 nm, corresponding to the interplanar distance of (200) planes of rutile TiO_2 and (101) planes of tetragonal SnO_2, respectively. Wide amorphous structure is observed between TiO_2 and SnO_2 nano-crystallines.

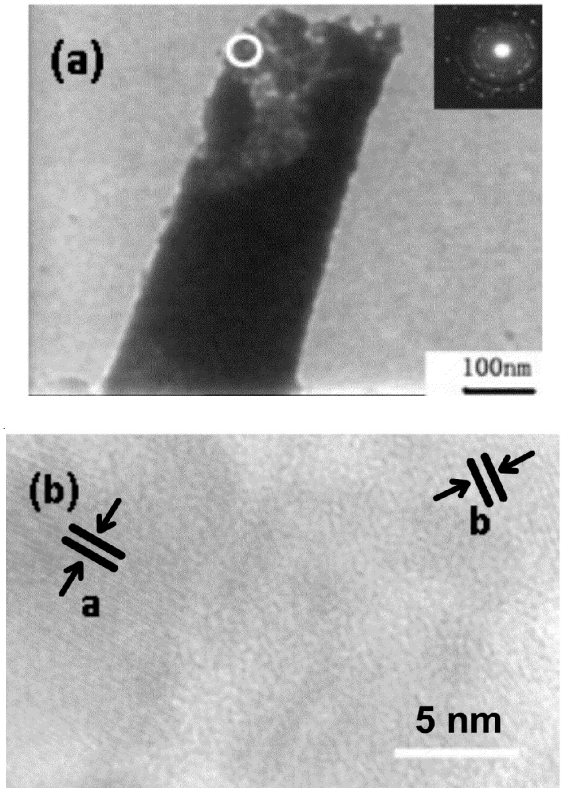

Fig. 2. (a) TEM image of TiO_2/SnO_2 nanowire, the insert is the ED pattern of the carcled part, (b) HRTEM image of the circled part in Fig (a)

The XPS spectrum of the samples is shown in Fig. 3. As shown in Fig. 3(a), Sn 3d has two peaks at 486.8 and 495.2 eV, corresponding to $3d_{5/2}$ and $3d_{3/2}$ peak of Sn in SnO_2, respectively. The two peaks separate clearly, which indicates all Sn itoms are Sn^{4+}. In Fig. 3(b), the bind energy of Ti 2p is 458.7 and 464.7 eV respectively, corresponding to the $2p_{3/2}$ and $2p_{1/2}$ peak of Ti in TiO_2. The bind energy of O 1s (Fig. 3. (c)) is 530.3 eV, corresponding to the bind energy of oxygen element in oxide. In the XRD pattern (Fig. 4.) of the nanowire arrays, all the diffraction peaks of SnO_2 are well corresponding to the literatures of tetragonal SnO_2 (PDF#77-0452) and the six TiO_2 peaks corresponds to the (110), (101), (211), (220), (301) and (312) diffraction peaks of rutile TiO_2 (PDF#88-1175), respectively. The characterization results suggest that the obtained nanowires are composed with crystalline rutile TiO_2 and tetragonal SnO_2.

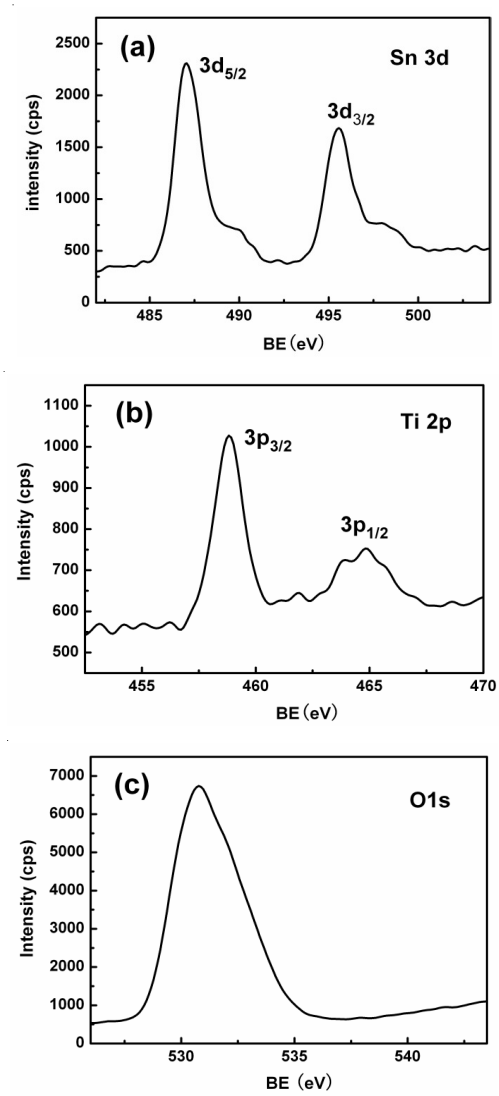

Fig. 3. XPS spectrum of TiO_2/SnO_2 nanowire arrays: (a) Sn 3d, (b) Ti 2p, (c) O 1s

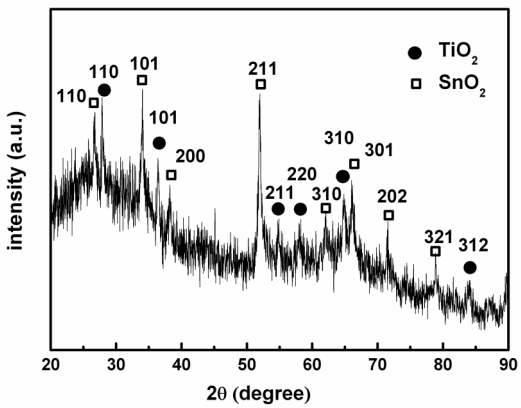

Fig. 4. XRD spectrum of TiO_2/SnO_2 nanowire arrays embeded in anodic aluminium oxide template

The mechanism of the electrophoretic deposition can be explained as follows. When Ti^{4+} sol and Sn^{4+} sol were mixed, they combined to form composite colloid. Since the pH value of the colloid is carefully tuned, both the two colloidal particles had typical double-layer structure and positively charged (inside of the slip plane). As illustrated in Fig. 5, the colloidal particles with a little adsorbed liquid moved to cathode when the external electric field was applied to the electrodes. At the beginning of the deposition, a colloidal tube formed on the surface of the anodic aluminium oxide template wall due to the adsorption effect. Then the tube was filled from the bottom to the top with the the extending of the deposition time. At the same time, the colloidal particles gelated in the anodic aluminium oxide template hole for a condensation process. After enough deposition time, the anodic aluminium oxide template holes were filled up and solid composite nanowires were obtained. During the annealing process, the Ti^{4+}/Sn^{4+} composite gel were dehydrated and crystallized, leading to the formation of crystalline SnO_2 and TiO_2 nano-crystallines and amorphous grain boundary area. The diameters of the prepared nanowires are a little smaller than those of the anodic aluminium oxide template pores due to the densification reaction during sintering process.

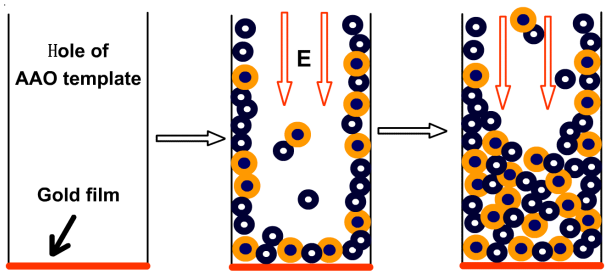

Fig. 5. Schematic diagram of the electrophoretic deposition process of the TiO_2/SnO_2 composite nanowires

Conclusion

Highly ordered TiO_2/SnO_2 composite nanowire arrays have been synthesized by electrophoretic deposition method using anodic aluminium oxide as template. Careful characterization indicates that the obtained composite nanowires are composed of rutile TiO_2 and tetragonal SnO_2 nano-crystallines with amorphous grain boundaries. Subsequent investigations indicate that the gas-sensing sensitivity of prepared TiO_2/SnO_2 composite nanowires is higer than that of SnO_2 nanowires and high absorbance and photocatalytic performance in UV-VIS region is observed. The detail will be reported elsewhere.

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