Self-Organized Synthesis and Mechanism of SnO₂@Carbon Tube-Core Nanowire

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 $SnO_2@$ carbon tube-core nanowire was synthesized *via* a facile self-organized method, which was *in situ* by one step *via* Chemical Vapor Deposition. The resulting composite was characterized by scanning electron microscopy, X-ray diffraction and transmission electron microscope. The diameter of the single nanowire is between 5 nm and 60 nm, while the length would be several tens to hundreds of micrometers. Then X-ray diffraction pattern shows that the composition is amorphous carbon and tin dioxide. Transmission electron microscope images indicate that the nanowire consists of two parts, the outer carbon tube and the inner tin dioxide core. Meanwhile, the possible growth mechanism of $SnO_2@$ carbon tube-core nanowire is also discussed.

Key Words : SnO₂@carbon, Tube-core nanostructure, Nanowire, Self-organized

Introduction

Recently, carbon-encapsulated metal or metallic oxide composite materials have attracted extensive attention due to their broad potentially application in lithium-ion batteries,¹⁻⁴ biology medicine^{5,6} and so on. Presently, various useful and novel structures of carbon-encapsulated metal or metallic oxide have been reported, such as core-shell nanochains,^{4,7} hollow spheres,⁸ and nanotube.^{3,9,10} Meanwhile, various synthesis methods have been developed, such as ultrasonicelectrodeposited,¹ hard template,⁸ the diffusion method,³ the sonochemical method,² sol-gel method,¹¹ the supercritical fluids method,¹² and feeding catalytic precursor during Chemical Vapor Deposition growth.^{13,14} Although the majority of carbon-encapsulated metal or metallic oxide composite materials were obtained, the various production routes always can be divided into more than two main stages and metal or metallic oxide is mainly deposited on the exterior surfaces of CNTs or the filling continuity is weak.¹³ However, it is rare to report SnO₂@carbon tube-core nanowire (STNW) and explain the growth mechanism.

In this paper we report a facile and effective method to synthesize STNW which is one step self-organized method *via* Chemical Vapor Deposition (CVD) *in situ*. An ideal SnO₂@carbon tube-core structure nanowire (STNW) composite was controlled synthesis, and the resulting composite is characterized by several effective testing instruments. Furthermore, the growth mechanism is also discussed in detail.

Experiment Section

Materials. Raw materials used in the experiment as following: Stannic oxide (\geq 99.8%, Kelong), activated carbon, Ni(NO₃)₂ (\geq 98%, Kermel), and Cetyl trimethyl ammonium chloride (CTAC) (\geq 98%, Kelong)

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site. The synthesis of the products was carried out in a hightemperature tube furnace. In a typical procedure, firstly, the substrates, washed several times in absolute ethyl alcohol and acetone, were dipped into the mixture solution Ni(NO₃)₂ and Cetyl trimethyl ammonium chloride (CTAC), extracted quickly and dried in air naturally. Secondly, the mixture of active carbon powder and fine tin dioxide at the mole rate of 2:1 were grinded and diverted into a ceramic boat. Thirdly, the ceramic boat and the substrates were serially placed on the supporting base, transferred into the quartz tube mounted inside the furnace. After that the quartz tube was evacuated by a vacuum pump. Subsequently, under a argon flow in the furnace at the rate of about 0.12 L/min, the guartz tube was heated from the room temperature to 300 °C at the rate of 10 °C/min, and then heated to 1200 °C at the rate of 8 °C/min and kept 4 hours. Finally, turn off the power, the quartz tube was cooled down to the room temperature under a steady argon feed rate (0.12 L/min) atmosphere naturally. The samples were observed on the surface of the substrate.

Characterization Techniques. The morphology of products was observed on the Navie600i field emission scanning electron microscope (FE-SEM), the XRD patterns were gained by the Panlytical X'Pert PRO X-ray diffraction (XRD) employed with Cu-K α radiation. The results of TEM were carried out on JEOL 2010 transmission electron microscope (TEM) at the accelerating voltage of 200 kV.

Results and Discussions

Figure 1 shows the typical scanning electron microscopy (SEM) images and the X-ray diffraction (XRD) patterns of the SnO₂@carbon tube-core nanowire (STNW) sample on substrates. Figure 1(a) clearly reveals the general view of the morphology of the as-prepared samples like nanograss. The local magnified images (Fig. 1(b) and (c)) obviously show



Figure 1. (a-c) The SEM images of the STNW in the different magnification (d) X-ray diffraction patterns of the STNW.

that nanograss consists of countless straight single feature nanowire rather than nanobelt, because the width-to-thickness aspect ratio is smaller than nanobelt obviously. At the same time, the branched nanowires are existed, so the nanograss is likely the crown of trees. From the high magnification SEM images of the nanowire, the external diameter ranges from 5 nm to 60 nm and the length varies from several tens to hundreds of micrometers. The surface of nanowire is smooth and uniform along the fiber axis as shown in Figure 1(c). From the XRD patterns (Fig. 1(d)), compared with the basic peak of SnO₂, most of the diffraction peaks of the as prepared nanowire could be attributed to tetragonal SnO₂ (JCPDS card No. 21-1250, SG: P42/ mnm(136), $a_0 = b_0 = 4.7380$ Å, $c_0 = 3.1880$ Å). The diffraction peaks located at 26.6°, 33.8°, 37.9°, 51.8° and 54.7° are corresponding to the (110), (101), (200), (211) and (220) of the tetragonal SnO₂ phase respectively. It can be observed that the peaks were sharpened, indicating the high crystalline products of SnO₂. Only a broad peak was observed located at 23° to 43°, illustrating amorphous nature of carbon. The sample is consisted of tetragonal SnO₂ and amorphous carbon. There is no Sn or other impurities in the samples obviously.

To investigate further information of the nanowire, the representative TEM and HRTEM images are appeared in Figure 2. These images show the inner structure of STNW. Figure 2(a) image is naturally confirmed the tube-core nano-structure of integrated special single nanowire contained in STNW. It is clearly appears that SnO_2 nanowire is filling the whole inner cavity which is formed by the outer carbon layer, without any space in the core. The nanowire structure contains parts: the branch part and the stem part. Both the stem and the branch are uniform. For example, external diameter of ~30 nm cavity is filled with SnO_2 nanowire

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Figure 2. (a) The TEM of the branched nanowire (b) Local magnified TEM image of the branch part (c) HRTEM image of the branched part (d) HRTEM image of the stem part.

whose length is up to hundreds of micrometers and a tubecore structure is formed, as marked in Figure 2. However, SnO₂ nanowire, encapsulated in thinner cavity with the diameter no more than 60 nm, is uniform growth along one orientation, in addition to the branch part. Figure 2(b) shows the typical branched structure. The character of the nanowire is confirmed in Figure 2(c) and (d), which show HRTEM images of tube-core structure in the branch part and the stem part separately. On the one hand, the local magnified TEM would be depicted the two layers obviously by contrast. The thickness of the two layers is different, the outer is about 2 nm, and the inner is about tens of nanometers. On the other hand, these are clearly to illustrate that amorphous carbon is located in the outer layer. In the inner, the aligned lattice fringes of the nanowires are obviously displayed about the stem. In detail, the interplanar spacing is measured to be 0.264 nm, which corresponds to the (101) plane of SnO_2 lattice. So in the stem the lattice fringes are along with the growth direction of nanowires regularly, the growth direction of the stem [101] crystalline orientation. While in the branch part the lattice fringe distances are 0.264 nm as well, but the intersection angle between the growth direction and the plane is measured to be 68°, the result of further calculating and analysis indicates that the growth direction of the branched part is [110] crystalline orientations. With the continuous growth, the growth direction is incline to [101] crystalline orientations.

In order to precisely investigate the growth mechanism of inserting SnO_2 into the interior cavity, those conditions, such as the resource without SnO_2 , the substrates dealt only with $Ni(NO_3)_2$ solution and the substrates dealt only with CTAC, have been researched respectively. These conditions are used to show the function of $Ni(NO_3)_2$ and CTAC to the

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Figure 3. The morphology of the sample (a) When there was no resource and the substrate was dealt only with CTAC solution (b) when there was no resource and the substrates were dealt only with the mixed solution of Ni(NO₃)₂ and CTAC. (c) when there was only active carbon as the resource and the substrates were dealt with the mixed solution. (d) While the resource consists of SnO₂ and active carbon.

growth of STNW. The SEM images show the produce on the substrates in Figure 3. Figure 3 images show the morphology of the sample. When there was no resource and the substrate was dealt only with CTAC solution, monodisperse particles were gained as Figure 3(a) shown. Figure 3(b) shows the sample, when there was no resource and the substrates were dealt only with the mixed solution of Ni(NO₃)₂ and CTAC. The monodisperse particle was formed the inner cavity structure with the Ni(NO₃)₂ molecule in the core. Figure 3(c) is the morphology of the sample when there was only active carbon as the resource and the substrates were dealt with the mixed solution. A large amount of nanowires, unsmooth surface and out-of-straight, grow up on the substrate. To analyze the composition, the nanowire is carbon. These springs-like rough carbon nanowires also display the importance of Ni catalyst. In Figure 3(d) image, it contains a large amount of uniform and straight nanowires, which is the sample taking the SnO₂ and active carbon as resources.

From those detail process above, the mechanism of the growth process revealed in Figure 4 has been concluded. In the synthesis process of $SnO_2@$ carbon tube-core nanostructure composition, $Ni(NO_3)_2$ and CTAC play crucial roles. At first, $Ni(NO_3)_2$ molecules are dispersed uniformly with the cationic surfactant CTAC on the substrates. Then CTAC clusters are formed when the substrates dry in the air naturally such as the feature of Figure 4(a) shown. The $Ni(NO_3)_2$ molecules bundle in the CTAC cluster, due to CTAC is a macromolecular long-chain structure. Subsequently, $Ni(NO_3)_2$ decompose into Ni at high temperature,¹⁵



Figure 4. Schematic diagrams for the synthesis the preparation procedure of $SnO_2@$ carbon nanocomposite.

which is the catalyst in the growth process of SnO_2 nanowires. The long carbon chain of CTAC is formed to carbon nanowires preferentially at relatively high temperature in initial stage shown in Figure 4(b). With the increasing of gaseous carbon, the carbon shell is smoother gradually. The liquid Ni catalytic particles at the high temperature are absorbed SnO_2 gas from the gas mixture to form a Ni-SnO₂ solid state solution, and SnO_2 nanowires grow in the cave shown in Figure 4(c). So, the mechanism belongs to vapourliquid-solid (V-L-S) mechanism. Whereas, at 1200 °C the following chemical reaction would take place during the thermal evaporation process:

$$2\operatorname{SnO}_2(s) + \operatorname{C}(s) = 2\operatorname{SnO}(v) + \operatorname{CO}(v) \tag{1}$$

$$CO(v) + SnO(v) = Sn(s) + CO_2(v)$$
⁽²⁾

$$2\operatorname{SnO}(v) = \operatorname{SnO}_2(s) + \operatorname{Sn}(l)$$
(3)

And the principal reaction is SnO₂ gasify. Meanwhile on the carbon tube internal surface, there might be plenty dangling bonds of oxygen, which provide the activity sites for adsorption SnO₂ vapor. The abundance of SnO₂ vapor is beneficial for crystal SnO2 growth along a certain orientation. In this condition, the outer carbon is uniform in the entirety growth process. As the raising supersaturation accumulated, the growth direction of SnO₂ nanowires tends to be consistent as shown in Figure 4(d). So the nanowire is straighter than the carbon nanotube shown in Figure 3(d). The SnO₂ nanowires are facile to form branched part. So the nanowies constitute nanograss such as Figures 3(d) shown. Like the growth of the branched structure SnO₂ nanowire, which has been reported,¹⁶ the branched SnO₂@carbon nanowire is formed as Sn particles the nucleation sites depositing on the SnO₂ nanowire. Though the crystal orientation is changing in the junction, the branch nanowire also grows along the definite directions soon and then result in uniform branched nanowire shown in Figure 2. The branched nanowires are straight and uniform, so the deposition carbon layer is homogeneous. In brief, a perfect SnO₂@carbon tube-core nanostructure composition is obtained in our experiment.

Conclusion

The ideal composite of SnO₂@carbon tube-core nanowire

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(STNW) has been successfully synthesized *via* a facility self-organized method *in situ* by one step. The special tubecore nanostructure composite is novel, and the filling rate is improved greatly. In addition, the growth mechanism of the STNW is discussed in detail, which coincides with vapourliquid-solid (V-L-S) mechanism. This novel structure STNW could offer a new path for the design of low-cost functional composites containing nanoparticles with controllable morphologies, structures, and compositions as well as promising applications.

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