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RESEARCH PAPER

Synthesis of hollow carbon nanostructures using a ZnO template method

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Abstract: A ZnO template approach for the large scale synthesis of hollow carbon nanostructures was developed. A diluted ethylbenzene stream was used to form a carbon layer on the template at a high temperature and a dilute HCl solution was used to etch the template. Hollow carbon nanotubes and hollow carbon nanospheres were fabricated using ZnO nanorods and nanospheres as the respective templates. The present process is simple, efficient and low cost, and may be extended to fabricate other hollow carbon nanostructures used in catalytic reactions and energy storage.

Key Words: Nanocarbon; Hollow structure; Template method; Coking reaction

1 Introduction

Recently, the design and synthesis of hollow carbon nanostructures have attracted considerable attention owing to their potential applications in catalyst supports, gas storage and separation, and lithium-ion batteries[1, 2]. Up to now, the hollow carbon nanostructures have been synthesized by a template method and a hydrothermal method. Among them, the template method is more acceptable because the structure of as-prepared hollow carbon nanomaterials could be controlled by tuning the size or the morphology of the templates[3, 4]. In general, for the template method, a core-shell structure is synthesized by coating a carbon precursor on a hard template core, followed by carbonization and core removal to obtain the hollow carbon nanostructures. The template approach based on the use of solid molds also provides opportunities for synthesizing various carbon nanostructures[5-8]. However, the expensive surfactant is usually required by functionalizing or modifying the template due to the incompatibility between the template surface and shell material, resulting in a complicated fabrication process and high cost[9]. Thus, developing an efficient and low cost process to synthesize the hollow carbon nanostructures is still challenging.

Herein, we reported a facile and scalable synthesis of hollow carbon nanostructures by a template method assisted with a fast coking process at high temperatures. Through this efficient and low cost method, the hollow carbon nanotubes and hollow carbon nanospheres can be fabricated by using ZnO nanostructures as templates. The various ZnO nanostructures as template materials can be used to fabricate complex carbon nanostructures. In addition, the ZnO templates can be easily dissolved and removed in mild acids or bases[10, 11]. The synthetic procedure of hollow carbon nanostructures is illustrated in scheme 1. Firstly, the as-prepared ZnO nanorods and commercial available ZnO nanospheres were chosen as the templates. Subsequently, a carbon layer was uniformly coated on the surface of ZnO templates (C@ZnO) by a fast coking process with diluted elthylbenzene at 700 °C for just 2 min. Afterwards, the C@ZnO nanocompsite was treated with HCl solution at room temperature, and the hollow carbon nanotubes and hollow carbon nanospheres were obtained.

2 Experimental

The ZnO nanorod was synthesized by a typical physical vapor deposition method under atmosphere pressure[12]. The source materials, consisting of a mixture of 0.5 g of ZnO powder and 0.5 g of active carbon, were loaded into a ceramic boat that was positioned in the middle of a quartz tube. The silica wafer was used as the substrate to collect samples, which was placed downstream the source material in the temperature zone of 700 °C. Prior to heating, the quartz tube was purged with Ar (30 mL/min) for 30 min. Then, it was heated up to 1000 °C under the mixture of Ar (50 mL/min) and O_2 (10 mL/min) for 1 h. The surface of the silica substrate became white after the reaction, indicating that ZnO nanorod was deposited on it. The ZnO nanospheres with sizes of50-100 nm were bought from Sinopharm Chemical Reagent Co., Ltd. The C@ZnO nanocomposite was prepared by a fast coking process with the ZnO template under a mixed gas flow (100 mL/min) of 2% ethylbezene balanced with He at 700 °C for just 2 min. After the ZnO template was removed with a 5% HCl aqueous solution for 2 h, the hollow carbon naostructures were successfully collected. Transmission electron microscopy (TEM) was performed by a Tecnai G 2

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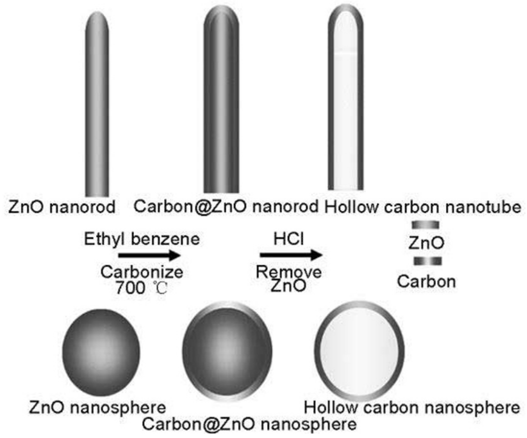

Fig. 1 A schematic illustration of the preparation of hollow carbon nanostructures.

F20 S-TWIN electron microscope operated at 200 kV. Raman spectroscopy was performed on a LabRam HR 800 using a 633 nm laser.

3 Results and discussion

Fig. 1a and 1d show typical SEM and TEM images of the ZnO nanorods prepared by the traditional chemical vapor deposition method. Note that the as-synthesized ZnO nanorods are uniform in shape and size. The average length and width of the ZnO nanorods is 2-10 μm and 50-200 nm, respectively. The as-prepared ZnO nanorods were then employed as templates for the growth of the carbon layer by a fast coking process of ethylbenzene at 700 °C for just 2 min. Our previous study demonstrated that the coking reaction of ethylbenzene on the metal oxide catalyst surface can be quickly happened at high temperatures[13]. Fig. 2b and 2d present the TEM images of the ZnO nanorods after they are coated by the fast coking process. It can be seen that a carbon layer is uniformly coated on the middle part and even the tip of one individual ZnO nanorod. There is no gap between the carbon layer and ZnO nanorods as displayed in the HRTEM images in Fig. 2c and 2f. The average thickness of the carbon layer is around 5-10 nm. In addition, it is found that the morphology and the structure of ZnO nanorods are well maintained after being coated by the carbon layer. The TEM image in the Fig. 1 provides further the evidence that the whole of one single ZnO nanorod is completely covered by a uniform carbon layer through this fast coking process.

Fig. 3a shows a representative TEM image of the finally obtained hollow carbon nanotubes after ZnO nanorods are leached away by the diluted HCl solution at room temperature. Note that all the as-prepared carbon nanostructures exhibit tubular structures (Fig. 3b). In particular, these tubular structures almost are replicated from the initial morphologies of the ZnO nanorods. The hollow carbon nanotubes resulting from the ZnO nanorods have inner diameters of 50-200 nm, and thickness of 5-10 nm with quite smooth walls. Meanwhile, there are big holes generated on the tip of some hollow carbon nanotubes (Fig. 3c). HR-TEM image in Fig. 3d presents that the graphitic layers fabricated in the hollow carbon nanotubes are inconsecutive. All the above TEM results indicate that we have developed an efficient and facile way to prepare hollow carbon nanotubes though the feasible template method.

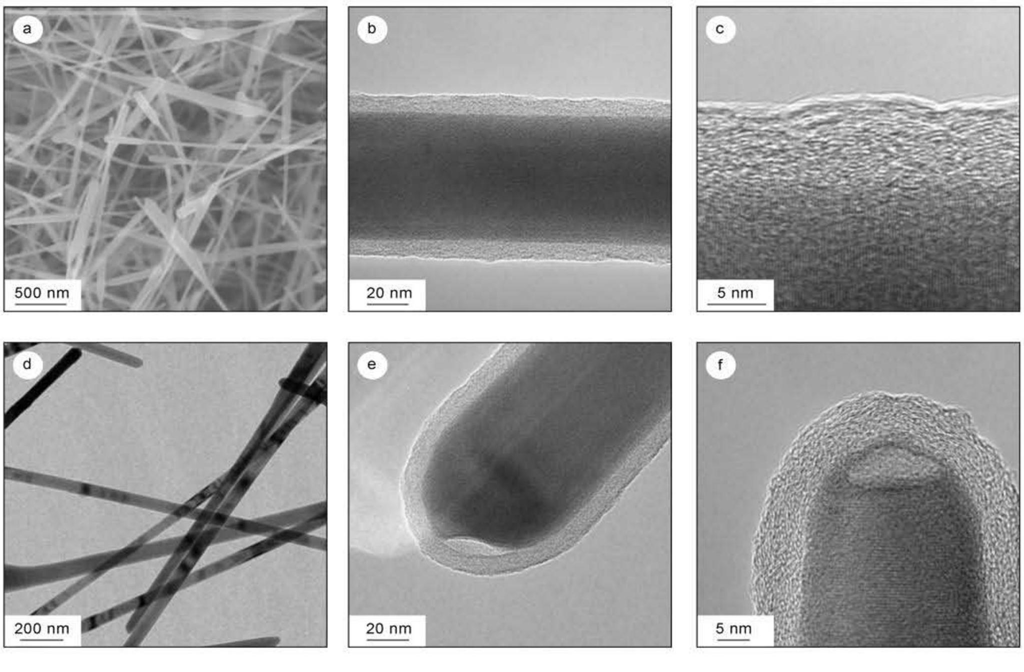

Fig. 2 (a, d) SEM and TEM images of the ZnO nanorods as the template, TEM images of the carbon layer coated on one single ZnO nanorod (b-c) in the middle part and (e-f) in the tip part.