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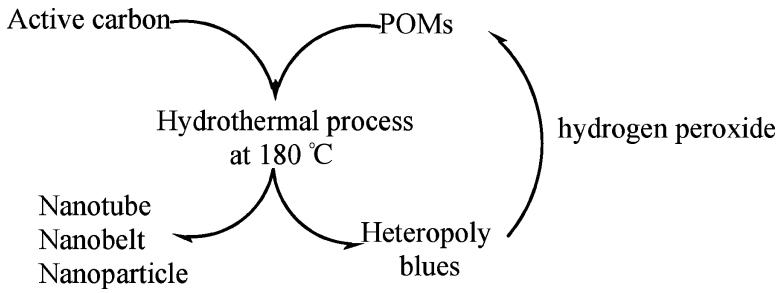

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Controllable Fabrication of Carbon Nanotube and Nanobelt with a Polyoxometalate-Assisted Mild Hydrothermal Process

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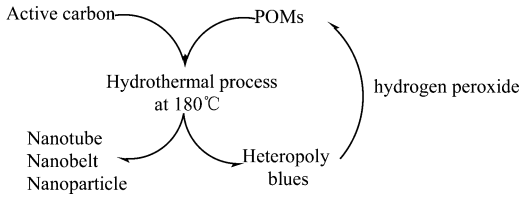
Since the discovery of carbon nanotubes (CNTs) in 1991, one-dimensional (1D) carbon nanomaterials have attracted considerable attention due to their distinctive geometries, novel physical and chemical properties, and potential applications in numerous areas such as nanoscale electronics and photonics.[1−6] Considerable efforts have been devoted to study the preparation and growth mechanism of 1D carbon materials. For example, metal-catalyzed chemical vapor deposition (CVD), arc evaporation, and laser ablation of carbon[7−12] are widely used to obtain CNTs. Recently, some new methods have been consecutively developed for the synthesis of CNTs. Examples include high-temperature hydrothermal processing, solvothermal route, sonochemical route, and solid-state metathesis reaction.[13−19] However, they suffer from the limits of high temperature and pressure, special equipment and conditions, or tedious procedures. Therefore, exploring general and simple methods to fabricate 1D carbon materials is still a challenge.

The hydrothermal technique occupies a unique place in modern science and technology. Recent studies verify that mild hydrothermal processes show extraordinary ability in the fabrication of the 1D nanostructured materials.[20−23] Especially the participation of water can simplify the synthesis and purification process of nanostructured carbon based on the complex chemistry in the C−H−O system.[17,24−27] On the other hand, polyoxometalates (POMs) represent an attractive class bearing many unique functions in catalysis. Besides their structural robustness, the electronic characteristics of POMs have played an important role in their catalytic behavior. Dumesic et al. successfully applied POM compounds for power generation reactions in a C−H−O reaction system.[28−34] Here, based on the above studies, a POMs-assisted hydrothermal system was developed for the controllable synthesis of 1D carbon nanostructures. The results demonstrate that carbon nanotubes, nanobelts, and nanoparticles can be directly prepared from active carbon powder, and the POMs used are renewable.

Adding tungstosilicic acid ($H_4SiW_{12}O_{40}$) or tungstophosphoric acid ($H_3PW_{12}O_{40}$) to the hydrothermal system leads to the formation of carbon nanoparticles (CNPs). When $H_3PMo_{12}O_{40}$ (or $H_4SiMo_{12}O_{40}$) was used, CNTs can be obtained. Using phosphovanadomolybdate ($H_5PV_2Mo_{10}O_{40}$) results in the formation of carbon nanobelts (CNBs). After the hydrothermal reaction, the POMs used were changed into heteropoly blues, and active carbon powder was converted partially into CNTs, CNBs, and CNPs. The obtained heteropoly blues can be converted back to the POMs with the addition of a small amount of H_2O_2 solution. Thus, this approach can be considered as a green and renewable synthesis strategy, which will be valuable toward research in the nanometer regime. Scheme 1 shows this controllable and renewable synthesis route.

Scheme 1. Controllable and Renewable Synthesis Route



In a typical experiment, 8 mL of POMs solution (0.05−0.5 M) and 0.3−0.5 g of carbon powder were placed into in a stainless steel autoclave of 12-mL capacity (Teflon-lined reactor). The autoclave was sealed and maintained at 160−180 °C for 72 h and then allowed to cool to room temperature naturally. The dark precipitate was collected and washed with distilled water and absolute ethanol, respectively. After that, the obtained sample was dried in a vacuum at 65 °C for 2 h. Electron microscopy studies were carried out using a JEM-2010 at an operating voltage of 200 kV. Samples were prepared by ultrasonic dispersion of the amorphous particles in ethanol. After ultrasionication, a drop of the suspension was placed on a microgrid and dried in air.

The observations revealed the formation of the CNTs after the hydrothermal process assisted by $H_4SiMo_{12}O_{40}$ (or $H_3PMo_{12}O_{40}$). Typical transmission electron microscope (TEM) images of the CNTs are shown in Figure 1. The individual fiber exhibits a middle-hollow structure (Figure 1b). The hollow nanotubes have diameters in the range of tens and lengths in the range of hundreds of nanometers. The inner diameters are between 5 and 10 nm, and the outer diameters are between 20 and 30 nm. Figure 1c show the high-resolution TEM (HRTEM) images for the wall structure of a carbon nanotube. The walls are composed of graphite sheets aligned to the tube axis. The interlayer spacing in the walls, about 0.34 nm, corresponds to the 002 distance of graphitic carbon lattice.

The TEM observations revealed the formation of the CNBs after the $H_5PV_2Mo_{10}O_{40}$-assisted hydrothermal process. A typical nanobelt has a width ranging from 200 to 500 nm, and a length up to several micrometers. The thickness of the belts is about 10 nm, as estimated from the TEM images, and the width-to-thickness ratios are about 20−60. The single-crystalline nature of CNBs was further confirmed with electron diffraction (ED) measurements. The selected area electron diffraction (SAED) pattern (inset in Figure 2a and b) taken from a single nanobelt indicates that the nanobelts were single crystals. Images a and b of Figure 2 show the selected SAED patterns taken from different areas (the trunk and the top, respectively) in a single belt. It was found that the SAED patterns recorded from different areas of the individual CNB were almost identical. The SAED patterns can be indexed to the 002 planes of hexagonal phase of carbon orienting perpendicular to the electron beam. Figure 2c shows a crooked nanobelt. The typical thickness

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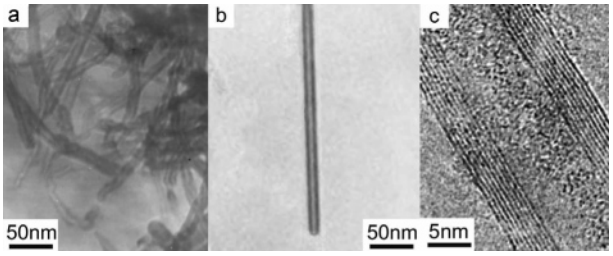

Figure 1. TEM images (a and b) of CNTs and HRTEM image of the CNTs.

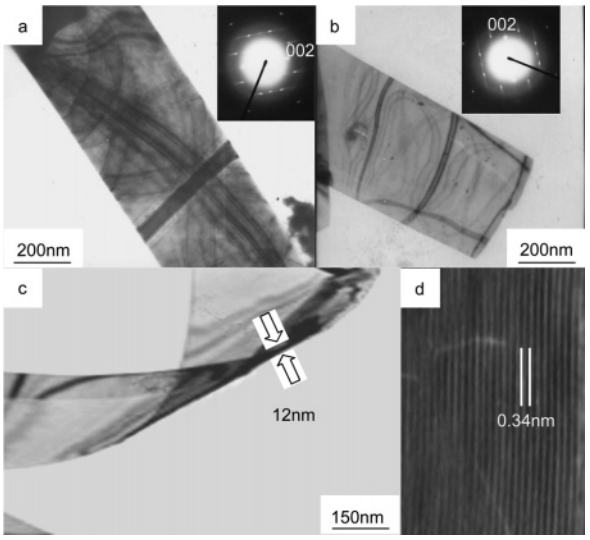

Figure 2. (a) TEM image of the trunk of a single CNB. Right inset: SAED pattern of the same nanorod. (b) TEM image of top of a single CNB. Right inset: SAED pattern of the same nanorod. (c) TEM image of a crooked nanobelt. (d) HRTEM image of a single-crystalline carbon nanobelt as the same one in c.

estimated from TEM observations was about 10−15 nm as shown in Figure 2c. Figure 2d is a representative HRTEM image of a single-crystalline CNB, showing the clearly interplanar distance d_{002} = 0.34 nm. It also reveals that the belt is free from dislocation and stacking fault. The evolution of the carbon nanobelts was also studied with TEM of the carbon nanostructures at various stages of the hydrothermal process. TEM images of the products after a reaction for 24 h revealed that products mainly consist of sheetlike particles with sizes about several tens of nanometers. After heating for 48 h, nanobelts could be clearly observed. Further extending the heating period led to the formation of longer nanobelts.

Experiments using tungstosilicic acid ($H_4SiW_{12}O_{40}$) or tungstophosphoric acid ($H_3PW_{12}O_{40}$) lead to the formation of carbon nanoparticles. The typical TEM image of the CNPs (see Supporting Information) shows that CNPs are uniform with the average sizes of about 8−10 nm.

In series of control experiments, sodium phosphomolybdate etc. used as additives cannot lead to the formation of well-defined nanostructured carbon, which indicates that the aqueous acids are helpful for the formation of nanostructured carbon by a hydrothermal process.[35,36] Although the fundamental basis of these hydrothermal reactions in this system is still to be further understood, it is important to point out that the excellent properties (unique electronic characteristics) of POMs may play a major role in determining the formation of those nanostructured carbons. It can be foreseen that unique electronic characteristics of POMs may be indicative for the synthesis of many nanostructured materials that can be obtained through redox.

In summary, a simple POMs-assisted mild hydrothermal method was developed to fabricate CNPs, CNTs, and CNBs. This is a convenient, controllable, and renewable approach for the synthesis of carbon nanomaterials with the participation of POMs. Further work is now in progress to evaluate the possibility of synthesizing oxide nanostructures using a similar method.

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Supporting Information Available: Detailed characterization results, experimental details, and complete refs 3 and 25. This material is available free of charge via the Internet at http://pubs.acs.org.

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