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Synthesis of Carbon Nanotube Bundles with Mesoporous Structure by a Self-Assembly Solvothermal Route

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A kind of carbon nanotube bundle has been synthesized by a simple one-step solvothermal reaction between Na and hexachlorobenzene (HCB) using NiCl_2 as catalyst precursor. Before the reaction, NiCl_2 was initially dispersed ultrasonically in cyclohexane then prereduced by Na at 230 °C to produce small Ni particles in reduced state. The tubes thus-produced have a uniform outer diameter of about 20 nm, an inner diameter of 4 nm, and are highly ordered assembled as bundles which have a 2D hexagonal arrangement as proven by SAXS and TEM experiments.

Introduction

In the past decade, the study of synthesis of new porous carbon materials has made great breakthroughs mainly in two aspects: synthesis of carbon nanotubes via different kinds of methods after the first observation of carbon nanotubes with graphite-like structure,^{1–5} and synthesis of ordered porous carbon materials with certain kinds of ordered porous silica templates. The latter have been successfully synthesized with microporous zeolite Y, as well as mesoporous molecular sieves such as MCM-48, etc., by successive procedures of infiltration, carbonization of carbon precursors in the template pores, and template removal.^{6–11} Usually these mesoporous carbon materials have amorphous structures, whereas walls of most of carbon nanotubes consist of crystallized graphitic cylindrical layers. Because of the promising applications of carbon materials, researchers are seeking new synthetic routes and new forms of carbon materials.

Recently, Lee et al. reported the synthesis of carbon materials with graphitic structure through a Wurtz-like reaction of hexachlorobenzene (HCB) and sodium, but no porous structure was obtained.¹² Before their en-

deavors, Qian's group reported the formation of carbon nanotubes from a similar reaction between HCB and potassium with a mixed catalyst.¹³ However, the tubes in this work grew with random orientation and in insignificant amounts.¹³ In the present paper, we report an improved method to synthesize highly ordered tube-like carbon materials with high yield and good arrangement.

Experimental Section

Synthesis. In this experiment, 200 mg of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was first dehydrated at 230 °C, then ground and dispersed ultrasonically in ca. 40 mL of cyclohexane for 30 min. The as-prepared NiCl_2 was added together with 2.0 g Na to a stainless steel autoclave lined with glass. The autoclave was sealed and heated at a temperature of 230 °C for 6 h and then cooled. A 2.0-g portion of HCB was added to the autoclave, which was at the same time filled with cyclohexane to $\frac{2}{3}$ of its capacity. The autoclave was sealed again and heated at 230 °C for 10 h. The product was removed from the autoclave after it cooled to room temperature, and was treated sequentially with ethanol, hot cyclohexane, diluted sulfuric acid, and hot water. The as-treated product was finally dried at 80 °C.

Characterization. SEM pictures of the samples were taken on a HB-600 electron microscope with an accelerating voltage of 25 kV. HRTEM pictures were taken on Philips CM 200 with an accelerating voltage of 200 kV. XRD patterns were recorded on a Rigaku D/max-rb diffractometer equipped with a $\text{Cu K}\alpha$ X-ray source operating at 40 kV and 100 mA. SAXS intensities were recorded on MX Labo (MAC Science) with $\text{Cu K}\alpha$ radiation (1.54056 Å) at 40 kV and 20 mA. UV Raman experiments were carried out on a homemade apparatus described elsewhere.^{14,15}

Results and Discussion

During the study, a sodium slice was put directly into cyclohexane, together with HCB, and this was heated immediately at a temperature of 230 °C without any

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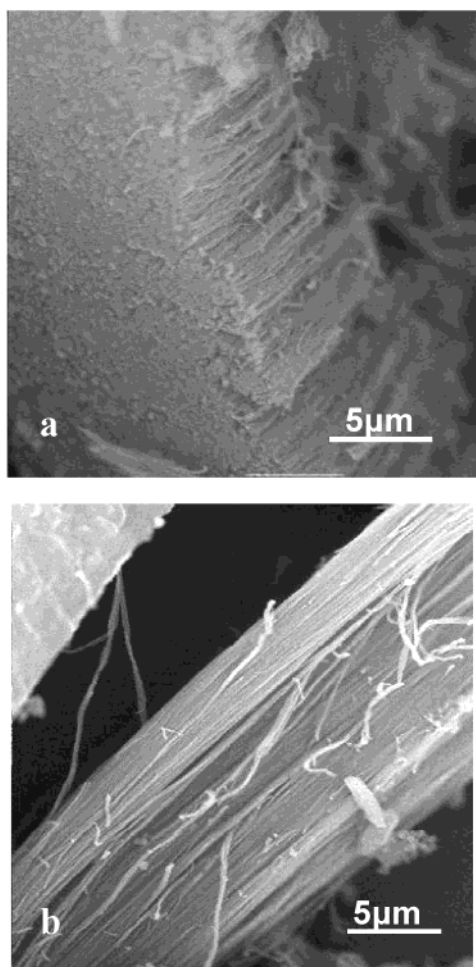


Figure 1. SEM images of the as-synthesized products with different lengths (a, b).

catalyst. The products were black carbon slices without any ordered structure, which indicated that the two reactants underwent a very rapid reaction, such that the sodium slices could not even melt to form spheres at such a temperature before they were consumed. Also, the yield of carbon tubes by such a method was poor. The planar graphitic structure of the product reported by Lee et al. also confirms that tubular structures cannot be formed successfully without catalyst.¹²

Thus, a direct mixture of NiCl_2 with the two reactants in the experiment will not bring the catalytic function of the reduced nickel to an effective degree because of the rapid reaction. With this consideration, NiCl_2 was first dispersed by ultrasonication and added with sodium to the autoclave, then the autoclave was closed and heated to 230 °C, and held at that temperature for 6 h. This process ensured that the precursor of the real catalyst, NiCl_2 , was able to be fully reduced by metallic sodium and that tiny particles of nickel would deposit on the surface of Na. The catalytic function of nickel could thus be fully realized in the subsequent reaction between sodium and HCB, and the possibility of a reaction between the two reactants without catalysis would be decreased to a minimum.

SEM images (Figure 1) show that the products (side view) are tube-like structures in highly aligned arrangements with a length of a few tens of micrometers (Figure 1a) to many hundreds of micrometers or even longer

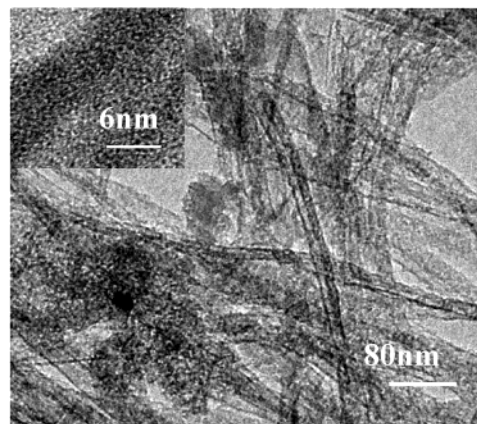


Figure 2. HRTEM pictures of the tube-like morphology of the separated product. The inset shows the amorphous wall structure.

(Figure 1b). Some shell-like blocks were also observed within the scope. The content of tube-like carbon is over 70% in the as-synthesized product.

A HRTEM image (Figure 2) shows that the large bundles of tubes can be separated ultrasonically into single tubes. The tubes were found mostly straight with open ends; neither closed caps nor encapsulated metal particles were observed in the scope. This is quite different from those reports about carbon nanotubes with closed tips or with helix shapes synthesized by some catalytic methods.^{12,16,17} During the present reaction, the reduced nickel particles depositing on the surface of sodium spheres perform as active centers, and they are expected to stay on the surface of the sodium all through the reaction which guarantees the continuous catalytic growth of the tube-like structure from the bottom end during the reaction. The open-tip morphology of the product confirms this proposal. And the size of the nickel particles is believed to have determined the pore size of the carbon materials. The outer diameter of the tubes is about 25 nm with a wall thickness of about 7~10 nm (Figure 2 inset). Thus, the inner diameter of these tubes should be less than 10 nm.

The pore-size-distribution measurement determined by the nitrogen adsorption–desorption isothermal and BJH methods (Figure 3) indicates that these tubes have pores of diameter ~5 nm (the BET surface area is 1087 m^2/g). This is in good agreement with the TEM result and shows that the carbon tube bundles obtained here are a kind of mesoporous carbon material. But the present mesoporous carbon material is different from those reported in refs 6–11, which could not be separated from each other by the ultrasonic treatment used here. At the same time, the inset picture shows no sign of a stratified graphene-layer-like structure in the wall structure as reported of carbon nanotubes in other studies,^{1,12,18} and indicates instead an amorphous wall structure of our product.

Figure 4 shows that the as-synthesized sample was not in crystalline form, with only a weak and very broad

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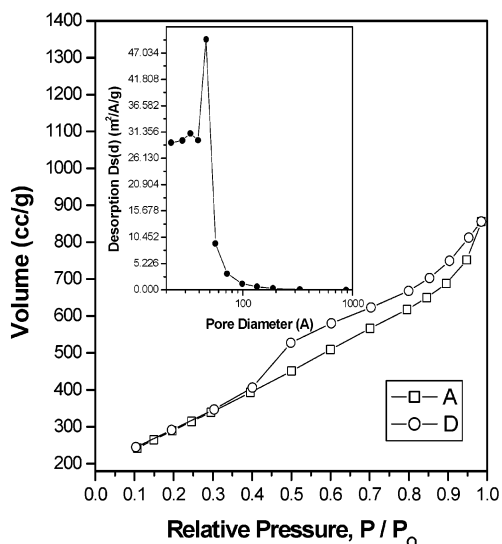


Figure 3. Nitrogen adsorption-desorption isotherm measured at 77 K for the sample treated with He flow at 800 °C for 5 h. The inset shows the pore size is about 5 nm by BJH method. The BET surface area is 1087 m²/g.

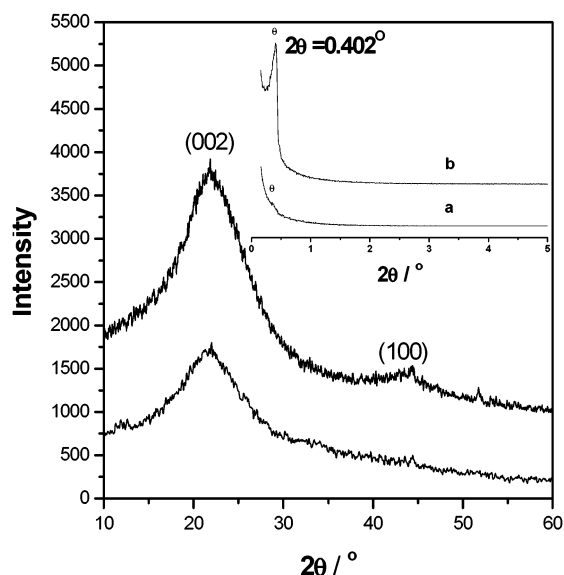


Figure 4. XRD patterns of the (a) as-synthesized product and (b) product treated with helium flow at 800 °C for 5 h. Inset shows SAXS patterns of the two samples, with diffraction peaks at $2\theta = 0.402^\circ$ (marked by \blacktriangledown) indicating a d value of 21.98 nm.

hump at about $2\theta = 23^\circ$ (Figure 4a). No other characteristic graphitic diffraction peaks appear at higher reflection angles as in other reports.^{18,19} After the 800 °C treatment, the 23° hump strengthened but kept its broad nature, and a new broad signal at about $2\theta = 44^\circ$ appeared (Figure 4b) corresponding to the (002) and (100) diffraction peaks, respectively. The appearance of these very broad peaks indicates that the amorphous structure of the as-synthesized sample somehow became ordered after the high temperature treatment. Meanwhile, in the inset SAXS patterns, the as-synthesized product (a) shows only an insignificant signal at $2\theta = 0.402^\circ$, which increases remarkably after the treatment at 800 °C under helium flow for 5 h (b), indicating a d

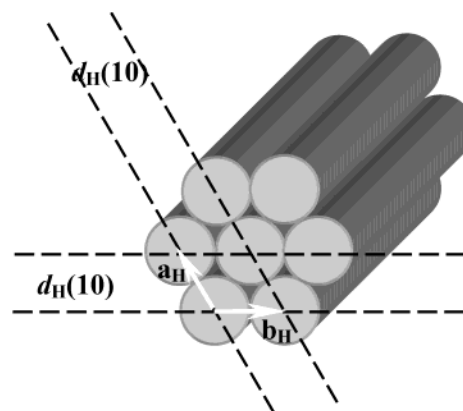


Figure 5. Schematic representation of the 2-dimensional hexagonal ($p6m$) arrangement of the carbon tubes, in which $a_H = b_H = D$, D is the outer diameter of the tubes. (For convenience, only the outer shells of the walls are illustrated here.)

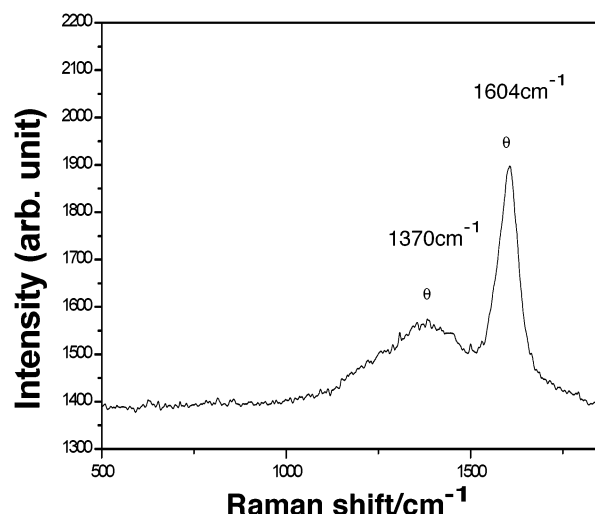


Figure 6. UV Raman spectrum of the as-synthesized product.

value of 21.98 nm. This is in good agreement with a two-dimensional hexagonal ($p6m$) arrangement as shown schematically in Figure 5. In this representation, $d_H(10) = (3/4)^{1/2} a_H$. For the product of this experiment, the value of a_H is the outer diameter of one tube, i.e., about 25 nm as indicated in the HRTEM picture, and thus $d_H(10) = 21.65$ nm in this case. This value agrees quite well with the value obtained by SAXS. The low intensity of the $2\theta = 0.402^\circ$ peak of the as-synthesized product may be due to some depositions of polyaromatic species within the pores, which weakens the ordered arrangement. When heated at a high temperature, these species were either transformed into more ordered structure or driven away, and the 2-D hexagonal arrangement became clearer and enhanced.

In the UV Raman study shown in Figure 6, a strong absorption peak appeared at about 1604 cm⁻¹ and a broad hump at around 1370 cm⁻¹. The 1370 cm⁻¹ hump is reasonably informational for the disordered amorphous structure or the very small graphitic fragments. The 1604 cm⁻¹ peak was attributed to the presence of disordered sp^2 hybridized carbon in polyolefinic, polyaromatic, or substituted aromatic species as attributed in some other studies.^{14,15,20} Considering hexagonal carbon rings are assembling units for the products in this study, the appearance of this 1604 cm⁻¹ peak is

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quite understandable and indicates that the fabricating units did not assemble in a very ordered way but only underwent a random cross-linking process.

Conclusion

In summary, a kind of highly ordered tube-like carbon bundle with mesoporous structure (the pore size is around 5 nm) is synthesized through a hydrothermal route by catalytic assembling of carbon rings at a low temperature. SEM, N₂ isotherm, HRTEM, and SAXS experiments reveal the size and wall structure of the

product. XRD and UV Raman confirm that this kind of carbon tube has amorphous wall structure, which is quite unique and different from those graphitic cylindrical structures of carbon nanotubes reported before.

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