

Fabrication and Characterization of Mesoporous Carbon Nanosheets Using Halloysite Nanotubes and Polypyrrole via a Template-Like Method

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ABSTRACT: A novel synthesis route for mesoporous carbon (MC) nanosheets were developed using halloysite nanotubes (HNTs), a type of natural clay that is structurally and chemically similar to mineral kaolinite, as inorganic matrix and using polypyrrole (PPy) as carbon precursor by a template-like method. First, PPy/HNT hybrids were prepared by *in situ* oxidative polymerization. Carbon (C)/HNT hybrids were further obtained by pyrolysis of the PPy/HNT hybrids. MC was obtained after the removal of inorganic template by hydrochloric acid/hydrofluoric acid mixture at the end. Both the C/HNT and the MC were characterized by Fourier transform infrared spectroscopy analysis, X-ray diffraction, Raman spectra measurement, and high-resolution transmission electron microscopy. The MC was also characterized with specific surface area (BET). The results showed that the MC obtained was almost amorphous carbon. The increase in the ratio of [HNTs template]/[pyrrole monomer] led to an increase in the BET-specific surface area. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Since the discovery of fullerenes and carbon nanotubes (CNTs),¹ synthesis of carbon nanostructures has attracted a great deal of attention both for basic scientific research and industrial applications. The structural characteristics and physicochemical properties of CNTs^{2,3} and related graphitic nanofibers or nanofilaments⁴ have been received a lot of interest for a wide range of applications, including fuel cells,⁵ hydrogen storage,^{6,7} and electrochemical energy storage and conversion.^{8,9} Many carbon precursors have been used for the preparation of carbon materials via pyrolysis, such as aromatic polyimide,^{10,11} polyacrylonitrile,^{12,13} and so forth. Polypyrrole (PPy) is a conducting polymer, which can also be used as carbon precursor to prepare graphitic carbon nanostructures.¹⁴ Jang et al.¹⁵ reported on the easy synthesis of PPy nanotubes via a template-mediated vapor deposition polymerization and the process into CNTs through the carbonization process. They also fabricated magnetic CNTs using PPy nanotubes as the carbon precursor.¹⁶ Jang et al.¹⁷ produced CNTs by high-temperature (900°C) treatment under nitrogen atmosphere with PPy nanotubes. This synthesis

method of the as-prepared CNTs is simple and could be widely used.

Halloysite nanotubes (HNTs), which are a type of naturally deposited hydrated aluminum silicate structurally and chemically similar to mineral kaolinite, have a predominantly hollow tubular structure in the submicrometer range with a high aspect ratio.¹⁸ Like most of the natural clays, the size of HNTs vary from hundreds nanometers to several micrometers in length and have an inner diameter of 10–150 nm depending on the different deposits. Many active agents could be entrapped into the inner lumen of the HNTs, such as marine biocides,¹⁹ drugs,²⁰ and nicotinamide adenine dinucleotide,²¹ followed by their retention and release. Recently, it was found that halloysite could also be used as adsorbents,²² nanocomposites,^{23–25} biomimetic nano-reactors,²⁶ and nanotemplates²⁷ or nanoscale reaction vessels instead of CNTs or boron nitride nanotubes.²⁸

In this work, we report the fabrication of mesoporous carbon (MC) using PPy as precursor and HNTs as template. First, PPy/HNT hybrids were fabricated by *in situ* oxidative polymerization,²⁹ and then the C/HNTs were obtained after carbonization

of the hybrids. After removal of the inorganic template by hydrochloric acid (HCl)/hydrofluoric acid (HF) mixture solution, the MC was obtained at the end. Different from the synthesis of CNTs using PPy nanotubes as the carbon precursor, MC with different specific areas could be obtained by adjusting the ratios of [pyrrole monomer]/[HNTs template] using this method.

EXPERIMENTAL

Raw Materials

Halloysite clay was obtained from Hebei Province, China. Pyrrole (analytical grade reagent; Tianjin Chemical, Tianjin, China) was freshly distilled under pressure before use. Concentrated HCl, HF, and ammonium persulfate (APS) were analytical grade reagents received from Tianjin Chemical and were used without further purification as received. Deionized water was used throughout the experiment.

Preparation of the Core–Shell Structure of PPy/HNT Hybrids

Halloysite was pretreated by the followed procedure: 250 g of raw halloysite clay and 500 mL of water were mixed and milled with SF400-type wit sand-grinding dispersing machine at 4000 rpm for 2 h. The HNT suspension was centrifuged (3000 rpm for 3 min) to remove the deposit. The halloysite was dried in vacuum oven for further experiments. The detailed preparation of PPy/HNT hybrids synthesized by *in situ* oxidative polymerization was previously described by Liu et al.²⁹ Briefly, HCl (6 mL) was added into 450 mL of distilled water, and 3.0 g halloysite was dispersed into the mixture in ultrasonic bath for 30 min, and then, a stable suspension was obtained. Then certain amount of pyrrole (1.5, 1.0, 0.75, or 0.5 mL) was added into the suspension. The mixture was stirred under magnetic stirring overnight and used for further experiments directly. Then 100 mL of the acidic aqueous solution of APS [containing certain amount of APS (6.80, 4.54, 3.4, or 2.27 g and 1.00 mL of concentrated HCl)] was added dropwise into the mixture for 30 min with magnetic stirring in an ice-water bath. Then the mixture was stirred for another 12 h. After the polymerization, the mixture was centrifuged and the black powder was obtained. The products were washed by water for several times until neutral and dried under vacuum (0.1 mmHg) at 40°C overnight.

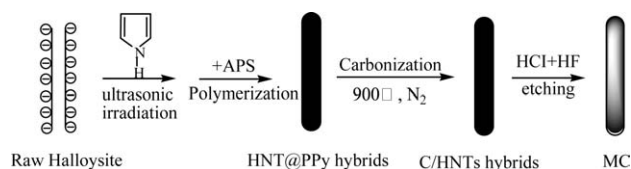
Preparation of C/HNT Hybrids and MC

The obtained PPy/HNTs were placed in a quartz tubular furnace to be carbonized to fabricate C/HNTs under nitrogen atmosphere, then vacuum sealed, and heated at a rate of 1°C/min. After 5 h of carbonization at 900°C, the quartz tube was naturally cooled to room temperature. C/HNTs were obtained after opening the sealed tube.

The C/HNTs (1.0 g) were immersed in 100 mL of water containing 10 mL of concentrated HCl and 10 mL of concentrated HF overnight. The MC produced was obtained by centrifugation and then washed with water for several times until neutral and dried under vacuum (0.1 mmHg) at 40°C overnight.

Characterization and Analysis

The chemical structure of HNTs, C/HNTs, and the MC were conducted by recording infrared spectra using Bruker IFS 66 v/s (Germany) infrared spectrometer in the range of 400–4000



Scheme 1. The formation mechanism of the MC.

cm^{-1} with the resolution of 4 cm^{-1} . The KBr pellet technique was adopted to prepare the sample for recording the IR spectra.

The X-ray diffraction (XRD) patterns were recorded in the range of $2\theta = 3.0^\circ\text{--}80^\circ$ by step scanning with a Rigaku D/Max-III A diffractometer (Japan). Nickel-filter $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) was used with a generator voltage of 40 kV and a current of 30 mA. Each sample was scanned with a scanning speed of $1^\circ/\text{min}$.

Raman spectroscopy was performed on a Via Reflex (Renishaw) micro-Raman spectrometer (UK) with a crystal laser excitation of 633.1 nm.

The transmission electron microscopy (TEM) observation was performed on a JEOL JEM-2010 F electron microscope (Japan) operating at 200 kV. The powders were dispersed in ethanol in an ultrasonic bath for 5 min and then deposited on a copper grid covered with a perforated carbon film.

The BET-specific surface area (BET) of MC was analyzed in a Chemisorb-2750 measurement (Micromeritics Instrument Corp., USA) by measuring N_2 isotherms at 77 K for the determination of surface area. For such study, the samples were out-gassed at 423 K for 6 h, and the surface area was determined in the 0.05–0.3 relative pressure range.

RESULTS AND DISCUSSION

Preparation of MC

PPy/HNT hybrids were fabricated by *in situ* oxidative polymerization of the pyrrole monomer absorbed on the surface of HNTs. As PPy is one of the carbon sources,³⁰ PPy shell of the PPy/HNTs can be converted to the corresponding carbon shell by thermal carbonization. The PPy/HNT hybrids were carbonized at 900°C for 5 h in a quartz tubular furnace under nitrogen atmosphere, and the C/HNTs were successfully prepared. The MC can be obtained after the removal of inorganic template by HCl/HF mixture. The mechanisms have been shown schematically in Scheme 1.

Spectroscopic Analyses

The Fourier transform infrared (FTIR) spectra of the raw halloysite, PPy/HNTs, C/HNTs, and the MC are shown in Figure 1. The main characteristic peaks of the PPy/HNT hybrids are assigned as follows: the bands at 1554 and 1474 cm^{-1} are attributed to typical pyrrole rings vibration; the bands at 1307, 1193, and 1036 cm^{-1} are attributed to $=\text{C}-\text{H}$ in-plane vibration, and the bands at 791 and 910 cm^{-1} are attributed to $=\text{C}-\text{H}$ out-of-plane vibration.³¹ These characteristic bands due to the PPy component were observed in the spectrum of PPy/HNTs. To confirm the conversion to the carbon materials, C/HNTs and MC were also characterized by FTIR. All the peaks in the FTIR spectra of

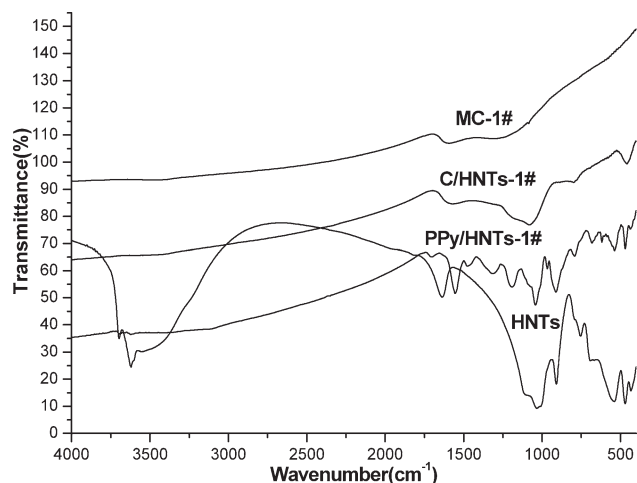


Figure 1. FTIR spectra of the HNTs, PPy/HNTs, C/HNTs, and MC.

PPy shell were removed completely following the thermal treatment (C/HNTs-1#; Figure 1). This suggests that all the functional groups in PPy have been eliminated, leaving behind symmetric carbon that shows no IR absorption in this region. In the spectrum of MC, the bands at 3710, 3650, 1640, 1040, 910, 750, 550, and 460 cm^{-1} disappeared after removal of inorganic template by HCl/HF mixture solution. It showed that the inorganic template was etched after the treatment with the HF/HCl mixture.³²

The XRD patterns of the HNTs, C/HNTs, and MC are shown in Figure 2. We note that there is a broad peak between $2\theta = 15^\circ - 35^\circ$ in curve C/HNTs-1# and curve MC-1#, which is assigned to the (002) reflection of carbon material, indicating that the products also contain a number of amorphous compounds. The halloysite structure collapses and forms a spinel phase after thermal treatment at 900°C, most likely amorphous at this temperature, and contributing to the broad peak. After the removal of inorganic template by HCl/HF mixture solution, the XRD peak at about 13° disappeared, indicating that the crystal structures of the HNTs were destroyed.²⁷ In curve MC-1#, the reflections

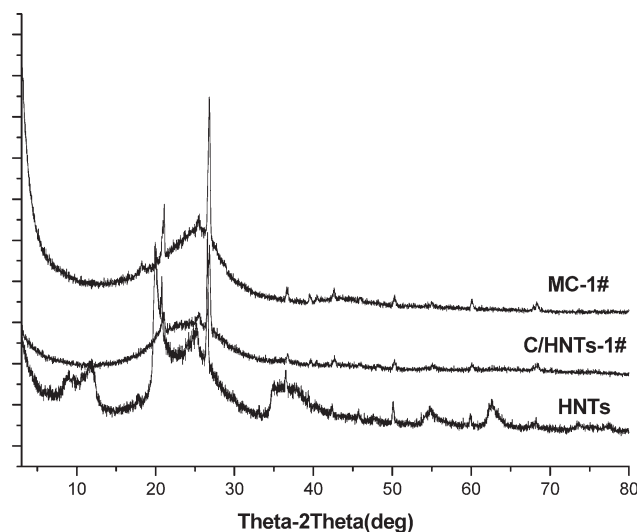


Figure 2. XRD patterns of HNTs, C/HNTs-1#, and MC-1#.

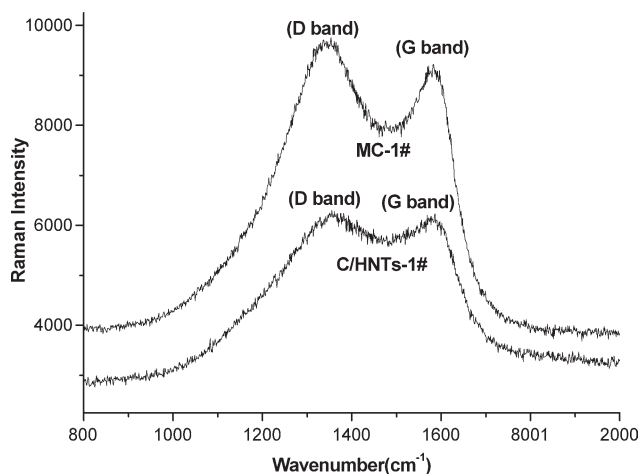


Figure 3. The Raman spectrum of C/HNT hybrids and MC.

stem from quartz that is present in raw HNT sample still remaining in the carbon because the inorganic templates were encapsulated by carbon shell very well after carbonization and could not be removed completely.

A typical Raman spectrum is shown in Figure 3. The structure of the C/HNT hybrids and MC can also be observed, with a characteristic strong, relatively narrow band around 1583 cm^{-1} corresponding to the stretching modes of carbon sp^2 bands of the typical graphite (E_{2g} mode), whereas the band at 1341 cm^{-1} corresponding to the vibrations of carbon atoms with dangling bonds in disordered graphite planes.³² The two bands at 1583 and 1341 cm^{-1} may be ascribed to the graphite-like and disordered structure of carbons, respectively.³³ The D-band showed increased intensity relative to that of the G-band in the both XRD patterns. This result indicates a semicrystalline carbon structure containing some lattice edges or plane defects within the analyzed MC.¹⁸ It has been reported that the highly crystalline carbon material with high conductivity occurs through the carbonization process when carbonized at 2200°C.³⁴ These results also indicated that the as-prepared MC was the disordered amorphous carbon phase.

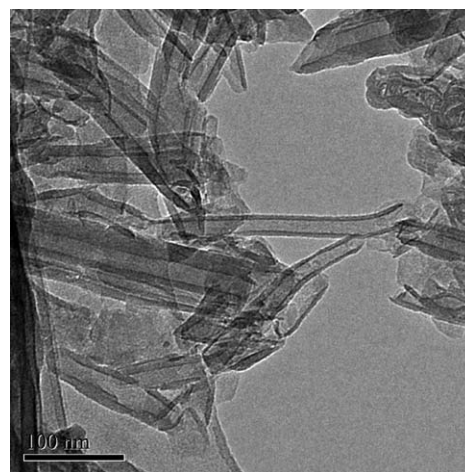


Figure 4. The TEM image of halloysite nanotubes.

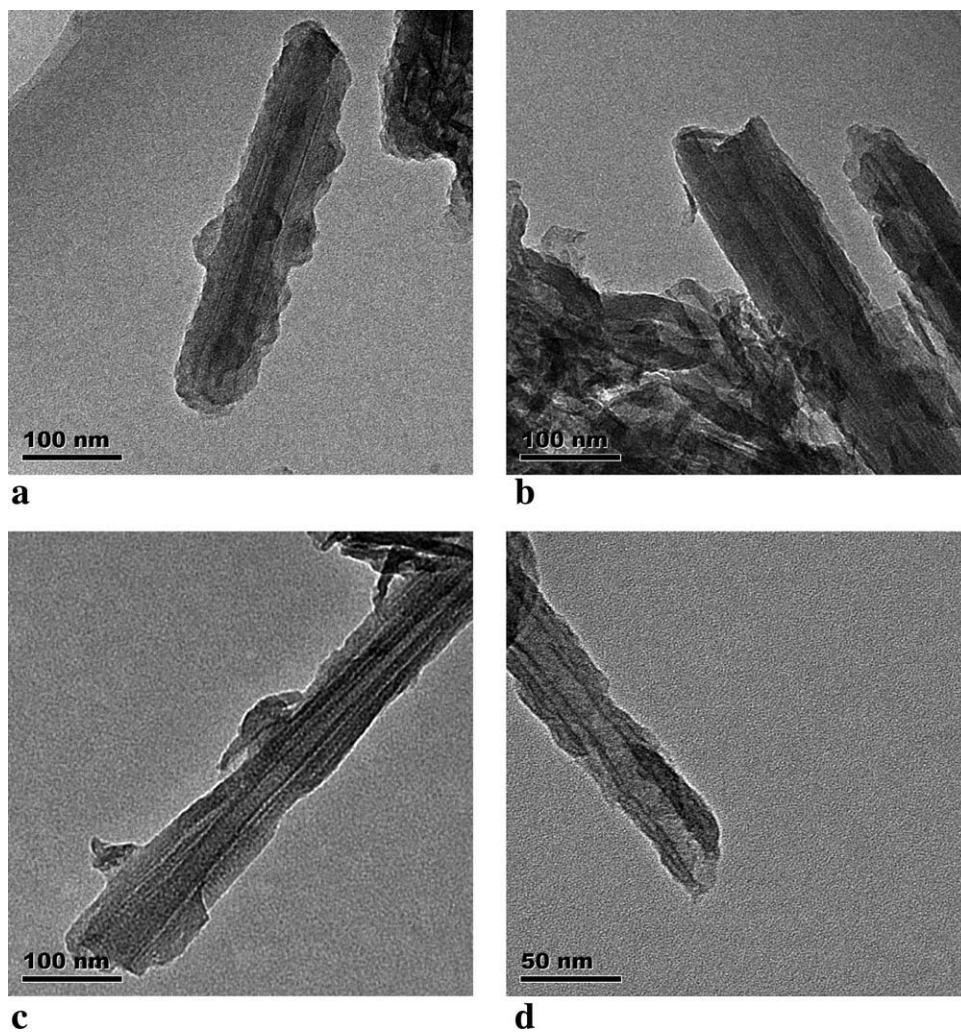


Figure 5. The TEM images of the C/HNT hybrids: (a) C/HNTs-1; (b) C/HNTs-2; (c) C/HNTs-3; and (d) C/HNTs-4.

Morphological Analysis

The TEM image of the raw HNTs is shown in Figure 4, and the TEM images of the C/HNT hybrids are shown in Figure 5. The morphologies of the C/HNT hybrids prepared with different amounts of pyrrole monomer were similar, but a little different in the thickness of the carbon layers. It indicated that the concentration of HCl and the pyrrole monomers had no effect on the morphologies of the C/HNT particles. The adsorption amount of the PPy molecules onto the surfaces of the HNTs might affect the thickness of the layer. The more pyrrole monomers added, the thicker carbon layers of the C/HNTs are obtained. The HNT nanotubes were different in length, and therefore, the morphologies of the C/HNTs were different for the different length. When compared with that of the raw HNTs shown in Figure 4, direct evidence for the formation of the carbon shells on the surfaces of the HNTs is shown in Figure 5. It is clear from the images that in the C/HNT hybrids [Figure 5(a–d)], the inner hollow cavity of the C/HNT hybrids remained as the raw HNTs, but the outer diameters of the C/HNTs decreased. It is clear that the carbon shell coated only onto the outer surface of the HNTs and that the thickness of

the carbon shell decreased by the decreased amount of the pyrrole monomers added.

The TEM images of the MC are shown in Figure 6. It was evident that the mesoporous and tubular structures were obtained after etching the template by HF/HCl mixture solution. The images of MC-1 are shown in Figure 6(a, b). It is clear that the inner diameter of MC is equal to the outer diameter of HNTs and that the thickness of the MC layer is about 5 nm. The high-resolution TEM (HRTEM) images are shown in Figure 6(c-1,c-2). It shows that there are some ordered graphitic layers on the wall of the MC. The graphitization might occur at higher temperature such as 2200°C,³⁴ and thus, the main activity that occurred at 900°C should be described as carbonization but not graphitization. Above all, these MCs were found to be mostly amorphous in structure. The images of MC-2, MC-3, and MC-4 are shown in Figure 6(d–f). The CNTs could also be obtained by the direct carbonization of the PPy nanotubes; however, in our previous study,²⁹ it was shown that uniform PPy nanotubes could be obtained only when 1.5 and 1.0 mL of pyrrole monomer was added, and PPy nanotubes could not be

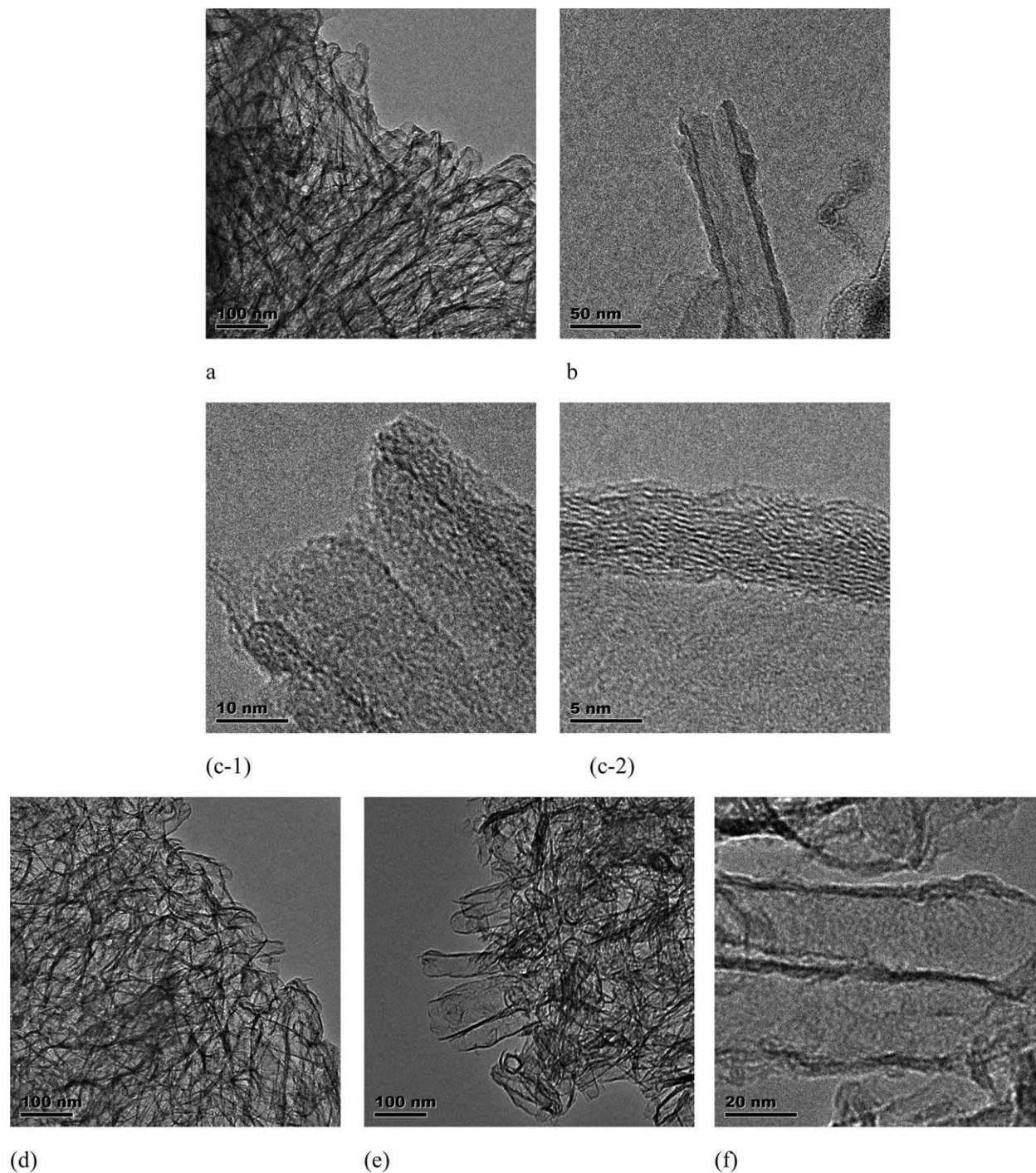


Figure 6. The TEM images of the MC: (a and b) MC-1; (c) HRTEM image of MC-1; (d) MC-2; (e) MC-3; and (f) MC-4.

Table I. Preparation Conditions for the C/HNT Hybrids

Samples	HNTs (g)	Pyrrrole (mL)
C/HNTs-1	3	1.5
C/HNTs-2	3	1.0
C/HNTs-3	3	0.75
C/HNTs-4	3	0.5

Table II. BET Analysis

Samples	BET (m ² /g)
MC-1#	401.72
MC-2#	462.61
MC-3#	489.11
MC-4#	620.71

obtained when 0.5 mL of pyrrole monomer was added using the HNTs as template. Moreover, the MC-4 with 0.5 mL of pyrrole monomer could also be fabricated using this method. Therefore, we developed a novel method to fabricate the mesoporous and tubular carbon materials with less monomer (0.75 and 0.5 mL) added (Table I).

BET Analysis

The data of the BET are shown in Table II. The surface area of the MC using the same template might be determined by the thickness of the carbon shell. The MC sample with the thinner carbon shell should own the bigger surface area. Thus, the more pyrrole monomer added, the thicker carbon shell of the MC is obtained. Therefore, the MC-4 fabricated with 0.5 mL of pyrrole monomer own the thinnest wall and the biggest area of 620.71 m²/g.

CONCLUSIONS

MC nanosheets with large BET-specific surface area were fabricated by using HNTs as template and PPy as carbon precursor. The obtained carbon nanosheets possess abundant tubular cavity due to the replication of the inorganic template effect of HNTs during carbonization. The results indicated that the mesoporous structure of MC can be tuned by adjusting the ratio of [HNTs template]/[pyrrole monomer]. With the increase in the ratio of [HNTs template]/[pyrrole monomer], the BET surface area is increased.

REFERENCES

- Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, R. D. *Nature* **1990**, *6291*, 354.
- Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *5582*, 787.
- Endo, M.; Hayashi, T.; Kim, Y. A.; Muramatsu, H. *JSP Int.* **2007**, *15*, 4.
- Liang, C. H.; Li, Z. L.; Qiu, J. S. *J. Catal.* **2002**, *211*, 278.
- Dillon, A. C.; Heben, M. J. *Appl. Phys. A* **2001**, *72*, 133.
- Hirscher, M.; Becher, M.; Haluska, M.; Quintel, A.; Skakalova, V.; Choi, Y. M.; Dettlaff-Weglikowska, U.; Roth, S.; Stepanek, I.; Bernier, P.; Leonhardt, A.; Fink, J. *J. Alloys Compd.* **2002**, *330*, 654.
- Lee, K.; Zhang, J.; Wang, H.; Wilkinson, D. P. *J. Appl. Electrochem.* **2006**, *36*, 507.
- Liu, C.; Cheng, H. M. *J. Phys. D: Appl. Phys.* **2005**, *38*, 231.
- Frackowiak, E.; Beguin, F. *Carbon* **2002**, *40*, 1775.
- Tang, N. J.; Zhong, W.; Au, C. T.; Gedanken, Y. Y.; Du, Y. W. *Adv. Funct. Mater.* **2007**, *17*, 1542.
- Laskoski, M.; Keller, T. M.; Qadri, S. B. *Polymer* **2007**, *48*, 7484.
- Chae, H. G.; Minus, M. L.; Rasheed, A.; Kumar, S. *Polymer* **2007**, *48*, 3781.
- McCann, J. T.; Lim, B.; Ostermann, R.; Rycenga, M.; Marquez, M.; Xia, Y. *Nano Lett.* **2007**, *7*, 2470.
- Yang, L. C.; Shi, Y.; Gao, Q. S.; Wang, B.; Wu, Y. P.; Tang, Y. *Carbon* **2008**, *46*, 1816.
- Jang, J.; Oh, J. H.; Stucky, G. D. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 4016.
- Jang, J.; Yoon, H. *Small* **2005**, *1*, 1195.
- Jang, J.; Yoon, H. *Chem. Commun.* **2003**, *6*, 720.
- Joussein, E.; Petit, S.; Churchman, J.; Theng, B.; Righi, D.; Delvaux, B. *Clay Miner.* **2005**, *40*, 383.
- Price, R.; Gaber, B.; Lvov, Y. *J. Microencapsulation* **2001**, *18*, 713.
- Levis, S. R.; Deasy, P. B. *Int. J. Pharm.* **2003**, *253*, 145.
- Lvov, Y.; Price, R.; Gaber, R. B.; Ichinose, I. *Colloids Surf. A* **2002**, *198*, 375.
- Zhao, M. F.; Liu, P. *Microporous Mesoporous Mater.* **2008**, *112*, 419.
- Zhou, C.; Du, X.; Liu, Z. *J. Mater. Sci.* **2011**, *46*, 446.
- Dong, Y.; Chaudhary, D.; Haroosh, H. *J. Mater. Sci.* **2011**, *46*, 6148.
- Zhang, L.; Wang, T. M.; Liu, P. *Appl. Surf. Sci.* **2008**, *255*, 2091.
- Shchukin, D. G.; Sukhorukov, G. B.; Price, R. R.; Lvov, Y. M. *Small* **2005**, *1*, 510.
- Wang, A. P.; Kang, F. Y.; Huang, Z. H.; Guo, Z. C.; Chuan, X. Y. *Microporous Mesoporous Mater.* **2008**, *108*, 318.
- Antill, S. J. *Aust. J. Chem.* **2003**, *56*, 723.
- Liu, Y. S.; Nan, H. M.; Cai, Q.; Li, H. D. *J. Appl. Polym. Sci.* **2012**, *125*, E638.
- Han, C. C.; Lee, J. T.; Yang, R. W.; Han, C. H. *Chem. Mater.* **2001**, *13*, 2656.
- Zhang, L.; Liu, P. *Nanoscale Res. Lett.* **2008**, *3*, 299.
- Dresselhaus, M. S.; Dresselhaus, G.; Pimenta, M. A.; Eklund, P. C. In *Analytical Applications of Raman Spectroscopy*; Pelletier, M. J., Ed.; Blackwell: Oxford, UK, **1999**; Chapter 9.
- Sonobe, N.; Kyotani, T.; Tomita, A. *Carbon* **1991**, *29*, 61.
- Han, C. C.; Lee, J. T.; Chang, H. *Chem. Mater.* **2001**, *13*, 4180.