Research paper

Controllable modification of nanostructured carbon with hollow macroporous core/mesoporous shell and its application as templates in aqueous solution

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ABSTRACT

Controllable modification of hydrophilic groups on tubular nanostructured carbon with hollow macroporous core/mesoporous shell (TNC-HMC/MS) was systematically studied and the mesoporous structure of TNC-HMC/MS has been kept. Different oxidants were used to modify the TNC-HMC/MS. Results revealed that the TNC-HMC/MS could be modified with carboxyl or hydroxy by different oxidants. More importantly, the BET/BJH results indicated that the mesoporous shell of TNC-HMC/MS has not been destroyed. In addition, water-soluble ammonium metatungstate has been encapsulated into the hollow core of TNC-HMC/MS and formed nanodot, bamboo-like and nanowire morphology.

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1. Introduction

Nanostructured carbon with hollow macroporous core/mesoporous shell (NC-HMC/MS) has drawn considerable attention due to its relatively high chemical and thermal stability, low density, high strength, large surface area, uniform particle size and narrow pore size distribution [1,2]. Besides, NC-HMC/MS possesses unique hollow core and mesoporous shell structure, which allows it to encapsulate materials in the hollow core via the mesoporous in the shell. In this case, materials could be effectively encapsulated without destroying the shell. Therefore, it shows a great potential to be applied in many fields [3], such as supercapacitors [4], drug delivery [5,6], catalyst supporter [7], low-threshold field emitters [8], battery [9], electromagnetic wave and microwave absorption materials [10], or metal/nonmetal nanoparticles encapsulation [11–13].

Unfortunately, the feature of hydrophobia limited applications of NC-HMC/MS. what's more, due to the low activity of carbon, to modify NC-HMC/MS with hydrophilic groups is not easy. One way to solve this problem is oxidizing the carbon by grafted O-containing hydrophilia groups on the shell of mesoporous carbon [3], such as oxidized through hydrogen peroxide [14,15],

thermal treatment [16], nitric acid [15,17], etc. However, the mesoporous shell of NC-HMC/MS which could allow materials encapsulate in is easily been attacked during oxidative treatment [3]. Whereas, integrity is very important for the mesoporous shell of NC-HMC/MS, especially for the encapsulated materials hosted within the hollow core with carbon shell, in order to preserve the physical properties which enable the promised applications (Li-S battery [18], drug delivery [5,6], conductive polymer [19]). Therefore, controllable surface modification of NC-HMC/MS without destroying the integrity of shell is highly desirable.

What's more, most of the reports about hollow macroporous core/mesoporous shell carbon concern sphere-shaped particles [1,15,16,20,21]. And to the best of our knowledge, tubular nanostructured carbon with hollow macroporous core/mesoporous shell (TNC-HMC/MS) has been seldom reported. Furthermore, by comparing with carbon nanotubes (CNTs), the advantage of mesoporous shell of TNC-HMC/MS it's that it could allow materials encapsulated in via the shell. And for the CNTs which also need to be modified with hydrophilic groups, there are four basic modification ways, i.e. mixture of acids [19,22–29], mono-acid [19,30–35], alkaline reagent or gas [36–38] and H_2O_2 included oxidation mixture [19,33,34]. Hence, referred to the aforementioned modification methods of mesoporous carbon and CNTs, we have controllable modified the TNC-HMC/MS with carboxyl or hydroxy by different oxidants without destroying its carbon surface or pore structure. In addition, by controllable stirring, nanodot, nanowire

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and bamboo-like AMT were formed in the hollow core of TNC-HMC/MS, which indicated that TNC-HMC/MS has the potential to be used as supporter/template for catalyst, drug delivery, supercapacitors, Li-S battery or nanowires of metal/non-metal.

2. Materials and methods

2.1. Materials

Pristine TNC-HMC/MS was self-prepared by catalytic pyrolysis of Teflon with $FeCl_2$ at circa 700 °C. The liquid reagents included HCl (36~37%, AR), H_2O_2 (30.0%, AR), $NH_3 \cdot H_2O$ (25~28%, AR), H_2SO_4 (95~98%, AR) and HNO_3 (65.0~68.0%, AR).

2.2. Modification of the TNC-HMC/MS

The purified TNC-HMC/MS (pristine TNC-HMC/MS soaped in HCl for about 72 h) was modified via 4 different ways: (1) Strong acid mixture oxidation, ultrasonic treatment in H_2SO_4 and HNO_3 (volume ratio with 3:1) mixture for 2 h, then stirred for 5 h at room temperature, centrifuged by distilled water to neutral and dried in oven. (2) Diluted strong acid oxidation, ultrasonic in 20 wt.% HNO_3 for 30 min and dried directly. (3) Stirred in H_2O_2 at room temperature and dried. (4) Stirred in H_2O_2 and $NH_3 \cdot H_2O$ (volume ratio with 1:1) at room temperature and dried. (5) Refluxed and condensed in H_2O_2 and $NH_3 \cdot H_2O$ (volume ratio with 1:1), dried. Identification of modified TNC-HMC/MS was shown in Table 1.

2.3. Characterization

XPS was carried out in high vacuum on PHI -5300 ESCA. TGA was performed using SDT Q600 V20.9 Build 20 in N_2 with a heating rate of 10 °C/min to 800 °C. BET results were obtained from AUTOSORB-1 (Quantachrome Ins.) in N_2. SUPRA™ 55 FESEM was applied to get the morphology of TNC-HMC/MS.

2.4. Application as template in aqueous solution

Water-soluble ammonium metatungstate (AMT) was used to be encapsulated into the hollow core of TNC-HMC/MS. After controllable stirring in aqueous solution for about 24 h, AMT encapsulated in TNC-HMC/MS with different morphology were obtained.

3. Results and discussion

The purified and modified TNC-HMC/MS were dispersed in water, ethyl alcohol and N,N-dimethyl formamide (DMF) respectively, and pictures of the dispersed samples were shown in Fig. S1. As can be seen, the purified S2 and modified S6 were hydrophobic. S3, S4, S5 and S7 have dipped down to the bottom in water, which indicated their good hydrophilic performance. Results revealed that oxidant selected in this work could effectively modify TNC-HMC/MS with hydrophilic property, except modification in H_2O_2 and $NH_3 \cdot H_2O$ mixture through stirring.

Table 1
Identification of the samples.

No.	Modification
S1	Pristine
S2	Purified
S3	H_2SO_4 and HNO_3
S4	Diluted HNO_3
S5	H_2O_2
S6	H_2O_2 and $NH_3 \cdot H_2O$ (stirring)
S7	H_2O_2 and $NH_3 \cdot H_2O$ (refluxed and condensed)

3.1. Hydrophilic detection by XPS and TGA

Fig. 1 showed the C1s, O1s and N1s spectra of the pristine, purified and modified samples. As shown in Fig. S2, all samples possessed C and O peaks. However, as revealed in Figs. S1 and S2 was hydrophobic, and S1 was intrinsically hydrophobic, so the following atom content details were consisted of hydrophilic samples only.

For C1s spectra, the main peak in all samples at 284.8 eV was corresponded to C—C of the basic TNC-HMC/MS structure. Peaks at 286.2 ± 0.2 eV, 287.5 ± 0.2 eV, 288.9 ± 0.2 eV and 290.2 ± 0.2 eV were attributed to different O-containing moieties [33,39,40]. Besides, peak at 286.2 ± 0.2 eV may be caused by sp^3-hybridized carbon atoms in the amorphous carbon shell [41,42] or C—N/C=N [42,43]. And peak at 291.5 eV may originate from the π-π* transition loss [33].

In the case of O1s spectra, all modified samples have been introduced O-containing groups, but possessed different peak features. To be specific, O1s spectra of strong oxidant modified samples (Fig. 1(a) and (b), sample S3 and S4) contained two peaks at 531.7/532.0 eV and 533.3/533.6 eV [39,44,45] which was attributed to the two O atoms in —(C=O)—O. And spectra of weak oxidant modified samples (Fig. 1(c)–(e), sample S5, S6 and S7) showed one peak at 532.7 ± 0.2 eV which was derived from hydroxyl [40,44]. Besides, the relative intensity of peaks could give more details of the sample, namely, O1s spectra of S3 (modified by the mixture of H_2SO_4 and HNO_3) showed relatively proximate peak intensity, which means only carboxyl have been introduced. Whereas, the relative intensity of O from C—O bond was higher than that of O from C=O bond in sample modified by diluted HNO_3 (S4, Fig. 1 (b)), which indicated that S4 possessed both carboxyl and hydroxyl. Of particularly interesting, O1s spectra of S6 (Fig. 1(d)) showed a peak at 532.7 ± 0.2 eV, but its O content (4.31%) was relatively low, so the O may come from O groups in air.

The $NH_3 \cdot H_2O$ contained modification results (N1s spectra) were insert in Fig. 1(d) and (e). As indicated from inserts of Fig. 1 (d) and (e), hydrophilic N-containing groups [40,45] were detected in S7 (insert of Fig. 1(e)), but no obvious N-containing groups were observed in S6 (insert of Fig. 1(d)). Associated with the results in Fig. S3 (N element detected in S6 was about 0.46%) and the dispersion picture in Fig. S1 (S6 in water), the detected N may attribute to the residual of absorbed $NH_3 \cdot H_2O$ in S6.

In addition to the XPS detection, thermogravimetric analysis was applied to support the results and reveal the thermostability of TNC-HMC/MS before and after modification procedures, especially the thermostability of hydrophilic groups. Fig. 1(f) was the thermogravimetric data of purified sample (S2) and samples modified with hydrophilic groups (sample S3, S4, S5 and S7, Fig. S5 shows more clearly about the weight changes). As indicated in Fig. 1(f), the first weight loss stage below 100 °C in the TG curves of all samples may be caused by the evaporation of absorbed water [33,46–48].

The second stage from 250 °C to 300 °C in samples S3 and S4 were attributed to the decarboxylation of the functionalized TNC-HMC/MS by acid [33], comparing with the loss of hydroxyl groups at the stage from 200 °C to 400 °C from S5 and S7 [33]. Besides, at the stage from 150 °C to 200 °C in S7, the weight loss was about 3%, it could be the result of losing N-containing groups. Thermogravimetric results indicated that different functional groups with different thermostability could be effectively grafted on TNC-HMC/MS by different oxidants.

3.2. Carbon surface and pore structure detection

As what aforementioned, oxidizing process could damage the carbon surface or pore structure of TNC-HMC/MS [3]. However,