SiO₂@MgO nanoparticles templated mesoporous carbon with rich electro-active oxygenic functionalities and enhanced supercapacitive performances

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Abstract:

As a member of carbon-based materials, ordered mesoporous carbon (OMC) still suffers from poor capacity for supercapacitive applications. Functionalization the skeleton with pseudocapacitive functionalities is an efficient way to enhance the capacity of OMCs. Herein, a designed SiO₂@MgO nanoparticle with uniform diameters was employed as template towards the synthesis of pseudocapacitive oxygen functionalized OMC. The obtained carbons possess ordered mesoporous structure, large surface area, and rich pseudocapacitive oxygen species. As electrode for supercapacitor in 1.0 M H₂SO₄, the SiO₂@MgO templated OMC achieves higher

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capacitance (257 F/g) than pure SiO₂ templated OMC (180 F/g), surfactant templated OMC (152 F/g) and commercial activated carbon (110 F/g) owing to the high pseudocapacitive oxygen functionalities, providing more capacity by reversible Faradaic reaction.

Keywords: mesoporous carbon, pseudocapacitive oxygen, hard template, SiO₂@MgO, supercapacitor

1. Introduction

Due to the unique features of ordered mesoporosity, uniform pore size, large surface area, open-accessed structure, low cost, superior chemical/physical stability, ordered mesoporous carbons (OMCs) have attracted wide interests in many fields such as sorption [1-4], catalysis [5, 6], energy storage [7-10] and etc. To date, ordered mesoporous carbonaceous materials (OMCs) with various morphologies have been successfully prepared by hard- and soft-templating methods. Generally, hard templating method [11-14], also called nanocasting method, employs mesostructured silica-based substrates as rigid template. The starting materials are introduced into the pores of the template followed by carbonization at high temperature and then the hard template is removed by chemical etching to generate mesoporous carbon replicating the silica-based mesochannels. To date, the hard template growth of porous carbons have exhibit an appealing application in energy storage fields [15, 16]. As to soft-templating method [17-19], amphiphilic surfactant molecules, such as block copolymers, which are soft and can be decomposed during calcination, are used as templates, in which the block copolymers could form a soft micelle structure in the synthesis solution and the micelle could interact with the oxygen-containing

carbonaceous precursors mainly via hydrogen bonding or coulombic force to form the mesophase. After calcination at high temperature, the mesophase is carbonized and the block copolymers template is removed resulting in the formation of mesopores.

Recently, great efforts have been made to functionalize the carbon surface or framework by introducing heteroatom containing functionalities to enhance/expand the properties and applications of OMCs. To date, various heteroatom (e.g., N, P, S and B) doped mesoporous carbon materials [20-23] have been widely investigated and have exhibited superior performances in many areas such as catalysis, sorption and electrochemistry, etc. Though, various hetero-atom doped OMC have been explored by hard- or soft templating method, most of the reported approach lies in selection/design of a hetero-atom containing precursor to fabricate doped OMC. As a result, in most cases, the effect of template towards the surface species was omitted. However, a recent reported result shows that surface properties of template exerts a remarkable effect on the surface species variation of carbon nitride [24]. Hence, template induced formation of functionalities on OMC would be a promising alternative approach towards the fabrication of functional mesoporous carbon.

Herein, we fabricated a pseudocapacitive oxygen functionalized ordered mesoporous carbon with a designed silica@MgO nanoparticles as template. As shown in Fig. 1, in our approach, the as-made uniform silica nanoparticles (Fig. S1 in supplementary data) was firstly coated by MgO via an incipient impregnation method. The coated silica (denoted as SiO₂@MgO) nanoparticle was employed as template, onto which the precursor of phenolic resin was introduced by an incipient impregnation method. After carbonization and template removal, the obtained mesoporous carbons (denoted as MS-OMCs) possess ordered mesoporosity, large surface area and rich pseudocapacitive oxygenic functionalities. As electrode for

supercapacitor (SC) in 1.0 M H_2SO_4 , the MS-OMCs achieve an enhanced SC performance with high capacitance (257 F/g) vs SiO_2 templated OMC (180 F/g).

2. Experimental section

Synthesis

The as-made $\text{SiO}_2@\text{MgO}$ nanoparticles (details in supplementary data) was added to 10.0 ml phenolic resin solution till an incipient state and subsequently underwent further thermo-polymerization at 373 K for 24 h to get a rigid composite. The rigid composite was carbonized at 973, 1073 and 1173 K for 2 h with the ramp rate of 2 K/min. After carbonization, the template was removed by mixed acid solution of HCl and HF. The obtained ordered mesoporous carbons templated by as-made $\text{SiO}_2@\text{MgO}$ nanoparticles were denoted as MS-OMCT (M: MgO, S: SiO_2 , OMC: ordered mesoporous carbon, T: carbonization temperature/K). As comparison, pure silica nanoparticles templated OMC was also prepared by the similar method and denoted as S-OMCT(S: SiO_2 , OMC: ordered mesoporous carbon, T: carbonization temperature/K).

Characterization

Transmission electron micrograph (TEM) and high-resolution electron micrograph (HRTEM) images were obtained with a JEOL 2100 microscope operated at 200 kV. X-Ray diffraction (XRD) patterns were recorded on a Philips X'Pert X-ray diffractometer with a $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). Raman spectra of the products were measured on LabRAM Aramis with a 532 nm laser as the excitation source. N_2 sorption isotherms were measured using a Micromeritics ASAP2020 analyzer at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the Barrett-Joyner-Halenda (BJH) model, the pore size distributions and pore volumes were calculated from the adsorption branches of

isotherms. Before measurements were taken, all samples were degassed at 573 K for 4 h. Elemental analysis was carried out with an instrument of vario EL II. FTIR spectra were recorded on a VECTORTM 22 spectrometer.

Electrochemical test for supercapacitor

Electrochemical measurements were carried out in a 1.0 M H₂SO₄ aqueous electrolyte at room temperature, using a three-electrode cell with an Ag/AgCl reference electrode and a platinum coil counter electrode. The testing electrode was prepared by mixing the obtained carbon powder, carbon black and polytetrafluorethylene (PTFE) together at a mass ratio of 80:10:10, and dipping the resulting mixture into steel mesh (1 cm×2 cm, current collector) before being pressed together at 10.0 M Pa. The areal loading amount of electrode materials is about ~4 mg/cm². The electrochemical performances of samples were determined by cyclic voltammetry (CV) and galvanostatic charge/discharge curves (GDC). The mass specific capacitance was calculated by the discharge curve according to the formula of $C_m = \frac{I\Delta t}{m\Delta V}$ (F/g), where I is the current density (A), Δt is the discharge time (s), m is the weight of active material, ΔV is the potential window of discharging (V).

3. Results and discussion

3.1 Morphology and structure of the derived MS-OMCs

The morphology of the designed silica@MgO nanoparticles templated mesoporous carbon was characterized by transmission electron micrograph (TEM). After template removal, as shown in Fig. 2, the TEM image of MS-OMC973 displays an ordered mesoporous structure with the pore size of ~19.0 nm, originated from the inverse replication of the closely packed structure of silica@MgO nanoparticles. The high-resolution TEM image of MS-OMC973 (Fig. 2b) shows disordered lattice fringes, indicating that MS-OMC973 owns a graphitic structure resulted from the

catalytic graphitization of MgO in the designed template. The crystallinity of the MS-OMCs was characterized by wide angle X-ray diffraction (XRD) shown in Fig.3a. All the XRD patterns of MS-OMCs exhibit two diffraction peaks around 25° and 44° that can be indexed to (002) and (100) diffractions of graphitic carbon, which is consistent with the HRTEM result. The XRD pattern of MS-OMC1173 shows a sharper diffraction peak than MS-OMC1073 and MS-OMC973, indicative of an enhanced graphitization degree resulted from higher carbonization temperature. Raman spectra (Fig. 3b) of the three MS-OMCs all show two peaks around 1350 and 1590 cm⁻¹ ascribed to ‘D-band’ and ‘G-band’ of graphitic carbon [25], respectively. The emergence of ‘2D-band’ around 2860 cm⁻¹ in Raman spectrum of MS-OMC1173 further confirms its superior graphitization degree to MS-OMC1073 and MS-OMC973. The textural structure of the three MS-OMCs was investigated by nitrogen sorption isotherms shown in Fig. 4. The nitrogen sorption isotherms of MS-OMC973, MS-OMC1073 and MS-OMC1173 are all IV-type isotherms with a clear condensation step and a hysteresis loop at relative pressure of 0.4–0.6, indicative of the existence of uniform mesopores in the three carbons. The detailed textural parameters of the three MS-OMCs are shown in Table 1. The specific surface areas are 896 m²/g for MS-OMC973, 1115 m²/g for MS-OMC1073, 879 m²/g for MS-OMC1173 and the corresponding pore volumes are 1.83, 2.55 and 1.79 cm³/g, respectively. As depicted in the insets of Fig.4, the pore size distribution (PSD) curves calculated from the adsorption branches all show bimodal distributions with the pore size around 3.87 and 18.7 nm for MS-OMC973, 3.69 and 18.7 nm for MS-OMC1073, 3.65 and 23.2 nm for MS-OMC1173, respectively.

3.2 Surface chemistry and elemental component of the derived MS-OMCs

The surface chemistry of the three MS-OMCs were investigated by FTIR

spectroscopy (Fig. 5) The peak around 1728 cm^{-1} corresponds to -C=O stretching vibrations related to carbonyl-containing groups, which are active in electrolyte by Faradic reaction ($\text{-C=O} + \text{e}^- \leftrightarrow \text{-C-O-}$) and thus provides pseudocapacitive contributions [26]. Obviously, MS-OMC973 exhibits a sharper and larger absorption peak of carbonyl than MS-OMC1073 and MS-OMC1173, implying that the obtained MS-OMC973 possesses more pseudocapacitive oxygenic functionalities. The elemental components of the derived MS-OMCs was confirmed by elemental analysis (EA). The EA results listed in Table 2 show that MS-OMC973 possesses the highest oxygen content (15.6 wt. %) than MS-OMC1073 (14.2 wt. %) and MS-OMC1173 (12.0 wt. %), which is consistent to the FTIR results. The EA results display that high temperature carbonization would lead to the decrease of content. While, as compared to pure silica templated S-OMC973, the designed $\text{SiO}_2\text{@MgO}$ nanoparticles templated MS-OMCs all owns much more oxygen content than S-OMC973 (7.7 wt. %), indicating that the $\text{SiO}_2\text{@MgO}$ template may favors the conservation of oxygenic functionalities during carbonization.

3.3 Supercapacitive (SC) performances of the derived MS-OMCs

The mesoporous carbon with open-accessed and regular arranged mesopores has many potential applications such as catalysis, sorption, electrochemical supercapacitors and etc. Here, the electrochemical capacitive performances of the derived MS-OMCs are evaluated by cyclic voltammogram (CV) and galvanostatic charge/discharge curve (GDC) in 1.0 M H_2SO_4 electrolyte. As shown in Fig. 6a-6c, the CV curves of MS-OMCs at various scan rates all exhibit a rectangular shaped pattern with a redox peak around 0.3 V, ascribed to the Faradaic reaction [27]

The CVs patterns of the three MS-OMCs indicates that their capacitances are

contributed by the electrochemical double layered capacitive (EDLC) and pseudocapacitive behaviors. While, the CV plots for S-OMC973 (Fig. 6d) only exhibit a rectangular-shaped pattern without any redox signs, showing that the capacitive performance of the pure silica templated OMC is mainly contributed by the EDLC. The emergence of redox peaks in the CV plots of MS-OMCs further confirms the successful construction of pseudocapacitive oxygenic functionalities on MS-OMCs by the designed silica@MgO template. The galvanostatic charge/discharge curves (GDC, Fig. 7a-7c) of the three MS-OMCs all show an obvious deviation from the typical triangular shape of non-Faradaic electric double-layer capacitor (EDLCs), further evidencing the Faradaic characteristics of the charge storage. The GDC curve (Fig. S3) of pure silica nanoparticle templated S-OMC973 shows an inconspicuous deviation from the typical triangular shape of non-Faradaic electric double-layer capacitor (EDLCs), further confirming the capacitance of S-OMC973 mainly contributed by EDLC. Fig. 7d shows the specific capacitances of the four carbons at various current densities. For MS-OMC973, the capacitances (from 0.5 to 20 A/g) calculated from GDC curve are 257, 243.7, 235.8, 225, 215, and 200 F/g, respectively, the values are higher than those of pure silica templated S-OMC973 (maximum capacitance of 180 F/g) at every current density. Moreover, the capacitances retention of the three MS-OMCs are 77.8 % for MS-OMC973, 73.6% for MS-OMC1073 and 70.7 % for MS-OMC1173, respectively, indicative of an excellent rate capability. In sharp contrast, the capacitance retention for S-OMC973 is as low as 47.7 %.

To find the SC level of the derived MS-OMC, the capacitance of MS-OMC973 as compared to pure silica nanoparticles templated S-OMC973, surfactant templated OMC973-EISA [18] (BET surface area of 522 m²/g), commercial activated carbon

(AC, BET surface area of 891 m²/g) [28] and flower-like hierarchical mesoporous carbon [29] at various current densities are compared and shown in Fig. 8. It is obvious that the designed SiO₂@MgO nanoparticles templated MS-OMC973 achieves the higher capacitance ($C_{\max}$: 257 F/g) at every current densities than that of S-OMC973 ($C_{\max}$: 180 F/g), OMC973-EISA ($C_{\max}$: 152 F/g), AC ($C_{\max}$: 110 F/g) and FMCS ($C_{\max}$: 226 F/g) making the obtained MS-OMCs a promising candidate for SC application. The superior SC performances of MS-OMCs can be attributed to the rich pseudocapacitive oxygenic functionalities, providing pseudocapacitive capacity and surface wettability, thus contributing to large capacitance and high rate capability.

4. Conclusion

A magnesium oxide coated silica nanoparticles (SiO₂@MgO) was designed and employed as template for the synthesis of pseudocapacitive oxygenic functionalities doped ordered mesoporous carbon. The obtained mesoporous carbon possesses ordered structure, large surface area and rich oxygenic functionalities. As electrode for supercapacitor in 1.0 M H₂SO₄, the SiO₂@MgO templated mesoporous carbon achieves higher capacitance (257 F/g) than pure SiO₂ templated OMC (180 F/g), surfactant templated OMC (152 F/g) and commercial activated carbon (110 F/g) owing to the high pseudocapacitive oxygen functionalities, providing more capacity by reversible Faradaic reaction. The developed strategy affords a novel approach for the synthesis of pseudocapacitive oxygen functionalized mesoporous carbon and the derived mesoporous carbon may find utility in many other applications e.g. catalysis, adsorption, separation, etc..

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Figures and Tables:

Fig. 2. TEM image (a) and high resolution TEM image (b, HRTEM) of MS-OMC973.

Fig. 3. X-ray diffractions patterns and Raman spectra of MS-OMCs.

Fig. 4. Nitrogen sorption isotherms of MS-OMC973 (a), MS-OMC1073 (b) and MS-OMC1173 (c).

Fig. 5. FT-IR spectra of MS-OMC973, MS-OMC1073 and MS-OMC1173.

Fig. 6. Cyclic voltammogram (CV) of MS-OMC973 (a), MS-OMC1073 (b) MS-OMC1173 (c) and S-OMC973 (d) in 1.0 M H_2SO_4 electrolyte.

Fig. 7. Galvanostatic charge/discharge curves under various current densities of MS-OMC973 (a), MS-OMC1073 (b), MS-OMC1173 (c) and specific capacitances of the four carbons at various current densities (d).

Fig. 8 Capacitance of MS-OMC973 compared to S-OMC973, OMC973-EISA commercial activated carbon (AC) and flower-like hierarchical mesoporous carbon superstructures (FMCS) at various current densities.

Table 1. Structural parameters of MS-OMC973, MS-OMC1073 and MS-OMC1173.

Sample	S_{Total} (m^2/g)	V_{Total} (cm^3/g)	Pore size (nm)	S_{Micro} (m^2/g)	S_{Exter}^a (m^2/g)
3DOMC973	896	1.83	3.87	105	791
3DOMC1073	1115	2.55	3.69	224	891
3DOMC1173	879	1.79	3.65	119	760

^a S_{Exter} represents the surface area outside microporosity.

Table 2. Elemental analysis (EA) results of MS-OMC973, MS-OMC1073, MS-OMC1173 and S-OMC973.

Sample	C	H	O
MS-OMC973	83.7	0.7	15.6
MS-OMC1073	85.4	0.4	14.2
MS-OMC1173	87.4	0.6	12.0
S-OMC973	90.8	1.5	7.7

Graphical abstract: