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Preparation and electrochemical hydrogen storage of mesoporous carbons by degradation of polyethylene in supercritical water

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Abstract Mesoporous carbons were prepared by treating waste polyethylene film in supercritical water at 550 °C. High-resolution transmission electron microscopy images reveal that the pore wall has a thickness of 3–4 nm and is composed of discontinuous graphitic layers, which are parallel to the tangent direction of the mesopore. Electrochemical measurements show the discharging capacity of mesoporous carbon is up to 348 mAh/g (corresponding to 1.3 wt% hydrogen storage). When temperature is lower than 450 °C, only carbon nanofibers were obtained; on the other hand, if reaction temperature is higher than 650 °C, carbon nanotubes are the main products. The possible conversion mechanism from polyethylene to mesoporous carbons and other carbon materials is tentatively discussed.

Introduction

As one of the important commercial plastic, polyethylene (PE) is widely used in various fields for its excellent chemical stability, low dielectric constant and little water absorption [1]. However, waste PE materials are persistent solid pollutants. How to dispose them has been recognized as a worldwide environmental problem [2]. The traditional landfill is becoming undesirable due to rising costs, the release of explosive greenhouse gases (such as methane) and the poor biodegradability [3]. Recently, several methods have been developed to treat PE, such as thermolysis [4–6], photo-degradation [7, 8] and biodegradation [9]. Among these methods, supercritical water treating of polymers have been widely focused, because water has many environmental and technological advantages in the state about its critical point ($T_c > 374$ °C, $P_c > 22.1$ MPa) [10–12]. Bi et al. [13] reported the degradation of PE to oil in a continuous supercritical water reactor. Bae et al. [14] investigated the decomposition reaction of polystyrene (PS) in supercritical water at temperature ranging from 370 to 420 °C. Goto's group have studied the depolymerizations of polymers such as polyethylene terephthalate or nylon 6 in supercritical fluids [15]. Their results all indicated that supercritical water is a superior medium for the decomposition reaction.

Actually, polymer wastes are cheap sources for fabricating carbon materials. Among various carbon materials, mesoporous carbons have attracted increasing attention [16] owing to their broad applications in catalyst supports [17–19], adsorbents [20–22], biofiltration [23, 24], sensors [25], electrodes [26] and energy storage [27]. Especially, because interconnected pores can fast transport and efficiently adsorb mass gas, porous carbons are expected to be an ideal hydrogen storage materials [28–30].

Usually, mesoporous carbons are prepared by templating method. For example, Ryoo et al. [31] obtained mesoporous carbons by carbonizing sucrose inside the pores of MCM-48 silica molecular sieves. Li and coworkers and Fuertes fabricated ordered mesoporous carbons by templating SBA-15 silica molecular sieves [32, 33]. Bein and coworkers synthesized mesoporous carbon nano-filaments by replication of Fe-containing silica-based mesoporous nano-filaments prepared in the channels of anodic alumina membranes [34].

Herein, we present a template-free strategy to convert PE into mesoporous carbons and other carbon materials in supercritical water. Investigation of their electrochemical hydrogen storage behaviors indicates mesoporous carbons

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have high hydrogen storage capacity (348 mAh/g, corresponding to 1.3 wt%).

Experimental

Preparation of mesoporous carbons, carbon nanofibers and carbon nanotubes

In a typical experiment, 1 g commercial PE film was added into a 60 mL stainless steel autoclave, which was then filled with distilled water up to 80% of the total volume. The autoclave was sealed and maintained at the target temperature (mesoporous carbons: 550 °C, carbon nanofibers: 450 °C and carbon nanotubes: 650 °C) for 6 h, and then allowed to cool to room temperature naturally. After being centrifuged at 8,000 rpm, the dark precipitate was washed with absolute ethanol, dilute HCl and distilled water. Finally, the products were collected and dried in vacuum at 50 °C for 4 h.

Characterization of the carbon materials

The phase structure and purity of the samples were characterized by X-ray diffraction (XRD; Phillips X'Pert SUPER with Cu Kα radiation, $\lambda = 1.5418$ Å). The morphology and crystallization were analyzed by transmission electron microscopy (TEM; Hitachi H-800, using an accelerating voltage of 200 kV) and high-resolution TEM (HRTEM; JEOL-2010, also at 200 kV). Raman spectrum was recorded on a LABRAM-HR Confocal Laser MicroRaman Spectrometer (Ar^+ laser, $\lambda_{ex} = 514.5$ nm) at room temperature. The specific surface areas of were evaluated from nitrogen adsorption data (Micromeritics Instrument Corp., ASAP 2000).

Electrochemical measurements of the carbon materials

Electrochemical measurements were performed in a three-electrode cell, in which carbon sample was used as the working electrode, $Ni(OH)_2/NiOOH$ as the counter electrode, Hg/HgO as the reference electrode, and 6 mol/L KOH as electrolyte. The working electrode was fabricated by pressing the mixture of 90 wt% carbon and 10 wt% poly(tetrafluroethylene) onto a copper foil. The electrodes were cycled galvanostatically between −1.2 and −0.4 V (vs. Hg/HgO) at a current density of 50 mA/g.

Results and discussion

Figure 1 shows the XRD pattern of the samples prepared at different temperatures. At lower reaction temperature (450 °C), no diffraction peak can be clearly identified (Fig. 1(a)), indicating that the products are amorphous. In the XRD pattern of the sample obtained at 550 °C (Fig. 1(b)), two intense peaks are observed, which coincide with the (002) and (010) reflections of graphite, respectively. At higher reaction temperature (650 °C), the sample exhibits better crystallinity than lower temperature (Fig. 1(c)).

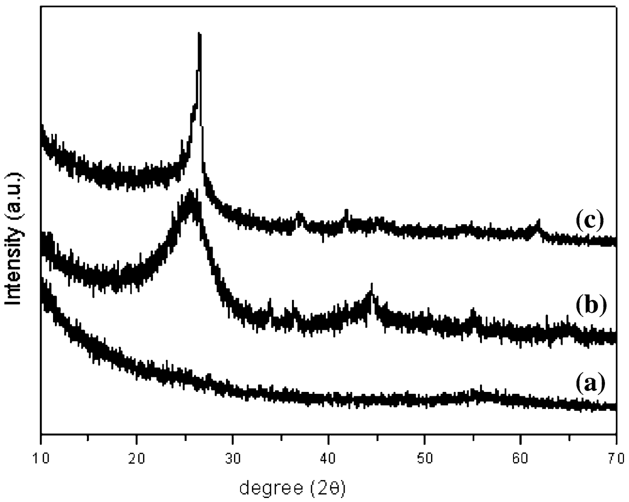

Fig. 1 XRD patterns of the samples prepared in supercritical water at 450, 550 and 650 °C (from the bottom to top)

Figure 2(a) gives the typical TEM image of the products prepared at 550 °C. In this case the as-prepared products are porous carbons. The pore sizes concentrate in the range of 8–12 nm, which are in the mesopore range. The TEM image of the products prepared at 450 °C (Fig. 2(b)) show that no mesoporous carbons but a large amount of carbon nanofibers are observed. As conversion temperature at 650 °C, carbon nanotubes are the main products (Fig. 2(c)).

The microstructures of mesoporous carbons were further investigated by HRTEM. From Fig. 3(a), one can see the products are porous films. By analyzing the image contrast, we deduced that the thickness of a layer of carbon film is not more than 10 nm. Figure 3(b) demonstrates the details of a pore with a wall thickness about 3–4 nm, and the pore wall is composed of discontinuous graphitic layers that are parallel to the tangent direction of the pore. Note that there exist interstices among graphitic layers. These voids seem to be in favor of storing hydrogen because of their large volume.

Raman spectroscopy of the mesoporous carbons is shown in Fig. 4. The peak at 1,590 cm^{-1} (G-band) is associated with an E_{2g} mode of graphite and related to the vibration of sp^2-hybridize carbon atoms in a two-dimensional graphite layer [35]. Compared with the G-band at 1,580 cm^{-1} for the graphitic carbons, the G-band of the

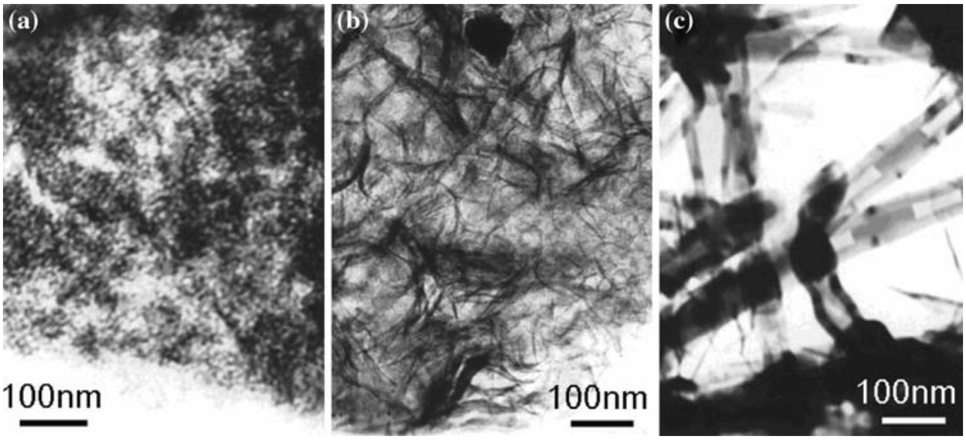

Fig. 2 TEM images of (**a**) mesoporous carbons, (**b**) carbon nanofibers and (**c**) nanotubes

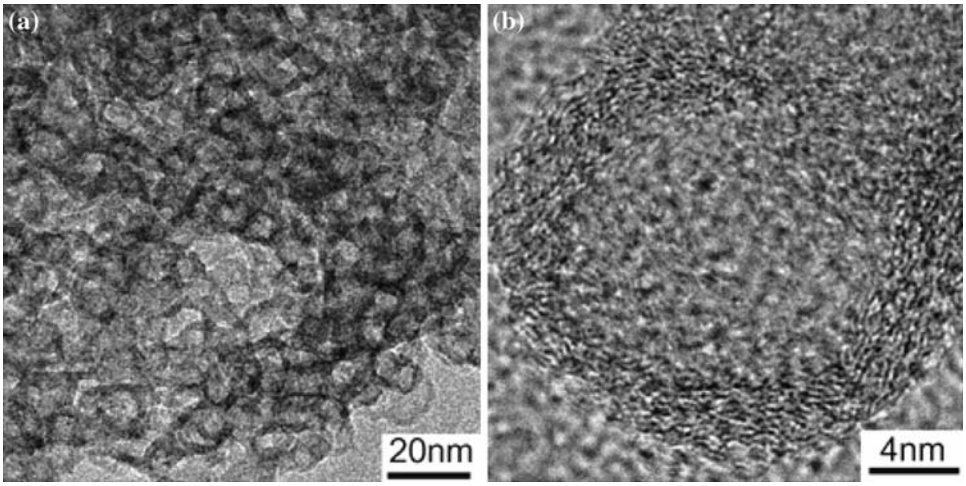

Fig. 3 HRTEM images of (**a**) mesoporous carbons and (**b**) a representative mesopore

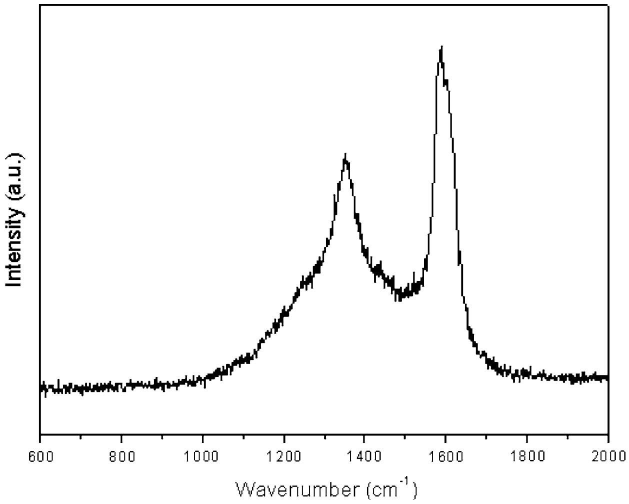

Fig. 4 Raman shifts of mesoporous carbons

mesoporous carbons shifts towards a higher wavenumber because of the less orderly arrangement of the carbon atoms [36]. The D-band at about 1,351 cm^{-1} corresponds to the vibrations of carbon atoms with dangling bonds at the plane termination of disordered graphite or glassy carbon [37]. For low crystalline degree of graphitic carbons, the relationship $L_a = 4.4I_G/I_D$ (in nm) may be used to obtain relative information on the microcrystalline planar [35], where I_G and I_D are the integrated intensities of the G and D bands, respectively. The crystal size L_a of mesoporous carbons, calculated from above equation is about 3.1 nm.

To investigate the effects of different reaction conditions on the formation of mesoporous carbons, we carried out a series of comparative experiments. It is found that the reaction temperature and medium are vital factors in the synthesis mesoporous carbons degraded by PE.

The suitable temperature range to generate mesoporous carbons is 530–570 °C; neither lower nor higher temperature is in favor of forming mesoporous carbons (Fig. 2(b, c)). In addition, only gray gel was obtained when reaction temperature was deceased to 350 °C. This is because the relatively low temperature cannot provide enough energy required for the decomposition of PE.

Supercritical water, which exhibits both a density close to that of liquid and high diffusivity and low viscosity similar to that of gas, is a promising media to degrade polymeric compounds. In our sealed system, water easily reaches the supercritical state that can promote the decomposition of PE. Besides, supercritical water provides a constant environment and slows the cracking rate of molecule chain during the conversion from PE to carbon [38]. That may be helpful for the formation mesoporous carbons. In fact, without any water added in the autoclave, the product was mainly irregular carbon particles. This is due to the thermal cracking of PE proceeding too fast to effectively control the growth of neonatal carbon clusters.

Based on the above experiments, a possible reaction process is proposed as follows. Firstly, PE is decomposed to low molecular weight hydrocarbons via random chain-breaking reaction in supercritical water system (Eq. 1). To our knowledge, PE could degrade to hydrocarbons (the number of carbon atoms: 5–11) ~400 °C in an isolated atmosphere [39], so the above speculation is reasonable. Subsequently, with the increase of temperature and pressure, these hydrocarbons are further decomposed to carbon clusters [38] (Eq. 2a and 2b). Eventually, the carbon clusters grow multiform carbon products (nanofibers, mesoporous carbons and nanotubes) in different temperature ranges. The whole reaction could be summarized as Eq. 3.

$$-CH_2CH_2CH_2CH_2- \rightarrow -CH_2CH_2 + CH_2CH_2- \rightarrow C_nH_{2n} + C_nH_{2n+2} \tag{1}$$

$$C_nH_{2n} + n/2O_2 \rightarrow nC + nH_2O \tag{2a}$$

$$CnH_{2n+2} + (n+1)/2O_2 \rightarrow nC + (n+1)\ H_2O \tag{2b}$$

$$-(CH_2)-_n + n/2O_2 \rightarrow nC + nH_2O \tag{3}$$

Electrochemical hydrogen storage behaviors of as-prepared carbon material have been investigated by the galvanostatic charge–discharge technique. In this technique, the carbon sample is used as working electrode, which can adsorb nascent hydrogen when electrolyzing water. During the discharging process, carbon electrode releases the adsorbed hydrogen atom, which becomes water again under alkaline conditions. This charge/discharge mechanism is formulated in the following equation:

$$C + H_2O + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} C/H_{ad} + OH^-$$

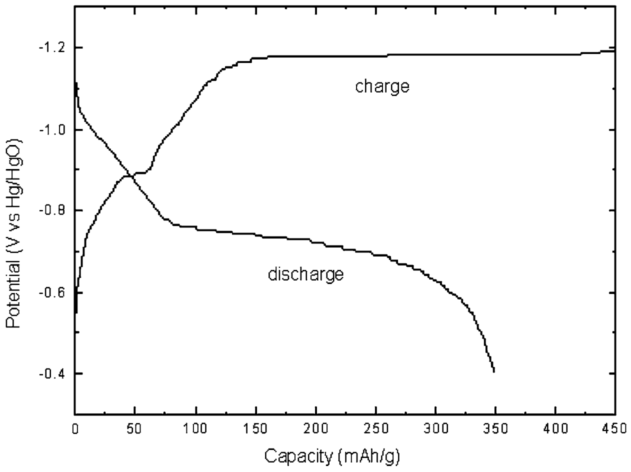

Fig. 5 Charge/discharge curves for mesoporous carbons as electrodes

Figure 5 displays the galvanostatic charge–discharge cycle of mesoporous carbons at a current density of 50 mA/g. The charge curve reveals a voltage plateau around −1.15 V, which accords with electrochemical reduction of H_2O to H atom in aqueous alkaline solution (the theoretical value of equilibrium potential is −0.87 V vs. NHE, i.e., −0.97 V vs Hg/HgO electrode). Other voltage plateau can be found around −0.88 V from 34 to 63 mAh/g. This two-plateaus phenomenon implies there are two different hydrogen-adsorption sites in mesoporous carbons. The hydrogen initially adsorbed into the mesopores of carbon and then entered the intercrystallite voids of carbon particles (~1–2 nm, pertain to micropores). A similar phenomenon was also reported previously [40, 41]. The plateau of the discharging potential is observed at approximately −0.58 V and the discharging capacity up to 348 mAh/g, amounting to a hydrogen-storage capacity of 1.3 wt%, which is comparative to those of some electrochemical hydrogen storage materials, such as Ni_xB nanoparticles (1.24 wt%) [42], Co–P ultrafine particles (1.1 wt%) [43], MoS_2 nanotubes (0.95 wt%) [44], selenium submicrotubes (0.97 wt%) [45], carbon nanotubes (1.0 wt%) [46] and ordered porous carbons (1.95 wt%) [30]. It means that as-prepared mesoporous carbon is an efficient electrode material for electrochemical hydrogen storage.

Figure 6(a, b) give the charge–discharge curve of the other carbon samples. The discharge capacity of carbon nanofibers and nanotubes are 47 and 95 mAh/g, respectively, which reveal that the electrochemical hydrogen storage capacity of carbon samples is highly sensitive to their morphology.

The data derived from N_2 adsorption as listed in Table 1 exhibits the influence of the specific surface area and micropore area on the hydrogen storage capacity. No close relationship exists between the hydrogen storage capacity and the specific surface area. However, the hydrogen storage capacity has an increscent trend with the increase of micropore area. These findings suggest that hydrogen adsorption mainly take place in micropores, therefore, the

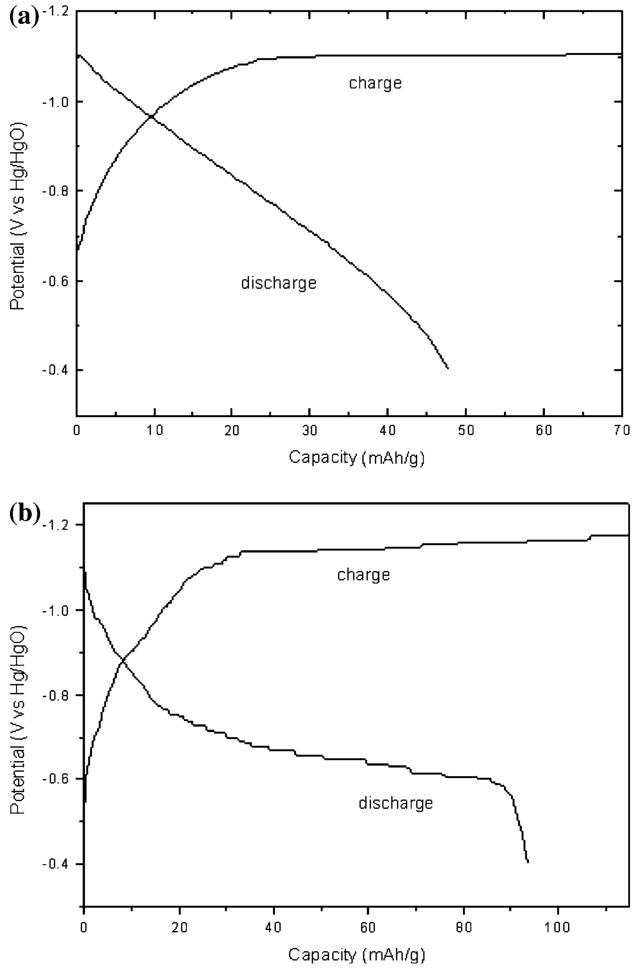

Fig. 6 Charge/discharge curves for (**a**) carbon nanofibers and (**b**) nanotubes as electrodes

Table 1 Impact of the specific surface area and micropore area on the hydrogen storage capacity

Carbon samples	BET surface area (m^2/g)	Micropore area (m^2/g)	Hydrogen storage capacity (mAh/g)
Mesoporous carbons	571	112	348
Carbon nanofibers	411	21	47
Carbon nanotubes	389	27	95

presence of micropores is very important to enhance the hydrogen storage capacity.

Conclusions

In summary, PE films have been successfully converted into mesoporous carbons in supercritical water at 550 °C. Carbon nanofibers and nanotubes could also be obtained by varying reaction temperature. We expect that this supercritical water method can be extended to the degradation of other polymer wastes. A discharging capacity up to 348 mAh/g was achieved for mesoporous carbon, which may be applied as the material of electrochemical hydrogen storage.

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