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Metal-Organic Framework as a Template for Porous Carbon Synthesis

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Carbon, which has different allotropes (graphite, diamond, fullerenes/nanotubes) and various microtextures as well as ability for existence under different forms, represents a very attractive material for use as adsorbents,[1] catalyst supports,[2] and electrode materials.[3] Extensive methods have been employed to prepare carbon materials, including laser ablation,[4] electrical arc,[5] chemical vapor decomposition (CVD),[6] and nanocasting,[7,8] as well as chemical or physical activation methods.[9] Among these methods, the nanocasting method is an effective way to prepare microporous and mesoporous carbon materials, for which porous inorganic templates, such as zeolites[7] and SBA-15,[8] have been used with carbon precursors, such as furfuryl alcohol (FA)[10] and sucrose.[11] On the other hand, there has been a rapid development in metal-organic frameworks (MOFs) in the past decade; especially, porous MOFs have attracted much attention as they have been used for gas separation and storage and heterogeneous catalysis.[12] Porous MOFs have permanent nanoscaled cavities and open channels offering congenital conditions for small molecules to access and, therefore, exhibit a potential for use as a template to synthesize nanoporous carbon materials. Herein, we report the first example of the use of a MOF as a template for preparing nanoporous carbon, which exhibits high surface area and hydrogen adsorption capacity as well as excellent electrochemical performance as an electrode material for electrochemical double-layered capacitor (EDLC).

The MOF-5 framework ($Zn_4O(OOCC_6H_4COO)_3$),[12k] one of the most representative MOFs, which has a three-dimensional intersecting channel system (cavity diameter 18 Å), was used as template and FA (molecular dimensions $8.43 \times 6.44 \times 4.28$ $Å^3$)[13] as carbon precursor in this work. MOF-5 was prepared according to the reported method[14,15] and pretreated under dynamic vacuum at 200 °C for 24 h. The degassed MOF-5 was heated at 150 °C for 48 h under the atmosphere of FA vapor, during which FA was polymerized in the pores of MOF-5. The carbonization of the PFA/MOF-5 composite was performed at 1000 °C for 8 h with an Ar flow.[10] The as-synthesized sample was identified to be carbon (designated as NPC) by the energy-dispersive X-ray spectroscopy (EDS).

The PXRD pattern for NPC (Figure 1a) displays two broad peaks at $2\theta = 25$ and 44°, corresponding to the diffractions for carbon. No diffractions were observed for Zn species in the sample obtained by carbonizing at 1000 °C. The absence of Zn is further conformed by the EDS measurement (Figure 2c). The Cu signal is originated from the Cu-mesh supporting the TEM sample. It is noted that sharp diffractions due to ZnO appeared in a sample obtained by carbonizing at 800 °C.[15] The observed ZnO was formed owing to the decomposition of the MOF-5 framework between 425 and 525
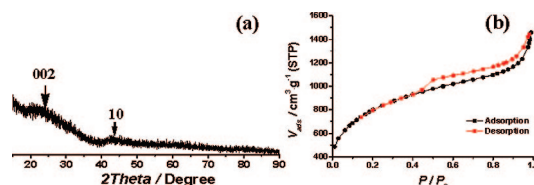

Figure 1. (a) PXRD pattern and (b) N_2 sorption isotherms of NPC.
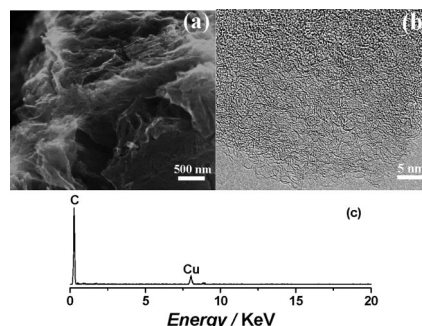

Figure 2. (a) SEM and (b) HRTEM images and (c) EDS of NPC.

°C as observed in the TG measurement.[15] At temperature higher than 800 °C, ZnO was reduced during the carbonization process,[16] and subsequently, Zn metal (boiling point 908 °C) vaporized away along with the Ar flow, leaving carbon species alone in the resulting NPC sample.

The general shape of the N_2 sorption isotherms for NPC (Figure 1b) suggests the existence of different pore sizes spanning from micro- to macropores. Especially, the steep increase in the adsorbed volume at low relative pressure reveals the presence of microporosity in the sample, and the following small slope observed at medium relative pressure as well as the desorption hysteresis denotes the existence of developed mesoporosity, while the final almost vertical tail at the relative pressure near 1.0 points to the presence of macroporosity. The ratio of macropore$_{d>50\ nm}$/mesopore$_{2<d<20\ nm}$/micropore$_{d<2\ nm}$ (d, pore diameter) for the NPC sample is approximately 1.0:15:5.0 as calculated from the nitrogen adsorption isotherm. The BET surface area and pore volume are 2872 $m^2 \cdot g^{-1}$ and 2.06 $cm^3 \cdot g^{-1}$, respectively. It is noteworthy that such a value is close to the theoretical surface area of a double-sided separated graphitic sheet (2965 $m^2 \cdot g^{-1}$).[17] In contrast, the sample obtained by carbonizing at 800 °C gives rise to a much lower BET surface area (417 $m^2 \cdot g^{-1}$) and pore volume (0.63 $cm^3 \cdot g^{-1}$).[15] It reveals that the carbonization temperature is critical for the structural evolution of the resultant carbon. The role of MOF-5 as template in the present work has been further investigated by carbonizing the sample at 530 °C. At this temperature, the MOF-5 framework decomposes to produce ZnO species, which is observed by XRD measurements[15] and the reduction of ZnO needs higher tempera-
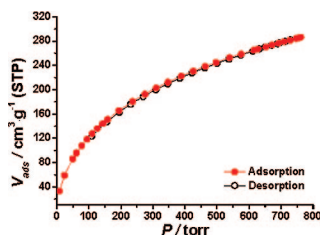
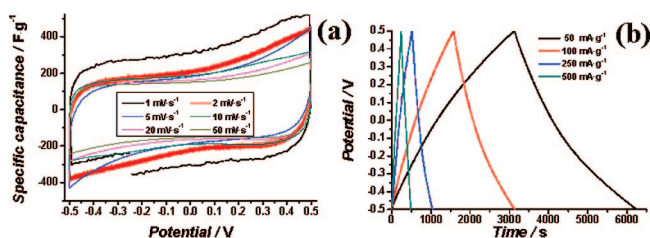**Figure 3.** Hydrogen sorption isotherm of NPC at −196 °C.

Figure 4. (a) Cyclic voltammograms at different scan rates and (b) galvanostatic charge/discharge at different current densities. Electrochemical properties measured in a two-electrode cell with 2.0 mg of active material NPC on each electrode.

ture. The sample prepared by carbonizing at this temperature has a low surface area ($S_{BET} = 217$ m$^2 \cdot$g^{-1}).[15] Washing the sample with HCl to remove ZnO gives rise to a high BET surface area of 1732 m$^2 \cdot$g^{-1}.[15] This observation reveals that the pores have been formed during the carbonization at 530 °C with ZnO included in the material, indicating that the pore formation is not based on the evaporation of the Zn. More structural details for NPC were investigated by SEM and HRTEM observations (Figure 2), which show sheet-like structure. In the present work, weight losses during the polymerization of FA and subsequent pyrolysis of PFA in the pores of MOF-5 result in incomplete filling and leave a free space in the pores where carbonization takes place. During the carbonization process, the MOF-5 framework decomposes, behaving as a self-sacrificed template and resulting in the formation of the nanoporous carbon with a large pore volume and high specific surface area.

The resultant nanoporous carbon displays a high hydrogen storage capacity. The hydrogen adsorption/desorption isotherms were measured at −196 °C, as shown in Figure 3. It should be noted that the same hydrogen adsorption/desorption behavior was observed by repeating measurements four times. The hydrogen uptake at 760 Torr is as high as 2.6 wt %, which is much higher than the H$_2$ uptake (1.3 wt %) by MOF-5 under the same condition.[12f] The as-synthesized NPC exhibits excellent electrochemical performance as an electrode material for EDLC. A two-electrode NPC-based capacitor (electrolyte, 1.0 M H$_2$SO$_4$) cycling potentiodynamically between −0.5 and 0.5 V at various sweep rates behaves like an ideal capacitor by showing rectangular voltammograms without any redox peaks in the chosen potential range (Figure 4a). At high sweep rates, the specific capacitance is attributed to meso/macropores of the active material NPC. The specific capacitance decays ca. 22% (from 204 to 159 F$\cdot$g^{-1}) with the increasing sweep rates from 5 to 50 mV$\cdot$s^{-1}, indicating the excellent mesoporosity of NPC. The observed sharp increase in specific capacitance from 233 F$\cdot$g^{-1} (2 mV$\cdot$s^{-1}) to 312 F$\cdot$g^{-1} (1 mV$\cdot$s^{-1}) is connected with diffusion limitation within the micropores of NPC. In comparison, it has been reported that the carbon materials synthesized using SBA-15 as a template show capacitances at a sweep rate of 5 mV$\cdot$s^{-1} ranging from 102 to 163 F$\cdot$g^{-1},[18] which are much lower than that of NPC (204 F$\cdot$g^{-1}). Galvanostatic charge/discharge curves are also measured for

specific capacitance evaluation. Figure 4b shows the galvanostatic charge/discharge curves at different current densities. Typical triangular shapes confirm good capacitive properties of NPC. The specific capacitance is maintained as high as 258 F$\cdot$g^{-1} even at a current density of 250 mA$\cdot$g^{-1}.

In summary, we have for the first time employed a metal-organic framework (MOF) as a template to prepare nanoporous carbon, which exhibits a high specific surface area and important hydrogen uptake as well as excellent electrochemical property as an electrode material for electrochemical double-layered capacitor (EDLC). The present finding provides us a new example of application of the rapidly growing MOF family. The structural diversity of MOFs will show high potential as templates for synthesizing functional carbon materials.

Supporting Information Available: XRD and TG of MOF-5 used in this work, XRD and N$_2$ sorption isotherms for the sample obtained by carbonizing at 530 and 800 °C as well as the electrochemical measurement details of NPC. This material is available free of charge via the Internet at http://pubs.acs.org.

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