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In situ construction of carbon nanotubes/nitrogen-doped carbon polyhedra hybrids for supercapacitors

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ABSTRACT

Recently utilizing metal-organic frameworks (MOFs) as precursors to prepare porous carbons for supercapacitors application has attracted enormous attention. Unfortunately, such MOFs-derived porous carbons are mostly microporous and of low graphitization degree, which are considered unfavorable for the ion and electron transport. Further efforts need to be made to address this issue. Here we propose a new hybrid carbon nanotubes (CNTs)/nitrogen-doped carbon polyhedra (NCP) structure, which was fabricated via using CNTs as substrate for in situ growth of MOFs, [Zn(2-MeIM)$_2$] (2-MeIM: 2-methylimidazolate, ZIF-8) with a subsequent annealing process. The resultant CNTs/NCP hybrid possesses a high specific surface area of 898.0 $m^2\ g^{-1}$ and a nitrogen content of 9.43 wt%. When applied as supercapacitor electrode, it exhibits a maximum specific capacitance of 308.0 $F\ g^{-1}$ at a scan rate of 5 $mV\ s^{-1}$ in 1 M H_2SO_4 aqueous electrolyte measured in a three-electrode system, and even at a high scan rate of 200 $mV\ s^{-1}$, the capacitance still reaches 200.6 $F\ g^{-1}$. Furthermore, the CNTs/NCP-based symmetric supercapacitor exhibits a high energy density of 12.0 W h Kg^{-1} and good cycle ability. It is believed that CNTs/NCP should be promisingly applicable as a high performance supercapacitor electrode material.

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1. Introduction

Supercapacitor is an emerging energy storage technology which has gained rapidly increasing attention for supplementing existing battery technology [1–5]. Among different types of supercapacitors, electrical double layer capacitor (EDLC) that usually uses carbon as active materials exhibits several merits, such as low cost and long cycle life, and is the most commonly used supercapacitor at present. Recent advances in EDLC have been focused on the design and synthesis of porous carbon materials with novel nanostructures. Although there have been many approaches being reported for the synthesis of nanostructured carbon (including direct carbonization of polymer aerogels, templating method using zeolite and mesoporous silica, etc.) [6–9], exploring and seeking novel and facile strategies to prepare nanostructured carbon with high specific surface area and good electrical conductivity is still an urgent need for the development of EDLC.

Metal organic frameworks (MOFs), as a new class of crystalline porous materials with multiple functionalities have received enormous interests in various applications such as gas storage and separation, catalysis, ion exchange and chemical sensors [10–14]. Recently, MOFs have emerged as a new platform for the synthesis of new porous carbons [15–18]. As a subclass of MOFs, zeolitic imidazolate frameworks (ZIFs) are excellent precursors for nitrogen-doped porous carbons in view of the existence of abundant carbon and nitrogen species [19–22]. Especially, ZIF-8, [Zn(2-MeIM)$_2$] (2-MeIM: 2-methylimidazolate) derived porous carbons exhibit several attracting features, including well-defined shape, high nitrogen-content and large surface area, and thus may be promising electrode materials for supercapacitor application [23]. Unfortunately, the ZIF-8 derived nitrogen-doped carbon polyhedra (NCP) is mostly microporous and of low graphitization degree, which are considered unfavorable for ion and electron transport [24]. Although currently some progresses have been achieved, the obtained capacitive performances are still unsatisfied.

In order to solve the above-mentioned problem, here for the first time carbon nanotubes (CNTs)/NCP hybrid structures (CNTs/NCP) have been fabricated via using CNTs as substrate for in situ growth of ZIF-8 with a subsequent annealing process. The obtained CNTs/NCP with a novel CNTs-inserted NCP hierarchical porous structure exhibits an improved graphitization degree, pore volume and specific surface area compared to pristine NCP. Furthermore, the obtained CNTs/NCP was used as an active material to demonstrate its supercapacitor application. Control experiments of constructing supercapacitors using pristine NCP or CNTs as the active material were also carried out for comparison.

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2. Experimental

2.1. Preparation of CNTs/ZIF-8

Before the synthesis of CNTs/ZIF-8, CNTs purchased from Nanotech Port Co., Ltd. (Shenzhen, China) were pre-treated according to the chemical method described in the literature [25]. The synthesis process of CNTs/ZIF-8 is illustrated in Fig. 1. Typically, CNTs (20 mg) were dispersed in 50 mL methanol solution with the assistance of ultrasonication for 1 h. The resultant solution was mixed with $Zn(NO_3)_2 \cdot 6H_2O$ (350 mg), and then stirred for 1 h to form a black solution A. Subsequently, 526 mg 2-MeIM was dissolved in 50 mL methanol to form a clear solution B that was subsequently slowly added to solution A under stirring for 1 h. After being kept still for 24 h, CNTs/ZIF-8 was collected by centrifugation, washed thoroughly with methanol several times, and finally dried at 60 °C for 24 h. For comparison, ZIF-8 was synthesized by a similar process without the addition of CNTs.

2.2. Preparation of CNTs/NCP

CNTs/NCP and NCP were obtained by direct carbonization of CNTs/ZIF-8 and ZIF-8 at 1000 °C for 4 h with a heating rate of 5 °C under N_2 atmosphere, respectively.

2.3. Characterization

The surface morphology and structure of the samples were characterized by scanning electron microscopy (SEM, JEOL JSM-LV5610) and transmission electron microscopy (TEM, CM200). The pore size distribution and Brunauer–Emmett–Teller (BET) specific surface area were deduced from the nitrogen physical adsorption measurement data obtained using ASAP 2010 Accelerated Surface Area and Porosimetry System (Micrometitics, Norcross, GA). Raman spectra were obtained by Renishaw inVia microscope. A He-Ne laser (633 nm) was used as the light source for excitation. X-ray photoelectron spectroscopy (XPS) was performed on Imaging Photoelectron Spectrometer (Axis Ultra, Kratos Analytical Ltd.) with a monochromatic Al Ka X-ray source. X-ray diffraction (XRD) measurements were conducted on X-ray powder diffractometer (Rigaku D/Max2550, Cu Kα radiation).

2.4. Electrochemical experiments

Electrochemical analyses were performed using a three-electrode system equipped with a Ag/AgCl (3 M KCl) reference electrode and a platinum counter electrode. Working electrodes were prepared as described in the literature [22] by pasting a mixture of active material (CNTs, NCP or CNTs/NCP) with polymeric binder, polyvinylpyrrolidone/polyvinyl butyral onto graphite paper. The mass loading of each electrode is ~2 mg cm^{-2}.

All of the electrochemical measurements including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS, 10 mHz–100 kHz, 10 mV AC amplitude) were carried out using an electrochemical workstation (Autolab PGSTAT 302N) in a H_2SO_4 electrolyte (1 M) by using a three-electrode system. The specific capacitance ($\boldsymbol{C}$, F g^{-1}) can be obtained from CV curves using the following equation:

$$\boldsymbol{C} = \tilde{\boldsymbol{i}}/(v \times m) \tag{1}$$

where $\tilde{i}$ is the average current (A), $\boldsymbol{v}$ is the scan rate (V s^{-1}) and $\boldsymbol{m}$ is the mass of electrodes (g).

The electrochemical performances of CNTs, NCP and CNTs/NCP were further investigated in a two-electrode system. In such a two-electrode system, one electrode acted as working electrode and the other electrode with same weight and size was used as the counter and reference electrodes. The cell was composed of two sandwiched electrodes separated by a polypropylene membrane filled with 1 M H_2SO_4 electrolyte. The energy density (E) and power density (P) can be calculated from CV tests according to the following equations:

$$\boldsymbol{E} = \frac{1}{2} \times \boldsymbol{C}_s \times (\Delta \boldsymbol{V})^2 \tag{2}$$

$$\boldsymbol{P} = \frac{\boldsymbol{E}}{\Delta \boldsymbol{t}} \tag{3}$$

where C_s is the specific capacitance in a two-electrode system, ΔV is potential change during the discharge process, and Δt is the discharge time.

3. Results and discussion

The surface morphology and structure of CNTs/ZIF-8 were first characterized by SEM and TEM. From the SEM images shown in Fig. 2a and b, it can be clearly seen that CNTs/ZIF-8 hybrid is composed of uniform CNT-inserted polyhedra with a perfectly smooth surface and a size of approximately 250 nm. Further observation by TEM analysis shown in Fig. 2c reveals that the homogeneously distributed ZIF-8 is solid polyhedra intertwined with CNTs. The magnified TEM image in Fig. 2d confirms that the intertwined CNTs are inserted in ZIF-8 polyhedra, forming a novel CNTs/ZIF-8 hybrid structure. The original structures of CNTs, ZIF-8 and CNTs/ZIF-8 were further investigated by XRD measurements, as shown in Fig. 3. Obviously, both CNTs and ZIF-8 display typical diffraction peaks, indicating that they are highly crystalline. With the introduction of CNTs into ZIF-8, the obtained CNTs/ZIF-8 exhibits similar diffraction peaks with ZIF-8, and moreover, no obvious diffraction peaks of CNTs can be observed. This is ascribed to

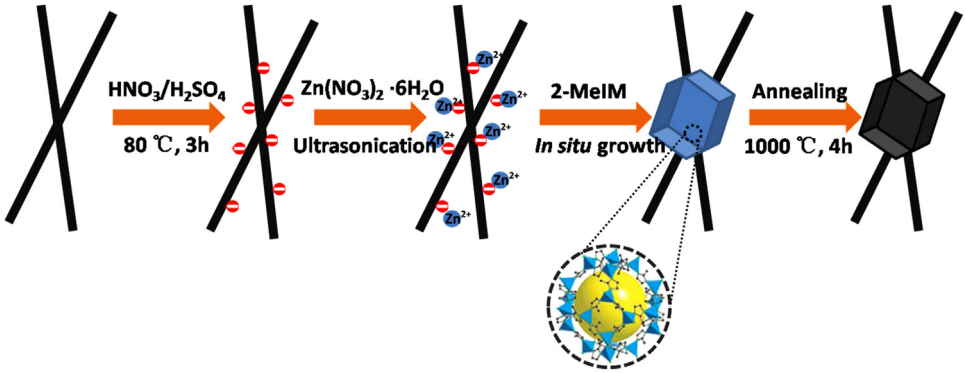

Fig. 1. Schematic illustration of the synthesis process of CNTs/ZIF-8.

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