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Nitrogen-doped mesoporous carbon thin film for binder-free supercapacitor

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ABSTRACT

Free-standing nitrogen-doped mesoporous carbon films were successfully prepared by carbonizing gelatin/HKUST-1 composite films, which converted from gelatin/copper hydroxide nanostrands composite films. Gelatin provides the sources of both carbon and nitrogen. The formation of HKUST-1 crystals expanded the gelatin matrix and produced porous structures which were reserved during the carbonization process. The mesoporous structures of the prepared carbon film were easily wetted by electrolytes and more suitable for rapid ionic migration. This mesoporous nitrogen-doped carbon film was explored as a binder-free electrode for supercapacitor, which exhibited highest specific energy of 28.1 W h kg^{-1}, specific capacity of 316 F g^{-1} at a current density of 0.5 A g^{-1}, 168 F g^{-1} at a current density of 5 A g^{-1}, and high capacitance retention of 92.9% with degrading of 0.00064% after charging/discharging 11,000 cycles.

1. Introduction

Porous carbon materials are of great importance and promising applications in electrode materials [1–5]. Various methods have been developed to synthesize porous carbons, including chemical vapour decomposition, laser ablation, chemical or physical activation, carbonization of polymer aerogels, carbide-derived carbon, template procedures [6–10]. Besides the high surface area and porosity, pseudocapacitance also contributed to the specific capacitance. Doping nitrogen (N) into carbon material has been an effective way to enhance the electrochemical performance, mainly due to the extra faradaic redox reactions, and the strong electron donor behavior of nitrogen, and strengthening the wettability of the interface between the electrolyte and electrodes [11–15]. In most cases, nitrogen-containing carbon materials have been achieved through reaction with nitrogen-containing reagents [16,17]. However, the post-treatment processing (such as treating with NH_3 gas) generally leads to low nitrogen content. This drawback might be overcome by carbonization of nitrogen-rich carbon precursors [18].

Gelatin, a low cost and abundant fibrous and nitrogen-rich protein, is expected to be an ideal precursor for the synthesis of nitrogen-doped carbon for supercapacitor [19,20]. In order to further enhance the performance, harsh activation processes were explored. Very recently, gelatin has been carbonized to carbon by using SBA-15, and sepiolite as templates, respectively [21–23]. However, most of the prepared nitrogen-doped carbons were in powder form. Typically, non-electrochemical active binders are requested to assemble them into electrodes for supercapacitors. This could result in less active materials loading and lower power density. In addition for thin film like electronic devices, free-standing binder-free thin films electrodes are highly demanded. Up to date, free-standing mesoporous nitrogen-doped carbon thin film for binder-free supercapacitor electrode has scarcely reported.

Herein, we demonstrate a novel way for the synthesis of free-standing mesoporous nitrogen-doped carbon films (mp-NCF) through carbonizing gelatin/HKUST-1 porous composite film without activation process. The gelatin/HKUST-1 film was prepared by reacting gelatin/copper hydroxide nanostrands (CHNs) thin film with H_3BTC at room temperature. Because of the growth of HKUST-1 crystals, the compacted gelatin/CHNs film (about 1 μm thick) was converted to 4.8 μm thick and porous gelatin/HKUST-1 thin film. After carbonization under argon at different temperature and removing away the remained copper particles, free-standing mesoporous nitrogen-doped carbon film was obtained and used as binder-free electrode for supercapacitor. It shows 168 F g^{-1} at current density of 5 A g^{-1} and retained 156.2 F g^{-1} after cycling 11,000 cycles with 0.00064% degradation per cycles.

2. Experimental

2.1. Materials

Gelatin and 1,3,5-benzenetricarboxylic acid (BTC) were purchased from Sigma–Aldrich. The gelatin was generated from pork

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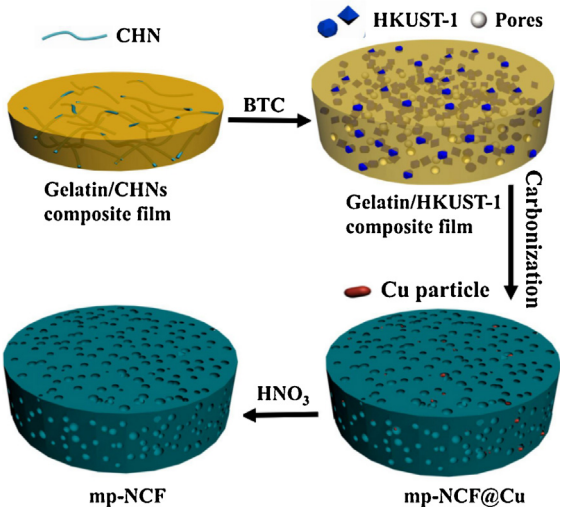

Scheme 1. Schematic illustration of the synthesis process of the mp-NCF from gelatin/CHNs composite films.

skin, type B with 150 blooms, 100–115 free carboxyl groups per 100 g, molecular weight 33 kDa. Copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), aminoethanol ($NH_2CH_2CH_2OH$) (AE) and glutaraldehyde (GA) (50 wt%) were obtained from Acros Chemicals. Polycarbonate membranes (PC) (9 cm diameter with 200 nm pores, 11 μm thick and porosity 10%) were purchased from Whatman. Ultrapure water of 18.2 MΩ was produced by a Millipore Direct-Q system.

2.2. Synthesis of free-standing mesoporous nitrogen-doped carbon films

As shown in Scheme 1, CHNs were synthesized by quickly mixing 1.4 mM AE aqueous solution with equal volume of 4 mM $Cu(NO_3)_2$ aqueous solution using a magnetic stirrer, then the mixed solution was aged for 1 or 2 days to form CHNs [24]. A mixture of 4 ml of gelatin aqueous solution (0.1 wt%) and 250 ml CHNs solution was filtered on a PC support (effective diameter 7.2 cm) to form a gelatin/CHNs composite film, and cross-linking by 3 ml 2.5 wt% GA aqueous solution for 1 h. The obtained gelatin/CHNs composite film was peeled off from the support to be free-standing. After that the free-standing gelatin/CHNs composite film was immersed into 10 ml, 10 mM H_3BTC ethanol–water (vol/vol, 1:1) solution at room temperature. After 1 h, a free-standing porous gelatin/HKUST-1 composite film was obtained. Three prepared free-standing gelatin/HKUST-1 composite films were carbonized in a horizontal tube furnace at a rate of 10 °C min^{-1} under argon flow at 600, 800 and 900 °C for 2 h, respectively. Finally, the free-standing and black films were obtained and further immersed into HNO_3 aqueous solution (0.1 M) to remove Cu compounds resulting from HKUST-1, and produced free-standing mesoporous nitrogen-doped carbon films named as mp-NCF-600, mp-NCF-800 and mp-NCF-900, respectively. For comparison, a nitrogen-doped carbon film (g-NCF) was carbonized from pure gelatin film at 600 °C after removing away CHNs from gelatin/CHNs composite film using 10 mM HCl.

2.3. Characterization and electrochemical test

X-ray diffraction (XRD) patterns were recorded by an X'Pert PRO (PANalytical, Netherlands) instrument with Cu Kα radiation at 0.02° steps. The morphologies were investigated using scanning electronic microscopy (SEM) (Hitachi S4800). X-ray photoelectron spectroscopy (XPS) was obtained by an ESCALAB_250Xi X-ray photoelectron spectrometer using Al Kα (λ = 1.5406 Å) X-ray as the excitation source. The nitrogen sorption and desorption measurements were recorded in Micromeritics instrument (ASAP 2020) after activating at 150 °C for 12 h. Fourier transform infrared spectra (FTIR) were recorded by using a Tensor 27 FTIR spectrometer (Bruker Inc.) in the form of KBr pellets. One piece of the prepared mp-NCF film folded into 1 cm × 1 cm (1 mg) and pressed between two pieces of Ni foams (1 cm × 1 cm) and served as electrode for supercapacitor. All electro-chemical tests were carried out by using a CHI 660D (Chenhua Shanghai, China) electrochemical workstation in a 1 M Na_2SO_4 aqueous solution with a platinum counter electrode and a standard calomel reference electrode (SCE).

3. Results and discussion

3.1. Structures and morphology

The XRD results (Fig. 1) indicate the main peaks of the gelatin/HKUST-1 composite film are attributed to the HKUST-1, indicating the CHNs are converted into HKUST-1 in gelatin film (Fig. 1a) [25]. The XRD patterns of both the mp-NCF carbon films converted from gelatin/HKUST-1 composite films at different temperatures and g-NCF film converted from pure gelatin display broad carbon (002) diffraction peak located around 24° (Fig. 1b) [26]. However, before immersing mp-NCF carbon films in 0.1 M HNO_3, several obvious diffraction peaks of Cu crystals are observed apart

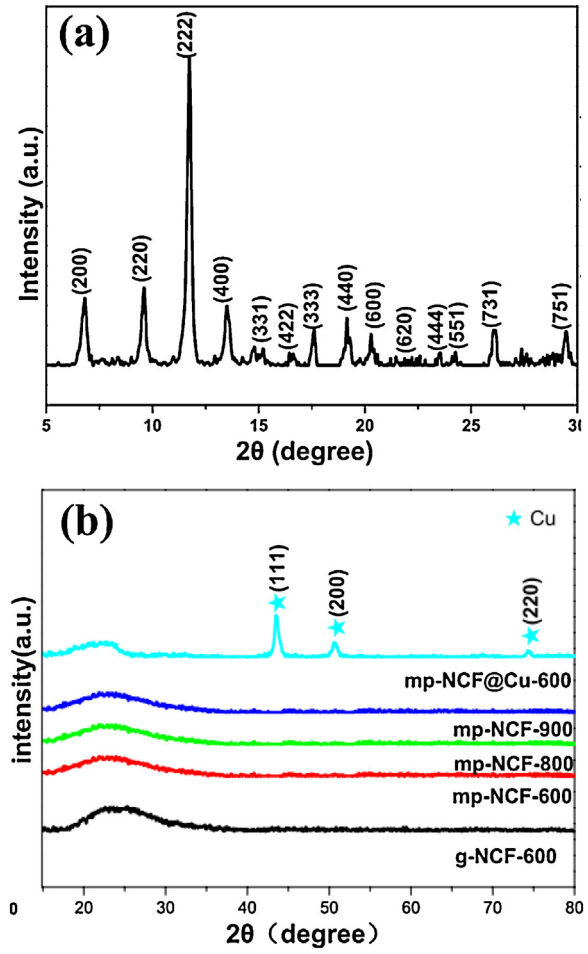

Fig. 1. XRD patterns of (a) gelatin/HKUST-1 composite film, (b) g-NCF-600 (black), mp-NCF-600 (red), mp-NCF-800 (green), mp-NCF-900 (royal blue), mp-NCF@Cu-600 (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)