



Synthesis and supercapacitive performance of hierarchically porous graphitic carbon monoliths containing cobalt nanoparticles



Yurong Liu^{a,b,*}, Baoping Lin^{a,*}, Dan Li^a, Tong Xu^a, Xueqin Zhang^a, Ying Sun^a, Hong Yang^a

^a School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, PR China

^b Chongqing Key Laboratory of Micro/Nano Materials Engineering and Technology, Research Center for Material Interdisciplinary Science, Chongqing University of Arts and Science, Chongqing 402160, PR China

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ABSTRACT

The hierarchically porous graphitic carbon monoliths containing cobalt nanoparticles (HPGCM-Co) have been successfully fabricated through multi-component co-assembly in polyurethane (PU) foam scaffold associated with a direct carbonization process from triblock copolymer F127, phenolic resol and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. *In situ* generated Co nanoparticles during the carbonization process act as catalysts for graphitization of carbon materials at relatively low carbonization temperatures (<1000 °C). The obtained graphitic monolithic materials exhibit large macropores (100–450 μm) and mesopores (5.1 nm), high surface area (747 m² g⁻¹) and pore volume (0.60 cm³ g⁻¹). Their supercapacitive performances have also been systematically studied. The galvanostatic charge–discharge results indicate that the specific capacitance of HPGCM-Co (231.6 F g⁻¹) is 42% higher than that of cobalt-free hierarchically porous carbon monolith (HPCM) at current density of 1 A g⁻¹ in 6 M KOH aqueous solution, revealing a promising application in supercapacitors. The excellent supercapacitive performance of HPGCM-Co is attributed to its unique hierarchical porous structure and high graphitization degree.

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1. Introduction

Supercapacitors are attractive energy storage devices suitable for a number of applications (e.g. hybrid electric vehicles, power tools, mobile electronic devices, etc.) because they can provide energy density higher than dielectric capacitors, greater power density and longer cycling ability than batteries [1–3]. However, the current applications of supercapacitors are still limited by their low energy density, and developing better electrode materials for supercapacitors has been an essential but challenging topic [4]. Transition metal oxides [5,6], conducting polymers [7,8] and carbon materials [9–12] are the fundamental candidates for supercapacitor electrode materials. Among these materials, porous carbon materials turn out to be the most promising candidates because of high conductivity, electrochemical stability, open porosity and low cost [13,14]. Unfortunately, commercial carbon electrode materials have some inappropriate factors for supercapacitors. For example, activated carbon is the most widely adopted electrode material. But the slow ion transportation in the small micropores limits their

effective utilization [15,16]. For ordered mesoporous carbon electrodes, because small mesopores are embedded in big particles, ions must diffuse to long distance and inner pores are not sufficiently accessible [17]. Therefore, the porosity of carbon materials plays an important role in the electrochemical capacitive performance of supercapacitors.

Recently, hierarchically porous carbons containing two or three types of pores have exhibited great potential for high performance supercapacitor applications due to the increased mass transport through macropores and mesopores and maintenance of high specific surface area on the level of micropore systems [18–23]. It is well known that macropores serving as ion-buffering reservoirs are able to minimize the diffusion distances, mesopores can decrease ion-transport resistance, and micropores are capable of increasing the electric-double-layer capacitance [24–26]. In general, hierarchical porous carbon materials are prepared in powder form. In contrast to carbon powders, carbon monoliths possessing an integrated structure and controlled pore structure are much easier to be used in supercapacitors [27,28]. However, carbon monoliths usually have amorphous carbon frameworks with poor electronic conductivity, a drawback that limits their applications in electrochemical systems. By contrast, graphitic carbon shows advantages over amorphous carbon because of well-developed crystalline structure and high electric conductivity, which make

* Corresponding authors. Address: School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, PR China (Y. Liu). Tel./fax: +86 25 52090616.

E-mail addresses: liuyr1978@163.com (Y. Liu), lbp@seu.edu.cn (B. Lin).

them more attractive in the application of supercapacitors [29,30]. Thus, a hierarchically porous structure and higher graphitization degree are favorable to enhance the capacitance of carbon materials. The combination of these two factors in one material could provide a supercapacitor electrode with high electrochemical properties. However, until now there have been few reports regarding carbon monoliths of this type. Sevilla et al. [31] have prepared graphitized macro/mesoporous carbon monoliths by carbonizing polymeric monoliths of poly(benzoxazine-co-resol). The overall synthesis process consists of the following steps: (a) the preparation of polymeric monoliths by co-polymerization of resorcinol and formaldehyde with a polyamine (tetraethylenepentamine), (b) doping the polymer with a metallic salt of Fe, Ni or Co, (c) carbonization and (d) the removal of inorganic nanoparticles. The obtained materials have a dual porosity made up of macropores and mesopores, with a BET surface area in the 280–400 m² g⁻¹ range. In addition, they show a specific capacitance of up to 35 F g⁻¹ in organic electrolyte. This synthesis procedure is complicated. What's more, the relatively low surface area and specific capacitance limit the practical use of these carbon materials. Therefore, it is still an urgent and important issue to explore facile methods to prepare hierarchically porous graphitic carbon monoliths for supercapacitors.

In this report, we demonstrate the synthesis of hierarchically porous graphitic carbon monoliths containing cobalt nanoparticles (HPGCM-Co) through multi-component co-assembly in PU foam scaffold associated with a direct carbonization process from triblock copolymer F127, phenolic resol and Co(NO₃)₂·6H₂O. *In situ* generated Co nanoparticles during the carbonization process act as catalysts for graphitization of carbon materials. The advantage of this method is that the two processes of formation of hierarchical pores and graphitic structure are simultaneously carried out in one process, which makes the synthesis very simple and time-saving in comparison with the conventional preparation methods. In addition, this synthetic procedure is an economical and practical pathway for the large-scale production of hierarchically porous graphitic carbon monolithic materials for supercapacitors because PU foam is inexpensive and commercially available. Furthermore, the electrochemical performance of HPGCM-Co-based electrodes has been systematically investigated. To the best of our knowledge, this is the first report of fabrication of hierarchically porous graphitic carbon monoliths containing cobalt nanoparticles for supercapacitors using PU foam as macroporous monolithic scaffold.

2. Experimental

2.1. Chemicals

PU foam with the density of 0.014 g cm⁻³ was purchased from Nanjing Chunhua Xinfei Sponge Factory. Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly-(ethylene oxide) triblock copolymer F127 (*M_w* = 12,600, PEO₁₀₆PPG₇₀PEO₁₀₆) was purchased from Acros Corp. Hydrated cobalt nitrate [Co(NO₃)₂·6H₂O], phenol, formalin (37 wt%) and ethanol were purchased from Nanjing Wanqing Chemical Corp. All chemicals were used as received without purification.

2.2. Synthesis of HPGCM-Co

The resol precursor (*M_w* < 500) was prepared according to the literature method [32]. The detailed fabrication process of HPGCM-Co was carried out as follows. Firstly, the PU foam slab with a total volume of 10 cm³ (4.3 cm × 1.5 cm × 1.5 cm) was cleaned with distilled water and dried at 100 °C for 6 h. The mixed solution composed of 1.0 g F127, 5.0 g 20 wt% resols' ethanol

solution and 0.25 g Co(NO₃)₂·6H₂O are coated onto the PU foam. The weight percentage of Co was 5% with respect to resol. It took 5–8 h at room temperature to evaporate ethanol. Then the coated PU foam was thermocured in an oven at 100 °C and 150 °C for 24 h each. The product, denoted as HPGCM-Co-as made, was pyrolyzed at 350 °C for 3 h and 900 °C for 2 h with a ramping rate of 1 °C min⁻¹ below 600 °C and 5 °C min⁻¹ above 600 °C. The obtained sample was denoted as HPGCM-Co-900, where 900 was the pyrolysis temperature. As a comparison, we synthesized the hierarchically porous carbon monolith (HPCM) by similar approach without adding cobalt nitrate.

2.3. Characterization

Small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu K_α radiation (40 kV, 35 mA). Wide-angle X-ray diffraction (XRD) patterns were collected on Bruker D8 Advance X-ray diffractometer using Cu K_α radiation (40 kV, 200 mA). Raman spectra were obtained with a Renishaw inVia Raman spectrometer (England), using a He–Ne laser with an excitation wavelength of 532 nm. Scanning electron microscopy (SEM) images were collected with a Hitachi S-3400N electron microscope operated at 20 kV. Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2011 microscope (Japan) operated at 200 kV. N₂ adsorption/desorption was determined using a Tristar-3020 surface area analyzer.

2.4. Electrochemical measurements

Supercapacitive performances were evaluated by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) tests and electrochemical impedance spectroscopy (EIS) in 6 M KOH aqueous solution. All electrochemical experiments were performed on CHI 660D electrochemical workstation (Shanghai CH Instruments Co., China) using a three-electrode system with Pt foil and Hg/HgO electrode as counter electrode and reference electrode, respectively. The working electrode was prepared by mixing 90 wt% active materials (as-prepared HPCM or HPGCM-Co) and 10 wt% polyvinylidene fluoride (PVDF) with N-methyl-2-pyrrolidone (NMP) to form slurry. Then the above materials (5 mg) were coated onto a 1 cm × 1 cm nickel-foam current collector, and dried at 60 °C for 8 h. The CV measurements were conducted with a potential window from –0.9 V to 0 V at different scan rate ranging from 1 mV s⁻¹ to 50 mV s⁻¹. GCD tests were run on from –0.9 V to 0 V at different current densities from 1 A g⁻¹ to 5 A g⁻¹. EIS measurements were recorded from 100 kHz to 10 mHz with an alternate current amplitude of 5 mV. Specific capacitance values were calculated from GCD curves according to the equation as follows:

$$C = \frac{I \times \Delta t}{\Delta E \times m} \quad (1)$$

where *C* is the specific capacitance (F g⁻¹), *I* is the constant discharging current (A), Δt is the discharging time (s), ΔE is the discharging potential window (V) and *m* is the mass of active materials (g).

3. Results and discussion

3.1. Morphology and macroporous structure

The coated PU foam has the same volume as the PU foam scaffold (Fig. 1a). The thermally decomposable PU foam scaffold can be removed during the carbonization process. HPGCM-Co-900 shows about 55% volume shrinkage and 30% linear shrinkage (Fig. 1b), but

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