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Vapor deposition polymerization of aniline on 3D hierarchical porous carbon with enhanced cycling stability as supercapacitor electrode

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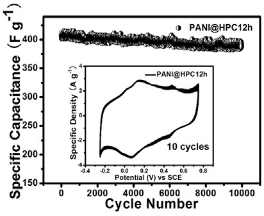
HIGHLIGHTS

- PANI was coated on to hierarchical porous carbon through VDP method.
- The PANI@HPC composite exhibited good electrochemical performance.
- The cycling stability is superior as compared to literature.
- Symmetric supercapacitor based on the composite displayed high energy density.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a polyaniline coated hierarchical porous carbon (HPC) composite (PANI@HPC) is developed using a vapor deposition polymerization technique. The as synthesized composite is applied as the supercapacitor electrode material, and presents a high specific capacitance of 531 F g^{-1} at current density of 0.5 A g^{-1} and superior cycling stability of 96.1% (after 10,000 charge–discharge cycles at current density of 10 A g^{-1}). This can be attributed to the maximized synergistic effect of PANI and HPC. Furthermore, an aqueous symmetric supercapacitor device based on PANI@HPC is fabricated, demonstrating a high specific energy of 17.3 Wh kg^{-1}.

1. Introduction

Supercapacitor, as an important energy storage device, has been paid abundant attention due to its high power density, high columbic efficiency, and excellent cycling stability [1–4]. In general, supercapacitors are classified into two types, according to the charge-storage mechanism, which includes electrochemical double-layer capacitors (EDLCs) based on carbon materials, and pseudocapacitors based on certain transition metal oxides or conducting polymers [5–9]. The EDLCs usually display perfect cycling stability, but low specific capacitance; on the contrast, pseudocapacitors present high specific capacitance, while poor long cycle life [10–12]. These undoubtedly limit their practical application as individual electrode material for supercapacitors. Therefore, developing composite materials combining both EDLC material and pseudocapacitor material becomes an inevitable trend.

Among various carbon materials, hierarchical porous carbons (HPCs) with well-defined macropores and interconnected meso-/micropores combined in one system, have attracted superior

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attention [13–19]. Such HPCs possess improved mass transport facilitated by the macropores, high surface area and pore volume from micro-/mesopores, which grant them superior capacitance performance [19–23]. For example, Qie et al. [19] developed functionalized three-dimensional (3D) HPC via a modified chemical activation route with polypyrrole microsheets as precursor, and achieved a specific capacitance (SC) of 224.5 F g^{-1}. Jeon et al. [24] developed a nitrogen doped HPC with high capacitance of 239 F g^{-1}. Recently, we reported an oxygen rich 3D HPC derived from Artemia cyst shells, demonstrating a high SC of 369 F g^{-1} [25,26], and excellent long cycle life. However, despite the good capacitance behavior of HPC, its energy density remains relatively low, and the capacitance can be further improved by hybridizing the HPC with some pseudocapacitance materials.

Polyaniline (PANI) with good electrical conductivity [27] and theoretical specific capacitance of as high as 2000 F g^{-1}, is considered as a promising pseudocapacitor electrode material [28–32]. Coating PANI onto certain carbon surface is proven as an effective approach to improving the capacitance behavior of carbonaceous materials [33–40]. For example, very high SC of 1191.8 F g^{-1} was achieved from 3D cross-linked carbon network wrapped with ordered PANI nanowires [39]. Zhou et al. [36] coated PANI on graphene-beaded carbon nanofibers, and achieved an SC value of 637 F g^{-1}. Fan et al. [40] fabricated mesoporous PANI film on ultra-thin graphene nanosheet (G-mPANI) with SC of 749 F g^{-1}, which is more than two folds as that of pure PANI. However, this promising improvement on SC values also accompanied with significantly sacrificed cycling performance. Therefore, it is necessary to develop a feasible way to fabricate a PANI@carbon composite which can maximize the synergistic effect, demonstrating both high capacitance and good long cycle life.

In this work, we report a set of sequential strategies to fabricate a conducting PANI coated HPC composites through a vapor deposition polymerization (VDP) method. By carefully controlling the reaction condition, PANI can be evenly coated on to the HPC carbon frame without blocking the hierarchical pores. Such unique structure can offer 3D highly efficient pathways towards electrons and ions, facilitating high specific capacitance and excellent cycling performance.

2. Experimental section

2.1. Materials

Prior to use, aniline monomer (AN, Shanghai Chemical Co.) was distilled under reduced pressure. Artemia cyst shells were attained from China Academy of Aquaculture and Sciences. Hydrochloric acid (HCl, Kermel Tianjing Chemical Co.), nitric acid (HNO_3, Tianjin Chemical Reagent Co.), sulfuric acid (H_2SO_4, Tianjin Chemical Co.) and ammonium persulfate$(NH_4)_2S_2O_8$, Tianjin Chemical Co.) were used without further purification.

2.2. Synthesis of hierarchical porous carbon (HPC)

The hierarchical porous carbon was prepared according to the reported method [25]. Specifically, Artemia cyst shells were cleaned with distilled water and dried at 80 °C for 24 h followed by ball-milled for 6 h at a speed of 300 rpm. The pre-treated shells were then heated to 700 °C at Ar atmosphere with a heating rate of 5 °C min^{-1} and held there for 4 h. The product was subsequently sonicated in 3M HNO_3 for 80 min and then cleaned with distilled water. The obtained product was further activated with KOH with a weight ratio of 1:3 (M_C:M_{KOH}) at 750 °C in Ar atmosphere. Finally, the final product was washed several times with HCl solution and deionized water, respectively, until PH = 7, and then dried at 80 °C, which was denoted as HPC.

2.3. Synthesis of a polyaniline coated hierarchical porous carbon composite (PANI@HPC)

The preparation procedure of PANI@HPC is schematically illustrated in Fig. 1. The two connecting flasks were used as the reactor for vapor deposition polymerization (VDP) [41], of which the total volume was 275 ml. First, 0.45 g APS was dissolved in 1 ml of 1M HCl as the initiator solution. After that, 0.1 g HPC was added into the initiator solution, and ultrasonically dispersed for about 30 min to obtain a homogeneous dispersion and then kept for 4 h at room temperature to wet the HPC thoroughly. In this step, the as prepared HPC went through a soaking process, the surface of HPC was etched by mixed HCl and APS solution, due to electrostatic and hydrogen bonding interactions between them. Thus APS was hence able to be dispersed evenly on the surface of HPC, providing a large number of active nucleation sites for further PANI growth.

The homogeneous mixture of HPC and APS was then centrifuged and transferred into one of above-mentioned flask equipped with a sealing apparatus. The reactor was evacuated at room temperature, till the inside pressure of the chamber below −0.06 MPa. Subsequently, certain amount of liquid AN monomers was introduced into a small flask and then vaporized by heating at 80 °C with water bath. The obtained AN vapor was then introduced into the other chamber of the reactor, which was cooled at 0–5 °C with an ice-salt bath. VDP was proceeded for a certain time at 80 °C in the atmosphere of vaporized AN monomers. Considering that HPC is an excellent electron acceptor, analogous to other forms of carbon, such as graphene or carbon nanotubes, while aniline is a very good electron donor, the aniline vapor could be easily absorbed onto the surface of HPC through the electrostatic attraction and the formation of weak charge-transfer complexes between the aniline monomer and the porous framework structure of HPC [42]. As a result, HPC was finally coated by the aniline vapor in the presence of the homogeneous initiator (APS) solution with HCl as dopant acid. Thus, it is aptly to believe that there was an equal opportunity for aniline monomer to adsorb and polymerize on the overall surface of HPC.

After polymerization, the residual monomer vapor was removed from the reactor. Finally, the product in the reactor was collected and washed several times with deionized water and ethanol, and then freeze-dried under vacuum at −120 °C. A series of PANI@HPC composite materials were fabricated by carefully controlling the VDP reaction time. The samples synthesized with different VDP reaction time of 6, 12 and 24 h, were denoted as PANI@HPC6h, PANI@HPC12h and PANI@HPC24h, respectively. For comparison, pure PANI was also synthesized through the in situ oxidative polymerization as described in literature [43].

2.4. Characterization

The morphology of samples was observed under a Carl Zeiss SUPRA 55 SAPPHIRE field emission scanning electron microscope (FESEM, Germany), under the acceleration voltage of 15 kV, and Hitachi-7650 transmission electron microscopy at 80 kV (TEM, Japan). Fourier transform infrared (FTIR) spectra from 500 to 4000 cm^{-1} were collected by NiCOLET IS10 FTIR spectrometer (America) operated at resolution ratio of 4 cm^{-1}. Powder X-ray diffraction (XRD) patterns between 10 and 60° (~2θ) were collected by Rigaku D/MAX-2500 powder diffractometer with Cu-Kα radiation (λ = 0.154 nm) operated at 40 kV, 200 mA. Thermogravimetric analyses (TGA) were carried out by a thermal gravimetric analyzer (DTG-60A, SHIMADZU, Japan), with a heating rate of 10 °C min^{-1} under the air atmosphere ranging from 100 to 800 °C. X-ray