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KOH Activated Hollow Hierarchical Porous Polyaniline-Based Nanospheres as Efficient Electrode Material for High Performance Supercapacitors

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Abstract

Hollow nanostructured materials have gained attraction due to their advantages in stability, enlarged surface area and enhanced electrochemical performance toward supercapacitors. In this study, we describe the synthesis of hollow polyaniline spheres (HPS) by one pot polymerization process using $FeCl3$ as a catalyst and $H2O2$ as oxidizing agents under hydrothermal conditions. The HPS are further activated by using potassium hydroxide (KOH) and heat treatment under $N2$. The obtained results have demonstrated that activated HPS samples possess unique well- balanced hierarchical porous structure with mesopores and micropores combination. Besides, activated HPS own easy-accessibly large surface area and high conductivity, which can result in ultrafast electrolyte ion transport and endow carbon materials outstanding capacitive performance. Furthermore, the KOH activated HPS exhibits a larger specific surface area of 311 m2 g–1, specific capacitance of 945 F g–1 at scan rate 2 mV s–1, high energy density 126 Wh kg–1 at 1 A g–1 current density and capacitance retention (96%) after completing 1000 cycles in 1.0 M KOH aqueous solution, indicating that HPS are a promising electrode material for high performance supercapacitor application.

Keywords: Hollow polyaniline spheres (HPS) • KOH activation• Heat treatment • Micro/meso– pores • Supercapacitors

Introduction

In response to energy and environmental challenges, extensive improvements have been made for the progress of renewable energy equipment. New and environmentally friendly energy storage device technologies have become a research issue for several decades to accommodate the growing sustainable energy applications. Electrochemical capacitors, which are also known as supercapacitors, are electrochemical energy storage devices with unique properties, such as high power density, long cyclic life, fast charge-discharge rates, and low maintenance costy, good reversibility, and broad energy storage application prospects. Electrode material is the critical component of supercapacitor. Nowadays, carbon-based materials conductive polymers and metal oxides have been widely studied in supercapacitors [1]. Metal oxides and conductive polymers display high specific capacitance, thus achieve high energy densities, high charge/discharge rate, and quite stable physicochemical properties. The pseudocapacitors or so-called redox supercapacitors undergo fast and reversible faradaic redox reaction at the surfaces of electroactive materials that store the charges. The large specific pseudocapacitance of faradaic electrodes exceeds that of carbon-based materials using double layer charge storage. Typical active pseudocapacitive materials include transition metal oxides, such as $RuO2$, $MnO2$, $Fe3O4$, NiO, and conducting redox polymers such as polyaniline (PANI), polypyrroles (PPY), and polythiophenes [2].

As an important conducting polymer, PANI has been widely studied as electrode materials for the supercapacitor applications due to its excellent capacity for energy storage, easy synthesis, high conductivity, low cost and numerous morphologies. PANI has different morphologies such as nanotubes, nanofibers, hollow nano/micro spheres, nanorods andnano/micro spheres dependent on their synthetic method. Among these morphologies, hollow micro/nanostructured materials have been recognized as one type of promising material with numerous applications in energy-related fields. The unique nanostructures, like porous or hollow structures, provide particular advantages to supercapacitors due to the enhanced surface-to volume ratio and reduced transport lengths for both mass and charge transport. Specifically, the microporous structure can enhance selectivity and maintenance of specific surface area, but limit fast mass diffusion and transport. By contrast, the mesoporous structure can reduce transport resistance of mass ions from electrolyte to the surface of interior pores in the carbon shell, thereby offering a good charge accommodation . While, the hollow

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macroporous cavity can acts as "ion-buffering reservoirs" to minimize the diffusion distances of electrolyte ions [3]. Therefore, considerable efforts have been made to design and fabricate a carbon material with hierarchical porosity, particularly mesopores in combination with macropores and micropores, because of the enhanced properties compared with single-pore-sized porous materials. For example, Han et al prepared the dispersed carbon hollow-spheres with micropore shells and meso/macropore cores using colloidal silica as template, and there was a high specific capacitance of 270 F g–1 at 0.5 A g–1 in KOH aqueous electrolyte . Bhattacharjya et al synthesized hollow core mesoporous shell carbon (HCMSC) capsules by nanocasting method, and the specific capacitance of HCMSC was 162 F g–1 at 0.3 A g–1 current density in non- aqueous electrolyte. Lei et al reported hollow carbon spheres (HCS) with specific surface areas of as high as 2239 m2 g–1 by chemical vapor deposition with ferrocene as the carbon precursor and colloidal silica spheres as the template. This unique hierarchical porous structure not only can enhance effective selectivity of ion and maintain high specific surface area through the fine pores of micro/mesopores, but also improve mass diffusion and transport through the macro/ mesopores during the charge/discharge process. Although significant advances have been achieved in the fabrication of a variety of porous nanomaterials with hierarchical pore architectures and simultaneously manipulation the pore texture and morphology, especially regarding to construction of spherical morphology with well-developed hierarchical pores owing to their suitability for a great number of applications. On the other hand, the nanomaterials should also possess suitable polarity adapted to the electrolytes [4].

Furthermore, the porosity properties of nanomaterial can also be significantly modified by activation processes that remove the most reactive carbon atoms from their structure. In particular, the chemical activation of various carbon materials using KOH as the activating reagent is very promising because of its higher yields and high specific surface area of the resulting porous carbons. The modified porous structure is favorable to enhance active specific surface area and pore volume for high performance supercapacitors [5].

In this work, we have synthesized hollow hierarchical porous polyaniline nanospheres with microporous/meso-porous through template free method, hydrothermal treatment is put forward in which FeCl3 (Fe2+) acts as catalyst and H2O2 as oxidizing agent. Furthermore, KOH activation was used to introduce more micropores and mesopores, leading to a large active surface area and pore volume.

Materials and methods

Chemical reagents

The ethanol (AR), Phosphoric acid (H3PO4), Hydrogen peroxide (H2O2), Aniline, and Iron chloride FeCl3, were gained from Damo Reagent, Tianjing, China. Water used in the whole experiment was doubly distilled.

Synthesis of hollow polyaniline spheres (HPS)

HPS were prepared by following literature protocol [31]. Briefly, in a typical experimental procedure, 0.82 ml H3PO4 dissolved in 40 ml H2O, then added 0.1 ml of aniline monomer under vigorous stirring at room temperature to form a uniform solution. 0.12 ml of H2O2 added after few minute. 0.617 mmole of FeCl3 dissolved in 2 ml H2O, added into above solution. After fully stirring, the mixture was transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed quickly and maintained at 140 °C for 19 h in a temperature-controlled oven. Then, the autoclave was cooled to room temperature. The precipitate was filtered and washed with deionized water and ethanol, respectively, until the filtrate became colorless. At last, the sample was dried in vacuum at 60 °C for 6 h.

Same procedure was used to obtain solid spheres and mixed hollow solid spheres just by changing the amount of FeCl3 1.84 and 1.25 mmole, respectively.

Carbonization and KOH activation

For carbonization, HPS sample was simply heated at 500 ℃under N2 flow at a heating rate of 5℃ min–1 for 2 h and obtained sample was named as HPS-500. Furthermore for KOH activation, HPS was mixed with solid KOH at mass ratio of 1/2. Then the mixtures were heated at 500 ℃ for 2 h under N2 flow at a heating rate of 5℃ min–1. The resulted mixture was washed with excess HCl (1 M) solution and deionized water successively until the pH value of filtrate was neutral. Finally, after dried at 60 ℃ overnight, the activated hollow porous spheres were obtained and named as HPS-KOH-500.

Characterization

The morphology and structure of all as-prepared HPS samples were examined by means of scanning electron microscopy (SEM), Fourier transforms infrared spectroscopy (FT–IR) and Brunauer–Emmett–Teller (BET). SEM images were taken using a QUANTA 450 (FEI, America) which was attached with energy dispersive spectroscopy (EDS) to observe the chemical composition of samples. N2 adsorption-desorption measurements were taken to examine the porosity structural properties of all samples. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method via a micromeritics JWBK 122W instrument. The pore size distribution was determined using the Barrett–Joyner–Halenda (BJH) method. The FT–IR spectroscopy was measured on Bruker–Tenson 27 in the 4000-400 cm–1 region to determine characteristic functional groups of the samples. The powder X-ray diffraction (XRD) patterns were recorded from 10° to 80° using a Netherlands' PANalytical X'pert power diffractometer at room temperature employing Cu Kα (λ=0.15408 nm) radiation generated at 40 kV and 40 mA with a scan rate of 16° min–1. TGA was further carried out on TA instruments (TGA–Q50) in nitrogen flowing (40 ml min–1) with a linear heating rate of 10 °C min–1 to study the thermal stability of samples [32].

Electrochemical measurements

The electrochemical experiments were carried out using a conventional three-electrode cell. The working electrode was prepared as followed: all HPS products, carbon blacks, and binder (60% of polytetrafluorethylene aqueous suspension) at a mass ratio of 8:1:1 were added and mixed well in N–methyl–2–pyrrolidone (NMP) until it formed the slurry with proper viscosity, and then the slurry was uniformly coated on a disk-like nickel foam (with the active area of 1 cm2) by dipping, dried at 80 °C for 12 h in a vacuum drying oven, then pressed at 4 M Pa for 30 s in order to assure a good electronic contact. Thus, the working electrode obtained. The electrochemical measurements were performed on a CHI 760e electrochemical workstation (CHENHUA, Shanghai, China) detailed in our previous work [33].

Result and discussion

Morphology-Controlled Synthesis of PANI Particles

A control set of experiments were performed to investigate the role of important synthetic parameter, i.e., the amount of catalyst, molar ratio of monomer to catalyst, on the morphology of these PANI particles. The amount of catalyst was found to be the dominant parameter for morphology control. When the concentration of catalyst was 0.145 g ml–1 solid spheres in 300- 500 nm range were obtained (Fig. 1a). In contrast, with decreasing the catalyst concentration

0.05 g ml–1, well-defined HPS with relatively uniform sizes were produced (Fig. 1b,c and Supporting information S1a,b). Mixed hollow as well as solid spheres were obtained by using mass concentration of catalyst of about 0.1 g ml–1 as shown in Fig. 1d. Fig. 1e shows the HPS after heat treatment at 500 °C. It displays that heat treatment makes the surface rough and creates some pores on the HPS (Fig. S1c,d). Etching process after KOH activation further enhances the amount of pores and makes surface more rough. The size of all HPS as well as activated samples is about 200-400 nm range.

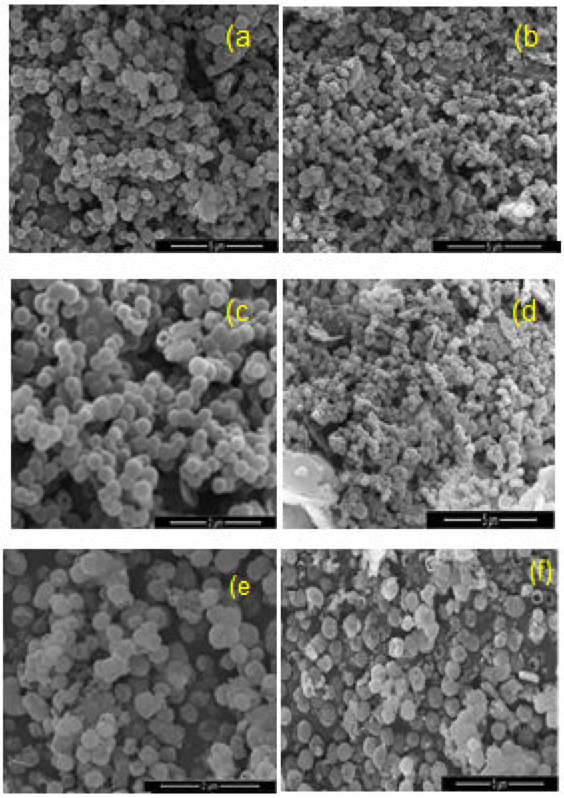

Figure 1: SEM images of (a) Solid PANI spheres, (b, c) Hollow PANI spheres (HPS), (d) Mixed hollow and solid spheres, (e) HPS-500 and (f) HPS-KOH-500.

Thermal Stability and Structural Characterization

TGA was performed to check the thermal stability of HPS. TGA spectra shows gradual weight loss may be due to (i) removal of water at temperature 100°C and (ii) decomposition of polymer . The total weight left after 800°C is 15%. Based on TGA results, we conducted thermal treatment to obtained more suitable and higher electrochemical activity.

The EDS analysis describes the elemental composition of polyaniline samples as shown in Fig. S3. Results show that PANI samples have elemental composition as carbon, nitrogen and oxygen with almost similar weight and atomic %. Absence of metal (Fe) in EDS analysis describes that iron chloride is used as catalyst just to facilitate the polymerization, without taking part in elemental composition of PANI samples.

illustrates the FT-IR spectra of different polyaniline samples. Peaks at 1551 cm-1 and 1411 cm-1 are associated with C=N and C=C stretching modes of quinonoid and benzenoid rings, respectively . The peak at 1344 cm-1 is related to C-N stretching vibrations of secondary aromatic amines. The sharp peak at 1126 cm-1 is due to results from N=Q=N (Q denotes quinoid ring) stretching mode and is indication of electron delocalization in PANI. Peak in range 889 cm- 1 is attributed to out of plane bending of C–H. Peak at 3384 cm-1 shows secondary amine, single N-H stretching vibrations .

The prepared samples are further analyzed by XRD patterns., one broad peak centered at 23.4° (2θ) which can be approximately indexed as (002) plane of standard graphite, is observed in the XRD patterns, revealing the characteristics of amorphous carbon usually derived from KOH activation procedure.

Conclusion

N2 adsorption–desorption isotherms and the corresponding pore size distributions in Fig. 2d of different as–synthesized HPS samples. The Brunauer–Emmett–Teller (BET) surface areas for the HPS, HPS-500 and HPS-KOH-500 samples are found to be ~41 m2 g–1, 66 m2 g–1, and 311 m2 g–1, respectively. Interestingly, the sharp increases for the nitrogen uptake of the HPS-KOH-500 are more drastic comparing with other samples, suggesting more micropores are induced by KOH activation, and overusing KOH also could result in the collapse of micropores and formation of small size mesopores . The abundant interconnected pore structures are favorable to rapid ion transfer/diffusion and charge accumulation. The pore size distribution curves of all samples are shown in Fig. 2d. A broad pore size distribution ranging from micropores to mesopores can be observed. Especially, KOH activated HPS owns the highest content of micropores and mesopores in which the pore size concentrates at 1.3 to 5.0 nm. The unique hierarchical porous structure concluded by nitrogen adsorption/desorption measurements is in good agreement with the results of SEM observations. After KOH activation, the BET surface area and total pore volume of KOH activated HPS rise to 311 m2 g–1 and 0.26 cm3 g–1, respectively, which could provide a huge amount of “ion-adsorption sites”. Notably, it shows a promise to explore the synthesized HPS- KOH-500 as an electrode material for advanced supercapacitor.

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