Synthetic Metals 246 (2018) 23–30

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Magnetic-field assisted synthesis of carbon dots-doped polyaniline nanotubes with a high-performance supercapacitance

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ARTICLE INFO

Keywords:
Polyaniline
Carbon dots
Magnetic field
Supercapacitance
Nanotubes

ABSTRACT

Carbon dots-doped polyaniline nanotubes (CDs@PANI-0.5 T) have been synthesized under an applied magnetic field (MF) of 0.5 T. Not only the applied MF has improved the morphology, crystallinity, and conductivity of PANI nanotubes, but also the doped CDs with large specific surface area increase the electron mobility and electron density of the PANI nanotubes. Which eventually reduce both the charge transfer resistance (R_{ct}) and internal resistance (R_s) of the electrode materials, and thus enhance the supercapacitance behavior of the electrodes. The supercapacitor assembled from CDs@PANI-0.5 T electrodes shows a superior specific capacitance, high energy density, and cycle stability to control samples of PANI-0.5 T, CDs@PANI-0 T, and PANI-0 T.

1. Introduction

As an outstanding new-generation energy storage system, supercapacitor energy storage devices have received more and more attention due to their advantages of high specific capacitance, high energy density, and good cycle stability. In recent years, this energy storage device has been widely used in electric vehicles, portable electronic devices, wearable electronic devices, and so on. [1,2]. Compared to traditional batteries, supercapacitors are easy to prepare, safe, environment-friendly, lightweight, and energy-efficient. Which considered the most powerful competitors in the field of energy storage. [3]. However, the problem with supercapacitors is they attain low energy density and relatively low voltage, which keeps the barrier of wide-spread use of super capacitor in potential applications [4]. To improve the performance of supercapacitors, a new work focuses on the hollow structure and improve the conductivity of electrode has begun recently.

The charge storage capacity of the double layer capacitor mainly comes from the enrichment of ions and electrons between the electrode and electrolyte interface also effectively improves the charge storage capability of pseudocapacitor [5,6]. High specific capacitance is dependent on a large number of components, for example, effective surface area, electrode structure, adsorbed ion concentration, active sites for ion transport and most importantly the amount of pseudocapacitance [7,8]. Therefore, preparing conductive polymers under external magnetic fields is an effective way to improve their crystallinity and conductivity. In addition, it was found that the hollow structure not only improved the specific surface area and the specific capacitance but also improved the cycle stability of the electrode material [5,9].

To achieve high electrochemical performance, the active electrode material used for the supercapacitor should have a large electrolyte-accessible surface area and high electrical conductivity [6]. In recent years, while maintaining the maximum the energy density, the power density of supercapacitors was also desired to be increased [10,11]. Conductive polymer supercapacitors such as polythiophene (PTP), polypyrrole (PPy), and polyaniline (PANI) are of popular research materials because of their merits of highly conductive, low density, large specific capacitance and charge/discharge efficiency [12,13]. Among all, PANI has excellent electrical conductivity and large specific surface area, which is consider as the best candidate for supercapacitor electrode materials [14–16]. Polyaniline has been widely studied due to its low density, environmental friendliness, high specific capacitance, low density, and ease of preparing [17,18]. The research on PANI-based hybrid supercapacitors have been progressed rapidly in the last several years. However, there are still some issues that remain to be overcome to achieve the device performances, like increase in both specific power and energy densities, developing eco-friendly electrolyte systems, and synthesis of electrode materials with desirable electrical/mechanical properties for intelligent and wearable devices [19–21]. Therefore, improve the specific capacitance and power density of polyaniline supercapacitors, make them applicable to practical production is of great significance [22].

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https://doi.org/10.1016/j.synthmet.2018.09.015
Received 12 May 2018; Received in revised form 25 July 2018; Accepted 26 September 2018

In order to improve the physical properties of PANI, different fabrication methods have been employed in past. By changing the experimental conditions such as doping, reaction temperature, reaction time, *etc.* have influenced on morphology and magnetic properties [23,24]. Among other physical parameters during growth of materials, external applied magnetic field (MF) is an important parameter. Compared to traditional synthesis, the sample prepared under MF will generate a new type of materials, because MF might be more effective than conventional preparation parameters [25,26]. The applied MF continuously transfer a uniform amount of energy to atoms and molecules through the lines of forces from north to south pole of magnetic field, causing the alignment of atoms, molecules, and dipoles in the direction of magnetic force. [27–30]. Apart from the improved crystallinity, the MF also can control the morphologies and specific surface area of samples [29]. Therefore, it expected to realize the morphology change and crystalline improvement in PANI and PANI-based materials using MF during synthesis.

As small carbon nanoparticles (< 10 nm), carbon dots (CDs) including carbon nanodots and carbon quantum dots (CQDs) are becoming new research hot topic in nearly fifteen years. Usually, they consist of a carbon core with sp^2-hybridization and a plenty of functional groups at the surface [31,32]. CDs have extraordinary optical properties, can act as a good electron donor, and also a good electron acceptor [33]. Maity et al. prepared PANI-GQD composites, which improved the conductivity three times compared with GQDs, and they also found the charge transfer between conductive polymer and GQDs by the fluorescence quenching phenomenon [34]. Recently, our group has prepared a composite of CDs/PPy/GO and investigated the role of CDs in the enhancement of supercapacitance [35]. We found from our previous knowledge that doping of CDs had a great influence on the supercapacitor properties like high capacitance and energy density.

In this work, CDs-doped PANI nanotubes were prepared under a low static MF (0.5 T). The specific capacitance of the sample prepared under the MF achieves 609 F g^{-1} at 0.5 A g^{-1}, and after charge-discharge for 2000 cycles, the capacitance can still keep 76.51% retention, which shows a much better cycle stability than the control sample obtained without MF.

2. Experimental section

2.1. Materials

Aniline (Ani), ammonium persulfate (APS), camphorsulfonic acid (CSA) were purchased from Aladdin Chemical Co., Ltd. The food-grade konjac flour (KF) bought from Sinopharm Chemical Regent Co., Ltd. Before use, aniline was distilled, APS and CSA have not been treated, the distilled water was used in the synthesis process.

2.2. Synthesis of CDs

According to the previous literature, the CDs were prepared by thermolysis method [36]. 3 g of KF powder was heated at 350 °C for 90 min in the air. Next, the resulting black solid was ground and the resulting fine powder was stirred with 100 ml of absolute ethanol for 6 h. CDs were extracted from the above solution through a 0.22 mm filter, and the resulting mixed solution dried at 60 °C for 24 h. After that, CDs re-dispersed and filtrated again to remove hydrophilic organic components and residual inorganic salts. Finally, after drying the filtrate, the yellow solid CDs powder was collected. The TEM image (Fig. S1) confirms that as-synthesized CDs are fairly uniform, and the narrow size distribution histogram shows it has an average diameter of about 2.46 nm [37].

2.3. Synthesis of CDs-doped PANI nanotubes (CDs@PANI nanotubes)

As shown in Scheme 1, CDs@PANI nanotubes were synthesized under 0.5 T MF by *in-situ* polymerization. First of all, a uniform (homogeneous) solution was obtain by 0.2 g CDs, 0.93 g CSA and 2.23 g aniline and 500 mL deionized water, then the mixed solution stirring for 10 min at 5 °C. Next, keep the mixed solution under a 0.5 T MF for 1 h without stirring, and then add 500 mL mixture solution which contains 5.47 g APS. After stirring to make sure complete mixing, the reaction solution keep under a 0.5 T MF for 24 h at 5 °C. After reaction finished, washed the products with ethanol and deionize water repeatedly, finally dried it for overnight at 50 °C under vacuum. The obtain CDs@PANI nanotubes named as CDs@PANI-0.5 T A similar synthesis process to that of CDs@PANI hybrid without MF during the polymerization was done, and then the CDs@PANI with nanofiber morphology, namely, CDs@PANI-0 T was obtained as a control. In addition, the similar synthesis process synthesized PANI-0.5 T and PANI-0 T without CDs.

2.4. Characterizations

Scanning electron microscope (SEM, S-4800) and a transmission electron microscope (TEM, JEM-2100) has been employed for the morphology of samples. Raman spectra was characterized by a LabRAM HR800 Raman spectroscopy (λ_{ex} = 532 nm). XRD patterns were recorded by an X'Pert PRO diffractometer with Cu *K*α radiation (λ = 1.54056 Å), and the scanning rate was 2° min^{-1}. The operation current and voltage maintained at 20 mA and 36 *k*V, respectively. The BET surface area data was recorded by N_2 adsorption at −196 °C (Micromeritics ASAP 2020 analyzer). Thermo-gravimetric analysis (TGA) done by SDT Q600 from ambient temperature to 800 °C in N_2 atmosphere at 10 °C min^{-1}. The real permittivity (ε′) of the samples was measured by using an Agilent E5071C vector network analyzer in the frequency range of 2–18 GHz at room temperature.

2.5. Electrochemical tests

The electrochemical measurement of samples were taken by a CHI 660E electrochemical workstation. In a three-electrode system, the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) tests were measured in 0.5 mol L^{-1} Na_2SO_4 aqueous solution. The Nafion impregnated sample casting onto a glassy carbon electrode (GCE, d = 4 mm) which was prepared as a working electrode. To keep the electrode sensitivity, it was polished with 0.03 μm α-alumina powder. The saturated calomel electrode (SCE) were used as reference electrodes, and platinum wire employed as counter electrodes. The EIS test was recorded from 100 mHz to 100 kHz and performed at 0 V (*vs.* SCE) using an AC amplitude of 5 mV. The potential windows of CV and GCD tests had set in the range from 0 to 1.0 V (*vs.* SCE). A linear sweep voltammetry (LSV) at a scan rate of 20 mV s^{-1} were used for current-voltage (*I-V*) measurements. In order to evaluate the electrochemical performance of supercapacitors in practical applications, two-electrode systems were used for CV and GCD tests. The symmetrical supercapacitor is prepared as follows (1) the electrodes were composed of 10 wt. % polytetrafluoroethylene (PTFE) binder, 10 wt. % acetylene black and 80 wt % as-synthesized hybrid; (2) the mixture smeared on a piece of round nickel foam (diameter 1.7 cm) with a loading of *ca.* 5.0 mg cm^{-2}. After that, the nickel foam was dried in vacuum for 12 h at 60 °C and compressed by *ca.* 10 MPa for 5 min; (3) immerse the electrodes into the electrolyte for 5 min, and assembled as a button capacitor with cellulose separator. 0.5 mol L^{-1} Na_2SO_4 aqueous solution was used for the electrolyte [38].

3. Results and discussion

The influence of MF on the synthesis of CDs@PANI-0.5 T can be easily observed by the SEM and TEM results. Fig. 1 shows an obvious induction of MF in the synthesis of the polymer. The MF lines aligned the PANI main chain molecules in direction of field lines and finally formed a tube-like structure in both CDs@PANI-0.5 T (Fig. 1a) and