



In situ synthesis of polyaniline/sodium carboxymethyl cellulose nanorods for high-performance redox supercapacitors

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ARTICLE INFO

Article history:

Received 22 November 2011

Received in revised form

1 March 2012

Accepted 16 March 2012

Available online 11 April 2012

Keywords:

Polyaniline

Sodium carboxymethyl cellulose

Nanorods

Supercapacitors

ABSTRACT

Polyaniline/sodium carboxymethyl cellulose (PANI/CMC) nanorods have been synthesized via in-situ oxidation polymerization of aniline in the presence of sodium carboxymethyl cellulose as a polymerization template. The structure and morphology of the nanorods are characterized by TEM, FE-SEM and XRD. The size and shape of the composite nanorods are uniform with a diameter of 100 nm. Their electrochemical properties are also investigated using cyclic voltammetry and galvanostatic charge/discharge measurement. The specific capacitance of PANI/CMC nanorods prepared with 20 wt% CMC can be as high as 451.25 F g^{-1} . Its capacitance remains higher than 300 F g^{-1} after 1000 cycles at a current density of 1 A g^{-1} . These novel nanorods are desirable for applications in supercapacitor devices.

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1. Introduction

Supercapacitors have been extensively studied as one type of the most promising candidates for next generation energy storage systems [1]. Compared with electrostatic supercapacitors or batteries, electrochemistry supercapacitors have several advantages, such as a large specific capacitance, a high power density, a long cycle life and rapid charging-discharging rates [2]. In addition, materials used in electrochemistry supercapacitor are often non-toxic and safe, while many types of batteries, e.g. nickel-cadmium batteries, are toxic.

Material for electrochemistry supercapacitors recently employed can be divided into three types: (1) metal oxides or metal hydroxides [3–5], (2) conducting polymers [6], and (3) carbon materials [7,8]. Among them, noble metal oxides such as RuO_2 and conducting polymers have shown a capacity to deliver higher specific capacitance than carbon materials, since they store charges through both double-layer and redox capacitive mechanisms [9]. However, due to the low abundance and the high cost of RuO_2 , conducting polymers have attracted more intensive interests as alternative materials for electrochemical energy storage applications and they exhibit a continuous range of oxidation states with increasing electrode potential [10].

Polyaniline (PANI) is generally considered suitable for the next generation of supercapacitors because of its high energy density, low cost, environmental friendliness and easy synthesis [11,12]. However, it has a relatively poor cycling stability and temperature dependence [13]. Therefore, it is often hybridized with inorganic materials (carbon materials, metal oxides or hydroxides) to prepare a composite to be used in the supercapacitors with an improved conductivity, better cycleability, specific capacitance and mechanical stability [14]. Mujawar and Lee [15] prepared a composite via electropolymerization of polyaniline on TiO_2 nanotubes, which had a specific capacitance of 740 F g^{-1} and a 13% loss over 1100 cycles. Feng et al. [16] obtained a graphene/polyaniline composite film used as the supercapacitor electrode with a specific capacitance of 640 F g^{-1} and a retention life of 90% after 1000 charge/discharge cycles. Snook et al. [17] suggested that one significant drawback of some materials is the relatively low power due to the slow diffusion of ions within the bulk of the electrode. If the dimension of the electrode materials becomes smaller, the diffusion of ions in the electrode is accelerated to improve electrochemical properties of these electrode materials. In recent years, polyaniline was template-synthesized in order to reduce its dimension. Xing et al. [18] reported the synthesis of polyaniline in the reversed micelles of CTAB as a surfactant. Zhou et al. [19] synthesized PANI nanofibers with high electrical conductivity using the CTAB-SDS binary surfactants as a soft templates and a dispersion reagent. Li et al. [20] synthesized porous and mat-like polyaniline/sodium alginate nanostructured composite with good electrochemical properties in an aqueous solution with sodium alginate as a template.

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Sodium carboxymethyl cellulose (CMC) is polysaccharide composing the fibrous tissue of plants. Because hydroxyl groups on 2-glucopyranose residue of cellulose are replaced by carboxymethyl groups, CMC has a number of sodium carboxymethyl groups ($-\text{CH}_2\text{COONa}$) and dissolves in water. CMC is commonly employed in food processing, flocculation, drag reduction, detergents, textiles and drugs [21]. Recently, CMC is successfully used as an effective stabilizer in preparing nanoparticles, such as Ag nanoparticles [22]. $\alpha\text{-Fe}_2\text{O}_3$ electrodes with CMC binder show excellent cycling performances [23]. He et al. [24] employed CMC as pre-agglomeration stabilizers and obtained highly dispersed zero valent iron nanoparticles. Among all polysaccharides, CMC is available easily and it is also affordable and environmentally friendly.

In the present paper, we used one step in-situ oxidation polymerization method to prepare polyaniline/sodium carboxymethyl cellulose nanorods using rod-like CMC as a polymerization template. The composite nanorods have a uniform diameter of 100 nm. The nanorods showed an enhanced specific capacitance and excellent cycling stability.

2. Experimental

2.1. Materials

Aniline monomer (Shanghai Chemical Works, China) was distilled under reduced pressure. Sodium carboxymethyl cellulose (CMC, Tianjing Yuanli Chemical Co., China), ammonium persulfate (APS, Tianjing Damao Chemical Co., China) were used as received. All solutions were prepared in deionized water. All Other chemical reagents were in analytical grade.

2.2. Synthesis of polyaniline/sodium carboxymethyl cellulose nanorods

Polyaniline/sodium carboxymethyl cellulose nanorod was synthesized as follows: 0.1 g sodium carboxymethyl cellulose was dissolved in 30 ml deionized water at ambient temperature. 0.4 g aniline monomer and 10 ml 1 M HCl solution were introduced into the above solution, and then the mixture was sonicated for 15 min to facilitate the adsorption of aniline onto the sodium carboxymethyl cellulose. 1.25 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 10 ml deionized water was added into the above system after being stirred for 30 min. The polymerization was performed for at least 12 h at room temperature. Reaction product was collected by centrifugation and washed successively with deionized water and ethanol until the filtrate was colourless, and then dried at 60 °C for 24 h in vacuum to obtain a dark green powder.

For comparison purpose, pure polyaniline without sodium carboxymethyl cellulose was also synthesized under the same conditions.

2.3. Characterizations

X-ray diffraction (XRD) of samples was performed on a diffractometer (D/Max-2400, Rigaku) using Cu K α radiation ($k = 1.5418 \text{ \AA}$) at 40 kV, 100 mA. The 2θ range used in the measurements was from 5 to 80°. Morphology of the pure PANI and PANI/CMC nanorods was examined with field emission scanning electron microscopy (FESEM, JSM-6701F, Japan) at an accelerating voltage of 5.0 kV. The structure of the samples was characterized by a transmission electron microscopy (TEM, JEM-2010 Japan). FT-IR spectra were recorded on a Nicolet Nexus 670 Fourier transform infrared spectrometer using KBr tableting technique and the spectra was in the range of 4000 - 400 cm^{-1} .

2.4. Electrochemical measurements

A typical three-electrode test cells in electrolyte was used for electrochemical measurement on the electrochemical working station (CHI650D, Chenghua, Shanghai China). All the measurements were carried out in 1 M H_2SO_4 electrolyte at room temperature. The glassy carbon electrode with a diameter of 3 mm was used as the working electrode. Platinum electrode served as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The fabrication of the working electrodes refers to Ref. [20]. Typically, 4 mg of PANI/CMC was ultrasonically dispersed in 1 mL of deionized water, and 10 μL of the polytetrafluoroethylene (PTFE) emulsion (60 wt%) was added to this dispersion. 3 μL of the above suspension was dropped onto the glassy carbon electrode using a pipet gun and dried at room temperature.

Cyclic voltammograms were recorded from -0.2 to 0.8 V at scan rates of 10, 20, 30, 50 and 80 mV s^{-1} . The measurements of the galvanostatic charge/discharge property and cycle-life stability were performed with a computer controlled cycling equipment (LAND CT2001A, Wuhan China). The galvanostatic charge/discharge property was measured at the current densities of 1, 2, 3, 5, and 10 A g^{-1} with cutoff voltage of $0-0.8 \text{ V}$.

3. Results and discussions

3.1. Mechanism of the formation of the nanorod structure

The one-pot synthesis of PANI/CMC composites was conducted through in-situ oxidation polymerization, as described in Scheme 1. Since sodium carboxymethyl cellulose hydrolyses in strongly acidic condition, it can be completely dissolved at room temperature. Therefore, HCl solution of low concentration was rapidly added into sodium carboxymethyl cellulose solution immediately after the addition of aniline monomer. The addition of HCl solution into the CMC solution promotes the dissociation of neutral $-\text{COONa}$ into negatively charged $-\text{COO}^-$. As a result, the negatively charged CMC chains easily adsorb $-\text{NH}_2$ groups of aniline monomer via an electrostatic interaction to form biopolymer-monomer complexes [13]. This operation will keep the structure of sodium carboxymethyl cellulose intact during hydrolysis but promote the dissociation of $-\text{COONa}$ to $-\text{COO}^-$. Furthermore, it was observed that the electrical conductivity of polyaniline synthesized in acidic conditions is better than that obtained in basic or neutral conditions [25].

After the oxidant ammonium persulfate was introduced into the system, polyaniline was synthesized and it was attached onto the surface of sodium carboxymethyl cellulose. As a result, the PANI/CMC composite was thus prepared. CMC not only serves as a dopant for PANI but also acts as a polymerization template during the polymerization.

3.2. Morphology

Fig. 1 shows the typical morphology of the pure PANI and PANI/CMC products. One can see that pure PANI particles (Fig. 1a) aggregate into lumps with diameters ranging from 200 nm to a few microns. Their surfaces are very rough because aniline polymerization is a multi-level growth process. However, as shown in Fig. 1b, the PANI/CMC particles are of a uniform rod-like structure with a diameter of 100 nm, and a random netlike structure rather than the dense accumulation is observed in lower magnification (Fig. 1c). The PANI/CMC products structure was further characterized by transmission electron microscopy (TEM). As shown in Fig. 1d, the rod-like structure of PANI/CMC products can be clearly visible.

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