Materials Letters 139 (2015) 145–148

Contents lists available at ScienceDirect

Materials Letters

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

Synthesis of polypyrrole/sodium carboxymethyl cellulose nanospheres with enhanced supercapacitor performance

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ARTICLE INFO

Article history:
Received 13 August 2014
Accepted 14 October 2014
Available online 22 October 2014

Keywords:
Polypyrrole
Sodium carboxymethyl cellulose
Nanocomposites
Polymeric composites
Supercapacitors

ABSTRACT

Polypyrrole/sodium carboxymethyl cellulose (PPy/CMC) nanospheres have been synthesized via in-situ oxidation polymerization of pyrrole in the presence of sodium carboxymethyl cellulose as a polymerization template. The size and shape of the composite are uniform with a diameter of about 100 nm. The electrochemical properties of the nanocomposite are investigated using cyclic voltammetry and galvanostatic charge–discharge measurements. The specific capacitance of PPy/CMC nanospheres can be as high as 184 F g^{-1} at a current density of 0.25 A g^{-1}. Moreover, the hybrid electrode showed good cyclic stability of 80% retention after 200 cycles of charge/discharge after introducing CMC as template. These results indicate a promising potential application of the PPy/CMC nanocomposite used as an effective electrode material in supercapacitors.

1. Introduction

In recent years, supercapacitors have been extensively studied as one of the most promising candidates for the next generation energy storage device with the advantages of large specific capacitance, long cycle life, high power density and rapid charging–discharging rates [1,2]. It is well-known that the electrochemical performance of the supercapacitors is largely depends on the electrode materials. Therefore, looking for new electrode materials has become a pivotal issue for the supercapacitors development.

Currently, the electrode materials for supercapacitors contain carbon materials [3,4], metal oxides [5] and conducting polymers [6,7]. Polypyrrole (PPy), as a promising conducting polymer, has attracted more intensive interests as alternative materials for supercapacitor application because of its high electrical conductivity, high energy storage capacity, easy synthetic procedure, enhanced thermal and chemical stability, environmental friendliness, and low cost [8–10]. However, the poor processability and the inferior mechanical property which may be due to the collapse of the polymer backbone during a limited number of charge–discharge cycles, have limited its applications [11]. Therefore, PPy is often hybridized with other materials to prepare compounds with versatile and tunable properties that are superior to the individual materials [12]. For example, PPy has been hybridized with carbon nanotubes and transition metal oxide to form composite which has been used as supercapacitor electrode material and displayed excellent electrochemical performance [13,14]. Compared with these expensive template, the widely available sodium carboxymethyl cellulose (CMC) is a kind of polysaccharide and has a number of sodium carboxymethyl groups ($-CH_2COONa$). Recently, CMC is successfully used as an effective stabilizer in preparing nanocomposites [15–17]. Herein, PPy/CMC nanocomposite is fabricated using CMC as a polymerization template which can protect the backbone of the PPy layer during the charge–discharge process. Electrochemical tests indicate that the PPy/CMC nanocomposite exhibits high capacitance and excellent cycling stability as electrode material for supercapacitors in 1 M Na_2SO_4 electrolyte which makes them be promising candidate for the fabrication of electrochemical energy storage devices.

2. Experimental section

Materials synthesis: PPy/CMC nanospheres was synthesized as follows: 0.1 g CMC (Kaitong Chemical Reagent Co., Ltd, Tianjin) was dissolved in 30 ml deionized water at ambient temperature. 0.4 g pyrrole (Py) monomer (Sinopharm Chemical Reagent Co., Ltd) and 10 ml HCl (1 M) solution were introduced into the above solution, and then the mixture was sonicated for 15 min to facilitate the adsorption of Py onto the CMC. 1.25 g $(NH_4)_2S_2O_8$ (Kaitong Chemical Reagent Co., Ltd, Tianjin) 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. The fabrication process was illustrated in

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http://dx.doi.org/10.1016/j.matlet.2014.10.074
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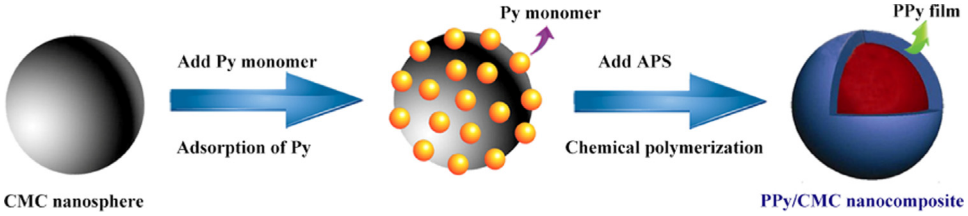

Scheme 1. Schematic illustration of the fabrication process for PPy/CMC nanocomposite.

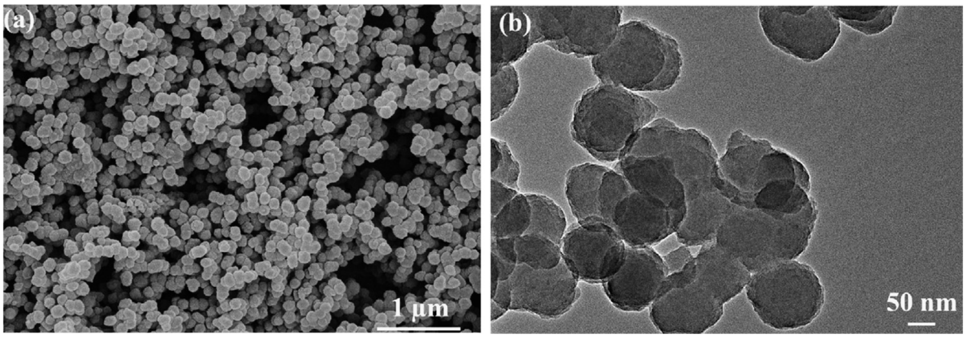

Fig. 1. (a) SEM and (b) TEM images of PPy/CMC nanostructures.

Scheme 1. 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 PPy without CMC was also synthesized under the same conditions.

Materials characterization: The obtained materials were characterized by X-ray powder diffraction (XRD) on Rigaku D/Max-3B diffractometer with Cu $K\alpha$ radiation. The microstructure was studied by transmission electron microscopy (TEM, JEM JEOL 2100) and field emission scanning electron microscopy (FESEM, JSM-6701F). The qualitative information was obtained by Fourier transformation infrared spectroscopy (FTIR, Thermo Nicolet 5700).

Electrochemical measurement: A typical three-electrode test cells was used for electrochemical measurement on CHI660E (Chenhua, Shanghai China) electrochemical working station. All the measurements were carried out in 1 M Na_2SO_4 aqueous solution electrolyte at room temperature. The working electrode was fabricated by mixing the electroactive material, carbon black and poly(tetrafluoroethylene) at a weight ratio of 80:15:5 to form homogeneous slurry. The resulting slurry was coated onto the nickel foam current collector using a blade. Then the electrode was dried at 80 °C for 12 h. Platinum sheet and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Cyclic voltammograms were recorded at different scan rates from 5 to 80 mV s^{-1} within the potential window of −0.4 to 0.8 V. Galvanostatic charge–discharge curves were performed at different current densities within the potential range of −0.4–0.6 V.

3. Results and discussion

Fig. 1 shows the FESEM and TEM images of the synthesized PPy/CMC composite. The obtained PPy/CMC composites are globular shaped and the sizes are relatively uniform (Fig. 1(a)). As shown in Fig. 1(b), the surface of the composite is very rough which may be due to a multi-level growth process for the Py polymerization. According to the plotting scale, the diameter of the nanospheres is approximately 100 nm.

The XRD patterns of pure PPy, CMC, and PPy/CMC nanospheres are compared in Fig. 2(a). It can be seen that diffraction of CMC shows a typical peak at 20.2° and the pure PPy has a characteristic peak at about 22°. The diffraction peak of PPy/CMC composite is similar to pure PPy, and no obvious diffraction peak appears at about 20°, since the content of CMC in the composite is very small and is uniformly dispersed in the composite materials.

FTIR spectra for pure PPy, CMC, and PPy/CMC are presented in Fig. 2(b). For CMC, the peaks at 3440, 2925 and 1057 cm^{-1} correspond to O–H stretching vibrations, aliphatic C–H stretching vibrations and C–O–C stretching vibrations, respectively [18]. And the ones at 1616 and 1423 cm^{-1} are assigned to the asymmetric and symmetric stretching of the carboxylate group ($-COO^-$). The spectrum for pure PPy exhibits the characteristic absorption bands at 1542, 1456, 1299, 779 and 673 cm^{-1}, which are assigned to pyrrole ring stretching, =C–H in-plane deformation and C–H outer-bending vibrations, respectively, and is well consistent with the reported bands [19]. Importantly, the spectrum for PPy/CMC sample with presence of CMC characteristic peaks is similar to the bands of PPy, implying the formation of PPy backbone chains onto the CMC surface.

In order to evaluate the electrochemical properties of the pure PPy, CMC, and PPy/CMC composite, cyclic voltammetry (CV) test is performed. The CV curves for the pure PPy, CMC and PPy/CMC nanosphere electrodes are presented in Fig. 3(a) at a scan rate of 10 mV s^{-1}. The CV curve area of PPy/CMC composite is evidently larger than that of the PPy at the same scan rate in 1 M Na_2SO_4, verifying that PPy/CMC composite has a higher specific capacitance than pure PPy. Otherwise, the CV curve of the CMC is a horizontal straight line, which indicates that CMC only possesses a negligible capacitance. Fig. 3(b) presents CV curves for the PPy/CMC composite electrodes at various scan rates. CV curve area increases as the scan rate increased from 5 to 80 mV s^{-1} and the shapes of these CV curves do not significantly change, revealing the ideal capacitive behavior and good charge collection as well as the facilitated diffusion of Na^+ in the PPy/CMC nanocomposite electrode [20].

The galvanostatic charge–discharge test is a reliable method to evaluate the electrochemical capacitance of the electrode materials. Fig. 3(c) presents the charge–discharge curves of the PPy/CMC