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Soft template interfacial growth of novel ultralong polypyrrole nanowires for electrochemical energy storage

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ABSTRACT

In this paper, novel ultralong interconnected polypyrrole (PPy) nanowires were synthesized by an interfacial reaction of pyrrole in organic phase and ammonium persulfate in aqueous phase using cetyltrimethylammonium bromide (CTAB) as soft template. The morphology of as prepared PPy was investigated by field emission scanning electron microscopy and transmission electron microscopy. The electrochemical performance of as prepared PPy was evaluated as electrode materials for electrochemical capacitor by the means of cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. It was shown that the size and morphology of as prepared PPy can be optionally controlled by varying the concentration of CTAB in aqueous phase, and CTAB concentration played a crucial role in improving the electrochemical performances of as prepared PPy nanowire at high charge/discharge rate. In the presence of 6.25 ~ 12.5 mM CTAB, ultralong interconnected PPy nanowire bonded with spherical PPy nanoparticles can be perfectly prepared. The diameter of PPy nanowire was in the range of 20 to 100 nm with length up to about several micrometers. A higher specific capacitance was obtained up to 328.7 F g^{-1} at current density of 0.3 A g^{-1}. 75.7% of initial capacitance was retained even after 600 cycles at current density of 1.0 A g^{-1}.

1. Introduction

The demands for sustainable and clean energy are becoming more and more critical owing to the emergence of electric vehicles and many new types of portable electronic devices currently available. Hence, searching for new energy storage devices is of realistic significance [1]. As a new type of energy storage devices, electrochemical capacitors (ECs) have been investigated intensively in recent decades on account of higher power density, faster charge/discharge rate and longer term stability. Generally, three kinds of electrode materials are used for the fabrication of ECs, i.e., carbon-based materials [2,3], transition metal oxides [4,5] and conducting polymers [6,7].

Progress towards ECs technologies can benefit from continuous development of a variety of different structure materials [8]. Nanostructured electrode materials have demonstrated their better rate capabilities, obvious size effects and significantly enhanced kinetics [9,10]. For nanostructured electrode materials, the distance within the materials over which the electrolyte must transport ions is dramatically smaller compared with the conventional electrodes composed of chemically similar bulk materials [11]. Nowadays, the fabrication of multitudinous morphologies such as core/shell [12], sandwich-like [13] and nanowire [14] has been a novel strategy design trend to meet various demands. Within this context particular emphasis has been devoted to understand the fabrication of well-defined electroactive materials within micro- and nanometric scales by various techniques, as well as the influences of these techniques on their morphologies and structure properties.

Directed self-assembly of nanoparticles opens new avenues of technology through the controlled fabrication of nanoscopic materials with a wide variety of applications. Organic/aqueous interfacial synthesis is an alternative useful and more convenient approach than conventional homogeneous reaction system. During the formation process of nanoparticles at interface, thermal energy causes spatial fluctuations of particles, and the energy balance results in a weak interfacial aggregation of nanoparticles [15]. Liquid/liquid interface has been proved to be ideal for the assembly of nano-sized particles and offers potential for the chemical manipulation of nanoscale materials due to the high mobility and rapid equilibrium at interface [16]. In this sense, the

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control of morphology, size and texture of electroactive materials with higher power density, faster charge/discharge rate and longer term stability for ECs is very interesting and especially important.

Conducting polymers, especially polypyrrole (PPy), polyaniline and polythiophene, are playing a vital role in the construction of high performances ECs because of the ideal capacitance behaviour they have represented [17]. PPy has received most attention due to its ordinary preparation, benign conductivity and that it can be easily converted between various oxidation states [18]. To improve the capacitive performance of PPy, recent studies have focused on the morphology designs that allow the access of electrolyte in three dimensions. Electropolymerization and in situ polymerization have been widely employed in the preparation of PPy nanowires [19,20]. Previously researches always based an ordinary in-situ chemical oxidative polymerization, a one-phase method was employed for preparing PPy nanowires, which was then used as electrode materials for supercapacitor.

In this paper, we focused on the development of a simple organic/aqueous interface synthesis route using CTAB as soft template for the preparation of PPy nanowires. The aqueous/organic interface opens avenues to size-selective particle assembly, two-dimensional phase behaviour and functionalization. The size and morphology of as prepared PPy can be optionally controlled by varying the concentration of CTAB in aqueous phase, and CTAB concentration played a crucial role in improving the electrochemical performances of as prepared PPy nanowires at high charge/discharge rate. In the presence of 6.25 ~ 12.5 mM CTAB, ultralong interconnected PPy nanowires bonded with spherical PPy nanoparticles can be perfectly prepared.

2. Experimental

2.1. Reagents and materials

Pyrrole monomer (Py), ammonium persulfate (APS), cetyltrimethylammonium bromide (CTAB), tetrachloromethane, ethanol and hydrochloric acid (HCl) were analytically pure grade. Py was purified through distillation under reduced pressure and stored refrigerated before use. All the chemicals were purchased from Aldrich Chemical Reagent Co. Distilled water was used throughout the experiments.

2.2. Synthesis of PPy samples

PPy samples were prepared at organic/aqueous interface at temperature of 0 ~ 5 °C. Firstly, 5.0 mmol Py was dissolved into 50 mL tetrachloromethane (0 °C) as the organic phase. Secondly, different amounts of CTAB (0, 0.625, 1.250, 2.500 and 5.000 mmol) were added into 200 mL 0.20 M HCl solution (0 °C). After vigorous stirring for 10 min to form a homogeneous solution, 5.0 mmol APS was added into the above aqueous solution, and immediately the solution turned milky white and very viscous. Then, the aqueous solution was poured slowly into the beaker containing organic phase, and a static organic/aqueous interface was formed. Subsequently, the reaction system was placed in an ice-bath to control the temperature below 5 °C for 24 h. It was found that some black flocculent products appeared at organic/aqueous interface after a short introduction period. As the puce products were produced continuously, the colour of aqueous phase turned darker until a black homogeneous solution was obtained eventually. Finally, the resulting black precipitate was suction-filtered in air and washed with copious amounts of distilled water and ethanol and dried in 60 °C overnight.

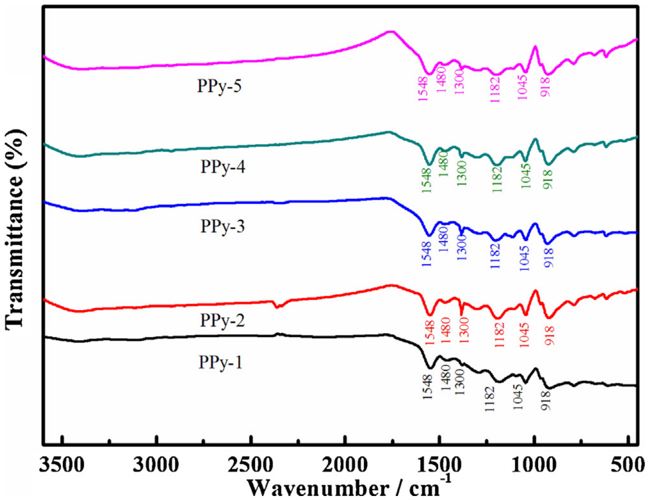

Fig. 1. FTIR spectra of PPy prepared in the presence of CTAB with different concentrations.

PPy samples prepared in the presence of CTAB with different concentrations (0, 3.125, 6.250, 12.500 and 25.000 mM) were marked as PPy-1, PPy-2, PPy-3, PPy-4 and PPy-5, respectively.

2.3. Characterization of materials

SEM images of PPy samples were investigated using Ultra 55 microscope (Carl Zeiss AG, Germany). TEM images were investigated using Libra 200FE microscope (Carl Zeiss AG, Germany). Fourier transform infrared (FTIR) were obtained with Nicolet 5700 (Nicolet Instrument Co. USA) in the wavelength range of 4000 ~ 400 cm^{-1} with KBr pellet method.

2.4. Electrochemical tests

Electrodes for ECs were prepared by mixing electroactive materials with 10 wt.% acetylene black and 5 wt.% polytetrafluoroethylene (PTFE) emulsion to make homogeneous slurry in the presence of absolute ethyl alcohol. The slurry was pressed onto a stainless steel fiber felt with an apparent area of 1 cm^2 under the pressure of 5.0 MPa. The mass load of every electrode is approximate 3 mg. Subsequently, the as prepared electrodes were dried at 80 °C for 24 h before use.

1.0 M H_2SO_4 solution was used as electrolyte in all experiments at room temperature. All electrochemical measurements were carried out by introducing a three-electrode test system using platinum sheet as counter electrode, as prepared electrode as working electrode referred to saturated calomel electrode (SCE) immersed in 1.0 M H_2SO_4. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed with PARSTAT 2273 electrochemical workstation (Princeton Applied Research, USA). CV tests were preformed between -0.2 and 0.8 V. EIS measurements were preformed at open-circuit potential in the frequency range from 100 kHz to 0.01 Hz with an ac perturbation of 5 mV. Galvanostatic charge/discharge tests were performed between -0.2 and 0.8 V using CHI 760 C electrochemical workstation (CH Instruments, China).

3. Results and discussion

Shown in Fig. 1 were FTIR spectra of PPy prepared in the presence of CTAB with different concentrations. The broad peak at 3000 ~ 3500 cm^{-1} was stretching vibration of C-H and N-H of pyrrole