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Coral reef-like polyanaline nanotubes prepared by a reactive template of manganese oxide for supercapacitor electrode

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Abstract

Coral reef-like PANI nanotubes composed of nanopaticles were successfully synthesized by a reactive template of manganese oxide. The structure was characterized by using SEM, TEM, and FT-IR, and the supercapacitive behaviors of these nanotubes were investigated with cyclic voltammetry (CV), and charge–discharge tests, respectively. A maximum specific capacitance of 533 F/g could be achieved in 1 mol/L aqueous H_2SO_4 with the potential range of −0.2 to 0.8 V (*vs*. the saturated calomel electrode) in a half-cell setup configuration for PANI electrode, suggesting its potential application in the electrode material for electrochemical capacitors.

Keywords: Electrochemical capacitors; PANI; Reactive template; Specific capacitance

Electrochemical capacitor is a kind of device which combining the advantages of the high power of dielectric capacitors and the high specific energy of rechargeable batteries. In recent years, a lot of research interest was focused on conducting polymer-based supercapacitors owing to their high capacitive characteristics and low material cost [1,2]. Among various applications of conducting polymers, PANI is unique in nature from the viewpoint that it has the advantage of environmental stability, low cost and great potential in device application and its electrical behaviour can be reversibly controlled by charge-transfer doping and by protonation [3–5]. Recently, the studies of PANI have been made rapid progress [6,7].

Nanotubes of PANI can be fabricated by using self-assembly or template-assisted methods. Self-assembly methods produce nanotubes by forming nanostructural micelles. Template-assisted method shaped the PANI structure easily. The templates for making PANI include track-etched polycarbonate and porous alumina [8,9], and silica or polystyrene microspheres for producing hollow shells [10–13]. However, these templates are not involved in the reaction and must be selectively removed from the final products and the property of PANI would be affected at the same process. Wan and co-workers have schemed out a method by which PANI could be synthesized with a reactive template [14]. Recently, the study by Zheng *et al*. has shown that manganese oxide could act as a chemical oxidative initiator for polymerization of aniline, hence the template would be spontaneously removed after the reaction [15].

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Here we synthesized coral reef-like PANI nanotubes by using manganese oxide as oxidative initiator, which was prepared via a facile, one-step hydrothermal synthesis process using $K_2Cr_2O_7$ and $MnSO_4$ at low temperature. The PANI nanotubes were characterized through SEM, TEM and FT-IR techniques. The primary electrochemical characterization was investigated by cyclic voltammetry (CV) and galvanostatic charge–discharge test.

Preparation of manganese oxide was according to the literature procedure but with a lower temperature of 60 °C [16]. In a typical experiment, 0.0880 g manganese oxide was dispersed in 60 mL DI water, and then the mixture was put in an ice bath and stirred slowly. At the same time, 192 μL aniline monomer was added to the solution of 34.4 mL DI water and 5.6 mL sulfuric acid to make the aniline solution mix with sulfuric acid. After being cooled to room temperature, the aniline solution was mixed with the manganese oxide solution quickly. The reaction was carried out at the ice bath for 6 h. The resulting green powder was rinsed with DI water and anhydrous ethanol several times to remove excess ions and monomers. The product was dried in a vacuum oven at 60 °C for 12 h. Electrochemical measurements were carried out using an electrochemical working station (CHI660C, Shanghai) in a half-cell setup configuration. A platinum gauze electrode and a saturated calomel electrode served as the counter electrode and the reference electrode, respectively. The used electrolyte was 1 mol/L H_2SO_4 solution.

The morphologies of the manganese oxide nanowires template and coral reef-like PANI are shown in Fig. 1. The manganese oxide nanowires interlace with each others and form an interaction network (Fig. 1a) and the structure of synthesized PANI basically replicate that of the template (Fig. 1b). The PANI interaction network structures with tube diameters 100 nm and lengths 1 μm were obtained using templates rods with diameters of 55 nm and lengths 900 nm. It should be noted that the surface of PANI nanotubes are covered with nanoparticles which have diameters of about 30 nm (Fig. 1c), the specific surface area is large and the coral reef-like PANI nanotubes are obvious. The resultant structure is hollow, with one round closed end (Fig. 1d).

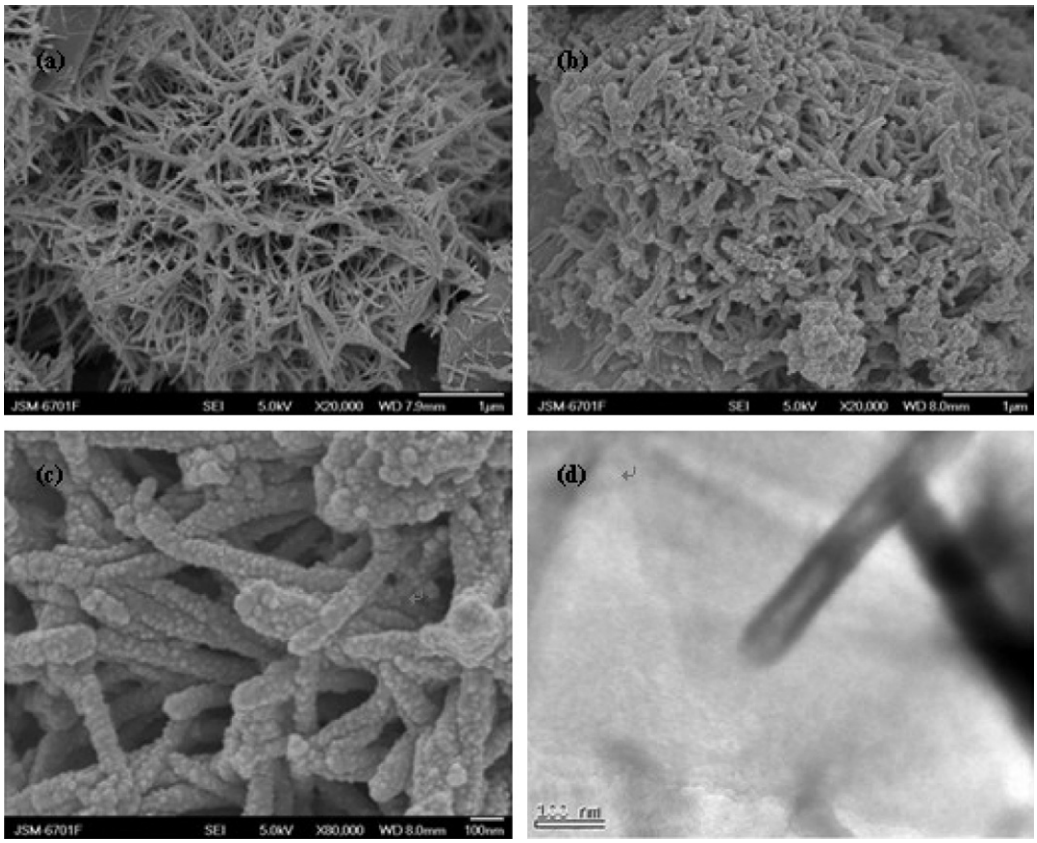

Fig. 1. FESEM image of manganese oxide nanowires template (a) and coral reef-like PANI nanotubes (b and c). TEM image of coral reef-like PANI nanotubes (d).