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Effects of monomer solvent on the supercapacitance performance of PANI/TiO_2 nanotube arrays composite electrode

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ABSTRACT

Polyaniline/TiO_2 nanotube arrays composite electrodes were achieved by depositing polyaniline onto TiO_2 nanotube arrays through cyclic voltammetry method. Neutral sodium sulfate aqueous solution was used as a testing electrolyte and the effects of monomer solvent on the electrode performance were studied. Results show that the sample prepared in ethanol solution has much better capacitance performance than that in acetone or aqueous solutions. The potential window of the electrode could be enlarged to 2 V (−0.2–1.8 V) and the highest energy density of the active material reached 727.3 J/g. The composite electrode also has excellent rate and cycling performance.

1. Introduction

Polyaniline (PANI) is a commonly used conductive polymer with advantages of high capacitance and simple synthesis method. However, it exhibits weak electrochemical stability during charge–discharge process [1–4]. Titania is an important semiconductor material which shows good chemical stability, low toxicity and less environmental damage [5–9]. Titania nanotube arrays (TNTA) synthesized by anodic oxidation method have large specific surface area and highly ordered structure. The composite electrodes achieved by depositing PANI onto TNTA exhibit better capacitance performance [10–12]. In previous reports, electrodeposition of the PANI onto TNTA were generally carried out in aqueous [13,14] or acetone solution [15] containing aniline monomer and sulfuric acid. In addition, properties of the electrodes were generally tested in aqueous solutions containing sulfuric acid [16,17] or potassium hydroxide [18,19] and the working potential windows were generally lower than 1.2 V [20–22]. In this paper, to further improve the performances, the PANI/TNTA composite electrode was prepared in ethanol solution containing aniline monomer and sulfuric acid by cyclic voltammetry method for the first time. The effects of monomer solvent on the performance of PANI/TNTA composite electrode are discussed. Composite electrode prepared in ethanol solution has great rate and cycling performance in Na_2SO_4 aqueous solution at the potential window of −0.2–1.8 V.

2. Experimental

TNTA were prepared in ethylene glycol solution containing 0.25 wt% NH_4F and 10% H_2O according to the literature method [5], and then calcined at 450 °C for 2 h in the air. The composite electrode was prepared through electrodeposition method in a three-electrode system with the TNTA as the working electrode, the Pt foil as the counter electrode and the saturated calomel electrode (SCE) as the reference electrode. The deposition process was conducted by cyclic voltammetry method in ethanol solution containing 0.1 M aniline monomer and 0.5 M sulfuric acid for 40 min. The applied potential window and scan rate was −0.2–1 V and 50 mV/s. Whereafter, the sample was rinsed with ethanol and deionized water and then dried at 100 °C for 2 h to obtain the PANI/TNTA-e composite electrode. As comparison, PANI/TNTA-w and PANI/TNTA-a were prepared in aqueous and acetone solution when other conditions remained unchanged. The morphology, structure and chemical composition of the samples were characterized using a scanning electron microscope (SEM, Quanta 450 FEG), an X-ray diffractometer (XRD, D/maxRB, Rigaku), and a Fourier transform infrared spectroscopy (FTIR, V80) respectively. The electrochemical properties of the samples were studied by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurement using an electrochemical workstation (CHI660e,

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Chenhua). The electrochemical tests were performed in a three-electrode system composed of the sample as the working electrode, the platinum foil as the counter electrode, and the SCE as the reference electrode. The testing electrolyte was a 0.5 M Na_2SO_4 aqueous solution.

3. Results and discussion

The top view of the TNTA with opening nozzle is shown in Fig. 1a. The average inner diameter of the nanotubes is about 110 nm, and the average wall thickness is about 15 nm. As seen

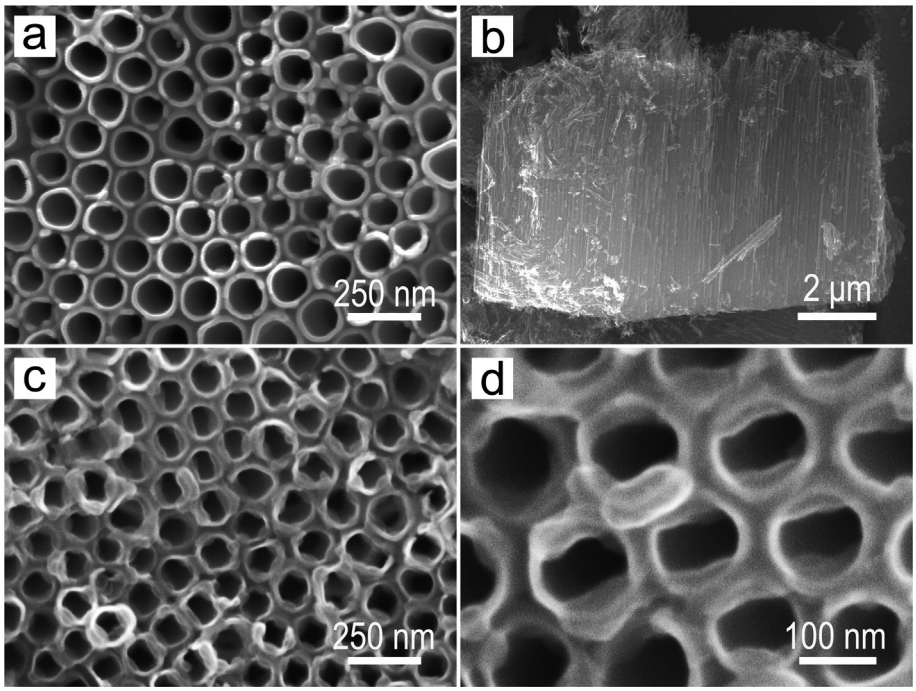

Fig. 1. SEM images of the samples (a, b: TNTA; c, d: PANI/TNTA-e).

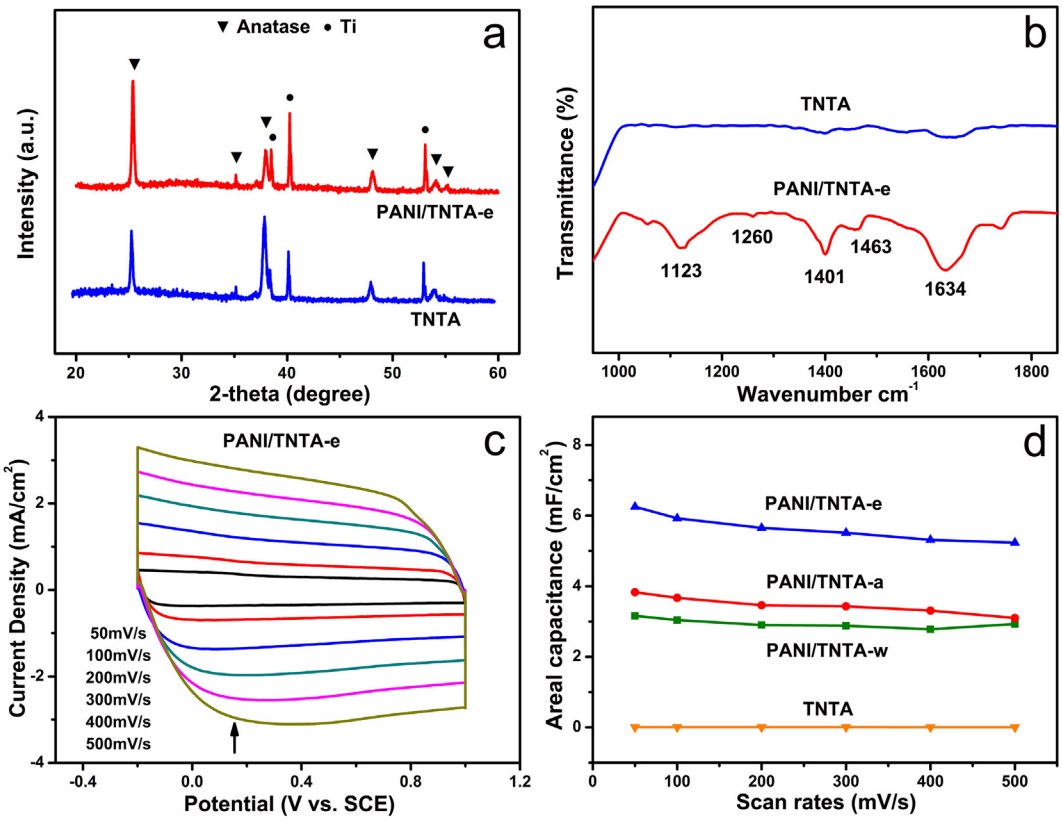

Fig. 2. XRD (a), IR (b), CV curves (c) and capacitance-scan rate curves (d) of samples.