Amorphous nickel oxide and crystalline manganese oxide nanocomposite electrode for transparent and flexible supercapacitor

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HIGHLIGHTS

- Amorphous NiO and crystalline MnO_2 nanocomposite positive electrode was prepared.
- The resultant positive electrode delivered high specific capacitance.
- Amorphous Fe_2O_3 negative electrode was prepared.
- A transparent and flexible supercapacitor was assembled.
- The supercapacitor achieved an outstanding integrated electrochemical properties.

ARTICLE INFO

ABSTRACT

Among numerous active electrode materials, transition metal oxides are promising electrode materials in supercapacitors. Here, we fabricated amorphous nickel oxide and crystalline manganese oxide nanocomposite positive electrode for transparent and flexible supercapacitor. The nanocomposite was prepared via a two-step method. First, the amorphous nickel oxide film was prepared using a room-temperature chemical solution deposition and photochemical method. UV light irradiation causes condensation and densification of nickel oxide film by photochemical activation at room temperature. Second, the crystalline manganese oxide was prepared by chemical bath deposition method. The synergistic effect of the two components provides high electrochemical activity. A high-performance, transparent and flexible asymmetric supercapacitor was made of the nanocomposite positive electrode and worked in a wide voltage window of 1.2 V. An area capacitance of 48.1 mF/cm^2 and an energy density of 9.62 $\mu Wh/cm^2$ at a power density of 28.9 $\mu W/cm^2$ were achieved. After a 10,000 cycles, the capacitance of the device retains about 90% of its initial value. The high integrated electrochemical performances of the device were attributed to higher storage and transport capacity of the nanocomposite for both ions and electrons. These findings make amorphous and crystalline transition metal oxide nanocomposites as advanced electrode materials for transparent and flexible supercapacitors.

1. Introduction

Supercapacitors have gradually become very promising energy storage device because of their excellent properties such as high power density, fast charge-discharge rate and long cycle life [1–3]. Transparent and flexible supercapacitors are key components in transparent and wearable electric devices [4,5]. However, most of previous reports on transparent and flexible supercapacitors were based on carbon-based nanostructures, and these devices usually suffered from poor specific capacitance. Thus now we focus on exploring other electrode materials used in transparent and flexible supercapacitors. Transition metal oxides have been widely used in energy storage devices [6,7,8,9]. And

it has been confirmed that amorphous nanomaterials possess unique electrochemical behaviors which are comparable to those of crystalline materials [10,11]. Among these materials, nickel oxide (NiO) has been explored as electrode material of supercapacitor due to its high electrochemical activity, rich redox reactions and high theoretical capacitance of 2573F/g [12–14]. Unfortunately, the practical application of NiO is limited due to its poor electrical conductivity and narrow potential window, which is usually smaller than 0.5 V [15,16]. Manganese oxide (MnO_2) is an excellent Faradaic material with a high theoretical capacitance of 1370 F/g, which can extend the potential window and improve the electrical conductivity for the electrode materials [17,18].

In this contribution, we prepared amorphous nickel oxide and

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crystalline manganese oxide nanocomposite positive electrode for transparent and flexible supercapacitor. In this case, a nanocomposite of NiO fabricated with photochemical method and MnO_2 fabricated with chemical bath is used as the positive materials and iron oxide (Fe_2O_3) with photochemical method is used as the negative material. It is noticed that NiO and Fe_2O_3 are amorphous, and MnO_2 is crystalline. Interestingly, the transparent and flexible asymmetric supercapacitor made of the NiO@MnO_2 nanocomposite positive electrode and amorphous Fe_2O_3 negative electrode exhibits excellent performance. It is also found that the synergistic effect of the amorphous and crystalline composite materials can improve the electrochemical performance, making them promising electrode materials for transparent and flexible supercapacitors.

2. Experimental

2.1. Preparation of transparent and flexible positive electrode

In our case, Indium Tin Oxides/Polyethylene terephthalate (PET/ITO, 15 Ω/square) substrate was first cleaned ultrasonically in the mixture of 20 ml deionized water, 5 ml ethanol and 5 ml acetone for 10 min. Then cleaned ultrasonically several times in deionized water and dried at room temperature. Tapes were stuck to the substrate leaving an active area of $1 \times 1 \, cm^2$. The amorphous NiO and Fe_2O_3 films were prepared by chemical solution deposition and photochemical method. The NiO precursor solution was composed of 0.115 g of nickel (II) 2-ethylhexanoate (78% w/w) and 0.284 g of n-hexane. The Fe_2O_3 precursor solution is composed of 0.888 g of iron (III) 2-ethylhexanoate (50% w/w) and 0.304 g of n-hexane. Then, the resultant precursor solutions were spin-coated on PET/ITO substrate at 1500 rpm for 20 s. The mass of the resultant film can be determined by the volume of dropped solution and times of repetition. The films were then irradiated under UV light (Philips TUV 8 W) with a wavelength of 185 nm (10%) and 254 nm (90%) for 24 h in air at room temperature. For the synthesis of NiO@MnO_2 nanocomposite, MnO_2 was synthesized by chemical bath deposition method. The reaction solution was composed of 0.05 M $KMnO_4$ and 0.2 M $NH_3 \cdot H_2O$. The prepared NiO film was vertically immersed in the mixed solutions for 2 h. Then the MnO_2 particles began to grow on the surface of NiO film. Finally, the as-prepared NiO@MnO_2 film was washed with deionized water for several times and dried at a temperature of 60 °C for 1 h.

2.2. Fabrication of asymmetric supercapacitor

The Polyvinyl alcohol/potassium hydroxide (PVA/KOH) gel electrolyte was prepared according to the following steps: Firstly, 2 g PVA powder was mixed with 15 ml deionized water under magnetic stirring at constant temperature (90 °C) until the mixed solution became clear. Then, the resulting solution was cooled at room temperature. At the same time, 1.2 g KOH powder was dissolved in 5 ml deionized water under magnetic stirring at room temperature until the mixed solution became clear. Afterward, two solutions were mixed under magnetic stirring, and the transparent gel electrolyte was acquired. The NiO@MnO_2 electrode and the Fe_2O_3 electrode were immersed into the gel electrolyte for 5 min, and then taken out and dried at 50 °C for 1 h. After that, two electrodes were pressed together and dried for another 1 h, forming a transparent and flexible supercapacitor.

2.3. Materials characterization

Transmission electron microscopy (TEM) images were acquired with a microscope (FEI Tecnai G2 F30) at an accelerating voltage of 300 kV. Scanning electron microscopy (SEM) images were acquired with a Quanta 400F thermal FE environment electron microscope operated at 20 kV. X-ray diffraction (XRD) was performed on D-MAX 2200 VPC with Cu Kα radiation (40 kV, 26 mA, 10°/s). X-ray photoelectron

spectroscopy (XPS) patterns were recorded on a Thermo Fisher ESCALab250 spectrometer with Al-Kα (20.0 eV) radiation X-ray source. Infrared spectroscopy was recorded on a Nicolet6700-Contiuμm Fourier transformation infrared spectrometer coupled with an infrared microscope within the wavelength range 400–4000 cm^{-1}. The static water contact angles measurement was carried out by a SDC-200 contact angle measuring equipment with a CCD camera. The transmission spectra were measured using a Lambda950 UV–Vis-NIR spectrophotometer. The loading mass of the active materials were measured using a XP2U Ultra-microbalance (d = 0.1 μg).

2.4. Electrochemical characterization

All the electrochemical tests were measured using a CHI660D electrochemical workstation.

From the cyclic voltammetry (CV) curves, the areal capacitance can be obtained using following equation:

$$C = \frac{1}{sv\Delta V} \int_{v_0}^{v_a} I(V) dV \tag{1}$$

where ΔV (V_0-V_a) represents the potential window (V), I represents the response current (A), s represents the active area (cm^2) of the active materials and v represents the potential scan rate (V/s).

From the galvanostatic charging and discharging (GCD) curves, the areal capacitance can be obtained using following equation:

$$C = \frac{I \times \Delta t}{s \times \Delta V} \tag{2}$$

where I represents the discharge current (A), Δt represents the discharge time (s), ΔV represents the potential window (V), and s represents the active area (cm^2) of the active materials.

In order to obtain a good electrochemical performance for supercapacitor, the ratio of the mass of positive/negative materials should follow the following equation:

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \tag{3}$$

where ΔV represents the potential window (V) of positive electrode and negative electrode, C represents the specific capacitances (F/g) and m represents the loading mass (g) of the active materials.

The energy density (E) and power density (P) are calculated according to following equations:

$$E = \frac{C(\Delta V)^2}{2} \tag{4}$$

$$P = \frac{E}{\Delta t} \tag{5}$$

where C represents the specific capacitance (mF/cm^2) of the device, ΔV represents the potential window (V), Δt represents the discharge time (s).

3. Results and discussion

Fig. 1a shows the XRD patterns of PET/ITO substrate, NiO film and Fe_2O_3 film on substrate, respectively. There is no difference among the three curves, and only the diffraction peaks related to ITO are observed. These results indicate that the NiO and Fe_2O_3 materials are amorphous. Fig. 1b shows the XRD patterns of NiO@MnO_2 composite film. The diffraction pattern exhibits four peaks indexed to (0 0 1), (0 0 2), (1 0 0) and (1 1 0), which are in accordance with K-birnessite MnO_2 (JCPDS, Card No. 52-0556) [19]. Fig. 1c and 1d show the high-resolution XPS spectra of Ni 2p and Fe 2p. The Ni 2p region contains two easily identifiable main peaks: the Ni $2p_{1/2}$ peak at 872.5 eV and the Ni $2p_{3/2}$ peak at 854.8 eV, respectively. And two Ni satellite peaks resulting from shake-up processes are located at the higher binding energy by the side of the double Ni 2p peaks at 878.7 and 860.2 eV, respectively. The Ni