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The Ti@MoO_x nanorod array as a three dimensional film electrode for micro-supercapacitors

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ABSTRACT

Ti@MoO_x core–shell nanorod arrays with diameters within 100 nm were fabricated by electrodepositing MoO_x on a Ti nanorod array prepared by oblique angle deposition. A high areal capacitance of 27 mF cm^{-2} and satisfactory cycling stability were obtained. After post-annealing, MoO_2 grains were introduced to enhance the rate capability, suggesting a potential pseudocapacitive micro-electrode.

1. Introduction

Micro-supercapacitors (m-SCs) are miniaturized supercapacitors to serve as energy storage units in micro-power systems, which possess high power density and long cycle life with moderate energy density [1–5]. Hence, specific-surface energy and power density become important metrics for m-SCs and high areal capacitance is required. Transition metal oxides could potentially provide high capacitance due to their pseudocapacitive properties. However, the poor conductivity restricts their future application [6–8]. One promising solution is to distribute active materials on a three dimensional (3-D) current collector possessing large real surface area [9–11]. For example, MnO_2/Mn/MnO_2 sandwich-like nanotube arrays synthesized based on Mn nanotube arrays exhibit high specific capacitance and charge/discharge rate [12]. However, the indispensability of ZnO nanorod array as a template to prepare Mn nanotube array complicates the fabrication process. Furthermore, the manufacture of m-SCs has to be compatible with present microelectronic technology [1,4,7,13]. Thus a facile and complementary metal oxide semiconductor (CMOS)-compatible technique for appropriate current collectors is crucial for future application.

Oblique angle deposition (OAD) is a nanorod array growing technique based on physical vapor deposition. By enlarging the incident angle of the deposition flux, discretely aligned nanorods could be formed as a result of self-shadowing effect [14,15]. Herein, OAD was employed to prepare Ti nanorod arrays (TiNA) as a 3-D current collector for deposition of MoO_x pseudocapacitive layers, producing a TiNA@MoO_x structure as a micro-electrode. The electrochemical performance was studied. Post-annealing in reductive atmosphere was also carried out to improve the electronic conductivity.

2. Experimental

TiNA was prepared by electron beam evaporation technique. A compact Ti film of 130 nm was pre-deposited on a Si-(001) substrate. Then, the TiNA was deposited using OAD mode, with the incident angle of 85° and a deposition rate of 5 Å s^{-1}, during which the substrate was cooled by liquid nitrogen. Afterwards, MoO_x was coated on TiNA by electrodeposition. The electrolyte was composed of 0.1 M Na_2MoO_4, 0.1 M Na_2EDTA and 0.1 M CH_3COONH_4. A Pt foil was used as the counter electrode. The electrodeposition was carried out at 70 °C in chronopotentiometry mode with a cathodic current density of 0.45 mA cm^{-2}. Samples deposited for 170, 260 and 350 s are denoted as TiNA@MoO_x-170s, TiNA@MoO_x-260s and TiNA@MoO_x-350s, respectively. As a comparison, a flat MoO_x film was directly deposited on the top of Ti film at 0.3 mA cm^{-2} for 230 s. Post-annealing was carried

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out on a TiNA@MoO_x-350s sample at 350 °C for 1.5 h in the atmosphere of H_2 and Ar, whose flow rates were 30 and 345 sccm, respectively.

The morphology was examined by field-emission scanning electron microscopy (SEM, JEOL-JMS-7001 F). X-ray diffraction (XRD) patterns were acquired on a Rigaku X-ray diffractometer using the continuous scan mode with a scan step of 0.02°. Transmission electron microscope (TEM) image, high-resolution TEM (HRTEM) image and selected area diffraction (SAD) pattern were taken with a JEOL 2010 TEM.

A CHI660D electrochemical workstation was used for electrochemical test. A three-electrode assembly was constructed using the sample as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Pt foil as the counter electrode. The electrolyte was a 2 M Li_2SO_4 aqueous solution (pH = 4.1).

3. Results and discussion

As shown in Fig. 1a, discrete Ti nanorods, with diameter of 30–50 nm and length of 600–700 nm, have been grown on a Ti-coated Si substrate. The diameter increases due to the coating of MoO_x (Fig. 1b). For TiNA@MoO_x-350s after annealing in Fig. 1c, certain conglutination was observed and small grains (dozens of nanometers) appear. More information could be obtained from the XRD results (Fig. 1d). Similar XRD patterns between the samples before and after electrochemical coating indicate the coated MoO_x to be amorphous. However, after annealing, diffraction peaks of monoclinic MoO_2 (JCPDS: 32-0671, m-MoO_2) appear, which coincides with the small grains shown in Fig. 1c. The formation of MoO_2 nanocrystallites could be further confirmed by the annealing experiment of electrodeposited MoO_x in literature [16].

Fig. 2a reveals a core–shell configuration of amorphous MoO_x (~25 nm) uniformly coating Ti nanorods. The dark fringes in the core are Ti branching rods, which is validated by the corresponding dark field image in Fig. 2b. After annealing, the core–shell configuration is not obvious due to the growing of nanocrystallites (Fig. 2c). The SAD pattern in the insert is indexed to m-MoO_2, in good agreement with XRD analysis and the HRTEM image (Fig. 2d).

All the as-deposited samples show triangular cyclic voltammetry (CV) curves with lowest potential of −1 V vs. SCE (Fig. 3a). It is a cation insertion/extraction process in hydrous MoO_x, which could be presumably described as: $MoO_x \cdot yH_2O + \delta H^+ + \delta e^- \leftrightarrow MoO_{x-\delta}(OH)_\delta \cdot yH_2O$, and $MoO_x \cdot yH_2O + \delta Li^+ + \delta e^- \leftrightarrow Li_\delta MoO_x \cdot yH_2O$ [17,18]. However, after annealing, the negative potential limit is extended to −1.12 V vs. SCE, and a rectangular curve was obtained, with a cathodic partial peak around −1.05 V and an anodic peak around −0.15 V vs. SCE, which indicates the coexistence of MoO_2 grains and amorphous MoO_x [19]. The capacitive characteristic of these TiNA@MoO_x are illustrated by the galvanostatic charge/discharge curves in Fig. 3b. The Coulomb

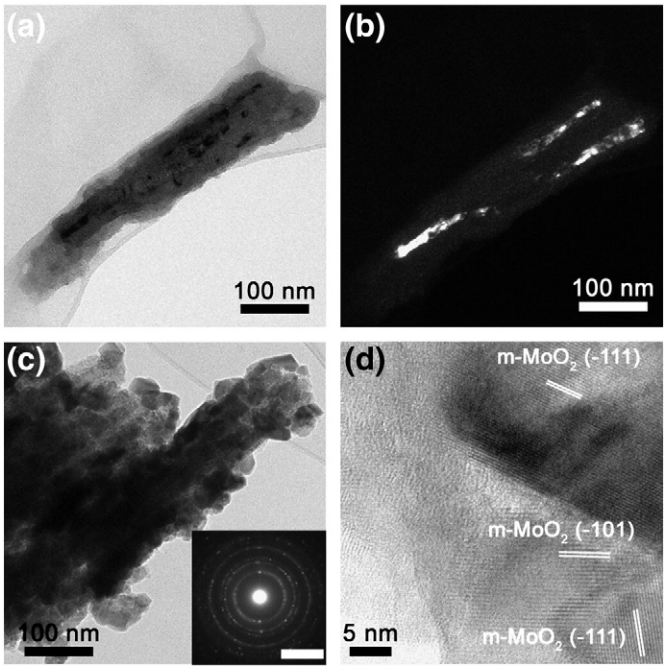

Fig. 2. (a) Bright field and (b) dark field TEM images of as-deposited TiNA@MoO_x-260s individual nanorod; (c) TEM image and (d) HRTEM image of the annealed TiNA@MoO_x-350s nanorod. The insert image in (c) is the SAD pattern from the same area.

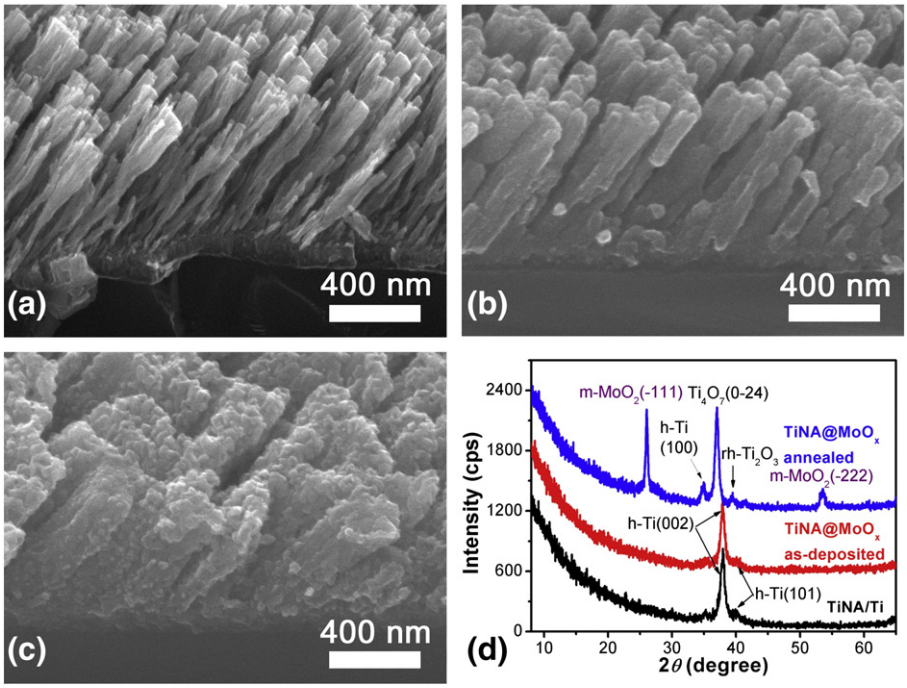

Fig. 1. SEM images of (a) TiNA, (b) as-deposited TiNA@MoO_x-260s and (c) TiNA@MoO_x-350s annealed in H_2/Ar; (d) XRD spectra of the three samples.