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Ultrahigh supercapacitance in cobalt oxide nanorod film grown by oblique angle deposition technique

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A B S T R A C T

Nanorod films of cobalt oxide (Co_3O_4) have been grown by a unique oblique angle deposition (OAD) technique in an e-beam evaporator for supercapacitor electrode applications. This technique offers a non-chemical route to achieve large aspect ratio nanorods. The fabricated electrodes at OAD 80° exhibited a specific capacitance of 2875 F/g. The electrochemically active surface area was 1397 cm^{-2}, estimated from the non-Faradaic capacitive current region. Peak energy and power densities obtained for Co_3O_4 nanorods were 57.7 Wh/Kg and 9.5 kW/kg, respectively. The Co_3O_4 nanorod electrode showed a good endurance of 2000 charge-discharge cycles with 62% retention. The OAD approach for fabricating supercapacitor nanostructured electrodes can be exploited for the fabrication of a broad range of metal oxide materials.

1. Introduction

Nanostructured metal oxides, such as nickel oxide, cobalt oxide, manganese oxide, titanium oxide, and ruthenium oxide, have been widely studied for supercapacitor applications [1]. Cobalt oxide (Co_3O_4) is an outstanding material among other transition metal oxides owing to its high theoretical capacity (3560 F/g), good transport properties, and excellent electrochemical performance [2–4]. Availability of maximum active surface area in a Co_3O_4 supercapacitor is vital to the charge storage via efficient ions and electrons transport process [4,5]. Nanorod metal thin films can be grown by oblique angle deposition (OAD), where the substrate is held at a particular selected angle to the vapor deposition direction. Oblique angles $> 70°$ to the normal are generally employed for obtaining two dimensional nanostructures, where the initially formed metal islands function as shadow masks for the oncoming vapor flux, impeding deposition in the shadowed regions [6]. Herein, we report the preparation of Co_3O_4 nanorod electrode for supercapacitors via OAD. In this method, by controlling the growth conditions such as deposition angle, time of deposition, and substrate temperature, the diameter, density, and physical structure can be effectively tailored at the nanoscale level. The fabricated electrodes exhibited an excellent supercapacitance value (2875 F/g) and a good retention capability after 2000 charge-discharge cycles.

2. Experimental methods

Co_3O_4 thin films were grown on a nickel foam (NiF) substrate ($5 \times 1\ cm^2$) by OAD technique in an e-beam evaporator. A series of oblique deposition angles between the substrate and incident beam was studied (65° to 85° in steps of 5°). The optimal deposition angle was identified as 80° based on the observed supercapacitance value. The distance between the source material (Co purity 99.99%) and the substrate was fixed at 90 cm. Initially, the substrates were cleaned with acetone, isopropanol, deionized water, and dried with N_2 gas. The propounded results were also compared and contrasted with normal deposition without OAD. All the depositions were performed in a clean room (Class 1000) at room temperature. The depositions were carried out at a chamber pressure of $\sim 1 \times 10^{-6}$ Torr and deposition rate of ~ 2 Å/s. The details of the experimental setup have already been presented in the previous report [7]. Co oxidation was achieved by annealing the samples in air at 396 °C for 2 h.

The samples were characterized by X-ray diffractometer (XRD: Rigaku-Ultima IV) and field emission scanning electron microscope (FE-SEM: Hitachi-S-4800). Electrochemical characterization was carried out using a standard three-electrode electrochemical cell. Co_3O_4 served as the working electrode, saturated calomel electrode was used as a reference electrode, and graphite rod served as the counter electrode. The galvanostatic charge-discharge electrochemical studies were performed in 2 M KOH aqueous solution in a typical three-electrode system. All the

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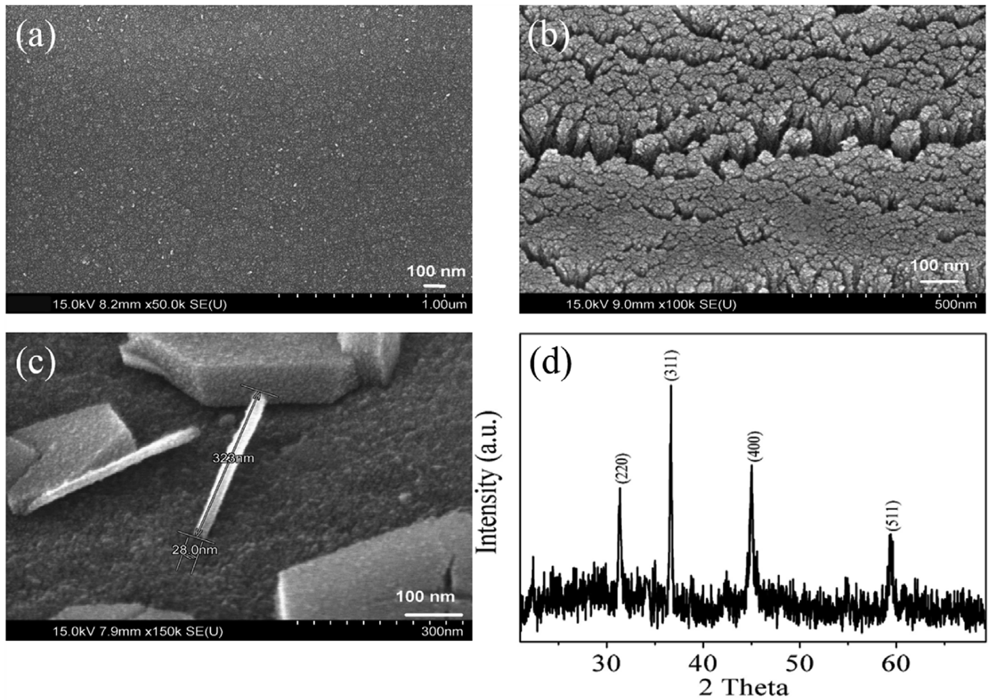

Fig. 1. FE-SEM images of Co_3O_4 nanorods grown by (a) normal, (b) OAD at an angle of 80°, (c) dimensions of a typical Co_3O_4 nanorod, and (d) X-ray diffraction pattern of the OAD 80° sample annealed at 396 °C.

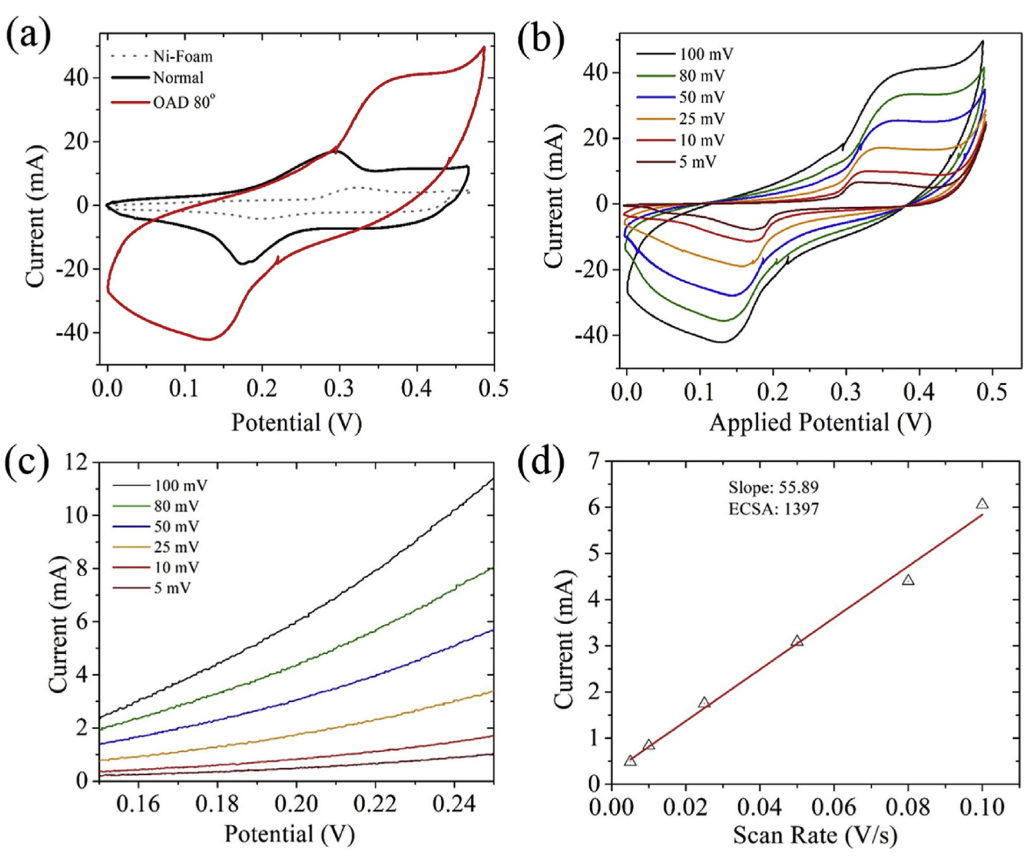

Fig. 2. (a) CVs of the substrate with a Co_3O_4 electrodes grown by normal and OAD 80° within a potential window of 0 V to +0.48 V at 100 mV/s scan rate, (b) CVs of the OAD 80° sample at various scan rates, (c) CVs of the OAD 80° sample at various scan rates in the non-Faradaic voltage region from 0.15 V to 0.25 V, and (d) currents measured at 0.2 V as a function of scan rate for the OAD 80° sample.

measurements were carried out in Versa-stat-3.

3. Results and discussion

FE-SEM images of the Co_3O_4 films grown at normal and OAD angle of 80° are shown in Fig. 1(a) and (b). A typical Co_3O_4 nanorod is shown in Fig. 1(c). SEM image of Co_3O_4 nanorods shows that the nanorods grown at an OAD angle of 80° are relatively denser and uniformly distributed, while the normally grown Co_3O_4 film does not have noticeable nanostructures. The length and diameter of the Co_3O_4