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The cobalt oxide/hydroxide nanowall array film prepared by pulsed laser deposition for supercapacitors with superb-rate capability

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ABSTRACT

The aluminum doped cobalt oxide thin film was prepared through crossed-beam pulsed laser deposition (PLD) of aluminum and cobalt metals in the low-pressure O_2/H_2 atmosphere. The thin film was etched by NaOH to remove aluminum oxide and then cobalt oxide/hydroxide nanowall array film was obtained. The pseudocapacitive performances of the nanowall array film are tested by cyclic voltammetry (CV) and galvanostatic charge–discharge measurements in 1 M KOH aqueous solution. When deposited in the atmosphere of O_2:H_2 = 2:1, the thin film displays a high specific capacitance (690 F g^{-1}) and a superb rate capability (75% capacitance retention from 1 A g^{-1} to 120 A g^{-1}). In addition, excellent cycling stability is achieved for the film electrode and the specific capacitance degradation is only 0.3% after 1000 cycles.

1. Introduction

Supercapacitors, an important alternative energy/power source, can fit the time-dependent power needs of modern electronics and power systems due to their higher power density and longer life cycle than conventional dielectric capacitors [1–7]. These new power sources manifest potential applications in many fields such as electric vehicles, portable electronics and other devices [3,8]. It is well known that electrode materials play a critical role to developing the performance of supercapacitors. Among the various electrode materials, transition metal oxides have been widely researched as they can provide a variety of oxidation states for efficient redox charge transfer. Particularly the Ru-based oxides show promising materials for supercapacitors due to their high pseudocapacitance. However, the expensive cost of Ru has limited their commercial application [9]. Nickel oxide, a low-cost alternative to RuO_2, has been investigated for energy storage applications. Recently, we fabricate the nanostructured NiO thin film by pulsed laser deposition (PLD), which shows a high specific capacitance of 835 F g^{-1} at 1 A g^{-1} with excellent rate performance [10]. Cobalt oxides are also considered as promising electrode materials for supercapacitors due to their high redox activity, environmental friendliness and low cost. It is remarkable that the theoretical specific capacitance of Co_3O_4 is up to 3560 F g^{-1} [11–13]. Qian et al. prepared Co_3O_4 nanosheets and microspheres assembled from nanosheets by using a facile EA-directed solvothermal method and sequential thermal decomposition at atmospheric pressure, which gave a specific capacitance of 92 F g^{-1} at 5 mA cm^{-2} [14]. Wang et al. selectively prepared one-dimensional and layered parallel folding of cobalt oxalate nanostructures by a water-controlled precipitation approach by altering the solvents that showed a maximum specific capacitance of 202.5 F g^{-1} at a current density of 1 A g^{-1} [15]. More recently, Yan et al. synthesized Co_3O_4/MWCNT composites by chemical co-precipitation method followed by thermal treatment process which exhibited a maximum specific capacitance of 418 F g^{-1} at a current density of 0.625 A g^{-1} [16]. Unfortunately, in these cases, the observed specific capacitances are much less than theoretical value, especially at high rates, as the Co_3O_4-based electrodes are commonly binder-enriched electrodes made by the traditional slurry-coating technique for electrochemical evaluation, where a large portion of surface of electroactive Co_3O_4 is blocked from the contact with the electrolyte ions to participate in Faradaic reactions for energy storage.

The present work is to utilize the PLD method to prepare cobalt oxide/hydroxide nanowall array using a precursive aluminum doped cobalt oxide thin film. The test results suggest that the nanowall array electrode affords dramatic rate capability during the charge–discharge of very high current density (120 A g^{-1}). The cycling stability is also excellent, which suggest this material has huge potential application in developing the rate capability and cycling ability of supercapacitors.

2. Experimental

All reagents in the experiment are analytical grade, which were used as received without further treatment. The aluminum doped

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cobalt oxide thin film was deposited by PLD technique on the Mo substrate in the stainless steel chamber. Two laser beams (Nd:YAG @1064 nm, 8 ns pulse width, repetition rate 10 Hz) were synchronously focused onto two pure solid targets, namely Co (99.995%, Alfa Aesar) and Al (99.999%, Alfa Aesar), respectively. The ratios of two metals in the plasma plume were adjusted by intensities of two laser beams. The plasma plumes are directed toward a substrate that was held at equal distance (3 cm) from the two targets. Both targets were kept in continuous rotation to obtain a uniform ablation over their entire surface. The chamber was evacuated by mechanical pump and turbomolecular pump to the residual pressure of 10^{-4} Pa before deposition. During the deposition process, the pressure of the ambient gas in the chamber was kept at 30 Pa and the substrate temperature was maintained at 250 °C. The plasma plume reacted with the ambient gas (mixture of O_2/H_2) and deposited on the substrate to form the aluminum doped cobalt oxide thin film. The ratio of O_2 and H_2 was selected as pure O_2, 2:1, 1:1 and 1:2, respectively. Afterwards, the cobalt oxide/hydroxide nanowall array was obtained by immersing the aluminum doped cobalt oxide thin film in 3 M NaOH (Chinasun Specialty Products Co., Ltd.) solution overnight, and then the sample was rinsed several times by distilled water, dried at 100 °C for 1 h.

The morphology and chemical composition of the thin film were characterized by field emission scanning electron microscopy (FESEM; Philips XSEM30, Holland) and energy dispersive X-ray spectroscopy (EDS), respectively. Raman spectroscopy (Rainshaw-Invia) was collected using a 514 nm laser with RM50 under ambient condition. The electrochemical properties were evaluated with the three-electrode setup: the thin film electrodes of samples served as the working electrode, a platinum gauze electrode and a saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. The measurements were performed on a CHI 660D electrochemical workstation in 1 M KOH (Chinasun Specialty Products Co., Ltd.) electrolyte at room temperature.

3. Results and discussion

The schematic of the experimental apparatus is shown in Fig. 1. The laser beam was focused on the rotated targets to evaporate the Co and Al, which produce energetic atomic species. These species reacted with O_2/H_2 in the expanding ablation beam and then condensed on the Mo substrate forming Co oxide and oxhydroxide thin film doped by Al oxides. The obtained thin film was fabricated by removal of the Al oxides by alkali etching. The molar ratio of Co and Al is about 5:1, which give the best quality of nanowall array after etching.

Fig. 2 shows the Raman spectra of the cobalt oxide/hydroxide nanowall array, aluminum oxide doped Co oxide film and cobalt

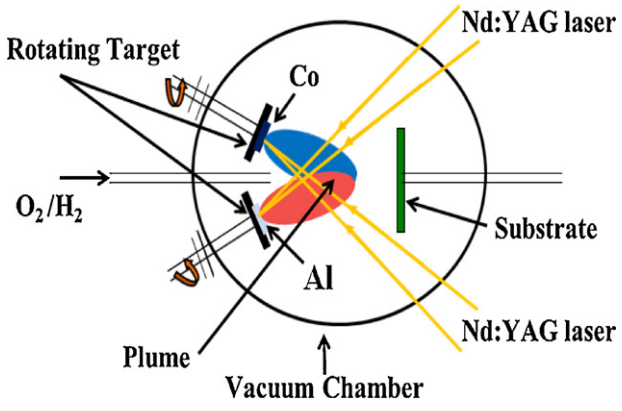

Fig. 1. The PLD system used for fabricating the aluminum doped cobalt oxide film.

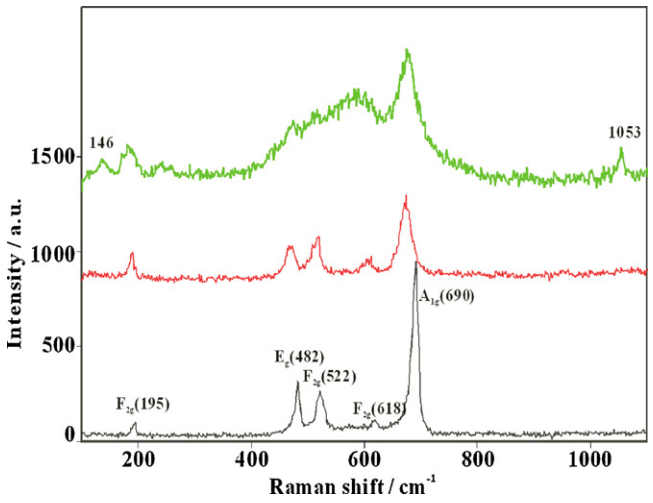

Fig. 2. The Raman spectra of the cobalt oxide thin film (the black line), aluminum doped cobalt oxide film (the red line) and the cobalt oxide/hydroxide nanowall array film (the green line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

oxide thin film (the ratio of O_2 and H_2 in deposition atmosphere is 2:1). Five distinguishable Raman bands are located at approximately 195, 482, 522, 618, and 690 cm^{-1}, which correspond to the F_{2g}, E_g, F_{2g}, F_{2g} and A_{1g} modes, respectively, of the crystalline Co_3O_4 phase in agreement with the literature values [14,17,18]. The result confirms the formation of the spinel structure. In comparison with cobalt oxide thin film, the Raman peaks of the aluminum oxide doped thin film have little shifts but display relatively broader Raman bands. However the peaks for aluminum oxide were not observed because of band weakness, which indirectly demonstrates substitution of Al^{3+} for Co^{3+} in the spine lattice. The Raman peaks of alkali etched nanowall array become broader in the range of 400–800 cm^{-1}. In addition there are new peaks at 1053 and 146 cm^{-1}, which are the typical peaks for $Co(OH)_2$ in solid [19], indicating small amount of cobalt hydroxide formed after etching.

The obtained metal oxide film and nanowall array film were checked by FESEM, as shown in Fig. 3 (a–d). Fig. 3 (a, b) are the SEM images of the as-synthesized aluminum doped thin film taken at different magnifications. The FESEM images reveal a dense thin film composed of uniform nanoparticles in addition to the tiny interval between particulates of submicrometer size. Similar kind of morphology is observed for the deposited in different ratios of O_2 and H_2 atmosphere. After immersion in 3 M NaOH solution, the surface morphology of the sample changed dramatically (Fig. 3c and d). The SEM results indicated that the arrays consisted of crisp-like nanowalls, typically 0.4–0.8 μm in length and 20–30 nm in thickness. The nanowalls grew vertically and arranged as a dense film with obvious holes on the substrate. Similar morphology was reported by Sun et al. [20,21] and Liu et al. [22]. This unique structure has high surface area due to the free standing nanowalls and consequently provides high specific capacitance due to easy access of the active species in the redox process to the interface of the electrode [7]. The energy-dispersive X-ray spectroscopy (EDS) reveals the existence of Al, Co and O species in the precursor (inset of the Fig. 3a), which forms the Al doped Co oxide film. However, only Co and O can be observed in the etched electrode (inset of the Fig. 3c), which shows that the Al had been almost extracted from Al doped Co oxide films by the highly concentrated NaOH solution.

The pseudocapacitive performances of the cobalt oxide/hydroxide nanowall array film electrode were evaluated using cyclic voltammetry (CV) and galvanostatic charge–discharge measurements in 1 M KOH aqueous solution. The cobalt oxide thin film was also investigated for comparison. Fig. 4(a) shows the CV