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Intense pulsed light-assisted facile and agile fabrication of cobalt oxide/nickel cobaltite nanoflakes on nickel-foam for high performance supercapacitor applications

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ABSTRACT

We report an extremely efficient method for fabricating high-performance supercapacitive $CoO/NiCo_2O_4$ nanoflakes on Ni-foam substrate by using intense pulsed light (IPL) technology. Structural and morphological characterization is carried out using X-ray diffraction (XRD) and scanning and transmission electron microscopies (SEM and TEM). These reveal that hierarchically structured $CoO/NiCo_2O_4$ nanoflakes of 150–200 nm in size and a thickness around 10 nm are formed on Ni-foam substrate by IPL irradiation with energy of 20 J cm^{-2} for 15 ms. The electrochemical behavior of the composites is analyzed by cyclic voltammetry and galvanostatic charge–discharge experiments. The IPL-induced $CoO/NiCo_2O_4$/Ni-foam electrode exhibits a very high specific capacitance of 2163 Fg^{-1} at a discharge current density of 1 Ag^{-1} and a good rate performance of 908 Fg^{-1} even at 50 Ag^{-1}.

1. Introduction

Supercapacitors have attracted a great deal of attention because they can serve as energy storage devices that could overcome the drawbacks of conventional capacitors and batteries. Supercapacitors not only exhibit rapid charging/discharging, superior cycling life, and high reliability, but they can also provide higher energy density than conventional capacitors and higher power density than batteries [1–3]. Because supercapacitors often bridge the gap between conventional capacitors and batteries, they have been utilized in a wide range of applications including electric vehicles, electronic appliances, digital communication devices, and mobile phones. Supercapacitors can be categorized into two types based on the energy storage mechanism: electric double layer capacitor (EDLC) or pseudocapacitor. The EDLC, which stores electrical energy by electrostatic accumulation of charges at the electrode/electrolyte interface, can provide ultrahigh power and excellent cycle life due to a fast and nondegrading energy storage process [4,5]. However, the amount of energy stored in an EDLC is relatively low due to the finite surface area of the electrode materials. Carbon-based active materials with a high surface area, such as active carbons, carbon nanotubes, graphenes, carbon fabrics, and carbon papers are used as electrode materials in EDLCs. Another type is the pseudocapacitor, which stores electrical energy by fast and reversible Faradaic redox reactions with several oxidation states. Pseudocapacitors can provide higher energy density than EDLCs because the Faradaic redox reactions occur within the active electrode materials. However, their power density and cycling stability are inferior compared to EDLCs. Transition metal oxides and conducting polymers are primarily used as electrode materials in pseudocapacitors [6–9].

Among various transition metal oxides, ruthenium oxide is one of the most promising pseudocapacitor electrode materials because of its superior electrochemical response [10]. However, in spite of the superior performance of ruthenium oxide, it is still limited in its application as an industrial supercapacitor due to its high cost [11]. Hence, considerable effort is being devoted to developing inexpensive metal oxide electrode materials with excellent supercapacitive performance. Among various alternative materials investigated, cobalt- and nickel-based materials are thought to be quite promising as the next generation of supercapacitors because of their high specific capacitance, environmental stability, cost effectiveness, and natural abundance. Various methods have been employed for synthesizing cobalt- and nickel-based oxide nanostructures, including chemical bath deposition [12],

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hydroxide decomposition [13,14], thermal decomposition of carbonates [15], nanocasting [16], electrodeposition [17], combustion [18], coprecipitation [19] and the sol–gel method [20]. The drawbacks of these methods are that they contain multiple, time-consuming steps and involve high-temperature processes for the synthesis of metal oxides. All methods require calcinations/heat treatment at 200–600 °C for 1–24 h. Therefore, faster, more facile and energy-efficient methods for metal oxide production are of interest.

Recently, we reported an intense pulsed light (IPL) irradiation process for the formation of metal nanoparticle-alloys on various supporting materials [21–23]. The high intensity of pulsed white light is used in the IPL irradiation process, which is generated from a xenon lamp emitting a spectrum of light with a wide range of wavelengths from 380 nm to 1000 nm through arc plasma generation (Fig. 1a) [21]. To form metal nanoparticles on the supporting materials, the flash light was irradiated on the target materials for a few milliseconds at room temperature under ambient conditions. Since the IPL irradiation technique is an ultra-fast and environmentally benign process, interest in the IPL technique has recently increased and it may replace the conventional chemical process. Yoo et al. utilized the IPL method coupled with the sol–gel process to synthesize ruthenium oxide nanoparticles [24]. First, ruthenium hydroxide nanoparticles were synthesized by the sol–gel process then these were transformed to ruthenium oxide nanoparticles using the IPL method. In the present research, the IPL method was utilized to directly synthesize metal oxide nanoflakes from the precursor solution on a Ni-foam substrate and the prepared substrate was further used as a supercapacitor electrode. The IPL-assisted $CoO/NiCo_2O_4$ nanoflakes show a maximum specific capacitance of 2163 Fg^{-1} at a current density of 1 Ag^{-1}. They also exhibited good long term cycling stability with only a 25% degradation after 3000 cycles under a scan rate of 50 mV s^{-1}

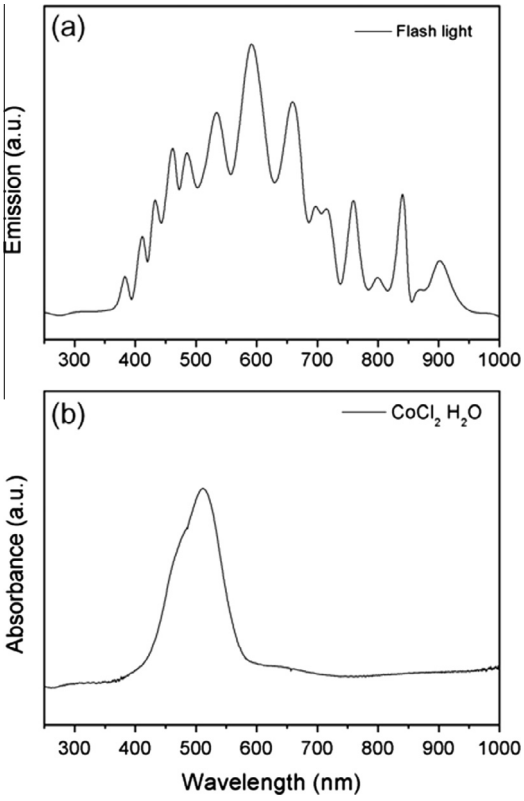

Fig. 1. UV–vis–IR (a) emission spectrum of the flash light and (b) absorbance spectrum of $CoCl_2$.

2. Experimental

2.1. Synthesis of the $CoO/NiCo_2O_4$ nanoflakes and electrode fabrication

A Ni-foam substrate with pore sizes of 300–400 μm was cleaned in methanol and acetone for 10 min, and dried under a nitrogen stream. Then, the Ni-foam substrate was immersed in an aqueous metal oxide precursor solution of 1 M $CoCl_2$ for 30 min and dried at 40 °C for 1 h in an oven. The metal oxide precursor-coated Ni-foam substrate was irradiated under intense pulsed light of 20 J cm^{-2} for 15 ms. The IPL irradiated sample was rinsed with distilled water to remove the unreacted metal oxide precursor and dried under a flow of nitrogen. The as-prepared substrate was used as a working electrode for electrochemical analysis. The mass loading of the active material ($CoO/NiCo_2O_4$) used was 0.71 mg cm^{-2}.

2.2. Characterization and electrochemical measurements

The morphological analysis was performed using a field emission scanning electron microscope (FESEM, Hitachi S 4800) and transmission electron microscope (TEM, TECNAI 20). The elemental composition in the as-prepared samples was determined using X-ray photoelectron spectroscopy (XPS, VG Multilab ESCA 2000 system). All electrochemical measurements were conducted by three-electrode configurations using a CHI 660D electrochemical workstation (CH instrument, USA) in a 1 M KOH solution. For the three-electrode configuration, the $CoO/NiCo_2O_4$/Ni-foam acted as the working electrode. Ag/AgCl served as the reference electrode and platinum was used as the counter electrode. A cyclic voltammogram (CV) and galvanostatic charge–discharge (CD) were obtained to investigate the supercapacitive properties of the electrodes.

3. Results and discussion

3.1. Surface morphological studies

The surface morphology and crystal structure of the electrode materials before and after IPL irradiation were investigated by scanning and transmission electron microscopy (SEM and TEM). Fig. 2a shows a representative SEM image of a cobalt oxide precursor ($CoCl_2$) film on a Ni-foam substrate. To prepare the cobalt oxide precursor film on the Ni-foam substrate, the substrate was immersed in an aqueous solution of 1 M $CoCl_2$ for 30 min and dried at 40 °C for 1 h in an oven. As seen in the figure, $CoCl_2$ nanocubes ranging from 20 nm to 80 nm in size were formed on the Ni-foam substrate. Fig. 2b shows an SEM image of cobalt oxide nanoflakes on the Ni-foam substrate after IPL irradiation with an energy of 20 J cm^{-2} for 15 ms. As seen from the figure, the nanocubes have been transformed into nanoflakes by IPL irradiation. The IPL-irradiated film exhibits a hierarchical morphology of interconnecting nanoflakes of 150–200 nm in size and a thickness around 10 nm. The nanoscale thickness of the flakes has the advantage of shortening the diffusion distance, increasing the utilization of active material and being able to accommodate the volume change during faradaic reaction. The interconnecting nanoflakes compose channels connected with nanoscale pores that are about 50 nm in size, which may be formed by the momentary evaporation of gas molecules in the nanocubes during IPL irradiation for 15 ms. The channels with nanoscale pores can facilitate penetration of the electrolyte, providing reduced contact resistance and enhanced mass/charge transfer at the electrode/electrolyte interface. The structure of the IPL-irradiated film is further analyzed by TEM. Fig. 2c shows a TEM image of a single nanoflake. Note that the nanoflake was collected from the top part of the film, which was not in direct contact with the Ni-foam. The selected-area electron diffraction (SAED) pattern of the nanoflake is shown in Fig. 2d and exhibits highly resolved bright spots (dot patterns) indicating a single crystalline characteristic. The calculated *d*-values from the spots are 2.62, 2.29, 1.59 and 1.36 (±0.02) Å and these correspond to the (hkl) values (111), (200), (220) and (311) of CoO (JCPDS No. 75-0419), respectively. This result confirms that the cobalt chloride nanocubes were