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Hydrothermal preparation of ZnO electrodes synthesized from different precursors for electrochemical supercapacitors

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ABSTRACT

In this work, zinc oxide (ZnO) particles have been synthesized by hydrothermal technique using three different types of precursor solutions namely; zinc acetate, zinc chloride and zinc nitrate for active materials of supercapacitor (SC) electrode. The SC properties of ZnO powders were studied as a function precursor solution. The physical properties of the ZnO particles were analyzed with X-ray diffraction, scanning electron microscopy, and Raman spectroscopy. The electrochemical properties of the ZnO particles obtained from different precursors were investigated through cyclic voltammetry, galvanostatic charge/discharge measurements in a 6 M KOH electrolyte at a scan rate of 5 mV/s. The specific capacitance values of the ZnO electrodes obtained from nitrate, acetate and chloride precursor solutions were measured to be 5.87 F/g, 5.35 F/g and 4.14 F/g, respectively.

1. Introduction

Supercapacitors (SCs), also known as electrochemical capacitors or ultracapacitors, have drawn intensive attention in recent years due to their significant potential for energy storage [1–5]. Based on the charge-storage mechanism, SCs store energy in two different ways: (i) electrical double-layer capacitors (EDLCs) and (ii) pseudocapacitors [1]. The energy storage mechanism for EDLC capacitance is based on electrostatic charge diffusion and accumulation at the electrode/electrolyte interface. Due to their high surface area, electrochemical stability, good conductivity, low cost and availability in various different forms, carbon materials like activated carbon, carbon aerogel, carbon nanotubes graphene, etc., are widely used in EDLC electrodes. Whereas the pseudocapacitors are based on fast, reversible Faradic redox reactions which occur between the electrode and the electrolyte materials [6,7]. Compared to EDLCs, pseudocapacitors can provide much higher capacitance and energy density through Faradic reaction. Various materials such as transition metal oxides (RuO_2 [8], Co_3O_4 [9], NiO [10], SnO_2 [11], MnO_2 [12], V_2O_5 [13]), metal hydroxides ($Ni(OH)_2$ [14], $Co(OH)_2$ [15], $Co_xNi_{1-x}(OH)_2$ [16]) and polymeric materials (PANI [17], PPy [18]) have been explored for pseudocapacitor applications. Although ruthenium oxide (RuO_2) exhibits the best pseudocapacitive properties high cost, limited availability and the polluting effect on the environment make this material not so attractive for large-scale production.

Zinc oxide (ZnO) has been viewed as one of the most promising active materials with high energy density of 650 A h/g for supercapacitors, due to its significant advantages of low cost, abundant availability, environment friendly nature and electrochemical activity. Recently, ZnO has been used as a potential candidate for supercapacitor electrodes. Fang et al. [19] have synthesized ZnO–graphene nanocomposites as an electrode material for high-performance supercapacitors which exhibited a specific capacitance of 786 F/g. Similarly, Kim and Kim [20] have fabricated ZnO-activated carbon nanofiber composite electrodes which showed a specific capacitance of 178.2 F/g and high energy densities of 22.71–17.77 Wh kg^{-1} in the power density range of 400–4000 W kg^{-1}. Zhang et al. [21] have successfully synthesized carbon nanotube (CNT) and zinc oxide (ZnO) composite as the electrode for supercapasitors which exhibited a specific capacitance of 126.3 F/g. As seen above studies and many other studies in literature, ZnO composite materials have been widely studied as a component of hybrid materials for supercapacitors. But, there are very limited reports on ZnO as a pseudocapacitive electrode material for supercapacitors. In addition, it is well known that the particle properties such as morphology and size affect supercapacitive properties of electrode material. In this study, we prepared ZnO particles via hydrothermal method by using three different precursors, and investigated the supercapacitive properties of as-synthesized ZnO particles as a function of the precursor solution.

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2. Experimental

ZnO particles were grown by hydrothermal method from zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), zinc nitrate hexahydrate ($(Zn(NO_3)_2{\cdot}6H_2O$) and zinc chloride ($ZnCl_2$) precursors. The precursor solutions were prepared by dissolving 0.1 M of zinc salts (acetate, chloride and nitrate) and 0.1 M of hexamethylenetetramine (HMT, $C_6H_{12}N_4$) in 100 mL deionized water. Hydrothermal growth was carried out at 140 °C in a Teflon lined sealed stainless steel autoclave placed in a furnace for 4 h. After cooling naturally to room temperature, the resulting white solid products were filtered and washed with distilled water several times and dried at room temperature in air for further characterization. All experimental conditions were kept the same for all samples. The crystal structures of synthesized particles were investigated by Philips X'Pert Pro X-ray diffractometer (XRD), with Cu-Kα radiation, the surface morphologies were observed using a Zeiss EVO-LS10 scanning electron microscopy (SEM) and surface-enhanced Raman spectra of the samples were obtained by a portable Raman spectrometer (BWS465 B&W Tek Inc.) with a 302 mW diode laser at 785 nm, a resolution of 3 cm^{-1}.

The working electrodes were prepared by mixing ZnO particles with graphite powder and polytetrafluoroethylene (PTFE) in a mass ratio of 70:20:10. In order to obtain slurry, a small amount of butanol was added drop wise into the above mixture. Then the obtained slurry was coated onto the nickel foam (1 cm × 1 cm) with a spatula and dried at room temperature for 24 h. The capacitive properties of the samples were studied by cyclic voltammetry, namely an Iviumstat potentiostat/galvanostat. All experiments were carried out in a three electrode cell. A typical three-electrode cell equipped with a working electrode ZnO particles, a platinum foil counter electrode, and a standard calomel electrode (SCE) reference electrode was used for measuring the electrochemical properties of working electrode. All electrochemical measurements were carried out in 6 M KOH solution used as electrolyte.

3. Results and discussions

Typical XRD patterns of the ZnO particles produced with different precursor are shown in Fig. 1. As shown in Fig. 1, while ZnO particles fabricated from zinc nitrate and zinc acetate precursor have a hexagonal wurtzite structure, particles fabricated from zinc chloride precursor have a plate-like structure namely; zinc chloride hydroxide monohydrate, ($Zn_5(OH)_8Cl_2{\cdot}H_2O$), simonkolleite (PDF-2: reference code:00-076-0922). The formation of zinc chloride hydroxide should be related higher concentration (>0.01 M) of Zn^{2+} ion in precursor solution of $ZnCl_2$ [22]. XRD analysis of the as-synthesized ZnO particles obtained from nitrate and acetate salts showed the diffraction peaks at 31.70, 34.37, 36.14, 47.58, 56.58,62.82, 66.37, 67.89 and 69.04°, which were indexed to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2) and (2 0 1) crystal planes of pure ZnO with a

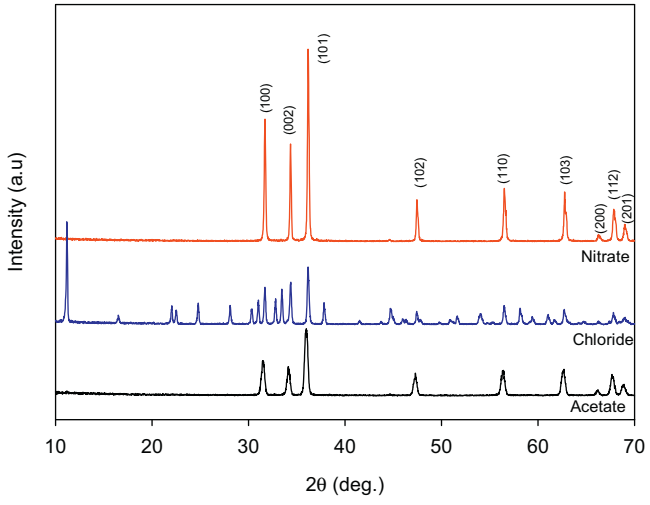

Fig. 1. Typical XRD patterns of ZnO particles obtained from zinc acetate zinc chloride and zinc nitrate at 140 °C.

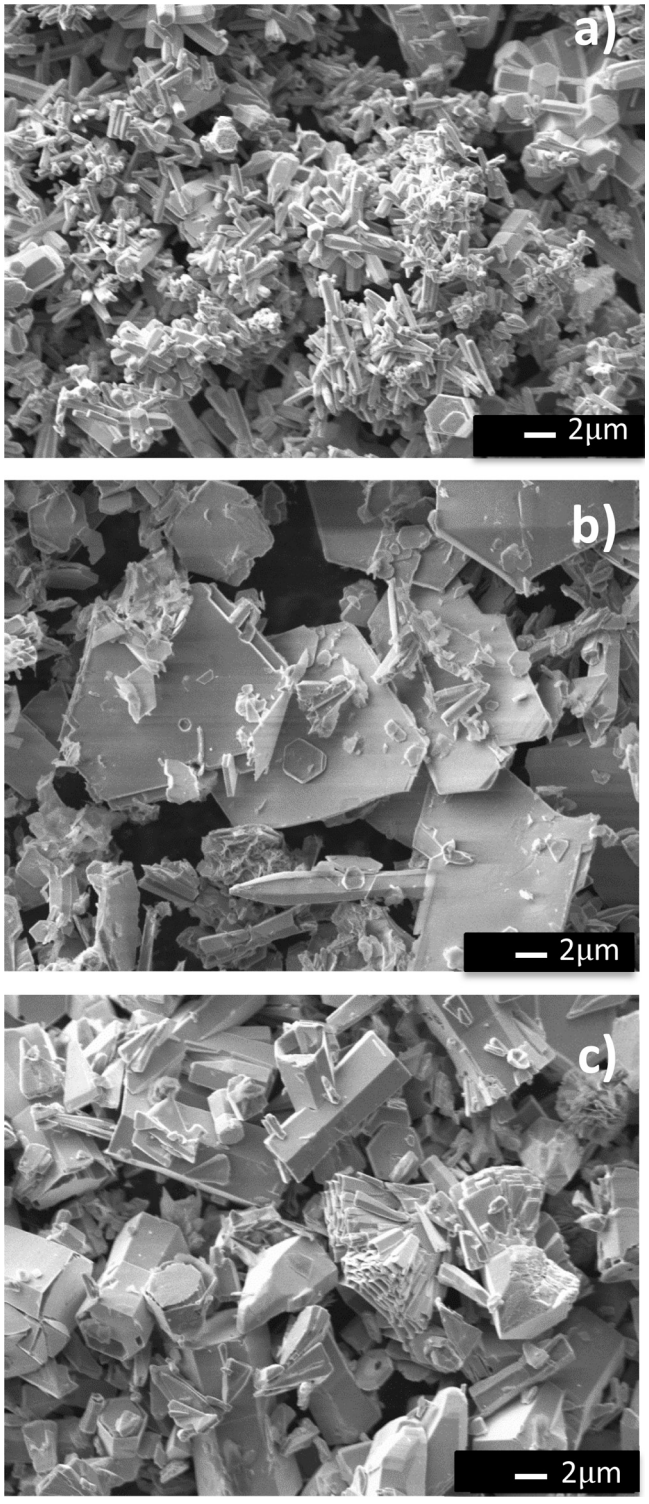

Fig. 2. SEM images of the ZnO particles obtained from zinc nitrate (a), zinc chloride (b) zinc acetate (c) precursor solutions.