Effect of ion concentration in enhancement of super capacitive behavior of ZnO nano-platelets

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Abstract

ZnO nano-platelets have been prepared using a high pressure reactor via hydrothermal route. The as-formed fine platelets morphology of the as-synthesized powder was confirmed from the scanning electron microscopy (SEM) images. The elemental analysis using energy dispersive X-ray (EDAX) analysis indicated the presence of Zn, O, Na and Cl which confirms the presence of ZnO as major and NaCl as the minor phase. The precipitation of this minor phase after growth and catalytic induction in nano-platelet (NP) morphology during growth has been elucidated. The electrochemical performance of this as-synthesized powder is quite promising. Additionally, the effect of this minor NaCl phase in changing the ionic equilibrium of the electrolyte in capacitance measurement has been analyzed. Copyright © 2016 VBRI Press

Keywords: Zinc oxide, hydrothermal synthesis, nano-platelets growth, cyclic voltammetry, SEM

Introduction

Supercapacitors, also electrochemical capacitors have attracted considerable attraction as future energy storing devices by virtue of their high power density, long pertained cycle life, good and stable charge discharge rates **[1]**. Transition metal oxides are considered to be promising materials as electrode materials for supercapacitor applications among which Zinc oxide (ZnO) has been found to be a desirable candidate for supercapacitors material because of its high specific surface area, biocompatibility and excellent electrochemical activity **[2-3]**. Zinc oxide with various morphologies and different synthesis routes has already been reported since long **[4]**. A lot of research has been carried out recently on ZnO based composites for improving the overall capacitance and energy capabilities **[5-6]** but no recent work significantly reports the role of the minor impurity phase in enhancing the capacitive behavior of the Zinc oxide.

In this paper ZnO particles have been prepared by hydrothermal route and calcined at 450ºC. The structure and morphology of the grown ZnO nanostructures has been reported. This report on the effect of impurity phases in the enhancement of electrochemical properties of the nano-platelets is new and the reported enhanced capacitance can find possible application in energy storing devices.

Experimental

Materials details

Zinc chloride ($ZnCl_2$), sodium hydroxide (NaOH), potassium nitrate (KNO_3) (all with assay 95%) were purchased from Fisher Scientific and ammonium hydroxide(NH_4OH) (assay-28 to 30%), hydrochloric acid(HCl)(assay-36.5%)from Finar chemicals and used without any further purification.

Material synthesis

ZnO nanoparticles were synthesized by the hydrothermal route using zinc chloride ($ZnCl_2$) as the starting precursor. In brief, 14.03 g of $ZnCl_2$ was mixed with 7.015 g of NaOH in 100 ml of distilled water and was stirred vigorously to obtain a clear solution. Subsequently, 5 ml of concentrated HCl was added drop wise and 11.3 ml of ammonium hydroxide was added to the solution and stirred for about 30 minutes. Now, the obtained solution was transferred to a teflon autoclave and treated in high pressure reactor for one hour at 80 °C. The obtained precipitate was repeatedly washed with distilled water and filtered and heated in air oven at 80 °C to obtain a dry powder. The resulting powder was allowed to calcine at 450 °C. Finally, white-colored ZnO nanostructures were obtained and stored in vacuum for morphological and electrochemical characterizations.

Characterizations

The morphology of as-synthesized ZnO powders was observed by scanning emission microscopy (SEM; JEOL-JSM-6510). The elemental composition was investigated by energy dispersive spectroscopy (EDS) attached with SEM. For the measurement of electrochemical behavior of the prepared ZnO nano-platelets, first the prepared ZnO powder were coated on the surface of glassy carbon electrode (GCE; Surface area=0.001cm^{-1}). The analytical performances of the fabricated sensors were measured by CV technique, three electrode system. In three electrode system Ag/AgCl was used as reference electrode, modified GCE was used as working electrode and pt wire used as auxiliary/counter electrode. For all measurements, 10ml 0.1M KNO_3 was used as electrolyte.

Results and discussion

SEM analysis

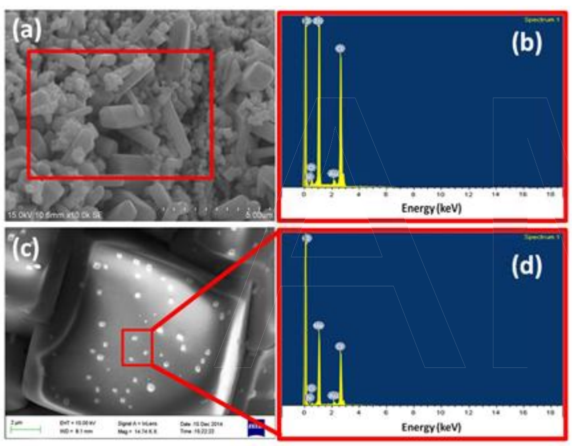

Fig 1. (a) and (c) Low magnification and High magnification SEM images (b) and (d) EDAX spectra of as-synthesized 450°C calcined ZnO NP's.

SEM images of the as synthesized sample calcined at 450 °C with Energy Dispersive X-ray (EDAX) spectra are shown in **Fig. 1**.The growth of nano-platelet structure is evident from the image shown in Fig.1a and its subsequent EDAX spectrum confirmed the presence of nano-dotted sodium ions on the surface of the as synthesized ZnO nano-structures. The EDAX spectra of low magnification image clearly shows the presence of Zinc Oxide while the specific area scan of the high magnification image confirms the presence of NaCl. The effect of these nano-dotted impurities on the electrochemical activity of the as-synthesized ZnO nano-platelets has been discussed further.

Electrochemical characterization

Fig. 2 shows the cyclic voltammograms (CV) of ZnO electrodes recorded at a scan rate of 25 mVS^{-1} in 0.1M KNO_3 solution with the potential window of 0.0 to 1.0 V. The rectangular shape of CV curves is the peculiar behavior of the electric double layer capacitor (EDLCs) i.e. the non-faradic charge transfer condition. In present case, the rectangular and symmetric current-voltage (I-V) characteristic behaviour follows the reported literature **[7]**. Thus, the equivalent circuit of double layer capacitance is represented by a serial combination of equivalent series resistance (R) and double layer capacitance (C). The shape of the voltammogram depends on the time constant τ (RC) of the electrochemical cell. τ (RC) ≠0, indicates current containing both transient part as well as a steady state part, resulting non-rectangular shape of the CV. The forward scan of oxidation generates electrons which accumulate on the solid side and K^+ ions tend to accumulate on the solution side of the double layer, producing a polarizable double layer that acts as the ideal electrochemical capacitor.

The number of active ions involved is more in the as-synthesized ZnO NP compared to commercial ZnO. The presence of NaCl impurity phase led to the increased ion concentration in the electrolyte contributing to the increase in the specific capacitance which is evident from the increase in sweep area of the CV curves as indicative in Fig 2. The symmetrical charge discharge curves nearly triangular in shape even for 900 seconds indicates excellent electrochemical reversibility confirming superior capacitive behavior thus establishing the as-synthesized nano-platelets as potential candidate for energy storing devices as shown in the inset of **Fig. 2.**

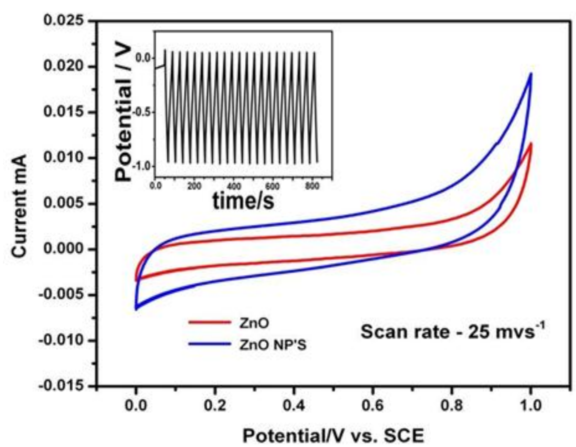

Fig. 2 Cyclic voltammetry curves of ZnO nano-platelets with impurity phase and commercially available ZnO and Charge/Discharge curve of 450°C calcined sample at constant current density 2mAcm^{-2} in the inset.

Growth mechanism

The plausible growth mechanism of the ZnO nano-platelets structures comprises of two steps: nucleation or formation of spherical molecules and its growth into platelets structure. When the solution of zinc chloride and sodium hydroxide is stirred for a certain

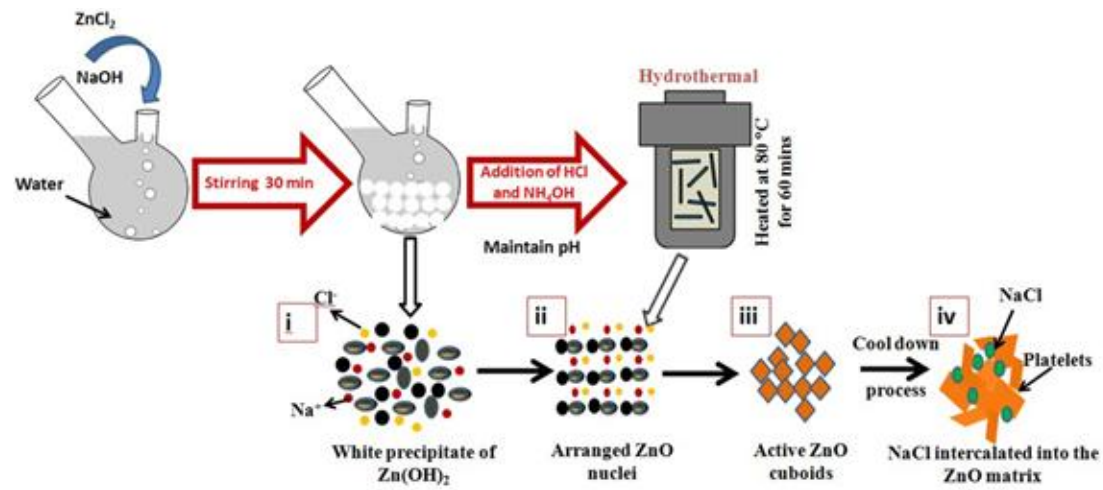

Fig. 3. Possible growth mechanism of the as-synthesized ZnO nano-platelets.

extent of time, a white precipitate is observed which is $Zn(OH)_2$. Further, addition of ammonium hydroxide and dilute hydrochloric acid to this white precipitate, raises the pH of the system to an acidic value which when heated in a hydrothermal reactor dissociates $Zn(OH)_2$ forming ZnO nuclei which reacts with water molecules to form ZnO by following the reaction:

$$Zn(OH)_2 + H_2O \longrightarrow Zn^{2+} + 2OH^-$$
$$Zn^{2+} + H_2O \longrightarrow ZnO + 2H^+$$

Extending this growth temperature for a prolonged period of time, there starts the grain growth and formation of faceted ZnO platelets due to more preferable interaction of H^+ ions with hydroxyl ions OH^- ions at the surface of ZnO molecule due to acidic medium with mobile Na^+ and Cl^- ions in the solvent at the upper part of the reactor. Subsequently, cooling down the system to room temperature resulted in the intercalation of the NaCl crystals into the ZnO matrix. These intercalated NaCl crystals are in the form of fine nano cuboids shape which are present as impurity phase even after repeatedly washing with de-ionized water.

Conclusion

This report demonstrates the growth of ZnO nano-platelets using a simple hydrothermal route. The presence of impurity phase NaCl led in enhancement of specific capacitance. This suggests impurity phases could play a vital role in augmenting the electrochemical activity of transition metal oxides.

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