

Hydrothermal Synthesis of Hydrated Zinc Oxide Nanoparticles and its Characterization[†]

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Abstract: Hydrated zinc oxide nanoparticles were successfully prepared by hydrothermal method using zinc acetate and sodium hydroxide as the zinc and hydroxide sources along. The synthesized zinc oxide nanoparticles were characterized by XRD, FTIR and SEM in order to confirm the phase purity and morphology of the sample. Zinc oxide nanoparticles exhibit hexagonal wurtzite structure, which was revealed by the XRD analysis. The synthesized hydrated zinc oxide was used to modify glassy carbon electrode (GCE). The electrochemical property of the modified electrode (ZnO/GCE) was tested in a pH 7.4 phosphate buffer solutions (PBS) by cyclic voltammetry (CV). There is no peak observed in the voltammogram which indicated that the material can be used as an electrochemical sensor.

Keywords: ZnO, Nanoparticles, X-ray diffraction, Cyclic voltammetry

Introduction

Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 mV) and one of the most widely used and studied functional oxides^{1,2}. Zinc oxide readily forms into noncentral symmetric wurtzite nanocrystal structures with self-polarized crystal surfaces. The thermodynamically stable crystallographic faces of ZnO include a polar-terminated (001) face and nonpolar low-symmetry (100) faces. The low-symmetry surfaces are more stable than the polar face, leading to faster growth along the polar surface. As a result, a variety of one-dimensional (1D) ZnO nano-structures including nanorods/nanowires, nanobelts, nanorings and other hierarchical nanostructures can be readily synthesized and these materials have been examined for applications in photovoltaic energy conversion, optics, optoelectronics, catalysis, piezoelectric systems, photocatalysts, chemical sensors and solar cells³⁻⁷.

In this study, we have reported the synthesis of ZnO nanoparticles using hydrothermal method and characterized its structural, morphological properties. Additionally we have performed the electrochemical activity of the synthesized ZnO.

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Experimental

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and sodium hydroxide were purchased from Qualigens. Double distilled water was used as the solvent throughout the experiment.

Characterization methods

The crystal structure of ZnO nanoparticles was analyzed by a Rich Siefert 3000 diffractometer with $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). FT-IR spectrum of the ZnO was recorded on Shimadzu FT-IR 8300 series instrument by using potassium bromide pellets. The morphology of the materials was analyzed by SEM HITACHI SU6600 scanning electron microscopy respectively. The electrochemical experiments were performed on a CHI 600A electrochemical instrument using the as-modified electrode and bare GCE as working electrode, a platinum wire was the counter electrode and saturated calomel electrode (SCE) was the reference electrode.

Synthesis of ZnO nanoparticles

0.070 g of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 0.400 g of NaOH were dissolved into 40 mL of distilled water. After the mixture was magnetically stirred for 20 min and this solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. It was then sealed and maintained at 180°C for 2 h. After slowly being cooled to room temperature, obtained powders were collected by centrifugation and washed with distilled water and absolute ethanol. The powders were finally dried at 60°C for 12 h.

Electrode modification

Ultrasonically dispersed ZnO nanopowder in 5 mL of water was drop coated onto the GCE and dried at room temperature. CV's were run in electrochemical cell containing 50 mL of 0.1 M KOH in presence of SCE as a reference electrode and Pt wire as counter electrode.

Results and Discussion

Structural characterization

XRD patterns of the ZnO nanoparticles prepared by hydrothermal method is shown in Figure 1, which indicates the ZnO has hexagonal wurtzite phase structure. The peak and relative intensities obtained for the ZnO match with the literature values⁸. There was no characteristic peaks of impurity were observed. The average grain size of ZnO is determined using Scherrer relation⁹ and it was found to be around 72 nm.

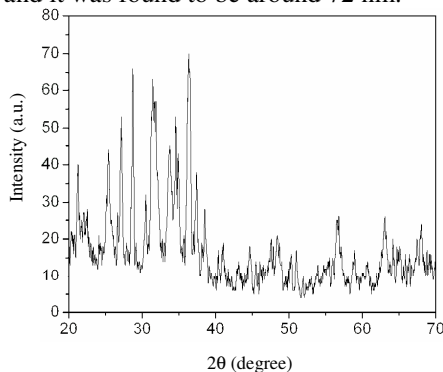


Figure 1. XRD pattern of ZnO nanoparticles

FT-IR spectrum of ZnO nanoparticles (Figure 2) showed significant absorption peaks at 3457 and 1598, 452 cm^{-1} . The absorption band at 452 cm^{-1} was assigned to Zn-O stretching vibration¹⁰. The weak band near 1598 cm^{-1} is assigned to H-O-H bending vibration mode were presented due to the adsorption of moisture, when FTIR sample disks were prepared in an open air atmosphere. These observations provided the evidence for the presence of hydration in the structure¹¹.

The SEM micrograph of the ZnO by hydrothermal method is shown in Figure 3. It can be seen that the particles adopt irregular morphology with different sized particle whose size is in the nm range. It is expected that the formation of agglomerates were purely due to the synthetic condition.

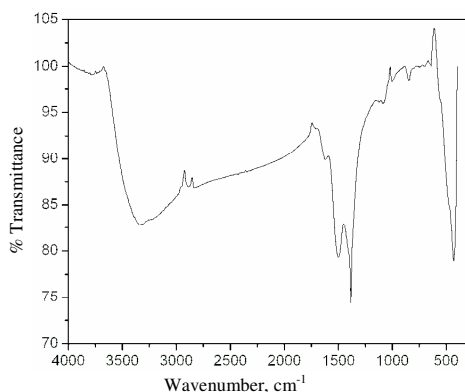


Figure 2. FT-IR spectrum of ZnO nanoparticles

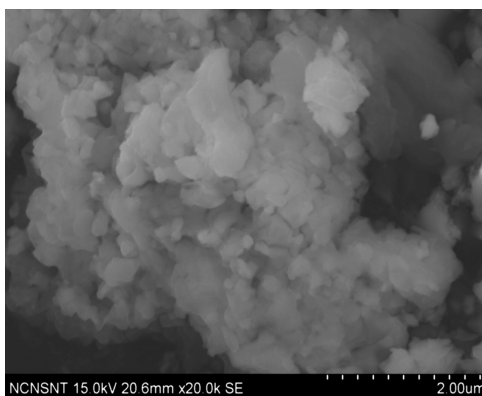


Figure 3. FESEM image of ZnO nanoparticles

The electrochemical behaviour of ZnO/GCE was examined by cyclic voltammetry. Figure 4 shows the CV of bare and ZnO/GCE in 0.1 M KOH as a supporting electrolyte. It can be seen that the ZnO is non-electroactive in the selected potential region. However, it shows enhanced peak current than the bare GCE which indicated that the modified electrode can be further used for the determination of biologically important molecules.

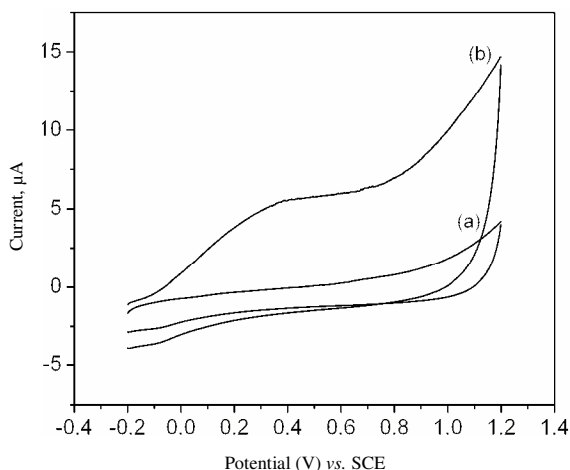


Figure 4. CV of (a) bare (b) ZnO/GCE in 0.1 M KOH at 50 mV/s

Conclusion

The ZnO nanoparticles were successfully prepared by hydrothermal method. FT-IR analysis confirms the formation of the Zn-O bond in the ZnO nanoparticles. The XRD confirms the crystal structure and phase purity of the sample. The SEM of ZnO nanoparticles shows the spherical agglomerated particles. The electrochemical property of the ZnO nanoparticles modified GCE was investigated by cyclic voltammetry. The results conclude that the ZnO nanoparticles will have potential application in the electrochemical sensor.

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