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Synthesis and Characterization of ZnO Nanopowders and ZnO-CNT Nanocomposites Prepared by Chemical Precipitation Route

D. Gültekin*, M. Alaf and H. Akbulut

Engineering Faculty, Metallurgical & Materials Engineering Department, Sakarya University
Esentepe Campus, 54187, Sakarya, Turkey

The aims of this work are synthesis of ZnO nanopowders and producing nanocomposites by mixing with carbon nanotubes. ZnO nanopowders have been synthesized by chemical precipitation route. Different amount of collected nanosized Zn-based precipitates and chemically oxidized carbon nanotubes powder have been mix together and annealed at 400 °C. Characterization of produced nanopowders and nanocomposites have been carried out by X-ray diffractometer and scanning electron microscope.

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1. Introduction

Zinc oxide (ZnO) is an important material and has received considerable attention due to its applications in electrical, optical, mechanical, and scientific research. ZnO is a wide band gap (3.37 eV) semiconductor and has a large binding energy (60 meV) [1, 2], low resistivity and high transparency in the visible range and high light trapping characteristics [3]. The synthesis of nanoparticles has become a highly developed field owing to the scientific and technological interest due to the structural peculiarities and unusual physical and chemical properties they may lead to [4]. In recent years, it has been found that ZnO can be synthesized by various routes such as electron beam evaporation technique [5], chemical spray pyrolysis technique [1], RF thermal plasma evaporation [6], sol–gel method [3, 7], and precipitation [1, 7] methods. Among these methods, precipitation has many advantages over the other methods, for example, it is unsophisticated and a low cost method. Moreover, the morphology of ZnO powders can be controlled easily by using an appropriate surfactant or capping agent such as polyethylene glycol, monoethanolamine (MEA), diethanolamine or triethanolamine [7].

Over the past few years, great efforts have been made toward the syntheses of nanocomposites of inorganic materials and carbon nanotubes (CNT) [8] with the aim of exploiting the unique properties of CNTs (such as a high theoretical electrical conductivity, high aspect ratio, remarkable thermal conductivity, and good mechanical properties) [9]. In this work, ZnO nano powders and ZnO/multi-walled CNT (ZnO/MWCNT) nano--composites were synthesized and characterized.

*corresponding author

2. Experimental

Figure 1 represents the process flow chart used for synthesis of nanostructured ZnO powders by homogeneous precipitation and producing of ZnO/MWCNT nanocomposites. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) (Merck) was used as a precursor whereas distilled water was used as solvents. Monoethanolamine (MEA) (Merck) was used for adjusting of sol pH. MEA was added to homogeneous and transparent solution until white precipitates are obtained. The pH value was recorded as 10. The addition of MEA changes the alkaline nature of the prepared sols that give ZnO films with improved crystalline quality [10]. After the precipitation, collected nanosized powders were dried at 100 °C.

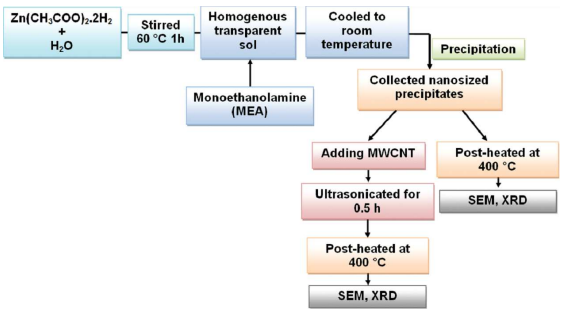

Fig. 1. The process flow chart used for synthesis of nanostructured ZnO and ZnO/MWCNT nanocomposite.

MWCNTs of over 10 l'm in length with outer diameters of 50 nm were purchased from Arry Nano. In order to eliminate ofamorphous carbon and remove impurities, MWCNTs were annealed to 350 °C and then treated with hydrochloric acid for one hour. Chemical oxidation of CNTs was carried out with a mixture of sulphuric acid and nitric acid in ratio 3:1 for 3 h. In order to enhance the efficiency, it is necessary to attach other substances

to the surface of MWCNTs. Therefore, the surface modification of MWCNTs has been a focus of many environmental scientists [11].

An appropriate amount of ZnO nanopowders and functionalized MWCNTs (ZnO/MWCNT ratios are 5:1 and 2:1, respectively) were first dispersed into water by magnetic stirrer and ultrasonicated for 30 min to form a well dispersed. Since the boiling point of MEA and the thermal decomposition temperature of zinc acetate dihydrate are 170 and 240 °C, respectively, a heat treatment temperature of 300 °C is sufficient for the complete evaporation of organics and to initiate the process of formation and crystallization of the ZnO film [10] fabricated coatings annealed at 400 °C.

3. Results and discussions

The formation of ZnO particles from the hydrolysis of Zn^{2+} ions in aqueous media is known to be a complex process. Many polyvalent cationic species can be formed between Zn^{2+} ions with OH^- ions and are strongly dependent upon the pH of the solution. However, the precipitation of ZnO particles has been usually described through a growth unit that might be either $Zn(OH)_2$ or $Zn(OH)_4^{2-}$ ions depending on the pH, temperature, and synthetic methods. The growth of ZnO from $Zn(OH)_2$ has been usually suggested to occur through the dissolution-reprecipitation mechanism [12]. ZnO will be formed through the chemical reaction [10]: $Zn(OH)_2 \rightarrow ZnO + H_2O$.

Figure 2 presents the X-ray diffraction (XRD) patterns of synthesized powder and nanocomposites. The peak positions in each product agree well with the reflections of bulk ZnO and ZnO/CNT composites with all peaks corresponding well to standard crystallographic data (ZnO: JCPDS 01-076-0704, C: JCPDS No. 00-026-1080). As could be seen from the XRD patterns, all products have polycrystalline nature and peaks belonging to the (100), (002), (101) (102), (110), (103), (112) and (201) reflections were seen in ZnO powders, also (002) reflection for C. No other peak related to impurities was detected in the spectrum, which further confirms that the synthesized products are of high purity. The ZnO powders show a highly oriented (101), (100) and (002) peaks, respectively. Although it was obtained that there has been slight changing in orientation and peak intensities with an increasing amount of CNT.

TABLE

XRD diffraction peaks information 2Θ of ZnO and ZnO/CNT nanocomposites.

(*hkl*)	ZnO	ZnO/CNT 5:1)	ZnO/CNT 2:1)
(100)	31.680	31.680	31.680
(002)	34.320	34.339	34.380
(101)	36.160	36.158	36.141

As could be seen in Table, the XRD peaks shifting of ZnO and ZnO/MWCNT nanocomposites were investigated and reveal the effect of the amount of CNT. It

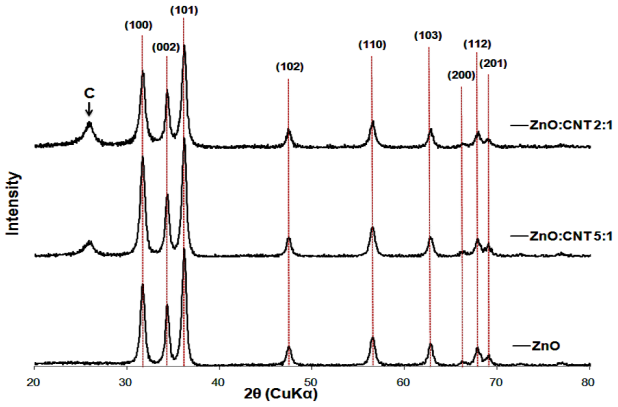

Fig. 2. The XRD diffraction patterns of ZnO and ZnO/MWCNT products.

was observed that there have been slight increases/decreases between XRD peaks angle belonging to ZnO and ZnO/MWCNT nanocomposites. While a peak was observed at 34.320° from the XRD 2θ scan data of the pure ZnO nanopowders corresponding to ZnO (002), ZnO/MWCNT nanocomposites resulted in shifting XRD peaks to a higher angle. Furthermore, ZnO/MWCNT (5:1) and ZnO/MWCNT (2:1) nanocomposites peak shifts to 36.158°, and 36.141°, respectively. The peak shift in the XRD curves originates from difference between ZnO and ZnO/MWCNT lattice constants. These peaks shifts may indicate a lattice strain between ZnO and CNTs.

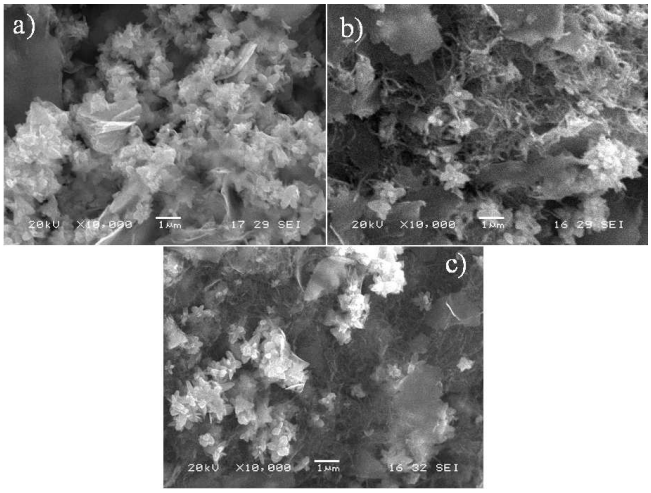

Fig. 3. SEM micrographs of (a) ZnO, (b) ZnO/CNT 5:1, (c) ZnO/CNT 2:1.

Grain morphologies of ZnO powders can be observed from SEM images represented in Fig. 3. The grain sizes of the ZnO powders were calculated by using Scherrer's formula and the crystallite size is 26 nm. In the literature, ZnO nanostructures having 9–250 nm have been reported [13]. The nanostructure has both approximately 0.1–1 μm sized agglomerated nanoparticles and

prism-like nanoflowers. It was observed that nanocomposite structures have well-dispersed carbon nanotubes network.

4. Conclusions

Polycrystalline and nanostructured ZnO powders were successfully produced by homogeneous precipitation route, then ZnO/MWCNT nanocomposites were prepared by physically mixing with nanopowders. The effects of amount of CNT on the properties of powders have been presented. The XRD patterns of all products were of polycrystalline nature. Experimental results showed that although the crystal orientations and particle sizes of the prepared ZnO particles were not affected with amount of CNT, slight increases/decreases in XRD peaks angle were observed. The intensity of the (101) orientation is predominant for ZnO and ZnO/MWCNT products. ZnO nanoparticles and CNTs combined together and results showed that ZnO and nanotubes kept their structure and formed a nanocomposite. ZnO and nanotubes have not reacted with each other.

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