Synthesis and Characterization of ZnO–MgO Nanocomposite by Co-precipitation Method

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ABSTRACT

Co-precipitation along with aging at 80 °C has been used to synthesize zinc-magnesium nanocomposite. Obtained materials were characterized by scanning electron micrograph, point energy dispersive X-ray analysis (EDX), Fourier transform infrared spectroscopy, X-ray diffraction analysis (XRD) and UV–visible diffuse reflectance spectra (UV-DRS) so as to determine its various physico-chemical characteristics. EDX analysis confirmed the presence of Zn, Mg, and O elements within ZnO–MgO nanocomposite. Formation of magnesium oxide along with zinc oxide nanocomposite has been confirmed by XRD analysis which has been reaffirmed by point EDX analysis. Optical properties investigated by UV-DRS showed decrease in maximum reflectance (~25%) due to incorporation of MgO within ZnO nanoparticle. Electrochemical study showed higher electrochemical activity of ZnO–MgO nanocomposite than bare ZnO nanoparticle.

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1. Introduction

A wide range of various metal oxide semiconductors have a great potential in practical applications. [1] Nanocrystalline zinc oxide (ZnO), an n-type metal oxide semiconductor, is one of the metal oxides which comprises wide band gap energy of 3.37 eV, large excitation binding energy of 60 meV along with good optical, electrical, and piezoelectric responses. [2] ZnO has a lot of important applications in the field of solar cell, optoelectronics, microelectronics, light emitting devices, gas sensing device transistor, and medical sectors. [3–5] Tuning of excitation wavelength of this semiconductor is essential so as to tune its optical, electrical, and magnetic properties which play important roles during practical applications. Doping (or mixing) of one metal oxide semiconductor with other helps in tuning of the properties. Doping of ZnO with magnesium (bandgap of 7.3 eV) could enhance the UV luminescence intensity by adjusting its wavelength. ZnO–MgO nanocomposite exhibit enhanced optical properties that results partly from the different crystallites or electronic coupling between ZnO and MgO which enhances the bandgap. [6–10] Several synthesis techniques such as solid state mixing, [11] electrochemical method, [12] hydrothermal growth, [4] sonochemical, [13] sol gel technique, [14] high pressure synthesis technique, [15] glycine-nitrate combustion route, [16] and thermal evaporation techniques [5, 17–19] have already been reported for ZnO–MgO synthesis. Among all, co-precipitation method is the simplest and easy for the production of ZnO–MgO nanocomposite. In one study, ZnO–MgO has been prepared from alcoholic solution by consecutive precipitation or co-precipitation method followed by high temperature annealing. [20]

In this work, ZnO–MgO nanocomposite have been prepared by simple single-step co-precipitation method. Products were characterized by various sophisticated characterization techniques. Electrochemical performance of nanoparticles was studied in bare sodium hydroxide solution using three electrode single compartment cell setup.

2. Experimental details

Magnesium sulfate, heptahydrate and zinc sulfate, heptahydrate was purchased from HiMedia Laboratories Pvt. Ltd, India. Sodium hydroxide and distilled water (DI) was used as purchased from local sources. All chemicals used in this study were of analytical grade and were used without further purification.

Co-precipitation method was used to prepare ZnO–MgO nanocomposite by dissolving 0.58 g of ZnSO₄·7H₂O, 0.49 g of MgSO₄·7H₂O and 0.75 g of NaOH in DI water (60 ml) under constant agitation in a 100-ml glass beaker. Resultant solution was fasten for 24 h within a 100-ml glass conical flask at 90 °C. The precipitate was centrifuged at 8000 rpm at room temperature and repeatedly washed with de-ionized water. Obtained white color semi-solid samples were dried for 12 h at 80 °C. In a similar way, by using homogeneous precipitation method, individual ZnO and MgO nanoparticles were prepared, where 0.58 g of ZnSO₄·7H₂O (or 0.49 g of MgSO₄·7H₂O) and 0.75 g of NaOH were added in 60 ml of DI water. Finally, white color powder nanoparticles were formed. Nanoparticles formation can be described by the following equations:

\[
\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{NaOH} \rightarrow \text{Zn(OH)}_2 + \text{NaSO}_4 + 6\text{H}_2\text{O} \\
\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{NaOH} \rightarrow \text{Mg(OH)}_2 + \text{NaSO}_4 + 6\text{H}_2\text{O} \\
\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{NaOH} \rightarrow \text{Zn(OH)}_2 \cdot \text{Mg(OH)}_2 + \text{NaSO}_4 + 4\text{H}_2\text{O} \\
\text{Zn(OH)}_2 \cdot \text{Mg(OH)}_2 \rightarrow \text{ZnO–MgO} + 2\text{H}_2\text{O}
\]

Pure ZnO and MgO nanoparticles were formed via reaction (1) and (2), and (3) and (4), respectively. ZnO–MgO nanocomposite was formed via reaction (5) and (6).

Powder X-ray diffraction data of nanocomposites were obtained using an X-ray diffractometer (Bruker AXS, Diffractometer D8, Germany) diffraction unit. Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet 6700, NEXUS, USA) was used to obtain FTIR spectra using KBr pellet technique. To understand the morphology of nanocomposite, a scanning electron micrograph (SEM) (QUANTA, Model 200 FEG, Netherland) was used. Conductive sample were prepared by gold coating using a sputter coater (Edwards S150). After gold sputtering, SEM and energy dispersive X-ray analysis was done using an EDX spectrometry. Shimadzu UV-2100 spectrometer was used to determine the UV–visible diffuse reflectance spectra (BaSO₄ reference material) within range of 200–800 nm.

Electrochemical experiments were carried out using CHI-760c, USA Potentiostat with three electrode single compartment cell setup. Pt wire, Hg/HgCl₂ and glassy carbon electrode (GCE) were used as counter, reference, and working electrodes, respectively; and all the potentials were measured vs. GCE. Electrode modification by obtained nanoparticles was an important part of the experiments. GCE electrode was polished with 0.3 micron alumina slurry and washed with DI several times. Nanoparticles modified electrodes were prepared...
by rubbing the ethanol wetted sample over the polished GCE surface and dried at room temperature. Above treatment adhered some amount of produced nanoparticle sample on GCE electrode surface.

3. Results and discussion

SEM micrographs (shown in Figure 1) were used to analyze the morphology of nanoparticles prepared by co-precipitation method. Figure 1(B) shows formation of ZnO–MgO nanoflakes (with a diameter of about 200–300 nm) whereas pure ZnO was flower shaped (Figure 1(A)). Elemental distributions of the corresponding nanoparticles were determined by EDX analysis as indicated by arrow line in the Figure 1. Results show the presence of three elements: Zn, Mg, and O within ZnO–MgO; whereas, ZnO comprise mainly two elements, Zn and O. Furthermore, to reaffirm the nanocomposite formation, point EDX analysis (Figure 2) of ZnO–MgO was performed. At a very low resolution, at four different points (red, green, blue and yellow circle) EDX data was taken. Analysis confirmed the presence of Zn and Mg elements at every point which signifies the incorporation of MgO crystal within ZnO nanoparticle. In other word, obtained sample is not a mixture of ZnO and MgO nanoparticles but is a nanocomposite.

Figure 3(a) shows FTIR spectra of synthesized ZnO and ZnO–MgO nanoparticles. Peaks at 3353.65 and
3440.43 cm⁻¹ represent the bending vibration of H₂O and presence of OH stretching in ZnO and ZnO–MgO, respectively. Peaks at 2933.24 and 2925.53 cm⁻¹ stipulate the presence of residual organic component in ZnO and ZnO–MgO, respectively. [21] Peaks at ~1513, 1417 and ~1564, 1388 cm⁻¹ stipulate the presence of metal carbonyl groups which has been possibly adsorbed at the surface of resultant nanoparticles. [22] Peaks in the range of 400–600 cm⁻¹ represent the characteristic metal–oxygen (M–O) vibrational modes. [22] Peak at 470 cm⁻¹ indicates the development of pure ZnO,[23] whereas in ZnO–MgO, the peak has been shifted at 491 cm⁻¹ stipulating the incorporation of MgO crystal within ZnO nanoparticles. [3] In Figure 3(a) (I), broad peak at 470 cm⁻¹ is due to pure ZnO, whereas in Figure 3(a) (II), the peak has been shifted to 491 cm⁻¹ indicating incorporation of MgO within ZnO nanoparticles. [3]

Composition and purity of nanoparticles (ZnO and ZnO–MgO) were determined by X-ray powder diffraction analysis (Figure 3(b)). All the diffraction peaks in Figure 3(b) (I) match with standard patterns of hexagonal structure of pure ZnO (JCPDS No. 01–079–0207) which is in agreement with the previously reported 2θ values. [24] Figure 3(b) (II) exhibits peak of cubic MgO (JCPDS No. 00–004–0821) along with ZnO, illustrating incorporation of MgO within ZnO.[11] XRD studies revealed a high degree of purity and crystallinity of nanoparticles.

Optical properties of pure ZnO and mixed metal oxide (ZnO–MgO) were analyzed by determining UV–visible diffuse reflectance spectra. Figure 4(a) shows the UV–visible absorption spectra of nanomaterials. Pure ZnO nanoparticle showed maximum ~55% reflectance in the visible region (410–800 nm) which is in agreement with previous literature. [25] Reflectance decreased by ~25% after incorporation of MgO with ZnO. The band gap energy (Eg) of the nanoparticles has been calculated using the following equations [26, 27]:

\[(h\nu\alpha)^{1/n} = A(h\nu - E_g)\]  

(7)

where, \(h\nu\), \(\alpha\), and \(E_g\) is photon energy, proportional constant, absorption co-efficient, and band gap energy, respectively. Exponent \(n\) has a values of 3, 2, 1.5, and 0.5 which represent indirect forbidden, indirect allowed, direct forbidden, and direct allowed transitions, respectively. [27, 28] Here, the exponent value has been taken as 0.5 as the nature of direct allowed transition in ZnO.

Further, the Equation (7) was modified with Kubelka-Munk function \(F(R) = (1 - R)^{2/2R}\) (where, \(R\) is the diffuse reflectance). [28] Hence, the equation has been written as:

\[(h\nu F(R)^{2})^{1/n} = A(h\nu - E_g)\]  

(8)

Using Equation (8), Tauc plot has been drawn to calculate band gap energy values of nanomaterial as shown in Figure 4(b). Analysis shows that ZnO–MgO nanocomposite exhibited band gap energy of 2.9 eV which is in agreement with literature. [29] The results show that the \(E_g\) value of pure ZnO has been increased from 2.75 [30] to 2.9 eV with metal doping. [31]

The cyclic voltammetry curve of pure ZnO electrode and ZnO–MgO nanocomposite electrode in 0.1 M NaOH electrolyte solution at a scan rate of 50 mV/s in the potential range ~-2 to +2 V has been shown in Figure 5. ZnO–MgO electrode showed reduction peak at around +1.7 V whereas, pure ZnO electrode has almost negligible reduction peak. As ZnO has no specific property of redox reaction like MgO, therefore, the pure ZnO has no response. [31, 32] At the positive end of the potential range, the peak current intensity and

| Sl No. | Zn (Wt %) | Mg (Wt %) | O (Wt %) |
|--------|-----------|-----------|-----------|
| Spot 1 | 71.1      | 11.68     | 17.23     |
| Spot 2 | 47.95     | 23.12     | 28.93     |
| Spot 3 | 75.12     | 16.35     | 8.53      |
| Spot 4 | 72.87     | 16.99     | 10.29     |

Figure 2. Point EDX spectra of ZnO–MgO nanocomposite were shown by green, red, blue, and yellow circle.
been observed for ZnO–MgO electrode than pure ZnO electrode, in other word, ZnO–MgO electrode shows better electrochemical performance.

4. Conclusion

In the present study, co-precipitation method has been used for the synthesis of ZnO–MgO nanocomposite. XRD analysis showed standard hexagonal wurtzite structure of ZnO accompanied by small signature of cubic MgO. The incorporation of MgO within ZnO has been confirmed by point EDX analysis. UV-DRS analysis exhibited that ZnO has a maximum reflectance of ~55% which has been decreased to ~20% in ZnO–MgO. Obtained band gap energy values of ZnO and ZnO–MgO were 2.75 and 2.9 eV, respectively. Higher electrochemical activity of ZnO–MgO nanocomposite than bare ZnO nanoparticle exhibited its possible utilization in various electronic devices.

Figure 3. (a) FTIR spectra (b) XRD spectra of nanoparticles. Note: Where, curve I and II represent the ZnO and ZnO–MgO, respectively.

Figure 4. (a) UV–vis diffuse reflectance spectra of (I) ZnO–MgO and (II) ZnO. (b) ($h\nu F(R)^2$ vs. photon energy plot (Tauc plot) of ZnO.

Figure 5. Electrochemical behavior of nanoparticle electrode in NaOH solution.

current signal increases drastically for ZnO–MgO electrode which signify the enhanced electric surface area of ZnO–MgO nanocomposite. Higher integrated area has been observed for ZnO–MgO electrode than pure ZnO electrode, in other word, ZnO–MgO electrode shows better electrochemical performance.
Disclosure statement
No potential conflict of interest was reported by the authors.

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