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ORIGINAL ARTICLE

EFFECT OF SOLVENTS ON THE STRUCTURAL, SIZE OF THE NIO/ZNO NANOCOMPOSITES BY THE WET CHEMICAL METHOD AND THEIR OPTICAL PROPERTIES

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ABSTRACT

The (NiO-ZnO) nanocomposite has been synthesized by the wet-chemical method using as solvents. The structural, optical and size of the NiO-ZnO samples have been characterized by XRD, UV, PL, SEM and TEM studies. The phase purity was confirmed by the XRD patterns. The prepared samples were calculated to average crystalline size of the different solvents such as organic and polar, were (22-48) and (34-76) nm, which were confirmed by the XRD results. The SEM and TEM reveal the information of almost spherical and aggregated spherical shaped NiO-ZnO samples. The UV-visible absorption peak was occurred at 353 nm with the band gap values of two different solvents were calculated to 3.62 and 3.54 eV and it could be used for optical devices. UV emission band were observed from the luminescence spectra at 350 nm. Hence, it should be suitable for optoelectronic devices.

Keywords: Semiconductor; Nanocomposites; Structural; Optical Properties

1.INTRODUCTION

Nickel oxide (NiO) is the most exhaustively investigated transition metal oxide. It is NaCl-type anti ferromagnetic oxide semiconductor. It offers promising candidature for many applications such as solar thermal absorber, catalyst for oxygen evolution, photo electrolysis and electro chromic device. Nickel oxide is also a well studied material as the positive electrode in batteries. NiO is a P-type semiconductor and its electrical conduction is almost entirely contributed from electron hole conduction. NiO is preferred for high electro chromic efficiency, low cost and high dynamic dispersion (Nguyen et al., 2014; Lin et al., 2011;Qi et al., 2016). Zinc oxide (ZnO) is n-type semiconducting metal oxide materials due of its tunable & multi functional morphological, photonic and spintronic, gas sensing and optoelectronics devices and it is a wide direct band gap of 3.37 eV (Zadi et al., 2016; Huang et al., 2010; Xuan et al., 2016; Behera and Chandra,2016; Horng et al., 2015; Huang et al., 2016). The synthesized of nanoscaled ZnO is dominated by physical and chemical process. The physical methodologies include thermal evaporation, chemical vapour deposition and molecular epitaxial and etc. Generally such process requires high vacuum and are energy consuming. While the chemical methods such as auto combustion, solvothermal, wet-chemical, reflux and hydrothermal processes. In this process ZnO is preferred for easy manipulation, low cost and high dynamic dispersion (Hana et al., 2016; Hana et al., 2016; Kumar et al., 2014; Hong et al., 2008; Wang et al., 2006; Sahoo et al., 2011;Mousa et al., 2013 Qu et al., 2016). The NiO/ZnO nanocomposites are predicted to show improved optical properties, viz., luminescence efficiency and band edge emission, with respect to the particle size and morphologies. The metal mixed semiconductor NiO/ZnO nanocomposites has also emerged because of the two metallic oxides are mixed, it might be useful for new applications in materials science, such UV-sensor, lithium batteries, gas sensor, UV photo detector and optoelectronics devices (Qu et al., 2016; Huang et al., 2015;Li et al., 2015;Echresh et al., 2015). The Composites have good potential for various industrial fields because of their excellent properties such as high hardness, high melting point, low density, high thermal conductivity and improved mechanical properties (Sahoo et al., 2011;Mousa et al., 2013 Qu et al., 2016). It has been reported that NiO/ZnO nanocomposites can be synthesized through hydrothermal, radio-frequency reactive magnetron sputtering, Electro spinning, MOCVD methods (Wang et al., 2015; Lia et al., 2015; Luoa et al., 2016; Longa et al., 2014). Among the

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various chemical synthetic methods for the preparation of metal oxides nanocomposites of a large surface area, a wet-chemical method offers several advantages viz, better homogeneity, high crystallinity, high-purity, high yielding powders.

The present work is to study the polar and organic solvents effect on the structural, size and optical properties of the synthesized NiO/ZnO nanocomposites by the wet chemical method. In addition, the possible mechanism of NiO/ZnO nanocomposite has also been proposed.

2.Experimental

In a typical experiment, 0.1M of nickel acetate tetra hydrate ($Ni(CH_3COO)_2{\cdot}4H_2O$) and zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) were separately dissolved in 50 ml of distilled water. All the chemical reagents were commercial with AR purity, and used directly without further purification. After dissolved completely, 3 ml of ammonia (NH_3) was added to the above solution. Then, the colloidal solutions were mixed and stirred for 60 min. The resultant mixed solutions washed with distilled water and absolute ethanol to remove the impurities, and dried at 120ºC for 1440 min. Then, light greenish coloured nanocomposites powder was obtained, when it was calcined at 500ºC for 120 min. The same procedure was followed for the preparation of NiO/ZnO by using organic as solvent.

$$Ni(CH_3CHOO)_2.2H_2O + 2NaOH \longrightarrow Ni(OH)_2 + 2CH_3COONa + 2H_2O \quad (1)$$

$$Zn(CH_3CHOO)_2.2H_2O + 2NaOH \longrightarrow Zn(OH)_2 + 2CH_3COONa + 2H_2O \quad (2)$$

$$Ni(OH)_2.Zn(OH)_2 \xrightarrow{\Delta} NiO/ZnO + 2H_2O \quad (3)$$

The prepared NiO/ZnO samples were characterized by the powder XRD, XPERT PRO with Cukα X-ray radiation (λ=0.15496 nm). The morphologies were carried out by the HR-SEM JOEL-JEM-2010 studies. The magnification images were observed by the TEM (Philips model CM 20) analysis. The absorption study of the prepared samples has been carried out by the Varian Cary 5E UV-vis spectrophotometer. The PL spectra of the (NiO-ZnO) samples were studied by the Fluoromax 4 spectrofluorometer, with a Xe lamp as the excitation light source.

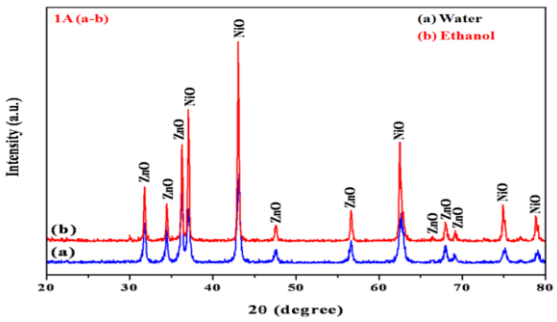
3. RESULTS AND DISCUSSION

Structural properties

Figure 1A (a) and (b) shows the XRD patterns of NiO/ZnO nanocomposites prepared in organic and polar, respectively. All the peaks in the XRD patterns could be indexed to the NiO/ZnO nanocomposites. The existence of strong diffraction peaks at 2θ values located at 73.78º, 43.10º, 62.64º, 75.92º, and 79.88ºcorresponding to (111),(200),(220), (311) and (222) cubic structure of NiO crystal planes (JCPDS No. 04-0850) (Fang et al., 2013) with diffraction peaks at 31.78º, 34.41º, 36.27º, 47.55º, 56.62º, 63.23º, 67.97º, 68.21, 72.5º and 77.1ºcorresponding to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) hexagonal phase wurtzite structure of ZnO crystal planes (JCPDS Card No. 36-1451), respectively (Fang et al., 2013). This fact indicates that the prepared samples are not a single phase but a composite. Moreover, no impurity such as $Ni(CH_3COO)_2$, $Ni(OH)_2$, $Zn(CH_3COO)_2$ and $Zn(OH)_2$ were detected, and the diffraction Peaks were indicates that the smaller crystallites size of the prepared NiO/ZnO samples (Lia et al., 2015; Luoa et al., 2016; Longa et al., 2014; Fang et al., 2013).

In any preparation of nanomaterials, the solvent is an important parameter for determining the crystal size. In the present work, the organic mediated samples (Fig. 1A (a)) shows broadening of diffracted peaks compared to the peaks of the aqueous mediated sample, as shown in Fig.1A (b). This clearly reveals that using organic media can produce fine particles and using Scherer's formula, the average crystallite sizes of the NiO/ZnO samples synthesized in organic and polar are found to be ~ (22-48) and (34-76) nm, respectively. From the result it's concluded that the organic mediated NiO/ZnO sample are most ultra-fine, owing to their best dispersing and capping ability.

Fig.1. 1A (a-b) XRD pattern of the NiO-ZnO samples calcined at 500 ^{0}C.

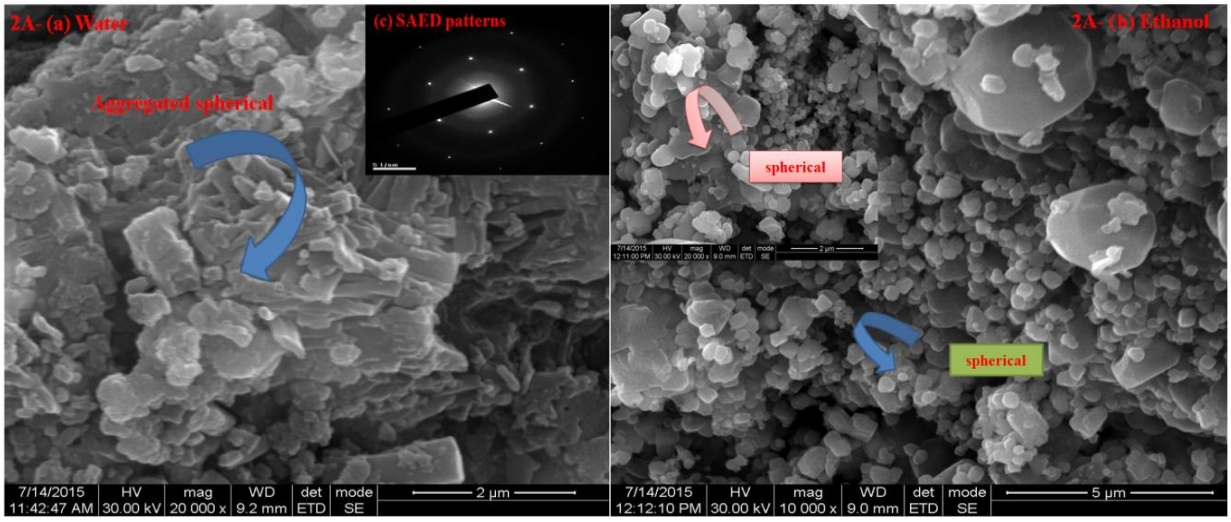


Topographical Properties

Figure 2A (a-b) shows the SEM images of the NiO/ZnO nanocomposites calcined at 500 ^{o}C with corresponding SAED patterns inserted left top corner of the figure 2A (c). This SAED pattern identifies the poly crystalline nature for the NiO/ZnO samples. It shows the samples are presented of spherical and aggregated spherical morphology in organic and polar. The average particle sizes of the NiO-ZnO samples were found to be ~22-48and 34-76 nm for respectively (Yuan et al., 2009; Cho et al., 2015), it is comparable with the average crystallite size calculated from the XRD result. It is clearly seen that organic have a crystallite size improvement compared to polar mediated sample. It could be observed from the figure that the nanocrystallite showed extra fine an agglomerated status (Huang et al., 2015).

Figure 3B (b) shows the HR-TEM image of as-synthesized NiO/ZnO nanocomposites calcined at 500 ^{o}C. The size of the spherical and aggregated spherical particles calculated from the Tem images were about ~22-48 and 34-76 nm corresponding to the NiO/ZnO nanocomposites samples, which was good aggrement with the lattice spacing of plane in the samples (Wang et al., 2014; Kumar et al., 2014). The spherical morphology with a highly foam-like structure, porous can be observed with the particle size of the nanoparticles was drastically decreased from ~22-48 nm (organic) and 34-76 nm (polar) by the preparation of NiO/ZnO samples. This is perfectly in agreement with the XRD analytical results, and indicates that the NiO/ZnO samples with small average particle sizes were well crystallized (Huang et al., 2015).

Fig.2. 2A (a-b) SEM images and of the NiO-ZnO samples calcined at 500 ^{0}C.



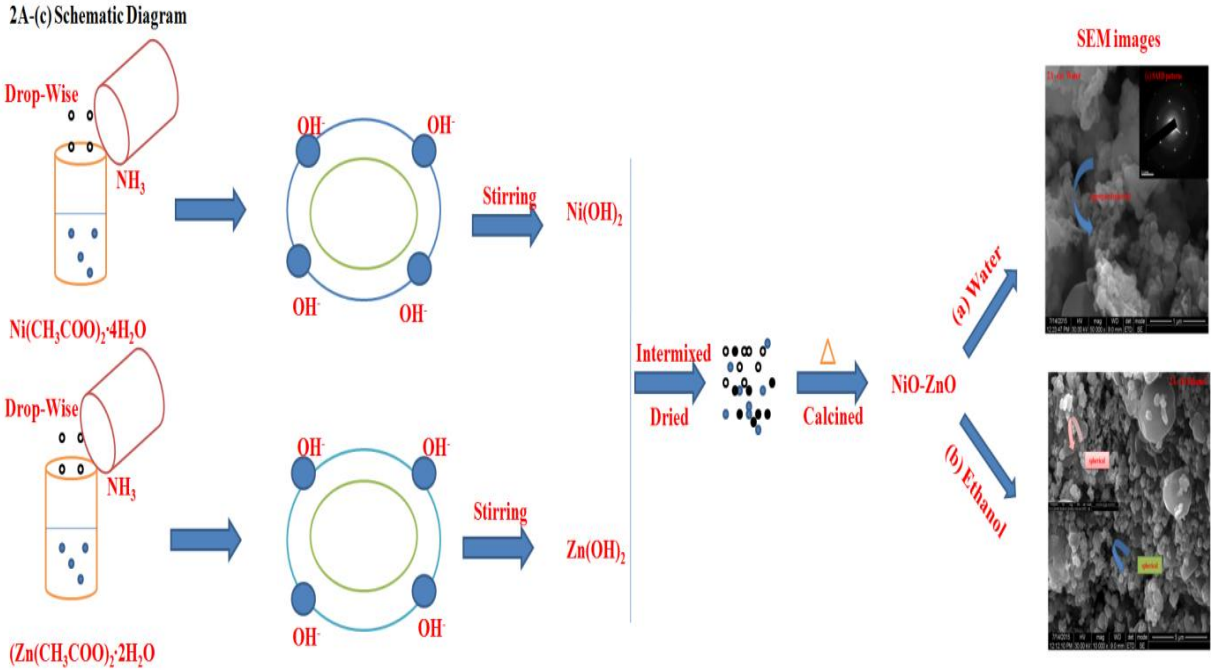


Fig.3. 3A (b) TEM (HR-TEM insert) image of the NiO-ZnO samples calcined at 500 ^{0}C.

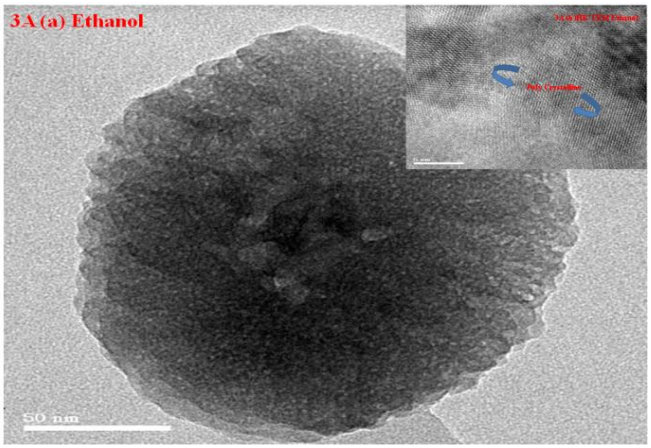


Fig.4. 4A (a-b) UV-visible absorption of the NiO-ZnO samples calcined at 500 ^{0}C.

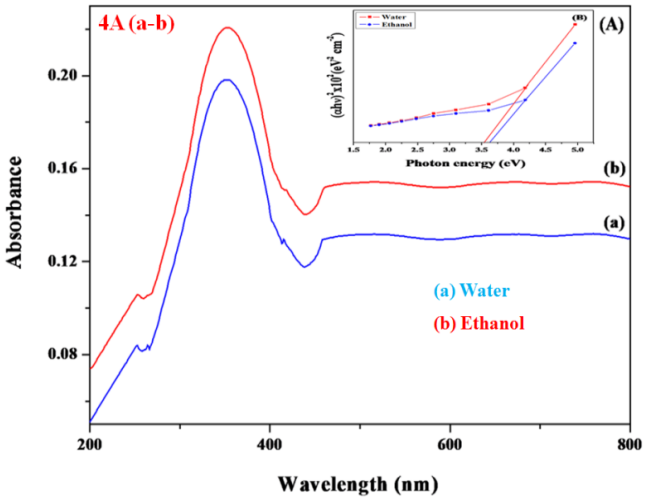
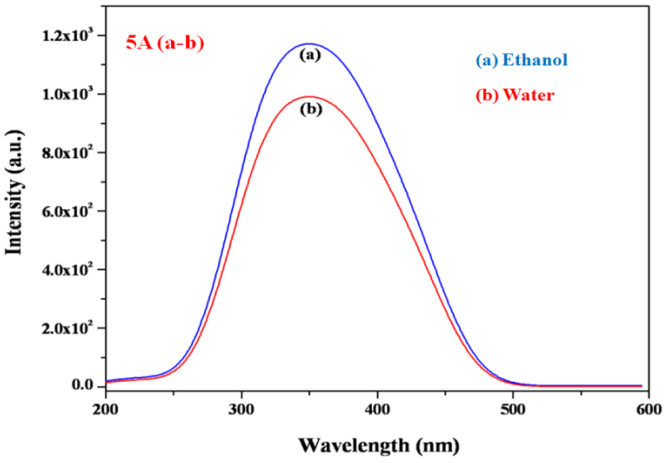


Fig.5. 5A (a-b) PL emission spectra of the NiO-ZnO samples calcined at 500 ^{0}C.



Optical Properties

Fig. 4A (a-b) shows the UV-visible absorption spectrum of the NiO/ZnO samples prepared in organic and polar, respectively. It can be seen in all the spectra that the strong absorption peaks were appeared at around 353 nm, which is attributed to the band gap absorption in NiO/ZnO [25] with the calculated values of the band gap energies of organic and polar mediated NiO/ZnO samples are 3.62 and 3.54 eV respectively, which are good agreement with reported band gap values of NiO/ZnO samples. The appearance of two kinds of characteristic bandgap values also confirms that the NiO-ZnO sample is a composite material composed of NiO[1-3] and ZnO (Zadi et al., 2016; Huang et al., 2010; Xuan et al., 2016; Horng et al., 2015; Huang et al., 2016).

According to the data of the absorption spectra, the optical band gap (E_g) of the NiO/ZnO samples can be estimated, by using the following equation:

$$\alpha h\nu = C\,(h\nu - Eg)^n.$$

α - is the absorption coefficient; $h\nu$-is the photon energy, C-is the constant, n=1/2 for a directly allowed transition (Aslania et al., 2011). For the indirect transitions, the plots of $(\alpha h\nu)^2$ versus photon energy of the NiO/ZnO samples are shown in Fig. 4A (a-b). Hence, the optical band gap for the absorption peak can be obtained by the linear portion of the $(\alpha h\nu)^2$-$h\nu$ curve (Qu et al., 2016; Huang et al., 2015;Li et al., 2015;Echresh et al., 2015; Wang et al., 2015; Lia et al., 2015).

Photoluminescence (PL) Properties

Fig. 5A (a-b) shows the room-temperature PL emission spectra of organic and polar mediated NiO/ZnO samples were measured at 300 nm excitation wavelength. The nanocomposite samples exhibit strong as well broad UV emission at 350 nm, which can be attributed to the near band edge emission that comes from the free hole–electron pair transition (Zhao et al., 2014). The emission peak also decreases with increase in crystallite size as resulted from UV-visible absorbance spectrum and indicating that the prepared NiO-ZnO samples have a good quality of the crystal (Aslania et al., 2011). Since, it was observed from the PL emission spectra that there was a change in the intensity of the emission peak by the alcoholic medium mediated sample (Fig. 5A (a)) than that of aqueous medium, which lead us to conclude that the alcoholic solvents changed the crystalline size or increased the intrinsic and surface defect (Mousa et al., 2013 Qu et al., 2016; Huang et al., 2015;Li et al., 2015).

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