HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF ZnO, MgO AND ZnO/MgO NANOCOMPOSITES

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ABSTRACT

Nano Zinc oxide (ZnO) with different morphologies including spherical-like, granular shapes, have been hydrothermally synthesized at low temperature at 100°C using stainless steel autoclave. It was found that the volumes of added Sodium hydroxide and Zinc acetate dihydrate in water play a crucial role in the morphological control of ZnO nanostructure. Based on structural information provided by FTIR, XRD and SEM, a possible growth mechanism for the formation of spherical ZnO structures was discussed. The optical properties of the synthesized nanoparticles were studied by Ultraviolet-visible spectroscopy and strong absorption peaks at 279 nm for all synthesized nanoparticles. From that study, the band gap was also calculated and it was 3.79, 3.64 and 3.55 eV respectively for ZnO, MgO and ZnO/MgO nanocomposites. Nanoparticles of MgO are prepared by using the sol-gel route. The MgO nanograins were sphere-like and needle-like and had a large surface area. The grain size was obtained using XRD data. The X-ray diffraction patterns revealed the formation of nanoparticles of MgO. The structural morphology and optical properties of the nanoparticles were studied using SEM. The formation of the nanostructure is confirmed using FTIR. A process was proposed for the synthesis of ZnO/MgO nanocomposites using sol-gel preparation of ZnO and magnesium with an alkali solution following by annealing in the range of 400°C. X-ray powder diffraction showed crystalline ZnO and MgO phases in the resulting composite. The zinc oxide nanoparticle size was weakly affected by the molar ratio of zinc to magnesium.

Keywords: ZnO, MgO, XR-D, FT-IR, Hydrothermal, Nanocomposites

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INTRODUCTION

The optimum preparation of nanoparticles was perilous for the production of nanotechnologies regarding the shape and size. Particularly Zn-O nano-systems, such as nanowires, nanobelts and thin-films can be simply shaped by physical or chemical methods such as chemical vapor deposition, pulsed laser-deposition, sol-gel process, thermal-annealing method and solvothermal analysis. Zn-O has polar surfaces that help in the production of a wide range of nanomaterials such as nanowires, nanobelts and thin-films rings, springs, bows and helices.¹ Zn-O has established substantial care since of its unique optical, semi-conducting, piezo-electric and magnetic properties. Zn-O nanostructures show remarkable properties such as large catalytic effect and sturdy adsorption capacity. The array of morphologies such as rods, tubes, rings, tetra-pods, spirals is the field of Zn-O that produces the base of its versatile applications. MgO has spacious structures, which can carry a great deal of effective catalytic compositions to form a carrier compound catalyst. Based on the technology for the preparation of Nano MgO, a new technology to produce nano-MgO under simple conditions. Alkaline earth metal-oxides are well known for their fundamental characteristics. Although Mg-O displays the most fundamental characteristics of this group,

no acid property have ever been inspected in detail.² Zn-O/Mg-O nanoparticles can be used as the photo-catalyst for the degradation of effluents, electrode nanomaterials in super-capacitor, antibacterial agent and microwave absorbing materials. Numerous skills for synthesizing Zn-O and Mg-O nanomaterials have been described, like alkoxide-hydrolysis, gas-phase thermal-decomposition, core-sheath and micro-emulsion technologies.³

EXPERIMENTAL

Preparation of Nano-ZnO

0.5 g of zinc acetate dehydrate $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 110 ml of deionized water under 10 mins vigorous stirring. Subsequently, the dissimilar solution, 10ml of Sodium hydroxide (2 molar) was presented in it, resultant in a slurry white-precipitate produced. Afterward, five mins stirring, the solution was transported into a stainless-steel auto-clave of 200 ml volume and closed. The auto-clave was continued at 100°C for 5 hrs and cooled in the air at room temperature. The resultant colorless products were centrifuged, cleaned then rinsed with dehydrated water and ethyl alcohol many times to eliminate the ions probably residual in the last product and dried at 70°C in air.

Preparation of Nano-MgO

Magnesium chloride (0.5 mol) and sodium carbonate (0.5 mol) were dissolved in 100 ml deionized water separately. Under room temperature, the 100 ml of Na_2CO_3 solution was slowly added to the MgCl_2 solution with stirring to obtain $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. After the vigorous stirring, the products were transferred into a Teflon-lined stainless steel autoclave. Sealed and hydrothermally treated at a constant temperature of 60°C . The products were aged for 3 to 96 h. After filtration, the precipitated particles were washed with distilled water and ethanol several times and drying the products were calcined for 2 hours at 200°C to get nano MgO.

Preparation of Nano-ZnO/MgO composites

Solutions were prepared by dissolving 0.5g of zinc acetate dihydrate in 110 ml of dehydrated water under 600 seconds by forceful stirring. Formerly 10 ml of sodium hydroxide (2 M) solution was added into that solution and the solution is kept at 100°C for 5 hrs. MgCl_2 (0.5 mol) and Na_2CO_3 (0.5 mol) were dissolved in 100 ml deionized water. These two solutions were slowly mixed to get $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and this solution was added to the first solution in drop-wise and dried at 150°C to get ZnO/MgO nanocomposite.

RESULTS AND DISCUSSION

ZnO NPs

The X-Ray Diffraction spectra of the synthesized nanomaterials are shown in Fig.-1. All the diffraction peaks are confirmed with JCPDS- No 361451, which can be indexed to the structure of hexagonal-wurtzite Zn-O. The strong, sharp peaks specify that the Zn-O nanomaterials were well crystallized. The nano-size of the nanoparticles was determined by following Debye-Scherrer's formula.

$$D = 0.9\lambda / \beta \cos\theta \quad (1)$$

From the eqn.-1, Where D is crystallite-size, λ is the X-ray-wavelength, β is the full-width at half maximum (FWHM) and θ the half diffraction angle. The nanosize of the synthesized nanomaterials calculated using FWHM.

Fig.-1: The XRD pattern of synthesized (a) nano ZnO (b) nano MgO and (c) ZnO/MgO Nanocomposites

Table-1: Particle Size estimated from the Diffraction Spectrum of ZnO, MgO and ZnO/MgO by using full width half maximum (FWHM)

NPs	Pos. [°2Th.]	FWHM [°2Th.]	d-spacing [Å]	Particle size
ZnO	20.6070	0.1624	4.30666	
	21.1017	0.3767	4.20680	49.75
	31.7168	0.2223	2.81892	21.46
	32.2752	0.2204	2.77141	37.17
	36.2111	0.3289	2.47869	37.55
	37.8471	0.1952	2.37522	25.43
	39.4328	0.2219	2.28328	43.05
	40.2274	0.2581	2.23999	38.05
	46.2716	0.3002	1.96049	30.82
	47.5163	0.3934	1.91199	28.79
	51.9470	0.3629	1.75885	22.08
	61.5732	0.3442	1.50496	24.37
MgO				26.88
	15.4289	0.2689	5.73839	29.83
	21.3730	0.2720	4.15400	29.74
	23.4882	0.5796	3.78450	14.01
	25.5503	0.4588	3.48354	17.76
	27.0762	0.5220	3.29059	15.66
	30.9597	0.4331	2.88610	19.04
	33.4133	0.4854	2.67957	17.10
	39.2598	0.5674	2.29294	14.87
	41.0206	0.6017	2.19850	14.10
ZnO/MgO	47.1339	0.4798	1.92661	18.08
	15.3311	0.3657	5.77478	21.93
	21.2522	0.3312	4.17735	24.42
	45.4803	0.3462	1.99274	24.90
	75.3208	0.3428	1.26076	29.29

Characteristic FT-IR spectra of Zn-O were revealed in Fig.-2, in which the peak at 3403 cm^{-1} was assigned to the O-H stretching vibration. Symmetric C=O stretching of zinc acetate dehydrate at 1543 cm^{-1} , C-H out-of-plane bending group at $898\text{--}865\text{ cm}^{-1}$ O-H bending of hydroxyl group at 558 cm^{-1} and ZnO stretching of ZnO at 420 cm^{-1} .⁴ Figure-3(a, b, c) shows the SEM images of the synthesized nanoparticles. From the figure. one can observe that the products are mainly composed of spherical nanostructures. From Fig.-3(b) displays some imperfect micro-spheres also exist in the products are observed in $5\text{ }\mu\text{m}$. The ZnO nanoparticles have spherical structures. In SEM figure ($1\text{ }\mu\text{m}$ and 500 nm) a large number of granular shapes are found.

Fig.-2: FT-IR Spectrum of synthesized (a) nano ZnO (b) nano MgO and (c) ZnO/MgO Nanocomposites

MgO NPs

MgCl₂ solution reacts with Na₂CO₃ solution to produce MgCO₃ · 3H₂O, if the reaction temperature is high, it would favor forming a large number of the core in a short time. It makes the cores do not have enough time to grow up. So, MgCO₃ · 3H₂O in larger size could not be obtained, this is unfavorable to the further reaction to getting MgO. The aging time also affects the grain size of MgCO₃ · 3H₂O. The axis and length of MgCO₃ · 3H₂O were increased as the aging time was prolonged. MgO showed amorphous X-ray diffraction patterns as reported by Bokhimi et al., 1995, where the evaluation of the crystalline structure is chiefly related to the calculations hours. All diffraction peaks of MgO could be indexed as the hexagonal structure (Fig.-1b) confirmed by JCPDS card No 40829. From X-Ray Diffraction, peaks arising from impurities were spotted. Therefore, the preparation phase agrees to pure MgO, suggesting a comprehensive synthesis reaction. Total development of the intensity of the XRD peaks is a visible indication that the upsurge in crystallinity of nanomaterials after hydro-thermal reaction⁶. The particle size of nano MgO was 19.01nm. Figure-2(b) shows infrared spectra of MgO. Characteristic MgO hydroxyl stretching vibration bands are observed at 3689-3629 cm⁻¹. The absorption bands due to CH₂ bending and symmetric C-O-C stretching of MgO at 1483 and 1120 cm⁻¹. C-C out of the plane and C-H bending vibration of MgO at 715 and 668 cm⁻¹. The SEM micrograph in Fig.-3(a, b, c) demonstrates that, during magnesium chloride calcination at 200°C, the globular-like structure of the particles persists in 10 μm. Even though it is a non-equilibrium shape for MgO was observed for 4 μm and 2μm (Fig.-1). At 2 μm the irregular flake-like structures were observed.

ZnO/MgO NPs

The X-ray diffraction pattern of the nanocomposite is presented in Fig.-1(c). The peaks at 21.10° and 51.94° are attributed to standard diffraction of wurtzite ZnO peaks and also cubic MgO peaks at 75.32 in the detection limit. The MgO structure (with Miller indices 111, 110, 102, (JCPDS card No 74-1225) and those associated with zinc oxide (Wurtzite indices 100, 002, 101 and 110 (JCPDS card no 79-205). The unit cell parameters for MgO and ZnO phases almost coincide with the literature values. This means that, there are no noticeable interactions between the magnesium and zinc oxides at this low annealing temperature. In this work, the effect of concentration of the precipitated component and the zinc-to-magnesium molar ratio on the zinc oxide nanoparticle size.⁷

Fig.-3: SEM images of ZnO (a), MgO (b) and ZnO/MgO (c) Nanocomposites

There are no systematic variations in the crystallite size as a function of that treatment. This result indicates the co-existing of ZnO and MgO in the composites.^{8,9} The X-ray diffraction patterns of the corresponding composite in Fig.-1c indicate that besides ZnO, there still exists zinc acetate dehydrate and magnesium chloride. This fact indicates that the nanocomposites are not a single phase but a composite. The particle size of ZnO/MgO nanocomposites was 25.13nm.¹⁰ Figure-2 shows the infrared spectra for ZnO/MgO nanocomposites. The spectra are more similar to those of MgO. The pronounced peaks at 3628 cm⁻¹ are also observed in ZnO/MgO and suggest that the surface may be composed mainly by MgO. The symmetric C=O stretching of ZnO at 1635 cm⁻¹. The hydroxyl bands at around 1500 cm⁻¹ also support this hypothesis.¹¹ The coverage of ZnO particles by MgO can be observed by SEM. A typical SEM micrograph in Fig.-3(a, b, c) shows the several nanospheres connected. When comparing the micrograph

of ZnO and MgO, one may suggest, by observing the particles morphologies, shows a ZnO particle with small MgO ones located around it. The MgO particles are tightly attached since an electrostatic interaction between ZnO and MgO is expected. Figure-3(a) reinforces this hypothesis showing a micrograph using lower magnification to observe a larger number of particles. Note that the surface of the observed particle is rough (and not smooth as MgO particles) in Fig.-3(b) probably due to the adhesion of the smaller porous MgO particles on the surface of ZnO. The inset of Fig.-3(c) indicates that the nanospheres grown on the inside surface of the sphere appear to be needle-like, and their diameters decrease from the root to the tip.¹² Figure-4 evinces the Ultraviolet-visible spectroscopy of the nano ZnO, nano MgO and ZnO/MgO nanoparticles. From this, all spectra show that strong absorption peaks at 279 nm, which is accredited to the absorption in ZnO/MgO nanoparticles. From that data, the optical band gap (E_g) of the synthesized nanoparticles can be calculated using the below equation:

$$\alpha h\nu = C (h\nu - E_g)^n \quad (2)$$

Where α -absorption coefficient, $h\nu$ - Photon energy, C - Constant and $n=1/2$ for a directly allowed transition and it was 3.79, 3.64 and 3.55 eV respectively, which are good agreement with conveyed of ZnO/MgO nanoparticles band gap values.

Fig.-4: UV-Visible Spectroscopy of nano ZnO (a), nano MgO (b) and (iii) ZnO/MgO (c) nanoparticles

CONCLUSION

In summary, a simple hydrothermal technique without the addition of any surface-active agent and polymers was put forward to prepare Zinc oxide nanocomposites. A uniform Zn-O nanosphere is detected from several magnifications 10 μm , 5 μm , 4 μm , and 3 μm . The aforementioned is the hydrothermal process zinc-acetate dihydrate reacted with sodium hydroxide to produce a complex, and the complex gradually disintegrated in the hydro-thermal process. All these features are promising to this condiments-free hydro-thermal development of ZnO nanocomposites. The preparation route to Zinc Oxide nanoparticles was capable of enormous scale and cheapest method of production of Zn-O nanomaterial. A technique is developed for the synthesis of MgO nanocomposites via MgCl_2 and Na_2CO_3 form a solution. The particle shape is shown to persist during magnesium chloride conversion to magnesium oxide. The calculations hour is too high, the products would be easily sintered and the surface area and activity of MgO would be declined. The ZnO/MgO nanocomposites are successfully produced by the hydrothermal process. The XRD patterns show the hexagonal phase of ZnO and the cubic phase of MgO. The sizes and the morphology of ZnO spheroidal and hexagonal particles were found to be from 21.46-49.75 nm, whereas those of MgO spheroidal and flake (or) rectangular particles are in the range of 14.10-29.83 nm. ZnO and MgO nanocomposites are found to approximately 21.93-29.29 nm.

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