Surface characteristics and structural properties of sol-gel prepared ZnO-SiO₂ nanocomposite powders

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Abstract. Zinc oxide-silica (ZnO-SiO₂) composite powders with different surface morphologies were synthesized via sol-gel process using rice husk ash as silica source. Micrograph results revealed the surface modification of bare ZnO from hexagonal tips to hemispherical tips after incorporation of SiO₂ to ZnO. After annealing at 400 and 500 °C, the hemispherical tips became more apparent due to the removal of the flaky particles associated to the complexes of zinc. Annealing the sample powders to 600 °C sharp tips was observed on the morphology of ZnO-SiO₂. Infrared spectroscopy further support that SiO₂ was incorporated to ZnO due to the Si-O-Zn band observed in the IR spectra. X-ray diffraction results verify the presence of amorphous SiO₂ and the polycrystalline nature of the samples having particle size in nanometer scale. Furthermore, diffraction spectra show that thermal annealing removes the zinc complexes resulting to more pronounced hemispherical tips of ZnO-SiO₂.

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor that acquired great interest due to its attractive properties such as 3.37 eV wide band gap [1], large exciton binding energy (60 meV), good piezoelectric characteristics and good optical and electrical properties [2]. It has potential applications in the field of optoelectronics for making devices like photodetectors, light emitting diodes, electroluminescence devices, solar cells, flat cathode ray tubes [3] and short wavelength devices [4]. However, the photocatalytic activity of ZnO [5] and its poor compatibility to organic compounds that makes it to agglomerate in organic solution [6] are just some problems that hinder some potential applications of ZnO. Fortunately, these disadvantages of ZnO are avoidable through the process of surface modification [7] and this can be achieved by coating ZnO particles by surface modifiers like alumina and silica. But silica is given much attention by most scientists due to its important properties such as high transparency for visible light, low chemical activity and compatibility to ZnO [5].

Various methods were used to incorporate SiO₂ to ZnO such as double jet precipitation [8, 9], hydrolysis method [10], sonochemical synthesis [11], and spray drying [4]. However it is difficult to obtain small size and large scale production of incorporated material with these techniques due to the need of faster chemical reaction. On the other hand, the chemical solution (sol-gel) process is of great

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advantage due to its capability to mass produce and the chemical reaction can be controlled and is a low cost method [12].

Different studies have been reported in the preparation of ZnO-SiO₂. The group of K. Han studied zinc oxide coated with silica for its application as interconnector or nanoelectronic devices and biochemical capsules [13]. Eunice S., et al. performed random laser action in SiO₂/ZnO composite films which consist of ZnO clusters placed on silica matrix [14]. The coating of SiO₂ on ZnO is also applied to protect organic material from the photocatalytic reaction of ZnO where the effect of polyelectrolyte dispersants for obtaining uniform composite particles is studied by Wang, H., et al [15]. However in their studies they used tetraorthosilicate (TEOS) as a source of their silica which is very expensive and very toxic chemical.

In this particular work, we incorporated SiO₂ extracted from rice husk ash (RHA) to ZnO using sol-gel process for the synthesis of ZnO-SiO₂ composite material. We present the effects of SiO₂ to the morphology of bare ZnO and the effects of thermal annealing to the surface morphology and structural characteristics of the composite powders.

2. Experimental methods
The ZnO-SiO₂ composite powders were synthesized through sol-gel process. A solution of 0.03 M zinc sulphate (ZnSO₄) and 2.0 M ammonium hydroxide (NH₄OH) together with amorphous SiO₂ powders were magnetically stirred in a beaker for 30 minutes and the pH of the solution was measured. After 30 minutes the solution was heated and constantly stirred for 5 hours with bath temperature maintained at 70°C. After 5 hours of stirring and heating, the solution with the precipitates was cooled at room temperature (25°C). The powders were filtered and washed with distilled water in order to removed unnecessary residues present in the powders. The sample powders were thermally annealed at 400°C, 500°C and 600°C in a furnace keeping as-grown (un-annealed) powder as control sample. The morphological characteristics of the samples were studied using JEOL JSM-6510LA analytical scanning electron microscope and the structural characteristics of the powders were analysed by X-ray diffraction (XRD) using CuKα1 radiation (λ=0.154 nm) at 0.010 increment per step and by Perkin Elmer Spectrum 100 infrared spectrometer for functional groups determination.

3. Results and discussions
3.1. Surface morphology
Figure 1 shows the micrographs of bare ZnO and as grown ZnO with SiO₂ from RHA. The bare ZnO rods show hexagonal tips, but upon adding SiO₂, the surface of hexagonal ZnO was modified to hemispherical tips. Since all the growth parameters were held the same for both samples, it is very apparent that SiO₂ from RHA modified the surface structure of ZnO. SiO₂ possibly capped the surface of the ZnO nanorods. Also observed in the figure are some flaky particles associated to the complexes of zinc.

As the ZnO-SiO₂ composite powders were annealed at 400°C, 500°C and 600°C, more apparent hemispherical tips were observed. Annealing the samples at 400°C and 500°C, flaky particles present in the as-grown ZnO-SiO₂ were removed and the tips of the nanorods are more pronounced hemispherical tips, which further suggest the dissociation of the weakly bonded zinc complexes (zinc sulphate and zinc hydroxide) as seen in figure 2 (a) and (b). However, annealing the sample at 600°C, a disintegration of the nanorods was observed. The hemispherical tips were modified to sharp tips with remarkable decrease of the diameter of the nanorods after thermal annealing at this elevated temperature. It can be said from the surface properties of the samples that the formation of the hemispherical tips depends on the chemical activity on the surface, which relies on the concentration of the OH⁻ groups and the presence of the silanol (Si-OH) and siloxane (Si-O-Si) functional groups of SiO₂ that act as the center of molecular adsorption. The functional groups of silica were formed during the synthesis through rehydroxylation process inside an aqueous solution allowing it to bind with the Zn(OH₂), which is the seed nuclei for the formation of ZnO nanorods. The resulting hemispherical tips
evidently show the integration of amorphous SiO$_2$ at the surface of ZnO allowing for the formation of ZnO-SiO$_2$ composite powder with SiO$_2$ capping the surface of ZnO.

**Figure 1.** SEM micrographs of (a) as grown bare ZnO powder and (b) as grown ZnO-SiO$_2$ composite powder.

**Figure 2.** SEM images of ZnO-SiO$_2$ composite powder annealed at (a) 400°C, (b) 500°C, and (c) 600°C.
To supplement the morphological result on the capping of SiO$_2$ at the surface of ZnO, FTIR spectroscopy was done on the samples. As presented in figure 3, the presence of characteristic peaks of amorphous SiO$_2$ in as-grown and annealed samples is observed. These peaks are found at 961 cm$^{-1}$ for Si-OH stretching, 1099 cm$^{-1}$ for Si-O-Si asymmetric stretching 471 cm$^{-1}$ for Si-O-Si bending and 803 cm$^{-1}$ for Si-O-Si symmetric stretching. The broad band at 3476 cm$^{-1}$ is attributed to the O-H stretching vibration. The appearance of absorption band at 933 cm$^{-1}$ in the IR spectra is associated to the Si-O-Zn absorption band which confirms that SiO$_2$ indeed binds with ZnO. The Si-O-Zn band weakens as the annealing temperature increases from 500°C to 600°C and along with it is the appearance of Si-OH stretching and ZnO$_4$ (605 cm$^{-1}$). Noticeable also is the shifting of Si-O-Si asymmetric stretching band to a lower frequency at temperatures 500°C and 600°C. The shifting of Si-O-Si asymmetric stretching band is probably due to the bonding change around the SiO$_4$ tetrahedral and can be directly associated to the binding of ZnO and SiO$_2$ causing the hemispherical tips formation. The presence of peaks corresponds to Si-O-Zn bond and ZnO$_4$ at 500°C and 600°C suggests a possible formation of zinc silicate (Zn$_2$SiO$_4$). This might be the reason also for the change in surface morphology of ZnO with amorphous SiO$_2$ sample when annealed at 600°C. Further investigations are being done to support this effect.

**Figure 3.** FTIR spectra of ZnO, SiO$_2$ and ZnO-SiO$_2$ composite powders at different annealing temperatures.

### 3.2. Structural characteristics

Figure 4 shows the diffraction patterns of amorphous SiO$_2$ and the polycrystalline nature of as grown ZnO-SiO$_2$ and ZnO-SiO$_2$ powders annealed at temperature range of 400-600°C. The ZnO-SiO$_2$ powders exhibit strong 2$\theta$ peak centred at 31.74 which corresponds to the (101) peak of highly c-axis oriented wurtzite ZnO. The sample also has other peaks which correspond to (002), (102) planes, etc., which may be attributed to the rodlike nature of the samples as observed in the micrographs result. Furthermore, the presence of Zn(OH)$_2$, Zn(HSO$_4$)$_2$ and ZnSO$_4$$\cdot$H$_2$O for the as-grown ZnO-SiO$_2$ powder were observed indicating that the as-grown powder is indeed composed of zinc complexes while annealing the samples at 400-600°C shows the removal of these complexes supporting our results in the SEM images. Additionally, investigation on the XRD patterns of the sample showed that as the ZnO-SiO$_2$ powders were annealed, the full width at half maximum (FWHM) of the (101) plane decreases which indicate increase of crystallinity of the samples. However, it is worth noting that even without annealing the as-grown ZnO-SiO$_2$ exhibits high crystallinity.
Figure 4. X-ray diffraction spectra of amorphous SiO$_2$ and ZnO-SiO$_2$ composite powder at varying temperatures.

Figure 5 (a) shows the dependence of the FWHM at the (101) plane to annealing temperature. To further determine the effect of SiO$_2$ and annealing temperature to the structural characteristics of ZnO, we calculated the lattice parameters of the samples. The calculated lattice parameters were slightly greater than the standard lattice parameter of wurtzite ZnO may be due to the attachment of SiO$_2$ to ZnO that results to the realignment of ZnO atoms onto SiO$_2$ atoms. Figure 5 (b) shows the plot of the difference between the standard lattice parameters of ZnO and calculated lattice parameters of the ZnO-SiO$_2$ powders. The calculated particle sizes ranges from 13.62 nm to 24.24 nm which clearly shows that the synthesized powder samples are in nanometer scale. These samples have promising potential applications in nanotechnology like in sensor technology.

4. Conclusions
Nanocomposite powders of ZnO-SiO$_2$ were successfully synthesized through sol-gel process. The surface properties based on SEM images showed that the tips of ZnO-SiO$_2$ powders were hemispherical, far different from bare ZnO which is hexagonal in form. Infrared spectra show the
functional groups of SiO₂ and Si-O-Zn absorption band indicating the attachment of SiO₂ to ZnO. XRD analysis affirmed that the composite powder was polycrystalline and were indexed to wurtzite nature of ZnO with strong peak at (101) plane suggesting the c-axis orientation of the nanorods with hemispherical tips due to SiO₂ capping. Annealing the samples removes the complexes of zinc and made the sample more crystalline indicative of the decrease of full width at half maximum. The particle sizes ranges from 13.62 nm to 24.24 nm which can be a promising material for nanotechnology applications.

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