Surface modification of nanostructured hexagonal ZnO powder using amorphous silica powder via low temperature sol-gel process

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INTRODUCTION

Over these past decades, zinc oxide (ZnO) nanoparticles were given a lot of interest by many scientists and researchers because of its fascinating physical and chemical properties compared to its bulk form. In fact, ZnO was exploited in the field of optoelectronics for making devices like photodetectors, light emitting diodes, electroluminescence for making devices like photodetectors, light emitting diodes, and solar cells (Xiang, J., et.al., 2006) flat cathode ray tubes (Lu, Y., et.al., 2000) and short wavelength devices (Wang, Y., et.al., 2003). However, not much interest was given to ZnO in the field of industry and cosmetic due to its photocatalytic activity and poor compatibility to organic compounds that makes it to agglomerate in organic solution. Fortunately, these limitations of ZnO can be averted through the process of surface modification (Cao, Z., et.al., 2010). On this process, ZnO nanoparticles were coated with surface modifiers like alumina and silica (SiO2) in order to alter its physical and chemical attributes resulting to improved properties. But silica is preferable due to its interesting properties such as high transparency for visible light, low chemical activity and compatibility to ZnO (Cao, Z., et.al., 2009).

Different techniques were employed in order to prepare SiO2 modified ZnO. Some of these are double jet precipitation (Xia, X., et.al., 2003 and Tang F., et.al., 2003), hydrolysis method (Abdullah, M. et.al., 2004), sonochemical synthesis (Sounderya, N., et.al., 2008), and spray drying (Wang, Y., et.al., 2003), to name a few. But due to complexity and a need of faster chemical reaction of these techniques, it is very difficult to obtain small size and a large scale production of composite material. On the other hand, sol-gel method is of great advantage due to its capability to mass produce and the chemical reaction can be controlled and it’s a low cost method (Cui, H., et.al., 2009).

Different studies have been reported in the preparation of SiO2 and ZnO as composite. The group of K. Han studied zinc oxide coated with silica for its application as interconnector or nanoelectronic devices and...
biochemical capsules (Han, K., et al., 2007). Eunice S., et al. performed random laser action in SiO2/ZnO composite films which consist of ZnO clusters placed on silica matrix (Leong, E., et al., 2004). 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 (Wang, H., et al. 2002). However in their studies they used tetraorthosilicate (TEOS) as a source of their silica which is very expensive and very toxic chemical.

In this work, investigation on the effects of incorporating crystalline and amorphous SiO2 from rice husk ash (RHA) on the surface morphology of as grown hexagonal ZnO powder is reported. Variation in the mass of SiO2 was employed in order to determine their effects on the surface of ZnO. The samples underwent several characterization techniques like scanning electron microscopy (SEM), energy dispersive X-ray (EDX), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction.

**MATERIALS AND METHODS**

A solution of 0.03M zinc sulphate (ZnSO4) and 2.0 M ammonium hydroxide (NH4OH) together with crystalline and 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 with bath temperature maintained at 70°C. After constant stirring and heating, the solution with the precipitates was cooled at room temperature. The powders were filtered and washed with distilled water in order to removed unnecessary residues present in the powders. The sample powders were then air dried. The morphological characteristics of the samples were studied using JEOL JSM-6510LA analytical scanning electron microscope and the crystal phase of the powders were analyzed by X-ray diffraction (XRD) using CuKα1 radiation (λ=0.154 nm) at 0.010 increment per step. Perkin Elmer Spectrum 100 infrared spectrometer was used for functional groups determination.

**RESULTS AND DISCUSSIONS**

A. **Effects of silica powders to the surface morphology of ZnO through SEM:**

Scanning electron micrographs showed the difference between amorphous and crystalline in terms of their surface attributes. Crystaline SiO2 possesses spherical shape of diameter ranges from 1.8 to 2.0 µm, but amorphous SiO2 does not have uniform size and shape as observed in Figure 1. Chemically synthesized ZnO powders have nanorod features with hexagonal tips as showed in Figure 2a. These ZnO nanorods formed a flower-like structure, which grows cluster by cluster. By incorporation of 0.05g crystalline SiO2, flaky particles dominates the surface with few appearance of ZnO nanorods and the absence of flower-like structure. These flaky particles are believed to be zinc complexes such as Zn(OH)2, (NH4)2ZnO2, and zinc. But increasing the mass of crystalline SiO2, ZnO nanorods become dense as observed in Figure 2b-d.

![Fig. 1: SEM micrographs of (a) crystalline SiO2 and amorphous SiO2 in 5,000 magnifications.](image)

Incorporation of amorphous SiO2 in bare ZnO resulted to surface image different from using crystalline SiO2. As clearly observed in Figure 3, increasing the mass of amorphous SiO2 causes ZnO nanorods to disappear. Among the mass of amorphous SiO2 using 0.1g is the most interesting. Compared to bare ZnO, the tip of ZnO nanorods are not hexagonal but it tends to sharpen. Its magnified image clearly revealed that the ZnO tip is hemispherical. The growth formation of these rods is the same to bare ZnO, which is a flower-like structure. It can be observed also the absence of flaky particles suggesting that many zinc complexes are
converted to ZnO. To determine the distribution of Si, O, and Zn that supports further the presence of SiO$_2$ and ZnO on the surface, elemental mapping was done.

**Fig. 2:** Surface images of as grown (a) ZnO; (b) ZnO with 0.05g crystalline SiO$_2$; ZnO with 0.1g crystalline SiO$_2$; and ZnO with 0.5g crystalline SiO$_2$ scanned at 5,000 magnifications.

**Fig. 3:** SEM micrographs of (a) ZnO with 0.1g amorphous SiO$_2$, (b) magnified image, (c) with 0.3g amorphous SiO$_2$, and (d) with 0.5g amorphous SiO$_2$.

**B. Elemental composition analysis via energy dispersive X-ray spectroscopy:**

Table 1 shows the quantitative EDX data of all the samples. It can be seen that elements Si, O, and Zn were present on the surface of the samples that can be attributed to SiO$_2$ and ZnO. This result further supports the elemental mapping claiming that SiO$_2$ and ZnO really exist on the surface. Knowing that the stoichiometric ratio of Si, O, and Zn is 1:2:2; it is concluded that the distribution of these elements on the surface is non-
stoichiometric. But only the ZnO sample with 0.1 g amorphous SiO$_2$ is close to the stoichiometric ratio of Zn and O (1:1). This means that at this mass of amorphous SiO$_2$ the growth of ZnO particles is not disrupted. Additionally, it is clearly seen in SEM images the formation of well-aligned ZnO nanorods. This implies that 0.1 g is the suitable amount of amorphous SiO$_2$ used to modify the surface of ZnO without interrupting its growth among amount considered in this work.

**Table 1:** Quantitative EDX data analysis for as grown ZnO with crystalline and amorphous SiO$_2$ powders in atom percent.

<table>
<thead>
<tr>
<th>Sample I.D</th>
<th>Atom percent</th>
<th>Si</th>
<th>O</th>
<th>Zn</th>
<th>Si:O:Zn</th>
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<tr>
<td>Crystalline</td>
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<td>CP1(0.05g)</td>
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<td>CP2(0.1g)</td>
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<td>CP6(0.5g)</td>
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<tr>
<td>Amorphous</td>
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<tr>
<td>CP7(0.1g)</td>
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<td>CP11(0.3g)</td>
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<tr>
<td>CP12(0.5g)</td>
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</table>

![SEM micrographs](image1)

**Fig. 4:** Elemental mapping of as grown ZnO incorporated with 0.1 g amorphous SiO$_2$.

**C. Compositional analysis via Fourier transform infrared spectroscopy:**

IR spectra appeared in Figure 5 shows peaks centered at 1103 cm$^{-1}$, 805 cm$^{-1}$, 477 cm$^{-1}$, 949 cm$^{-1}$, 3434 cm$^{-1}$, and 1631 cm$^{-1}$ that correspond to Si-O-Si asymmetric stretching, Si-O-Si symmetric stretching, Si-O-Si bending, Si-OH stretching, O-H stretching, and O-H bending. The presence of these peaks pointed out that SiO$_2$ is in the samples. Notice the peak at 933 cm$^{-1}$ of ZnO with 0.1 g amorphous SiO$_2$ sample, which is not found in ZnO with 0.1 g crystalline SiO$_2$. This peak is attributed to Si-O-Zn stretching confirming that SiO$_2$ really adhered on ZnO nanoparticles. The bonding of SiO$_2$ to ZnO modified its surface that is changing its tip from hexagonal to hemispherical, which was clearly seen in SEM results.
Fig. 5: IR spectra of ZnO with SiO$_2$ compared to ZnO and crystalline and amorphous SiO$_2$.

**D. X-ray diffraction analysis:**

The characteristic peak of amorphous SiO$_2$ is centered at 2θ value 21.12°. The lack of intense peak in its spectrum suggested that it is really amorphous. Notice a strong 2θ peak centered at 36.25° which corresponds to the (101) peak of highly c-axis oriented wurtzite ZnO. The sample also has other peaks which correspond to (100), (002), (102) planes, etc., which is attributed to the rod-like nature of the samples as observed in the micrographs result. Furthermore, the presence of Zn(OH)$_2$, Zn(HSO$_4$)$_2$ and ZnSO$_4$H$_2$O for the as-grown ZnO-SiO$_2$ powder are observed indicating that it is indeed composed of zinc complexes as also claim by SEM results. Choosing (101) plane, the particle size of ZnO-SiO$_2$ composite powder is 24.24 nm.

Fig. 6: XRD spectra of ZnO with 0.1g amorphous SiO$_2$ as grown and amorphous SiO$_2$ as comparison. The indices are for ZnO, Zn(OH)$_2$, Zn(HSO$_4$)$_2$ and ZnSO$_4$H$_2$O compared to PDF#36-1451, PDF#20-1435, PDF#20-1437, PDF#50-0412, and PDF#34-0320.

**Conclusions:**

Surface modification of hexagonal ZnO powder was successfully done using amorphous silica powder via low temperature sol-gel process. Hexagonal ZnO powders turned to hemispherical tips upon SiO$_2$ capping especially when using 0.1 grams of SiO$_2$. Crystalline silica powders however disrupt the growth of ZnO nanostructures producing flaky structural features.

**ACKNOWLEDGMENT**

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