Characterization of ZnO/TiO₂ Nanocomposites Prepared via the Sol-Gel Method

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ABSTRACT

ZnO/TiO₂ nanocomposites were synthesized via a modified sol-gel technique by incorporating 30 and 70 wt% TiO₂ nanopowder into a ZnO sol-gel matrix. Zinc acetate dihydrate was used as the ZnO precursor and de-ionized water as the solvent, while titanium oxysulfate was employed for the synthesis of TiO₂ nanopowder. The synthesized ZnO/TiO₂ nanocomposites were characterized by x-ray diffraction, UV-vis spectroscopy, scanning electron microscopy, and transmission electron microscopy. The ZnO/TiO₂ nanocomposites showed both the ZnO (wurtzite) and TiO₂ (anatase) phases. The average ZnO crystallite size of the ZnO/TiO₂ nanocomposites was found to be about 26.3 nm. The TEM results confirmed that spherical TiO₂ particles were embedded in the ZnO matrix. TiO₂ particles attached onto the rod-like ZnO particles were also observed. The ZnO/TiO₂ nanocomposites exhibited optical absorption properties superior to those of pure ZnO and TiO₂.

Key words : ZnO/TiO₂, Nanocomposite, Sol-gel, Optical property

1. Introduction

Zinc oxide (ZnO) and titanium dioxide (TiO₂) are n-type semiconductor oxides that have attracted a lot of research interest. Both ZnO and TiO₂ possess outstanding physical and chemical properties such as non-toxicity and high reactivity at the nanoscale. Furthermore, both are highly earth-abundant, and hence cheap. ZnO and TiO₂ also exhibit wide bandgaps of 3.37 and 3.2 eV (anatase) respectively.¹⁻³⁾

TiO₂ in the anatase phase shows excellent photocatalytic activity and is widely used for photocatalytic processes like water-treatment and air-purification. This is because it has a high oxidizing potential for the photo degradation of organic and inorganic compounds and dyes. ZnO also exhibits high photocatalytic activity and can effectively decompose certain compounds even in the dark. Unfortunately, the photocatalytic efficiencies of both TiO₂ and ZnO are limited by certain factors. Their wide bandgaps permit UV light absorption only at wavelengths lower than or equal to 385 nm ($\lambda \leq 385$ nm). In addition, the high recombination rate of the electron-hole pairs generated by these oxides also degrades their photocatalytic efficiency.^{3,4)}

To overcome this limitation, various efforts have been made to develop nanocomposites containing both these oxides. Such nanocomposites can absorb visible light with wavelengths ≥ 400 nm and also offer enhanced charge separation.^{4,5)} There have been reports on the wet chemical syn-

thesis of ZnO/TiO₂ core-shell nanostructures.⁶⁾ These core-shell structures were found to be more effective for the photochemical degradation of acridineorange (in the presence of sunlight) than TiO₂ and ZnO nanostructures. These core-shell structures also exhibited a wide absorption spectrum extending up to the visible-light region. Kanjwal *et al.*⁷⁾ synthesized a ZnO/TiO₂ nanocomposite using electrospinning and a hydrothermal method. The resulting ZnO/TiO₂ nanocomposite showed better photocatalytic degradation of dye pollutants than pure ZnO and TiO₂. These results suggest that the optical and photochemical properties of pure TiO₂ and ZnO can be improved by developing nanostructures consisting of both of these oxides. In this study, we synthesized a ZnO/TiO₂ nanocomposite with excellent photocatalytic properties via a reproducible, cost-effective, and versatile modified sol-gel technique.⁸⁾

The ZnO/TiO₂ nanoparticles were synthesized by a sol-gel method using zinc acetate dihydrate. The titania content in the nanoparticles was varied and its effect on the morphology, crystal structure, and optical properties of the resulting nanoparticles was investigated.

2. Experimental Procedure

2.1. Materials

Zinc acetate dihydrate ($\geq 98\%$, Sigma-Aldrich) was used as the ZnO precursor without further purification. Sodium hydroxide was used as the precipitating agent and de-ionized water as the solvent for all the experiments. Titanium oxysulfate (29%, Sigma-Aldrich) was employed as the titania precursor while ammonium hydroxide (28%, Sigma-Aldrich) was used as the pH adjuster.

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Fig. 1. Schematic of the synthesis procedure for the ZnO/TiO₂ nanocomposites.

2.2. Synthesis of ZnO/TiO₂ nanocomposite

The ZnO/TiO₂ nanocomposites were synthesized by incorporating TiO₂ nanopowder into the ZnO sol-matrix. This TiO₂ nanopowder was synthesized by modifying the method proposed by Nankya *et al.*⁹⁾ The resulting TiO₂ nanopowder was dried at 100°C for 3 h. A weighed sample of zinc acetate dihydrate was dissolved in de-ionized water to form a 0.2 M solution, which was magnetically stirred at 80°C for 30 min. The TiO₂ nanopowder was then added to the ZnO solution. The resulting mixture was stirred for another 30 min before being cooled to room temperature. An aqueous solution of sodium hydroxide was prepared and stirred at 80°C for 20 min. This solution was then cooled to room temperature. The cooled sodium hydroxide solution was added drop-wise to the ZnO/TiO₂ solution at room temperature and the resulting solution was stirred vigorously for 5 h. The ZnO/TiO₂ precipitate so obtained was aged for 24 h, after which it was filtered and washed several times. It was then dried at 100°C for 24 h, calcined at 500°C for 2 h, and ground into powder. Fig. 1 shows the schematic of the procedure used for the synthesis of the ZnO/TiO₂ nanocomposites.

2.3. Characterization

X-ray diffraction (D/Max-2200, Rigaku, Japan) was carried out to examine the crystal structure and calculate the crystallite size of the nanocomposites. Field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6701F, Japan) and energy dispersive X-ray spectroscopy (EDX, line-scan mapping) analyses were carried out to examine the microstructure and elemental composition of the nanocomposites. The morphology of the ZnO/TiO₂ nanocomposites was examined using transmission electron microscopy (TEM, JEOL, JEM-2100F, Japan). UV-vis spectroscopy (Shimadzu, UV-2600) was carried out to investigate the optical properties of the nanocomposites.

3. Results and Discussion

3.1. Crystal structure

The XRD patterns of the calcined samples pure ZnO (Z) and TiO₂ (T) and the ZnO/TiO₂ nanocomposites (Z3T, Z7T) are shown in Fig. 2. The peaks observed at $2\theta = 31.69, 34.36, 36.17, 47.48, 56.52, 62.79, 66.34, 67.88, 69.04, 72.51,$ and 76.89 correspond to the ZnO hexagonal wurtzite phase (JCPDS card No. 36-1451). On the other hand, the peaks observed at $2\theta = 25.24, 37.82, 47.91, 53.92, 62.78, 68.87,$ and 75.17 correspond to the TiO₂ anatase phase (JCPDS card No. 21-1272). Z3T showed the (101) and (004) diffraction planes, while Z7T showed the (101), (004), and (105) diffraction planes. This indicates that the anatase phase was present in the synthesized nanocomposites. No impurity peaks were observed, indicating that the samples were pure.

The intensity of the XRD peaks decreased with an increase in the weight percentage of the TiO₂ nanopowder added to the ZnO sol-matrix. The Z3T sample with 30 wt% TiO₂ nanopowder showed intense XRD peaks. An increase in the TiO₂ content increased the sharpness and intensity of the anatase phase peaks, as shown in the inset of Fig. 2.

3.2. Crystallite size

The crystallite sizes of the nanocomposites were calculated using the Scherrer equation:

$$t = \frac{k\lambda}{\beta \cos \theta}$$

where t is the crystallite size (nm), k the Scherrer constant (equal to 0.94), λ the wavelength of the incident Cu-K α radiation ($1.54059 \text{ \AA}$), β the line broadening at full width at half maximum, and θ Bragg's diffraction angle.¹⁰⁾

The calculated average crystallite sizes of the samples are

Fig. 2. X-ray diffraction patterns of pure ZnO (Z) and TiO₂ (T) powders and the ZnO/TiO₂ (Z3T, Z7T) nanocomposites calcined at 500°C. The inset shows the (101) anatase peak of the nanocomposites.

Table 1. Crystallite Sizes of the Samples Calcined at 500°C

Sample	ZnO (101)		ZnO (100)	
	FWHM	Crystallite Size(nm)	FWHM	Crystallite Size(nm)
Z(ZnO)	0.3102	25.4	0.3143	25.4
Z3T	0.3072	25.7	0.2864	27.9
Z7T	0.3138	25.1	0.2910	27.4
T(TiO ₂)	TiO ₂ (101)		TiO ₂ (004)	
	FWHM	Crystallite Size(nm)	FWHM	Crystallite Size(nm)
T(TiO ₂)	0.8604	9.4	0.9121	8.3

given in Table 1. The Z3T and Z7T nanocomposites showed ZnO crystallite sizes of 26.8 and 26.3 nm, respectively. The crystallite size of the TiO₂ nanopowder incorporated in the ZnO sol-matrix was about 9 nm.

3.3. Microstructure of ZnO/TiO₂ nanocomposites

The morphology of the ZnO/TiO₂ nanocomposites was examined by FE-SEM and TEM. The FE-SEM images of the ZnO/TiO₂ nanocomposites calcined at 500°C are shown in Fig. 3. It was found that the ZnO/TiO₂ nanocomposite powders formed spherical agglomerates and consisted of rod-like ZnO particles (can be observed clearly from the FE-SEM image of Z5T). Fig. 3 also shows the line-scan mapping results of the nanocomposites, which give an insight into the microstructural composition of the nanocomposites. The EDX analysis results revealed that the ZnO/TiO₂ nanocomposites consisted of only Zn, O, and Ti. Following are the atomic ratios in which these elements were present in the nanocomposites: Z3T Zn (77.51), O (21.71), and Ti (0.78); Z7T Zn (63.55), O (23.27), and Ti (13.18).

Fig. 4. TEM images of pure ZnO (Z) and TiO₂ nanopowder (T) calcined at 500°C. **Fig. 5.** TEM images of the Z3T and Z7T nanocomposites calcined at 500°C. **Fig. 3.** SEM and line-scan mapping images and EDX results of the ZnO/TiO₂ nanocomposites calcined at 500°C.

Fig. 6. UV-vis absorbance spectra of ZnO, TiO₂, and ZnO/TiO₂ nanocomposites calcined at 500°C.

The TEM images of the samples are shown in Figs. 4 and 5. The TEM results showed that the nanocomposites were made up of rod-like ZnO and spherical TiO₂ particles. The images revealed that the ZnO and TiO₂ particles coexisted in the nanocomposites. It was also observed that some of the TiO₂ particles were embedded in the ZnO particles, while some were attached onto the ZnO surface. The images further confirm the rod-like shape of the ZnO particles in the nanocomposites. The TiO₂ particles on the other hand were spherical and had very small sizes.

3.4. Optical properties

Figure 6 shows the UV-vis absorbance spectra of the calcined samples (pure ZnO and TiO₂ and the Z3T and Z7T nanocomposites). Pure TiO₂ (anatase) and ZnO have wide bandgaps of 3.2 and 3.37 eV, respectively, which limits their use of the solar spectrum to only UV light ($\lambda \leq 385$ nm).⁶⁾ The ZnO/TiO₂ nanocomposites exhibited enhanced absorbance in the visible light region compared to pure ZnO and TiO₂. The ZnO/TiO₂ nanocomposites (Z3T, Z7T) showed a strong absorption edge between 380 and 390 nm. However, pure ZnO showed a strong absorption peak between 370 and 380 nm corresponding to ZnO bandgap absorption, while pure TiO₂ showed a broad peak at around 360 nm and a strong absorption peak between 240 and 260 nm ascribed to its 3.2 eV photon energy gap.⁹⁾ The ZnO/TiO₂ nanocomposites also showed enhanced light absorption (> 400 nm), while pure ZnO was more right-shifted compared to TiO₂. Thus, the combination of ZnO and TiO₂ to form ZnO/TiO₂ nanocomposites is an effective approach to improving the physicochemical properties of ZnO and TiO₂. This is because ZnO and TiO₂ have similar photocatalytic mechanisms.⁴⁾ They also have similar bandgap energies with the energy levels located at almost the same positions. The electron-hole recombination in pure ZnO and TiO₂ can also be suppressed by the enhanced charge separation in ZnO/TiO₂ composites.^{4,5)} Thus, on the basis of the results obtained in this study, it can be stated that the absorption properties of

ZnO/TiO₂ nanocomposites can be improved by increasing their TiO₂ contents.

4. Conclusions

In this study, we synthesized and characterized ZnO/TiO₂ nanocomposites consisting of 30 and 70 wt% TiO₂ nanopowder particles embedded in the ZnO sol-matrix. XRD results showed that both the TiO₂ anatase and ZnO wurtzite phases were present in the nanocomposites and no impurity compounds were observed. The crystallite sizes of the Z3T and Z7T nanocomposites were found to be 26.8 and 26.3 nm, respectively. SEM results showed that the nanocomposites consisted of spherical TiO₂ and rod-like ZnO particles. TEM results confirmed that spherical TiO₂ particles were embedded in the lattice. Some of the TiO₂ particles were also attached onto the surface of the rod-like ZnO particles. The ZnO/TiO₂ nanocomposites exhibited enhanced absorbance (with their light absorption extended to more than 400 nm corresponding to higher wavelengths) compared to that of pure ZnO and TiO₂.

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