Analysis of optical and structural properties of Ti-doped ZnO nanoparticles synthesized by co-precipitation method

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Abstract. In this study, we used the co-precipitation method to synthesize Ti-doped ZnO nanoparticles having different Ti contents. We then used energy dispersive X-ray spectroscopy to perform an elemental analysis, which revealed that the Ti content varied in its atomic percentages from 5 at.% to 16 at.%. We characterized the structural properties of the prepared samples using X-ray diffraction (XRD) spectroscopy and found Ti-doped ZnO to have an anatase structure in which the lattice parameters a = b = c decrease from 3.251 and 5.213 Å to 3.254 and 5.203 Å, respectively, when the Ti content increased from 5 at.% to 16 at.%. We also found the grain size of Fe-doped TiO to decrease from 12 nm to 10 nm with increasing Ti content. We characterized the molecular vibration of the samples using Fourier transform-infrared spectroscopy (FT-IR) and the optical properties using UV-Vis diffuse reflectance spectroscopy. The results show the band-gap energy of Ti-doped ZnO to decrease from 3.20 eV to 3.12 eV. We tested the photocatalytic activity of Ti-doped ZnO in the degradation of methylene blue from the aqueous solution under UV light irradiation and found the photocatalyst Ti-doped ZnO to have good degradation ability, with a degradation percentage of approximately 80%.

1. Introduction

Metal-oxide-semiconductor (MOS) are attracting the focus of researchers who are working in the fields of material applications. Few famous MOS includes titanium dioxide (TiO2), cobalt oxides (CoO and Co2O3), zinc oxide (ZnO) and copper oxides (CuO and Cu2O) [1], in which ZnO has proved itself as the first choice of researchers [2,3] due to its several advantages including (i) direct band gap of wide range (3.37 eV), huge exciton binding energy i.e. 60 meV at room temperature [4], great transparency [5], outstanding stability [6], low fabrication cost [7] and its notable optical and electrical characteristics at normal room temperature. ZnO is a preferable n-type MOS and has proven usability in the fields of nanoscience, solar cells, optoelectronics, photocatalysts and many more [2,3].

Moreover, applications of ZnO can be enhanced by changing the doping level and dopant element as it improves the optical and electrical characteristics.Titanium (Ti) has also been used as a dopant element and Ti-ions can be used in place Zn2+ as ionic radius of Ti (i.e. 0.068 nm) is smaller than the ionic radius of Zinc (Zn) (i.e. 0.074 nm) [8]. Therefore, ZnO can be doped with Ti to be used in different applications of microelectronics, spintronics and also as a photocatalyst with improved characteristics.

Photocatalytic activity of ZnO can be enhanced by transition metal (TM) doping under the photocatalytic process. TM doping improves the optical and structural properties of ZnO with further results in improved photocatalytic activity of TM-doped ZnO. With the addition of the dopant, the crystallite size of the samples can be decreased, which enhances the specific surface area of the
The addition of dopant can also create an additional energy level below the conduction band of ZnO, which can help prevent the recombination electron and holes.

In this endeavor, analysis of Ti-doped ZnO nanoparticles using the co-precipitation method is discussed and presented. We characterize the physical properties of the samples using XRD (X-Ray Diffraction) spectroscopy, EDX (Energy Dispersive X-Ray) spectroscopy, UV-Vis DRS (Diffuse Reflectance Spectroscopy), FTIR (Fourier transform–infrared) spectroscopy and ESR (Electron Spin Resonance) spectroscopy. We investigated the photocatalytic activity using methylene blue under UV light irradiation.

2. Experimental details
As initial materials, we used zinc (II) sulfate (ZnSO$_4$.7H$_2$O, 99%, Merck) and titanium chloride (TiCl$_4$, 99%, Merck) without further purification. We used ZnSO$_4$.7H$_2$O in distilled water with TiCl$_4$, and designated these solutions as solution A to find the required degree of Titanium doping. Then solution A is placed in an ultrasonic cleaner for about 2 hours, which was operating at about 57 kHz frequency. After that solution B is obtained by mixing NaOH of about 44 mmol to deionized water of about 440 mL. Then sonication is applied. Further, solution A is mixed with solution B after being stirred with magnetic mixer at room temperature. pH level of 12 should be achieved of the mixture of solution A and solution B. Furthermore, this solution is again stirred with magnetic mixer for about 30 minutes and the solution is left alone at room temperature for about 18 hours. Further, centrifugal technique and washing are applied for removing the unwanted particles and residues. Washing may be performed many times if required. Generally, ethanol and distilled water are used for washing. Finally, fabricated product is dried and kept in a vacuum oven at temperature of about 200 °C for at least 60 minutes.

Standard X-ray diffractometer (Philips PW1710) is used to analyse structural characterization with monochromatic Cu-Kα ($\lambda = 1.5406$ Å) radiation operated at 40 kV voltage and 20 mA current ranging from 10° to 80°. We calibrated the diffractometer using silicon powder. To verify the XRD patterns of the designed nanoparticles, we compared them with JCPDS data. We performed the optical characterizations by diffuse reflectance spectroscopy, in which Shimadzu UV-Vis spectrophotometer is used to observe all the spectra in the range of about 250–800 nm. A spherical attachment is also integrated with Spectralon reflectance standard. We took measurements from the 0–71 T field. For analysing the composition of the samples, EDX spectroscopy is used.

We tested the photocatalytic activity by examining the decay of methylene blue from the dissolved solution. Typically, we dissolved 0.3 g of the catalyst in aqueous MB solution of about 100 mL (20 mg/L) and then photocatalytic process is observed in a cylindrical glass vessel while placed on a magnetic mixer and a couple of UV-C lamps of 40 W are imposed on it. We then monitored the degradation of the methylene blue by UV-Vis spectroscopy. To analyze the photocatalytic experiment quantitatively, we performed calculations using the following equation (1) and equation (2).

\[
\text{Decolorization: } \frac{C_t}{C_0} \tag{1}
\]

\[
\% \text{ Degradation: } \frac{C_0 - C_t}{C_0} \times 100 \% \tag{2}
\]

where $C_0$ is the initial dye concentration and $C_t$ is the dye concentration after time t.

3. Results and discussion
Figure 1 shows the EDX spectra of Ti-doped ZnO with different Ti loadings. As we can see from the figure, the EDX spectra of the Ti-doped ZnO consist of Zn atoms at 0.93 eV, 8.45 eV, and 9.38 eV, oxygen atoms at 0.47 keV, and Ti atoms at 4.40 eV. After investigating the peak area of the corresponding peaks, we determined that the Ti atomic percentage of each sample was 5 at.%, 7 at.%, 12 at.%, and 16 at.%, respectively. The remaining carbon atom at 0.22 keV is probably due to environmental impurities. The existence of each atom clearly indicates the existence of Ti-doped ZnO in the samples. We detected no undesired peaks, which indicates that the samples had good purity.

To further confirm the existence of Ti-doped ZnO nanoparticles, we performed XRD spectroscopy, the results of which are plotted in figure 2. The XRD results for the Ti-doped ZnO nanoparticles show several diffraction peaks at 2θ = 31.72°, 34.38°, 36.15°, 47.50°, 47.50°, 56.64°, 62.83°, 67.99°, and 68.88°, which we attribute to the existence of a hexagonal wurtzite structure. We detected no undesired peaks, which indicates that all the samples were those desired. We found the peak intensity of the prepared samples to decrease with increasing Ti content, which means that the existence of Ti...
Table 1. Lattice constant and grain size of Ti-doped ZnO nanoparticles with different Ti loading concentrations.

| Sample                | Lattice parameters (Å) | Grain size (nm) |
|-----------------------|------------------------|-----------------|
| Ti-doped ZnO 5 at.%   | 3.2519                 | 5.2135          | 16              |
| Ti-doped ZnO 7 at.%   | 3.2515                 | 5.2127          | 15.7            |
| Ti-doped ZnO 12 at.%  | 3.2507                 | 5.2112          | 15.5            |
| Ti-doped ZnO 16 at.%  | 3.2452                 | 5.2029          | 15.2            |

Figure 1. EDX spectra of spectra Ti-doped ZnO with various Ti–doping loadings.

Figure 2. XRD spectra intensity of Ti-doped ZnO with various Ti–doping loadings.

Figure 3. W–H plot analysis of Titanium-doped ZnO with various Ti doping loadings.

atoms in the ZnO structure reduces the crystallinity of the ZnO nanoparticles. To qualitatively analyze the XRD measurements of the Ti-doped ZnO, we investigated the lattice parameters, grain size, and microstrain of the prepared samples. We calculated the lattice parameters of the prepared samples using the Rietveld-refinement method, the results of which are illustrated in table 1. While
studying this table, it is observed that lattice parameters a and c slightly change with the incorporation of Ti doping. This is probably due to the substitutions of the Ti and Zn atoms. The ionic radii of the Ti\(^{3+}\) ion are about 74.5 Å, whereas that of the Zn\(^{2+}\) atom is about 74 Å, so the Ti atom can replace the Zn atom [8]. To investigate the grain size of the prepared samples, we used the following Williamson–Hall (W–H) plot method in equation (3).

\[
\beta_{hkl} = \left(\frac{k\lambda}{D}\right) + 4\varepsilon \sin(\theta)
\]

where \(\beta_{hkl}\), \(D\), \(k\), \(\lambda\) and \(\varepsilon\) are full width at half maximum (FWHM), average crystallite size, shape factor, wavelength of the Cu–K\(\alpha\) radiation and microstrain parameter, respectively. Figure 3 shows a linear plot of \(\beta_{hkl}\) vs. \(\sin(\theta)\) for the prepared samples, from which we can see that the W–H plot method yields a better coefficient correlation for the prepared samples. We determined the grain sizes of the samples from the intercepts of this plot, the results of which are summarized in table 1. After observing the results summarized in this table, the grain size of Ti-doped ZnO product samples decreases with an increase in Ti content, which is probably due to the Ti atoms reducing the crystallinity of the ZnO.

Figure 4 shows a plot of the FT-IR spectra of Ti-doped ZnO, in which we can see several vibration modes at 430 cm\(^{-1}\), 885 cm\(^{-1}\), 1356 cm\(^{-1}\), and 3500 cm\(^{-1}\). We can attribute the absorption peaks ranging from 400–700 cm\(^{-1}\) to ZnO vibrational stretching modes [9]. We can also observe that weak absorption peaks are lying in the range of 1100–1600 cm\(^{-1}\), which correspond to the OH bending vibrational mode, C–OH bending in its own plane, and C–OH out-of-plane bending i.e. out of its plane [10]. According to first-principle theoretical and experimental studies of ZnO materials, hydrogen atoms usually form powerful OH covalent bonds with oxygen lattice, IR absorption peaks are achieved due to the stretching vibrational-mode OH covalent bonds. A wide band ranging from 2900–3700 cm\(^{-1}\) is obtained, which attribute in interweaving of O–H and C–H local vibration modes in the range of 1100–1600 cm\(^{-1}\) and 2900–3700 cm\(^{-1}\), respectively.

We investigated the ESR intensity spectra of the ZnO doped with Titanium to analyze the structural defects on the prepared samples. Figure 5 shows a plot of the ESR spectra, from which we can see that there are ESR signals at 3356 Gauss and 3363 Gauss, corresponding to \(g\) values of 2.01 and 1.99, respectively. The first signal at the \(g\) value of 1.99 is probably due to the existence of the Ti\(^{3+}\) ion in the samples [12], whereas the second signal at the \(g\) value of 2.01 is probably due to the existence of an oxygen vacancy in the ZnO lattice [13]. This clearly indicates that several parts of the Ti\(^{3+}\) ions had been deposited into the ZnO lattice.

We investigated the optical properties of the prepared samples using UV-Vis diffuse reflectance spectroscopy. Figure 6 shows plots of the UV-Vis reflectance spectra of the Ti-doped ZnO, from which we can see that the reflectance spectra increase with increasing Ti content. To further analyze
the optical characteristics of the fabricated samples, we performed a Kubelka–Munk analysis to obtained the optical band gap of the fabricated samples. Equation (4) is used to analyse the same:

\[ F(R) = \frac{(1 - 2R)^2}{2R} \]  

(4)

where R is the reflectance spectra of the samples. We obtained the band-gap energy by extrapolating F(R) = 0 vs. energy, the results of which correspond to the band-gap energy of the samples, as plotted in figure 7. As we can see from the figure, the band-gap energy of the Ti-doped ZnO slightly decreases with the incorporation of Ti doping. This decrease in the band-gap energy is probably due to the following reasons: (1) The oxygen vacancy, as detected by the ESR measurement, may act as an electron acceptor below the conduction band of ZnO, which influences the band structure of the ZnO structure. (2) The crystallite structure of ZnO, which decreases with decreased Ti doping, may affect the optical properties of the prepared samples due to the quantum confinement effect.

Figure 8 shows plots of the photocatalytic activity of Ti-doped ZnO nanoparticles with respect to the decay of methylene blue under the environment of UV light irradiation, from which we can see that the decay of methylene blue gradually increases with irradiation time. Increasing dopant concentration results in higher photocatalytic performance. We can see an increase in the degradation percentage from 60 % to 80 %. The increasing photocatalytic performance of Ti-doped ZnO is probably due to the decreasing crystallite size of Ti-doped ZnO, which implies a higher specific surface area. Moreover, the existence of the Ti3+ ion followed by the existence of the oxygen vacancy could prevent the process of recombination of the electron and holes, which could enhance the photocatalytic activity. To investigate the photocatalytic mechanism, we added three different radical
scavengers: an electron scavenger (sodium sulfate), a hole scavenger (di-ammonium oxalate), and OH radical scavengers (tert-butanol). Figure 9 shows plots of the influence of these scavengers on the photocatalytic performance, from which we can see that the addition of radical scavengers reduces photocatalytic performance. This is because the active radicals in the photocatalytic process had been scavenged. The addition of hole scavengers resulted in the lowest photocatalytic performance, which indicates that holes are the most vigorous radical elements in the degradation of methylene blue under the environment of UV light irradiation.

4. Conclusions

In this study, we used the co-precipitation method to successfully synthesize Ti-doped ZnO. The XRD results indicate that the prepared samples had a hexagonal wurtzite structure with different lattice parameter values, which indicates the substitution of the Ti atom on the ZnO nanoparticle structure. From the ESR analysis, we can confirm the existence of Ti$^3+$ on the samples, in which the Ti$^3+$ ion replaced the Ti$^4+$ ion, as well as the oxygen vacancy in the prepared samples. We found the band-gap energy of the ZnO nanoparticles to decrease after being doped with Ti atoms, which is probably due to the decreasing crystallite size of the samples, thereby inducing the quantum confinement effect. Our photocatalytic performance test results for Ti-doped ZnO on the decay of methylene blue under UV light irradiation reveals its good degradation ability.

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