Effect of Ni doping on the structural and optical properties of TiO₂ nanoparticles prepared by co-precipitation method

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Abstract. In this study, Ni-doped TiO₂ nanoparticles with different dopant concentrations were fabricated using coprecipitation. The chemical compositions, and structural and optical properties were characterized using X-ray diffraction (XRD), electron dispersive X-ray spectroscopy (EDS), and UV-VIS diffuse reflectance spectroscopy. Identification of paramagnetic species was conducted using electron spin resonance (ESR). The XRD pattern shows that only a single phase of anatase appeared because Ni⁺ has a similar ionic radius to that of Ti⁴⁺ and replaced some of the Ti⁴⁺ ions in the TiO₂ lattice. The crystallite size decreased with increasing Ni content. This phenomenon probably arises from the introduction of Ni⁴⁺ ions which decreased crystalline growth. The UV-VIS diffuse reflectance spectra showed that the UV absorption moved to a longer wavelength (red shift) and the band gap energy decreased. This caused the doped Ni atoms to form a localized energy state below the conduction band of the TiO₂ lattice. The ESR studies on the Ni-doped TiO₂ nanoparticles revealed the presence of Ni⁺, Ti³⁺, and oxygen defects in all samples.

1. Introduction

Titanium dioxide (TiO₂) is used as a semiconductor and has several unique characteristics; it is chemically inert, inexpensive, and has high oxidation ability [1]. Due to its interesting properties, TiO₂ has been widely used in many applications such as the photocatalytic process for wastewater treatment reported in Cao et al. [2]. However, several aspects of TiO₂ still need improvement and these include absorbance ability under visible light irradiation and increased charge-carrier lifetime.

A lot of effort has been made by researchers to improve the physical properties of TiO₂ and includes modification of their structural properties including grain size, morphology, and defect creation [3–5]. However, recently it has been reported that modification of the crystal structure of TiO₂ by transition metal doping can significantly improve its physical properties. Several papers have confirmed that the band gap energy of TiO₂ can be reduced into the visible light region by incorporating a transition metal in its structure [6,7]. The reduction in the band gap energy of TiO₂ is due to substitution between the transition metal ions and the TiO₂ ions, which implies the creation of a new energy level (impurity level) below the TiO₂ conduction band. Moreover, the substitution process also creates an oxygen vacancy in the structure of TiO₂, which is very important for improving the lifetime of its charge carrier [7].

In this study, we investigated the formation of transition metal doped TiO₂, using nickel (Ni) as the transition metal, synthesized by co-precipitation. All the prepared samples were characterized using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), UV-Vis absorbance spectroscopy, and electron spin resonance (ESR).
2. Experimental detail

Ni-doped TiO₂ was synthesized by the co-precipitation method using TiO₂ (titanium dioxide), Ni(NO₃)₂·6H₂O (Nickel (II) Nitrate Hexahydrate), NaOH (Sodium Hydroxide), C₂H₆OH (Ethanol), and Ar (Argon). Typically, TiO₂ and Ni(NO₃)₂·6H₂O were dissolved in distilled water and sonicated for two hours. The solutions were mixed by a magnetic stirrer operating at 80 °C for 30 minutes. A 0.1 M NaOH solution was added until the pH = 13. The solution was then held for four hours to separate the Ni-doped TiO₂ and centrifuged to collect the precipitated sample. This sample was washed using distilled water and ethanol to remove any unwanted substances and the final product dried at 100 °C. During the synthesis the NiₓTi₁₋ₓO₂ dopant concentrations were varied as x = 0.03, 0.06, 0.1, and 0.2.

All samples were investigated using an X-ray diffractometer, Philips PW 1710, with Cu-Kα (λ = 1.54060 Å) and an irradiation source operated at 40 kV and 20 mA in the 2θ range 10° to 80°. The lattice parameters of the samples were calculated using the Rietveld refinement method and the grain size of the samples was calculated using the Debye-Scherer equation:

\[ \beta \cos \theta = \frac{k \lambda}{D} \]

where \( \beta_{hkl} \) is the full width at half maximum (FWHM), D is the average crystallite size, k is a shape factor (set to 0.9), and \( \lambda \) is the Cu–Kα radiation wavelength. Chemical analysis of the samples was conducted using an energy dispersive X-ray spectrometer, LEO 420, in the energy range 0.33–11 keV. The optical properties of the prepared samples were investigated using Shimadzu UV-Vis equipment in the wavelength range 250–800 nm. The band gap energies of the prepared samples were calculated using the Kubelka-Munk equation:

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

where R is the reflectance ability of the prepared samples. The band gap energies were determined after extrapolation of F(R)- with n = 2 for direct band gap energy vs. energy at y = 0. The structural defects in the samples were investigated using X-band Jeol-JES-REIX ESR equipment at room temperature over the magnetic field range of 2100–4900 gauss.

3. Results and discussion

Figure 1 shows the EDS spectra of Ni-doped TiO₂ with different dopant concentrations and several peaks, detected from the C, O, Ni, and Ti atoms, can be seen. The atomic concentration measurements show the atomic composition of Ni-doped TiO₂, which indicates that the sample was successfully formed. The intensity of the EDS spectra correlates with the number of atoms in the samples. The ratio intensities between Ti and Ni are plotted in figure 2, which shows that the atomic concentration of Ni increases with increasing dopant concentration. The Ni contents were found to be 3.53, 6.11, 11.39, and 21.56 atomic percent (at.%).
The structural properties of the samples were characterized using XRD measurements and the results are plotted in figure 3. These measurements reveal several diffraction peaks at 2θ ≈ 25.3°, 37°, 37.73°, 38.54°, 48°, 53.84°, 55°, 62.02°, 62.62°, 68.7°, 70.2°, 74.94°, and 76.06°, which could be attributed to the 101, 103, 004, 112, 200, 105, 211, 213, 204, 116, and 220 diffraction planes of an anatase structure from the TiO$_2$. No other diffraction peaks were observed and this indicates that the Ni atom was successfully doped into the anatase structure. To further investigate the structure of the Ni-doped TiO$_2$, the XRD spectra was enlarged over the 2θ = 23–30° range (figure 4). It can be seen that the position of the 101 peak shifts to a lower diffraction angle with the increasing Ni content and is probably due to the influence of the dopant concentration. This phenomenon shows the existence of strain and a change in structural properties due to cation dopant presence in the TiO$_2$ structure.

The lattice parameters and grain sizes of the samples were calculated using the Rietveld refinement and W-H plot methods. The lattice parameter results are plotted in figure 5 and can be seen to increase slightly with increasing dopant concentration. The change in lattice parameter values is probably a result of the deformation process caused by Ni atom substitution into the anatase structure, as the ionic radius of Ni$^{2+}$ (83 pm) is greater than that of Ti$^{4+}$ (74.4 pm). Manzoor et al. [8] reported that the position of the ion in the lattice could be determined by the size difference between the ionic radii of Ti$^{4+}$ and the ionic dopant. If the ionic radius of the dopant is smaller than that of the host semiconductor the dopant ion will be embedded in the structure of TiO$_2$ through substitution, however, if the ionic radius is larger its ions embed by the interstitial process. The interstitial process in Ni-doped TiO$_2$ causes a disturbance in the crystal and produces a positive charge around Ti$^{4+}$ or creates an oxygen vacancy. The grain sizes of the samples are plotted in figure 6. It can be seen that the grains size decrease with...
Table 1. Band gap energy of Ni-doped TiO₂

| Sample            | Atomic percent (at.%) | Energy gap (eV) |
|-------------------|-----------------------|-----------------|
| Ni-doped TiO₂     | 3.53 at.%             | 3.17            |
|                   | 6.11 at.%             | 3.13            |
|                   | 11.39 at.%            | 3.12            |
|                   | 21.56 at.%            | 3.10            |

Figure 7. UV-Vis diffuse reflectance measurement of Ni-doped TiO₂.

Figure 8. ESR measurement of Ni-doped TiO₂.

increasing Ni dopant. This is because the incorporation of the Ni dopant retards TiO₂ crystal growth. The dopant ions migrate into the TiO₂ crystal lattice and influence the bond distances in Ti-O-Ti and O-Ti-O [8].

The UV-Vis reflectance spectra of the Ni-doped TiO₂ are plotted in figure 7. The Ni-doped TiO₂ nanoparticles show strong reflectance in the visible light region (800–400 nm) and further decrease with increasing Ni dopant. This indicates that the absorbance ability of the Ni-doped TiO₂ improves with increasing Ni dopant. The decreasing reflectance with increasing Ni dopant is probably due to charge transfer between Ni²⁺ and Ti⁴⁺. This shows that there is a level of impurity from Ni 3d and also confirms that the Ni dopant successfully embedded into the TiO₂ nanoparticle structures. Table 1 shows the band gap energies of the Ni-doped TiO₂, which decrease with increasing Ni dopant. The narrowed band gap energy is due to the existence of a new energy level below the TiO₂ conduction band, which comes from the Ni²⁺/Ni⁺ transition that exists below it [9]. The new energy level exists due to a charge transfer between the dopant and the TiO₂ valence or conduction bands. Moreover, the existence of Ni in the structure of TiO₂ could create an oxygen vacancy that promotes the reduction of Ti⁴⁺ to Ti³⁺ and probably influences the band gap energy of the samples.

The ESR measurements from the Ni-doped TiO₂ in the samples are shown in figure 8 and reveal several signals that can be recognized as Ni²⁺, oxygen vacancies, and Ti³⁺ [10]. These results confirm the existence of impurities in the structure of TiO₂, such as Ni⁺, Ti³⁺ and oxygen vacancies, influences the optical properties of Ni-doped TiO₂.

4. Conclusions
Ni-doped TiO₂ was successfully synthesized by co-precipitation. XRD results confirm that the Ni dopant was successfully embedded into the structure of the TiO₂ nanoparticles. The UV-Vis diffuse reflectance spectra confirm that increasing Ni dopant content reduces the band gap energy of the samples, which is due to the existence of an additional energy level from the structure of anatase. The ESR measurements confirm the existence of Ni⁺, oxygen vacancies, and Ti³⁺, all of which influence the optical properties of Ni-doped TiO₂.
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