Structural and optical study of Cu-doped TiO₂ nanoparticles synthesized by co-precipitation method

H. Sokoidanto, A. Taufik and R. Saleh

Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Integrated Laboratory of Energy and Environment, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia

Corresponding author’s e-mail: rosari.saleh@ui.ac.id

Abstract. In this study, we synthesized Cu-doped TiO₂ nanoparticles using a coprecipitation method, with chemical TiO₂ as the base material and CuSO₄⋅H₂O as a dopant precursor. To characterize their compositional, structural, optical, and paramagnetic properties, we employed energy dispersive X-ray spectroscopy, X-ray diffraction spectroscopy, Fourier transform infrared spectroscopy, diffuse reflectance UV-Visible spectroscopy, and electron spin resonance (ESR) spectroscopy. The outcome of the research study showed the samples to have a tetragonal anatase structure with grain sizes of 52–54 nm. The secondary CuO phase in the 6 at.% and 12 at.% samples showed a Cu solubility limit in their TiO₂ lattice, which also influences the lattice parameters. We observed band-gap narrowing with an increasing concentration of the Cu dopant, as indicated by the redshift of the diffuse reflectance band edge. Substituting Ti with Cu atoms led to the detection of a paramagnetic species by ESR spectroscopy.

1. Introduction

TiO₂ is one of the most investigated semiconductors due to its wide range of applications [1]. As an n-type semiconductor with wide band-gap energy, TiO₂ is renowned for its potential application as a photocatalyst and photoelectrocatalyst [2,3]. TiO₂ has several unique characteristics, including good optical transmittance, a high refractive index, and stability. However, TiO₂ nanoparticles have several limitations in some applications, such as being photocatalytic. Therefore, modified TiO₂ represents a challenging research topic due to its interesting properties.

Doping TiO₂ with a transition metal has become the subject of extensive research in recent years due to the ability of these metals to modify the physical properties of TiO₂. Zhang et al. [4] used a sol–gel method to synthesize a copper (Cu)-doped TiO₂ semiconductor and found that the incorporation of Cu atoms on the TiO₂ structure could modify the optical properties of the samples, such as shifting their energy adsorption ability [4]. Lopez et al. [5] also reported that the formation of Cu-doped TiO₂ decreased the band-gap energy of TiO₂, which the authors found to be very effective in improving the performance of a photocatalytic wastewater removal process.

In the current study, Cu-doped TiO₂ nanoparticles were prepared utilizing coprecipitation method. We investigated in detail the effect of different Cu-doping concentrations by characterizing the physical properties of all the prepared samples using energy dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, UV-Vis diffuse reflectance spectroscopy, and electron spin resonance (ESR) spectroscopy.

2. Experimental method
We used the following initial materials without further purification: copper sulfate pentahydrate (CuSO₄·5H₂O), sodium hydroxide (NaOH, 99%, Merck), and titanium chloride (TiCl₄, 99%, Merck). In order to achieve the preferred level of Cu doping, we mixed the TiCl₄ in distilled water with CuSO₄·5H₂O and designated these solutions as solution A. These solutions samples were subjected to ultrasonic cleaning by exposing them to ultrasonic waves of frequency 57 kHz for 2 h. Solution B was prepared by mixing 44 mmol of sodium hydroxide with 440 mL of de-ionized water. After the ultrasonic treatment, solution A was constantly mixed using a magnetic stirrer at ambient temperature. Subsequently, solution B was gradually poured till a pH of 12 was attained. After magnetic stirring for 0.5 h, the solution was undisturbed for 18 h at room temperature. After this treatment, the solution was subjected to centrifugation and rinsed with ethyl alcohol and distilled water multiple times to ensure the removal of residual and unwanted impurities. We finally dried the resultant precipitate under vacuum condition in an oven at a temperature of 200 °C for 1 h.

The structural characteristics of the specimen were studied by X-ray diffraction technique (Philips PW1710) using a monochromatic Cu-Kα (λ = 1.5406 Å) radiation utilized at 40 kV and 20 mA. The 2θ range was set between 10°–80°. Standard Si powder was used to calibrate the diffractometer. To analyse the diffraction spectra of the nanoparticles, we compared them with Crystallography Open Database (COD) data. We performed optical characterizations using UV-Vis diffuse reflectance spectroscopy, in which we observed all spectra in the 250 to 800 nm range using UV-vis spectrophotometer (Shimadzu) coupled with an integrating sphere attachment and the Spectralon reflectance standard. We took measurements from the 0–1 T field for analyzing using ESR spectroscopy. The elemental composition of the specimens was observed using Scanning Electron Microscopy combined with EDX spectroscopy.

### Results and discussion

We quantitatively analyzed the chemical compositions of all the prepared samples by EDX measurement, the results of which are plotted in figure 1. As we can see in the figure, the atomic composition of all the prepared samples consists of Cu atoms at 0.94 keV and 7.99 keV, Ti atoms at 4.52 keV and 4.91 keV, Oxigen atoms at 0.51 keV, and C atoms at 0.25 keV. Figure 2 shows a plot of the atomic ratio of Ti and Cu, in which we can see that the ratio of the Cu and Ti atoms were 2 at.%, 4 at.%, 6 at.%, and 12 at.%.

We characterized the structural properties of all the prepared samples using XRD spectroscopy. Figure 3 shows plots of the XRD spectra of Cu-doped TiO₂, in which we can see that the Cu-doped TiO₂ has 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°. We fitted the XRD spectra of all the samples using the Crystallography Open Database (COD) data no. 9009086, which indicate that the Cu-doped TiO₂ has a tetragonal anatase structure. From these XRD results, we determined that doping TiO₂ with Cu atom concentrations of 2 at.% and 4 at.% produces no secondary phase from the Cu metal, CuO, or Cu₂O.
However, Cu atom concentrations of 6 at.% and 12 at.% yielded an additional peak at \(2\theta \approx 35.5^\circ\), which could be attributed to a monoclinic-phase diffraction peak from CuO. The diffraction peaks of CuO at 6 at.% and 12 at.% are due to having exceeded the Cu dispersion limit.

Figure 4 shows plots of the lattice parameters of Cu-doped TiO\(_2\) nanoparticles with different Cu concentrations, in which we can see that the lattice parameters \(a = b\) and \(c\) slightly decrease with increasing Cu concentration. These decreasing lattice parameter values are due to the Cu atoms that substituted those from the TiO\(_2\). The Cu\(^{2+}\) ionic radius is smaller than that of Ti\(^{4+}\), which affects the Cu atoms ability to substitute the Ti atoms in the TiO\(_2\) system and reduces the lattice parameters of the samples. We calculated the grain sizes of the samples using Williamson and Hall (W–H) plots in
Figure 7. FTIR spectra of Cu-doped TiO\(_2\) nanoparticles.

Figure 8. UV-Vis spectra of Cu-doped TiO\(_2\) nanoparticles.

equation (1) as follows:

\[ \beta = \beta_e + \beta_D \]

where \( \beta_e = 4\epsilon \tan \theta \), which reflects the line broadening due to the micro strain \( \epsilon \), and

\[ \beta \cos \theta = \frac{k\lambda}{D} + 4\epsilon \sin \theta \]  

The intercept between \( \beta \cos \theta \) and \( \sin \theta \) provides information about the grain size and the micro-strain values of the prepared samples. We determined the grain size from the intercept of equation (2) with \( K \) as the Scherer constant (0.89). Figure 5 shows a plot of the W–H analysis, in which we can see that there are good coefficient correlations (\( R^2 \)). Figure 6 shows plots of the obtained grain sizes, from which we can see that the grain sizes of the specimen reduce with increasing Cu content. The decreasing grain size of the Cu-substituted TiO\(_2\) is due to the Cu atoms reducing the crystal growth of TiO\(_2\).

Figure 7 shows the molecular vibrations of Cu-doped TiO\(_2\) with different Cu contents, from which we can see that the samples exhibit wide infrared adsorption around 400–1000 cm\(^{-1}\), which could be attributed to the molecular vibrations of Ti-O and Cu-O [6–7]. We can attribute the molecular vibrations around 2500–3900 cm\(^{-1}\) to the vibrations of C-H and O-H. The C-H vibration is probably due to the ethanol adsorbed in the synthesis process.

Figure 8 shows the UV-Vis diffuse reflectance spectra of Cu-doped TiO\(_2\), which range between 5–70 %. The 210–270 nm range has a small reflectance spectrum, which indicates strong adsorption in that region due to the transition from O\(^2-\) at the 2p energy level to Cu\(^{2+}\) at the 3d energy level [8]. The high and wide reflectance spectra in the 600–800 nm range indicate the low adsorption ability of the samples. However, doping TiO\(_2\) with Cu atoms decreases the reflectance spectra with increasing Cu-doping concentrations. Figure 9 reveals the energy band-gap of the prepared compositions, figure 9a that we computed by Kubelka-Munk analysis. As we can see in the figure 9b, the band-gap energy of Cu-doped TiO\(_2\) decreases with increasing Cu-doping concentrations. We can attribute this decreasing band-gap energy to the interfacial charge transfer (IFTC), in which the electrons transition from the valence band of TiO\(_2\) to an impurity level below the conduction range for TiO\(_2\).

We used ESR spectroscopy to investigate the paramagnetic behavior of Cu-doped TiO\(_2\) for different Cu concentrations, which are plotted in figure 10. From the figure, we can see that the signal at \( g = 2.07 \) corresponds to the existence of Cu\(^{2+}\), which is coordinated with oxygen on the TiO\(_2\) lattice. This coordinated form comes from Cu\(^{2+}\), which substitutes the ion Ti\(^{4+}\). This substitution causes instability in the TiO\(_2\) lattice charge and consequently creates an oxygen defect in the form of an oxygen vacancy at \( g = 2.005 \). This signal is very close to that from Ti\(^{3+}\) at \( g = 1.990 \). These results confirm the substitution process of the Cu\(^{2+}\) ion on the TiO\(_2\) structure [9].
Figure 9. (a) Kubelka-Munk analysis and (b) Band-gap energy of Cu-doped TiO₂.

Figure 10. ESR spectra of Cu-doped TiO₂.

4. Conclusions
In the current research, we successfully prepared Cu-doped TiO₂ by employing the co-precipitation method. The obtained structural behaviour of Cu-substituted TiO₂ confirms the existence of an anatase structure in TiO₂. The EDX measurement results confirm the presence of doped Cu on the TiO₂ structure. We investigated Cu loading concentrations of 2 at.%, 4 at.%, 6 at.%, and 12 at.%. The obtained ESR measurements also confirm the existence of the Cu²⁺ ion by the resulting structural defect in the TiO₂ crystal structure. The optical characteristics of Cu-doped TiO₂ confirm the redshift of the absorbance ability of Cu-doped TiO₂, when compared with pure TiO₂. This is due to the existence of the Cu²⁺ ion in the TiO₂ structure, which serves as an electron acceptor in the valence band of TiO₂.

References
[1] Rahmana M.M, Krishna K.M, Soga T, Jimbo T and Umenoa M 1999 J. Phys. Chem. Solids 60 201–10
[2] Jia T, Fu F, Yu D, Cao J and Sun G 2018 Appl. Surf. Sci. 430 438–47
[3] Zhang G et al. 2017 Appl. Surf. Sci. 391 345–52
[4] Zhang D 2010 Transition Met. Chem. 35 933–8
[5] López R, Gómez R and Llanos M E 2009 Catal. Today 148 103–8
[6] Hamadanian M, Reisi-Vanani A and Majedi A 2010 Appl. Surf. Sci. 256 1837–44
[7] Wang Z, Liu Q, Yu J, Wu T, Wang G 2003 Appl. Catal. A 239 87–94
[8] Yoong L S, Chong F K, Dutta B K 2009 Energy 34 1652–61
[9] Córdoba G, Viniegra M, Fierro J L G, Padilla J and Arroyo R 1998 J. Solid State Chem. 138 1–6