



DOI: doi.org/10.21009/SPEKTRA.051.03

SYNTHESIS AND CHARACTERIZATION OF STRUCTURAL NANOCOMPOSITE TITANIUM DIOXIDE COPPER-DOPED USING THE IMPREGNATION METHOD

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Received: 28 March 2020

Revised: 1 April 2020

Accepted: 4 April 2020

Online: 26 April 2020

Published: 30 April 2020

SPEKTRA: Jurnal Fisika dan Aplikasinya

p-ISSN: 2541-3384

e-ISSN: 2541-3392



ABSTRACT

Nanocomposite Titanium Dioxide (TiO₂) doped Copper (Cu), Cu-TiO₂ is synthesized by the impregnation method. This study aims to determine the effect of adding Cu to the TiO₂ structure. The 1, 3, and 5 Cu with% TiO₂ dissolved in 50 ml of deionized water, and 3 grams of TiO₂ added. The compound is then stirred for 2 hours at 90°C and dried in an oven at 110°C for 30 minutes. Drying samples were calcined at 500°C for 3 hours. Cu-TiO₂ nanocomposites were characterized by XRD, SEM-EDX Mapping, and FTIR. The XRD analysis results show that Cu-TiO₂ nanocomposite has a high level of crystallinity and has an anatase phase structure. The size of TiO₂ crystals decreased with Cu doping and increased from 49.66 nm to 49.68 nm, with an increase in the composition of the doping mass of Cu. The SEM-EDX Mapping results show that all samples tend to clot, and Cu dopants evenly distributed on the surface of TiO₂. FTIR analysis explained the presence of hydroxyl ions in the sample marked with the appearance of the absorption peak at 1658.78 cm⁻¹ associated with OH bending of Ti-OH.

Keywords: nanocomposite, copper, titanium, dioxide, impregnation

INTRODUCTION

Titanium dioxide (TiO_2) has many advantages compared to other types of semiconductors, including chemical stability, corrosion resistance, and non-toxic [1]. TiO_2 has three different phases, namely, anatase, rutile, and brookite. In general, the anatase phase is formed at 300-600°C, while rutile formed at high temperatures [2,3]. In its use, TiO_2 has the limitation of only being stimulated in some parts of the UV light from the sun. Therefore, surface modification of TiO_2 with transition metals [4], and non-metal elements [5,6] becomes very important.

Currently, copper metal, Cu, as one of the TiO_2 dopants, is the concern of many researchers. To improve the properties of TiO_2 can be done by doping with the element Cu. It is caused by high copper conductivity and low cost. Also, copper has a low level of toxicity [7]. Cu can also affect particle size and optical properties of TiO_2 , and the amount of oxygen on the surface of TiO_2 [8]. Cu- TiO_2 has been widely applied in various fields, including environmental remediation, degradation of organic pollutants [9,10], and bacterial disinfection [11].

Xin et al. [12], synthesized Cu- TiO_2 with dopant variations of Cu (0 to 3 mol%) made by the sol-gel method. It was found that at 0.06% mol had many electronic traps, such as the voiding of O and Cu (II) ions and compared with pure TiO_2 , the hydroxyl content on the surface of Cu- TiO_2 increased. Heciak et al. [13] studied the effect of modification procedures and copper precursors on the physicochemical and photoactivity on the formation of useful hydrocarbons from acetic acid. The synthesis of Cu- TiO_2 was carried out by different methods, namely impregnation, mechanical alloying, and photo deposition.

Reddam et al. [14], synthesized modified TiO_2 with cations of Fe, Mn, and Cu. The characterization results confirmed the presence of anatase and rutile phases, and well dispersed on the surface of the catalyst, which was verified by XPS analysis. Mathew et al. [15], synthesized Cu- TiO_2 by the sol-gel method and calcined at a temperature range of 500 - 700°C for antimicrobial applications. The characterization results explained the presence of anatase at a temperature of 500-600°C, and bandgap energy was obtained 2.8 eV. The calcination temperature treatment of 500°C was too carried out by Heider et al. [16]. They reported that at calcination temperature of 500°C, an anatase phase was obtained.

In this study, the impregnation method was used for the synthesis of Cu- TiO_2 nanocomposites. In the process, this method does not transpire anion or cation exchange. The method depends on the metal cation, which becomes a dopant. Queiroz and Barbosa [17] reported that the synthesis of Cu- TiO_2 by the impregnation method could be obtained by anatase phase TiO_2 . Behnajady and Eskandarloo [18] reported the same thing. Besides, the insertion of dopants by the impregnation method does not change the electronic structure of the catalyst material.

The micro characterization obtained was done by X-ray Diffraction (XRD) and Scanning electron microscopy (SEM) - energy dispersive X-ray (EDX). The functional group investigated by Fourier-transform infrared spectroscopy (FTIR).

METHOD

Cu-TiO₂ nanocomposites synthesized using the impregnation method. Copper sulfate, n% (n = 0, 1, 3, and 5) of the weight of TiO₂, was dissolved in 50 ml of distilled water as a solution of copper precursors and stirred with magnetic stirrers until homogeneous at room temperature for 30 minutes. After that, 3 g TiO₂ was added to the solution. Subsequently evaporated at 90°C for 2 hours while stirring. The sample was then dried in an oven at 110°C, crushed and calcined at 500°C for 3 hours. It is to obtain the anatase phase TiO₂ formed in the temperature range 400-500°C [19]. Also, the calcination temperature of 500°C can induce OH group deficiencies on the surface [20].

Nanocomposite samples characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM)-energy dispersive X-ray (EDX) Mapping, and Fourier-transform infrared spectroscopy (FTIR).

TABLE 1. Percentage of Cu and sample labels.

Sample	% Cu	Sample Labels
TiO ₂	0%	TiO ₂
TiO ₂ + Cu	1%	1%-CTO
TiO ₂ + Cu	3%	3%-CTO
TiO ₂ + Cu	5%	5%-CTO

RESULT AND DISCUSSION

FIGURE 1 displays the XRD diffraction pattern of TiO₂ and Cu- TiO₂. The XRD pattern was obtained from Cu radiation in the range of angle values 2θ from 10° – 80°. The XRD diffraction patterns of TiO₂ and Cu-TiO₂ characterized by the presence of diffraction peaks at an angle of $2\theta = 25.3^\circ$; 37.0° ; 37.8° ; 38.6° ; 48.1° ; 53.9° ; 55.1° ; 62.7° ; 68.8° ; 70.3° ; 75.1° ; and 76.1° correspond to lattice planes (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), (215)) and (301), respectively. All patterns assigned to the crystalline phase structure of TiO₂, according to (JCPDS no 21-1272) and Cu doping on TiO₂ does not change the shape of the anatase structure of TiO₂. The Cu²⁺ ion may enter to replace Ti on TiO₂ because the ionic radius of Cu²⁺ (0.73 Å) is almost the same as the Ti⁴⁺ ion (0.74 Å) [21].

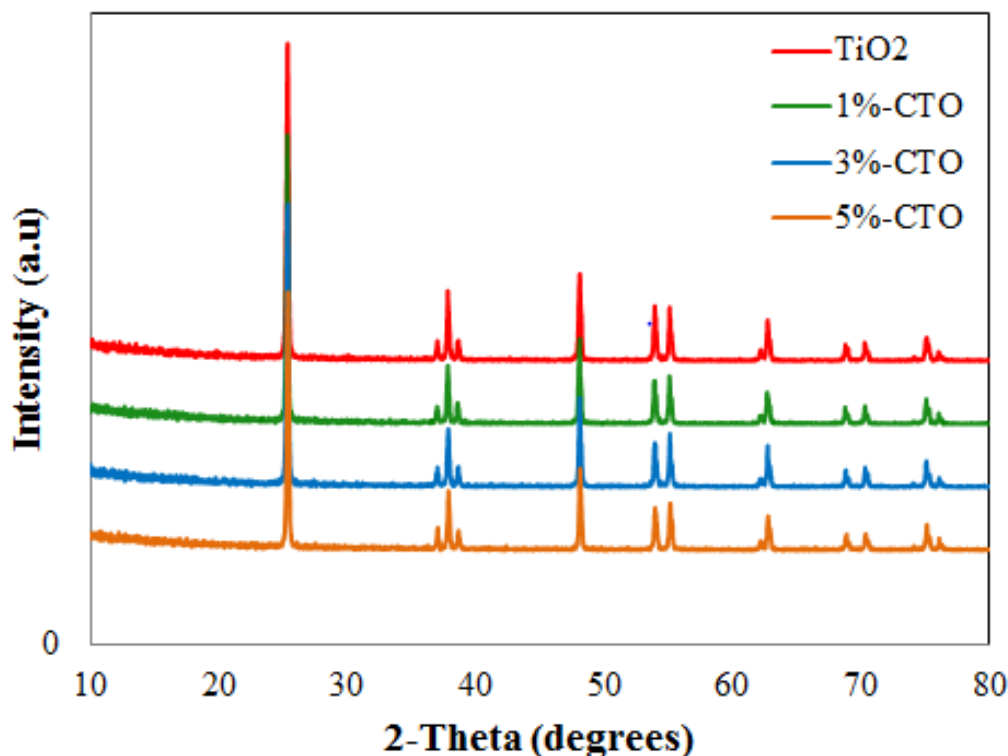


FIGURE 1. XRD patterns of (a) TiO₂, (b) Cu 1%-TiO₂, (c) Cu 3%-TiO₂, and (d) Cu 5%-TiO₂.

The average size of the crystallite sample is obtained from the half-width of the full maximum (FWHM) from the highest peak using the Debye-Scherrer equation,

$$t = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where t is the size of a crystal grain, k is the Scherrer constant (0.9), λ is the wavelength of X-rays (in Å), β is the width of half the peak (in radians), and θ is the Bragg diffraction angle (in radians). The results are shown in TABLE 2.

TABLE 2. Crystalline Size TiO₂ and Cu-TiO₂ nanocomposites.

Sample Labels	Lattice Parameters (Å)			Crystalline size (nm)
	<i>a</i>	<i>b</i>	<i>c</i>	
TiO ₂	3.7798	3.7798	9.5004	55.88
1%-CTO	3.7809	3.7809	9.5014	49.66
3%-CTO	3.7798	3.7798	9.4947	49.67
5%-CTO	3.7780	3.7780	9.4900	49.68

The size of the TiO₂ crystal was 55.88 nm, and the crystal size was smaller after Cu doped. The size of the crystals increases with enhancing doping Cu ions, which are 49.66 nm; 49.47 nm; and 49.68 nm respectively for 1% -CTO; 3%-CTO; and 5%-CTO samples. Navas et al. reported that crystal size decreased with an increase in Cu dopant in TiO₂ [22]. Rajamannan et al. reported that as Cu dopants increased in TiO₂, crystal size increased [23]. It explains that Cu doping can inhibit the growth of grains.

FIGURE 2 (a-c) shows the results of the characterization using SEM. The results explained that all Cu-TiO₂ samples tended to clot. In FIGURE 2a, small clumps of relatively uniform size appear, and they get more significant with the increasing composition of Cu dopants, as in FIGURE 2b and 2c. It indicated that Cu dopants are dispersed on the surface of TiO₂. XRD data confirmed this result. Nankya and Kim [24] reported that clumping particles and TiO₂ particle size decreased with the addition of Cu dopants. It is shown that Cu doping affects grain growth. FIGURE 3 shows the EDX Mapping image on a 5%-CTO nanocomposite sample. The elements shown in the image are colored spots. Cu dopants are evenly distributed on the surface of TiO₂. Zaid et al. [25] reported that the dispersed metal element indicated that doping Cu on the surface of TiO₂ by the method used was successful. Also, it shows that the calcination process influences the distribution of elements of Cu, O, and Ti that is evenly distributed in Cu-TiO₂, as reported by Tian [20]. This result was also reported by Singh and Dutta [26] with calcination temperatures of 600°C.

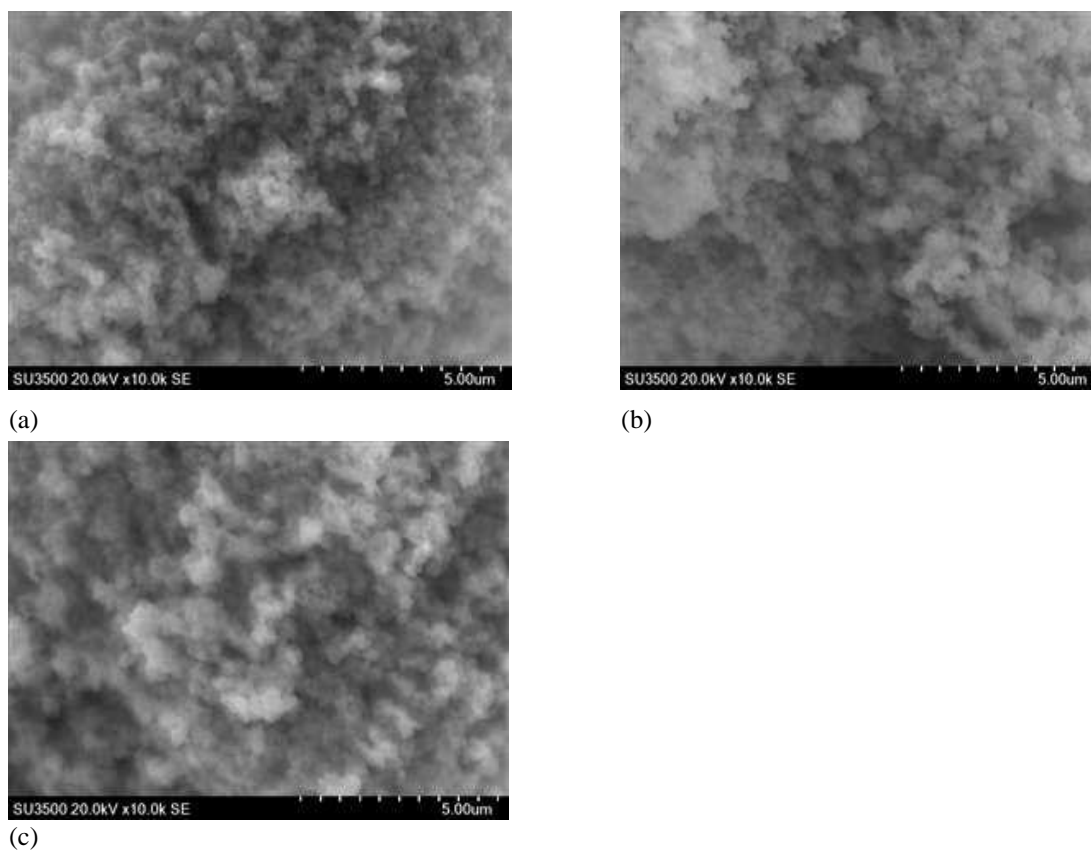
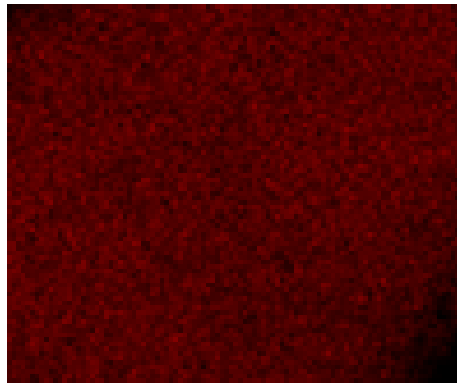
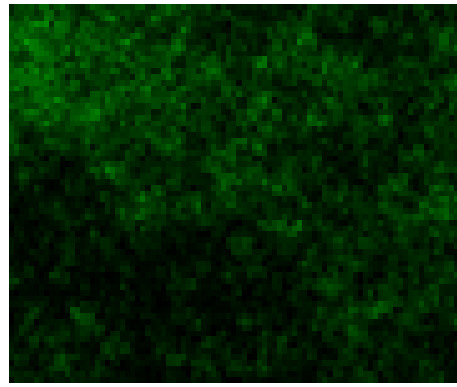


FIGURE 2. SEM micrographs of (a) 1%-CTO, (b) 3%-CTO, and (c) 5%-CTO



Ti Ka1



O Ka1



Cu Ka1

FIGURE 3. EDX and mapping images of 5%-CTO

FIGURE 4 shows the FTIR spectrum of 0%-CTO, 1%-CTO, and 5% -CTO. In all spectra, the Ti-O-Ti structure appeared in the absorption regions of 669.3 cm^{-1} and 501.49 cm^{-1} ; 677.01 cm^{-1} and 516.92 cm^{-1} ; and 684.73 cm^{-1} and 516.92 cm^{-1} , for samples of 0%-CTO, 1%-CTO, and 5% -CTO, respectively.. The absorption area of -OH stretching from Ti-OH on the surface of TiO_2 and water molecules shifted after Cu doping, i.e., from 3444.72 cm^{-1} (0%-CTO) to 3568.31 cm^{-1} (1%-CTO), 3562.52 cm^{-1} (5%-CTO).

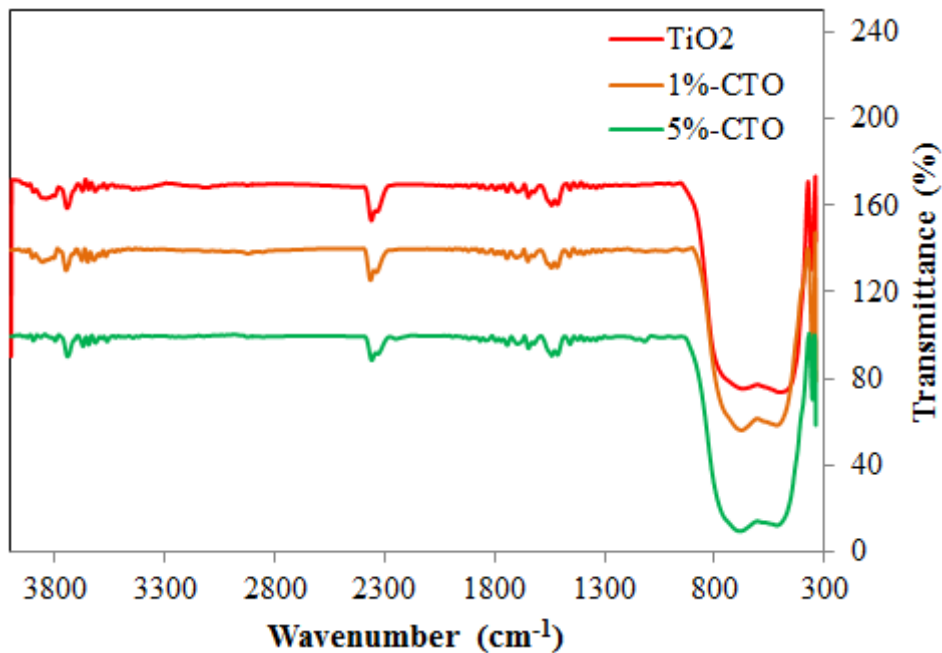


FIGURE 4. FTIR spectra of TiO₂; 1%-CTO; and 5%-CTO.

In 1658.78 cm⁻¹, it was related to the -OH bending of Ti-OH on the surface of TiO₂ and the water molecules adsorbed by the catalyst [27]. These results indicate the presence of hydroxyl ions in the sample. It thought that the existence of these peaks is because they are physically adsorbed. The absorption area of TiO₂ appears at 600-700 cm⁻¹ and changes with the addition of metals [28].

CONCLUSION

The Cu-TiO₂ nanocomposites were prepared using the impregnation method. From the observations, it was found that nanocomposites contain Cu on the surface of TiO₂. XRD measurements show that this doping material is an anatase structure phase with a high level of crystallinity and crystalline size ranges from 49.66 nm - 49.68 nm and 55.88 nm for TiO₂ without doping. SEM/EDX data show that agglomeration is increasing with the addition of Cu dopants and Cu, Ti, O elements evenly distributed on the surface of Cu-TiO₂. FTIR data showed that copper, Cu, entered the TiO₂ matrix, which was marked by the presence of hydroxyl ions at 1658.78 cm⁻¹.

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