ISSN: 1410-8917
Jurnal Kimia Sains & Aplikasi
e-ISSN: 2597-9914

Jurnal Kimia Sains dan Aplikasi 28 (8) (2025): 436-441
Jurnal Kimia Sains dan Aplikasi
Journal of Scientific and Applied Chemistry
Journal homepage: http://ejournal.undip.ac.id/index.php/ksa

Synthesis and Characterization of HDTMA-Br Modified TiO_2/ZnO/CuO Photocatalyst Composite for Photodegradation of Textile Dye (Methyl Orange)

Siti Fatika [1], Komar Sutriah [1,*], Mohammad Khotib [1]

[1] Department of Chemistry, Faculty of Sciences and Mathematics, IPB University, Bogor, Indonesia

* Corresponding author: komar.sutriah@yahoo.com

https://doi.org/10.14710/jksa.28.8.436-441

Article Info

Article history:

Received: 13th May 2025
Revised: 18th September 2025
Accepted: 22nd September 2025
Online: 31st October 2025

Keywords:
composite; hexadecyltrimethylammonium bromide; methyl orange; photodegradation; TiO_2/ZnO/CuO

Abstract

Methyl orange exhibits low biodegradability and is difficult to remove from aqueous solutions. Photodegradation using photocatalysts offers an efficient and practical alternative for treating methyl orange dye waste. Among various semiconductor materials, TiO_2 and ZnO have attracted considerable attention due to their strong photocatalytic activity. However, excessive use of TiO_2 can lead to turbidity in the solution, reducing light penetration and consequently diminishing the efficiency of the photoreduction and photooxidation processes. Numerous studies have been conducted to control the structure, morphology, and porosity of TiO_2 to enhance its photocatalytic performance. One effective approach involves the incorporation of surfactants into composites, which can modify the optical properties, structure, and morphology of the material, thereby improving its ability to degrade methyl orange. In this study, the composite was synthesized using the precipitation method. The highest degradation efficiency of 44% was achieved at 50 minutes for a methyl orange concentration of 30 mg/L, with a composite ratio of 1:1:0.3 and an HDTMA-Br concentration of 2 CMC. The addition of HDTMA-Br enhanced the photocatalytic performance by reducing electron–hole recombination, resulting in a band gap energy of 2.87 eV within the visible light range (1.77–3.1 eV).

1. Introduction

Textile industry wastewater contains dyes with aromatic structures that are difficult to degrade naturally and are harmful to the environment. One commonly used dye is methyl orange (MO), which exhibits high stability and low biodegradability. Due to its solubility in water, MO is challenging to separate from aqueous solutions using conventional purification or water treatment methods [1]. An alternative and practical approach for treating such wastewater is photodegradation, which utilizes photocatalysts. The photodegradation (photocatalytic degradation) process decomposes dye pollutants into simpler, less harmful compounds through photoinduced oxidation–reduction reactions [2]. Photodegradation typically employs photocatalysts composed of semiconductor materials [3].

Photocatalysis using TiO_2 and ZnO semiconductors has attracted widespread attention due to their high photocatalytic activity, excellent thermal, chemical, and biological stability, long lifespan, non-toxicity, and low cost [4]. ZnO is stable, non-toxic, and acts as an electron donor in the photocatalytic process. The photocatalytic activity of TiO_2 can be increased by the addition of copper metal (Cu), which broadens visible light absorption and promotes more efficient electron–hole separation. Using visible light is also safer than UV light, which can cause skin irritation, premature aging, and increase cancer risk. Thus, visible-light-driven photocatalysis not only enhances performance in photodegradation applications but also supports safer and more sustainable operation [5]. Various attempts have been made to control composite properties such as optical properties, structure, and morphology. One approach is to add surfactants.

The use of surfactants in the synthesis of metal oxides has attracted considerable attention as an effective strategy for controlling material surface properties. Particle stability and nanoscale size are crucial factors that determine their potential applications. In this study, the cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br) was employed as a stabilizing agent. The presence of a stabilizer prevents particle coalescence, thereby promoting the formation of uniformly distributed nanoparticles [6].

HDTMA-Br possesses a positively charged head group, enabling strong electrostatic interactions with the composite surface. Its long alkyl chain imparts hydrophobic characteristics, enhancing surface modification efficiency compared to shorter-chain surfactants. Previous research demonstrated that HDTMA-Br can improve the surface properties of zeolite, such as porosity and morphology, resulting in 66% removal of navy solophenyl dye within 78 minutes [7].

Minimized agglomeration leads to uniform particle distribution, maximizing the contact area between photocatalysts and pollutants. Particle aggregation and agglomeration significantly influence the optical properties of materials and, consequently, their ability to absorb and scatter incident radiation, which directly affects photocatalytic activity [8]. Therefore, a stabilizer is essential to ensure particle stability and uniform dispersion, thereby optimizing light absorption by the photocatalyst. To further evaluate this, the photocatalytic activity of the HDTMA-Br–modified $TiO_2/ZnO/CuO$ composite synthesized via the precipitation method was examined for MO degradation. The characteristics of the modified composite were analyzed using XRD, SEM, PSA, UV-Vis DRS, and FTIR techniques.

2. Experimental

2.1. Materials

The materials used in this study included distilled water, methyl orange dye (Merck), zinc chloride ($ZnCl_2$; Merck) as a ZnO precursor, titanium dioxide (TiO_2; Merck), copper nitrate ($Cu(NO_3)_2$; Merck), the cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br; Merck), sodium hydroxide (NaOH; 0.1 M; Merck), and potassium bromide (KBr; Merck).

The instruments employed were a Fourier Transform Infrared Spectrophotometer (FTIR; Shimadzu IR Prestige 21), oven (Wisconsin Oven), Particle Size Analyzer (PSA; Horiba Scientific SZ-100Z), centrifuge (Hermle Z206A), UV–Visible Spectrophotometer (Genesys 150), UV–Vis Diffuse Reflectance Spectrophotometer (DRS; Shimadzu UV-2450), furnace (Neycraft), Scanning Electron Microscope (SEM; Hitachi SU3500), ultrasonic bath (Elma), and X-ray Diffractometer (XRD).

2.2. Preparation of $TiO_2/ZnO/CuO$ Composite Photocatalyst Modified by HDTMA-Br Surfactant Using Sol-Gel Method

The $TiO_2/ZnO/CuO$ composite photocatalysts were prepared in various molar ratios, as listed in Table 1. TiO_2 (1 mol; 3 g), $ZnCl_2$ (1 mol), and $Cu(NO_3)_2$ (1 mol) were mixed in a molar ratio of 1:1:1 and dissolved in 600 mL of distilled water. Subsequently, 0.1 M HDTMA-Br was added at concentrations corresponding to 0, 2, and 5 times the critical micelle concentration (CMC) value (HDTMA-Br = 0.94 $mmol·L^{-1}$ or 342.6 $mg·L^{-1}$) [8]. The resulting solution was stirred magnetically for 10 minutes to ensure homogeneity.

Afterward, 0.1 M NaOH was added dropwise to the mixture under continuous stirring. The resulting precipitate was centrifuged at 4000 rpm for 10 minutes and washed three times with HDTMA-Br solution. The washed precipitate was then dried in an oven at 100°C, followed by calcination at 450°C for 3 hours to obtain the $TiO_2/ZnO/CuO$ composite photocatalysts.

2.3. Characterization of FTIR, PSA, SEM, UV-Vis DRS, and XRD

FTIR spectroscopy was performed using KBr pellets prepared with a sample-to-KBr ratio of 1:99. The spectra were recorded in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. PSA was conducted to confirm the nanoscale size of the composites. For measurement, approximately 2 mg of the composite powder was dispersed in 20 mL of dispersant, sonicated for 30 minutes, and analyzed using a Dynamic Light Scattering (DLS) instrument (Horiba Scientific SZ-100Z) at 25°C.

The surface morphology of the nanocomposites was examined using SEM (magnification 3.00 µm, accelerating voltage 15 kV). The phase composition was identified by XRD analysis using a step size of 0.05° and an integration time of 0.5 s over a 2θ range of 20°–80° to determine the diffraction patterns. Optical characterization was performed using UV–Vis DRS with $BaSO_4$ as the reference standard in the wavelength range of 200–1100 nm. The reflectance data (%R) were converted into Kubelka–Munk (F(R)) values, and the photon energy (hν) was calculated from the corresponding wavelength. The band gap energy was then estimated from the Tauc plot.

2.4. Optimization of $TiO_2/ZnO/CuO$ Composite Composition, HDTMA-Br Surfactant Concentration

2.4.1. Photodegradation of MO Solution with Variation of Irradiation Time

The photodegradation of MO solution was carried out under both UV and visible light irradiation at room temperature. A total of 20 mg of the $TiO_2/ZnO/CuO$ composite photocatalyst was added to 20 mL of MO solution with a concentration of 30 $mg·L^{-1}$, followed by magnetic stirring to ensure uniform dispersion. The mixture was then ultrasonicated for 15 minutes to enhance homogeneity.

Table 1. Comparison of $TiO_2/ZnO/CuO$ molar ratios

TiO_2	ZnO	CuO
1	1	0.3
1	1	1
1	0.3	1

Subsequently, the solution was irradiated using a 40 W visible light lamp and a 40 W UV lamp for 50 minutes in a black reactor with dimensions of 20 × 40 × 20 cm. After irradiation, the suspension was centrifuged to separate the $TiO_2/ZnO/CuO$ composite from the MO solution. The absorbance of the resulting filtrate was measured using a UV–Visible spectrophotometer at the maximum wavelength of 463 nm. The percentage of dye degradation was calculated using Equation (1).

$$\%\ \text{Degradation} = \frac{(C_0 - C_t)}{C_0} \times 100\% \qquad (1)$$

Where, C_0 is the initial concentration of MO dye before irradiation, C_t is the concentration of the dye at a given time.

3. Results and Discussion

3.1. Synthesis of TiO_2/ZnO Composite Photocatalyst

In this study, the $TiO_2/ZnO/CuO$ composite was synthesized using the precipitation method. $ZnCl_2$ was used as the ZnO precursor, while $Cu(NO_3)_2$ served as the CuO precursor. Each precursor was reacted in an alkaline environment by adding NaOH solution until the pH reached 12, leading to the formation of precipitates. The pH of the growth solution significantly influences the morphology, crystal quality, and optical properties of the resulting material. Previous studies have reported that pH plays a critical role in chemical precipitation processes, as hydroxide ions (OH^-) are directly involved in the formation of metal hydroxide intermediates [9]. Research by Ardiansyah and Wahyuni [10] demonstrated that ZnO synthesized at pH 12 produced purer particles with fewer impurities compared to synthesis at pH 7.

The addition of HDTMA-Br served to control the rate of reduction and minimize particle aggregation. The polar head groups of HDTMA-Br interact with water molecules, thereby stabilizing the particles and preventing agglomeration. After drying in an oven, a bright turquoise composite was obtained, as shown in Figure 1(a). However, after calcination at 450°C for 3 hours, the composite color changed to gray, as shown in Figure 1(b). According to Alawiyah and Maharani [11], calcination acts as the final step to remove residual organic molecules and to convert amorphous Ti–O–Ti bonds into crystalline TiO_2. Additionally, calcination eliminates impurities and unreacted precursor residues that cannot be removed at lower temperatures, thereby enhancing surface area and improving crystallinity [12]. As a result, a gray-colored composite powder was successfully obtained.

3.2. Characterization of $TiO_2/ZnO/CuO$ Composites

3.2.1. FTIR Profile of Photocatalyst Products

FTIR analysis was performed to identify the functional groups present in the composite and to evaluate the successful synthesis of both unmodified and HDTMA-Br–modified $TiO_2/ZnO/CuO$ composites. Based on the photodegradation results of $TiO_2/ZnO/CuO$ composites with a molar ratio of 1:1:0.3 and those modified with HDTMA-Br at 2 CMC, the modified composite demonstrated superior photocatalytic activity. The FTIR spectra of both samples are presented in Figure 2.

The FTIR spectrum of the unmodified composite (black curve) showed no characteristic absorption peaks in the wavelength range of 2915–2850 cm^{-1}, which correspond to the C–H stretching vibrations of the HDTMA-Br surfactant [13]. In contrast, the modified composite (HDTMA-Br 2 CMC) exhibited distinct absorption peaks within this range, confirming the presence of C–H groups originating from the alkyl chains of HDTMA-Br. This observation aligns with previous studies [14], indicating that the $-CH_3$ and $-CH_2-$ groups of the HDTMA-Br surfactant were successfully attached to the composite surface, thus verifying the success of the surface modification process.

Both unmodified and modified composites exhibited similar absorption bands at approximately 1600 cm^{-1}, which correspond to Ti–O–Ti stretching vibrations in TiO_2 [15]. The absorption bands observed at 750–760 cm^{-1} and around 500 cm^{-1} are attributed to Zn–O [16] and Cu–O [17] stretching vibrations, respectively. Additionally, the broad absorption band around 3500 cm^{-1} indicates the presence of hydroxyl (O–H) groups on the composite surface [17]. These results suggest that the modification with HDTMA-Br successfully introduced surfactant functional groups onto the composite surface without eliminating the primary functional groups of TiO_2, ZnO, or CuO.

Figure 1. Physical form of $TiO_2/ZnO/CuO$ composite (a) before calcination and (b) after calcination

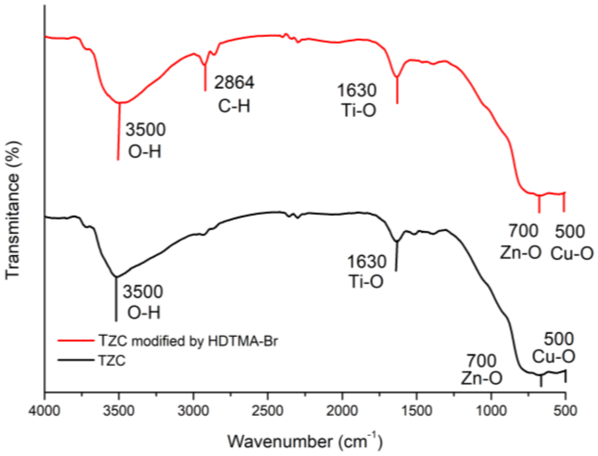

Figure 2. FTIR spectra of $TiO_2/ZnO/CuO$ composites

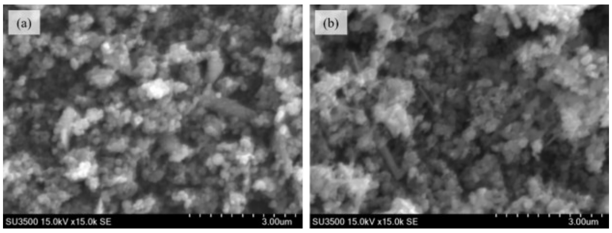

Figure 3. SEM images of (a) $TiO_2/ZnO/CuO$ composite and (b) HDTMA-Br–modified $TiO_2/ZnO/CuO$ composite

3.2.2. SEM Characterization

SEM characterization was performed to observe the surface morphology of the unmodified and HDTMA-Br–modified $TiO_2/ZnO/CuO$ composites, as shown in Figure 3. The unmodified composite (Figure 3a) exhibited a coarse and irregular surface due to particle agglomeration, indicating poor dispersion. After surface modification with HDTMA-Br (Figure 3b), the composite showed reduced clumping and a more uniform morphology. This suggests that the positively charged HDTMA-Br surfactant improved particle dispersion by reducing electrostatic attraction among particles and promoting a more controlled structure.

3.2.3. Characteristics of HDTMA-Br Modified $TiO_2/ZnO/CuO$ Composite by XRD

XRD analysis was performed to identify the crystalline phases formed in the $TiO_2/ZnO/CuO$ composite. The XRD pattern (Figure 4) exhibits sharp and intense peaks, indicating that the synthesized material possesses a high degree of crystallinity (57.76%). Based on comparison with the International Center for Diffraction Data (ICDD), three major crystalline phases were identified: anatase TiO_2 (ICDD 00-021-1272), zincite ZnO (ICDD 00-036-1451), and tenorite CuO (ICDD 00-048-1548). The highest diffraction peak was observed at 2θ = 25.38°, corresponding to the (101) plane of the anatase TiO_2 phase.

In addition, the diffraction peaks at 31.79°, 34.54°, and 36.28° correspond to the (100), (002), and (101) planes of the hexagonal wurtzite ZnO structure, respectively. A characteristic CuO peak was detected at 38.68°, associated with the (111) plane of the monoclinic tenorite structure. These results confirm that the three semiconductor oxides coexist within a single multiphase composite system.

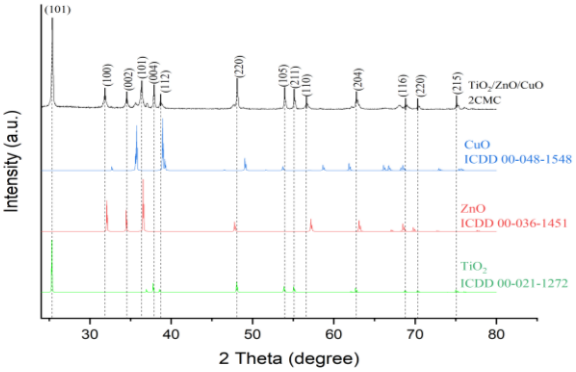

Figure 4. XRD diffractogram of HDTMA-Br-modified $TiO_2/ZnO/CuO$ (1:1:0.3) composite

The crystallite sizes calculated using the Debye–Scherrer equation for TiO_2, ZnO, and CuO in the HDTMA-Br modified composite (2 CMC concentration) were 51 nm, 33.1 nm, and 32 nm, respectively, with an average crystal size of 34.87 nm; an increase from 37 nm, 28 nm, and 26 nm in the unmodified composite. This increase may be attributed to the presence of HDTMA-Br, a cationic surfactant capable of forming micelle structures that facilitate controlled crystal growth.

3.2.4. Particle Size of $TiO_2/ZnO/CuO$ Composite Analyzed by PSA

PSA characterization was conducted to evaluate the effect of HDTMA-Br modification on the particle size of the composite. The analysis was performed using the DLS technique. As shown in Table 2, the polydispersity index (PI) decreased slightly from 1.148 to 1.122. However, since both values are greater than 0.1, the particle distribution of the composite remains polydisperse, indicating a high level of heterogeneity in particle size. Therefore, it can be concluded that the addition of HDTMA-Br surfactant slightly influences the particle size and distribution of the $TiO_2/ZnO/CuO$ composite.

3.2.5. UV Vis DRS Characterization

Characterization using UV–Vis DRS was conducted to determine the band gap energy of the HDTMA-Br-modified composite using the Tauc plot method and the Kubelka–Munk function. The results are shown in Figure 5. Before synthesis, TiO_2, ZnO, and CuO have reported band gap energies of 3.2 eV, 3.4 eV, and 1.3–1.7 eV, respectively [18, 19, 20]. After combining these oxides, the resulting composite exhibited a band gap energy of 2.87 eV, corresponding to approximately 432 nm (within the 400–450 nm range). This indicates that the modified $TiO_2/ZnO/CuO$ composite photocatalyst can effectively absorb visible light.

For a material to be photoactive under visible light, its band gap should fall between 1.77 eV and 3.1 eV, equivalent to wavelengths of 700–400 nm. A smaller band gap allows absorption of a broader portion of the visible spectrum. The observed reduction in band gap is attributed to the formation of heterojunctions and strong interactions between TiO_2, ZnO, and CuO phases, which modify the optical properties of the composite. Such interaction enhances photocatalytic performance by facilitating more efficient electron–hole pair generation during the photodegradation of MO dye.

Table 2. Particle size and PI value of unmodified and HDTMA-Br-modified $TiO_2/ZnO/CuO$ (1:1:0.3) composites

Parameter	Unmodified	Modified
Z-Average	340.2 nm	357.5 nm
Mean diameter	438.1 nm	441.3 nm
Polydispersity Index (PI)	1.148	1.122

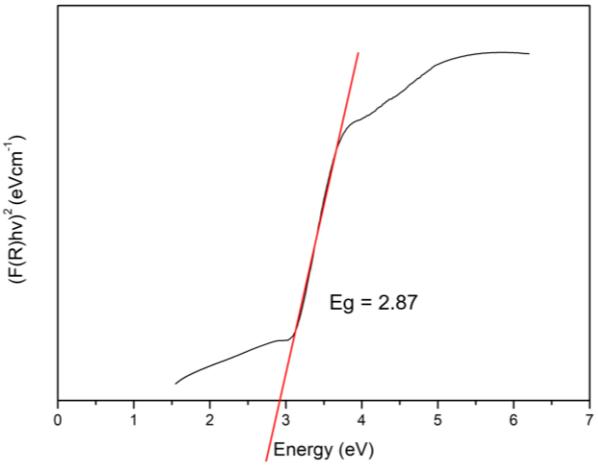

Figure 5. Band gap value of TiO_2/ZnO/CuO (1:1:0.3) composite

3.3. Optimization of TiO_2/ZnO/CuO Composite Performance at Different HDTMA-Br Concentrations

The photocatalytic performance of the HDTMA-Br–modified TiO_2/ZnO/CuO composite for methyl orange degradation was tested under UV and visible light using a 30 mg/L dye solution. As shown in Figure 6, the TiO_2/ZnO/CuO composite modified with 0 CMC HDTMA-Br exhibited lower degradation efficiency compared to the 2 CMC and 5 CMC–modified composites under both UV and visible light, with the highest degradation of 24% achieved under UV light. These results indicate that the addition of HDTMA-Br significantly influences the photocatalytic activity of the composite.

An improvement in degradation efficiency was observed at 2 CMC compared to 0 CMC; however, further increasing the surfactant concentration to 5 CMC reduced performance. This decline can be attributed to the excessive surfactant covering the active sites or forming aggregates that hinder charge transfer. The highest degradation efficiency (44%) was obtained for the 1:1:0.3 composite with 2 CMC HDTMA-Br under UV light, suggesting that 2 CMC is the optimum surfactant concentration for enhancing photocatalytic activity. According to Stefan *et al.* [21], the addition of 2 CMC effectively forms an optimal bilayer structure that enhances photocatalytic performance.

The photocatalytic process operates under specific optimal conditions that determine degradation efficiency. The presence of surfactants increases the interaction between the composite surface and methyl orange molecules, thereby improving degradation. In contrast, at higher CuO compositions (e.g., 1:1:1 and 1:0.3:1), the 5 CMC HDTMA-Br concentration resulted in higher degradation under both UV and visible light, which can be attributed to differences in ZnO and CuO composition ratios. The results show that the best-performing composite for methyl orange photodegradation was TiO_2/ZnO/CuO (1:1:0.3) with 2 CMC HDTMA-Br under UV light, achieving 44% degradation. The lower CuO content was more favorable, as higher CuO concentrations tend to promote electron–hole recombination, reducing photocatalytic efficiency.

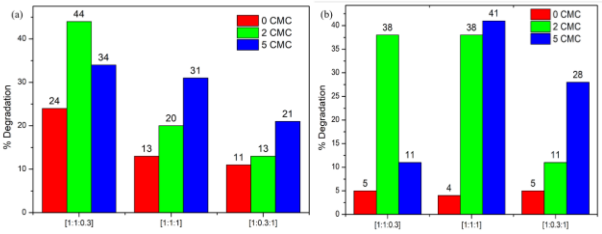

Figure 6. Photodegradation performance of TiO_2/ZnO/CuO composite without surfactant under UV light

The improvement in photocatalytic activity is attributed to the cationic surfactant (HDTMA-Br), which inhibits electron recombination by enhancing the generation of reactive oxygen species (ROS). These ROS act as strong oxidizing agents, decomposing organic pollutants during the photocatalytic process. Furthermore, the increase in crystallite size contributes to enhanced electron transfer and reduced electron–hole recombination, thereby improving photocatalytic activity. The modified composite also exhibits a narrower band gap in the visible region, enabling more efficient light absorption and charge separation. The positively charged HDTMA-Br molecules enhance photocatalytic performance by improving charge separation and optimizing the interaction between the photocatalyst and the dye. The improved performance of the surfactant-modified composites can also be associated with the increased crystallite size, which enhances charge transfer efficiency and minimizes recombination [22].

Additionally, the presence of surfactants increases surface hydrophobicity and promotes better separation of electron–hole pairs. SEM analysis further confirms that HDTMA-Br modification leads to more uniform and stable particles by reducing agglomeration, resulting in improved and more consistent photocatalytic performance.

4. Conclusion

The TiO_2/ZnO/CuO composite modified with HDTMA-Br was successfully synthesized, as confirmed by SEM and PSA analyses, which showed a slight improvement in particle dispersion and reduced agglomeration. FTIR confirmed the successful incorporation of HDTMA-Br without altering the main functional groups of the composite. The modified composite exhibited a band gap of 2.87 eV, making it active under visible light, and a crystallinity of 57.76% with an average crystallite size of 34.87 nm. The highest photocatalytic degradation efficiency of 44% was achieved for methyl orange (30 mg/L) after 50 minutes using the TiO_2/ZnO/CuO (1:1:0.3) composite with 2 CMC HDTMA-Br under UV light. These findings indicate that HDTMA-Br modification effectively enhances surface properties and light absorption, although further studies are needed to investigate charge carrier dynamics in more detail.

References

[1] Fortunate Phenyo Sejie, Misael Silas Nadiye-Tabbiruka, Removal of Methyl Orange (MO) from

Water by Adsorption onto Modified Local Clay (Kaolinite), *Physical Chemistry*, 6, 2, (2016), 39-48

[2] Mohamed A. Barakat, Rajeev Kumar, Photocatalytic activity enhancement of titanium dioxide nanoparticles, in: *Photocatalytic Activity Enhancement of Titanium Dioxide Nanoparticles: Degradation of Pollutants in Wastewater*, Springer, 2015, https://doi.org/10.1007/978-3-319-24271-2_1

[3] Tri Mawarni, Fadarina H. C., Martha Aznury, Muhammad Taufik, Degradasi Zat Warna Rhodamin B Menggunakan Sintesis Fotokatalis $ZnO/NiFe_2O_4$ dan Diaplikasikan pada Limbah Cair Industri *Pulp* dan Kertas, *KINETIKA*, 12, 3, (2021), 44-50

[4] Ardiansyah Taufik, Alfred Albert, Rosari Saleh, Sol-gel synthesis of ternary $CuO/TiO_2/ZnO$ nanocomposites for enhanced photocatalytic performance under UV and visible light irradiation, *Journal of Photochemistry and Photobiology A: Chemistry*, 344, (2017), 149-162 https://doi.org/10.1016/j.jphotochem.2017.05.012

[5] Annisa M. Dewi, Wahyu B. Widayatno, Yuly Kusumawati, Perbandingan Efektivitas Dekolorisasi Fotokatalitik Metilen Biru dan Metil Jingga menggunakan Semikonduktor ZnO pada Variasi pH, *Jurnal Riset Kimia*, 10, 2, (2019), 75-84 https://doi.org/10.25077/jrk.v10i2.328

[6] Hanae Abdelouahab Reddam, Rachad Elmail, Sara Cerro Lloria, Guillermo Monrós Tomás, Zinab Abdelouahab Reddam, Fernando Coloma-Pascual, Synthesis of Fe, Mn and Cu modified TiO_2 photocatalysts for photodegradation of Orange II, *Boletín de la Sociedad Española de Cerámica y Vidrio*, 59, 4, (2020), 138-148 https://doi.org/10.1016/j.bsecv.2019.09.005

[7] Patricia Cunico, Anu Kumar, Denise A. Fungaro, Adsorption of dyes from simulated textile wastewater onto modified nanozeolite from coal fly ash, *Journal of Nanoscience and Nanoengineering*, 1, 3, (2015), 148-161

[8] Ming Ge, Changsheng Guo, Xingwang Zhu, Lili Ma, Zhenan Han, Wei Hu, Yuqiu Wang, Photocatalytic degradation of methyl orange using ZnO/TiO_2 composites, *Frontiers of Environmental Science & Engineering in China*, 3, 3, (2009), 271-280 https://doi.org/10.1007/s11783-009-0035-2

[9] M. Rožić, Đ Ivanec Šipušić, L. Sekovanić, S. Miljanić, L. Ćurković, J. Hrenović, Sorption phenomena of modification of clinoptilolite tuffs by surfactant cations, *Journal of Colloid and Interface Science*, 331, 2, (2009), 295-301 https://doi.org/10.1016/j.jcis.2008.11.043

[10] Arie Ardiansyah, Sri Wahyuni, Sintesis Nanosilika dengan Metode Sol-Gel dan Uji Hidrofobisitasnya pada Cat Akrilik, *Indonesian Journal of Chemical Science*, 4, 3, (2015), 223-227

[11] Siti Tutik Alawiyah, Dina Kartika Maharani, Sintesis dan Karakterisasi Nano TiO_2 dengan Metode Sol-Gel Sebagai Agen *Self-Cleaning* pada Kain Katun, *Unesa Journal of Chemistry*, 7, 2, (2018), 64-67

[12] Indah Ilmiyatul Mufida, Rahmad Nuryanto, Taslimah Taslimah, Sintesis Elektrolit Padat $NaMn_{2-x}Co_xO_4$ dengan Variasi Suhu Kalsinasi Menggunakan Metode Sol-Gel dan Karakterisasinya, *Jurnal Kimia Sains dan Aplikasi*, 18, 1, (2015), 13-17 https://doi.org/10.14710/jksa.18.1.13-17

[13] U. O. Aroke, U. El-Nafaty, XRF, XRD and FTIR properties and characterization of HDTMA-Br surface modified organo-kaolinite clay, *International Journal of Emerging Technology and Advanced Engineering*, 4, 4, (2014), 817-825

[14] Wen-Bin Tsai, Jui-Yang Kao, Tzong-Ming Wu, Wen-Tung Cheng, Dispersion of Titanium Oxide Nanoparticles in Aqueous Solution with Anionic Stabilizer via Ultrasonic Wave, *Journal of Nanoparticles*, 2016, 1, (2016), 6539581 https://doi.org/10.1155/2016/6539581

[15] Hossein Asadzadeh Patehkhor, Moslem Fattahi, Mohammadreza Khosravi-Nikou, Synthesis and characterization of ternary chitosan–TiO_2–ZnO over graphene for photocatalytic degradation of tetracycline from pharmaceutical wastewater, *Scientific Reports*, 11, 1, (2021), 24177 https://doi.org/10.1038/s41598-021-03492-5

[16] M. Mohammadi, S. Sabbaghi, H. Sadeghi, M. M. Zerafat, R. Pooladi, Preparation and characterization of $TiO_2/ZnO/CuO$ nanocomposite and application for phenol removal from wastewaters, *Desalination and Water Treatment*, 57, 2, (2016), 799-809 https://doi.org/10.1080/19443994.2014.968877

[17] Indah Rohmah Wahyu Ningrum, Sintesis Nanopartikel Emas Menggunakan Kulit Jeruk Sunkist (*Citrus Sinensis*) dan Aplikasinya Untuk Elektroda Sensor Hidrokuinon dalam Krim Kosmetik, Kimia, Universitas Islam Indonesia, 2022

[18] F. Akbar Jan, Wajidullah, Rahat Ullah, Naimat Ullah, Salman, Muhammad Usman, Exploring the environmental and potential therapeutic applications of *Myrtus communis* L. assisted synthesized zinc oxide (ZnO) and iron doped zinc oxide (Fe-ZnO) nanoparticles, *Journal of Saudi Chemical Society*, 25, 7, (2021), 101278 https://doi.org/10.1016/j.jscs.2021.101278

[19] Dasol Jeong, Woohyeon Jo, Jaebum Jeong, Taegeon Kim, Seungyeon Han, Min-Kyu Son, Hyunsung Jung, Characterization of Cu_2O/CuO heterostructure photocathode by tailoring CuO thickness for photoelectrochemical water splitting, *RSC Advances*, 12, 5, (2022), 2632-2640 https://doi.org/10.1039/D1RA08863G

[20] Jenny Rizkiana, Hary Devianto, Tatang Hernas Soerawidjaja, Karakterisasi fotokatalis untuk fotoreduksi karbon dioksida menjadi asam format dalam fasa akuatik, *Indonesian Journal of Chemical Research*, 8, 1, (2020), 35-42

[21] Maria Stefan, Cristian Leostean, Ovidiu Pana, Adriana Popa, Dana Toloman, Sergiu Macavei, Ioana Perhaita, Lucian Barbu-Tudoran, Danut Silipas, Interface tailoring of SnO_2–TiO_2 photocatalysts modified with anionic/cationic surfactants, *Journal of Materials Science*, 55, 8, (2020), 3279-3298 https://doi.org/10.1007/s10853-019-04192-2

[22] Monika Bhattu, Jagpreet Singh, Recent advances in nanomaterials based sustainable approaches for mitigation of emerging organic pollutants, *Chemosphere*, 321, (2023), 138072 https://doi.org/10.1016/j.chemosphere.2023.138072