PREPARATION OF CuO-TiO_2 BINARY NANOCOMPOSITES FOR THE SUPERIOR PHOTOCATALYTIC DEGRADATION OF RHODAMINE B: MORPHOLOGICAL AND STRUCTURAL PROPERTIES

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ABSTRACT

Rhodamine B (RhB) belongs to the xanthene dye family that is commonly used in textiles and various applications, including photosensitizers, paper dyeing, and laser dye production, as well as biological staining and a fluorescent marker. There are examples of toxic cationic dyes, which are carcinogenic and mutagenic with high potential antagonistic effects on all living organisms. Consequently, the elimination of hazardous RhB is paramount before discharging into water streams to protect the environment and ecosystem. Semiconductor photocatalysis as a wastewater treatment technology may be promising for RhB high-efficiency removal. The coupling of semiconductors between p-type CuO and n-type TiO_2 semiconductors is expected to produce effective photoactive particles with improved properties. The p-n heterojunctions formed can lead to enhanced degradation of organic pollutants that persist in the environment.

The study focused on the preparation, characterization, and photocatalytic evaluation of CuO-TiO_2 binary nanocomposites in the photo-assisted degradation of RhB under UV irradiation. CuO-TiO_2 binary nanocomposites were synthesized via a simple solid-state dispersion method. The structure and surface morphology of CuO-TiO_2 binary nanocomposites were determined using FTIR, XRD, SEM, and Raman spectroscopy. SEM images revealed the morphologies of both CuO and TiO_2 catalysts. XRD diffractogram of CuO-TiO_2 binary nanocomposites clarified the characteristic monoclinic structure of the CuO phase and the anatase and rutile phases of TiO_2. The results could be beneficial for designing CuO-TiO_2 binary nanocomposites with superior photocatalytic degradation properties in wastewater management technologies.

Keywords: Binary nanocomposites, CuO-TiO_2, decolorization, Rhodamine B, semiconductor photocatalysis.

INTRODUCTION

RhB is a well-known member of the xanthene family dye, displaying a high molar absorptivity, tunable fluorescence, and high photostability. These properties make RhB usable for tracers in chemical and biological applications. Moreover, RhB is a cationic dye with a high water solubility that is widely used in the printing and textile industry, as well as in animal medicines, staining of biological trials, photosensitizers, and lasers (Al-Gheethi et al., 2022; Bar and Chowdhury, 2022; Li et al., 2023). This toxic cationic dye can be carcinogenic and mutagenic with high potential antagonistic results on all living organisms (Li et al., 2023). The untreated discharge of RhB can cause health problems to humans and animals, since it is classified as a carcinogenic and neurotoxic dye. Therefore, the efficient treatment of wastewater containing RhB is an environmental challenge facing the world today (Al-Buriahi et al., 2022; Al-Gheethi et al., 2022; Amalina et al., 2022).

Semiconductor photocatalysis is a promising water treatment process due to its easy handling, good reproducibility, simplicity, high efficiency, environmentally friendly, non-toxic, and cost-effective properties. In this technique, oxidizing species such as highly oxidized hydroxyl radicals are formed, and these radicals completely mineralize the hazardous and persistent pollutants into CO_2 and H_2O (Durodola et al., 2023; Jabbar and Graimed, 2022; Solayman et al., 2023).

Several catalyst development studies have focused on using a variety of binary oxides to improve visible light absorption capability, charge separation, and transportation (Raizada et al., 2020; Turkten and Bekbolet, 2020). Recently, Hamad et al. synthesized a binary system of S-scheme CuO@TiO_2 heterojunction nanocomposite for the efficient degradation of acid red 8 dye (Hamad et al., 2022). Likewise, another binary TiO_2-CuO system was reported as exhibiting a high photocatalytic activity in the degradation of tetracycline (Kubiak et al., 2020). Moreover, various organic pollutants and dyes such as acid yellow 36 (Wang et al., 2023), methylene blue (Li et al., 2008), methyl orange and cyanide (Koohestani and Sadrnezhaad, 2016) were used for the photocatalytic activity testing of CuO-TiO_2 binary nanocomposites.

In the present study, CuO-TiO_2 binary nanocomposite was prepared by using a facile mechanical mixing method. Fourier transform infrared spectrometer (FTIR) used with attenuated total reflection (ATR), Raman spectroscopy, X-ray diffraction (XRD), and Scanning electron microscopy (SEM) spectroscopic techniques were used to identify structural and morphological features of CuO-TiO_2 nanoparticles. RhB was employed as a representative dye to evaluate the photocatalytic activity of CuO-TiO_2 binary nanocomposite.

MATERIAL AND METHOD

Rh B ($C_{28}H_{31}ClN_2O_3$) was obtained from Merck. TiO_2 P-25 (Evonik) and CuO (Thermo Scientific, ACS) were used to prepare CuO-TiO_2 binary nanocomposite. All aqueous solutions were prepared with distilled water. The chemical structure and properties of RhB cationic dye were given in Figure 1.

CuO-TiO_2 binary nanocomposite was prepared by mechanical mixing method with weight ratio of CuO/TiO_2:1/1. Briefly, CuO (1 g) and TiO_2 (1 g) oxides were mixed in ethanol with mortar for 15 min and were sonicated in an ultrasonic bath for 30 min. Finally, CuO-TiO_2 binary oxide was dried in an air oven at 80 °C for 24 h, calcined in a muffle furnace at 500 °C for 3h, and grinded (Mohammadi et al., 2016).

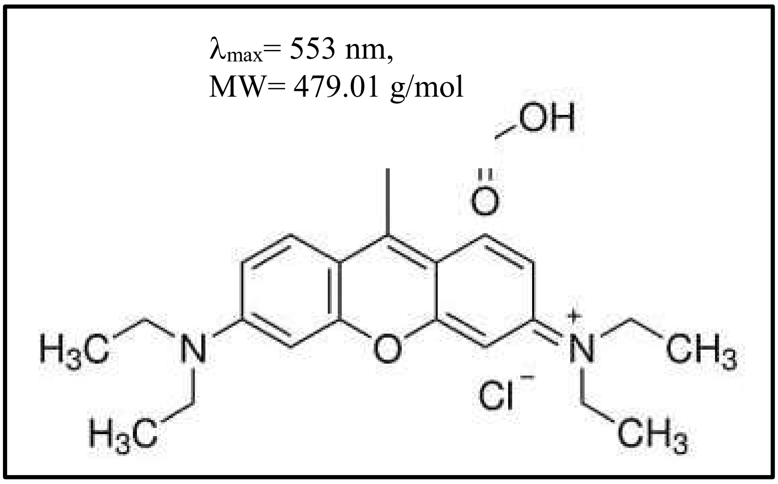
λ_{max}= 553 nm,
MW= 479.01 g/mol

Figure 1. The chemical structure of RhB.

FTIR spectroscopy was acquired by using Thermo Scientific Nicolet 6700 spectrometer equipped with an attenuated total reflection accessory. Dispersive Raman spectroscopic measurement was performed on a Thermo Scientific DXR Raman Microscope with an application of an Ar^+ laser power (10 mW, λ=532 nm). XRD diffractogram was carried out by a Rigaku-D/MAX-Ultima diffractometer with Cu Kα radiation (λ=1.54 Å) as X-ray source. SEM analysis was performed on FEI-Philips XL30 Scanning Electron Microscope with an accelerating voltage of 10 kV.

The photocatalytic activity experiments were carried out in a cylindrical Pyrex reaction vessel irradiated from the top. A 125W black light fluorescent lamp ($\lambda=_{max}$ 365 nm) was used as the light source. The photocatalytic activity tests were performed without pH adjustment in 50 mL of RhB (10 mg/L) upon using a 0.25 g/L catalyst dose. The irradiated solution was immediately filtered through 0.22 µm cellulose acetate filters. The absorbance values of the samples were monitored by a Thermo Scientific Genesys 10S double beam spectrophotometer using 1 cm quartz cells.

RESULTS AND DISCUSSION

FTIR spectroscopy was used to verify the functional groups of the synthesized CuO-TiO_2 binary nanocomposite, and the spectrum was shown in Figure 2. The observed peaks at 420 cm^{-1}, 482 cm^{-1}, 523 cm^{-1}, and 596 cm^{-1} were attributed to the characteristic Cu-O stretching vibration modes (Islam et al., 2021). The peaks observed below 800 cm^{-1} could be related to the stretching mode of Ti–O ($\nu_{Ti–O}$) that was the envelope of the phonon peaks of a Ti–O–Ti bond of the TiO_2 network (Kanna and Wongnawa, 2008).

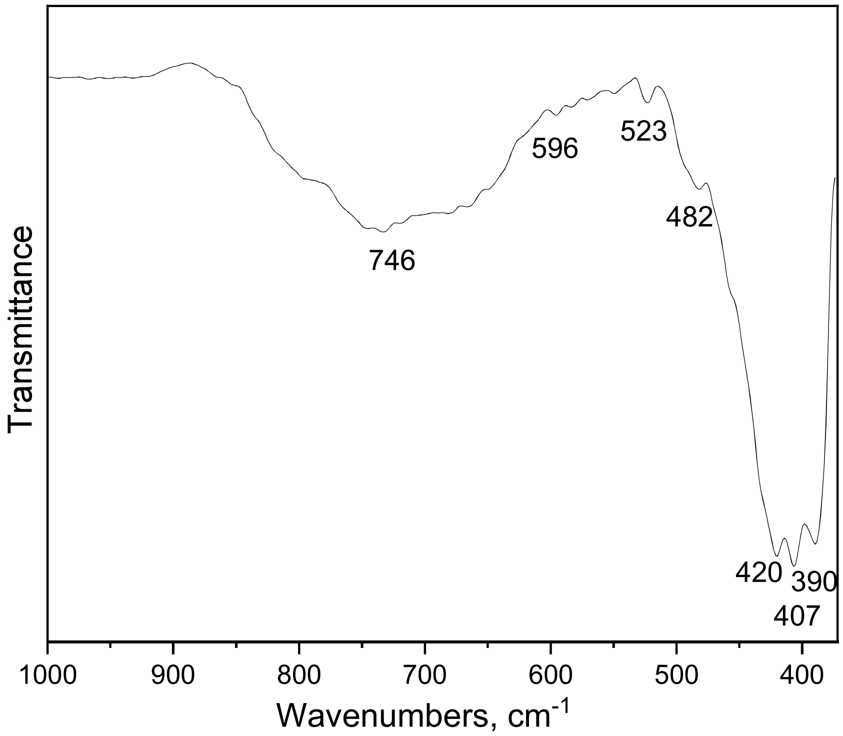

Figure 2. FTIR spectrum of CuO-TiO_2 binary nanocomposite.

The Raman spectrum of CuO-TiO_2 binary nanocomposite showed main bands as seen in Figure 3. The band centered at 637 cm^{-1} corresponded to the B_{g2} mode of CuO, while the bands located at 508 cm^{-1} was attributed to the characteristic A_{1g} anatase band of TiO_2 (Islam et al., 2021; Ohsaka et al., 1978).

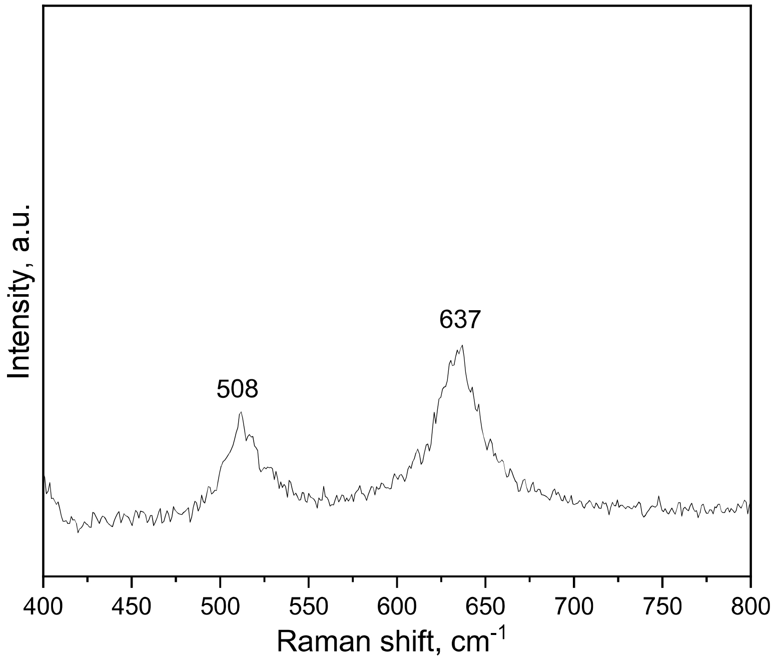

Figure 3. Raman spectra of CuO-TiO_2 binary nanocomposite.

The XRD spectrum of CuO-TiO_2 binary nanocomposite was presented in Figure 4. The diffractogram of CuO-TiO_2 exhibited the characteristic peaks at 2θ = 25.36°, 37.89°, 48.08°, 53.98°, 55.12°, 62.82°, 69.09°, and 70.38° were attributed to (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (0 0 2), (1 1 6), and (2 2 0) planes of anatase, while peaks at 2θ = 27.52°, 41.34° corresponded to (1 1 0), and (1 1 1) planes of rutile, respectively. The crystallite phases of TiO_2 were presented by anatase (JCPDS No. 73-1764) and rutile (JCPDS No. 99-0090) crystal structures.

A series of characteristic peaks of monoclinic CuO located at 2θ = 32.54°, 35.56°, 38.72°,48.80°, 53.36°, 58.32°, 61.56°, 65.84°, 66.30°, 68.12°, 72.44°, and 75.02° corresponded to the (1 1 0), (−1 1 1), (1 1 1) (−2 0 2), (0 2 0), (2 0 2), (−1 1 3), (0 2 2), (−3 1 1), (2 2 0), (3 1 1), and (0 0 4) planes. CuO data was in accordance with the standard (JCPDS card no. 89-5895).

SEM images of TiO_2, CuO, and CuO-TiO_2 binary nanocomposite were presented in Figure 5. TiO_2 nanoparticles (Figure 5 (a)) consisted of almost spherical shapes with a slight agglomeration while SEM image of CuO revealed a variety polyhedral-shaped particles (Figure 5 (b)). The presence of spherical and polyhedral-shaped particles indicated that CuO-TiO_2 binary nanocomposite exhibited both morphologies of TiO_2 and CuO (Figure 5 (c)).

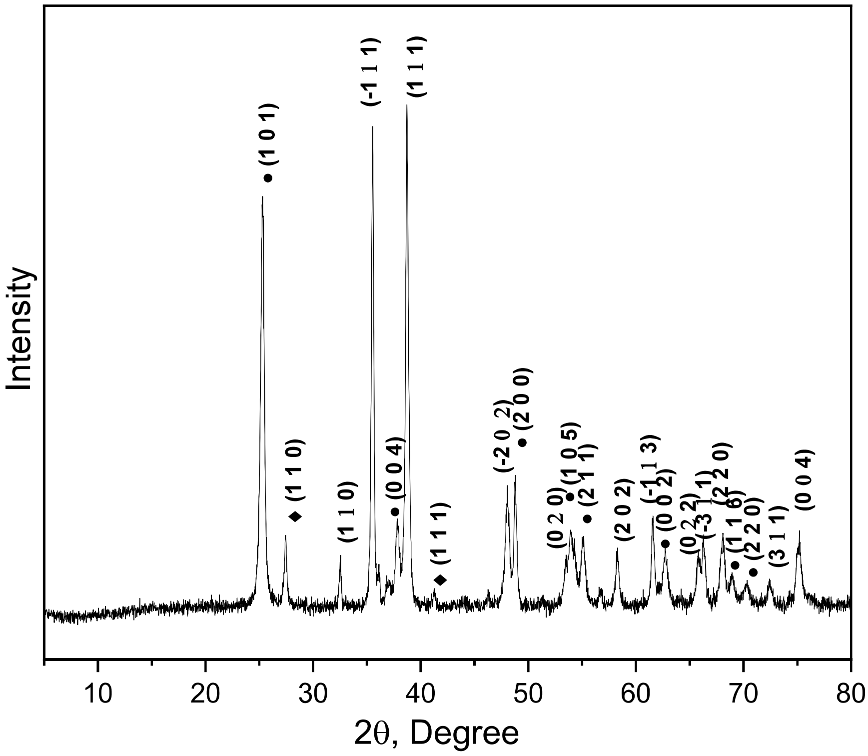

Figure 4. XRD spectrum of CuO-TiO$_2$ binary nanocomposite (● anatase, ◆rutile).

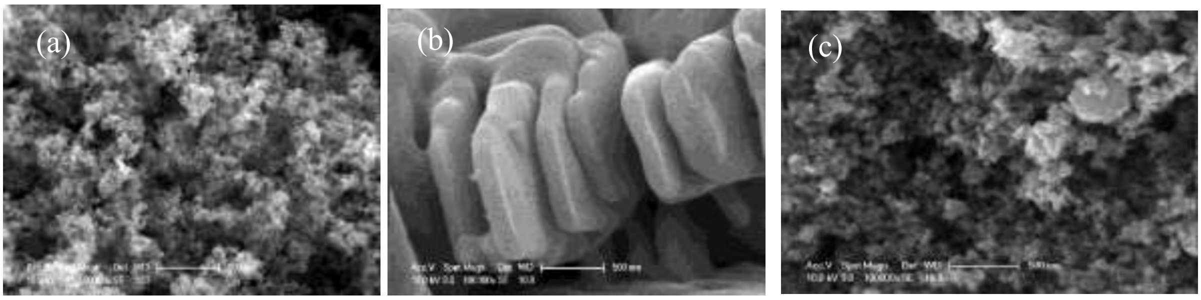

Figure 5. SEM images of (a) TiO$_2$, (b) CuO, and (c) CuO-TiO$_2$.

The degree of RhB decolorization by using CuO-TiO$_2$ nanoparticles (Figure 6) was calculated by the following equation (1).

$$\text{Decolorization, \%} = ((A_{,o} - A)/A_o)) \text{ x}100 \qquad (1)$$

where,

$A_{,o}$ = initial absorbance of RhB and A = absorbance of RhB at irradiation time t.

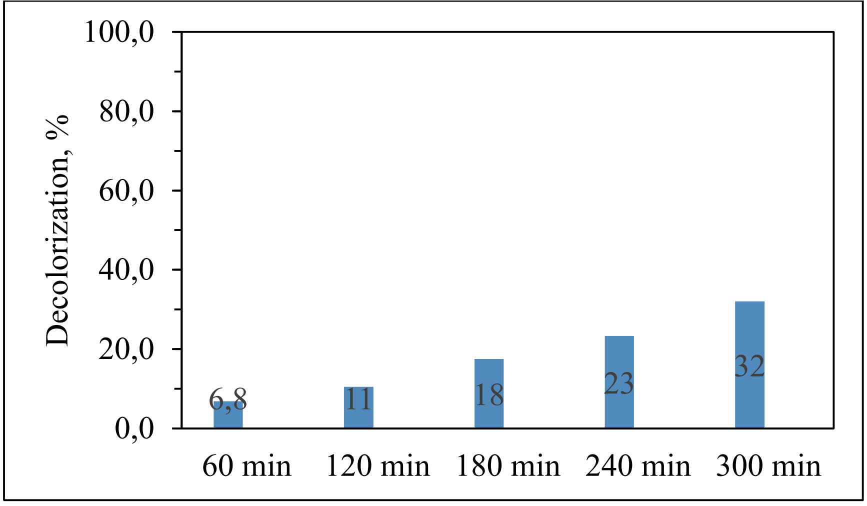

Figure 6. Removal efficiency of RhB upon using CuO-TiO_2 nanoparticles.

The removal efficiency of RhB in the presence of CuO-TiO_2 nanoparticles was found to be 32% after exposure light irradiation for 300 min.

CONCLUSIONS

In summary, CuO-TiO_2 nanoparticles were successfully synthesized via a mechanical mixing method. FTIR spectrum of CuO-TiO_2 binary nanocomposite confirmed the presence of characteristic peaks of CuO and TiO_2 in the structure of the composite. XRD results indicated evidence of anatase and rutile planes of TiO_2 and the monoclinic structure of CuO. The surface morphology feature of CuO-TiO_2 binary nanocomposite consisted of both TiO_2 and CuO particles. The photocatalytic activity of CuO-TiO_2 binary nanocomposite was investigated on the degradation of RhB dye. The removal percentage of degradation of RhB in the presence of CuO-TiO_2 nanoparticles was 32% upon 300 min irradiation.

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