

Article

Ce³⁺/Ce⁴⁺-Doped ZrO₂/CuO Nanocomposite for Enhanced Photocatalytic Degradation of Methylene Blue under Visible Light

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Abstract: In recent years, photocatalysis has been used as an environmentally friendly method for the degradation of organic pigments in water. In this study, Ce³⁺/Ce⁴⁺-doped ZrO₂/CuO as a mixed semiconductor oxide was successfully prepared by a one-step hydrothermal method. The Ce³⁺/Ce⁴⁺-doped ZrO₂/CuO has shown high degradation efficiency of methylene blue (MB), and the maximum degradation percentage was observed to be 94.5% at 180 min under irradiation visible light. The photocatalytic activity increases significantly by doping Ce³⁺/Ce⁴⁺ in ZrO₂/CuO for MB degradation. Ce³⁺/Ce⁴⁺ doping is shown to reduce the (e⁻/h⁺) recombination rate and improve the charge transfer, leading to enhanced photocatalytic activity of materials. The materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), FTIR, EDS, BET and diffuse reflectance spectroscopy (DRS).

Keywords: Ce³⁺/Ce⁴⁺; mixed semiconductor oxide; hydrothermal; photocatalysis; methylene blue



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1. Introduction

Water pollution is a global environmental problem as it can lead to the decomposition of aquatic ecosystems and can affect human health. Contaminants can include organic or inorganic compounds, metal ions, dyes, phenols, pesticides and detergents. In which the pollution of natural and synthetic organic dyes poses challenges because of their high carcinogenic nature due to the fact they contain azo functional groups that, during decomposition, can form amines and benzidine [1]. Organic dyes are persistent organic pollutants that are resistant to decomposition through chemical and biological processes. The dye molecules are practically non-biodegradable, so they persist longer in the environment, creating potential hazards [2].

Today, water pollution is treated by applying technologies such as adsorption, coagulation, filtration and photocatalysis. In which the heterogeneous photocatalysis method has gained wide scientific attention with high potential for applications [3]. Zirconia (ZrO₂)-based photocatalysis for wastewater treatment is of great interest because ZrO₂ is a semiconductor oxide with high mechanical strength, is non-toxic, and has high chemical stability and biocompatibility. However, ZrO₂ has a large band gap; the E_g of ZrO₂ ranges from 3.25 to 5.1 eV, depending on the fabrication method [4]. Therefore, ZrO₂ needs to be irradiated with UV radiation to have a photocatalytic activity. UV radiation constitutes

about 5% of the total electromagnetic radiation output from sunlight, limiting the practical applications of ZrO_2 .

To improve the photocatalytic performance of ZrO_2 , coupling with other semiconductor oxides has been shown to be an effective approach. The coupling produces mixed oxide semiconductors (MOS) that are capable of efficient charge separation due to the transition of electrons and holes generated from one semiconductor to another. CuO is often the semiconductor oxide of choice because it is a p-type semiconductor, has a small band gap of about 1.2 eV, is cheap and is environmentally friendly [5]. Renuka, L., et al., reported the synthesis of ZrO_2/CuO materials with excellent photocatalytic activity under visible light by a simple combustion method. The photocatalytic activity of ZrO_2/CuO obtained was 1.5 times higher than that of commercial P25 [6]. Nanda, B., et al., synthesized mesoporous $\text{CuO}/\text{ZrO}_2\text{-MCM-41}$ nanocomposites with high photocatalytic activity, the photoreduction of Cr(VI) to Cr(III) had a 99% degradation efficiency in 30 min [7]. The synergistic effect between ZrO_2 , CuO and TiO_2 oxides was also studied by Guerrero-Araque and Diana, et al. Co-catalysts are widely used to promote photocatalytic hydrogen production, especially CuO , which has shown a significant improvement in reaction rates [8].

Another use of low-photocatalytic activity is the electron-hole recombination process that occurs in the semiconductor oxide. In photocatalysis, the photocatalytic activity depends on the ability of the catalyst to create electron-hole pairs. Such an electron-hole pair is called an exciton. The excited electron and hole can recombine and release heat. Such exciton recombination leads to a decrease in photocatalytic activity. To reduce the recombination of electrons and holes, it is common to dope transition metal elements, especially rare earth, to prolongation of the exciton lifetime [9].

Recently, Piña-Pérez and Yanet, et al., doped $\text{Ce}^{3+}/\text{Ce}^{4+}$ into Al_2O_3 , showing significantly improved electron-hole pair separation efficiency. This catalyst was chosen for the photodegradation of other phenolic derivatives such as 4-chlorophenol, p-cresol and 4-nitrophenol. $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped Al_2O_3 synthesized by the sol-gel method showed better photocatalytic activity (TiO_2 , P25 Degussa) [10]. The redox pair of $\text{Ce}^{4+}/\text{Ce}^{3+}$ -doped α - β phase of Bi_2O_3 was reported by Akshatha, S., et al. The $\text{Ce}^{4+}/\text{Ce}^{3+}$ -doped Bi_2O_3 created a synergistic effect to enhance the photocatalytic activity to degrade Alizarin red S dye [11].

To the best of our knowledge, there are many studies on the doping of $\text{Ce}^{3+}/\text{Ce}^{4+}$ ions into oxide semiconductors for photocatalysis. However, the doping of $\text{Ce}^{3+}/\text{Ce}^{4+}$ ions into mixed semiconductor oxide is a topic that has not been fully investigated. In this paper, we use the hydrothermal method to prepare $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO . The $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO mixed oxide semiconductor was used for the photocatalytic degradation of methylene blue (MB). X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy, spectrophotometry UV-Vis and Brunauer-Emmett-Teller (BET) were studied.

2. Materials and Methods

2.1. Preparation of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -Doped ZrO_2/CuO Nanocomposites

The $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO nanocomposites were synthesized by the hydrothermal method. All chemicals were purchased from Merck (purity > 99%) and were used without further treatment: ZrCl_4 , $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, NaOH , $\text{C}_2\text{H}_5\text{OH}$, Methylene blue.

In a typical experiment, the molar ratio of ZrO_2/CuO was taken as 1:1, 10 mmol of ZrCl_4 and 10 mmol of $\text{Cu}(\text{NO}_3)_2$ were dissolved in 50 mL of deionized water, stirred in a magnetic stirrer at room temperature for 30 min. Next, 0–0.8 mmol $\text{Ce}(\text{SO}_4)_2$ was added to the above solution. The mixture is stirred vigorously to obtain a clear and homogeneous mixture. After stirring these mixtures for 30 min, they were added to 10 mL of 2 M NH_3 aqueous solution to gel.

The gel was then transferred into a Teflon-lined 100 mL stainless steel autoclave, which was heated in an oven at 200 °C for 12 h (heated with a Nabertherm furnace, heating rate

5 °C/min). For natural cooling, the entire solution was centrifuged to collect the precipitate and washed with deionized water, and then dried at 80 °C. Pure ZrO₂ and CuO were prepared with the same procedure. Finally, all the prepared powders were calcined at 600 °C for 2 h and then allowed to cool to room temperature for further experiments.

2.2. Characterization

The morphology of the Ce³⁺/Ce⁴⁺-doped ZrO₂/CuO nanocomposites was evaluated by using a field emission scanning electronic microscope (JEOL, JSM-7600F, JEOL Techniques, Tokyo, Japan). The surface morphology and microstructure of the nanocomposites were characterized by transmission electron microscopy (TEM) made with a (JEOL, JEM 1010, JEOL Techniques, Tokyo, Japan) operating at 200 kV. For the TEM analyses, the powders were dispersed in ethanol by sonication for 5 min.

FT-IR was performed in the range of 4000–400 cm^{−1} with the help of (FT-IR using a Perkin–Elmer Spectrum BX spectrometer (PerkinElmer Inc., Wellesley, MA, USA) using KBr pellets to identify the functional groups present in the sample. EDS (Hitachi TM4000Plus Tabletop Microscope (Hitachi High-Tech Corporation, Tokyo, Japan)) was the determining element in the composites. The UV-Vis absorption spectrum was recorded using a (UV-1700 PharmaSpec, Shimadzu, Kyoto, Japan) UV-Visible spectrophotometer. The X-ray powder diffraction patterns were characterized using (XRD, D8 Advance, Bruker, Germany) a diffractometer at room temperature (Cu-Kα radiation) with a nickel filter at a scan rate of 2°/min.

2.3. Dye Photodegradation

The photocatalytic activity of Ce³⁺/Ce⁴⁺-doped ZrO₂/CuO nanocomposites was evaluated by investigating the degradation of methylene blue (MB). Using 30 mL of the MB solution with a dye concentration of 10 mgL^{−1}, which was illuminated under a light-emitting 300W Xenon lamp (sunlight simulation) at irradiance (1 Wcm^{−2}). Light filters were used to remove wavelengths λ < 420 nm. The distance from the lamp to the MB solution was 10 cm. To limit the influence of external light, the entire experimental system was placed in a dark chamber. The nanocomposite powder loaded into the MB solution was 20 mg. Then the suspension was stirred for 60 min in the dark to obtain balance adsorption and desorption equilibration of the system. About 3 mL was taken from the suspension at different irradiation times, it was then centrifuged at 4000 rpm for 10 min, and degradation measurements were performed by a UV-Vis spectrophotometer. The photodegradation efficiency was calculated using Equation (1):

$$\%H = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (1)$$

where %H is the photodegradation efficiency, C₀ and C_t are the concentrations of MB at time 0 and t (min), respectively.

3. Results

3.1. X-ray Diffraction

The XRD pattern of the Ce³⁺/Ce⁴⁺-doped ZrO₂/CuO nanocomposites is shown in Figure 1. All the peaks in the XRD pattern are well indexed and have all crystallized as multiphase at Ce³⁺/Ce⁴⁺ different doping concentrations. ZrO₂/CuO and Ce³⁺/Ce⁴⁺-doped ZrO₂/CuO exists in three phases, namely tetragonal ZrO₂, monoclinic CuO and orthorhombic CuZrO₃.

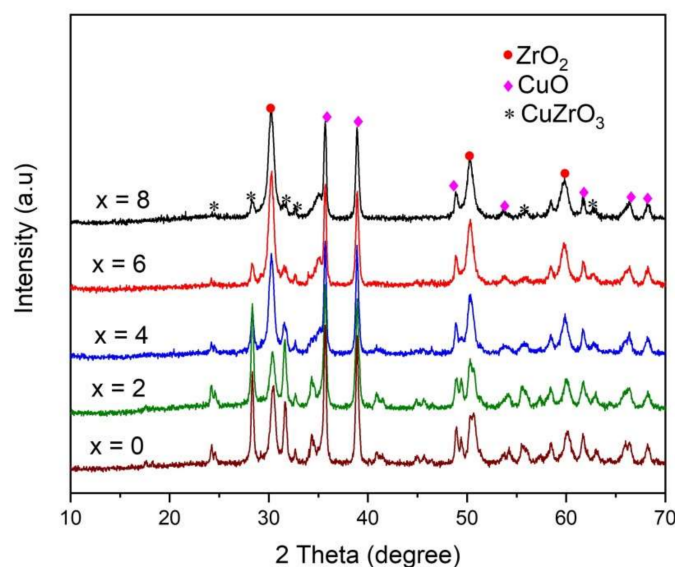


Figure 1. XRD patterns of the ZrO_2/CuO nanocomposite powder with doping of $\text{Ce}^{3+}/\text{Ce}^{4+}$ (0–8 mol%).

The diffraction peaks originating at $2\theta = \sim 30.48^\circ$, 34.35° , 50.30° , 50.65° and 60.09° correspond to (101), (200), (112), (220) and (202) planes of the tetragonal phase of ZrO_2 (JCPDS No. 00–050–1089), respectively. The diffraction peaks observed at $2\theta = \sim 35.68^\circ$, 38.89° , 48.93° , 53.62° , 61.70° , 65.97° and 68.20° are associated with (002), (111), (-202), (020), (-113), (022) and (113) planes, signifying the monoclinic phase of CuO (JCPDS No. 48–1548).

We also observed diffraction peaks at $2\theta = \sim 24.33^\circ$, 28.29° , 34.34° , 55.56° and 61.72° corresponded to (012), (112), (013), (313) and (402) planes of CuZrO_3 (PDF Card No. 00–043–0953), respectively. CuZrO_3 can be formed in a hydrothermal process, where the reaction between ZrO_2 and CuO occurs according to the chemical equation:



It is interesting that when the $\text{Ce}^{3+}/\text{Ce}^{4+}$ doping concentration changes, the ratio between the phases changes. In the absence of $\text{Ce}^{3+}/\text{Ce}^{4+}$ doping, the material exists in all three phases, including tetragonal ZrO_2 , monoclinic CuO and orthorhombic CuZrO_3 . However, when increasing the doping concentration of $\text{Ce}^{3+}/\text{Ce}^{4+}$, the diffraction intensity of the CuZrO_3 phase decreased. According to the authors Dean, James, et al., reported that CuZrO_3 has a perovskite structure; this structure is less stable due to its low energy, which has a thermodynamic preference to decompose into CuO and ZrO_2 [12]. We believe that increasing the concentration of $\text{Ce}^{3+}/\text{Ce}^{4+}$ doping increases the ability of phase segregation to CuO and ZrO_2 is preferred.

3.2. Microstructure and Morphology of ZrO_2/CuO -Doped $\text{Ce}^{3+}/\text{Ce}^{4+}$ Nanocomposites

The microstructure of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO synthesized by the hydrothermal method was analyzed by FE-SEM. Figure 2a–d show that the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO catalysts are spheres with non-uniform size distribution. When the $\text{Ce}^{3+}/\text{Ce}^{4+}$ doping concentration changed from 2 mol% to 8 mol%, the morphology of the catalysts was not significantly affected.

The size of the catalyst, as well as the surface area, greatly influence the photocatalytic efficiency. The small size of the material shows that the ability to adsorb the MB on the surface will be better, creating conditions for the oxidizing radicals to easily react with the colourant.

To better understand the shape, size and crystal formation of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO catalyst, we studied the transmission electron microscopy (TEM) images.

Figure 3 shows that the particle size of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO catalyst is larger than that of ZrO_2/CuO . According to the particle size distribution curves in

Figure 3c–d, ZrO_2/CuO concentrates around 20 nm, while $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO concentrates around 30 nm.

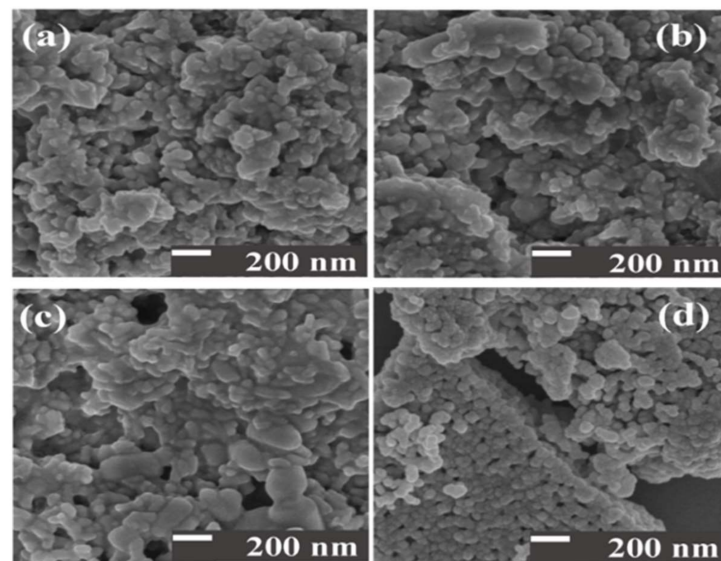


Figure 2. FE-SEM of x mol% $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO : (a) $x = 2$; (b) $x = 4$; (c) $x = 6$; (d) $x = 8$.

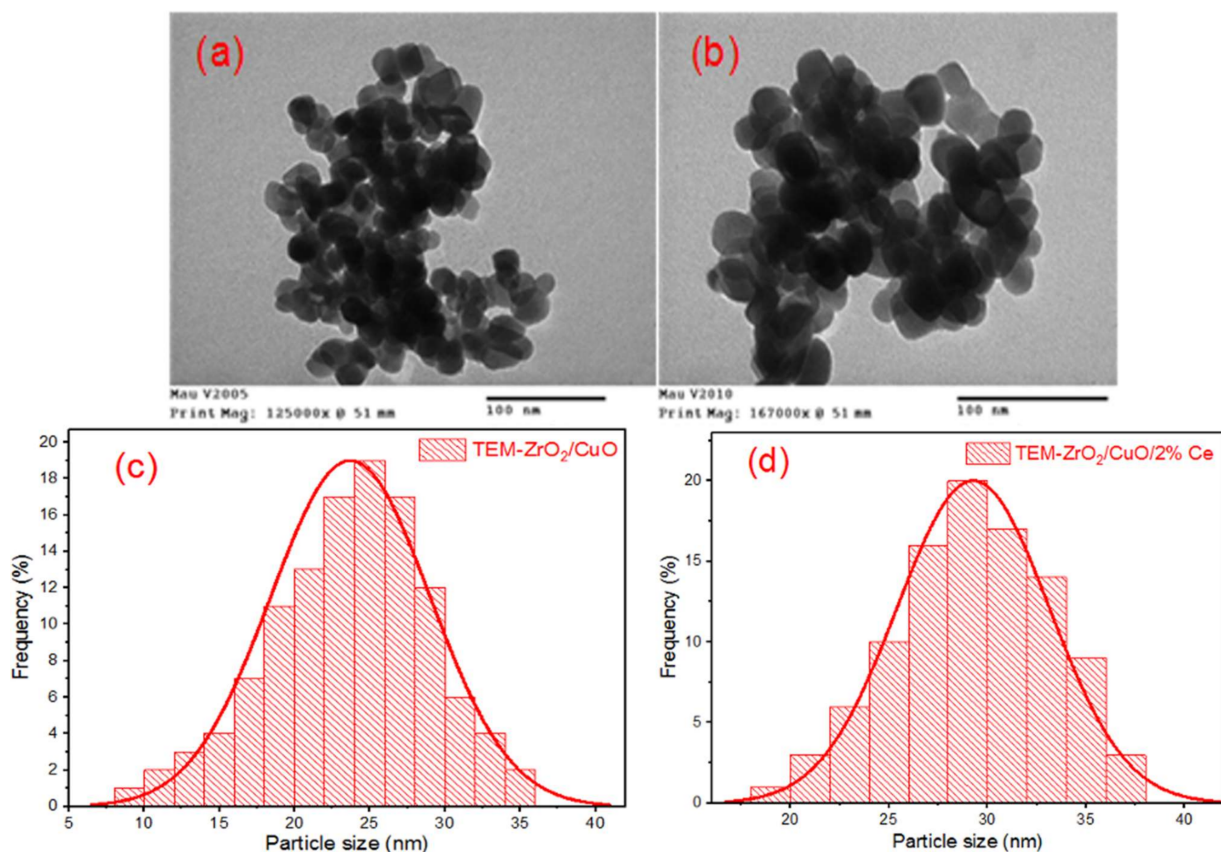


Figure 3. TEM and the particle size distribution curve of ZrO_2/CuO (a,c) and 2 mol% $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO (b,d).

3.3. Fourier Transform Infrared Spectroscopy and Energy Dispersive X-ray Spectroscopy of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -Doped ZrO_2/CuO Nanocomposites

Figure 4 shows the FT-IR spectra of ZrO_2/CuO and $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO . The $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO materials all have absorption maximums around $3113\text{--}3153\text{ cm}^{-1}$,

which is typical for the -OH group of wet water. The absorption peaks at $1710\text{--}1712\text{ cm}^{-1}$ and $1556\text{--}1566\text{ cm}^{-1}$ are characteristic of the vibrations of the Zr-O-H group in the material. In addition, the materials have an absorption maximum of $601\text{--}607\text{ cm}^{-1}$, which can be attributed to the vibrational stretching mode of the Cu-O bond. Bands at $424\text{--}524\text{ cm}^{-1}$ can be assigned to the Zr-O vibration mode in composites.

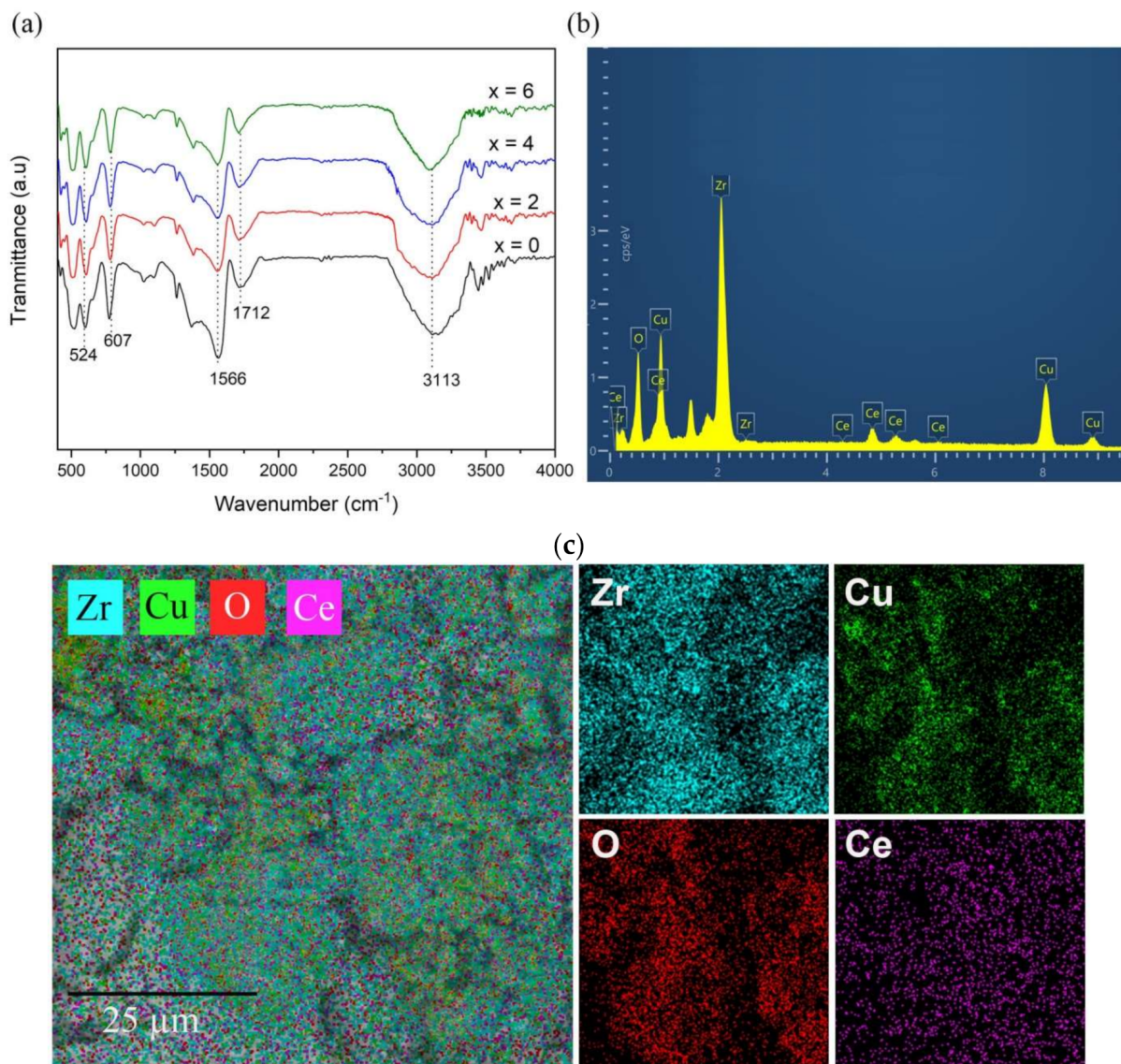


Figure 4. (a) FT-IR of x mol% $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO ($x = 0; 2; 4; 6$), (b) EDS, (c) mapping imaging of 8 mol% $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO .

Figure 4b shows the presence of elements Ce, Zr, Cu and O, confirming the presence of Ce doping in ZrO_2/CuO nanocomposites. We performed EDS mapping, which is equipped with SEM. Figure 4c clearly show the uniform spread of Zr, Cu, O and Ce elements.

3.4. Nitrogen Adsorption-Desorption Isotherms of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -Doped ZrO_2/CuO Nanocomposites

The specific surface areas of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO and ZrO_2/CuO nanocomposites were determined by measuring the nitrogen adsorption-desorption isotherms, as shown in Figure 5. All of them are all type III adsorption isotherms [13]. The BET surface areas of ZrO_2/CuO and $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO are 15.59 and $13.52\text{ m}^2\text{g}^{-1}$. The

large surface area of the catalyst facilitates the adsorption of the pigment to the surface of the material, thereby improving the photocatalyst efficiency.

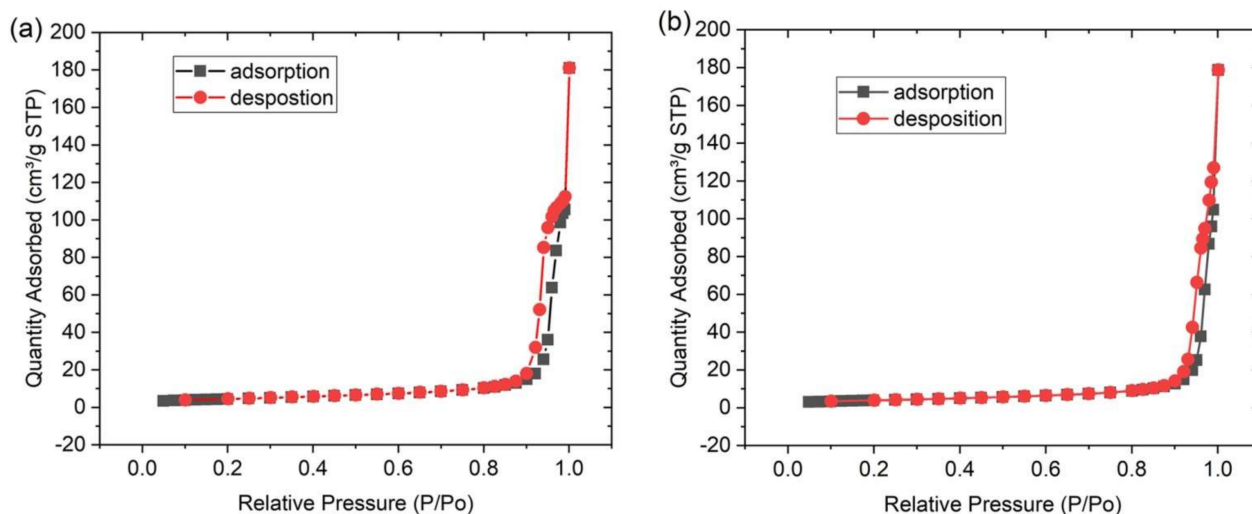


Figure 5. Nitrogen adsorption-desorption isotherms of (a) ZrO_2/CuO , and (b) 2 mol% $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO .

3.5. UV-Vis Absorption Spectrum of $\text{Ce}^{3+}/\text{Ce}^{4+}$ -Doped ZrO_2/CuO Nanocomposites

Figure 6 shows the UV-Vis absorption spectrum and the bandgap energy of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO . The results show that the $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO oxide composite material has an absorption region from UV to the visible region (200–1000 nm). To calculate the band gap, the Tauc relation is used:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (3)$$

where α is the absorption coefficient, h is the Planck constant, ν is the frequency of the incident photon, A is a constant that depends on the transition probability, E_g is the band gap energy and n is an index that depends on the transition probability of the nature of the electronic transition.

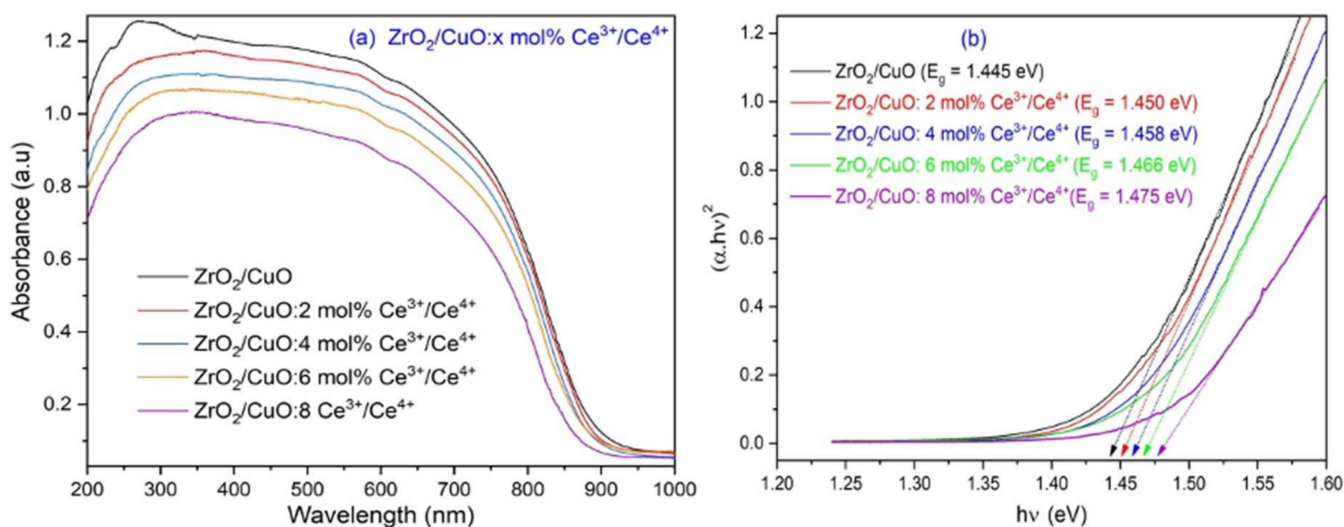


Figure 6. (a) The UV-Vis DRS and (b) The Kubelka-Munk energy curve versus the band gap (eV) of the x mol% $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO ($x = 0; 2; 4; 6; 8$).

The bandgap energy of $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO was found to be in the range of 1.445–1.475 eV. When increasing the $\text{Ce}^{3+}/\text{Ce}^{4+}$ doping concentration from 0 to 8 mol%, the band gap increased slightly from 1.445 to 1.475 eV. When Ce was doped into ZrO_2/CuO , the 5d and 6s orbitals of Ce overlapping with the d orbitals of Cu and Zr can increase the size of the valence band and also lower the position of its maximum, thereby increasing the band gap of mixed semiconductor oxide. The increase in the optical band gap upon Ce doping is similar to the increase in the band gap of Ag_2O upon Zn doping, as reported by De, Arup Kumar et al. [14]. The decrease in the band gap of the ZrO_2/CuO nanocomposites material compared with that of pure ZrO_2 is mainly due to the introduction of CuO into the ZrO_2 host matrix. It was found that when two metals combine, the band gap decreases and thus a shift to the visible region is observed [15].

The narrowing of the band gap can be attributed to the appearance of an impurity region (CuO) formed by overlapping impurity states and local states formed by the combination of Cu 2p and Zr 3p [7]. This result is similar to previous studies [16]. The photocatalytic reaction is initiated by the absorption of light with an energy equal to or greater than the band gap of the semiconductor. The band gap is in the range of 1.445–1.475 eV, so it is expected that the catalyst material can absorb visible light.

3.6. Photocatalytic Activity of $\text{Ce}^{3+}/\text{Ce}^{4+}$ -Doped ZrO_2/CuO Nanocomposites

To investigate the adsorption balance, 20 mg of 8 mol% $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO was added into 30 mL of 10 mgL^{-1} MB solution. The suspension was stirred in the dark; samples were measured via UV-Vis spectroscopy. Figure 7 shows that after the first 30 min, the concentration of MB strongly decreased, then at 60 min slightly decreased, and at 90 min, the concentration of MB increased slightly (desorption). It is shown that after 60 min of adsorption, equilibration has occurred.

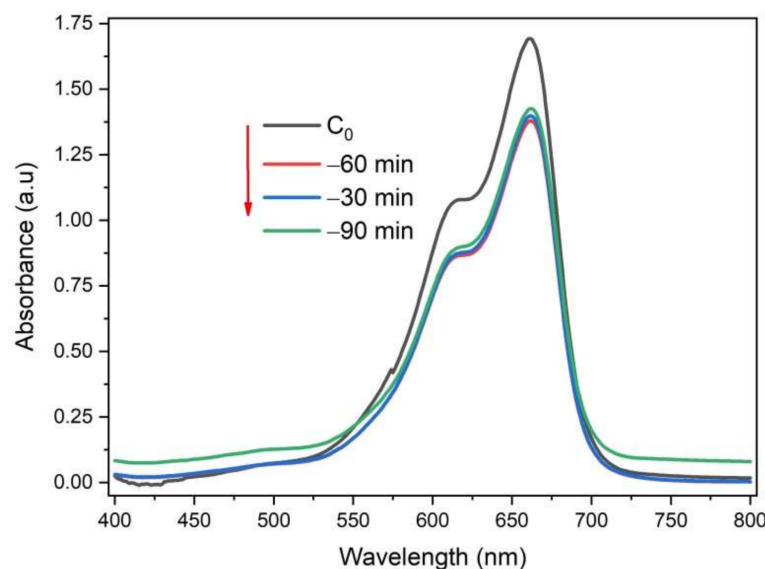


Figure 7. UV-Vis spectrum of MB after being adsorbed by ZrO_2/CuO -doped 8 mol% $\text{Ce}^{3+}/\text{Ce}^{4+}$.

Figure 8 shows the UV-Vis absorption spectrum of MB under visible light at different times in the presence of $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO . The evolution of MB photodegradation was monitored by measuring the absorbance at the wavelength of about $\lambda = 662 \text{ nm}$ at different times. The maximum absorption peaks of MB gradually decreased and almost disappeared in 180 min of illumination.

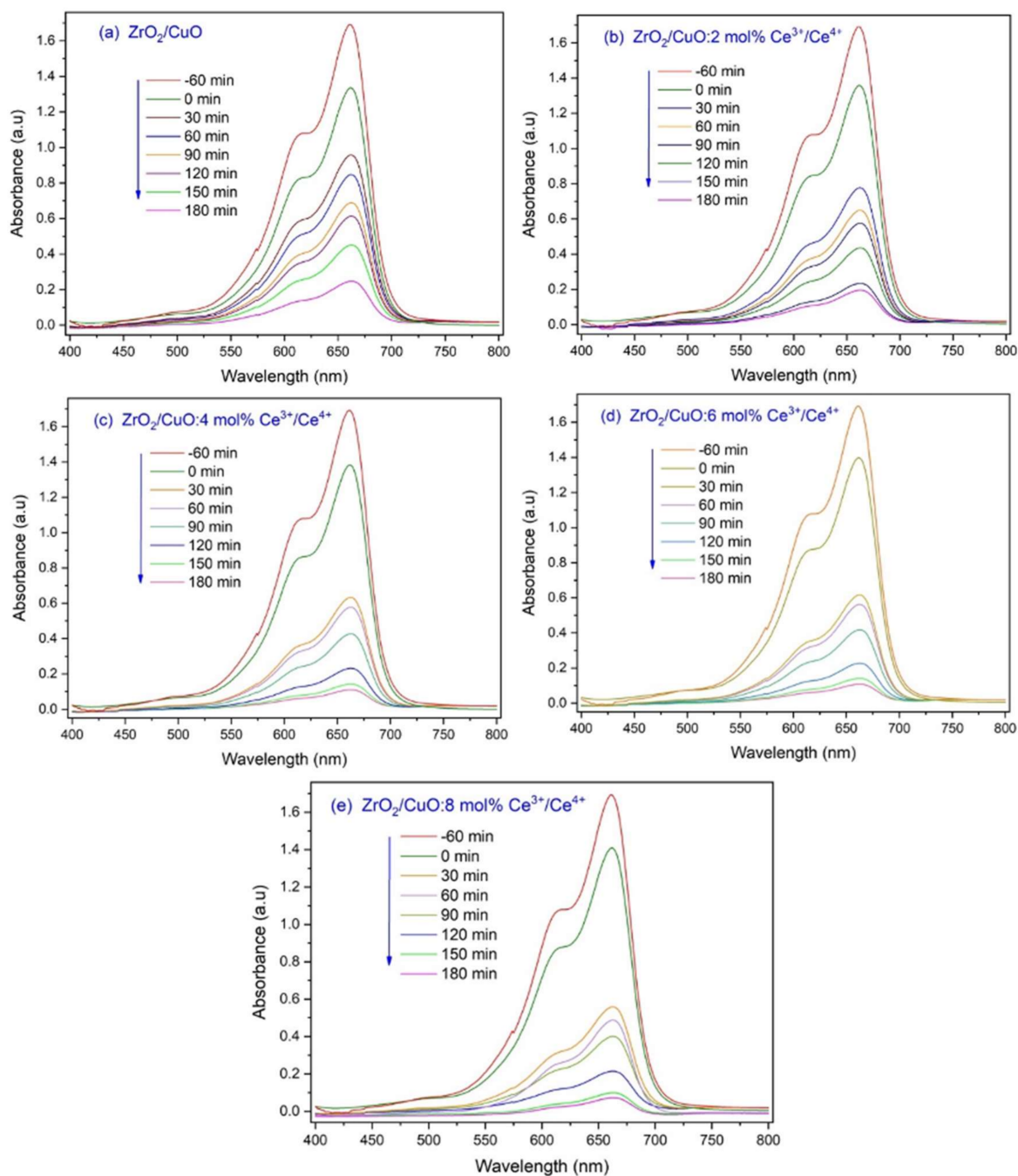
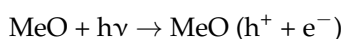
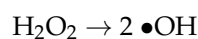
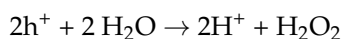
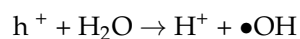


Figure 8. UV-Vis absorbance of MB under visible light at different times in the presence of x mol% $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO : (a) x = 0; (b) x = 2; (c) x = 4; (d) x = 6; (e) x = 8.

The reactions that occur during photocatalysis are described below. The reaction begins by generating excitons on the metal oxide surface (MeO) [17]:



Oxidation reactions due to the photocatalytic effect:



Reduction reaction due to the photocatalytic effect:

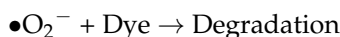
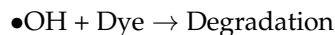
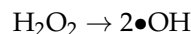
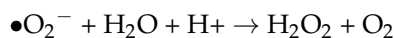
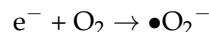


Figure 9a shows the ZrO_2/CuO catalyst, the photocatalytic efficiency of MB decomposition by Ce^{3+}/Ce^{4+} -doped ZrO_2/CuO increased significantly. The Ce^{3+}/Ce^{4+} doping concentration increased, and the photocatalytic efficiency under visible light also increased. Although the E_g values of ZrO_2/CuO and ZrO_2/CuO -doped Ce^{3+}/Ce^{4+} were not significantly different, the results showed that the photocatalytic degradation efficiency was enhanced by Ce^{3+}/Ce^{4+} doping. This could be due to the fact that as the Ce^{3+}/Ce^{4+} ion concentration increases, an increase in oxygen vacancy defects in the crystal lattice occurs. This leads to the redox pair Ce^{3+}/Ce^{4+} being capable of shifting between Ce_2O_3 and CeO_2 , which reduces electron-hole recombination [18].

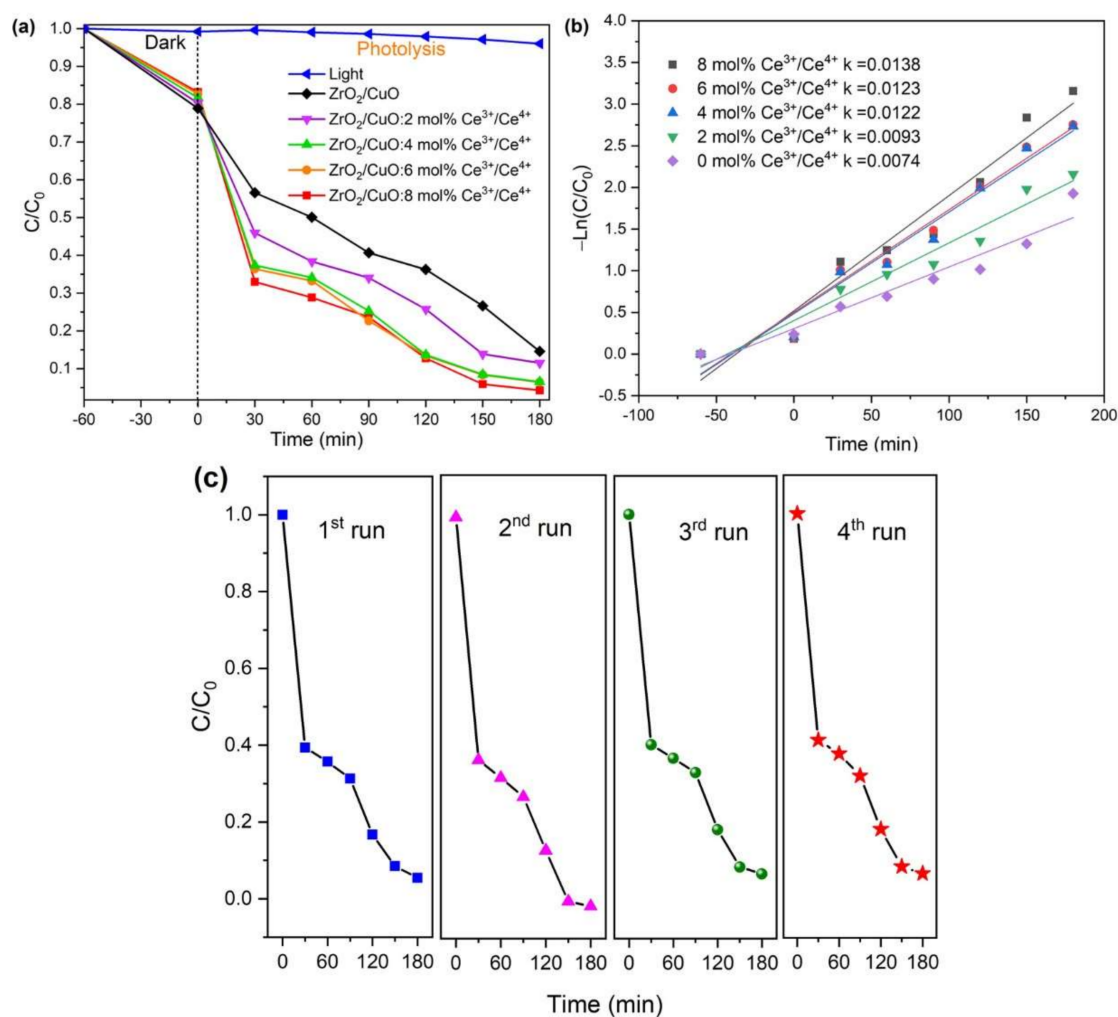


Figure 9. (a) Photodegradation of MB, (b) the reaction rate constant k of the MB degradation in the presence of x mol% Ce^{3+}/Ce^{4+} doped ZrO_2/CuO ($x = 0; 2; 4; 6; 8$), (c) reuse of 8 mol% of Ce^{3+}/Ce^{4+} doping ZrO_2/CuO .

The MB degradation processes all show first-order kinetics by plotting $\ln(C/C_0)$ versus irradiation time, t . The apparent response rate constant (k_{app}) was calculated from the slope of the curve, as illustrated in Figure 9b.

The k_{app} value continuously increased as the Ce^{3+}/Ce^{4+} doping concentration increased, with $x = 0$, $k_{app} = 0.0074 \text{ min}^{-1}$; $x = 2$, $k_{app} = 0.0093 \text{ min}^{-1}$; $x = 4$, $k_{app} = 0.0122 \text{ min}^{-1}$; $x = 6$, $k_{app} = 0.0123 \text{ min}^{-1}$; and $x = 8$, $k_{app} = 0.0138 \text{ min}^{-1}$. It was shown that 8 mol% Ce^{3+}/Ce^{4+} -doped ZrO_2/CuO exhibited the highest $k_{app} = 0.0138 \text{ min}^{-1}$, much higher than that of undoped ZrO_2/CuO with Ce^{3+}/Ce^{4+} .

Figure 9c shows the stability of the Ce^{3+}/Ce^{4+} -doped ZrO_2/CuO nanocomposites. The stability of the MOS material was evaluated by performing photocatalyst recycling experiments for a duration of 180 min. The activity was found to be roughly the same in the two repeated runs, and then there was a slight decrease in the third and fourth runs.

We assume that there is metal-to-metal charge transfer (MMCT). The MMCT effect is assumed to be: $Zr^{4+}-O-Ce^{4+}$ to $Zr^{4+}-O-Ce^{3+}$ and $Zr^{4+}-O-Cu^{2+}$ to $Zr^{4+}-O-Cu^{+}$. The effect is when two different metals in the mixture form an oxygen bridge, which helps electrons and holes move efficiently and avoid recombination, increasing the photocatalytic efficiency of the Ce^{3+}/Ce^{4+} -doped ZrO_2/CuO catalyst [19]. Furthermore, Ce^{3+}/Ce^{4+} ions act as electron-trapping sites reducing charge-pair recombination and thus enhancing photocatalytic activity [20,21].

Table 1 shows the photocatalytic degradation of MB using the various heterojunction photocatalyst. It shows that the combination of semiconductor oxides, or metal ion doping, shows an improved rate constant compared to single semiconductor oxides.

Table 1. Photocatalytic degradation of MB dye using the various heterojunction photocatalyst.

Photocatalyst	Synthesis Method	Light Source	Rate Constant (min^{-1})	Reference
$Fe_2O_3/\text{graphene}/CuO$	Solvothermal	Visible	72.5×10^{-3}	[22]
CuO/ZnO	Impregnation	UV lamp	182×10^{-3}	[23]
$ZrO_2/AgCl:Eu^{3+}$	Sol-gel	Visible	14×10^{-3}	[24]
C-doped ZrO_2	Sol-gel	UVC lamp	7.3×10^{-3}	[25]
N- TiO_2/ZrO_2	Hydrothermal	UV light	29×10^{-3}	[26]
ZrO_2/CuO	Combustion	Visible	11.19×10^{-3}	[6]
GO- ZrO_2	Co-precipitation	Visible	57.5×10^{-3}	[27]
CeO_2	Precipitation	UV light	12.1×10^{-3}	[28]
$V_2O_5-CeO_2$	Precipitation	Visible	108×10^{-3}	[29]
CeO_2/TiO_2	Precipitation	Visible	34×10^{-3}	[30]
Ce^{3+}/Ce^{4+} -doped ZrO_2/CuO	Hydrothermal	Visible	13.8×10^{-3}	This work

The ZrO_2/CuO -doped Ce^{3+}/Ce^{4+} photocatalyst can be reproducible and without destruction. This reproducible process can be confirmed by FT-IR, as shown in Figure 10. It is clear that the characteristic bands of MB, which are at 1383, 1324, 1245, 884 and 670 cm^{-1} , appear after adsorbing [31], while they disappear after 180 min of irradiation. Combined with the results of photocatalytic reuse experiments, it is proven that the Ce^{3+}/Ce^{4+} -doped ZrO_2/CuO nanocomposites have stability.

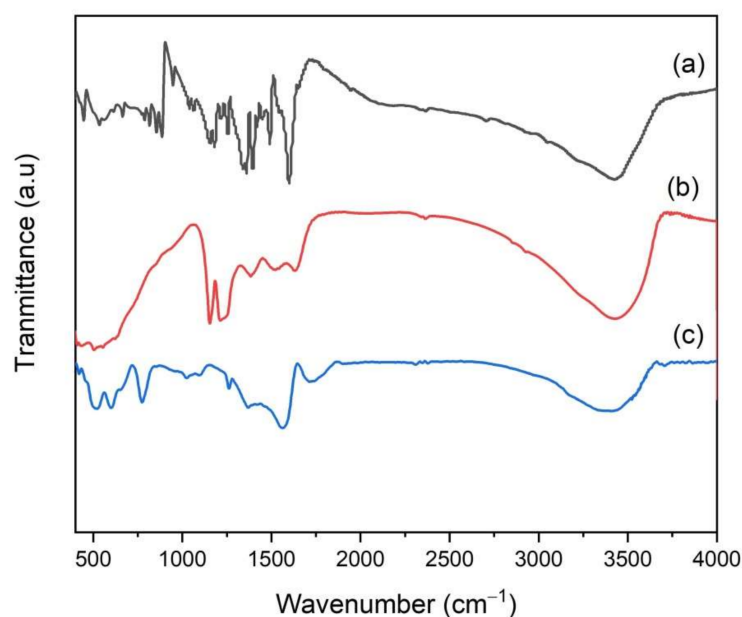


Figure 10. FT-IR spectrum of (a) MB, (b) MB adsorbed onto $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO before irradiation, (c) MB adsorbed on $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO 180 min after irradiation.

4. Conclusions

$\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO nanocomposites have been synthesized by the simple hydrothermal method. The obtained material is a mixed semiconductor oxide ZrO_2 and CuO . The coupling between CuO and ZrO_2 oxides has shown that the light absorption capacity is extended from UV to the visible region. Photocatalytic activity is enhanced when doping $\text{Ce}^{3+}/\text{Ce}^{4+}$ ions because $\text{Ce}^{3+}/\text{Ce}^{4+}$ ions have higher separation efficiency of charge carriers, which reduces electron-hole recombination. The $\text{Ce}^{3+}/\text{Ce}^{4+}$ -doped ZrO_2/CuO nanocomposites showed significantly improved photocatalytic activity. High photocatalysis activity with 94.5% degradation efficiency of MB was achieved after 180 min under visible light irradiation. It is believed that these materials will have promising applications in the wastewater treatment field.

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