Comparison of photocatalytic activity of ZnO, Ag-ZnO, Cu-ZnO, Ag, Cu-ZnO and TPPS/ZnO for the degradation of methylene blue under UV and visible light irradiation

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\textbf{ABSTRACT}

In this study, zinc oxide and silver and copper-doped zinc oxide nanorods were synthesized by a simple template-free precipitation technique. In addition, meso-tetrakis-(4-sulfonatophenyl) porphyrin (TPPS\textsubscript{4}) was prepared and immobilized on ZnO nanorods (TPPS/ZnO). The synthesized photocatalysts were characterized by various techniques such as X-ray powder diffraction, scanning electron microscopy, UV-visible spectroscopy, diffuse reflectance spectroscopy, and Fourier transform infrared spectroscopy. The potential of the obtained photocatalysts in the degradation of methylene blue was investigated under UV and visible light irradiation. The results revealed that the photocatalytic activity of TPPS/ZnO was higher than those of the pure ZnO and doped ZnO under visible light irradiation.

\textbf{Key words:} doped ZnO nanorods, methylene blue, photocatalyst, porphyrin, TPPS\textsubscript{4}

\textbf{HIGHLIGHTS}

- Zinc oxide and silver and copper-doped zinc oxide nanorods were synthesized by a simple template-free precipitation technique.
- In addition, TPPS\textsubscript{4} was prepared and immobilized on ZnO nanorods.
- The potential of the obtained photocatalysts in the degradation of MB was investigated under UV and visible light.
- The results revealed that the photocatalytic activity of TPPS/ZnO was higher than those of the pure ZnO and doped ZnO.

\textbf{GRAPHICAL ABSTRACT}

\textbf{1. INTRODUCTION}

In recent years, there has been an increased interest in searching for efficient techniques for decomposition of pollutants. Semiconductors such as TiO\textsubscript{2} and ZnO can act as sensitizers for light-reduced redox processes for the purpose of organic material mineralization (Hoffmann \textit{et al.} 1995; Gouvea \textit{et al.} 2000; Boer \textit{et al.} 2002; Li & Haneda 2003; Baruah \textit{et al.} 2019). ZnO is a nontoxic and biocompatible material with excellent chemical and thermal stability (Ozgur \textit{et al.} 2005; Zhao \textit{et al.} 2012).

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Semiconductors with one-dimensional shapes like rods or tubes appear to be attractive because of their novel optoelectronic properties (Hu et al. 1999; Cui et al. 2001; Kolmakov & Moskovits 2004; Kuchibhatla et al. 2007). The one-dimensional ZnO rod has the ability to provide natural channels resulting in little resistance for charges during the redox reactions (ZnO + h\textsuperscript{+} + e\textsuperscript{−}, which can facilitate the electron transfer and promote reaction rates (Pare et al. 2008).

Regardless of innovative fabrication techniques for use of ZnO for degradation of MB under solar light with good results (El Golli et al. 2021), the pure ZnO, with a large direct band-gap energy of 3.37 eV at room temperature with photoactivity at UV light, cannot efficiently make use of the solar spectra, because solar spectra contain only 4% UV light (Guillen & Herrero 2006). The doping of metal ions in ZnO nanostructures can lead to effects such as extending their optical absorption to the visible range (Wang et al. 2015; Ebrahimi et al. 2019), fluorescence enhancement, and controlling the concentration of surface defects. The doping of Cu and Ag in ZnO is expected to modify optical absorption and other physical or chemical properties of ZnO (Kuriakose et al. 2015; Heiba et al. 2020). Simultaneous doping of two kinds of atoms (co-doping) into semiconductor materials has recently been realized and it may result in higher photocatalytic activity and special characteristics compared with single element doping into semiconductor oxides (Sudash et al. 2012; Tunçal 2020, 2021).

Porphyins are purple conjugated heterocyclic compounds, composed of four pyrrole subunits interconnected at their α carbon atoms to form a planar porphyrin ring (Rayati & Malekmohammadi 2016). These compounds are suitable photosensitizers due to their very high absorption in the near 400 nm (Soret band) and absorption peaks in the 500–700 nm regions (Q bands). At this time, one of the important applications of porphyrin dyes is using them as sensitizers to extend the absorbance sensitizers due to their very high absorption in the near 400 nm (Soret band) and absorption peaks in the 500–700 nm regions (Q bands) of the semiconductors to the visible region (Gerdes et al. 1997; Sun et al. 2012). Porphyrins can participate in various photophysico-chemical processes that are promising solutions for photodynamic therapy of cancer (Nyman & Hynninen 2004).

Due to nontoxicity in the dark and photodegradation in aqueous media, porphyrins are attractive for the photodecontamination of chemically polluted waters (Rotomskis et al. 1997; Herath et al. 2008; Rabani et al. 2016a, 2016b; Sedghi et al. 2021). In this paper, a simple template-free precipitation method was used to synthesize ZnO and (Ag-, Cu- and Ag, Cu-) doped ZnO nanorods. Moreover, meso-tetrakis (4-sulfonatophenyl) porphyrin (TPPS\textsubscript{4}) has been immobilized on the surface of ZnO nanorods (TPPS/ZnO). The photocatalytic degradation of MB on TPPS/ZnO, ZnO nanorods, and doped ZnO nanorods was investigated under ultraviolet and visible light irradiation.

2. EXPERIMENTAL

2.1. Materials and methods

All the chemicals used in this work were analytical grade reagents and were used without further purification. Zinc nitrate (Zn(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O), silver nitrate (AgNO\textsubscript{3}), copper nitrate (Cu(NO\textsubscript{3})\textsubscript{2}.3H\textsubscript{2}O), ammonia (25%), pyrrole, propionic acid, benzoaldehyde and sulfuric acid were purchased from the Merck company. Deionized water was used for preparation of all solutions.

The samples were characterized by X-ray powder diffraction (XRD) using a JEOL X-ray diffractometer with Cu K\textsubscript{α} radiation. The particle morphologies of the ZnO powder were observed using an AIS2100 (Seron Technology) scanning electron microscopy (SEM). The FT-IR analyses were carried out on a Shimadzu FT-IR-8400S spectrophotometer using a KBr pellet for sample preparation. DRS spectra were prepared via a Shimadzu (MPC-2200) spectrophotometer.

2.2. The preparation of ZnO and doped ZnO nanorods

The amount of 5.94 g of Zn(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O was added to 500 mL distilled water to obtain a concentration of 0.04 M. The ammonia solution (25%) was added dropwise to the solution to achieve pH = 11; afterwards, the solution was refluxed under stirring. The white precipitate was deposited at the bottom of the flask. Finally, the mixture was centrifuged, and the white solid was collected and washed with distilled water. The obtained solid was dried at 100 °C in the oven for 3 h, followed by calcination at 450 °C for 3 h.

To prepare Ag-doped material, 5.71 g of Zn(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O and 0.18 g AgNO\textsubscript{3} were added to 500 mL distilled water to obtain a concentration of 0.038 M of zinc nitrate and 0.0016 M of silver nitrate (with the molar ratio Ag to ZnO of 4:96). To prepare Cu-doped ZnO with the same molar ratio, 5.71 g of Zn(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O and 0.19 g Cu(NO\textsubscript{3})\textsubscript{2}.3H\textsubscript{2}O were used. For the preparation of Cu,Ag-codoped ZnO, 5.71 g of Zn(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O, and 0.092 g AgNO\textsubscript{3} and 0.096 g Cu(NO\textsubscript{3})\textsubscript{2}.3H\textsubscript{2}O were added to 500 mL distilled water to obtain a concentration of 0.038 M of zinc nitrate, 0.0008 M of silver nitrate and 0.0008 M of copper nitrate, (a molar ratio Ag to Cu to ZnO of 2:2:96).

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2.3. Preparation of meso-tetrakis (4-sulfonatophenyl) porphyrin (TPPS₄)

The amount of 10 mmol of freshly distilled pyrrole (0.7 mL), 10 mmol of benzaldehyde, 100 mL of propionic acid and 15 mL of nitrobenzene were added together in a 250 mL flask. The mixture was allowed to reflux under stirring at 120 °C for 60 min. After that, the resulting mixture was cooled overnight at room temperature and filtrated under reduced pressure. The crude product was purified by column chromatography (silica gel, chloroform/ethyl acetate = 20:1 as eluent). As a result, the desired purple solid of meso-tetrakis (phenyl) porphyrin (TPP) was obtained (30%).

For the synthesis of meso-tetrakis (4-sulfonatophenyl) porphyrin (TPPS₄), 0.2 g of TPP was dissolved in 5 mL of concentrated H₂SO₄ (Figure 1). The mixture was heated in a steam bath for 4 h and then it was allowed to stand for 48 h. The resulting solution was neutralized by NaOH (3N) and then the solvent was removed under vacuum at room temperature. The product was washed with methanol until no TPPS₄ was detected in the solution using a UV–visible spectrophotometer.

2.4. The modification of ZnO nanorods by TPPS₄

The amount of 0.02 mmol of TPPS₄ was dissolved in 50 mL of H₂O. Then, this solution was added to 0.02 mmol of finely ground ZnO nanorods (2 mg). The resulting suspension was stirred under reflux for 5 h, and then the solvent was removed under vacuum at room temperature. The produced solution was cooled at room temperature for 24 h. Consequently, the product was washed with ethanol until no porphyrin was detected in the supernatant using a UV–visible spectrophotometer.

2.5. Photocatalysis procedure

Following the common practice among other studies, the catalytic reaction was performed in a 100 mL cylindrical Pyrex beaker as a photoreactor (Figure 2), which contains 20 mL of MB dye (10 mg/L) solution, and 0.02 g of catalyst (ZnO,

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**Figure 1** | Synthesis of the meso-tetrakis (4-sulfonatophenyl) porphyrin (TPPS₄).

**Figure 2** | Schematic representation of the photoreactor.
Ag-ZnO, Cu-ZnO, Ag,Cu-ZnO and TPPS/ZnO). Before irradiation, the solution was stirred in the dark (15 min) to allow equilibrium of the system. The photoreactor was placed in a box, whose inner walls were all covered with aluminum foil and a continuous air flow kept the indoor temperature constant. Irradiation was carried out using 400 W tungsten as a visible light source and 400 W high pressure mercury lamps as a UV light source and the intensity of emitted light for visible and UV sources were 40 and 60 mW·cm\(^{-2}\) respectively. All the photocatalytic experiments were carried out under the same conditions. The distance between photoreactor and light sources was 20 cm. The samples (5 mL) were collected during irradiation; then, the MB solution was separated from the photocatalyst by centrifugation. The degradation was monitored by measuring the absorbance amount using a double beam UV–Vis spectrophotometer (Shimadzu UV-1700) at 664 nm wavelength (Rahimi et al. 2016; Rabbani et al. 2017).

3. RESULTS AND DISCUSSION

3.1. Characterization of prepared photocatalysts

3.1.1. Morphological properties

The morphology of the ZnO particle was examined from SEM images. It was found that all synthesized ZnO nanorods were quite uniform in size. Figure 3(a) and 3(b) show the SEM images of the pure ZnO and TPPS/ZnO nanorods, respectively. Transmission electron microscopy (TEM) image of ZnO nanorods is inserted to its SEM image.

3.1.2. Structure properties

Figure 4 shows the XRD patterns of ZnO, Ag-ZnO, Cu-ZnO and Ag,Cu-ZnO nanorod powders. It can be seen that all peaks of these nanorods are in good agreement with hexagonal (wurtzite) ZnO (JCPDS Card No. 36-1451). For ZnO nanorods, impurity peaks were not observed, which indicates the high purity of the obtained ZnO nanorods (Hu et al. 2010). Overall, these diffraction peaks were sharp, narrow and symmetrical with a low and stable baseline, suggesting that the sample was well crystallized (Wen et al. 2012). For Ag-ZnO nanorods, the additional diffraction peak shown at 38.02° could be ascribed for face centered cubic structure of metallic Ag with the space group Fm-3 m (JCPDS Card No. 04-0783). The intensity of the Cu- and Ag-doped ZnO diffraction lines was decreased and a minor shift was also observed due to the substitution of Cu and Ag atoms in ZnO hexagonal lattices (Abinaya et al. 2016).

Table 1 shows that the calculated d-values are in good agreement with those taken from the JCPDS card file data for ZnO nanorod powder. There was no obvious difference between the XRD pattern of Ag-ZnO, Cu-ZnO, Ag,Cu-ZnO nanorods and the undoped ZnO, apart from the peak position which was slightly left-shifted ∼0.1° to 0.3°.

![Figure 3](image_url) | The SEM images of the synthesized (a) ZnO and (b) TPPS/ZnO nanorods. TEM image of ZnO nanorods is inserted to its SEM image.
3.1.3. Optical properties

The UV–Vis diffuse reflectance spectra (DRS) of the synthesized doped, undoped ZnO nanorods, TPPS/ZnO nanorods, and the UV–Vis spectrum of pure TPPS$_4$ (in methanol) at room temperature are shown in Figure 5(a). The spectrum reveals a characteristic absorption peak of ZnO at wavelength of 368 nm; this can be assigned to the intrinsic band-gap absorption of ZnO due to the electron transitions from the valence band to the conduction band (O$_{2p}$ → Zn$_{3d}$) (Zak et al. 2011).

In the semiconductor, the absorption coefficient is the result of the incident photon energy. Near the absorption edge, the absorption coefficient for direct transition is given by (Sze & Ng 2006):

$$a h\nu = A (h\nu - E_g)^n$$

| Table 1 | The XRD parameters of the synthesized ZnO nanorods

| h k l | Synthesized ZnO nanorods | JCPDS 36-1451 |
|-------|--------------------------|---------------|
|       | 2θ (degree) | d-Value (Å) | I (%) | 2θ (degree) | d-Value (Å) | I (%) |
| 1 0 0 | 31.8194 | 2.81239 | 61.23 | 31.770 | 2.81430 | 57 |
| 0 0 2 | 34.4762 | 2.6015 | 54.61 | 34.422 | 2.60332 | 44 |
| 1 0 1 | 36.2973 | 2.47505 | 100 | 36.253 | 2.47592 | 100 |
| 1 0 2 | 47.5898 | 1.9108 | 19.69 | 47.539 | 1.91114 | 23 |
| 1 1 0 | 56.6653 | 1.62443 | 22.6 | 56.603 | 1.62472 | 32 |
| 1 0 3 | 62.9221 | 1.47712 | 21.67 | 62.864 | 1.47712 | 29 |
| 2 0 0 | 66.4036 | 1.40787 | 1.83 | 66.380 | 1.40715 | 4 |
| 1 1 2 | 67.9976 | 1.3787 | 15.89 | 67.963 | 1.37818 | 23 |
| 2 0 1 | 69.1258 | 1.35893 | 7.95 | 69.100 | 1.35825 | 11 |
| 0 0 4 | 72.6191 | 1.30193 | 1.78 | 72.562 | 1.30174 | 2 |
| 2 0 2 | 76.9981 | 1.23743 | 2.21 | 76.955 | 1.23801 | 4 |

Figure 4 | The XRD patterns of the synthesized doped and undoped ZnO nanorods.
Figure 5 | (a) The diffuse reflectance spectra (DRS) of the synthesized TPPS/ZnO and doped and undoped ZnO nanorods and the UV–vis spectrum of pure TPPS₄ (in methanol) and (b) the plot for band-gap energy (E_{bg}) of doped and undoped ZnO nanorods.
where $E_g$ is the energy gap, $h\nu$ is the energy of the incident photon and constant $A$ varies for different transitions which is related to a couple of factors including the effectiveness of mass of carriers, refractive index, oscillator strength and so on. The symbol $n$ is an index which equals half of corresponding allowed direct transitions (Li et al. 2012).

When the transition in the semiconductor at certain wavelength scope is direct, the extrapolation method is commonly used to determine the band gap of semiconductors. In this work, when the index $n$ is 1/2, considering the relationship of reflectivity and transmission with wavelength, we calculated the square of the absorption coefficient as a factor of the incident photon energy (as shown in Figure 5(b)).

It can be seen in Figure 5(b) that the increase of Ag and Cu causes a slight red shift in band edge absorption peak. The calculated band gap of the Ag, Cu and co-doped Ag,Cu-ZnO nanorods and undoped ZnO nanorods were 3.20, 3.18, 3.14, and 3.22 eV, respectively (Table 2). The main reason is that the Zn$^{2+}$ ions are substituted by the Ag$^{+}$ or Cu$^{2+}$ ions. The substitution by the Cu$^{2+}$ ions of fewer radii than that of the Zn$^{2+}$ leads to a decrease in the optical band gap rather than by larger Ag$^{+}$ ions at the similar amount of dopant.

Ag and Cu codopants extend the absorbance of ZnO to cover the entire visible region. Doping of silver and copper in ZnO causes a red shift in the absorption edge that is interpreted as possible evidence for good contact between Ag and Cu ions and ZnO; this indicates that the presence of Ag-ZnO-Cu bonds and the creation of the new energy level in the band gap (Subash et al. 2012).

The absorption range of the TPPS/ZnO composite is wider in comparison with those of pure TPPS$_4$ and ZnO nanorods. The UV–visible spectrum of pure TPPS$_4$ has Soret peak in 413 nm and four Q peaks in 513, 553, 557 and 633 nm. In addition, the Soret and Q bands of the porphyrin of the composite are red-shifted, and related to those of the pure TPPS$_4$. Furthermore, the intensity ratio of the Soret band to Q bands of the TPPS/ZnO is lower than that of the pure TPPS$_4$. Based upon these observations, it was demonstrated that the porphyrin was assembled on the surface of ZnO nanorods, and there exists a strong interaction between ZnO nanorods and porphyrin in the TPPS/ZnO.

### 3.1.4. Fourier transform infrared spectroscopy

Figure 6 shows (i) the FT-IR spectra of the ZnO, Ag-ZnO, Cu-ZnO, Ag,Cu-ZnO and TPPS/ZnO nanorods, and (ii) TPPS$_4$ in the range of 390–4,000 cm$^{-1}$. The appearance of a sharp band at 401 and 501 cm$^{-1}$ in the FT-IR spectra confirms the synthesis of ZnO and doped ZnO, because it is the characteristic absorption band for the Zn–O stretching vibration (Al-Hajry et al. 2009). Additionally, broad absorption peaks centered at around 3,446 cm$^{-1}$ are caused by the O–H stretching of the absorbed water molecules. This is because the nanocrystalline materials compared a high surface-to-volume ratio.

For the FT-IR of TPPS$_4$, the stretching vibration of $\equiv$C–N and $-$C = N bands (pyrrole) appeared at 1,373 cm$^{-1}$ and 1,720 cm$^{-1}$, respectively. The stretching asymmetric and symmetric vibration bands that are attributed to the C-H (CH$_2$) band, are discernible in 2,846, 2,918 and 2,939 cm$^{-1}$. The appearance of the peaks at 890, 1,100 and 3,387 cm$^{-1}$ could be attributed to the C$_6$H$_4$ (phenyl), SO$_3$ group and N-H band, respectively.

For the FT-IR of TPPS/ZnO, the appearance of peaks that corresponded to TPPS$_4$ confirmed that porphyrin was immobilized on ZnO nanorods. However, these peaks make it difficult to give precise values because of very low intensities, which are attributed to small amounts of the macrocycle into the inorganic matrix.

### 3.2. Photocatalytic degradation of methylene blue

The photocatalytic activities of as-synthesized catalysts were evaluated by the degradation of organic dyes methylene blue (MB) in aqueous solution under light irradiation. The doped and undoped ZnO and TPPS/ZnO nanorods, with a high

| Photocatalyst   | ZnO | Cu-ZnO | Ag-ZnO | Ag-Cu-ZnO | TPPS/ZnO |
|-----------------|-----|--------|--------|-----------|----------|
| Band gap (eV)   | 3.22| 3.18   | 3.20   | 3.14      | -        |
| Light           | Visible | UV   | Visible | UV        | Visible  |
| Degradation (%) | 24.9| 41.8   | 81.42  | 84.49     | 94.9     |
| k (1/min)       | 0.0018 | 0.003 | 0.0104 | 0.0096    | 0.0069   |
| Regression      | 0.9432 | 0.9868 | 0.9988 | 0.9965    | 0.9983   | 0.9974 | 0.9997 | 0.9993 | 0.9961 |
specific surface area, were used as photocatalysts for the decomposition of MB. The characteristic absorption of MB at 664 nm was chosen to monitor the photocatalytic degradation process. Regarding the effect of initial MB concentration, it was observed that there was a decrease in the photodegradation of MB with increasing initial MB concentration. Figure 7 shows a typical photocatalytic degradation process of MB (initial concentration: 10 mg/L, 20 mL) using TPPS/ZnO (0.02 g) under visible light irradiation. The absorption peaks corresponding to MB diminished gradually as the exposure time was extended.

**Figure 6** | The FT-IR spectrum of the synthesized TPPS/ZnO and doped and undoped ZnO nanorods and pure TPPS₄.

**Figure 7** | The temporal evolution of the absorption spectra of the MB solution (initial concentration: 10 mg/L, 20 mL) in the presence of TPPS/ZnO catalyst (0.02 g) under visible light irradiation at 180 min.
Figure 8 shows the photocatalytic efficiency of samples in the dark and under visible and UV light irradiation. In the photocatalytic reaction, adsorption is one of the most important factors for a higher degradation percentage. According to Figure 8, this clearly shows that dye degradation percentage is enhanced only in the presence of a photocatalytic surface under light illumination (see Figures S1 and S2 in Supporting Information, also). Under UV light irradiation, the best photodegradation of MB was carried using Ag,Cu-ZnO (86%). However, under visible light irradiation, it can be seen that the TPPS/ZnO photocatalyst can lead to 99.9% decomposition of MB after 180 min illumination, which is significantly greater than that found using pure ZnO nanorods (Table 2). Also, the mineralization of MB was measured by total organic carbon analysis using the TPPS/ZnO catalyst under UV and visible irradiation. (see Fig. S5). The results showed that the degradation performance under UV irradiation can be overtaken by visible light (Ananpattarachai & Kajitvichyanukul 2015). After ZnO nanorods are sensitized by porphyrin, higher photoactivity is obtained under visible light irradiation, which indicates that porphyrin played a different role in the photoreactivity process (Gouvea et al. 2000).

Most of the photocatalytic degradation reactions follow the classical Langmuir–Hinshelwood kinetic model (Banerjee et al. 2004). For a detailed analysis of the decomposition reaction of MB, a pseudo first-order kinetic model was used:

\[
\ln \frac{C}{C_0} = -kt + \ln C_0
\]

where C is the concentration of MB, t is the irradiation time and k is the rate constant for the photocatalytic degradation reaction. The plot of \(\ln(C_0/C)\) versus t gives a linear relationship (Figure 9) between doped and undoped ZnO and TPPS/ZnO nanorods. This indicates that photocatalytic degradation of MB conformed to pseudo first-order kinetics.

The rate constant and the regression of kinetic plots of MB photocatalytic degradation using different catalysts under UV and visible light irradiation are listed in the Table 2. Making use of different catalysts, Table 2 compares the constant rate of kinetic plots of MB photocatalytic degradation against the regression rate; this comparison was carried out under UV and visible light irradiation.

Figure 10 draws a comparison between (i) the degradation efficiency, and (ii) the kinetics of MB photocatalytic degradation with different catalysts. We used the dark, and UV and visible light irradiation to perform this experiment.

The TPPS/ZnO photocatalyst has a higher degradation efficiency and higher rate constant than other catalysts. In order to understand the photocatalytic degradation mechanism, a possible proposed mechanism for the TPPS/ZnO photocatalyst was
shown in Figure 11. The porphyrins on the surface of the ZnO nanorods generate photoinduced electrons by absorption of the visible light. Also, among ZnO, doped ZnO and TPPS₄, only TPPS₄, i.e., the ground state of the sensitizer, is activated to its excited state, TPPS₄⁺ using one photon transition. The energy level of the excited TPPS₄ is higher than that of ZnO. The excited state electrons could readily be injected into the conduction band (CB) of ZnO. Meanwhile, TPPS₄⁺ takes the electrons from the solution to change into TPPS₄. The electrons present on CB of ZnO reacted with dissolved O₂ oxygen to
generate superoxides (\(\bullet O_2\)) and then hydroxyl (\(\bullet OH\)) radicals (Afshar et al. 2016). The generated superoxides and hydroxyl can oxidize MB absorbing on the catalyst surface into small molecules or CO\(_2\). The sensitization by porphyrin exhibits a better effect in the process of photocatalytic degradation of MB. Because the inhibition of electron–hole pair recombination increases, the number of the holes participating in the photooxidation reaction increases and it enhances the photoactivity of nanocomposite. Hence, this would result in higher charge carriers to form reactive hydroxyl radicals (\(\bullet OH\)) promoting the photodegradation of the adsorbed MB dyes.

The photocatalytic mechanism was investigated by measuring the photodegradation rate in the presence of N\(_2\) (O\(_2\) scavenger) and t-BuOH (\(\bullet OH\) scavenger, t-BuOH + \(\bullet OH\) → t-BuO\(^+\) + H\(_2\)O). In addition, iodine anions were used as the scavenger of positive holes (2 I\(^-\) + 2 h\(^+\) → I\(_2\)). The addition of N\(_2\) and t-BuOH, significantly reduced the photodegradation of MB while oxidation was slightly influenced by holes, suggesting that radicals were the principle oxidant.

Conversely, the doping of Ag and Cu in ZnO results in a lower band gap and the increase of defect sites. It has been also believed that the higher surface-to-volume ratio for the nanorods results in more surface oxygen vacancies (Huang et al. 2001; Yang et al. 2002; Banerjee et al. 2004; Lee et al. 2016; Huber et al. 2017; El-Nahas et al. 2021).

For Ag\(^+\) and Cu\(^{2+}\) when doped in ZnO, more surface defects could be produced and a space charge layer could be formed on the surface, which is beneficial for hindering the recombination of photoinduced electron–hole pairs. Ag or Cu can trap the electrons from the CB of ZnO during irradiation in the photocatalytic process.

The photocatalytic activity of Ag,Cu-ZnO is higher compared to Cu-ZnO and Ag-ZnO, too. This enhances the photocatalytic activity of Ag,Cu-ZnO due to a synergistic effect between Ag and Cu in ZnO.

4. CONCLUSION

The synthesis of doped (Cu, Ag and Cu,Ag) and undoped ZnO nanorods was successfully achieved using a simple precipitation method. The preparation of catalysts has been revealed by XRD, FT-IR, DRS and SEM images. Dopants shift the absorption of ZnO to the entire visible region. Ag-ZnO, Cu-ZnO, and Ag,Cu-codoped ZnO show lower reflectance in the visible region compared with ZnO and the shifting of the absorption edge to the visible region compared with ZnO. The photocatalytic degradation of MB in water was studied using TPPS/ZnO and doped and undoped ZnO nanorods under visible and UV light irradiation. The obtained results indicated that the photodegradation of MB was affected by the type of photocatalyst and light irradiation. Based on the Langmuir–Hinshelwood mechanism, a pseudo first-order kinetic model was illustrated. In this study, TPPS/ZnO nanorods were found to be more efficient than Ag-ZnO, Cu-ZnO, Ag, Cu-ZnO, and bare ZnO for MB degradation under visible light.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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