Optik - International Journal for Light and Electron Optics 303 (2024) 171722

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.com/locate/ijleo

Preparation and characterization of ZnO/CuO nanocomposites thin films for highly efficient visible-light photocatalysis of acriflavine dye

Fatima Allawi [a], M.A. Mahdi [b,*], Marwah J. Kadhim [b], Adel H. Omran Alkhayatt [c]

[a] Department of Chemistry, College of Science, University of Kufa, Najaf, Iraq
[b] Department of Physics, College of Science, University of Basrah, Basrah, Iraq
[c] Department of Physics, College of Science, University of Kufa, Najaf, Iraq

ARTICLE INFO

Keywords:
ZnO/CuO
Nanocomposite
Photocatalyst
Acriflavine dye

ABSTRACT

Chemical bath deposition (CBD) was used to grow ZnO nanorods on glass substrates. Grown ZnO nanorods are dipped in a copper nitrate trihydrate [$Cu(NO_3)_2.3\,H_2O$] solution at 90 °C for 30 min before being annealed at 400 °C for 1 h to convert Cu^{2+} ions to CuO nanoparticles, forming a ZnO/CuO thin films nanocomposite. Images obtained from a Field Emission Scanning Electron Microscope (FESEM) indicated that the ZnO structure consisted of nanorods coated in CuO nanoparticles. The optical absorption of both ZnO NRs and ZnO/CuO nanocomposites thin films was strongly edged, with an energy gap of 3.26 and 3.21 eV, respectively. The photodegradation rate of the manufactured ZnO NRs and ZnO/CuO nanocomposites thin films against Acriflavin dye was investigated at room temperature under varying pH conditions and period exposure to visible light. The rate of photodegradation of the dye was increased by increasing the time it was exposed to light and/or the pH of the solution. The photodegradation rates for AFN dye under visible light irradiation ranged from 36% to 100% as the pH value was increased from 4 to 10, and from 78% to 66% at a pH value of 12 and reduced to 78% at a pH value of 12 after 330 min of irradiation. Furthermore, the trapping experiments of reactive species for Acriflavin dye degradation by ZnO/CuO nanocomposites photocatalysts were also carried out

1. Introduction

Pollutants like organic material in the water have increased in recent years due to the massive growth of industry and the proliferation of factories along the banks of rivers, leading to severe environmental problems and the emergence of a number of diseases due to the pollutants' ability to bio-accumulate in the bodies of living organisms. The water must be purified from these pollutants, but only through processes that won't affect the environment [1]. Extraction, polymerization, the electro-Fenton process, and photocatalytic degradation are only some of the technologies discovered to rid water of toxic organic. In contrast, the use of a photocatalysis-based semiconductor degrading process is a relatively new technique that effectively treats water by eliminating organic and inorganic impurities [2,3]. The emergence of the Advanced Oxidation Process (AOP) has resulted in the development of a novel way to gather oxidative techniques within the fields of photocatalysis. These methods are specifically designed to achieve

* Corresponding author.
E-mail address: m.a.mahdi@uobasrah.edu.iq (M.A. Mahdi).

https://doi.org/10.1016/j.ijleo.2024.171722
Received 11 September 2023; Received in revised form 23 February 2024; Accepted 1 March 2024
Available online 6 March 2024

complete degradation of persistent organic pollutants by the generation of reactive oxygen species [4]. Due to its high catalytic activity, low cost, environmental friendliness, chemical stability, and ease of fabrication in nanostructured forms, zinc oxide (ZnO) is being looked at as a potential photocatalytic material. These features make ZnO an excellent candidate for use in numerous fields, including photocatalysis [5,6]. As a result of the broad bandgap of 3.37 eV and the fast rate of photo-induced electron (e^-)-hole (h^+) pair recombination, the photo-degradation reaction is strongly disrupted, and the material responds poorly to visible light [7]. Modifying ZnO with noble metals like Cu [8], Au [9], and Ag [10] increases its catalytic activity in visible light. Because of their numerous applications, metal oxide materials, in particular, have been widely used in environmental research, including catalysis for dye degradation [11]. Metal oxide nanocomposites, such as copper/zinc oxides (CuO/ZnO), have grown in popularity in these applications due to their optical, electrical, and magnetic properties, as well as their eco-friendliness and superior adjustable catalysis characterization [12]. Cupric oxide, a p-type metal oxide semiconductor with an optical band gap of 1.2–2.1 eV [13], is harmless and widely available in nature. In addition, the intrinsic high carrier concentration results in great physical stability and outstanding electrical conductivity. It's also a cheap material with a straightforward production method [14]. The heterojunction is formed when p-type CuO and n-type ZnO are coupled together. High photocatalytic efficiency can be achieved using heterostructures of nanostructured CuO-ZnO due to their large specific surface area and increased optical absorption [15]. Since World War II, Acriflavine (AFN) dye has been used as an antiseptic. Dr. Paul Ehrlich of Germany developed it and utilized it as an antibacterial agent, although it wasn't widely used until the 1960 s. Because of its solubility in water, acriflavine hydrochloride is frequently used to treat fungus infections in fish kept in aquariums. Its fluorescence makes it useful in biochemistry as well. Despite its usefulness in medicine, acriflavine has been linked to several negative side effects in humans, including skin irritation, eye discomfort, and breathing difficulties. It has been discovered that acriflavine is poisonous to aquatic plants as well. It also makes the water appear fluorescent, which must be corrected before it can be considered pure. Here, a simple chemical approach was used to construct a nanostructured ZnO-nanorods/CuO nanocomposite. Under visible light of varying durations and pH values, the produced nanostructures are used as a photocatalyst to degrade AFN dye.

2. Experimental part

2.1. Preparation ZnO Nanorods thin films

Chemical bath deposition (CBD) is used to grow a thin film of ZnO nanorods on a glass substrate. All chemicals used were analytical reagent grade and did not require further purification. After being ultrasonically cleaned in ethanol for 15 min, glass substrates were rinsed in deionized distilled water. The deposition of a seed layer composed of ZnO nanoparticles (NPs) is necessary for the growth of ZnO nanorods in alignment on glass substrates. That's why using an ethanol solution containing 5 mM zinc acetate dihydrate Zn $(OOCCH_3)_2$. The ZnO NPs were then formed by casting the solution onto clean glass substrates and heating them to 280 °C for 1 h. To grow ZnO NRs, zinc nitrate hexahydrate [$Zn(NO_3)_2.6\ H_2O$] and hexamethylenetetramine [$C_6H_{12}N4$ (99.9% purity)] with 0.1 M was dissolved in distilled water (DW) individually before being mixed. Substrates of glass covered with ZnO NPs were immersed into the prepared aqueous solution which was heated at 90±3 °C for 2 h. The substrates were taken out of the solution after the process of growth was finished, washed multiple times with DW, and then dried at room temperature. The grown ZnO NRs underwent an annealing process at 250 °C for 1 h to improve their crystallinity.

2.2. Preparation of CuO nanoparticles film

CuO nanoparticles were prepared by dissolving 0.48 g of 99.9% pure copper nitrate trihydrate [$Cu(NO_3)_2.3\ H_2O$] in 100 ml of DW. The ZnO NRs/glass substrates were dipped in the solution at 90 °C for 30 min to enable Cu ions to adhere to the ZnO NRs. The slides were then extracted from the solution, rinsed with DW, and allowed to dry before being annealed at 400 °C for one hour to convert Cu ions into CuO nanoparticles.

2.3. Mechanism of photocatalytic degradation of Acriflavine dye

Degradation tests were conducted using AFN dye at concentrations of 20 ppm at pH values of 4, 6, 8, 10, and 12. By oxidizing the AFN dye molecules that have been adsorbed onto their surfaces, the ZnO/CuO nanostructure can photo-catalytically eliminate the AFN dye. To achieve this, reactive species including hydroxyl (•OH) and superoxide ($\bullet O^{2-}$) radicals are generated. The mechanism for photocatalytic degradation of AFN dye by ZnO/CuO thin films nanostructures is depicted below [16]:

1. Light absorption: When ZnO and CuO absorb photons with energy equal to or greater than their bandgap energy, electron-hole pairs are formed.

$ZnO + h\nu \rightarrow ZnO^*$ (excited state)….(1)

$CuO + h\nu \rightarrow CuO^*$ (excited state)….(2)

2. Formation of reactive species: Electron-hole pairs can react with adsorbed water molecules or oxygen to generate highly reactive species such as hydroxyl ($^{\bullet}OH$) and superoxide radicals ($^{\bullet}O^{2-}$).

$ZnO^* + H_2O \rightarrow ZnO + {}^{\bullet}OH$ ….(3)

$ZnO^* + O_2 \rightarrow ZnO + {}^{\bullet}O^{2-}$ ….(4)

$CuO^* + H_2O \rightarrow CuO + {}^{\bullet}OH$….(5)

$CuO^* + O_2 \rightarrow CuO + {}^{\bullet}O^{2-}$….(6)

2. Adsorption of AFN dye: The molecules of AFN dye are adsorbed onto the surface of ZnO/CuO particles via electrostatic attraction or van der Waals forces.

AFN + ZnO/CuO → AFN -ZnO/CuO….(7)

3. Photocatalytic degradation: The highly reactive species can oxidize the adsorbed AFN dye molecules, resulting in the degradation of the dye. The oxidation of AFN dye molecules can occur via multiple mechanisms, including direct oxidation by $^{\bullet}OH$ radicals and indirect oxidation via the formation of peroxides.

AFN -ZnO/CuO + $^{\bullet}OH \rightarrow CO_2+H_2O$….(8)

AFN -ZnO/CuO + $^{\bullet}O^{2-} \rightarrow CO_2+H_2O$….(9)

However, the photocatalytic mechanism is determined by the locations of the nanocatalyst's valence band (VB) and conduction band (CB) edges. The following relationships estimate the nanocomposite's VB and CB locations [17]:

$$E_{CB} = \chi - E^e - 0.5E_g \ldots\ldots\ldots \quad (10)$$

$$E_{vB} = \chi - E^e + 0.5E_g \ldots\ldots\ldots \quad (11)$$

Where χ is the electronegativity, E^e is the energy of free electrons on the hydrogen scale, and Eg is the band gap energy. The value of E^e is 4.5 eV. The values of χ for ZnO and CuO are 5.79 eV and 5.81 eV, respectively [17]. The calculated band gap energies (Eg) of ZnO is 3.26 eV thus, E_{CB} and E_{VB} potentials are −0.36 eV and +2.92 eV, respectively. However, E_{CB} and E_{VB} potential of CuO are +0.265 eV and +2.355 eV, respectively when the energy band gap is 2.09 eV [17]. It is more difficult for electrons to move from the conduction band of CuO to the conduction band of ZnO due to the fact that the edge of CuO's conduction band is lower than ZnO's. When a ZnO/CuO thin films nanocomposite heterojunction is produced, electrons are transferred between the p-type CuO and n-type ZnO components, raising the Fermi level of CuO and decreasing the Fermi level of ZnO until equilibrium is reached. ZnO loses electrons, forming a depletion layer on the surface, and its Fermi level shifts in a positive direction, whereas CuO's Fermi level shifts in a negative direction. Finally, the Fermi levels of the two semiconductors match [18]. Meanwhile, as the Fermi levels rise and fall, the energy band of CuO rises while that of ZnO falls [19,20]. As a result, the conduction band edge of CuO in the nanocomposite is greater than that of ZnO. Fig. 1 shows the photo-degradation mechanism for AFN dye by ZnO/CuO thin films nanocomposite. To evaluate role of reactive species in photodegradation process, different scavenger like benzoquinone (BQ), isopropyl alcohol (IPA), ethylenediammine tetra acetate (EDTA) were used during photoreaction. The degradation efficiency is calculated using equation:

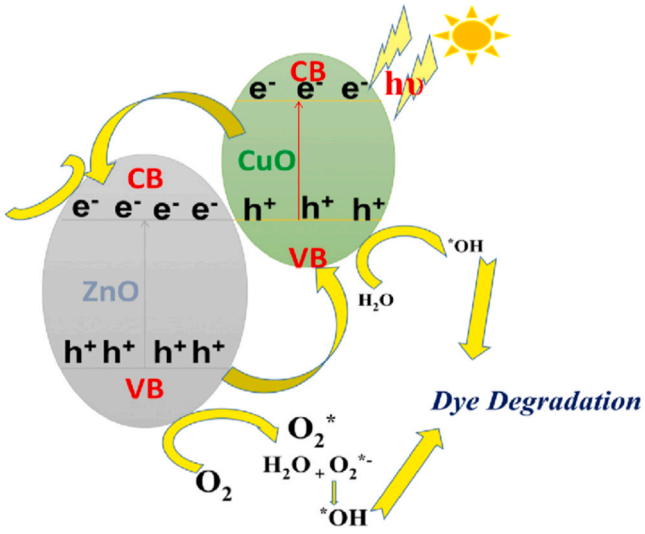

Fig. 1. The photo-degradation mechanism for Acriflavine dye in the presence of CuO@Zno nanocomposite [12].

$$Degradation \quad efficiency\% = (1 - C/C_o) \times 100..... \tag{12}$$

3. Results and discussions

3.1. Surface morphology

The FESEM images of the grown ZnO/glass nanorods and the ZnO/CuO thin films nanocomposites are displayed in Fig. 2. On the surface of the substrates, ZnO nanorods were grown in an orientation that resulted in a vertical alignment. The diameter of ZnO nanorods that have been prepared might range anywhere from 62 nm to 108 nm. On the other hand, as can be seen in Fig. 2B, the surface of the ZnO nanorods was entirely covered by the CuO nanoparticles. The statical distribution of the diameter of ZnO NRs displayed in Fig. 2C and noted a range of 62–175 nm.

3.2. Crystalline structure

The crystalline structure of prepared ZnO/CuO thin films nanocomposites was investigated using the XRD pattern as shown in Fig. 3. The XRD peaks that appeared at 2θ of 31.56, 34.28, 47.5, 56.55, 63.68, and 67.65 corresponding to ZnO lattice planes (100), (002), (102), (110), (103) and (112) respectively, of hexagonal wurtzite structure (JCPDS Card No. 36–1451). However, as illustrated in the SEM image, the high XRD intensity of (002) revealed that the ZnO NRs are alignment vertically onto the substrates. However, the XRD peaks which appeared at 2θ of 35.31, 38.59, 48.37, and 61.52 are corresponding to (002), (111), (202), and (113) of the monoclinic phase of CuO NPs (JCPDS Cards-00–04500937). The crystalline size (CZ) of the CuO nanoparticles was calculated by the Deby-Sherrar formula represented by the relation $CZ = \frac{K\lambda}{\beta\cos\theta}$ [21]. where θ, β, λ, and K are the angle between the incident beam and crystal plane, the FWHM diffraction peak, X-ray wavelength, and the incident Scherer constant, respectively. The CZ was estimated is a

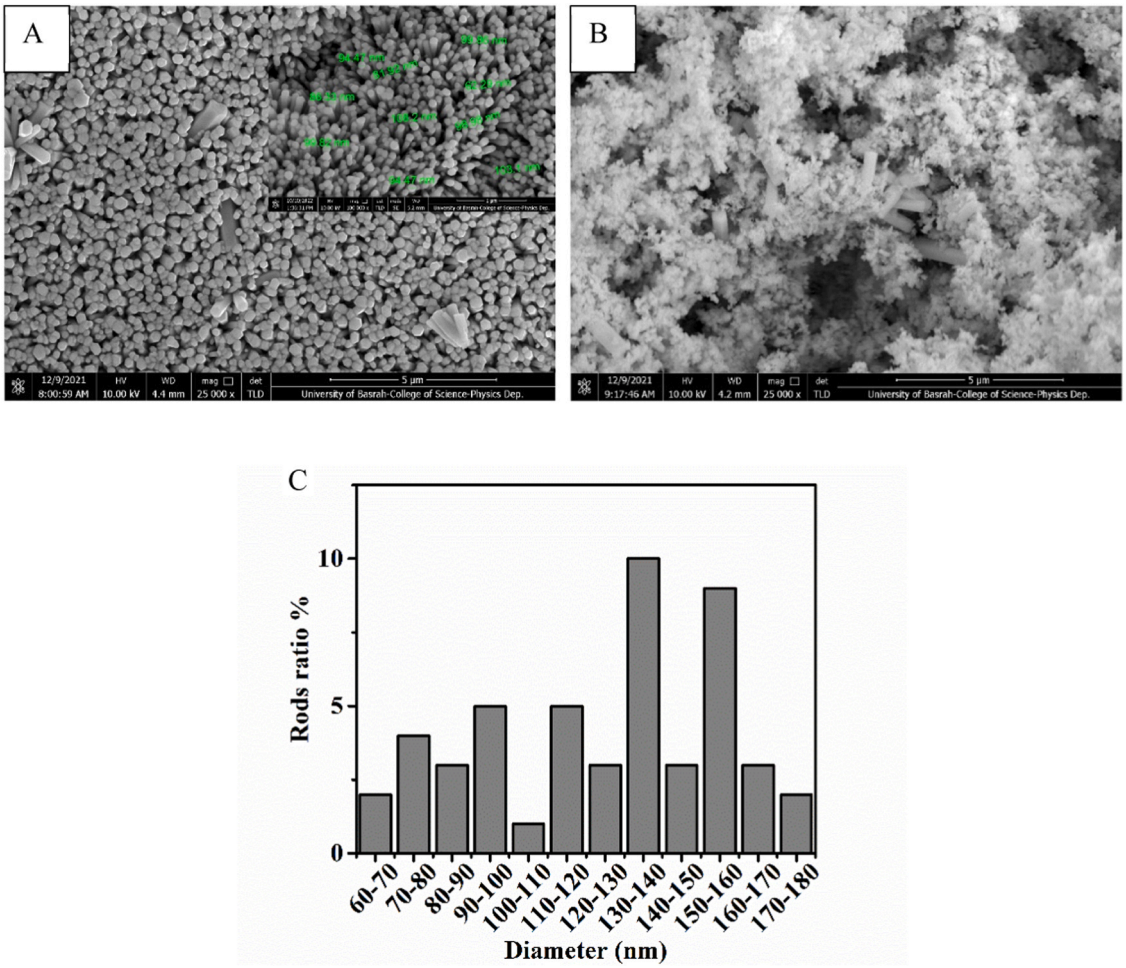

Fig. 2. The FESEM of the grown of (A) ZnO/glass NRs and (B) ZnO/CuO nanocomposites thin films (C) Diameter statical distribution of ZnO/glass NRs.

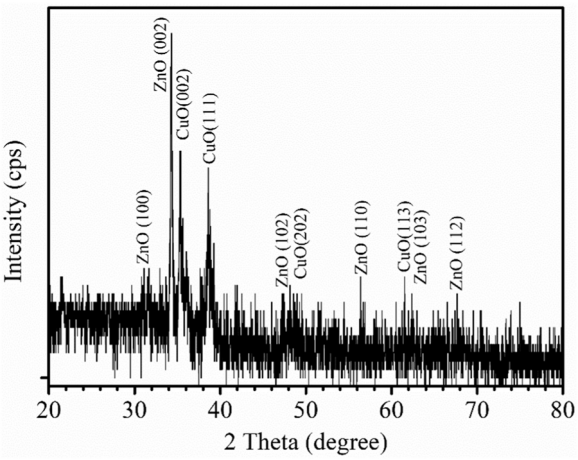

Fig. 3. The XRD pattern of the grown ZnO/CuO nanocomposite thin films on the glass substrates.

value of 44.05 nm of the ZnO/CuO nanocomposites thin films.

3.3. Optical properties

As shown in Fig. 4a, the optical properties of ZnO nanorods and ZnO/CuO nanocomposite thin films thin films were examined using optical absorbance. When compared to ZnO NRs, ZnO/CuO nanocomposites thin films exhibit strong light absorption. Moreover, the band gap calculated according to tauc plot is represented by the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ [22], where α, h, Eg, A, and ν are the coefficient of absorption, Planck's constant, band gap energy, constant, and frequency of vibration, respectively. Fig. 4b depicts the band gap values of ZnO nanorods as 3.26 eV, which is consistent with previous studies [23,24], and ZnO/CuO nanocomposites thin films as 3.21 eV. Meng et al. [25] prepared p-CuO/n-ZnO heterojunction nanofibers and they found that the Eg of ZnO reduced from 3.14 eV to 3.08 eV or less depending on the Cu contents in the samples.

3.4. Photocatalytic activity

Fig. 5 shows the photodegradation rate (PDR) of AFN dye that is catalyzed by ZnO NRs and ZnO/CuO nanocomposites thin films under visible light irradiation. After 330 min of irradiation by visible light, the ZnO NRs showed a modest photodegradation rate (PDR) of AFN dye, reaching roughly 19%, whereas the ZnO/CuO nanocomposites thin films showed 100% of PDR. CuO nanoparticles absorbs visible light and plays a dominant role in the photocatalytic activity, resulting in a significant electron-hole separation. Furthermore, the ZnO/CuO nanocompsites thin films reduces charge carrier recombination generated by photosynthesis [26]. In addition, ZnO surface defects are crucial in photocatalytic activity, since they may inhibit electron-hole recombination and lengthen the lifetime of the charge carrier [27]. Barman et al. [28] reported ZnO/CuO nanocomposites thin films reached a photodegradation rate is 66% in

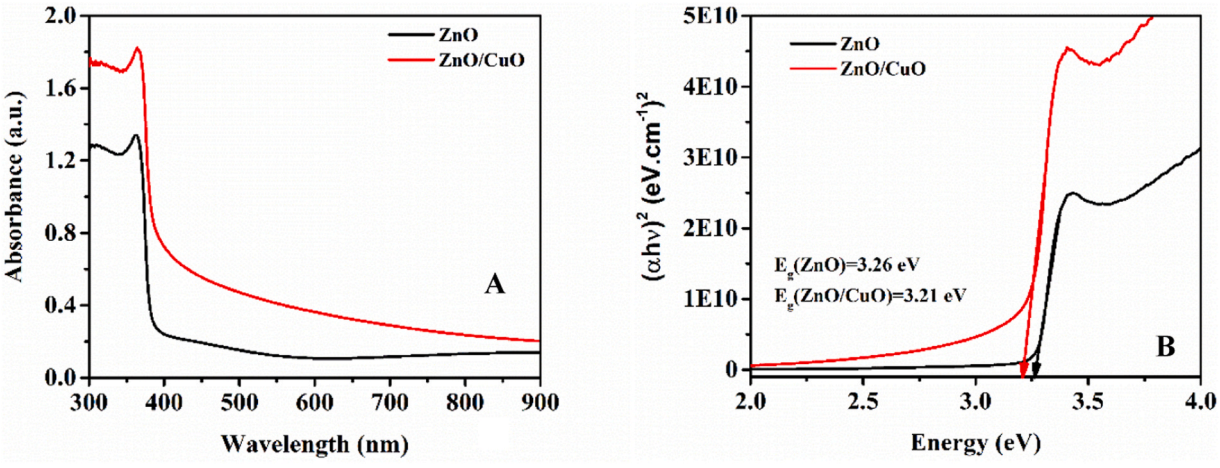

Fig. 4. (A) UV–vis spectra for ZnO and ZnO/CuO nanocomposites thin film (B) the plot of $(\alpha h\upsilon)^2$ vs. photon energy.

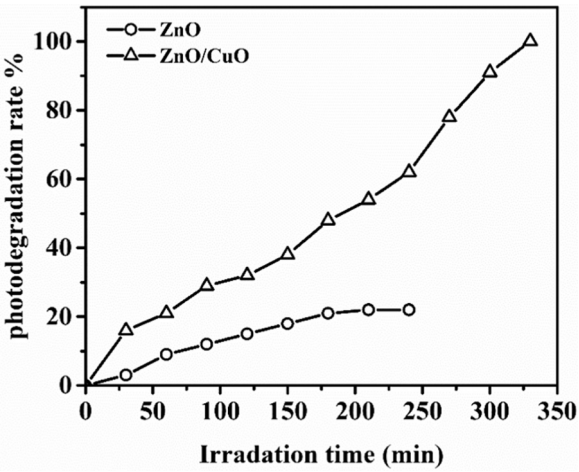

Fig. 5. Photodegradation rate of AFN dye by ZnO and ZnO/CuO nanocomposites thin film.

5 h from R6G aqueous under UV irradiation while Nami et al. [26] discovered that under visible illumination, the PDR of MB dyes catalyzed by ZnO/CuO nanocomposites thin films reached 49% after 300 min. Table 1 compares the current study to previously published works for ZnO/CuO nanostructures thin films used to degrade various dyes. Fig. 6A depicts the C/Co plot vs. irradiation duration of ZnO NRs and ZnO/CuO nanocomposites thin films for AFN dyes, revealing that the C/Co ratio is semi-constant when ZnO NRs are utilized and decreases with time when ZnO/CuO nanocomposites thin films are used to degrade AFN dye. The pseudo-first-order kinetics model of photodegradation is determined by the equation ln(C/Co) = -kt [29], where k represents the apparent rate constant and t represents the time of irradiation (Fig. 6B). The linear relationship yielded rate constant values of 0.0011 and 0.0068 min^{-1} for ZnO and ZnO/CuO nanocomposites thin films, respectively. The obtained rate constant is in agreement with the work that has been previously published [26,30].

3.5. *Effect of pH value*

The pH of dye solution is a significant parameter since it is related to the ionization state of the catalyst's surface, as illustrated in the equations [31]:

$M\text{-}OH + H^{+} \rightarrow M\text{-}OH_2^{+}$.....(12)

$M\text{-}OH + OH^{-} \rightarrow M\text{-}O^{-} + H_2O$.....(13)

Because of the reaction of heterogeneous photocatalytic takes occurs on the surface of semiconductors, the degradation of AFN dye was discovered to be significantly dependent on the pH solution. The pH of the solution is an important component that influences the degradation efficiency of organic pollutants [32]. Fig. 7 shows the effect of pH value on the degradation ratio of AFN dye catalyzed at different times. The photocatalytic activity of ZnO/CuO nanocomposites thin films increased as the pH increases from 4 to 10 but it reduced when the pH was 12. The highest value of the photodegradation was 100% obtained when the pH was 10 while the lowest value was at a pH of 4. However, the photocatalytic degradation of AFN dye can be increased with increasing pH due to several reasons. One of the main reasons is that the pH of the solution can affect the surface charge of both the photocatalyst and the dye molecules, which can influence their interaction and the photocatalytic process [33]. This tendency could be attributed to a stronger electrostatic interaction between cationic dye molecules and ZnO/CuO nanocomposites thin films which is an active species in alkaline conditions. However, in acidic conditions, the surface of the photocatalyst gains a positive charge, and so the electrostatic repulsion between ZnO/CuO nanocomposites thin films and cationic dye molecules does not favor adsorption on the photocatalyst surface leading to a slow photodegradation rate. In addition, the rate of production of hydroxyl radicals is faster in alkaline conditions, which

Table 1
Comparison of the current study with previously reported articles for ZnO/CuO nanocomposites thin films on the glass substrates.

Dye	Source irradiation	Photodegradation rat%	Time (min)	Ref.
RB	mercury lamp	98	400	[36]
MO	400 W	98	280	
RB	Xe lamp (300 W)	63.8	120	[37]
MB	tungsten	76	150	[38]
MB	UV	92	420	[39]
AFN	Visible light	100	330	Present work

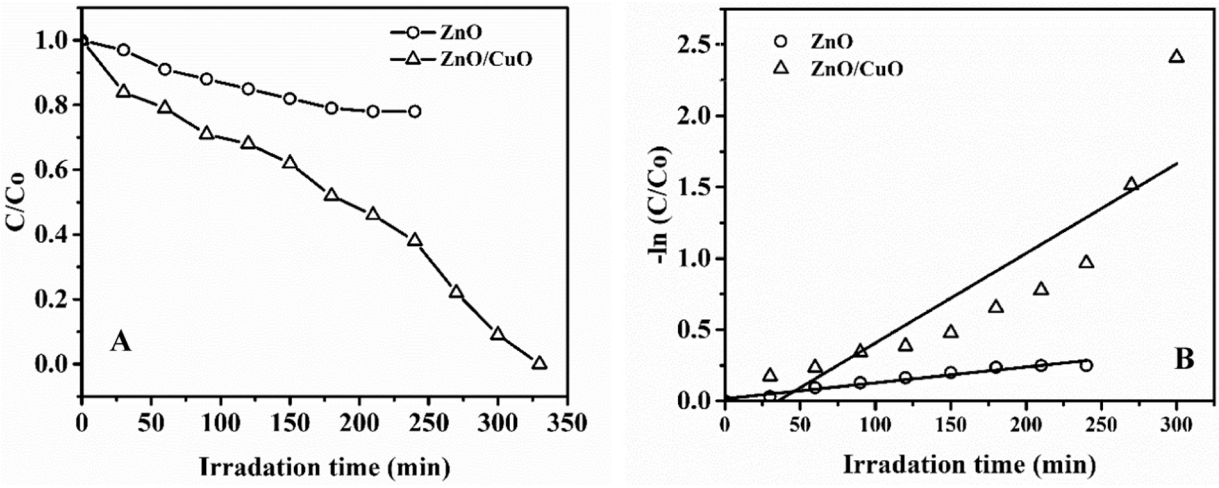

Fig. 6. (A) Kinetics of photocatalytic degradation and (B) variation of −ln (C/Co) with irradiation time of ZnO and ZnO/CuO nanocopmpositesthin films on the glass substrates.

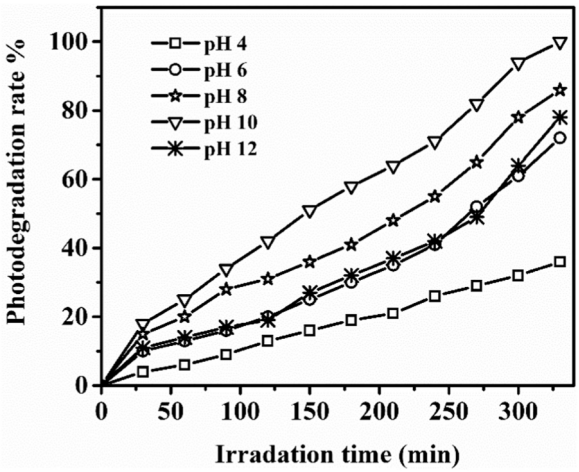

Fig. 7. Photodegradation rate of AFN dye under effect variance pH of ZnO/CuO nanocomposite thin films on the glass substrates.

favors photodegradation. U.R Bagwan et al. found that the rate constant of degradation AFN dye by Gd-doped TiO_2 nanostructures increased from 0.0074 to 0.0144 s^{-1} when the pH value increased from 4 to 10 [16]. Increasing the pH to 12 resulted in a high concentration of $^{\bullet}OH$ radicals. Under these conditions, radical-radical reactions occur, resulting in the deactivation of hydroxyl radicals and the formation of radicals $HO_2^{\cdot}$ and H_2O_2. The reactivity of these radicals with organic pollutants is extremely low at high concentrations of $^{-}OH-$ of high due to $^{-}OH-$ with $^{\bullet}OH$ interactions [34]. In other words, the repulsive columbic adsorption of ion hydroxide to the surface catalyst was avoided [35].

As shown in Fig. 8, it was found that the prepared ZnO/CuO nanocomposites thin films provided high stability were the degradation rate reached 94% after being reused six times for an irradiation time of 330 min and pH of 10. This confirmed the possibility of reusing the prepared samples multiple times without losing any material.

3.6. Role of active species

Scavengers such as EDTA, benzoquinone, and isopropanol alcohol were utilized during the photoreaction to investigate the involvement of active species such holes (h^+), superoxide radicals ($^{\cdot}O^{2-}$), and hydroxyl radicals ($^{\cdot}OH$) in the degradation reaction [40–42]. Photocatalytic activity decreased from 100% to 33%, 57%, and 69% when different scavengers (EDTA, BQ, and IPA) were added, as depicted in Figs. 9 and 10. The study concluded that holes are the predominant species responsible for the photocatalytic activity of the synthesized materials. Superoxide radicals are more effective than hydroxyl radicals in the photocatalytic destruction of dye compounds.

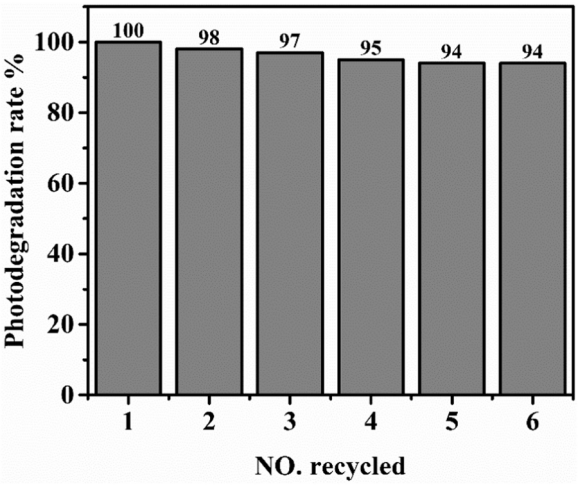

Fig. 8. The Reusability test of AFN dye degradation by ZnO and ZnO/CuO nanocomposites thin film.

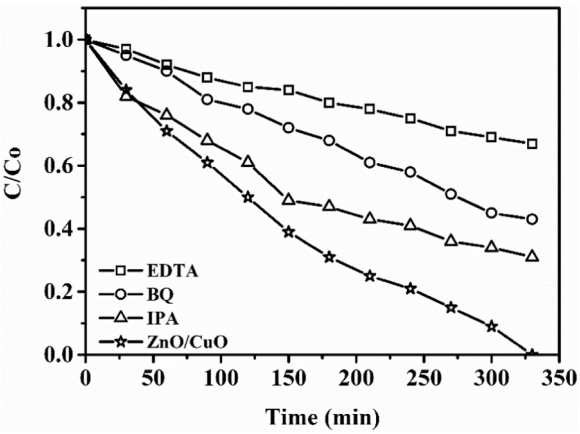

Fig. 9. Effect of different scavenger on C/C_O photodegradation of AFN dye by by ZnO and ZnO/CuO nanocomposites thin film.

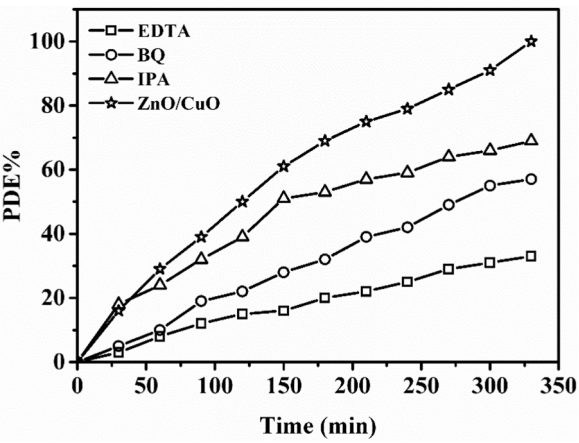

Fig. 10. Effect of different scavenger on photodegradation efficiency of AFN dye by ZnO and ZnO/CuO nanocomposites thin film.

4. Conclusions

In this work, ZnO NRs and ZnO/CuO nanocomposites were prepared onto glass substrates by CBD methods. The photocatalysis process against AFN dye was investigated under visible light irradiation at different times. The results show that the degradation rate of dye increased when used ZnO/CuO nanocomposites as catalysts compared to ZnO NRs. Although electrons find it difficult to move from the p-CuO conduction band to the n-ZnO conduction band because the edge of the CuO band is less than the edge of the ZnO band, the success of the junction between the two compounds causes a rise in the CuO compound's energy gap and its fall to the ZnO compound, which facilitates electron transitions between them. CuO absorbs visible light, and has a dominating role in photocatalytic activity, resulting in the greatest electron-hole separation. Furthermore, the degradation rate rose with a pH value from 4 to 10, and the basic medium yielded the best photocatalytic activity when compared to acidic media. After 330 min of irradiation and a pH of 10, the highest degradation rate was 100%. However, when the pH is 12, the breakdown rate slows due to the high concentration of •OH radicals. Radical-radical reactions occur under these conditions, leading to the deactivation of hydroxyl radicals, which prevents the repulsive columbic adsorption of ion hydroxide to the surface catalyst. Through using different types of scavenges, the study concluded that holes are the predominant species responsible for the photocatalytic activity of the synthesized materials. Superoxide radicals are more effective than hydroxyl radicals in the photocatalytic destruction of dye compounds.

CRediT authorship contribution statement

Adel H.Omran Alkhayatt: Writing – review & editing. **Marwah J. Kadhim:** Investigation, Methodology, Writing – original draft, Writing – review & editing. **Mazin A MAhdi:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **Fatima Allawi:** Data curation, Formal analysis, Investigation, Methodology, Writing – original draft.

Declaration of Competing Interest

We declare that the Submitted Research Paper is our original work and no part of it has been published anywhere else in the past. We take full responsibility, that if in future, the paper is found invalid according to basic rules, the last decision will be of the Authorities concerned. Any form of plagiarism will lead to disqualification of the paper.

Data Availability

No data was used for the research described in the article.

References

[1] M.J. Kadhim, F. Allawi, M.A. Mahdi, S.N. Abaas, High photocatalytic performance of ZnO/Fe3O4 and TiO2/Fe3O4 nanostructures nanostructures thin films against methylene blue dye under visible light irradiation, Iran. J. Mater. Sci. Eng. vol. 19 (2022) 1–15, https://doi.org/10.22068/ijmse.2461.
[2] M.J. Kadhim, M.A. Mahdi, J.J. Hassan, Influence of pH on the photocatalytic activity of ZnO nanorods, Mater. Int. vol. 2 (2) (May 2020) 0064–0072, https://doi.org/10.1007/s10854-016-4284-0.
[3] M. Karimi Shamsabadi, M. Behpour, Fabricated CuO–ZnO/nanozeolite X heterostructure with enhanced photocatalytic performance: mechanism investigation and degradation pathway, Mater. Sci. Eng. B Solid State Mater. Adv. Technol. vol. 269 (Jul. 2021), https://doi.org/10.1016/j.mseb.2021.115170.
[4] S. Raha, D. Mohanta, M. Ahmaruzzaman, Novel CuO/Mn3O4/ZnO nanocomposite with superior photocatalytic activity for removal of Rabeprazole from water, Sci. Rep. vol. 11 (1) (Dec. 2021), https://doi.org/10.1038/s41598-021-94066-y.
[5] M.J. Kadhim, M. Mahdi, J.J.J. Hassan, A.S. Al-Asadi, Photocatalytic activity and photoelectrochemical properties of Ag/ZnO core/shell nanorods under low-intensity white light irradiation, Nanotechnology vol. 32 (2021).
[6] J.E. Morales-Mendoza, F. Paraguay-Delgado, Widening UV–Vis absorption band by Cu doped ZnO and ZnO/CuO composite, Mater. Lett. vol. 291 (May 2021), https://doi.org/10.1016/j.matlet.2021.129494.
[7] T. Munawar, et al., Synthesis of novel heterostructured ZnO-CdO-CuO nanocomposite: Characterization and enhanced sunlight driven photocatalytic activity, Mater. Chem. Phys. vol. 249 (Jul. 2020), https://doi.org/10.1016/j.matchemphys.2020.122983.
[8] A.N. Kadam, T.G. Kim, D.S. Shin, K.M. Garadkar, J. Park, Morphological evolution of Cu doped ZnO for enhancement of photocatalytic activity, J. Alloy. Compd. vol. 710 (2017) 102–113, https://doi.org/10.1016/j.jallcom.2017.03.150.
[9] B. Peychev, P. Vasileva, Novel starch-mediated synthesis of Au/ZnO nanocrystals and their photocatalytic properties, Heliyon vol. 7 (6) (Jun. 2021), https://doi.org/10.1016/j.heliyon.2021.e07402.
[10] C.-Y. Lin, Y.-H. Lai, A. Balamurugan, R. Vittal, C.-W. Lin, K.-C. Ho, Electrode modified with a composite film of ZnO nanorods and Ag nanoparticles as a sensor for hydrogen peroxide, Talanta vol. 82 (1) (2010) 340–347, https://doi.org/10.1016/j.talanta.2010.04.047.
[11] P.T. Lum, K.Y. Foo, N.A. Zakaria, P. Palaniandy, Ash based nanocomposites for photocatalytic degradation of textile dye pollutants: A review, Mater. Chem. Phys. vol. 241 (Feb. 2020), https://doi.org/10.1016/j.matchemphys.2019.122405.
[12] A. Fouda, S.S. Salem, A.R. Wassel, M.F. Hamza, T.I. Shaheen, Optimization of green biosynthesized visible light active CuO/ZnO nano-photocatalysts for the degradation of organic methylene blue dye, Heliyon vol. 6 (9) (Sep. 2020), https://doi.org/10.1016/j.heliyon.2020.e04896.
[13] S. Harish, et al., Controlled structural and compositional characteristic of visible light active ZnO/CuO photocatalyst for the degradation of organic pollutant, Appl. Surf. Sci. vol. 418 (Oct. 2017) 103–112, https://doi.org/10.1016/j.apsusc.2016.12.082.
[14] P. Nandi, D. Das, ZnO-CuxO heterostructure photocatalyst for efficient dye degradation, J. Phys. Chem. Solids vol. 143 (Aug. 2020), https://doi.org/10.1016/j.jpcs.2020.109463.
[15] K. Sahu, A. Bisht, S. Kuriakose, S. Mohapatra, Two-dimensional CuO-ZnO nanohybrids with enhanced photocatalytic performance for removal of pollutants, J. Phys. Chem. Solids vol. 137 (Feb. 2020), https://doi.org/10.1016/j.jpcs.2019.109223.
[16] U.R. Bagwan, I.N. Shaikh, R.S. Malladi, A.L. Harihar, S.M. Hunagund, Effect of titanium dioxide and gadolinium dopants on photocatalytic behavior for acriflavine dye, J. Rare Earths vol. 38 (3) (Mar. 2020) 234–240, https://doi.org/10.1016/j.jre.2019.09.006.
[17] P. Nayak, S. Kumar, I. Sinha, K.K. Singh, ZnO/CuO nanocomposites from recycled printed circuit board: preparation and photocatalytic properties, Environ. Sci. Pollut. Res. vol. 26 (16) (Jun. 2019) 16279–16288, https://doi.org/10.1007/s11356-019-04986-6.

[18] Y. Bu, Z. Chen, W. Li, A ZnFe2O4-ZnO nanorod array p-n junction composite and its photoelectrochemical performance, Dalton Trans. vol. 42 (46) (Dec. 2013) 16272–16275, https://doi.org/10.1039/c3dt52000e.
[19] H. Chen, W. Liu, Z. Qin, ZnO/ZnFe2O4 nanocomposite as a broad-spectrum photo-Fenton-like photocatalyst with near-infrared activity, Catal. Sci. Technol. vol. 7 (11) (2017) 2236–2244, https://doi.org/10.1039/c7cy00308k.
[20] W. Wang, et al., P-n junction CuO/BiVO4 heterogeneous nanostructures: Synthesis and highly efficient visible-light photocatalytic performance, Dalton Trans. vol. 43 (18) (May 2014) 6735–6743, https://doi.org/10.1039/c3dt53613k.
[21] A.M. Selman, M.J. Kadhim, Fabrication of high sensitivity and fast response IR photodetector based on VO2 nanocrystalline thin films prepared on the silicon substrate, Opt. Mater. (Amst.) vol. 131 (Sep. 2022), https://doi.org/10.1016/j.optmat.2022.112664.
[22] A. Zare, A. Saadati, S. Sheibani, Modification of a Z-scheme ZnO-CuO nanocomposite by Ag loading as a highly efficient visible light photocatalyst, Mater. Res Bull. (Feb. 2023), https://doi.org/10.1016/j.materresbull.2022.112048.
[23] S. Akir, A. Barras, Y. Coffinier, M. Bououdina, R. Boukherroub, A.D. Omrani, Eco-friendly synthesis of ZnO nanoparticles with different morphologies and their visible light photocatalytic performance for the degradation of Rhodamine B, Ceram. Int vol. 42 (8) (Jun. 2016) 10259–10265, https://doi.org/10.1016/j.ceramint.2016.03.153.
[24] P. Bindu, S. Thomasa, Optical properties of ZnO nanoparticles synthesised from a polysaccharide and ZnCl2, Acta Phys. Pol. A vol. 131 (6) (Jun. 2017) 1474–1478, https://doi.org/10.12693/APhysPolA.131.1474.
[25] Q. Meng, W. Liu, J. Jiang, X. Zhang, Fabrication of novel p-CuO/n-ZnO heterojunction nanofibers by electrospinning for enhanced photocatalytic performance in the denitrification of fuel oil, Ceram. Int vol. 47 (14) (Jul. 2021) 19402–19413, https://doi.org/10.1016/j.ceramint.2021.03.277.
[26] M. Nami, S. Sheibani, F. Rashchi, Photocatalytic performance of coupled semiconductor ZnO–CuO nanocomposite coating prepared by a facile brass anodization process, Mater. Sci. Semicond. Process vol. 135 (Nov. 2021), https://doi.org/10.1016/j.mssp.2021.106083.
[27] E. Erdem, Microwave power, temperature, atmospheric and light dependence of intrinsic defects in ZnO nanoparticles: A study of electron paramagnetic resonance (EPR) spectroscopy, J. Alloy. Compd. vol. 605 (Aug. 2014) 34–44, https://doi.org/10.1016/j.jallcom.2014.03.157.
[28] D. Barman, J. Borah, S. Deb, B.K. Sarma, Design strategy for CuO-ZnO S-scheme heterojunction photocatalysts in the presence of plasmonic Ag and insights into photoexcited carrier generation and interfacial transfer in diverse structural configurations of the heterostructure system, Colloids Surf. A Physicochem Eng. Asp. vol. 663 (Apr. 2023), https://doi.org/10.1016/j.colsurfa.2023.131077.
[29] F. Ansari, S. Sheibani, M. Fernández-García, Characterization and performance of Cu2O nanostructures on Cu wire photocatalyst synthesized in-situ by chemical and thermal oxidation, J. Mater. Sci.: Mater. Electron. vol. 30 (14) (Jul. 2019) 13675–13689, https://doi.org/10.1007/s10854-019-01745-8.
[30] K. Mageshwari, D. Nataraj, T. Pal, R. Sathyamoorthy, J. Park, Improved photocatalytic activity of ZnO coupled CuO nanocomposites synthesized by reflux condensation method, J. Alloy. Compd. vol. 625 (Mar. 2015) 362–370, https://doi.org/10.1016/j.jallcom.2014.11.109.
[31] Y. Liu, Y. Kang, B. Mu, A. Wang, Attapulgite/bentonite interactions for methylene blue adsorption characteristics from aqueous solution, Chem. Eng. J. vol. 237 (Feb. 2014) 403–410, https://doi.org/10.1016/j.cej.2013.10.048.
[32] M.J. Kadhim *et al.*, The most important parameters that affect the photocatalytic activity of ZnO nanostructures against organic dyes: A Review, *Iranian Journal of Catalysis*, vol. 13, no. 1, pp. 1–21, doi: 10.30495/ijc.2023.1969439.1966.
[33] Z. Kalaycıoğlu, B. Özuğur Uysal, Ö. Pekcan, F.B. Erim, Efficient Photocatalytic Degradation of Methylene Blue Dye from Aqueous Solution with Cerium Oxide Nanoparticles and Graphene Oxide-Doped Polyacrylamide, ACS Omega (Apr. 2023), https://doi.org/10.1021/acsomega.3c00198.
[34] A. Nezamzadeh-Ejhieh, M. Karimi-Shamsabadi, Decolorization of a binary azo dyes mixture using CuO incorporated nanozeolite-X as a heterogeneous catalyst and solar irradiation, Chem. Eng. J. vol. 228 (Jul. 2013) 631–641, https://doi.org/10.1016/j.cej.2013.05.035.
[35] E. Abbasi, M. Haghighi, R. Shokrani, M. Shabani, Copper plasmon-induced Cu-doped ZnO-CuO double-nanoheterojunction: In-situ combustion synthesis and photo-decontamination of textile effluents, Mater. Res Bull. vol. 129 (Sep. 2020), https://doi.org/10.1016/j.materresbull.2020.110880.
[36] S. Pal, S. Maiti, U. Narayan Maiti, and K.K. Chattopadhyay, "Low temperature solution processed ZnO/CuO heterojunction photocatalyst for visible light induced photo-degradation of organic pollutants."
[37] F. Cao, T. Wang, X. Ji, Enhanced visible photocatalytic activity of tree-like ZnO/CuO nanostructure on Cu foam, Appl. Surf. Sci. vol. 471 (Mar. 2019) 417–424, https://doi.org/10.1016/j.apsusc.2018.12.034.
[38] N. Jalali, M. Nami, F. Rashchi, A. Rakhsha, Photocatalytic properties of ZnO/CuO nanocomposite prepared in acidic media, J. Ultra Graine Nanostruct. Mater. vol. 55 (1) (Jun. 2022) 21–30, https://doi.org/10.22059/jufgnsm.2022.01.04.
[39] H. Xu, W. Fang, L. Xu, F. Liu, Batch preparation of CuO/ZnO-loaded nanofiber membranes for photocatalytic degradation of organic dyes, Langmuir vol. 36 (47) (Dec. 2020) 14189–14202, https://doi.org/10.1021/acs.langmuir.0c02083.
[40] N. Verma, S. Yadav, B. Marí, A. Mittal, J. Jindal, Synthesis and charcterization of coupled ZnO/SnO2 photocatalysts and their activity towards degradation of cibacron red dye, Trans. Indian Ceram. Soc. vol. 77 (1) (Jan. 2018) 1–7, https://doi.org/10.1080/0371750X.2017.1417059.
[41] V. Kumari, N. Kumar, S. Yadav, A. Mittal, S. Sharma, Novel mixed metal oxide (ZnO.La2O3.CeO2) synthesized via hydrothermal and solution combustion process - A comparative study and their photocatalytic properties (Elsevier Ltd), *Mater. Today: Proc.* (2019) 650–657, https://doi.org/10.1016/j.matpr.2019.07.748.
[42] A. Mittal, et al., Surfactant-assisted hydrothermally synthesized novel TiO2/SnS@Pd nano-composite: structural, morphological and photocatalytic activity, J. Mater. Sci.: Mater. Electron. vol. 31 (3) (Feb. 2020) 2010–2021, https://doi.org/10.1007/s10854-019-02720-z.