Enhanced Structural, Optical, And Photocatalytic Activities Of CuO/TiO₂:ZrO₂ Catalysts For Degrading Methyl Orange (MO) Dye Under UV–Visible Irradiation.

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Enhanced structural, optical, and photocatalytic activities of CuO/TiO₂:ZrO₂ catalysts for degrading Methyl Orange (MO) dye under UV–Visible irradiation.

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Abstract.

On latest years, an emergency requirement for clean methods to improvement of environment worth has attracted attention in several researches' fields. The use of films on photocatalysis process is one of the most interesting alternatives due to its easily on separation of residual water and recovery of photocatalyst. In this study, CuO/TiO₂:ZrO₂ catalysts with various molar ratios of CuO were synthesized by sol-gel dip-coating process. The dip-coated thin films have been examined at different annealing temperatures 500, 800 and 1000 °C. The crystalline structures, morphology, constituent contents, optical and photocatalytic properties of the as-prepared catalysts were analyzed by X-ray diffraction (XRD), Raman spectroscopy, FT-IR spectra, UV-VIS, Photoluminescence spectroscopy (PL) techniques. X-ray diffraction (XRD) and Raman results indicated that an increase in annealing temperature from 500°C to 1000°C caused a transformation of crystallinity from anatase and brookite at 500°C to rutile and monoclinic CuO phases at 1000°C, accompanied by an increase in the particle sizes. The optical transmittance of the films, increased to over 90% in the visible region, indicate that copper loading decreases the band gap from 3.53 to 3.39eV. The PL experiments revealed that the recombination of photoinduced electrons and holes is hindered by copper adding effectively, which is favorable for photocatalytic performance. 5%CuO/TiO₂:ZrO₂ exhibits the highest photocatalytic activity and the degradation degree of methyl orange (MO) reaches more than 99% after 3h. Photocatalytic experiments confirmed that our catalysts displayed highly efficient and durable activity for the photodegradation of methyl orange under visible light.

Keywords: TiO₂:ZrO₂, CuO, Methyl orange, Photocatalytic activity, (e⁻/h⁺) recombination, Photodegradation.

1. Introduction:

With the advancement of industry and technology, air and water pollutions have become a major environmental problem issue and plagues the development of society [1], because large quantities of unwanted contaminants are being discharged into the environment from different industrial sources such as textile, dyeing, food, pharmaceuticals, plastics, leather, paper, sugar, petroleum, and metal works [2-3]. The more dangerous are the wastes from organic dyes, because they are poisonous and highly soluble in water and they produce various hazardous compounds upon treatment. Methyl orange (MO) is the most harmful dye among the other dyes and hence can be utilized in paper, textiles, food items, leather industry, etc. The hypersensitivity and allergy caused by MO is due to the presence of nitrogen in its structure and the water polluted with MO when comes in contact to an eye of a person can cause serious damage to the cornea in eye. Anemia, dizziness, mental confusion, huge sweating, and headache are the symptoms when a minor concentration of MO is present in the polluted water. Hence, the water must be purified from MO pollutants in order to prevent the harmful effects of its consumption [4].

Therefore, it is highly urgent to explore effective methods for the degradation of this organic dye wastewater. At present, the techniques like membrane separation, ozone oxidation, chemical oxidation, photocatalytic degradation, physical adsorption, ion exchange, flotation, electrochemical treatment, coagulation, biochemistry [5-9], have been successfully employed to treat the wastewater caused by dyes.

The photocatalytic degradation has been introduced as green and low-cost approaches for the effective elimination of dyes from wastewaters under mild conditions. This method has gained most attraction among all the techniques due to its easy operation, low energy consumption, low cost, low secondary pollution, and high efficiency and the organic dyes can be degraded successfully into safer products such as CO_2 , H_2O and inorganic acids under light conditions by using photocatalysts. The mechanism is based on the light activation of electron–hole pair formation in the semiconducting media [10]. The evolution of these photogenerated charge carriers to the contact surfaces induces the formation of radical species such as OH^- anions and superoxide's O_2^- . These active species interact with the organic products leading to progressive degradation of organic pollutants and subsequently their mineralization for achieved processes [11].

A wide range of semiconductors, such as TiO_2 , ZnO , SnO_2 , CuO , and ZrO_2 , are fully investigated as photocatalyst for the degradation of organic pollutants. Titanium dioxide (TiO_2) is one of the most widely studied semiconductors for photocatalytic applications due to its advantages, such as a suitable band gap for redox reactions, low cost, high chemical stability, high efficiency, availability and nontoxicity.

However, TiO_2 can absorb light within ultraviolet (UV) region only which is less than 5% of sunlight, so it is quite impractical to use TiO_2 under solar radiation. Besides, the high recombination rate of photoinduced charge carriers is another problem [12,13].

In order to solve these problems, several methods have been studied such as i) modifying the surface area, crystallinity, and porosity of TiO_2 particles, ii) doping and co-doping the surface with metals (Al, Se, Er, Ba, Cd, and Co) [14-19] and nonmetals (N, S, and C) [20-22], and iii) combining *p*-type materials with TiO_2 particles to be a *p-n* heterojunction semiconductor [23]. Among them, coupling TiO_2 with another semiconductor with a small bandgap such as CuO , PbS and CdS , is a promising strategy for increasing the activity in the visible-light region or allowing photogenerated electrons to be transferred from the conduction band to other semiconductors to inhibit recombination of the electron-hole pair.

The binary support was found to present the improved catalytic properties, ZrO_2 -doped TiO_2 support might be a better alternative to replace TiO_2 . The zirconia support was reported to supply the superior dispersion of active sites and better oxidation abilities than pure TiO_2 [24]. The strong thermostability, redox properties and surface acidity on the TiO_2 - ZrO_2 binary oxides were displayed [25]. Therefore, the ZrO_2 -doped TiO_2 should be an essential support to replace the pure TiO_2 for many catalytic reactions. In addition, a small amount of ZrO_2 doping may cause obvious change on the characteristic of the materials [26].

Copper oxide (CuO), a *p*-type semiconductor, is considered as a supporting material mixed with *n*-type photocatalysts such as TiO_2 [27,28]. Thus, metal oxides (*p*-type semiconductors) supported on titanium dioxide (*n*-type semiconductor) improve the absorption of visible light by titanium dioxide. Incorporation of CuO into TiO_2 enhances the photocatalytic activity of TiO_2 due to the formation of an inner electric field which could promote charge separation and minimize/inhibit charge carrier recombination [29]. The presence of CuO with low band gap (1.7 eV) on TiO_2 surface not only leads to visible light absorption but also increases the surface acidity for the absorption of more hydroxyl ion and organic reactants [30].

The aim of this work was to study the effect of CuO loading on the structural, optical, photoluminescence and photocatalytic properties of TiO₂:ZrO₂ thin films prepared by sol–gel method and annealed at 500, 800 and 1000°C. The catalysts were characterized by X–ray diffraction (XRD), Raman spectroscopy, FT-IR spectra, UV-VIS, Photoluminescence spectroscopy (PL) techniques. Moreover, the catalytic activity of the materials in the decomposition of Methyl Orange (MO) in water under UV light was investigated in detail to get information on the surface properties of the catalysts.

2. Experimental:

2.1. Synthesis of catalysts:

TiO₂:ZrO₂ and CuO co-doped TiO₂:ZrO₂ thin films were elaborated by sol-gel method using tetrabutyl-orthotitanate ((C₄H₉O)₄Ti), zirconium oxychloride salt (ZrOCl₂·8H₂O) and copper acetate (Cu(CH₃O₂)₂(H₂O)₂) as precursors. TiO₂:ZrO₂ solution were synthesized in a similar procedure to that disclosed in a recent patent [26]. First, TiO₂ sol was synthesized after the dissolution of 1 mol of butanol (C₄H₉OH) as solvent, 4 mol of acetic acid (C₂H₄O₂), 1 mol of distilled water and 1 mol of tetrabutyl-orthotitanate (C₄H₉O)₄Ti. The solution of ZrO₂ was prepared from the dissolution of 1 mol of zirconium oxychloride salt (ZrOCl₂·8H₂O) in distilled water and 2 mol of ethanol (95%) as catalyst. The mixture was stirred at room temperature for 2 h. Thus, 5 wt% of obtained ZrO₂ sol was added as doped into 95 wt% of TiO₂ solution. Then an appropriate amount of copper acetates was dissolved in 15 ml of absolute methanol and 5 ml of distilled water. finally, the obtained TiO₂:ZrO₂ sol was co-doped with 3 and 5 wt% of obtained CuO solution. Before dip-coated our thin films, solutions were aged for 24 h.

The sol-gel route was operated to achieve the deposition of CuO co-doped TiO₂:ZrO₂ thin films on single crystal silicon (001) substrates and glass substrates with refractive index equal to 1.52 and thickness of 2 mm. substrates were immersed and withdrawn at a constant rate of 6.25 cm.s⁻¹. In order to augment films thickness, the produced samples were composed of eight (8) layers. Each layer was dried at 100 °C for 15min and the final product (thin films) was annealed at 500, 800 and 1000 °C for 2 h.

The resulting CuO/TiO₂:ZrO₂ samples are hereafter labeled as xCu-TZ, where x represents the nominal copper concentration in weight % (x =3 and 5). The copper-free TiO₂:ZrO₂ material prepared with the same method is hereafter labeled as ZT.

2.2. Characterization:

Several instrumental techniques were employed to investigate structural and optical properties of our samples. The crystalline structure and phase stability of obtained xCu-TZ thin layers were characterized using X-ray diffraction (XRD). Brunkers Axs Advanced diffractometer with Cu(K α) wavelength radiation ($\lambda = 1.54056 \text{ \AA}$) was used. The patterns were scanned at room temperature, over the angular range $10\text{--}80^\circ 2\theta$, with a step length of $0.1^\circ 2\theta$. SENTERRA R200L and OPUS as software is used to perform the Raman spectra experiments in the vibrational region of $100\text{--}800 \text{ cm}^{-1}$. In the vibrational range of $400\text{--}4000 \text{ cm}^{-1}$, the functional groups present in the films were defined by the Infrared Spectrometer JASCO FT/IR 6300. UV–Vis spectrophotometer JASCO V-670 prepared with an integrating sphere UV–Vis–NIR ILN-725 is applied at room temperature to acquire the transmittance spectra in the visible light range. The PL spectra were obtained at 313 nm excitation (Hg lamp) and the signal was recorded using a TRIAX 190 Jobin-Yvon spectrometer.

2.3. Catalytic activity tests:

The ultraviolet light was emitted by an ultraviolet lamp with a power of 15 W and a voltage of 215 V. The evaluation of photocatalytic activity of TZ and xCu-TZ thin films was performed by photodegradation of methyl orange (MO) (10^{-5} M) at room temperature. The suspension was stirred in a darkroom for 30 min to achieve an adsorption equilibrium and desorption between MO and photocatalyst. Then the photocatalytic degradation of MO solution was carried out under the irradiation of a UV lamp with emission light of 365 nm ($\sim 3.39 \text{ eV}$). During the illumination period, 3 mL of suspension was taken every 30 min, and the absorbance of the solution was measured by a UV–vis spectrophotometer by observing the peak absorption at about 461 nm for 180 min (3h).

3. Results and discussion

3.1. Structural properties

3.1.1. XRD analysis:

Fig. 1. Shows diffraction patterns of TZ and xCu-TZ ($x = 3$ and $5 \text{ wt.}\%$) samples coated on glass substrates and annealed at 500°C . These patterns show a mixture of anatase (101) phase with tetragonal structure (JCPDS card N $^\circ$ 12-2172) and brookite phases (121) with orthorhombic structure (JCPDS card N $^\circ$ 16-617) in agreement with XRD results described by D. Guerrero-Araque et al. [31]. Whereas Morales-Anzures et al. [32], Reddy et al. [33] and Pérez-Hernández et al. [34], found that mixed xCu-TZ oxides prepared by the sol–gel method do not crystallize at temperatures below 600°C . The XRD patterns of xCu-ZT composites show no crystalline CuO diffraction peaks most likely due to the low contents of copper used in this

work (equal to or less than 5 wt%) [31]. The copper oxides species are highly dispersed on the surface of the TZ support and a successful substitution of Ti^{4+} ion by Cu^{2+} . In this present study, the oxidation stat of Cu is +2 and Ti is in +4 oxidation state. In turn, the radio of Cu^{2+} (0.73Å) is similar to that of Ti^{4+} (0.68 Å), hence Cu ions may be incorporated into the TZ lattice and occupied some of the titanium lattices [35]. Peak intensities corresponding to characteristic planes of anatase (101) obviously increased with the increase of copper content. This latter is interpreted as due not only to increase in proportion of titanium oxide but also to the improvement of the crystalline quality.

The XRD patterns of TZ and xCu-TZ (x = 3 and 5 wt.%) thin layers coated on Si substrates and annealed, respectively, at 800 and 1000 °C are presented in Fig. 2. A mixture of anatase and rutile (JCPDS card N° 21–1276) phases was observed from doped TZ pattern annealed at 800 °C. In case of copper loadings, the XRD patterns display new peaks reflection appeared at $2\theta = 23.48, 32.24$ and 50.98 corresponding to the monoclinic CuO (JCPDS card N° 41-0254) crystal [36–37], with a decrease of the relative intensities of the anatase peaks. The main diffraction peaks that are observed in all XRD patterns when the annealing temperature raised to 1000 °C are linked to the presence of TiO_2 rutile and CuO phases. For TZ, the absence of diffraction peaks corresponding to TiO_2 anatase stated a complete transformation to rutile structure. In case of copper addition, the XRD patterns demonstrate a combination of CuO and rutile phases, which their main diffraction peaks shifted toward lower angles with an increase in their intensities.

The structural parameters, which are listed in Table 1, are calculated from the following equations. The crystallite size has been calculated using Scherrer's relation [38]:

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

The strain (ϵ) and the dislocation density (δ) were calculated using the following formulas:

$$\epsilon = \frac{\beta \cdot \cos \theta}{4} \quad (2)$$

$$\delta = \frac{1}{L^2} \quad (3)$$

Where L is the crystallite size, k is a constant (k = 0.94), λ is the wavelength of the X-ray radiation, β is the full width at half maximum of (hkl) diffraction peak and θ is the angle of diffraction.

The incorporation of copper on TZ lattice, lead to increase in particle size and decrease the dislocation density (δ) and the strain (ϵ), This decrement reveals the reduction of lattice imperfections and thus the augmentation of both films' crystallinity and grain size.

Table 1 Grain size (L), FWHM, micro strain (ϵ) and the dislocation density (δ) undoped TZ, 3Cu-TZ and 5Cu-TZ thin films coated on Si substrates and annealed, respectively, at 800 and 1000 °C.

Annealing temperature T (°)	xCu-TZ	DRX					Raman	
		Phase	FWMH	L (nm)	$\delta \times 10^{-4}$ (line/nm ²)	$\epsilon \times 10^{-2}$	Raman shift (cm ⁻¹)	L (nm)
800 °C	TZ	Anatase	0.24	35,45	7,96	5,88	139.5	36.05
		Rutile	0.37	23,10	18,74	2,49	437.5	23.72
	3Cu-TZ	Anatase	0.35	24,31	16,92	8,50	138.2	25.04
		Rutile	0.29	29,48	11,51	1,60	435.3	29.38
		C	0.41	21,07	22,53	9,39	690.9	19.94
	5Cu-TZ	Anatase	0.47	18,10	30,51	11,42	139.0	18.77
		Rutile	0.27	31,66	9,98	1,49	436.1	30.73
		C	0.29	29,78	11,27	6,64	691.7	29.52
1000 °C	TZ	Rutile	0.34	25,14	15,83	2,28	440.7	26.02
	3Cu-TZ	Rutile	0.26	32,88	9,25	1,43	442.3	33.13
		C	0.28	30,85	10,51	6,41	704.9	29.84
	5Cu-TZ	Rutile	0.23	37,17	7,24	1,27	442.6	35.92
		C	0.24	35,99	7,72	5,50	716.8	34.97

3.1.2. Raman spectroscopy analysis:

The vibrational banding of TZ and xCu-TZ ($x = 3$ and 5 wt.%) thin films coated on Si substrates and annealed, respectively, at 800 and 1000 °C are presented in Fig. 3. They are acquired from Raman spectra in the characteristic frequencies' region from 100 to 800 cm⁻¹. The Raman spectrum of TZ films at 800 °C displays numerous combinations of TiO₂ anatase and rutile Raman active modes. Raman bands that are attributed to anatase are located at 137 (E_g), 196 (E_g), 303 (B_{1g}) and 390 (B_{1g}) and those for rutile are positioned at 435 (E_g) and 631 (E_g) cm⁻¹ [39-41]. In addition to that, more Raman bands are observed in both 3Cu-TZ and 5Cu-TZ films, these Raman bands are situated at 254 and 692 cm⁻¹ that are ascribed to the monoclinic CuO phase [42-44]. When the annealing temperature is raised to 1000 °C, the Raman active modes in all films are composed mainly of TiO₂ rutile and monoclinic CuO phases. The rutile Raman bands are observed at 147 (B_{1g}), 441(E_g), and 610 (A_{1g}) cm⁻¹[45-47] and those located at 304, 346 and 714 cm⁻¹ are assigned to CuO phase. Evidently, a significant increase in Raman bands could be observed in the peaks intensities after introducing copper species. the increasing intensity of peaks with the increasing of copper amount might result

from some agglomeration of dispersed CuO. Zeng et al. [48] reported that the formation of oxygen vacancies could result in the shift of E_g mode. A structural distortion occurs with Cu doping, and this distortion can cause changes in the Raman spectrum. It was found out that the E_g peak shows a shift towards lower wavenumbers, indicating the increase in oxygen vacancies and defects due to the substitution of Ti by Cu [49]. Also it was correlated to the change of crystalline size of xCu-TZ thin films. We conclude that the results obtained by X-ray diffraction and Raman analyses are in good agreement.

Grain size (L) and Raman bands FWHM can be related according the following equation [50]:

$$FWHM = A_1 \cdot e^{-\left(\frac{L-x_0}{t_1}\right)} + y_0 \quad (4)$$

Where (L) is the grain size in (nm), $y_0 = 12.7468$, $x_0 = 16.6998$, $A_1 = 12.4878$ and $t_1 = 0.2361$. The main vibrational modes of TiO₂ anatase, rutile and monoclinic CuO phases and the grain sizes are shown in Table 1.

3.1.3. Fourier transform infrared spectroscopy analysis:

The existence of the functional groups in FT-IR spectra of TZ, 3Cu-TZ and 5Cu-TZ thin films coated on Si substrates and annealed at 1000 °C are presented in Fig. 3. The peak at 2426 cm⁻¹ corresponded to the O–H stretching vibration of alcoholic groups as well as intercalated or adsorbed water molecular for all samples [51, 52]. The peak of 1729 cm⁻¹ was attributed to bending mode of surface –OH [53]. The peak positioned at 1450 cm⁻¹ correspond to elongating vibration of carboxylic linked to titanium atoms Ti–CO [54]. The peaks at 1322 cm⁻¹, 986 cm⁻¹ and 811 cm⁻¹ ascribed to stretching vibration of hydroxyl groups of Ti–OH [55]. SiO₂ presence in all FT-IR spectra is stated by the existence of strongest absorption peak situated at 1096 cm⁻¹ [56]. The absorption bands located, respectively, at 602 cm⁻¹, 479 cm⁻¹ are assigned to Ti–O–Ti and O–Ti–O polymers composing that are matching to both rutile and anatase phases of TiO₂ [57]. The absorption bands shape becomes sharper and they move slightly to an inferior frequency as the copper addition [58,59]. Likewise, no polymer bands associated to Cu–O liaisons were identified for our films.

The absorption bands shift observed in our FT-IR spectra to the lower frequencies can be influenced either by an augmentation in the nanoparticles size of both rutile TiO₂ and monoclinic CuO phase.

The increase in Cu content made the O-H vibrational bands at 2426 cm^{-1} and 1729 cm^{-1} very broad and intense, which confirms that our nanocomposite contains a large number of surface adsorbed hydroxyl (OH) species. These hydroxyl species play a vital part in the photodegradation process, and they can increase the degradation efficiency during the photocatalytic process.

3.2. Optical properties

3.2.1. UV-Vis analysis:

The transmission spectra of undoped TZ, 3Cu-TZ and 5Cu-TZ thin films deposited on glass substrates annealed at $500\text{ }^{\circ}\text{C}$ and examined using UV-vis in a spectral range between 300 and 800 nm wavelength range are presented in Fig. 5. The spectra reveal very pronounced interference effects which indicates that our films are sufficiently thick and the optical transmittance values are mainly over 90 % in the visible range. We note also a transmission decreases and the absorption edge shifts toward longer wavelengths as the copper concentrations increase. This indicates an increase in the gap of the $\text{TiO}_2\text{:ZrO}_2$ films, we calculated it using the Tauc formula [60]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (5)$$

where α is the absorption coefficient, A is the constant, $h\nu$ is the photon energy, h is Planck's constant, and E_g is the optical band-gap. When $(\alpha h\nu)^2 = 0$, $E_g = h\nu$, an extrapolation of the linear region of the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) on the x-axis gives the value of the optical band gap. The inset of figure 5 shows the plot $(\alpha h\nu)^2$ versus the incident energy ($h\nu$). The obtained band gap of TZ, 3Cu-TZ and 5Cu-TZ thin films are 3.53, 3.45 to 3.39 eV respectively. It can be noted that as Cu content increases, the E_g value decreases. This change can be likely due to the fusion of Cu ions into TiO_2 crystal structure, and the defect centers formed by the substitution of Ti^{4+} by Cu^{2+} ions in the TiO_2 crystal lattice resulting in changes in the optical absorption [61]. In Cu-TZ, when Cu ions are either located inside the bulk TiO_2 or on the surface sites, a rearrangement of the neighbor atoms takes place to compensate the charge deficiency, resulting in lattice deformation. This concludes that the Cu dopant narrow the electronic properties and alter the optical response of TiO_2 , causing a gradual decrease in the band gap energy with the increase of dopant concentration, which resulting in wide range absorber of visible light, which can be applied for different visible-light photocatalytic application. It is worth to mention that the incorporation of copper can act as a dopant in TiO_2 lattice due to electronic interaction between Cu^{2+} and Ti^{4+} ions, which lead to the creation trap states within TiO_2 band gap [62]. Thus, affects the electronic structure causing the band gap

shift [63]. We expected that such effective band gap lowering obtained by the doping may eventually leads to Fermi level reducing, enhancing the activity of the synthesized samples under study.

3.2.2. Photoluminescence analysis:

Since photoluminescence emission is derived from the recombination of photoinduced holes and electrons, it can provide the accurate data of separation of photoinduced pairs [64-66]. The PL spectra of TZ, 3Cu-TZ and 5Cu-TZ thin films are illustrated in Figure 5. They were examined in the wavelength range of 350–650 nm, the spectra display two emission peaks in the UV and green region and it is found that the addition of Cu does not bring new emission peak but only changes the peaks intensities and shifts them towards higher wavelengths. This shift may be related to the decrease of the band gap and to the increase in the grain size (Table 1). The emission at 412 nm is due to the recombination of holes and electrons between the valence band (BV) and the conduction band (BC) [66]. In addition, it can be observed a green emission peak at 587 nm in both TZ and xCu-TZ samples. These peaks are attributed to the electron-hole recombination via oxygen vacancies that can form new trapping energy levels in the band gap of TiO₂ [67,68].

We note that increasing Cu content shifts the PL peaks towards higher wavelengths and decreases their intensity, which indicates that the recombination of photoinduced electrons and holes is hindered by Cu adding effectively. Remarkably, the PL intensity decreases with the increase of Cu concentration, which implies that high content Cu doping is favorable to suppress the recombination of photogenerated electrons and holes which improves the photocatalytic effectiveness [69].

3.2.3. Photocatalytic properties:

The catalytic activity of photocatalyst depends on its active sites as well as concentration of dye. In the present work, effect of catalyst loading on degradation of Methyl Orange (MO) was examined under UV light radiation by using xCu-TZ films.

Fig. 7 shows the absorption spectrum of Methyl Orange (MO) dye as a function of wavelength (300-600 nm) for various time interval, which indicating a typical process for photodegradation of MO dye. The maximum absorbance peak of MO dye was observed at a wavelength of around 461 nm. The plots clearly demonstrate that the as prepared 3Cu-TZ films easily degrade the MO dye with slight increase of time. Here also the results revealed that the

3Cu-TZ nanoparticles are strong photocatalyst which degrade MO dye more than 98% at 3 hours.

The degradation rate is an important value that can yield the relative quantity of removed pollutant from the water. The degradation rate (D %) can be determined using the following formula [50]:

$$D\% = 100 \times (C_0 - C) / C_0 \quad (6)$$

where D is the decomposition rate of MO, C_0 is the initial concentration of MO before UV irradiation and C is the concentration of MO after an irradiation time t.

The degradation mechanism of organic dyes by photocatalytic reaction was suggested as follows: The pollutant organic dye molecules must be adsorbed sufficiently close to the catalyst surface. Then, the light is irradiated and the electrons are excited from the valence band (VB) of the catalyst to the conduction band (CB), and the reaction begins. When the electron is excited from the VB to the CB, the vacancies, or holes (h^+), are created in the VB. The electrons (e^-) excited to the conduction band meet the surrounding oxygen and produce superoxide radical anion ($\cdot O_2^-$) and hydrogen peroxide (H_2O_2).

The degradation rate of MO solution under UV irradiation for 3 h, is illustrated in Fig. 8. As shown, the degradation rates increase as a function of the exposition time to UV. In absence of photocatalyst and under UV irradiation (photolysis case), the degradation of pollutants was negligible, only 8.31 % of MO dye was removed after 3h. Using TZ, the degradation rate rises to 78 %. On the other hand, the degradation rates were 97% and more than 99% in the presence of 3Cu-TZ and 5Cu-TZ films, respectively. However, 5Cu-TZ films display the most improved photocatalytic performance. Obviously, the degradation rates of MO dye reach their maximum to 100 % after 3h, confirming the complete removal of these organic pollutant in water.

Besides, the photocatalytic degradation is a pseudo first order reaction and its kinetics can be defined as follows [50]:

$$\ln(C_0/C) = k t \quad (7)$$

Where k is the apparent rate constant (min^{-1}) and t is the irradiation time (min). The plots of $\ln(C_0/C)$ as a function of time are shown in the insets of Fig. 9. The slope of each plot was used to calculate the rate constant (k) of the reaction. The higher k values of 5Cu-TZ ($k=0.0238 \text{ min}^{-1}$) film confirm the faster removal of pollutants in water compared to TZ.

Chemically, the photochemical reaction between TiO_2 and UV light leads to the formation of $\cdot OH$ radicals and $\cdot O_2^-$ anions. As a result, photocatalytic reaction of MO occurs on the surface of TiO_2 , as mentioned by Jiang et al. [70]. Its gap energy of 3.2 eV was indeed

well matched to the photon energy of the UV light emitted by the lamp. When the anatase TiO_2 on the surface of the tested sample was exposed to UV irradiation, electron-hole pairs would therefore be produced, bringing about a series of oxidation-reduction reactions. The oxidizing power of $\cdot\text{OH}$ is able to decompose many organic molecules; hence, it allows decomposing the model pollutant (MO) into H_2O and CO_2 [71,72]. The porous structure, lifetime of electron-hole pairs, gap energy, and $\cdot\text{OH}$ radicals' concentration are essential parameters to ameliorate the effectiveness of photocatalyst [73]. So, the presence of copper acts as an impure substance in pure TZ crystal structure which improves the photocatalytic activity for the following reasons:

- The diminution of the band gap (E_g) by the addition of xCu-TZ matrix permits the absorption of more UV light energy and higher generation of electron-hole pairs [71,74]. This promotes the $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ concentrations and thus improves the effectiveness of the photocatalyst;
- The formation of new energy levels (trap states) between the conduction band and valence band as the dopant concentration increased also explained the enhanced photocatalytic activity;
- Cu acts as electron acceptor so that rapid charge diffusion was absorbed to form superoxide radical anions which enhance photocatalytic activity and inhibits charge carrier recombination ($\cdot\text{O}_2^-$);
- The contribution of more electron-hole pairs generated from Cu causes a higher creation of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals, and consequently accelerates the photocatalytic activity;
- From PL analysis, the sample with the least intense PL spectra underwent greater photo-degradation. The sample with a concentration of 5% of CuO had less intense and thus a higher degradation percentage which improves the electron-hole separation rate and increases their lifetime. As a result, more electrons and holes can contribute in the photoreaction and so rise the removal of organic molecules [75];
- The addition of copper may permit more Cu atoms to be penetrated in TiO_2 lattice structure that leads to increase visible light absorption [76,77].

These results suggest that CuO doped $\text{TiO}_2\text{:ZrO}_2$ have potential applications in industrial wastewater treatment as photocatalysts in the degradation of organic dyes.

Conclusion:

In this work, the performance of CuO/TiO₂:ZrO₂ photocatalysts, with various molar ratios of CuO (3 and 5 wt.%), prepared by sol-gel dip-coating process and annealed at different temperatures (500, 800 and 1000°C) are studied. The co-doping with CuO and the annealing temperature effects on the structural, optical and photocatalytic properties of TiO₂:ZrO₂ were investigated. The structural analysis confirmed the existence of triphasic structure of TiO₂ anatase/brookite/rutile and the monoclinic phase of CuO. XRD and Raman results indicated that an increase in annealing temperature from 500°C to 1000°C caused a transformation of crystallinity from anatase and brookite at 500°C to rutile and monoclinic CuO phases at 1000°C, accompanied by an increase in the particle sizes. The transmission spectra revealed that all the samples are transparent in the visible region and indicated that CuO loading decreases the band gap from 3.53 to 3.39 eV. PL spectra show that the recombination of photogenerated electrons and holes is inhibited effectively with CuO addition and the inhibition enhances with the increase of CuO doping concentration, which is favorable for photocatalytic performance. The photocatalytic efficiency of as prepared films was evaluated using Methyl Orange (MO) dye as contamination compound. It was found that 5%CuO/TiO₂:ZrO₂ films exhibits the highest photocatalytic activity and the degradation degree of methyl orange (MO) reaches more than 99% after 3h. These materials are very stable in the photocatalytic reactions, they degrade harmful dyes which are present in contaminated water through the photocatalytic activity because of the contribution of superoxides and hydroxyl radicals that form during photocatalysis. Therefore, they are promising and efficient catalysts for practical applications such as food industry, environmental, hospital, and wastewater treatment.

References:

- [1] Y. Cui, Y. Chen, Y. Jiang, J. Yang, Y. Wang, J. Alloy. Compd., 817, 152752, (2020). <https://doi.org/10.1016/j.jallcom.2019.152752>
- [2] Z. Jafari, N. Mokhtarian, G. Hosseinzadeh, M. Farhadian, A. Faghihi, F. Shojaie, J. Energy Chem., 25 (3), 393–402 (2016). <https://doi.org/10.1016/j.jechem.2016.01.013>
- [3] A. Gogoi, P. Mazumder, V.K. Tyagi, G.G.T. Chaminda, A.K. An, M. Kumar J. Groundw. Sustain. Dev., 6, 169-180 (2018). <https://doi.org/10.1016/j.gsd.2017.12.009>
- [4] L. Cheng, Q. Xiang, Y. Liao, H. Zhang, Energy Environ., 11, 1362–1391 (2018). <https://doi.org/10.1039/C7EE03640J>

- [5] W. Hu, L. Xie, H. Zeng, J. Colloid Interface Sci., 568, 36–45 (2020). <https://doi.org/10.1016/j.jcis.2020.02.028>
- [6] N. Hao, Y. Nie, Z. Xu, C. Jin, T. J. Fyda, J. X. J. Zhang, J. Colloid Interface Sci., 559, 254–262 (2020). <https://doi.org/10.1016/j.jcis.2019.10.042>
- [7] M. L. Baynosa, A. H. Mady, V. Q. Nguyen, D. R. Kumar, M. S. Sayed, D. Tuma, J. J. Shim, J. Colloid Interface Sci., 561, 459–469 (2020). <https://doi.org/10.1016/j.jcis.2019.11.018>
- [8] B. F. Mohazzab, B. Jaleh, M. Nasrollahzadeh, Z. Issaabadi, R. S. Varma., J. Mol. Catal., 473, 110401 (2019). <https://doi.org/10.1016/j.mcat.2019.110401>
- [9] F.G. Shahna, A. Bahrami, I. Alimohammadi, R. Yarahmadi, B. Jaleh, M. Gandomi, J. Hazard Mater., 324, 544–553 (2017). <https://doi.org/10.1016/j.jhazmat.2016.11.025>
- [10] J. Mermana, P. Sutthivaiyakit, C. Blaise, F. Gagné, S. Charnsethikul, P. Kidkhunthod, S. Sutthivaiyakit, Environ. Sci. Pollut. Res. Int., 24, 4077–4092 (2017). <https://doi.org/10.1007/s11356-016-8151-6>
- [11] D.L. Cunha, A. Kuznetsov, C.A. Achete, A.E. da Hora-Machado, M. Marques, J. Peer, 6, 4464 (2018). <https://doi.org/10.7717/peerj.4464>
- [12] S. M. Adyani, M. Ghorbani, J. rare Earth., 36, 72–85 (2018). <https://doi.org/10.1016/j.jre.2017.06.012>
- [13] N. Wei, H. Z. Cui, Q. Song, L. Q. Zhang, X. J. Song, K. Wang, Y. F. Zhang, J. Li, J. Wen, J. Tian, J. Appl. Catal. B Environ., 198, 83–90 (2016). <https://doi.org/10.1016/j.apcatb.2016.05.040>
- [14] W. Xie, R. Li, Q. Xu, J. Sci. Rep., 8, 1–10 (2018). <https://doi.org/10.1038/s41598-018-27135-4>
- [15] P. Margan, M. Haghighi, J. Sol. Gel Sci. Technol., 81, 556–569 (2017). <https://doi.org/10.1007/s10971-016-4217-7>
- [16] O. Beldjebli, R. Bensaha, Y. S. Oca, L. Amirache, R. Boukherroub, J. Mater. Res. Express, 6, 085036 (2019). <https://doi.org/10.1088/2053-1591/ab1d36>
- [17] H. Dehdouh, R. Bensaha, M. Zergoug, J. Mater. Res. Express, 4, 086408 (2017). <https://doi.org/10.1088/2053-1591/aa8068>
- [18] A. Doula, R. Bensaha, O. Beldjebli, J. Acta Physica Polonica A, 140, 421–426 (2021). <https://doi.org/10.12693/APhysPolA.140.421>
- [19] B. Toubal, R. Bensaha, F. Yakuphanoglu, J. Sol. Gel Sci. Technol., 82, 478–489 (2017). <https://doi.org/10.1007/s10971-017-4337-8>
- [20] S.A. Ansari, M.M. Khan, M.O. Ansari, M.H. Cho, New J. Chem., 40, 3000–3009 (2016). <https://doi.org/10.1039/C5NJ03478G>

- [21] M. Zhu, C. Zhai, L. Qiu, C. Lu, A.S. Paton, Y. Du, M.C. Goh, ACS Sustain. Chem. Eng., 3, 3123–3129 (2015). <https://doi.org/10.1021/acssuschemeng.5b01137>
- [22] Y. Park, W. Kim, H. Park, T. Tachikawa, T. Majima, W. Choi, Appl. Catal. B Environ., 91, 355–361 (2009). <https://doi.org/10.1016/j.apcatb.2009.06.001>
- [23] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, Chem. Rev., 114, 9919–9986 (2014). <https://doi.org/10.1021/cr5001892>
- [24] M. Yung, E. Holmgren, U. Ozkan, J. Catal., 247, 356–367 (2007). <https://doi.org/10.1016/j.jcat.2007.02.020>
- [25] C. Sun, J. Zhu, Y. Lv, L. Qi, B. Liu, F. Gao, K. Sun, L. Dong, Y. Chen, Appl. Catal. B, 103 206–220 (2011). <https://doi.org/10.1016/j.apcatb.2011.01.028>
- [26] H. Bensouyad, H. Sedrati, H. Dehdouh, M. Brahimi, F. Abbas, H. Akkari, R. Bensaha, J. Thin Solid Films, 519, 96–100 (2010). <https://doi.org/10.1016/j.tsf.2010.07.062>
- [27] Q. Yuan, X. Guan, X. Xue, D. Han, H. Zhong, W. Ji, J. physica status solidi (RRL), 13, 1800575 (2019). <https://doi.org/10.1002/pssr.201800575>
- [28] A.G. Escobar-Villanueva, V.M. Ovando-Medina, H. Martinez-Gutierrez, M.P. Militello, J. Mater. Sci. Mater. Electron. (2020) <https://doi.org/10.1007/s10854-019-02644-8>
- [29] A. L. Luna, M. A. Valenzuela, C. C. Justin, P. Vázquez, J. L. Rodriguez, J. R. Avendaño, S. Alfaro, S. Tirado, A. Garduño, J. M. D. Rosa, J. Appl. Catal. A: Gen., 521, 140–148 (2016). <https://doi.org/10.1016/j.apcata.2015.10.044>
- [30] S. J. A. Moniz, J. Tang, J. Chem-CatChem, 7, 1659–1667 (2015). <https://doi.org/10.1002/cctc.201500315>
- [31] D. Guerrero-Araque, P. Acevedo-Pena, D. Ramirez-Ortega, H. A. Calderon, R. Gomez, J. hydro. Ener., 42, 9744–9753 (2017). <https://doi.org/10.1016/j.ijhydene.2017.03.050>
- [32] F. Morales Anzures, P. Salinas Hernández, F. C. Ornelas-Gutiérrez, F.J. Tzompantzi-Moralesd, R. Pérez-Hernándezb, J. Catalysis Today, 349, 228–234 (2020). <https://doi.org/10.1016/j.cattod.2018.03.017>
- [33] B. M. Reddy, B. Chowdhury, I. Ganesh, E. P. Reddy, T. C. Rojas, A. Fernández, J. Phys. Chem. B, 102, 10176–10182 (1998). <https://doi.org/10.1021/jp9826165>
- [34] R. Pérez-Hernández, D. Mendoza-Anaya, M.E. Fernández, A. Gómez-Cortés, J. Mol. Catal. A Chem., 281, 200–206 (2008). <https://doi.org/10.1016/j.molcata.2007.11.008>
- [35] K. Sathishkumar, N. Shanmugam, N. Kannadasan, S. Cholan, G. Viruthagiri, J. Sol-Gel Sci. Techn., 74, 621–630 (2015). <https://doi.org/10.1007/s10971-015-3641-4>
- [36] M. You, T.G. Kim, Y. M. Sung, J. Cryst. Growth Des., 10, 983–987 (2010). <https://doi.org/10.1021/cg9012944>

- [37] M. Kikugawa, K. Yamazaki, H. Shinjoh, J. Applied Catalysis A, General, 547, 199–204 (2017). <https://doi.org/10.1016/j.apcata.2017.09.005>
- [38] E. Y. Kim, D. S. Kim, B. T. Ahn, J. Bull. Korean Chem. Soc., 30, 193–196 (2009). <https://doi.org/10.5012/bkcs.2009.30.1.193>
- [39] J. C. Colmenares, M. A. Aramendia, A. Marinas, J. M. Marinas, F. J. Urbano, J. Appl Catal A: Gen., 306, 120–127 (2006). <https://doi.org/10.1016/j.apcata.2006.03.046>
- [40] T. Onfroy, O. V. Manoilova, S. B. Bukallah, D. M. Hercules, G. Clet, M. Houalla, J. Appl Catal A: Gen., 316, 184–190 (2007). <https://doi.org/10.1016/j.apcata.2006.09.021>
- [41] P. Periyat, K. V. Baiju, P. Mukundan, P. K. Pillai, K. G. K. Warriar, J. Appl Catal A: Gen., 349, 13–19 (2008). <https://doi.org/10.1016/j.apcata.2008.07.022>
- [42] M. C. Mathpal, A. K. Tripathi, M. K. Singh, S. P. Gairola, S. N. Pandey, A. Agarwal, J. Chem. Phys. Lett., 2013, 555, 182–186 (2013). <https://doi.org/10.1016/j.cplett.2012.10.082>
- [43] K. Phiwdang, S. Suphankij, W. Mekprasart, W. Pecharapa, J. Energy Proc., 34, 740–745 (2013). <https://doi.org/10.1016/j.egypro.2013.06.808>
- [44] J. F. Xu, W. Ji, Z.X. Shen, W. S. Li, S. H. Tang, X. R. Ye, D. Z. Jia, X. Q. Xin, J. Raman Spectrosc., 30, 413–415 (1999). [https://doi.org/10.1002/\(SICI\)1097-4555\(199905\)30:5<413::AID-JRS387>3.0.CO;2-N](https://doi.org/10.1002/(SICI)1097-4555(199905)30:5<413::AID-JRS387>3.0.CO;2-N)
- [45] M. Li, X. Zhang, Y. Liu, Y. Yang, J. Appl. Surf. Sci., 440, 1172–1180 (2018). <https://doi.org/10.1016/j.apsusc.2018.01.227>
- [46] W. F. Zhang, Y. L. He, M. S. Zhang, Z. Yin, Q. Chen, J. Phys. D, 33, 912–916 (2000). <https://doi.org/10.1088/0022-3727/33/8/305>
- [47] T. T. Loan, N. A. Bang, V. H. Huong, N. N. Long, J. Opt. Mater., 69, 30–37 (2017). <https://doi.org/10.1016/j.optmat.2017.04.005>
- [48] Y. Zeng, T. Wang, S. Zhang, Y. Wang, Q. Zhong, J. Appl. Surf. Sci., 411, 227–234. (2017). <https://doi.org/10.1016/j.apsusc.2017.03.107>
- [49] M. Edelmannová, k.Y. Lin, J.C.S. Wu, I. roppová, L. Čapek, K. Kočí, Applied Surface Science, 454, 313–318 (2018). <https://doi.org/10.1016/j.apsusc.2018.05.123>
- [50] N. Mathews, E.R. Morales, M. Cortes-Jacome, J. Toledo-Antonio, J. Sol. Energy., 83, 1499–1508 (2009). <https://doi.org/10.1016/j.solener.2009.04.008>
- [51] K. Dong, L. Yu, Y. Zhang, Q. Wang, B. Neppolian, J. Sci. Adv. Mater., 6, 1828–1835 (2014). <https://doi.org/10.1166/sam.2014.1948>
- [52] U. J. Kim, C. A. Furtado, X. Liu, G. Chen, P. C. Eklund, J. Am. Chem. Soc., 127, 15437–15445 (2005). <https://doi.org/10.1021/ja052951o>

- [53] G. Li, L. Li, J. Boerio-Goates, B. Woodfield, *J Am. Chem. Soc.*, 127, 8659–8666 (2005).
<https://doi.org/10.1021/ja050517g>
- [54] N. T. Nolan, M. K. Seery, S. C. Pillai, *J. Phys. Chem. C*, 113, 16151–16157 (2009).
<https://doi.org/10.1021/jp904358g>
- [55] M. Liao, C. Hsu, D. Chen, *J. Solid State Chem.*, 179, 2020–2026 (2006).
<https://doi.org/10.1016/j.jssc.2006.03.042>
- [56] R. Parra, M. S. Góes, M. S. Castro, E. Longo, P. R. Bueno, J. A. Varela, *J. Chem. Mater.*, 20, 143–150 (2008). <https://doi.org/10.1021/cm702286e>
- [57] B. M. Reddy, I. Ganesh, *J. Mol. Catal. A: Chem.*, 169, 207–223 (2001).
<https://doi.org/10.1021/la00031a028>
- [58] P. Goswami, J. N. Ganguli, *J. Dalton Trans.*, 42, 14480–14490 (2013).
<https://doi.org/10.1039/C3DT51891D>
- [59] W. Khan, S. Ahmad, M. M. Hassan, A. H. Naqvi, *J. Opt. Mater.*, 38, 278–285 (2014).
<https://doi.org/10.1016/j.optmat.2014.10.054>
- [60] M. Sreemany, S. Sen, *J. Mater. Chem. Phys.*, 83, 169–177 (2004).
<https://doi.org/10.1016/j.matchemphys.2003.09.030>
- [61] V. Teodoro, E. S. Junior, M. V. Nogueira, M. A. Zaghet, E. Longo, L. A. Perazolli, *J. Sci Revs Chem Commun.*, 7 (3), 112 (2017).
- [62] S. Chahid, R. Alcántara, D.M. de los Santos, 940–946 (2019) https://doi.org/10.1007/978-3-030-11196-0_76
- [63] M. Sahu, P. Biswas, *J. Nanoscale Res Lett.*, 6 (1), 1–14 (2011).
<https://doi.org/10.1186/1556-276X-6-441>
- [64] Y. Z. Wang, Y. S. Wu, H. Yang, X. X. Xue, Z. H. Liu, *J. Vacuum*, 131, 58–64 (2016).
<https://doi.org/10.1016/j.vacuum.2016.06.003>
- [65] J. Singh, A. K. Manna, R. K. Soni, *J. Mater. Sci-Mater. El.*, 30, 16478–16493 (2019).
<https://doi.org/10.1007/s10854-019-02023-3>
- [66] X. Fan, J. Wan, E. Z. Liu, L. Sun, Y. Hu, H. Li, X. Y. Hu, J. Fan, *J. Ceram. Int.*, 41, 5107–5116 (2015). <https://doi.org/10.1016/j.ceramint.2014.12.083>
- [67] A. M. Selman, Z. Hassan, M. Husham, *J. Measurement*, 56, 155–162 (2014).
<https://doi.org/10.1016/j.measurement.2014.06.027>
- [68] L. Kernazhitsky, V. Shymanovska, T. Gavrillo, V. Naumov, L. Fedorenko, V. Kshnyakin, *J. Lumin.*, 146, 199–204 (2014). <https://doi.org/10.1016/j.jlumin.2013.09.068>
- [69] X. Zhu, Q. Zhou, Y. Xia, J. Wang, H. Chen, Q. Xu, J. Liu, W. Feng, S. Chen, *J. Mater. Sci.: Mater Electron*, 32, 21511–21524 (2021). <https://doi.org/10.1007/s10854-021-06660-5>

- [70] X. Jiang, G. Ding, L. Lou, Y. Chen, X. Zheng, *J. Mol. Catal. A Chem.*, 218, 187–195 (2004). <https://doi.org/10.1016/j.molcata.2004.02.020>
- [71] Y. F. Tu, S. Y. Huang, J. P. Sang, X. W. Zou, *J. Alloys. Compd.*, 482, 382–387 (2009). <https://doi.org/10.1016/j.jallcom.2009.04.027>
- [72] I. K. Konstantinou, T. A. Albanis, *J. Appl. Catal. B*, 49, 1–14 (2004). <https://doi.org/10.1016/j.apcatb.2003.11.010>
- [73] C. V. Reddy, B. Babu, J. Shim, *J. Phys. Chem. Solids*, 112, 20–28 (2018). <https://doi.org/10.1016/j.jpcs.2017.09.003>
- [74] J. Du, G. Zhao, H. Pang, Y. Qian, H. Liu, D.J. Kang, *J. Mater. Lett.*, 93, 419–422 (2013). <https://doi.org/10.1016/j.matlet.2012.11.134>
- [75] H. J. Lin, T. S. Yang, C. S. Hsi, M.C. Wang, K.C. Lee, *J. Ceram. Int.*, 40, 10633–10640 (2014). <https://doi.org/10.1016/j.ceramint.2014.03.046>
- [76] M. S. Adly, S. M. El-Dafrawy, S.A. El-Hakam, *J. Mater. Res. Technol.*, 8, 5610–5622 (2019). <https://doi.org/10.1016/j.jmrt.2019.09.029>
- [77] H. Khan, Z. Jiang, D. Berk, *J. Sol. Energy*, 162, 420–430 (2018). <https://doi.org/10.1016/j.solener.2018.01.055>

Figures:

Fig. 1. XRD patterns of the undoped, TZ, 3Cu-TZ and 5Cu-TZ thin films coated on glass substrates and annealed at 500 °C.

Fig. 2. XRD patterns of the TZ, 3Cu-TZ and 5Cu-TZ thin films coated on Si substrates and annealed, respectively, at (a) 800 and (b) 1000 °C.

Fig. 3. Raman spectra of the TZ, 3Cu-TZ and 5Cu-TZ thin films coated on Si substrates and annealed, respectively, at (a) 800 and (b) 1000 °C.

Fig. 4. FT-IR spectra of undoped TZ, 3Cu-TZ and 5Cu-TZ thin films coated on Si substrates and annealed at 1000 °C.

Fig. 5. Transmittance spectra of TZ and xCu-TZ thin films coated on glass substrates and annealed at 500 °C **(a)**. The plot $(\alpha h\nu)^2$ versus incident energy ($h\nu$) **(b)**.

Fig. 6. PL spectra of TZ and xCu-TZ thin films.

Fig. 7. Absorption spectra of Methyl Orange (MO) dye after 180 min of illumination in the presence of 3Cu-TZ thin films.

Fig. 8. Photocatalytic degradation of MO dye under different amounts of xCu-TZ photocatalysts (x=0, 3 and 5%).

Fig. 9. Plot of $\ln(C_0/C)$ versus time with different amounts of xCu-TZ photocatalysts (x=0, 3 and 5%).