# AN ENHANCED PHOTOCATALYTIC PERFORMANCE BASED ON MoO<sub>3</sub> AND Zn DOPED MoO<sub>3</sub> NANO STRUCTURES

N. R. CHANDAR<sup>a\*</sup>, S. AGILAN<sup>a</sup>, N.MUTHUKUMARASAMY<sup>a</sup>, R.THANGARASU<sup>b</sup>

<sup>a</sup>Department of Physics, Coimbatore Institute of Technology, Coimbatore- 641 014, Tamilnadu, India

<sup>b</sup>Department of Physics, PSG College of Arts & Science, Coimbatore- 641 014, Tamilnadu, India

The MoO<sub>3</sub> and transition metal of (Zn) doped MoO<sub>3</sub> nanostructures were synthesized by simple wet chemical method. In this article, we used for the high efficient  $Zn_x$  (x = 5, 10) &15%) for nanophotocatalyst in visible region. The process is simple, cost-effective and can be easily scaled-up. It is shown that the catalytic behavior of MoO<sub>3</sub> and Zn doped MoO<sub>3</sub> that are synthesized in this method has good efficiency for degradation. The MoO<sub>3</sub> and Zn/ MoO<sub>3</sub> photocatalysts are characterized by X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM) and Scanning Energy Dispersive X-ray spectroscopy (EDS).Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy. The obtained results of XRD and FE-SEM are confirmed the well dispersion of Zn nanoparticles and highly well improvement of the regular Zn nanoparticles on the surface of  $MoO_3$  nanostructures. The chemical nature of the bonding confirmation details about the Zn doped MoO<sub>3</sub> is analyzed through vibrational spectra of FTIR. The enhanced photocatalytic activities of Zn doped MoO<sub>3</sub> nanostrucutre are attributed to the degradation efficiency under UV-visible light irradiation inorganic segment. Also, evaluation of the photocatalytic degradation of Methyleneblue(MB) was done under UV-visible light irradiation. The results are showed that these structures exhibit promising candidates to degrade methylene blue (MB). Based on the characterization, it is found that Zn doped MoO<sub>3</sub>structure showed higher photocatalytic activity than MoO<sub>3</sub>. This relatively high photocatalytic activity may be attributed to the charge transfer between those bi-layered oxides. Besides, the kinetic studies revealed that the photocatalytic oxidation kinetic theory follows a pseudo-first-order reaction. Finally, the stability, cyclic efficiency and growth mechanisim of the Zn doped MoO<sub>3</sub>photocatalyst are investigated.

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### 1. Introduction

In recent years, different applications for advanced science and technology relating to industrial processes due to the strong demand for degradation of various kinds of organic and inorganic pollutants to that progress in the atmosphere [1]. ZnO[2], WO<sub>3</sub>[3], MoO<sub>3</sub>[4] and TiO<sub>2</sub>[5], they have been tested as photocatalysts, among them. MoO<sub>3</sub> has been reported many times due to its low cost, photochemical stability and non toxicity under irradiation[6-7]. However, MoO<sub>3</sub> has a large bangap (2.5 to 3.2 eV) and responds only UV light (k <390nm,accounts for only 5% of the total sunlight), which greatly restricts its convenient application for low consumption of solar energy. Molybdenum oxide (MoO<sub>3</sub>) as one of the interesting transition metal oxides, has attracted much attention with its distinctive properties. On the other hand,MoO<sub>3</sub> can be used in solar cell [8], supercapacitor[9], catalyst[10], gas sensor[11], battery[12], photocatalysis [13] Owing to the potential importance, the synthesis ofMoO<sub>3</sub> with diameter lesser than Bohr radius (2.7 nm) is important for latent research MoO<sub>3</sub>.In generally, it has three crystal phase: the stable

Corresponding author: nrajiv81@gmail.com

orthorhombic  $MoO_3(\alpha-MoO_3)$ , metastable monoclinic  $MoO_3(\beta-MoO_3)$  and hexagonal  $MoO_3(h-MOO_3)$ MoO<sub>3</sub>)[14].Among the diverse metal of Zn semiconductor photocatalysts, Zinc has few affirmative superiorities over lasting, namely low cost, nontoxicity. To solve the major technical issue the absorption of visible light and suppress their combination of photogenerated electron and hole pair into yield  $e^{-}/h^{+}$  pair. Besides the upper hand, the detriment is photogenerated  $e^{-}$  and  $h^{+}$ recombine very quickly. To run over this loss, bringing up new levels in the forbidden bands is favourable way semiconductor is combined with transition metals resulting in their formation of hybrid materials of doping. In the other way around, externally added metals are also called as catalyst[15-16] In this regard, we have synthesized Zn doped MoO<sub>3</sub> nanoparticles is analyzed its performance as photocatalyst in H<sub>2</sub> generation. We have reported that the improved way of wet chemical synthesis process of MoO<sub>3</sub> and Zn doped MoO<sub>3</sub> with adding the surfactant of SDS can be achieved good nanoparticles. However, it should be mentioned that the low dimensional nano scaled building blocks (such as nanoparticles, nanorods, nanosheets, and nanoplates) tend to combine during the preparation and photocatalys processes, resulting in reduction of their surface area and photocatalytic efficiency which the  $\alpha$ -MoO<sub>3</sub> has the multitype-nanostructure shape of the morphological studies was confirmation [17]. To obtained that  $MoO_3$  samples have been examined to photodegradation MB under visible light for evaluating their photocatalytic properties, with possible kinetic theory and photodegradation mechanism is also derived.

The present work aims to reach the relative characterization between pure and Zn doped  $MoO_3$  nanoparticles prepared by a simple wet chemical method. These nanoparticles have been investigated by using XRD, FE-SEM with EDS, FTIR, Raman technique, Finally, photocatalytic of pureand Zn doped  $MoO_3$  nanoparticles have been reported and their photocatalytic activity was evaluated in the degradation of MB under UV-Visible irradiation.

# 2. Experimental procedure

### 2.1. Preparation of Pure MoO<sub>3</sub> and Zn doped MoO<sub>3</sub> nanoparticles

The experimental setup for the synthesis of pure  $MoO_3$  and Zn-doped  $MoO_3$  nanoparticles is done by a wet chemical route. Ammonium heptamolybdatetetrahydrate (AHMT), sodium dodecyl sulfate (SDS), ethanol and Zinc nitrate Zn ( $NO_3$ )<sub>2</sub>.6H<sub>2</sub>O are used as dopant substances. The typical synthesis process consists of two steps.



Fig.1. Experimental process of wet chemical method.

Step I: The required amount of AHMT is dissolved in distilled water concentration of 0.5 M with the support of a magnetic stirrer for approximately 30 minutes. Tube light color precipitate is formed after adding the concentrated solution of SDS and stirred for 30 minutes. The mixture is constantly stirred for 20 minutes using a magnetic stirrer until a white color precipitate is formed. After that, the ethanol solution is added in drops to get a pure white color precipitate which later turns into a colloidal form. The precipitate is dried using a magnetic stirrer until a nucleation retort is formed keeping it for 24 hrs.

After the reaction hour, the solution is allowed to get settled with white yields. Besides, the obtained solid yields are filtered, washed with distilled water and ethanol by the centrifugation (9000 rpm/15min) several times and then dried in an oven at 150°C for 5hrs. Finally, the dried powder sample is calcined at 400°C for 2hrs with a heating rate of about 10°C/min in a muffle furnace. Then, the system is allowed to attain room temperature at a cooling rate of  $5^{\circ}$ C/min. Further, the prepared white coloured sample is turned into pale blue yield colored MoO<sub>3</sub> nanoparticles. The nanoparticle can be expected as shown in Fig. 1.

Step II: For the synthesis of Zn-doped  $MoO_{3}$ , a various concentration such as Zn(x=5%, 10% and 15%), an estimated amount of Zinc nitrate (x) is mixed with aqueous Ammonium heptamolybdate tetrahydrate solution. Besides, a required amount of SDS is added into the homogenous mixture in drops to get a light fluorescent white shade. After the achievement of light fluorescent white shade, the same procedure followed in Step I is adopted to obtain the Zn doped MoO<sub>3</sub> nanoparticles and an overview of the synthesis process is provided in Fig. 1.

### 2.2. Characterization techniques

The X-ray diffraction pattern is analyzed in crystallinity nature with Cu-Ka radiation ( $\lambda$ =1.5478) in the range of 20-90 degrees. The morphology of the nanoparticles is examined by Field Emission Scanning Electron Microscopy (FE-SEM, MIRA3 Model: TESCAN-2300) and the elemental confirmation analysis of the sample is performed using EDS spectra. The presence of the chemical bonding nature of Zn doped MoO<sub>3</sub> nanoparticles (as pellet mode in KBr) is studied by FTIR spectrometer (Model: 5TX FTIR) in the wavenumber ranging from 4000-400 cm<sup>-1</sup>. Micro-Raman analysis is also carried out using a Raman Analyzer-EZRaman N-532-C1S.

#### 2.3. Photocatalytic setup

A measured photocatalytic reactor system made of a double-walled reactor chamber of glass tube mock-up type is used for photocatalytic experiments. A 300W xenon lamp is used for the UV-Visible light source and the power of the reaction bottle on the plane window is placed at 20cm from the xenon lamp. The Methylene blue (MB) dye is used as photocatalytic degradation which is measured from pollutants. For the photocatalytic experiment, 30mg photocatalysts are suspended in a 30ml MB aqueous solution with a concentration of 15mg/l in a beaker. Before the reaction, the suspension is magnetically stirred for 30min to reach the adsorption/desorption equilibrium with light revelation. Subsequently, the photocatalytic reaction starts with the exposure of the preferred light source. The concentration of the aqueous suspension through MB dye in a sample is analyzed using a UV-Vis spectrophotometer at a wavelength of 664 nm. The photocatalytic efficiency is measured from the appearance  $\eta = (1-C/C_0)$ , where C is the concentration of the dye after a certain irradiation time and C<sub>0</sub> is the concentration dye. The time interval of the irradiation is 30min.

# 3. Results and discussion

#### 3.1. XRD analysis

The phase purity and the crystal structure of the pristine MoO<sub>3</sub> and Zn doped MoO<sub>3</sub> samples were determined by X-ray diffraction (XRD). Fig.2(a-b) shows the XRD pattern of MoO<sub>3</sub> and Zn doped MoO<sub>3</sub> samples were directly the diffraction peaks located at  $2\theta = 23.61^{\circ}, 25.90^{\circ}, 27.55^{\circ}, 33.70^{\circ}, 35.70^{\circ}, 39.14^{\circ}, 46.50^{\circ}, 49.50^{\circ}, 52.60^{\circ}, 56.60^{\circ}, 57.40^{\circ}, 58.97^{\circ}$  and  $64.72^{\circ}$  are respectively related to (110), (120), (021), (111), (121), (150), (061), (002), (211), (112), (081) and (062) crystal planes. The results exhibit that all the peaks are composed of orthorhombic MoO<sub>3</sub> crystal (JCPDS card No: 76-3210). No other peaks were detected in samples. As seen, the peaks of the Zn substituted MoO<sub>3</sub> samples show a significant shift of the diffraction peaks towards a higher angle concerning for that pure and doped samples. The slight shift of the XRD peaks with the Zn doped MoO<sub>3</sub> represents that Zn has been effectively doped into the MoO<sub>3</sub> host lattice at the MO site. We observed that most of the intense peaks around 23.54° in all the samples which imply that the MoO<sub>3</sub> and Zn substituted MoO<sub>3</sub> nanoparticles have preferred growth orientation along (110) direction.



Fig. 2.(a) XRD patterns of (a) Pure and Zn doped MoO<sub>3</sub> nanoparticles.

The results in Table.1 reveal that the crystalline size increases with Zn dopant concentration increases. This indicated that the increase in the doping concentration enhances the crystallinity which may be attributed to that difference in the ionic radii of Mo and zinc are similar ( $r_{Zn}=0.74$ Å:  $r_{Mo}=0.73$ Å) the interstitial incorporation of Zn is possible. Additionally, these changes in crystallinity might be due to the changes in the atomic environment as a result of Zn incorporation into the MoO<sub>3</sub> lattice. There is a slight lattice deformation in the Zn-MoO<sub>3</sub> lattice, as shown in Fig.2(b).



Fig. 2.(b) XRD shift position of pure MoO<sub>3</sub> and Zn doped MoO<sub>3</sub> nanoparticles.

The average grain size and micro-strain of the pure and  $Zn^{2+}$  samples are estimated from the broadening of the diffraction peaks using the debye-Scherrer formula (1) [18-20]:

$$D = \frac{K \lambda}{\beta \cos \theta} \tag{1}$$

where, D is a crystalline size,  $\beta$  - is a full width half maximum and  $\theta$  is the diffraction angle, The structural parameters of dislocation density ( $\delta$ ) and microstrain ( $\epsilon$ ) were resolved using the relations (2) and (3),

$$\delta = \frac{1}{D^2} \tag{2}$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \tag{3}$$

The estimated values of dislocation density ( $\delta$ ) and microstrain ( $\varepsilon$ ) are listed in Table 1 and it is showed that the dislocation density of the samples changed by increasing the doping level.

Pure and Zn doped MoO <sub>3</sub>	2 <del>0</del> (degree)	hkl	d-spacing (nm)	FWHM	Grain Size (D)	Micro- strain(ε) ×10 <sup>-3</sup>	Dislocation- density ×10 <sup>14</sup> cm <sup>-2</sup>	Stacking fault (×10 <sup>-2</sup> )
Pure	23.5410	110	3.7761	0.3859	21.9632	1.648400	0.002073	0.1933
	25.8502	120	3.4438	0.3330	25.5647	1.416173	0.001530	0.1545
	39.1021	150	2.3018	0.3924	22.4389	1.613451	0.001986	0.1494
Zn 5 %	23.6184	110	3.7639	0.4535	18.6919	1.936886	0.002862	0.2272
	26.5000	120	3.3608	0.4000	21.3107	1.698867	0.002202	0.1856
	39.2339	150	2.2944	0.4365	20.1802	1.794045	0.002455	0.1662
Zn 10%	23.7032	110	3.7506	0.4533	18.7031	1.935731	0.002858	0.2271
	25.9038	120	3.4368	0.3410	24.9677	1.450039	0.001604	0.1582
	39.1489	150	2.2991	0.4313	20.4181	1.77314	0.002398	0.1643
Zn 15 %	23.6988	110	3.7513	0.4092	20.7185	1.747425	0.002329	0.2050
	25.9922	120	3.4253	0.3221	26.4370	1.369427	0.001430	0.1495
	39.2379	150	2.2914	0.4051	21.7446	1.664968	0.002114	0.1543

*Table 1.To calculate the structural parameters of Pure and Ni doped MoO*<sub>3</sub>*samples at 400°C for 2 h.* 

It seems that the introduction of Zinc atoms into  $Mo^{6+}$  matrix inhibits the crystallite growth and induces the tensile strain. It is found that ' $\delta$ ' and ' $\epsilon$ ' decreased with the increasing dopant concentration which implied that lattice imperfection and strain were reduced due to an increase in crystallite size. The crystallite size increased by about 5%, 10% and 15% whereas dislocation density and microstrain decreased as Zn doped MoO<sub>3</sub> nanoparticles. In such structure, the interplanar spacing d<sub>hkl</sub> values are related to Miller indices h, k and l, V-volume and lattice parameters by the following relation (4-5)[21]

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$
(4)

$$V = a \times b \times c \tag{5}$$

It can be seen that the values of lattice parameters depend on [Zn]/[Mo] ratio, Table 2 summarizes the calculated lattices parameters values of  $MoO_3$ :Zn samples.

Also, it is found a maximum value of unit cells volume for 5%, 10 and 15% doping level. This phenomenon suggests that the incorporation of Zinc element in the  $MoO_3$  matrix can play an important role to improve the optical and morphological properties of these prepared nanoparticles.

Pure and Zn					Volume of unit
doped MoO <sub>3</sub> (%)	a (Å)	b (Å)	c (Å)	c/a	cell (Å3)
Pure	3.8916	14.1181	3.6768	0.9448	202.0091
Zn 5%	3.9235	14.1669	3.6743	0.9364	204.2342
Zn 10 %	3.9196	14.2086	3.6982	0.9435	205.9606
Zn 15 %	3.8772	14.1663	3.6697	0.9464	201.5587

Table 2. Structural parameters of  $Zn_xMoO_3$  samples at  $400^{\circ}C$  for 2 h.

# **3.2 FE-SEM analysis**

The surface morphology of the synthesized sample of pristineMoO<sub>3</sub> and Zn doped MoO<sub>3</sub> were confirmed by FE-SEM analysis.Fig.3(a-h) unveils the FE-SEM image of prepared MoO<sub>3</sub> and Zn doped MoO<sub>3</sub> samples.As shown in Fig.3(a-b) pure MoO<sub>3</sub>nanorods show up cubic plates, hexagonal nanorods, nanoneedles, nanosheets like structures with the length and diameter of about 45  $\mu$ m and 175 nm which are uniquecollections shape morphology. Fig.3(c-d) 5% Zn doping nanorods with bundle shape of the morphology interconnected images as nanowire with rods like structure. It is evident that some micro-wire, needle shape substructure existed along with the regular bundle nanorods.



SEM images of Zn doped MoO<sub>3</sub>nanostructure with a) and b)nondoped; c) and d) 5 wt% Zn; e) and f) 10 wt% Zn; g) and h) 15 wt% Zn.

Fig.3(e-f) at 10 % Zn doping, it is observed that nanorods with nanoplate is formed morphology. In this substructure, the nanowire shape morphology appeared regularly which is better that of the other morphologies. Finally, at 15% Zn doping concentration, nanorods, nanoneedle and nanopencil shape-like morphology is seen the Fig.3(g-h). It is improved that substructure at 15% Zn doping, nanorods, sheets, plates, disc with regular surface of the Zn:MoO<sub>3</sub> nanostructure are clearly well featured that the morphologywhich suggest that surface diffusion phenomenon plays an important role in the growth process of nanostructure.

Moreover, FE-SEM results suggest that these additives can be successfully converted into nanorods with different shapes of the structure growth are improvement in the Zn concentration adding as well-controlled distinct morphologies that belong to the narrative kind of Zn doped  $MoO_3$  nanostructure easily formed. The elemental analysis is done by EDS Fig.4(a-d) shows the Mo, O, and Zn as the mainelement and the concentration level of  $Zn^{2+}$  ions. No other impuritieswere observed in the EDS profile.



Fig. 4. Energy-dispersive spectra(EDS) of a) pure  $MoO_3$  nanostructure; b) dopped with 5 wt% Zn; c) dopped with 10 wt% Zn; d) dopped with 15 wt% Zn

#### 3.3. Raman analysis

Fig.5(a-d) shows the Raman spectra of pristine  $MoO_3$  and Zn doped  $MoO_3$  samples. The spectra of the  $MoO_3$  and Zn doped  $MoO_3$  nanorods show the main Raman bands around at 144 cm<sup>-1</sup>,177 cm<sup>-1</sup>, 263 cm<sup>-1</sup>, 306 cm<sup>-1</sup>, 355 cm<sup>-1</sup>, 396 cm<sup>-1</sup>, 684 cm<sup>-1</sup>, 837 cm<sup>-1</sup> and 1013 cm<sup>-1</sup>. The peak at144cm<sup>-1</sup> and 177 cm<sup>-1</sup> represents the lattice mode, the weak peak at 263 cm<sup>-1</sup> and 306 cm<sup>-1</sup> is assigned to the twist mode of O=Mo=O wagging vibration. The peaks at 355 cm<sup>-1</sup> and 396 cm<sup>-1</sup> represent the bending and scissoring modes of Mo<sub>3</sub>-O respectively.

It is known as the decrease in raman  $MoO_3$  peaks at 684 cm<sup>-1</sup> represent that stretching mode of triply corresponding oxygen (Mo<sub>3</sub>-O)[22]. The peak at 816 cm<sup>-1</sup> is assigned to the stretching mode of Mo<sub>2</sub>-O in this peak about pristine MoO<sub>3</sub> into Zn concentration increase with the

peak 837 cm<sup>-1</sup> decrease in lattice mode as well as stretching mode of vibration[23]. Further, the last peak at 1013 cm<sup>-1</sup> represents the stretching mode of terminal oxygen (Mo=O).

It can be seen that all the peaks described above couldbe originating in each Raman spectrum of pristine  $MoO_3$  and Zn doped  $MoO_3$ nanorods. The differences of the peak intensities of lattice mode as well as the stretching mode of terminal oxygen (Mo=O)imply that both of the lattice distortion and oxygen defects appear after Zn doped into  $MoO_3$  nanorods.



Fig. 5. Raman spectra of the pure and Zn doped MoO<sub>3</sub>a) MoO<sub>3</sub> b) 5 wt% Zn c) 10 wt% Zn d) 15 wt% Zn nanostructures

### 3.4. FTIR Analysis

FTIR technique is employed to examine the bonding environment of the prepared Zn doped  $MoO_3$  nanoparticles samples. Fig.6(a-d) shows the FTIR spectrum of  $MoO_3$  and Zn doped  $MoO_3$  with different doping concentration of Zn. The spectra of pristine and Zn doped  $MoO_3$ samples recorded in the range 400-4000 cm<sup>-1</sup> are shown in Fig.6(a-d). The result shows that the spectrum contains four important absorption bands. These studies are observed that clearly with a shift in the vibrational frequency mode of  $MoO_3$  nanoparticles ranging from 500-4000 cm<sup>-1</sup> due to the substitution Zinc ions into the  $MoO_3$  lattice structure. The vibrational bands at 1632 cm<sup>-1</sup> are attributed to the bending vibrations of the O-H bond. In the  $MoO_3$  nanoparticles, the CH<sub>2</sub> scissoring mode of SDS can be observed at 1405 cm<sup>-1</sup>[24].

The identified vibrational peaks at 1102 cm<sup>-1</sup>, 982cm<sup>-1</sup> can be attributed to the stretching vibrations of the terminal Mo=O bond indicator of the layered orthorhombic MoO<sub>3</sub> phase. The deformation band of Mo=O at around 1102 and 982 cm<sup>-1</sup> and the FTIR spectra indicating that good quality of our samples. The same absorption bands observed in FTIR spectra of pure and Zn doped MoO<sub>3</sub> nanoparticles of the present investigation are observed.



Fig. 6. FT-IR spectra of the pure and Zn doped MoO<sub>3</sub>a)pure MoO<sub>3</sub>b) 5 wt% Zn c) 10 wt% Zn d) 15 wt% Zn nanostructures

# 4. Photocatalytic studies

### 4.1. Absorbance and visible light driven photocatalytic performance

The photocatalytic activity of pure  $MoO_3$  and Zn doped  $MoO_3$  samples are tested for the degradation of the MB under UV-Visible irradiation during 0,15,30,45,60,75,90 and 100 min. The photo images and UV-Vis absorption curves of the MB solution at different time intervals are shown in Fig.7(a- d).

It can be seen that the intensity of the absorption peak corresponding to MB at 664 nm decreased with time, in accord with the color fading process. The influence of the  $MoO_3$  and Zn doped  $MoO_3$  samples, we can achive that the photocatalytic properties in variation of these parameters can modify the nanoparticles as stoichiometry, and subsequently, several  $MoO_3$  can be produced that some of in these compounds may display excellent photocatalytic properties. The peak maximum for the absorbance spectra of MB (at 664 nm) decreases gradually with increasing irradiation time, allowing the quantification of the photocatalytic discoloration of MB dye. In this color of the solutions like dark blue was turned to a light blue color of MB dye solution respectively.

The samples further tested for degradation efficiency under visible light irradiation with a regular interval of time in 15 mins and the corresponding sequential graph are shown in Fig.7(a-d).



Fig. 7. Photocatalytic degradation profile of (a) MB using pure MoO<sub>3</sub> nanostructure;
(b) MB using pure and Zndoped MoO<sub>3</sub> nanostructur e5 wt% Zn.
(c) MB using pure and Zndoped MoO<sub>3</sub> nanostructure 10 wt% Zn.
(d) MB using pure and Zn doped MoO<sub>3</sub> nanostructure 15 wt% Zn

To clearly understand the photocatalytic efficiency of the prepared pure and Zn doped  $MoO_3$  samples, an assumption has been made that MB dye degradation follows first-order-kinetics and it can be defined in the form of Langmuir–Hinshelwood model as follows (6)

$$\ln(C_0 / C_t = K_{app} t \tag{6}$$

where, k is the rate constant and  $C_t$  and  $C_0$  are the concentrations of MB at initial concentration time and at different time t, respectively [25].

The reaction kinetics for this different morphology of  $\alpha$ -MoO<sub>3</sub> for MB dye degradation is evaluated by plotting the curves between  $\ln(C_0/C)$  versus irradiation time Fig.8 (a-b). It found that pure and Zn doped MoO<sub>3</sub> samples show the rate constant are 0.00012 min<sup>-1</sup>, an increase in the Zn content from 5%, 10%, and 15% show an increase in rate constant from 0.00142 min<sup>-1</sup>,0.00156 min<sup>-1</sup> and 0.00362min<sup>-1</sup>. Thus, the synthesized pure MoO<sub>3</sub> and Zn doped MoO<sub>3</sub> nanoparticles are the promising materials the absolute result shows that the kinetics of MB dye degradation obeyed the pseudo-first-order as reported in Table 3.



Fig. 8 (a) Photo degradation test of the pure and Zn doped  $MoO_3$  nanostructure by using MB. (b) Kinetic degradation test of the pure and Zn doped  $MoO_3$  nanostructure by using MB.

It is found that the MoO<sub>3</sub> and Zn doped MoO<sub>3</sub>with various concentration are exhibited the photodegradation efficiency of 96.21, 78.88, 93.40, and 96.80 % of MB solution under visible light illumination. However, the MB degradation was not observed while in the absence of catalyst and/or light irradiation with the time taken are 100 minutes. The results are demonstrated that the Zn doped MoO<sub>3</sub> nanoparticles possessed exceptional photocatalytic activity towards the MB sample solution. It is also found that the 5 wt%, 10wt% and 15 wt% Zn-doped MoO<sub>3</sub> nanoparticles established in the highest activity in these series of Zn-doped MoO<sub>3</sub> photocatalysts. After 100 min of visible light irradiation, the MB degradation efficiency is found to be 96.21%, 78.88%, 93.40%, and 96.80 % for pure and Zn<sub>x</sub> (x = 5, 10 &15%) doped MoO<sub>3</sub> respectively. This results, indicates that Zn<sub>x</sub> (x = 5, 10 &15%) doped MoO<sub>3</sub> has higher photocatalytic activity for MB degradation. Due to the strong interaction of photo generated electron- holes, super oxide anion and hydroxyl groups can speed up the photocatalytic progression of MoO<sub>3</sub> nanocatalyst and improve its photocatalytic efficiency.

This might be attributed that in  $Zn^{3+}$  doping can supply them with exciting properties inherited from the synergetic effect as well as clearly depend upon the ionic stipulation . We can find out that as in activity of Zn-doped MoO<sub>3</sub> is enhanced tediously withthe  $Zn^{3+}$  content increasing. It can be attributed that among that situation as to relatively high doping concentrations of  $Zn^{2+}$ , which might cause an increased adsorption for MB become the recombination interior of photogenerated carriers, resulting in an increase of photocatalytic efficiency. When Mo<sup>2+</sup> ions are replaced by  $Zn^{2+}$  ions more hydroxide ions are adsorbed on the molybdenum surface defects, these excess hydroxide ions are acting as hole trapping agents, which delay electron-hole recombination reaction and hence enhances the photocatalytic activity. In addition, inhibitionof the (e<sup>-/</sup>h<sup>+</sup>) recombination and the increase in the absorption of visible light of  $Zn^{3+}$  doped MoO<sub>3</sub> is another considerable feature. In this clearly, photocatalyticactivity of MB using Zn-doped MoO<sub>3</sub> catalyst under visible light irradiation.

Materials	K (rate constant) min <sup>-1</sup>	R <sup>2</sup>	Maximum degradation efficiency (%)
MoO <sub>3</sub>	0.00012	0.9831	96.21
Zn 5%	0.00142	0.9491	78.88
Zn 10%	0.00156	0.9809	93.40
Zn 15%	0.00362	0.9101	96.80

Table 3. Stakeout the pseudo-first order rate constants (K),  $R^2$  values and maximum degradation (%) of the pure and Zn doped  $MoO_3$  nanoparticles.

They are observed only 96.80% degradation efficiency of Zn-doped MoO<sub>3</sub>catalyst. The above results, our newly prepared Zn-doped MoO<sub>3</sub>catalyst are showed highest the photocatalytic behavior towards Fig.8(a-b).

# 4.2. Recycle test

To confirm the stability and reusability of  $MoO_3$  and Zn doped  $MoO_3$ nanoparticles, we are conducted recurring photocatalytic tests running under the same experimental conditions are shown in Fig.9(a-b). Especially it explains the photo-stability of Zn doped  $MoO_3$  catalyst, more than 90% degradation of MB is still achieved after seven cycles of photodegradation, only small variation is observed in the photocatalytic efficiency. This suggest that Zn doped  $MoO_3$ samplesphotocatalyst exhibit sufficient stability during photocatalytic reaction.



Fig. 8. (a) recycling test of MB using Pure  $MoO_3$  nanostructure. (b) recycling test of MB using Zn doped  $MoO_3$  nanostructure.

# 4.3. Photocatalytic mechanism

It is concluded from Fig.10 that MoO<sub>3</sub> and Zn doped MoO<sub>3</sub>nanoparticles show enhanced photocatalytic activities towards the photodegradation of MB.



Fig.10. Schematic representation for photocatalytic mechanism of pure and Zn doped  $MoO_3$  catalyst under visible light irradiation.

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The results, a possible photocatalysis mechanism is improved that the efficiency of Zn doped  $MoO_3$  nanoparticles can be explained based on of the excitation of an electron from the valance band to the conduction band by absorbing the light of suitable energy resulting from the generation of equal number of hole in the valance band.Firstly,the dye adsorbs on the surface of  $MoO_3$  nanophotocatalysts. When the energy (hu) of a photon is equal to or higher than the bandgap energy of the  $MoO_3$  semiconductor materials, an electron (e<sup>-</sup>) in the VB can be excited to the CB with the simultaneous generation of a hole (h<sup>+</sup>) in the VB.

The photogenerated electrons and holes can react with the adsorbed  $O_2$  and  $H_2O$  to form the reactive oxygen species (ROS), in this superoxide anion ( $\cdot O^2$ -), hydroxyl radical ( $\cdot OH$ -) and  $H_2O_2[26]$ .The ROS are strong oxidative species and can oxidize dye and other organics absorbed on the active sites of the photocatalysts finally into the CO<sub>2</sub> and  $H_2O$  and mineral acids. The possible mechanism of photocatalytic degradation for the transition metal (Zn)doped MoO<sub>3</sub> photocatalysts are proposed as follows(7-12):

$$MoO_3 + h\upsilon \rightarrow MoO_3 (eCB^- + hVB^+)$$
(7)

$$e_{CB}^- + 0 \rightarrow 0^{-2} \tag{8}$$

$$Zn^+ + e_{CB}^- \to Zn \tag{9}$$

$$h_{VB}^+ + OH^- \to .OH \tag{10}$$

$$0^{-2} + 2H^+ \rightarrow 2. \ OH$$
 (11)

$$OH + MB \rightarrow Degradation \ products$$
 (12)

Overall since today, a few pieces of research have been made on Zn doped  $MoO_3$ nanophotocatalyst for degradation of organic dye of the MB in visible light irradiation in Table 3.We can evaluate the value of  $MoO_3$  and Zn doped  $MoO_3$ and found out the very small variation inbetween them. The  $Zn_x$  (x = 5, 10 &15%) doped in  $MoO_3$ has attained one of the right efficiency for degradation of MB was obtained.Thus, the separation of the charge carriers is attributed to such trapping by Zn dopant in  $MoO_3$ . Subsequently, it enhanced the yield of •OH quantities in the degradation of MB, which further improved the photocatalytic activity of Zn/MoO<sub>3</sub>.

# 5. Conclusions

In this work efficient  $MoO_3$  and Zn doped  $MoO_3$  based visible-light photocatalysts developed by using asimple wet chemical method.Our method would be important for the application of  $MoO_3$  photocatalytic materials due to the advantage of its simplicity,low cost, high production and excellent performance of the resulting products. Various concentrations of wt% of highly active Zinc-tailored and original  $MoO_3$  photocatalysts were prepared. The structural and morphological properties of the resultant materials were characterized by XRD, FTIR, FESEM, EDS and Raman studies, Photocatalytic activity of all samples were determined by analyzing the degradation of Methylene blue in the presence of the pure  $MoO_3$  and Zn doped  $MoO_3$ nanopartices. Zn concentration caused by the material to show considerable enhancement in the photocatalytic activity of  $Zn_x$  (x = 5, 10 &15%).

Zinc was considered as the optimum concentration. Also the effect of initial MB concentration, the amount of catalyst and the pH of solution on photo degradation of MB was investigated. The mechanism of photocatalytic activity was studied and it was found that the presence of Zn facilitates the interfacial charge transfer processes. These results show that Zinc has

an important role to play in the trapping of electrons in these materials. Moreover, oxygen defects play a key role in enhancing the photocatalytic efficiency. Therefore these materials applications could be extended to the development of a photocatalyst which is applicable in visible region.

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