



World Scientific News

An International Scientific Journal

WSN 94(2) (2018) 276-286

EISSN 2392-2192

Natural sun-light assisted photocatalytic and electrocatalytic activity of $\text{WO}_3\text{-TiO}_2$ novel nanomaterial

J. Kamalakkannan^{1,*}, N. Balraj²

¹PG and Research Department of Chemistry, Sri Vinayaga College of Arts Science, Ulundurpet - 637 002, Villupuram, India

²PG and Research Department of Economics, Sri Vinayaga College of Arts Science, Ulundurpet - 637 002, Villupuram, India

^{1,2}E-mail address: dr.jkamalakkannan@gmail.com , balraj.economics@gmail.com

ABSTRACT

The $\text{WO}_3\text{-TiO}_2$ novel nanomaterial was synthesized by precipitation method and sonication technique. The nanomaterial for the degradation of malachite green (MAG) dye under natural sun light irradiation. The synthesized nanomaterial is characterized by HR-SEM with EDX, PL and UV-Vis DRS analysis. The photodegradation of MAG at various parameters are reported. The mechanisms of dye degradation in natural sun light explain the higher photocatalytic activity of the catalyst. The result indicates the advantage of wastewater treatment by it. The electrochemical study from DSSC analysis showed increased current by $\text{WO}_3\text{-TiO}_2$ nanomaterial. It was proposed that the catalyst was found to be stable and reusable.

Keywords: Photocatalysis, Sun light, Reusability

1. INTRODUCTION

Malachite green is one of the most parts of materials for textile, dyeing, leather, pulp, paper, plastic, food and cosmetics industries [1]. TiO_2 is used in plastics paint and paper industries, for an outstanding to excellent optical properties and well-organized environmental

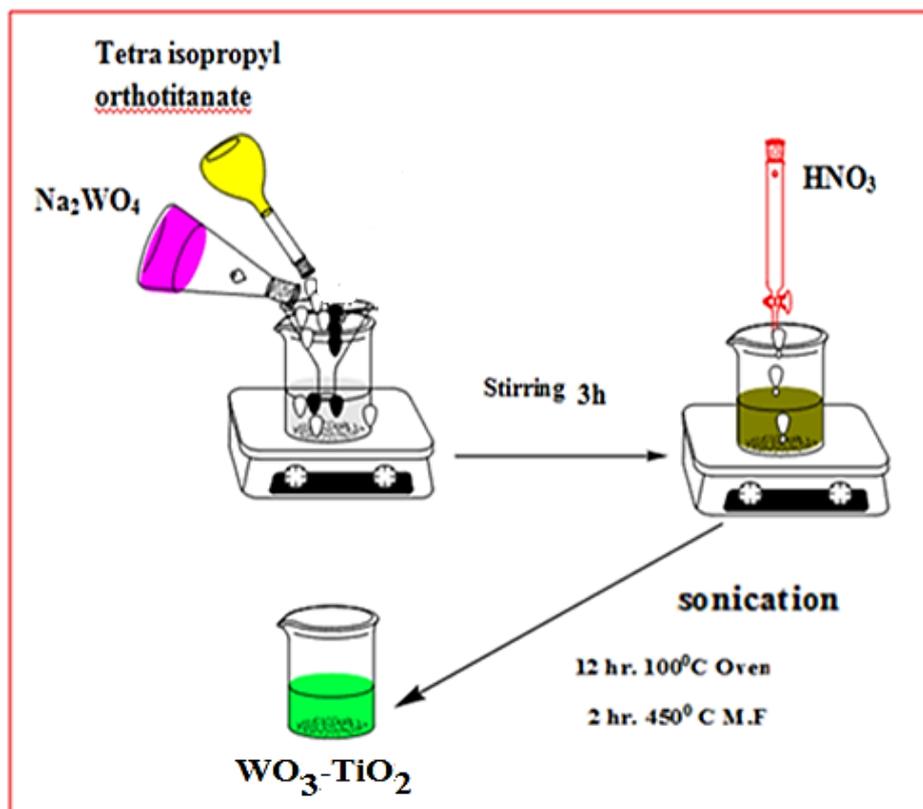
pollutants [2-5]. This recently metal complex oxide catalyst such as Ag_3VO_4 [6], BiWO_6 [7], ZnWO_4 [8] WO_3/TiO_2 [9], $\text{InCrO}_4\text{-TiO}_2$ [10], TiInCrO_6 [11], $\text{InMoO}_3\text{-TiO}_2$ [12] and MCrO_4 (M = Ba and Sr) [13,14] have been reported for the degradation of environment organic pollutants.

2. EXPERIMENT

2. 1. Synthesis of $\text{WO}_3\text{-TiO}_2$ nanomaterial

$\text{WO}_3\text{-TiO}_2$ nanomaterial was synthesized by the precipitation method and sonication technique. The amount of Sodium tungstate (Na_2WO_4) was first dissolved with deionized water. The resulting solution WO_3 was added but dropping by drops into tetra isopropyl orthotitanate solution at room temperature. The above solution was vigorous stirring for 3h and than three drops of con HNO_3 and 5 mL deionized water were added. The obtained solution was stirred for 2h and ultra-sonication for 20 min, until precipitate was formed. The precipitate was washed with deionized water and ethanol. Than it was collected and dried in an oven at 100°C for 12h. The resulting powder sample was calcined 500°C for 2h to achieve $\text{WO}_3\text{-TiO}_2$ nanomaterial is economically very very low cost and high stability elevated material is shown in Scheme 1.

2. 2. Chemicals



Scheme 1. Schematic representation for preparation of $\text{WO}_3\text{-TiO}_2$ nanomaterial.

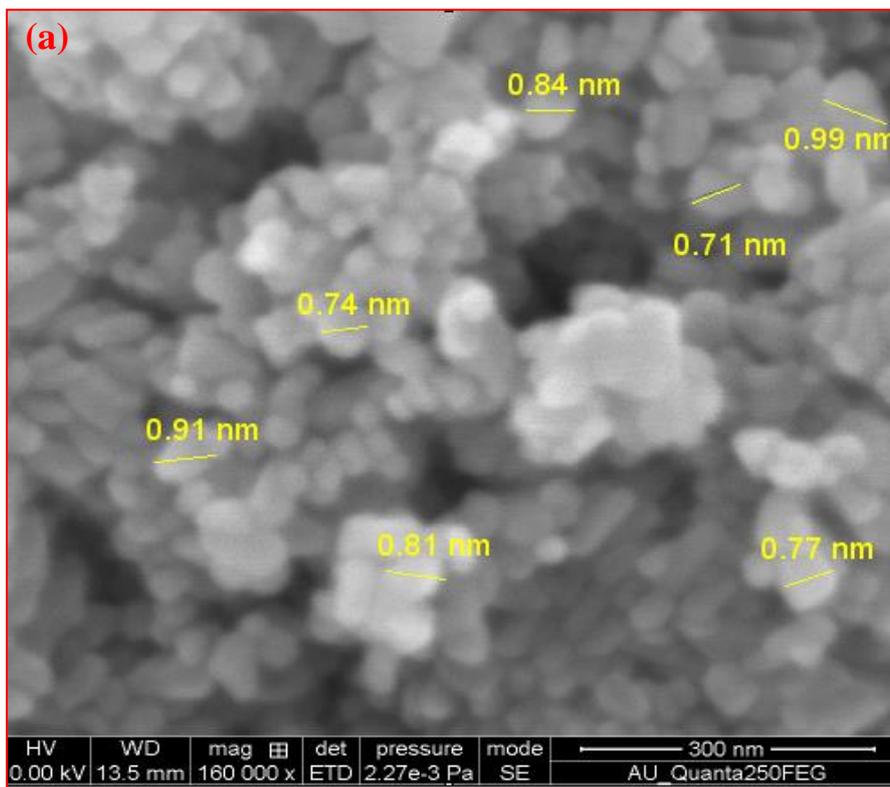
Tetra isopropyl orthotitanate ($C_{12}H_{28}O_4Ti$), Sodium tungstate (Na_2WO_4), nitric acid (HNO_3 -65%), were used as such. A gift sample of TiO_2 -P25 (80% anatase). Malachite green (MEG) are used, ethanol were the guaranteed reagents of Sigma Aldrich. The aqueous solutions were prepared by using double distilled water.

2. 3. Analytical Methods

The Scanning electron microscopy (HR-SEM) with elementary dispersive X-Ray analysis (EDX) was carried out on a FEI Quanta FEG 200 instrument with EDX analyzer facility at 25 °C. The sample was prepared by placing a small quantity of prepared material on a carbon coated copper grid and allowing the solvent to evaporate. Photoluminescence (PL) spectra at room temperature were recorded using a Perkin-Elmer LS 55 fluorescence spectrometer. The crystallinity of sample was characterized by an UV-Vis DRS and the direct band gap energy was analyzed by UV-visible (Shimadzu UV-1650 PC) spectrophotometer. UV spectral measurements were done using a Hitachi-U-2001 spectrometer. Fulorescence technique with coumarin (1 mM of 4-hydroxycoumarin) were measured on a Hitachi F-7000 fluorescence spectrophotometer. The Photovoltaic properties of the material was characterized by recording the photo current voltage (J-V) curve under illumination of A.M.1.5 (100 Mw/cm²).

3. RESULTS AND DISCUSSION

3. 1. Structural studies



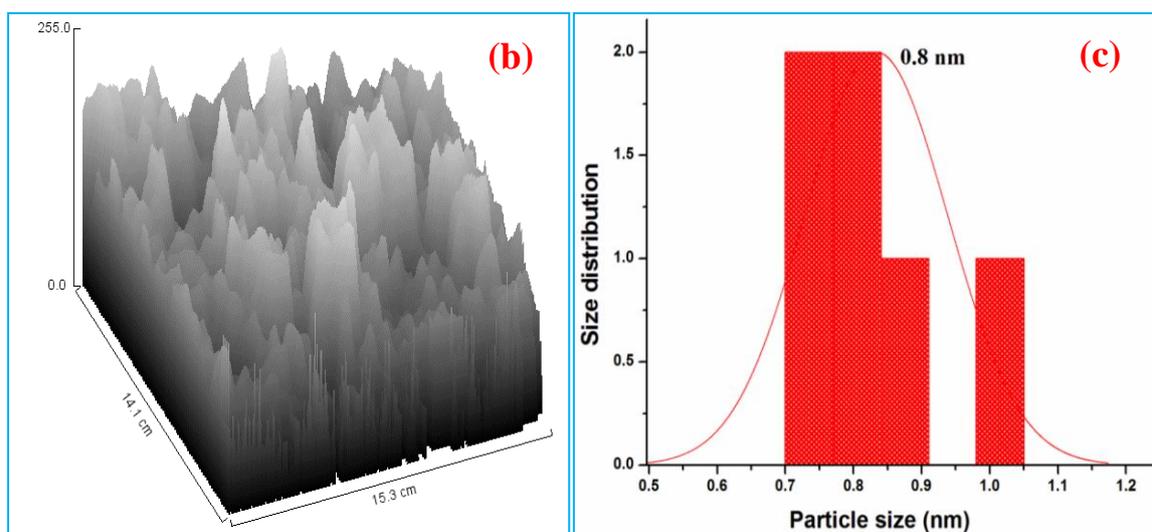


Fig. 1. HR-SEM image of (a) $\text{WO}_3\text{-TiO}_2$ (b) Surface plot and (c) Particle size in selected area highlighted in Fig. 1a

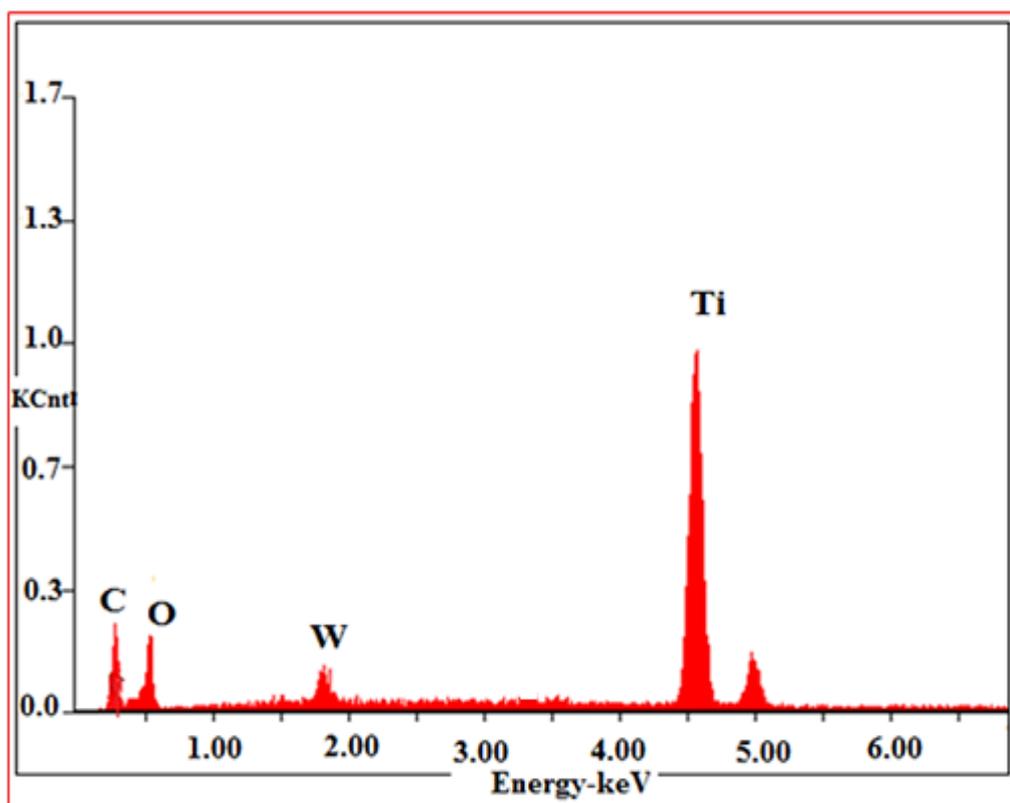


Fig. 2. EDX analysis of $\text{WO}_3\text{-TiO}_2$ nanomaterial

HR-SEM – analysis

Scanning electron microscopic image of supstract temperature at 500 °C respectively. The average grain size 300 nm as show in Fig. 1(a) 160 K. SEM micrographs reveal that the particles are nano spherical cage in chain shape. In TiO₂ the small particles have been agglomerated and the particles were slightly better in the size. The average particle size of WO₃-TiO₂ is 0.8 nm, hence WO₃-TiO₂ is effective due to less agglomeration which produces is more in the surface area so the high photocatalytic activity. Fig. 1b and 1c image profile and plot profile respectively. EDX analysis is shown in (Fig. 2). The presence of Ti, W and O is confirmed from the peaks at 4.5 KeV, 1.8 KeV and 0.8 KeV various respectively.

3. 2. The PL spectrum

The PL spectrum of prepared TiO₂ and WO₃-TiO₂ were emission band at 525 nm. The PL emission intensity decrease in WO₃-TiO₂ when compared to prepared TiO₂ is shown in Fig 3a and b respectively. This activity electron transfer is faster than the recombination of electron and hole in the valence band this lower energy state of WO₃. Thus due to definite quenching of electron and hole pairs in mixed catalyst of TiO₂ and calculated by was confirmed photocatalytic activity is increased.

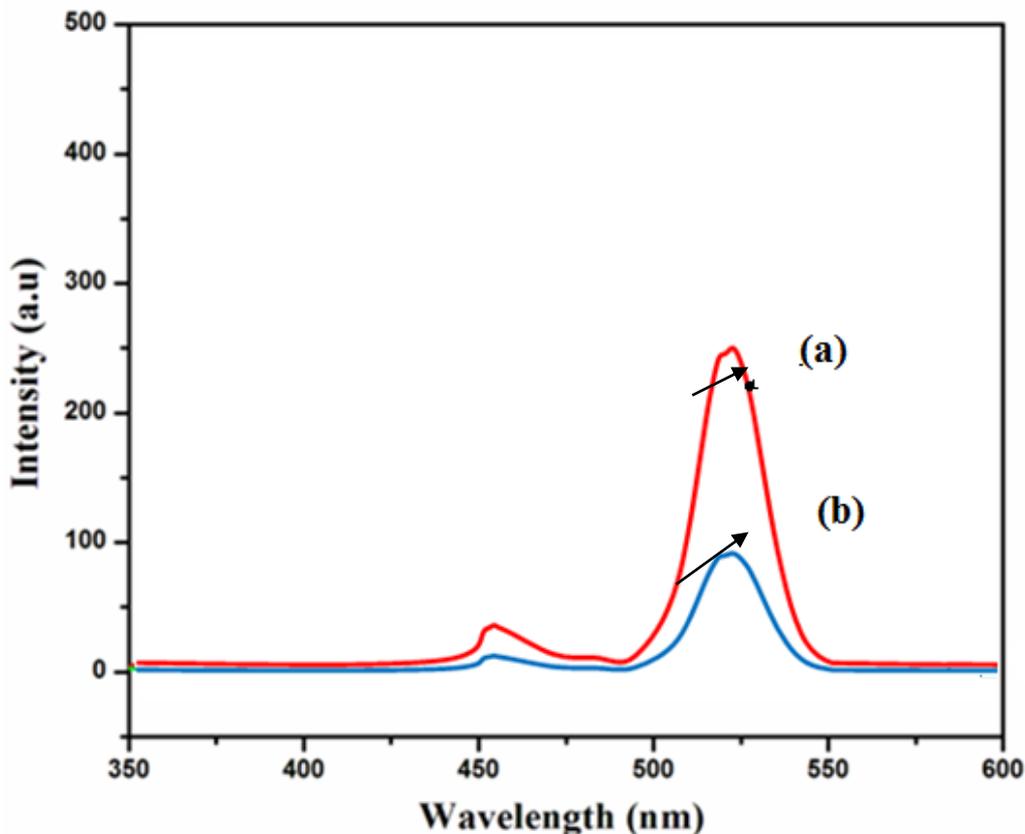


Fig. 3. Photoluminescence spectra of (a) TiO₂ (b) WO₃-TiO₂ nanomaterial

3. 3. UV-vis DRS Spectrum

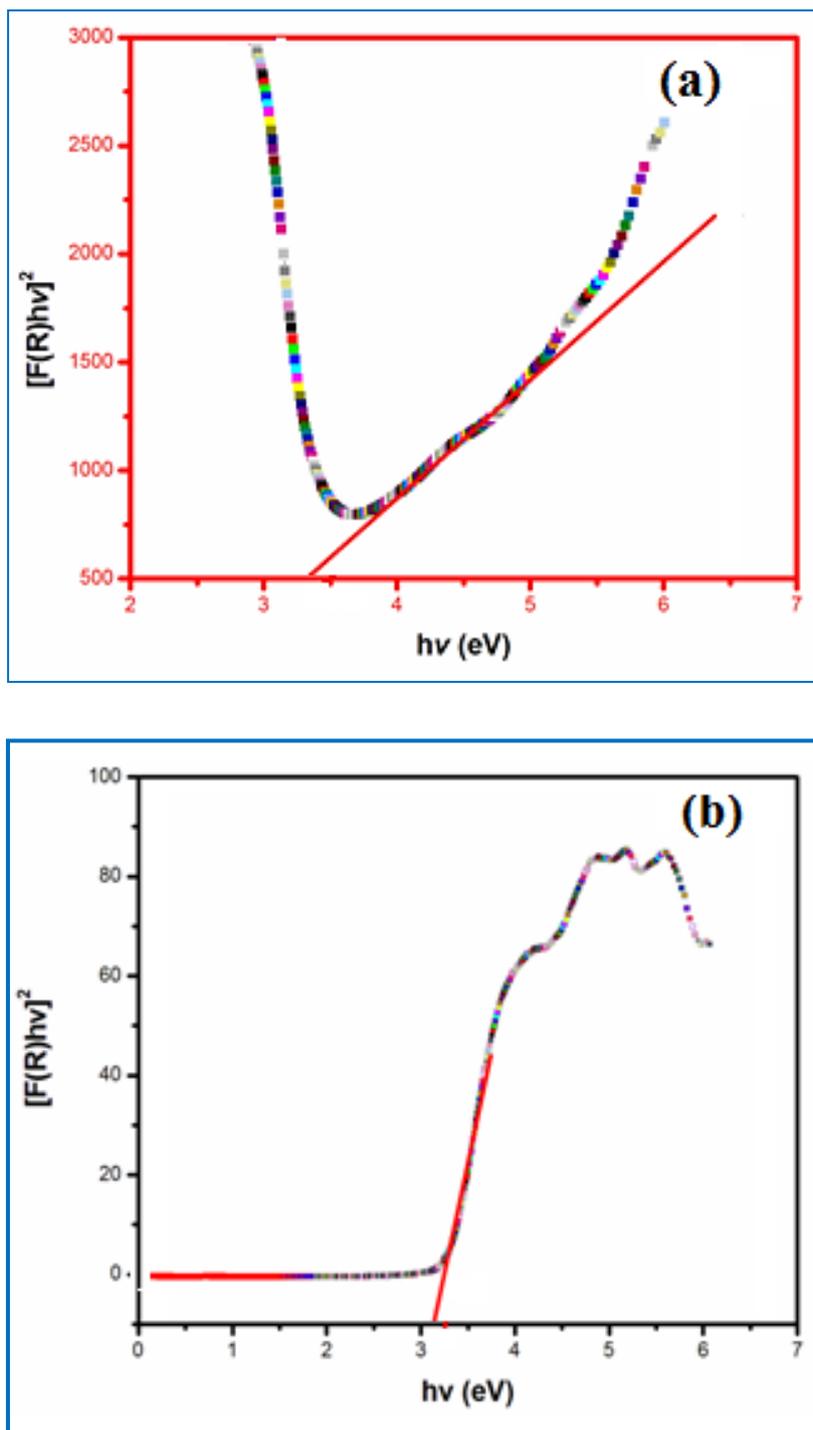


Fig. 4. Plot of Kubelka–Munk versus energy of the light absorbed of the (a) TiO_2 and (b) WO_3-TiO_2 nanomaterial

The UV-Vis DRS Spectrum of prepared TiO₂ and WO₃-TiO₂ as shown Fig. 4 a and b W strength covalently interacts with TiO₂ and decreases its band gap. WO₃-TiO₂ caused is a red shift in absorption edge from 400 to 422. The result indicate in UV-Vis spectrum in the diffuse reflectance mode (R) were trace formed to the Kubelka-Munk function F(R) to the wole the degree of light absorption from diffusion. The band gap energy was obtained from the plot of the modified Kubelka-Munk function (F(R) E)^{1/2} Vs the energy of the absorbed light (E) (eq 1) is shown in Fig. 4.

$$(F(R) \cdot E)^{\frac{1}{2}} = \frac{(1-R)^{1/2}}{2R} Xhv \text{ ----- (1)}$$

The final result indicates was band gap energy of the synthesized TiO₂ and WO₃-TiO₂ are 3.3 eV and 3.1 eV correspondingly. The lower band gap energy supports the higher photocatalytic activity [15-17].

3. 4. Photocatalytic study

3. 4. 1. Degradation of MAG dye

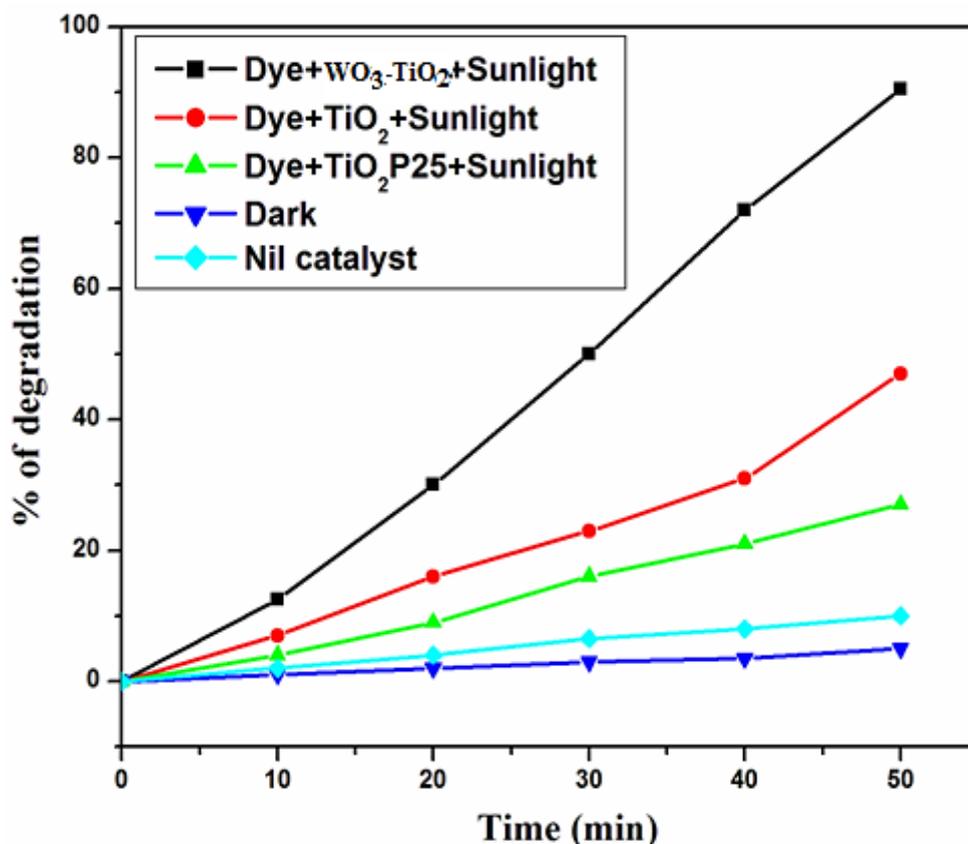
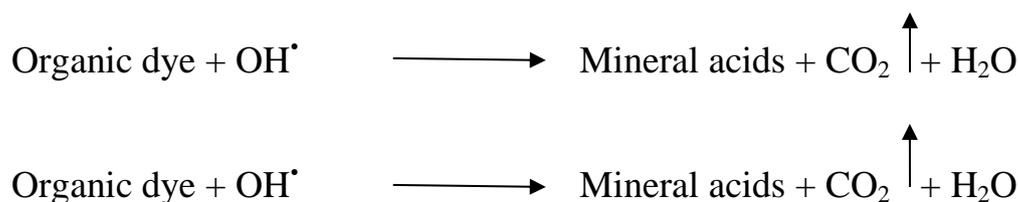
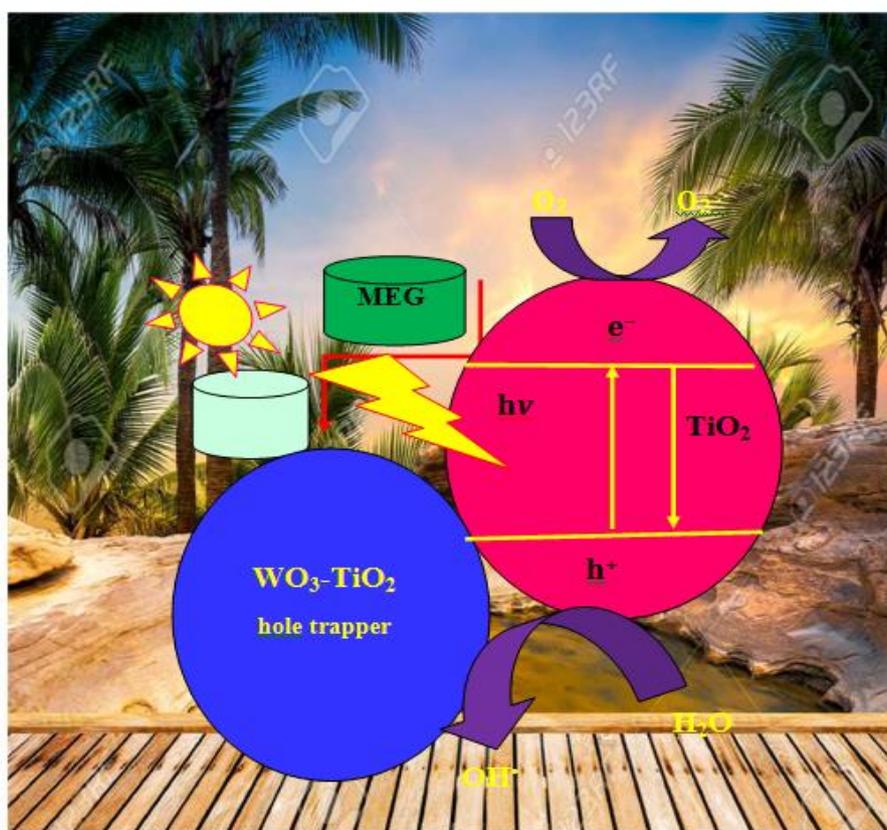


Fig. 5. Primary analysis under natural sun-light irradiation

WO₃-TiO₂ can be degradation of the MAG in aqueous solution up to 90.5 % when compared that of TiO₂ (47 %), TiO₂ P25, nil catalyst (10 %) and dark (5 %) The reaction of MAG undergoes % of degradation under Sun-light irradiation efficiency of MAG. The photocatalytic degradation is in the order of the catalyst material used WO₃-TiO₂ > TiO₂ P25 > TiO₂ > Nil catalyst > Dark shown in Fig. 5

3. 4. 2. Photocatalytic mechanism

Future for WO₃-TiO₂ nanomaterial under nature sun light as shows (Scheme 2). Wole generated Titanium dioxide by nature sun light trapped by WO₅. This hole trapping is faster than compared to electron-hole recombination of TiO₂ this proofed in OH[•] generation. These OH[•] and super-oxide radical on formed by electron in CB of TiO₂ powerful oxidizing agents photodegred the dye without difficulty



Scheme 2. WO₃-TiO₂ Photodegradation and Mineralization of MEG under natural sun light irradiation.

3. 4. 3. Reusability of the catalyst

The most important advantage of nanomaterial stability and reusability. The reusability of $\text{WO}_3\text{-TiO}_2$ was photodegradation tested by transporation out four successive cycles of MAG photodegradation under sun light result are shown in Fig. 6. The whole degradation was obtained in 50 min for the Ist (100), IInd (98), III^d (97) runs, but IVth and Vth runs gave 95 % degradation. There no considerable loss of activity up to IVth and Vth runs, the catalyst is stable and reusable.

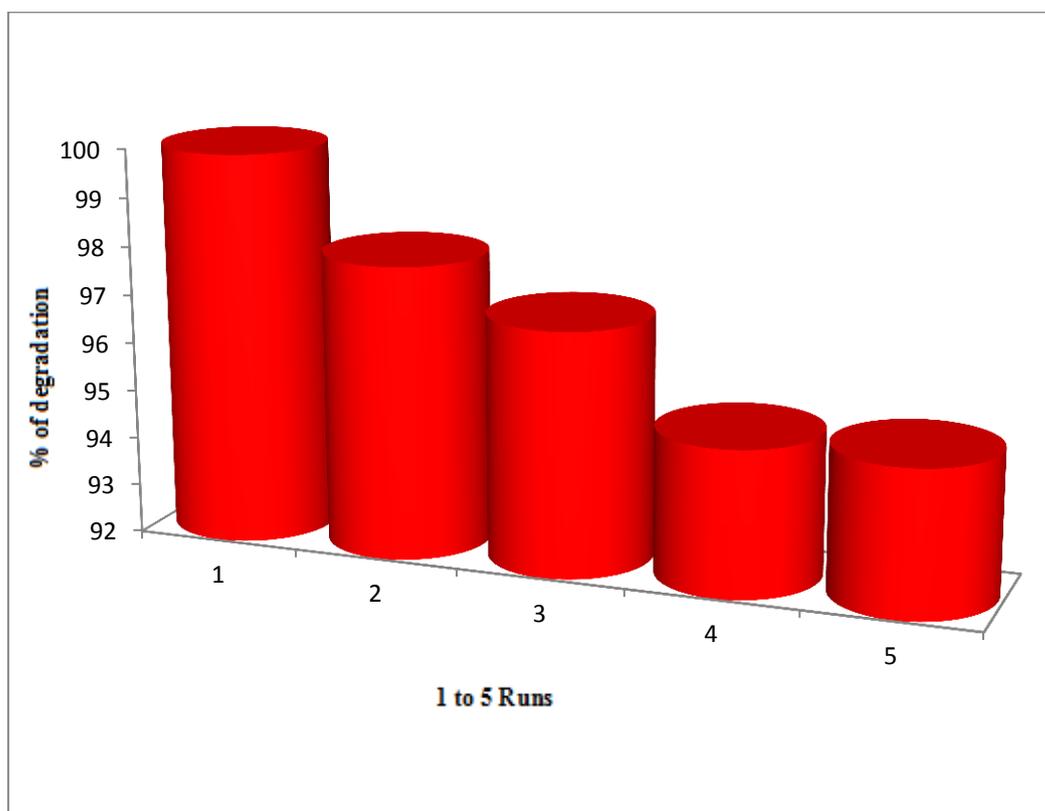


Fig. 6. Stability and Reusability on MAG dye degradation; (a) $\text{WO}_3\text{-TiO}_2$ nanocomposite material

3. 5. Photovoltaic properties

Fig. 7 shows the photo current voltage (J-V) characteristics of the dye Sensitized Solar cell (DSSCs). The prepared TiO_2 and $\text{WO}_3\text{-TiO}_2$ act as photoelectrode are coated on Fluorine doped Tin oxide (FTO-plate) glass substrate. The routine solar cell is fabricated with TiO_2 and $\text{WO}_3\text{-TiO}_2$ with Ruthenium dye (535-bis TBA, N719).

From the data, it is clear that (N719) $\text{WO}_3\text{-TiO}_2$ based cell gives the most brilliant performance with the use of dye as sensitizer reunite the highest value of short-circuit current density, J_{sc} (3.5 mA/cm^2), open-circuit voltage, V_{oc} (500 mV), fill-factor, FF (0.94 and efficiency, η (1.7%). It is observed that the effectiveness of doped photoelectrode based cell is much higher than TiO_2 and this is due to [5,25].

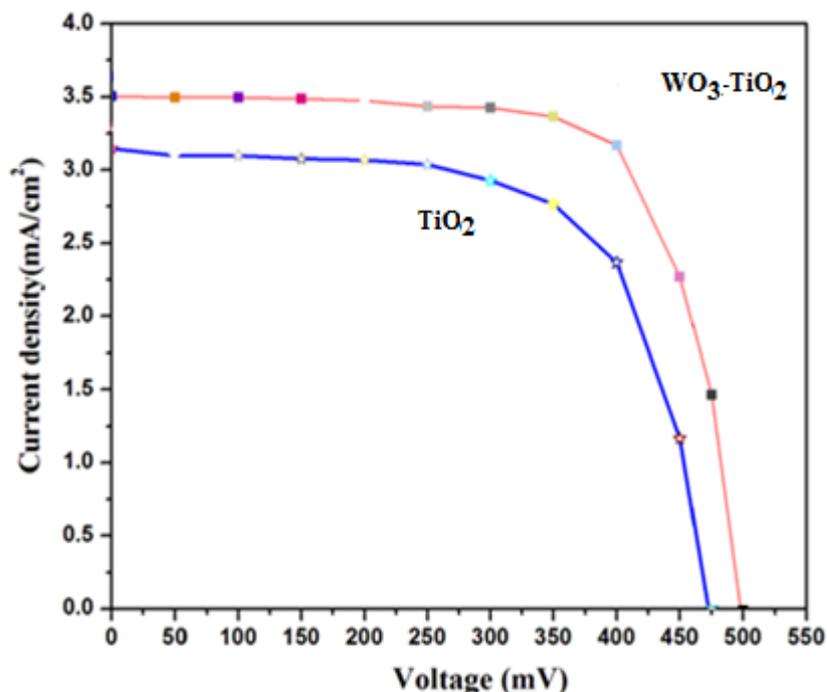


Fig. 7. Current density–voltage (J–V) curves for the DSSCs fabricated from nanomaterial by TiO₂ and WO₃-TiO₂ nanomaterial

4. CONCLUSION

WO₃-TiO₂ nanomaterial was synthesized by precipitation method. It was characterized by HR -SEM image showed spherical shaped structure with EDX spectra revealed the presence of Ti, W and O in the catalyst. PL analysis of a low electron and hole recombination rate implies a lower luminescence emission intensity and higher photocatalytic activity. WO₃-TiO₂ nanomaterial was higher photocatalytic activity when compared that of TiO₂ nnomaterial on MAG dye under sun-light irradiation. The WO₃-TiO₂ higher Photovoltaic property of the Dye Sensitized Solar Cells (DSSCs) was observed. WO₃ -TiO₂ nanomaterial is economically very low cost and high stability and nanomaterial shows elevated for expanded important industrial applications. The result indicates that the prepared nanomaterial is stable and reusable.

References

- [1] O. Gulnaz, A. Kaya, F. Matyar and B. Arikan, *J. Hazard. Mater.* 2004, 108, 183-188.
- [2] H. K. Shon, S. Phuntsho and S. Vigneswaran, *Desalin. Water Treat* 225, 235–248 (2008).

- [3] J. Kamalakkannan, V. L. Chandraboss, S. Prabha and S. Senthilvelan. *RSC Adv*, 5, 77000–77013 (2015)
- [4] H.K. Shon, S. Phuntsho, S. Vigneswaran, *Desalin. Water Treat* 225, 235–248 (2008)
- [5] Jayaraman Kamalakkannan, Vijayaragavan Lenin Chandraboss, Selvaraj Prabha, Bala Karthikeyan, Sambandam Senthilvelan, *J Mater Sci: Mater Electron*, DOI:10.1007/s10854-015-4050-8
- [6] H. Xu, H. Li, L. Xu, C. Wu, G. Sun, Y. Xu, J. Chu, *Ind. Eng. Chem. Res.* 48, 10771-10778 (2009)
- [7] C. Zhang, Y.F. Zhu, *Chem. Mater.* 17, 3537–3545 (2005)
- [8] G. Huang, Y. Zhu, *Cryst Eng Comm* 14, 8076–8082 (2012)
- [9] Papp J. Soled S. Dwight K. *Chem Mater.* 6, 496-500 (1994)
- [10] J. Kamalakkannan and S. Senthilvelan, *World Scientific News*, 62, 46-63 (2017)
- [11] J. Kamalakkannan, V.L. Chandraboss, B. Loganathan, S. Prabha, B. Karthikeyan, S. Senthilvelan, *Appl. Nanosci.* doi:10.1007/s13204-015-0474-y (2015).
- [12] J. Kamalakkannan, V.L. Chandraboss, S. Prabha, B. Karthikeyan, S. Senthilvelan, *Can. Chem. Trans.* 3, 327–339 (2015)
- [13] Yin, J Z, Zou J, Ye Yin J, Zou Z; Ye J. *Chem. Phys. Lett*, 378, 24-28 (2003).
- [14] Tanmay Ghorai, Niladri Biswas. *J. Mater. Res. Technol* 2, 10-17 (2013)
- [15] Subash, B.; Krishnakumar, B.; Velmurugan, R.; Swaminathan, M.; Shanthi, M. *Catal. Sci. Technol.* 2, 2319-2326 (2012).
- [16] Neppolian, B.; Wang, Q.; Yamashita, H.; Choi, H. *Appl. Catal. A: Gen*, 333, 264–271 (2007)
- [17] Swetha S., Balakrishna R. G. *Chin. J. Catal*, 32, 789-794 (2011).
- [18] Y. Zhang, L. Wang, B. Liu, J. Zhai, H. Fan, D. Wang, Y. Lin, T. Xie, *Electrochimica Acta* 56, 6517-6523, (2011)