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# W/Mo-doped TiO<sub>2</sub> for photo catalytic degradation of methylene blue

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*Abstract- Films of 1.0 wt% tungsten- and tungsten-molybdenum-doped TiO<sub>2</sub> on glass substrates were prepared by a simple sol-gel dip-coating using titanium peroxide gel and employed for photo catalytic degradation of methylene blue (MB) in sunlight. The influences of the dopants and annealing temperature on the size, morphology and optical properties of TiO<sub>2</sub>-based photo catalysts were investigated. Mo/W-codoped TiO<sub>2</sub> films heat-treated at 500°C showed the highest photo catalytic activity for degradation of methylene blue in sunlight. The photo catalytic study test showed this film to be very effective for adsorption and degradation of methylene blue. Almost 100% discoloration of methylene blue occurred within one hour sunlight irradiation. . Photo catalytic activity was recorded up to 10 cycles showing no significant reduction in activities.*

**Keywords:** W-Mo/TiO<sub>2</sub>; thin film; Methylene blue; photo catalyst.

## I. INTRODUCTION

Dyes are an important group of chemicals among different pollutants being released in the ecosystem. The use of dyes by many industries, such as textile, paper, rubber, plastics and cosmetic to colour their products is a common activity. Since these industries also use substantial amount of water in their processes, this results in highly colored effluent. During a chemical or biological reaction pathway, these dye compounds not only reduce the dissolved oxygen in water but also release some toxic compounds which are harmful to aquatic life. Increased environmental awareness and the relevant EPA restrictions on the organic content of industrial effluents makes it necessary to eliminate dyes from wastewater before they are discharged in the mainstreams [1-3].

Among the various types of dyes, methylene blue (MB) is one of the most commonly used substances for colouring cotton, wood, paper stocks, and silk [4]. It is utilized in medicine as well. Severe exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, mental confusion, painful micturition, methemoglobinemia, jaundice and quadriplegia, and tissue necrosis in humans [5-9]. Considering the above critical negative impacts and taking into account that many dyes including MB reaching the water source are difficult to decompose, therefore, it is important to remove these pollutants from wastewater before their final disposal.

In recent years, heterogeneous photo catalysts such as TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, CdS, GaP and ZnS offer high potential for elimination of ambiguous refractory organics. Among the semiconductor catalysts, titanium dioxide (TiO<sub>2</sub>) has received the greatest interest in photo catalysis technology. The TiO<sub>2</sub> is the most active photo catalyst under photon energy of 300 nm <math>\lambda</math> <math>< 390</math> nm and remains stable after repeated catalytic cycles, whereas CdS or GaP are degraded and to produce toxic products [10]. In addition, the multi-faceted functional properties of TiO<sub>2</sub> catalyst, such as their chemical and thermal stability or resistance to chemical breakdown and their strong mechanical properties have promoted its wide application in photo catalytic water treatment [11]. Since the band gap energy (E<sub>g</sub>) of TiO<sub>2</sub> is high, considerable efforts have been directed to extend the absorption edge of TiO<sub>2</sub> towards the visible part of the spectrum in the last three decades. Different solutions have been investigated and proposed by scientists such as doping titania with metallic [12-14] and non-metallic species [15-17] and loading other semiconductors [18-19] on the surface or into the crystal lattice of titania.

Titania powder is used for photo catalytic degradation of pollutants in aqueous solution using a photo catalytic reactor and it is difficult to separate them. Thin films of titania as an active photo catalyst would be an attractive alternative to overcome the catalysts separation problems. TiO<sub>2</sub> thin films have been receiving much attention in the past years as their chemical stability, high refractive index, and high dielectric constant allow their use as components in optoelectronic devices, sensors and photo catalysis [20].



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Titanium oxide films have been made by a variety of techniques. Among the different methods for the preparation of thin  $\text{TiO}_2$  electronic layer, sol-gel method has many advantages; particularly the possibility of producing large surfaces and the method is also suitable for deposition on different substrates [21-25]. This process is carried out at room temperature [26]. The sol-gel technique has emerged as one of the most promising techniques as this method produces samples with good homogeneity at low cost [27]. It is particularly attractive for thin films fabrication, because the liquid precursor can easily be applied on a substrate by dipping.

In this work,  $\text{TiO}_2$ , W-doped  $\text{TiO}_2$ , Mo/ $\text{TiO}_2$  and Mo/W-codoped  $\text{TiO}_2$  films on glass substrates were synthesized, characterized, and applied for photo catalytic sunlight degradation of methylene blue (MB). Here we are reporting synthesizing of  $\text{TiO}_2$  thin film doping with above mentioned metals with this method for the first time. Also the codoped MoW/ $\text{TiO}_2$  for the first time successfully used for treatment of dyes such as methylene blue, malachite green and methyl violet in this study.

Peroxopolytungsten acid for doping of  $\text{TiO}_2$  was obtaining via dissolution of tungsten acid into hydrogen peroxide which is reported elsewhere [28] Di Paolo et al (2002) prepared W, V and molybdenum doped  $\text{TiO}_2$  [29]. In another study later they concluded that  $\text{TiO}_2/\text{W}$  (which was prepared by using the wet impregnation method) was the most efficient sample for the photo degradation of benzoic acid [30]. The W addition causes a red shift of the optical absorption related to a decrease of the band-gap energy, which increases the photo catalytic activity of titania after UV radiation as well as in the visible-light region with respect to undoped Titania [31].

Matrilas and his colleagues found that Molybdenum species supported on anatase were less active for oxidation of toluene than vanadium and, in addition, the presence of molybdenum inhibited the interaction between vanadium and anatase leading to poor vanadium dispersion [32]. Haber et al (2008) reported that many aromatic compounds were effectively oxidized on  $\text{MoO}_3/\text{TiO}_2/\text{Ti}$  electrodes in either aqueous or non-aqueous (acetonitrile) solutions [33]. To best of our knowledge the photo catalytic activity of codoped W-Mo/ $\text{TiO}_2$  is not reported elsewhere.

## II. EXPERIMENTAL

### A. Preparation of $\text{TiO}_2$ and its doping with molybdenum, tungsten and molybdenum-tungsten

The sol-gel solution was prepared similar to the procedure explained in our earlier work [34], briefly as follows: 4.2 gram titanium but oxide was hydrolyzed by adding 100 ml distilled water and washed out 2 times (every time with 50 ml) and thus produced water-alcohol solution was removed by simply decantation of water from the formed white precipitate. To this formed white precipitate 15 ml of 30% hydrogen peroxide solution was added to produce the sol of titanium oxide; simultaneously 65 ml of water was added to this solution with continuous stirring to maintain the temperature of reaction and dilute the solution. When this solution got visibly viscous, the glass rings and slides were dipped into the solution and pulled up for single coating before gelling (gelling of solution at room temperature take place between 30-60 minutes). A known amount of the glass rings and slides also left in the solution till it get dry in the room temperature during 3-4 days (which gives the multilayer of coating). Process variables such as solution concentration ( $\text{Ti}(\text{OC}_4\text{H}_8)_4$ :  $\text{H}_2\text{O}_2$ :  $\text{H}_2\text{O}$ ), gelling time (30min) and annealing time (3hours) remained constant. The dip coated glass rings for photo catalytic test and slides for characterization were left to dry at ambient temperature for several days followed by heating up to  $500^\circ$  in a furnace at an ascending heating rate of  $2^\circ\text{C}/\text{min}$  (start point was  $2^\circ\text{C}/\text{min}$  when reach to  $100^\circ\text{C}$  then the temperature rate increased to  $5^\circ\text{C}/\text{min}$ , after 30 minutes it increased to  $10^\circ\text{C}/\text{min}$  and finally  $20^\circ\text{C}/\text{min}$  till it reached to  $500^\circ\text{C}$ ). Weights of the films formed on the glass rings were measured by the difference in weights gained by coating on known quantity of glass rings after heating. The film thickness on the rings estimated about 790nm.

14 mg of Molybdenum trioxide powder and/or 15 mg of tungstic acid (both from Merck) were separately dissolved in 2 ml of 30%  $\text{H}_2\text{O}_2$  solution and water at  $100^\circ\text{C}$  to obtain molybdenum peroxide and peroxopolytungstic acid solutions, respectively. The solutions were added to the titanium peroxy sol (above mentioned titanium peroxide solution) while stirring to prepare 1.0wt% tungsten, molybdenum and tungsten-molybdenum-doped titanium oxide separately. For co-doping of titanium peroxy solution, both molybdenum peroxide and peroxopoly tungsten were added together to the peroxy solution while stirring.



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### B. Characterization

The surface morphology and elemental analysis of the samples were obtained by using SEM (JSM 6360A, JEOL) operated at 20kV. The crystal structures of dried  $\text{TiO}_2$  powder and films were investigated by X-ray diffraction (Bruker AXS D8) (XRD). The dried powder and the films on glass slides that were gradually heated up to  $500^\circ\text{C}$  were characterized by XRD. Almost all the information about the crystal structure of the films comes from the lattice planes parallel to the substrate surface. For a film coated on glass, the X-ray diffraction pattern was obtained by grazing incidence angle (GIA) technique. The fixed grazing incidence geometry has the advantage of substantially limiting the substrate diffraction peak intensity, since the X-rays penetrate less into the layers [35]. The absorbance spectra of the powder and films were recorded by using UV-vis spectrophotometer (JASCO model V-670).

### C. Photo catalytic activity test

Aqueous MB ( $10^{-7}$  and  $10^{-4}$  M) solution was prepared and used to evaluate the photo catalytic activity and kinetic study of thin films. MB is used by most of the researches to test the activity of catalysts; therefore MB was chosen as a model pollutant for easier comparison of the results with previous works which are carried out in this area. For photo catalytic degradation of MB, the heat treated and coated glass rings with  $\text{TiO}_2$  or/ & doped  $\text{TiO}_2$  films were used as photo catalyst.

To a small glass bottle containing coated glass rings (3g of coated rings which contain 0.001g thin film) 10 ml of MB (10mg/l) solution was added and then was kept in the sunlight. UV-VIS spectra of sample were recorded at different time intervals by UV-Vis spectrophotometer and the MB concentration was estimated using these results.

## III. RESULTS AND DISCUSSION

### A. Characterization of $\text{TiO}_2$ and W- and Mo-W-doped $\text{TiO}_2$

The titanium oxide powder before heat treatment is amorphous in structure. Thermal treatment up to  $500^\circ\text{C}$  for 3 hrs, results in well crystallized anatase-type  $\text{TiO}_2$ .

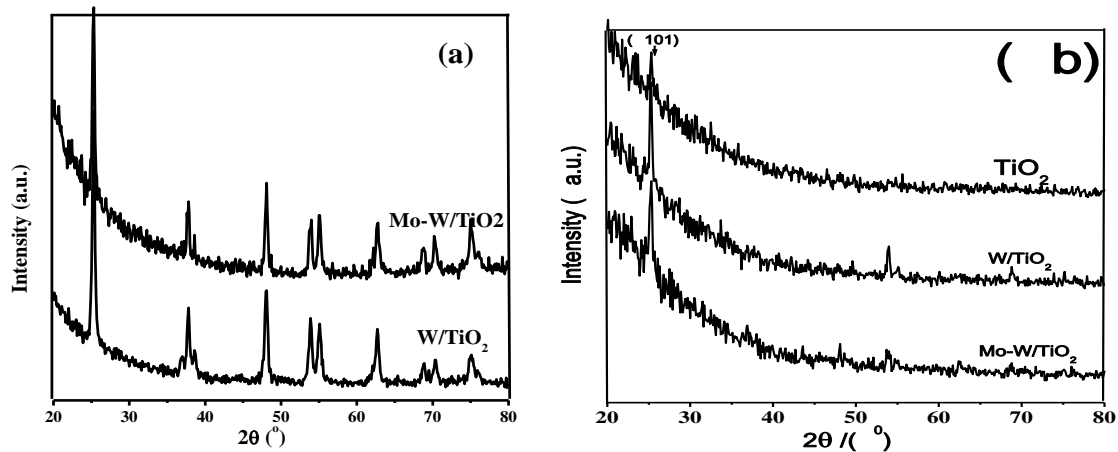


Fig. 1. XRD patterns of  $\text{TiO}_2$ , W- and Mo-W- doped powders (a) and films (b)

Fig. 1a shows the XRD patterns of the samples of W- and Mo/W-doped  $\text{TiO}_2$  in the form of powder (pure and Mo are not shown but available in different format), All samples show the anatase phase except  $\text{Mo/TiO}_2$  which shows forming of rutile phase too. Fig. 1b depicts the X-ray diffraction pattern of the sol-gel derived films coated on glass after heat treatment up to  $500^\circ\text{C}$ . Also, after doping, it is found that the major diffraction peaks are attributed to the anatase  $\text{TiO}_2$  phase and no other peaks related to dopants or impurities are observed that may incorporate in titanium dioxide anatase phase. Bragg reflections at angles of  $25.3^\circ$ ,  $48.1^\circ$  and  $55.6^\circ$  in doped film corresponded to (101), (200) and (211) tetragonal crystal planes of anatase phase of  $\text{TiO}_2$ , respectively. The anatase phase is the most active one for photo catalytic reactions [36]. From the full-width-at-half-maximum (FWHM) of the strongest peak (101) anatase phase, crystallite sizes were calculated using Scherrer's equation as follow:



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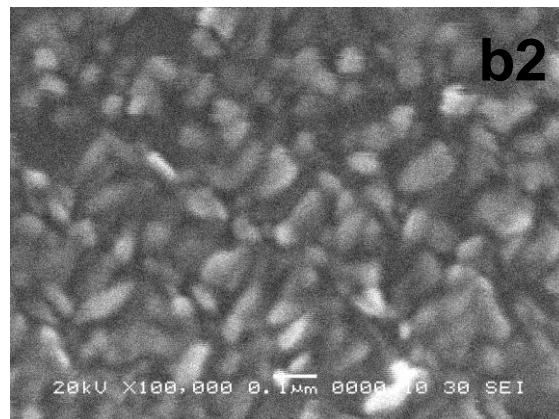
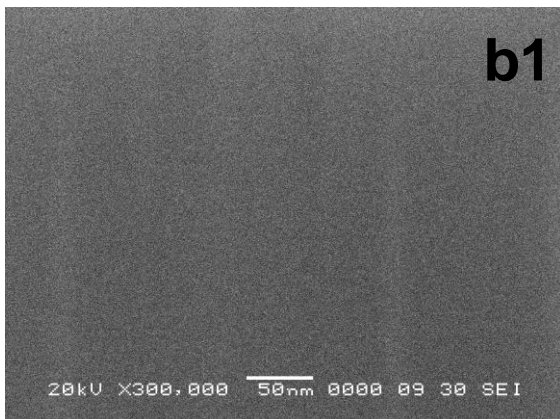
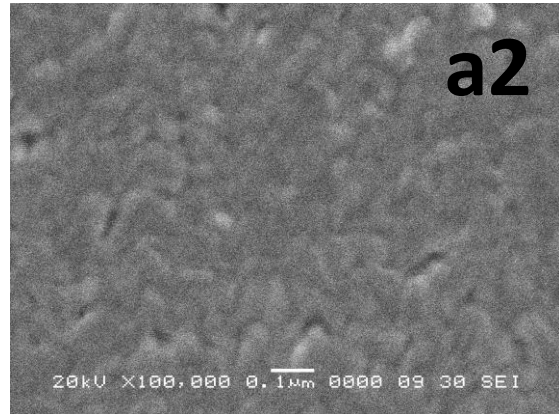
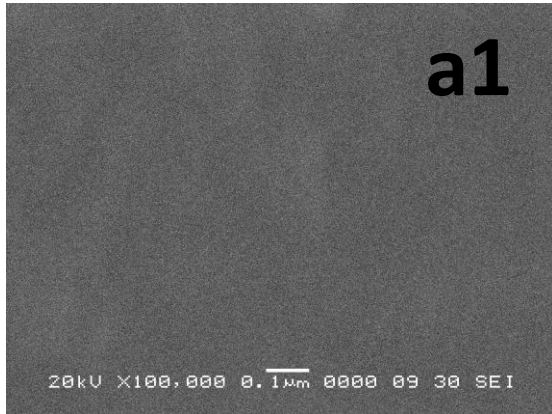
$$T = k\lambda / (\beta \cdot \cos\theta) \quad (1)$$

Where T is crystallite size and K,  $\lambda$ ,  $\beta$  and  $\theta$  are constant, wavelength, FWHM and angle, respectively. The calculated crystallite sizes of pure and W-and/or Mo- doped TiO<sub>2</sub> in the form of powder and film is shown in Table 1. However there was not a clear relation between doping and particles size.

Photo catalyst	TiO <sub>2</sub>	W/TiO <sub>2</sub>	Mo-W/TiO <sub>2</sub>
Powder crystallite size(nm)	12.3	21.4	27
Film crystallite size (nm)	35	19.8	20.3
Band gap (eV)	2.88	2.81	2.31

Table1: Crystallite sizes and band gap of TiO<sub>2</sub> and Mo and/or W-doped TiO<sub>2</sub> samples calcined at 500°C

A Pt thin film was sputtered on the photocatalysts films and examined by scanning electron microscopy (SEM) to investigate their surface morphology (Fig. 2). The single-coat samples of TiO<sub>2</sub> and W/TiO<sub>2</sub> show no distinguished particles and are transparent and homogeneous without any cracks over a wide area (Fig.2 a-1 and b-1). However, the multicoated samples of TiO<sub>2</sub> and W- and Mo-W- doped ones show rod-like nanoparticles of about 30 nm diameters and 100 nm lengths. The multicoated films are highly porous and allow diffusion of pollutants onto the photo catalyst surface with no limitation. The film thickness estimated from the weight gain of the glass substrate is about 790 nm for multicoated films. The films extended over the glass substrates enhance the easy access of pollutants to the photo catalyst surface and photo-efficiency. The adhesion and activity of multicoated films are enough for all cycles.





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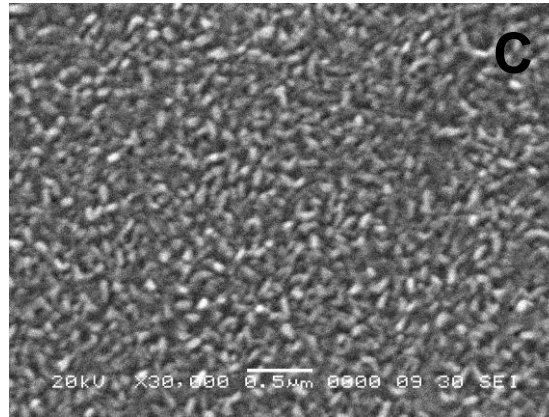


Fig. 2 SEM micrographs of films on glass calcined at 500°C, a-1) single and a-2) multicoatTiO<sub>2</sub> b-1) single and b-2) multi-coat W/TiO<sub>2</sub> c) multi-coat film of Mo-W/TiO<sub>2</sub>.

### B. UV-Vis spectroscopy

Fig 3 shows the absorption spectra of the samples in the form of powder. It shows the UV-Vis spectra of Degussa TiO<sub>2</sub> and synthesized TiO<sub>2</sub>, W- and Mo-W-doped TiO<sub>2</sub> powder samples, the cutoff wave lengths of which are 400, 430, 440 and 536 nm, respectively. The results show a significant absorption edge red-shift of TiO<sub>2</sub> powder and the one doped with tungsten, as compared to Degussa TiO<sub>2</sub> sample. A further considerable red-shift of about 100 nm is observed for the Mo/W-doped TiO<sub>2</sub> sample. An additional absorption peak shoulder from about 430 to 700 nm is observed for TiO<sub>2</sub> powder and the one doped with tungsten. The Mo/W-doped sample shows two absorption peaks in the range of about 536-850 and 850-1200 nm. Band gap estimation of samples was performed on the basis of equation (1) and the results are presented in Table 1, using Fig. 5 UV-Vis spectra.

$$E = hc/\lambda \quad (1)$$

Where, E is band gap energy, h is Planks constant ( $6.626 \times 10^{-34}$  Jouls.sec), C is the speed of light ( $3 \times 10^8$  m/s) and  $\lambda$  is cut off wavelength. The band gap of Degussa TiO<sub>2</sub> is estimated to be 3.09 eV, while those of the prepared TiO<sub>2</sub> and the ones doped with tungsten and molybdenum-tungsten are significantly lower. 0.78 eV narrowing of the band gap is observed for Mo/W-doped TiO<sub>2</sub> sample, due probably to synergetic effect of W and Mo doping.

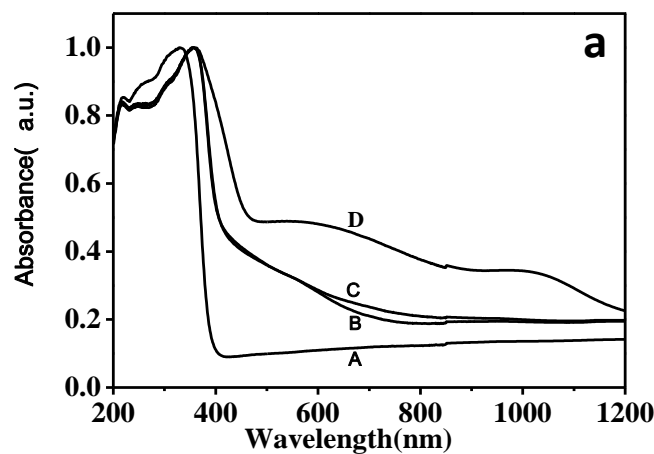


Fig. 3 Normalized UV-Vis spectra of A) TiO<sub>2</sub>Degussa, B) TiO<sub>2</sub>, C)W-TiO<sub>2</sub> and D) Mo/W-TiO<sub>2</sub> powder heat treated at 500°C

**C. Photo catalytic treatments of MB and kinetic**

Photo catalytic activity of films deposited on glass rings was tested for degradation of MB (8-32 mg/L solution) under UV and solar radiation. A cationic form of MB can be reduced and changed from blue to colorless by accepting a photo-catalytically generated electron [37]. The rate of discoloration of MB decreased with increasing initial concentration of MB when other parameters were kept unchanged. Therefore, the photo catalytic discoloration of MB was found to be pseudo-first order reaction and its kinetics may also be expressed as;

$$\ln(A/A_0) = kt$$

Here k is the apparent rate constant, A<sub>0</sub> is the initial absorption of methylene blue, t is the reaction time and A is the absorption of aqueous MB at time t. The rate constant, k is determined by a linear regression method.

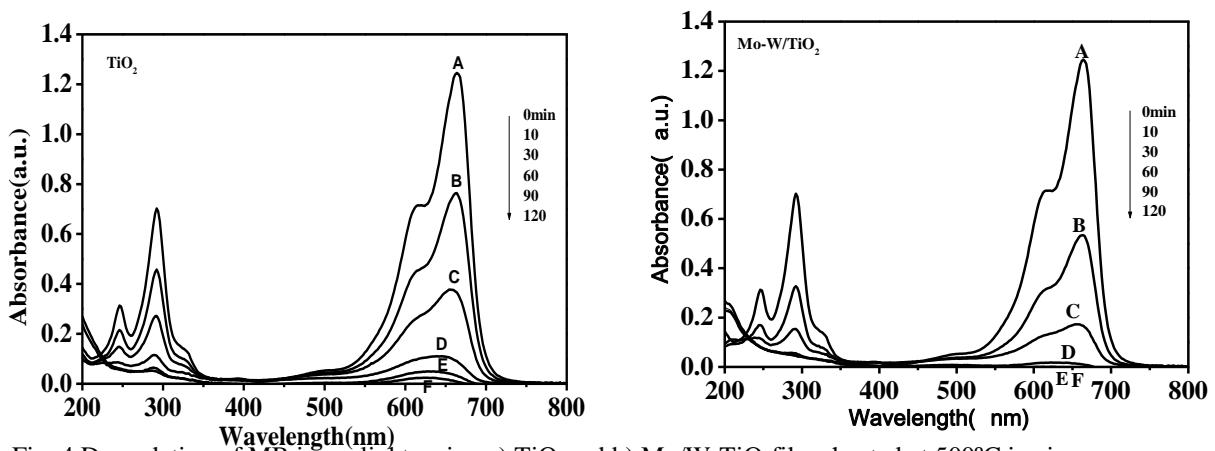


Fig. 4 Degradation of MB in sunlight, using a) TiO<sub>2</sub> and b) Mo/W-TiO<sub>2</sub> films heated at 500°C in air.

UV-Vis spectra of the MB in the presence of TiO<sub>2</sub> and Mo/W-doped TiO<sub>2</sub> films before and after solar light irradiation at different time intervals are presented in Fig. 4. The same experiment was carried out for the control sample at identical conditions. There is a sharp reduction in intensity of the peak at 664 nm during first 30 minutes of sunlight irradiation in the presences of photo catalyst.

664nm peak intensity of MB shows that about 100 % degradation of MB took place after 2 h exposure to sunlight in the presence of pure TiO<sub>2</sub> films. This time reduced to 1 h in the presences of Mo/W-doped photo catalyst. In the first 10 minutes the rate of MB removal in the presence of Mo/W-TiO<sub>2</sub> films was 52 % while it was 36% for pure TiO<sub>2</sub> films, showing photo catalytic activity enhancement due to co-doping. The plot of the percentage MB degradation in the absence of TiO<sub>2</sub> film for the same time of irradiation was done for comparison and it suggests that degradation of MB was quite slow without photo catalyst which occurs due to photolysis only. Based on the results of MB degradation, the first order kinetic plots were prepared. The plot of ln(A/A<sub>0</sub>) against time of irradiation for TiO<sub>2</sub> and doped TiO<sub>2</sub> is shown in Figs. 5. All the lines of kinetic plots are linear, which confirms the first-order reaction kinetics. These kinetic plots have been utilized for calculation of rate constant values for each degradation reaction. Result of the catalytic activity test shows the highest rate for degradation of MB in sunlight as well as UV light refers to Codoped W-Mo/TiO<sub>2</sub>. This degradation rate increased in the sunlight.



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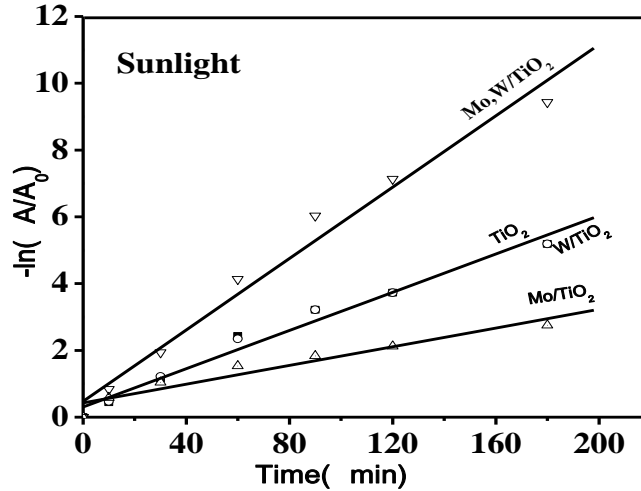


Fig. 5 kinetics of MB degradation in the presence of pure and doped titania film in sunlight

The absorption reduction in the case of using films heat treated at different temperatures was recorded. Rate constant of  $TiO_2$  calcined at  $500^\circ C$  was 1.3, 1.5 and 3.9 time faster than  $TiO_2$  calcined at 600, 300 and  $100^\circ C$  respectively (Table 2).

Films heat treatment at ( $^\circ C$ )	Rate constant ( $min^{-1}$ ) in sunlight	$R^2$
100	0.01097	0.87243
300	0.02875	0.99806
500	0.04258	0.99915
600	0.0335	0.97759

Table2: Reaction rate constants for the removal of methylene blue under sunlight using films prepared at 4 different temperatures

As comparison in the doped photo catalysts, the highest activity for degradation of MB was observed for co-doped Mo/W- $TiO_2$  heat treated at  $500^\circ C$ . It shows the activity of  $TiO_2$  after doping with W and Mo, W goes up comparing with pure  $TiO_2$  but doping of  $TiO_2$  with the Mo reduces the activity of photocatalyst. The results are summarized in Table 3.

Photo catalyst	$TiO_2$	Mo- $TiO_2$	W- $TiO_2$	Mo/W- $TiO_2$
% MB degradation after 1 h	91.2	78.4	93.6	99.2
Time for complete degradation (h)	2	4	1.8	1.2
Rate constant ( $min^{-1}$ )	$2.871 \times 10^{-2}$	$1.401 \times 10^{-2}$	$2.860 \times 10^{-2}$	$5.340 \times 10^{-2}$

Table3: Kinetics of photocatalysts for degradation of methylene blue (MB) in sunlight

#### D. Catalysts recycle for discoloration of MB

In order to find out the life span of the film and to check the recyclability of the photo catalyst after MB degradation, the procedure followed was: the colorless solution was decanted and fresh MB solution was added to the beaker containing film catalyst and was kept in the sunlight for decomposition of the fresh MB solution. After repeating this for 20 cycles the photo catalyst had almost the same capacity to degrade MB. The adsorbed MB on the film surface also did not remain for long time and it was degraded and films could be used for further cycles. Therefore in consecutive experiments, no appreciable decrease in catalytic activity was observed. The results of the 10 time photo catalyst recycle are shown in Fig. 6.



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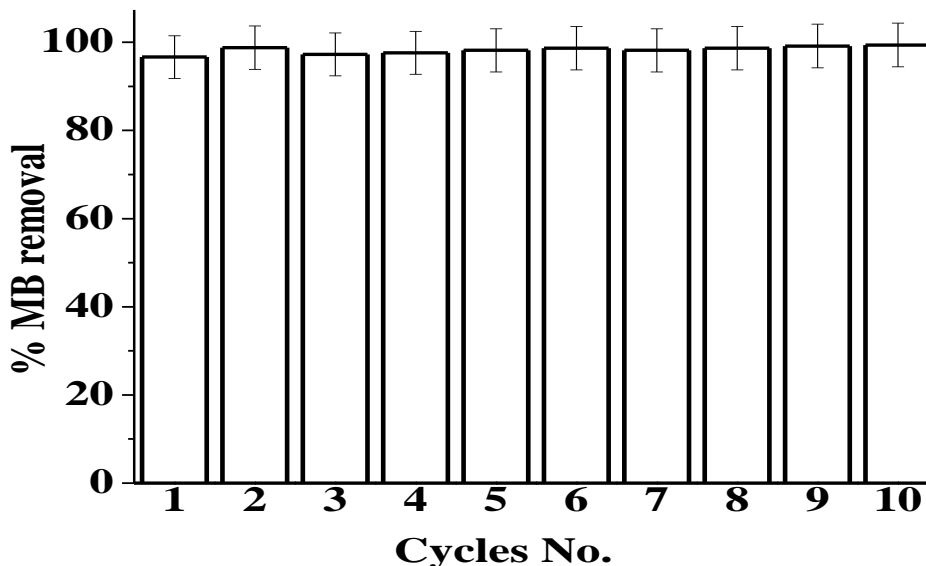


Fig. 6 Activity of catalyst in number of cycles is shown by %MB removal in each cycle.

#### IV. CONCLUSION

A long life, transparent, optically homogeneous TiO<sub>2</sub>-based films undoped and doped with W- Mo- and Mo/W were prepared by simple sol-gel dip coating method using titanium peroxide gel. The films consisted of anatase TiO<sub>2</sub> phase after heating at different temperatures and doping with W and both of Mo, W.

The band gap energy of the TiO<sub>2</sub> thin films was calculated to be about 2.91 eV, indicating band gap narrowing. Titanium based films photocatalyst prepared in this study has been found to be active for photocatalytic degradation of methylene blue. Among TiO<sub>2</sub> based thin films, TiO<sub>2</sub> films treated at 500°C and codoped Mo/W/TiO<sub>2</sub> were found to be the most active photocatalyst for degradation of methylene blue. This result could be correlated to the red shift in optical absorption.

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