

Photocatalytic performance of Sn-doped TiO₂ nanostructured mono and double layer thin films for Malachite Green dye degradation under UV and vis-lights

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Abstract

Nanostructure Sn⁴⁺-doped TiO₂ based mono and double layer thin films, contain 50% solid ratio of TiO₂ in coating have been prepared on glass surfaces by spin-coating technique. Their photocatalytic performances were tested for degradation of Malachite Green dye in solution under UV and vis irradiation. Sn⁴⁺-doped nano-TiO₂ particle a doping ratio of about 5[Sn⁴⁺/Ti(OBuⁿ)₄; mol/mol%] has been synthesized by hydrothermal process at 225 °C. The structure, surface and optical properties of the thin films and/or the particles have been investigated by XRD, BET and UV/vis/NIR techniques. The results showed that the double layer coated glass surfaces have a very high photocatalytic performance than the other one under UV and vis lights. The results also proved that the hydrothermally synthesized nano-TiO₂ particles are fully anatase crystalline form and are easily dispersed in water. The results also reveal that the coated surfaces have hydrophilic property.

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1. Introduction

Textile industry wastewater is heavily charged with unconsumed dyes, surfactants and sometimes traces of metals. These effluents cause a lot of damage to the environment. In most countries researchers are looking for appropriate treatments in order to remove pollutants, impurities and to obtain the decolourization of dyehouse effluents [1–3]. Usually, the conventional biological treatment processes do not readily remove dyes from textile wastewater, because of their resistance to biological degradation [4,5]. Various chemical, physical and biological processes are currently used such as flocculation, ultrafiltration, adsorption, ozonation and chlorination [6]. These processes are not efficient because they appear in solid wastes, thus creating other environmental problems requiring further treatment. Therefore, it is necessary to find an effective method of wastewater treatment in order to remove hazardous dyes and organics

from industry effluents [4]. One of the effective methods of wastewater treatment containing dyes is their photocatalytic degradation in solutions illuminated with UV irradiation, which contains a suitable photocatalyst, mainly TiO₂ sold commercially as Degussa P25 and Hombicat UV100. These are recognized as excellent photocatalysts and have good prospects in water and air purification [7–9]. The photodegradation of the hazardous materials in colloidal and particulate TiO₂ catalyst suspensions has been well studied [10,11]. However, this application has not been successfully commercialized, in part because of the costs and difficulties in separating the TiO₂ nanoparticles from the suspension after degradation has occurred. To solve this problem, TiO₂ film photocatalysts have been widely researched in photodegradation [12–14]. In recent years, nano-TiO₂ based thin films with super-hydrophilic and photocatalytic characteristics have attracted a great deal of attention. They have many advanced functions and features, including self-cleaning, antifogging, deodorizing and sterilizing. When exposed to UV light, organic compounds can be break down with TiO₂ films and enable water to spread evenly on their super hydrophilic surface to easily realize surface self-cleaning. Many researchers

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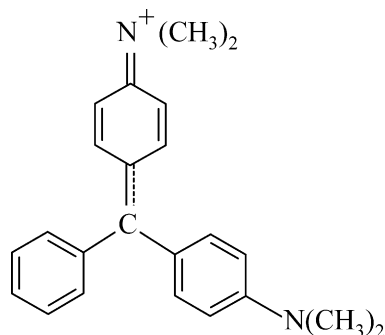
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have focused on this subject [15–18]. In order to synthesize of TiO_2 , different processes have been reported, such as sol–gel process [19], hydrolysis of inorganic salts [20], ultrasonic technique [21], microemulsion or reverse micelles and hydrothermal process [22–24]. A multitude of polar or non-polar solvents have been used in these processes. In these processes, high calcination temperature above 450°C is usually required to form regular crystal structure, except for the hydrothermal process. However, in the meantime, the high temperature treatment can decline the surface area and surface hydroxyl or alkoxide groups on the surface of TiO_2 , which provide easy dispersion, are lost. Thus, in this work, the hydrothermal process was selected to synthesize of Sn^{4+} -doped nanosized TiO_2 particles at low temperature, which seems to be really attractive to further improve the photocatalytic activity of TiO_2 . Compared with the other TiO_2 powders, these TiO_2 nanoparticles have several advantages, such as being in fully pure anatase crystalline form, having fine particle size with more uniform distribution and high-dispersion ability either in polar or non-polar solvents, stronger interfacial adsorption and easy coating on different supporting material. In this work, photocatalytic activity of hydrothermally synthesized nanostructure Sn-doped TiO_2 based mono and double layer thin films supported on glass surfaces were examined for degradation of Malachite Green (MG), which one of the hazardous dye, in aqueous solutions under UV and vis-lights and the results were compared.

2. Experimental

2.1. Chemicals and apparatus

The reagents employed were titanium (IV)-*iso*-propoxide, $[\text{Ti}(\text{OPr}^i)_4]$, 97%, Fluka], as TiO_2 source; tin (IV) chloride (Alpha, 98%) as dopant; deionized water as hydrolysis agent; tetraethylorthosilicate (TEOS, Aldrich, 98%) as a binder agent; hydrochloric acid (Merck, 37%) as catalyst; 2-butoxyethanol (2-BuOEtOH, Aldrich, 99%) and ethyl alcohol (EtOH, 96%) as solvents. The glass plate (5 cm \times 5 cm) as substrate. Malachite Green (MG), which was used as a model pollutant and purchased from a local textile factory was of analytical reagent grade; its chemical formula can be presented as:



Malachite Green

Nano- TiO_2 particle was synthesized by Berghoff model hydrothermal unit interfaced with a temperature (up to 240°C) and time controller unit. In order to determine the crystal phase,

Rigaku Geigerflex D Max/B model X-ray diffractometer (XRD) with Cu $\text{K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$) in the region $2\theta = 10\text{--}70^\circ$ with a step size of 0.04° was used. The average crystallite size of TiO_2 nanoparticles were estimated according to the following Scherrer's equation:

$$d_{hkl} = \frac{k\lambda}{\beta \cos(2\theta)}$$

where d_{hkl} is the average crystallite size (nm), λ the wavelength of the Cu $\text{K}\alpha$ radiation applied ($\lambda = 0.154056\text{ nm}$), θ the Bragg's angle of diffraction, β the full-width at half maximum intensity of the peak observed at $2\theta = 25.20$ (converted to radian) and k is a constant usually applied as ~ 0.9 . The BET surface area, average pore diameter and micropore volume of the nanosized- TiO_2 particle was calculated from the N_2 adsorption isotherm using ASAP 2000 model BET analyzer at liquid N_2 temperature. During the BET analysis, sample was degassed at 150°C for 4 h before N_2 adsorption. Pore size distribution of nano- TiO_2 was computed by DFT plus method. Contact angles of coatings with water were measured by using a goniometer (RAME HART 100-00 model). Film thickness on the coated glass surface was measured by Perthometer (MAHR-M1 Model).

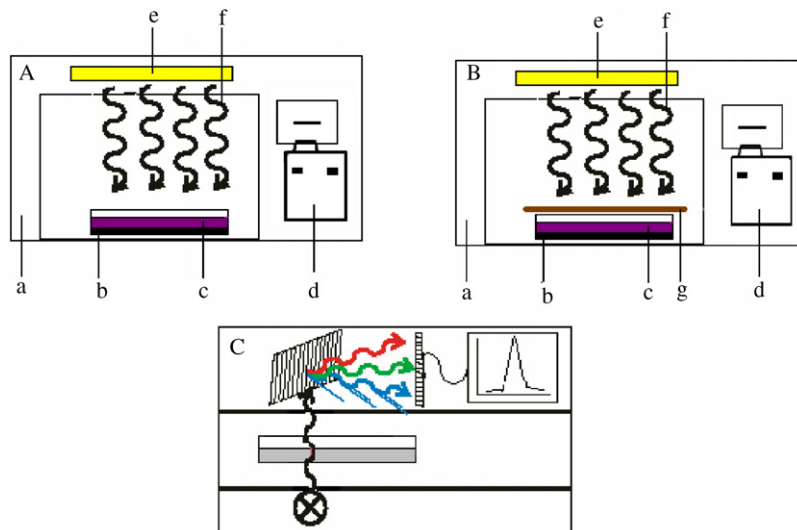
Dye concentration in the aqueous solution after irradiation was measured by a Varian Carry 5000 model UV–vis–NIR spectrophotometer. Coated glass/dye solution was irradiated with Solar Box 1500 model (Erichsen, Germany) radiation unit with Xe-lamp (690 W/m^2) and a controller to change the irradiation time and power input from 390 to 1100 W/m^2 for different time without cut-off filter and with 400 nm cut-off filter without shaking.

2.2. TiO_2 powder synthesis

$\text{Ti}(\text{OPr}^i)_4$ was dissolved in *n*-propanol. After stirring for 5 min at ambient temperature, the HCl solution (0.1N) was added. After stirring a few minute, tin (IV) chloride was added. The last solution was stirred until it formed a clear and homogeneous solution at ambient temperature. Then, water was added within 10 min into the last solution dropwise by burette. HCl/ $\text{Ti}(\text{OPr}^i)_4$, Sn^{4+} / $\text{Ti}(\text{OPr}^i)_4$ and $\text{H}_2\text{O}/\text{Ti}(\text{OPr}^i)_4$ ratios (mol/mol) were 0.19, 0.05 and 2, respectively. The reaction was allowed for 2 h, then the homogeneous and transparent solution was obtained. Sol-solution was then transferred into a 250 ml Teflon crucible, then left in a pre-heated (220°C) stainless steel autoclave device. The reaction allowed at 220°C for 2 h. After this time, autoclave was removed from the hydrothermal unit and cooled to room temperature. The as-obtained powders were dried using rotary evaporator at 40°C for 5 h. Thus, nanosized and white colour TiO_2 crystallite was obtained.

2.3. The preparation of coating solutions

Before preparing the coating solutions, the TiO_2 sol was prepared. For this purpose, required amount of TiO_2 was dispersed ultrasonically in deionized water without using dispersant. For preparing coating solution, EtOH was added to TEOS and stirred for 10 min at room temperature. HCl was allowed to react with



Scheme 1. Photoreactor system. (A) UV irradiation applied without filter, (B) vis irradiation applied with UV cut-off filter, (C) UV measurement after irradiation. (a: Solar Box irradiation unit, b: Sn-doped TiO₂ coated glass plate, c: dye solution, d: control unit of the Solar Box, e: UV lamp, f: UV lights, and g: glass UV filter.)

TEOS/EtOH system for 10 min and finally H₂O was added to TEOS/EtOH/HCl system and allowed to react for 10 min. Molar composition of each item in the coating solution were 1/5/0.06/0.18.

After preparing the coating solution, it was divided into two portions. TiO₂ sol was added dropwise into one portion of this solution in an ice-bath and the mixture was stirred for 10 min. After this time, the solution was removed from ice bath. Then, the 2-BuOEtOH (5 ml) was added into the both portions separately and stirred for 3 days at room temperature. The solutions are referred hereafter as TEOS and TiO₂-TEOS, respectively. At first, one of the glass plate (5 cm × 5 cm) was coated with TEOS using spin-coating technique (1000 rpm, 10 s) and dried for 10 min at room temperature. Then, the surface was coated with TiO₂-TEOS using the same technique. The other glass plate was only coated with TiO₂-TEOS using the same technique. Thus, mono and double layer coated glass surfaces were prepared. The solid ratio of TiO₂ in coatings was 50%.

2.4. Photocatalytic degradation of Malachite Green

Malachite Green (MG) is a common chemical that is used extensively in a variety of industrial applications. Therefore, it is chosen to be as a model pollutant. The photocatalytic degradation intermediates of MG solution were not determined. The photocatalytic performance of the films was determined by the degradation of Malachite Green dye solution. The coated glass was immersed into 25 ml aqueous MG solution with a concentration of 5.2 mg/l in a polystyrene reaction cell, which has six separate sample compartments and one cover. The cell was immediately located in the Solar Box ready for UV irradiation inducing the photochemical reaction to proceed. The coated glass/dye solution was irradiated in the horizontal direction and the distance between the UV lamp and the glass/dye solution was kept within 20 cm. The change of MG concentration in accordance with the irradiation time was measured

by UV/vis/NIR spectrophotometer after UV and vis irradiation. The photocatalytic reactor system used for testing the photocatalytic performance of Sn-doped TiO₂ coated surfaces are shown in Scheme 1.

2.5. Catalyst re-use studies

Photocatalytic nano-TiO₂ based mono layer (ml) and double layer (dl) coated surfaces were repetitively used to degrade the MG solution under UV-light. After the first use, so-used coated surfaces were employed to degrade a fresh MG solution under the same conditions. The process was repeated for two times under UV light. Before using repeatedly, the coated surfaces were stored in the dark at room temperature for a night.

3. Results and discussion

The XRD of hydrothermally synthesized Sn⁴⁺-doped TiO₂ particulate, as presented in Fig. 1, indicates that the TiO₂ is in the anatase crystalline form, which corresponds well with the PDF#21-1272 data files. The other crystalline forms of TiO₂, i.e.

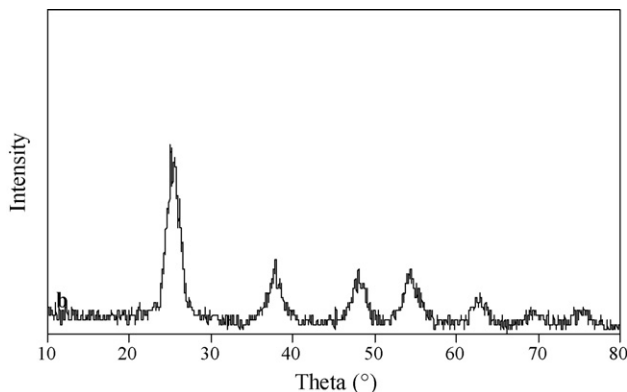


Fig. 1. XRD pattern of Sn⁴⁺-doped TiO₂ nanoparticulate powder.

Table 1
Some physicochemical characteristics of the synthesized Sn-doped TiO₂ particle and prepared mono and double layer films

Particle property		
Crystalline type	Anatase	
Crystallite size (nm)	9.70	
BET Surface area (m ² /g)	83.0	
Micropore area (m ² /g)	46.56	
Micropore volume (cm ³ /g)	0.024	
Adsorption average pore diameter (nm)	2.26	
Film property		
Film property	Mono layer	Double layer
Film thickness	12 μm	15 μm
Contact angles with water (before/after irradiation)	68°/15°	58°/9°

rutile and brookite, were not detected, as reported in our previous work [25]. The present and previous works show that Sn-doped TiO₂ photocatalysts, which have same crystallite structure can be synthesized by the different crystallization routes from different precursor [25]. In addition, no Sn phase, examined according to the sensitivity of XRD method, was found in XRD pattern. Based on the main chemical state of Sn⁴⁺, it can be concluded that Sn ions completely dissolved among the anatase crystallite in the studied composition [26].

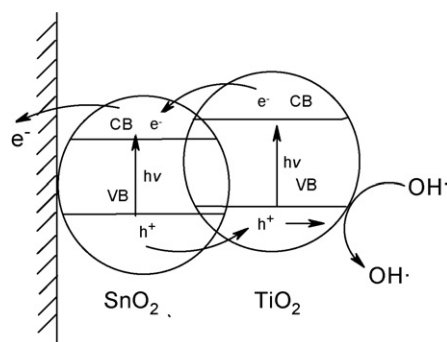
Some physicochemical characteristics of the synthesized Sn-doped TiO₂ particle and prepared mono and double layer films are shown in Table 1.

The BET surface area and micropore area of the Sn⁴⁺-doped nano-TiO₂ are bigger but adsorption pore diameter is smaller than undoped TiO₂ synthesized in our previously work [25]. The crystallite size is a lot smaller than that of undoped TiO₂. It is very well known that the photocatalytic effect of a catalyst is dependent on these properties.

According to the result of DFT plus method, TiO₂ particulate has pores in the range of 1.18–3.0 nm, which include macro and mesoporous. When considered surface area, TiO₂ sample is rich as mesoporous (56%) while volume is rich as microporous (59%). At the same time, adsorption average pore diameter is 1.96 nm obtained from (4V/A by BET) consistent with these results.

UV/vis absorption spectra of TiO₂ particle synthesized in this work are identical to the spectra reported in a previous work [25]. The doping Sn⁴⁺ results in a sharp increase in the absorption of TiO₂ photocatalyst in visible region, leaving unaffected intrinsic band gap of anatase TiO₂. The band edge absorption at <380 nm is accompanied by a broad and continuously decreasing absorption in the range 380–560 nm. The greatly red-shift (380–560 nm) can be attributed to the charge-transfer transitions between doped Sn⁴⁺ electrons and the TiO₂ conduction band. The extended absorbance of Sn-doped TiO₂ photocatalyst in the visible region provides a possibility for enhancing the photocatalytic performance of TiO₂.

While the of SnO₂ and TiO₂ are quite similar spectral responses as both are large bandgap semiconductors, SnO₂ has a wide band gap energy than TiO₂ (E_g , bandgap energy, for SnO₂ = 3.8 eV while E_g for TiO₂ = 3.2 eV) [27]. Though



Scheme 2. Schematic representation of the electron transfer process in case of SnO₂-TiO₂.

the band gap of SnO₂ is wider than that of TiO₂, its conduction band is at a lower energy level than that of TiO₂ as shown in Scheme 2. The electrical conductivity of SnO₂ is better than that of TiO₂. Hence, in a mixture of TiO₂ and SnO₂, it could be expected that the photogenerated electrons from TiO₂ is transferred easily into the SnO₂ underlayer, [(TiO₂)e_{CB}⁻ → (SnO₂)e_{CB}⁻], and holes oppositely flow into the TiO₂ overlayer, [(SnO₂)h_{VB}⁺ → (TiO₂)h_{VB}⁺], as shown in Scheme 2 [28,29]. Consequently, more holes reach the TiO₂ surface to oxidation thereat in surface. The electrons would be accumulated in the SnO₂ underlayer. In addition, as the molar ratio of SnO₂ is lower than that of TiO₂, each SnO₂ particle is surrounded more by TiO₂ particles, the photogenerated electron from TiO₂ conduction band may be passed to the SnO₂ conduction band or the electrons from the SnO₂ valence band may be excited to its conduction band by illumination. However, since SnO₂ particle is surrounded by many TiO₂, to which it cannot transfer the photogenerated electron, the electrons cannot further travel to the outer circuit and so. It can be concluded that this phenomenon important plays in the photocatalytic performances of these type semiconductors.

Curing of the coated surfaces, they were treated at 100 °C for 60 min. Then, the coated surfaces were irradiated under UV lamp (8 W, Xe lamp) for 20 min. For obtaining hydrophilic surfaces, they were again irradiated under the other UV lamp (960 W, Xe lamp) for 60 min. As can be also seen from Table 1, the film thickness were found to be 12 μm for mono and 15 μm for double layer coating. In addition, the contact angles of the irradiated surfaces with water were found to be 15° and 9°, respectively. As can be seen from the results, the contact angles decrease during the irradiation. For example, while the contact angle was 15° on the irradiated mono layer coated surface, it was 68° on the unirradiated coated surface. The decrease in the contact angle can be attributed to the reaction of produced electrons and holes in a different way. According to Fujishima et al. [15], the electrons tend to reduce the Ti(IV) cations to the Ti(III) state and the holes oxidizes the O²⁻ anions. In the process oxygen atoms are rejected, creating oxygen vacancies. Water molecules can then occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic. Therefore, we can conclude that the irradiated surface has almost superhydrophilic property. This property has an important role for photocatalytic performances.

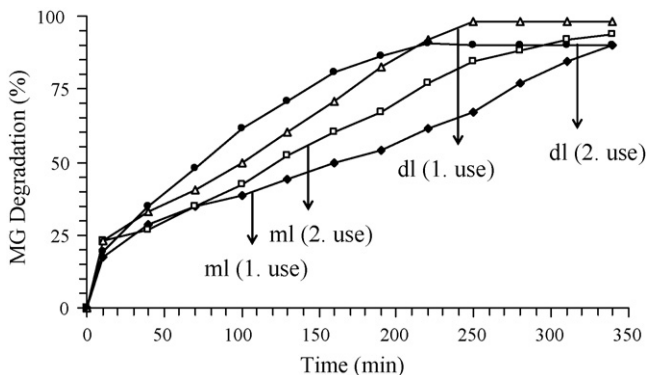


Fig. 2. Photocatalytic performance of mono layer (ml) and double layer coated (dl) surfaces for MG degradation under UV irradiation.

The mono and double layer coated surfaces generally exhibited good photocatalytic activity for the degradation of MG under both UV and vis-lights irradiation as shown in Figs. 2 and 3.

As shown in Fig. 2, the photocatalytic performance of double layer (dl) coated surface for the degradation of MG is higher than that of the mono layer (ml) coated surface in accordance with the irradiation time under UV-light both in first and second uses. According to the results of repeated usage experiments performed under both irradiation conditions, the double layer coated surface showed a high photocatalytic performance than the mono layer coated surface for degradation of MG from first to second use under UV irradiation. The photocatalytic performance of double layer (dl) coated surface for the degradation of MG is also higher than that of the mono layer (ml) coated surface in accordance with the irradiation time under vis-light (Fig. 3).

When the first uses of mono and double layer coated surfaces under UV irradiation is considered, MG was degraded as 50 and 71%, respectively, after irradiation for 160 min. According to the results of repeated usage experiments performed under this irradiation condition, the double layer coated surfaces showed a high photocatalytic performance for degradation of MG from first to second use. For example, after irradiation for 160 min, MG was degraded as 60% by mono layer coated surface and was degraded 81% by double layer coated surface, respectively. After irradiation for 220 min, the MG was degraded as 61.5 and 92% after first

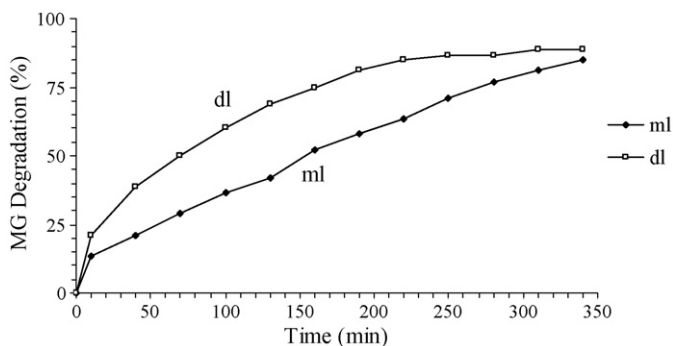
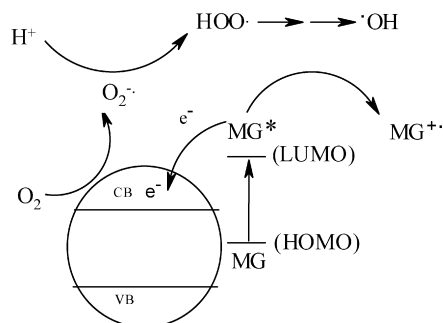


Fig. 3. Photocatalytic performance of mono layer (ml) and double layer (dl) coated surfaces for MG degradation under vis irradiation.

use and degraded 77 and 90% after second use of mono and double layer coated surfaces, respectively. After irradiation from 220 to 340 min, the MG was degraded as 98 and 90% by double layer coated surface at first and second use, respectively, while it was degraded by the mono layer coated surfaces at different amounts at the same conditions, such as 61.5, 67.3, 77, 84.5 and 90% at first use and 77, 84.5, 88.5, 92 and 94% at second use. When the first uses of mono and double layer coated surfaces under vis irradiation is considered, MG was degraded as 52 and 71%, respectively, after irradiation for 160 min. However, only 70 min is needed for 50% degradation of MG with double layer-coated surface. After irradiation for 340 min, MG was degraded as 85 and 89% by mono and double layer coated surfaces, respectively. Thus, one can conclude that the photocatalytic performance of the double layer coated surface is higher under UV or vis irradiation. The same results obtained in both irradiation observed in our previous works. In addition, in our previous works, undoped TiO_2 coated glass [25] and stainless steel surfaces showed markedly decreased the photocatalytic performances than Sn-doped TiO_2 surfaces under the same conditions.

There are various reasons in the increase photocatalytic performance. These are: (a) the high photocatalytic activity of Sn-doped TiO_2 film may be related to high surface area of the nano Sn^{4+} -doped TiO_2 particles as well as their mesoporous structure. (b) Sn^{4+} ion in coating improves electron transfer efficiency from the LUMO band of MG to the conduction band of TiO_2 , subsequently increasing the amount of radicals as shown in Scheme 3. (c) It has been presumed that the high photocatalytic performance can be ascribed to the Sn ions located in the TiO_2 lattice. In this case, some of the lattice Ti in TiO_2 is substituted by Sn^{4+} ions, the cell volume increases and lattice distortion and deformation are induced. This will result in the formation of more surface defects including coordinatively unsaturated surface cations such as Ti^{4+} and Sn^{4+} on the film surface. During the photocatalytic reaction, dye molecules can be captured by the surface defects on the Sn-doped TiO_2 film and are immediately oxidized by photogenerated holes from the valence band of the catalyst [30]. At the same time, these surface defects can efficiently capture O_2 molecules to form O_2^- active species for further photocatalytic degradation of dye molecules. The photogenerated electrons on the conduction band of TiO_2 must experience energy leaping over a potential barrier to reach the



Scheme 3. Schematic representation of electron transfer from MG (LUMO) to TiO_2 (CB).

surface and be captured by the surface adsorbed O_2 molecules. At the same time, accumulated photogenerated electrons at the bottom of the bent conduction band $[(SnO_2)_eCB^-]$ will increase the probability of electron–hole recombination during the photocatalytic reaction. After Sn-doping, since the conduction band energy level of SnO_2 is lower than that of TiO_2 , photogenerated electrons on the particle surface generated by visible light at the conduction band of SnO_2 can be captured directly by the efficiently adsorbed O_2 molecules on the Sn-doped TiO_2 surface. In the case of UV light, the photogenerated electrons at the conduction band can be transferred to the conduction band of SnO_2 can then be captured by adsorbed O_2 molecules on the Sn-doped TiO_2 surface. This will accelerate the separation of the holes and electrons, prohibiting their recombination. As a result, more photogenerated electrons and holes contribute to the photocatalytic reaction, improving the photocatalytic performance activities under both UV and vis lights. Moreover, Sn ions might be in the substitutional sites of Ti, as forming a solid state compound like $Ti_{1-x}Sn_xO_2$ [31]. $Ti_{1-x}Sn_xO_2$ may have a high photocatalytic performance causing a high tendency to degrade the MG. Besides, the Sn-doped TiO_2 particle has strong UV-light absorption ability, denoting that it can effectively be utilized for photocatalytic applications under vis irradiation. At the same time, it is seen that the Sn-doped TiO_2 particle has strong UV-light absorption ability. This also denotes that the Sn-doped TiO_2 particle can effectively be utilized under vis irradiation for photocatalytic applications. (d) All the nano- TiO_2 particles in coating can be transferred onto the coated surface during the irradiation resulting in a high photocatalytic performance. (e) The high photocatalytic performance of the coated surfaces is also related to its surface has almost super hydrophilic property (described previous) and related to TEOS is occurred a superior barrier for Na ions in double layer coating.

Generally, the logarithmic plot of concentration data gives a straight line, which its slope helps to predict the rate constant of reaction. That is $\ln(C_0/C) = kt$ [32,33], where C is the dye concentration (mg/l) at instant t (min), C_0 the dye concentration (mg/l) at $t = 0$ (min), and k is the reaction rate constant (min^{-1}). The regression curve of natural logarithm of normalized MG concentration versus reaction time was approximate straight line.

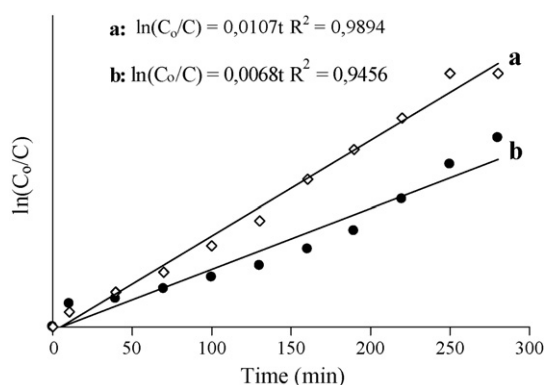


Fig. 4. Pseudo first order reaction kinetics curve for photodegradation of MG with (a) double layer coated and (b) mono layer coated surfaces under UV irradiation.

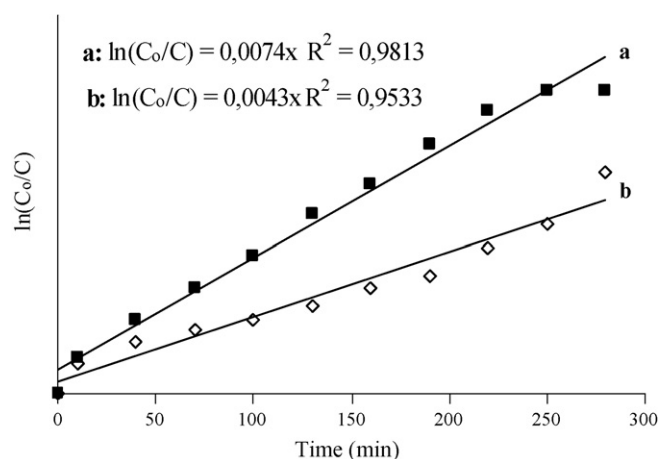


Fig. 5. Pseudo first order reaction kinetics curve for photodegradation of MG with (a) double layer coated and (b) mono layer coated surfaces under vis irradiation.

As shown in Figs. 4 and 5, as obtained by re-plotting Figs. 2 and 3, in the $\ln(C_0/C) - t$ coordinates, $\ln(C_0/C)$ are linear with the irradiation time, meaning that photodegradation of MG obeys the rules of a pseudo-first order reaction kinetics under UV and vis irradiation. The rate constants are 0.0107 and 0.0068 for double layer coated and mono layer coated surfaces under UV irradiation and are 0.007 and 0.0043 under vis irradiation. These results fall into line with MG degradation under UV irradiation as described above.

4. Conclusion

Nanostructure TiO_2 based mono and double layer thin films on glass substrate were prepared by spin-coating technique. Nano-sized Sn-doped TiO_2 particle was synthesized by hydrothermal process at low temperature. It was found that the synthesized nano- TiO_2 particle has an amphilic and the coated surfaces have hydrophilic property. High photocatalytic performance obtained by double layer coated surfaces, because, the diffusion of Na ions within the glass is restricted by earlier coating of the glass surface with TEOS as a thick film, i.e., TEOS is a superior barrier for Na ions, in both under UV and vis-lights. It can be suggested that, this coated surfaces prepared in our experiments can be used for cleaning of the pool water, deodorizing the interior of room air and preparing self-cleaning and/or antibacterial surfaces, and degrading of hazardous materials in waste water.

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