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Studies on Optical and photocatalytic properties of surfactant assisted silver deposition on TiO_2 thin films prepared by microwave irradiation technique

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ABSTRACT

This paper describes the development of nanostructured thin films of Ag-TiO_2 *by the Mw-glycol irradiation of silver ions on* TiO_2 *thin films prepared by sol–gel spin-coating (SGS) methods. Where the effect of silver containing* TiO_2 *nanoparticles were tested in photocatalytic applications. For increasing the photocatalytic activity was related to associate effects: the electron transfer from* TiO_2 *to Ag, reducing the electron–hole recombination, thickness of the film and silver distribution. From the experimental results without surfactant Ag-*TiO_2 *films exhibited much better photoactivity than the surfactant (PEG-2000) Ag-*TiO_2 *films due to excess of silver composition this has been explained in terms of SEM morphology and EDX Analysis.*

Keywords: Thin films, Microwave irradiation technique, Photocatalytic activity.

INTRODUCTION

In recent years, titanium dioxide as one of the most important photocatalytic material has been investigated extensively due to its wide applications in environmental purification [1–3]. As a semiconductor material, TiO_2 has raised a great interest for its photochemical properties that have led to many industrial applications. Modification of nano-crystalline TiO_2 films by metal-doping is increasingly being considered to maximize the photocatalytic efficiency because of increased electron traps and decreased TiO_2 band gap [4, 5]. The optical absorption of the modified nanocrystalline films in the UV–visible region caused by the surface Plasmon resonance (SPR) originating from collective oscillations of free electrons [6]. However, one of the main challenges to optimizing TiO_2 nanostructures is the high rate of recombination of the electron–hole pairs, which reduces significantly the photocatalytic efficiency. A reduction in the recombination rate and consequent increase in the efficiency can be achieved by the incorporation of noble metal into the structure of the semiconductor [7]. There have been several reports on metal incorporation to inhibit the recombination processes [8]. Sang Chul Kim [9] showed that the incorporation of small amounts of Pt in the TiO_2 structure dramatically increases the photocatalytic activity of the semi-conductor, because the metal centers enhance the charge. The most common and promising methods of Ag-TiO_2 preparation, which make possible approaching the systems are sol-gel [10], PRT [11],Chemical vapor deposition [12] and photoreduction method, Bin Zhao b et.al preparaed the Ag-TiO_2 nanocomposites by photoreduction method. This method requires 2h UV-irradiation to in-situ reduce Ag^+ ions on the surface of TiO_2 leading to Ag-TiO_2 composite nanoparticles (NPs) [13]. Li, X; Wang et al. reported about microwave irradiation method for the preparation of Ag-TiO_2 nano particles [14]. Feng Peng et.al reported the preparation of Ag-sensitized ZnO nanoparticles by microwave reduction method [15].To the best of literature not that much of work has done on the preparation of Ag-TiO_2 nanocomposite thin films by glycol reduction using microwave irradiation method.

Hence, this paper reports the synthesis of surfactant and without surfactant TiO_2 films by simple spin coating technique and loading of silver ions on nanostructured TiO_2 thin films by simple glycol reduction using microwave irradiation method. The effect of Ag doping on the structure and optical properties of TiO_2 films has been studied .The photocatalytic activity of the thin films was assessed by degradation of MB in aqueous solution under UV illumination. The results presented here may assist in the understanding of the phenomena involved in the photocatalytic degradation of pollutants using immobilized materials supported as thin films.

MATERIALS AND METHODS

2.1.Experimental

a) **Preparation of without surfactant TiO_2 thin films:** Titanium tetra isopropoxide (sigma Aldrich 99.9%) has been used as the titania precursor, the matrix sol was prepared by mixing titanium tetra isopropoxide (TTIP) with absolute ethanol (Aldrich 99.9%) and acetyl acetone at room temperature. Here the absolute ethanol has been used as a solvent. Acetyl acetone and PEG-2000 has been used to control the pH of the hydrolysis/condensation reactions in the sol–gel solution. The final composition of the solution in molar ratio was TIP: ethanol: acetyl acetone1:9:0.5.TiO_2 films have been spin coated onto well cleaned soda lime glass substrates using the above solution. The sol was put in drops on the substrate, which was rotated at a speed of 3000 rpm for 60 s resulting in the formation of a thin film. The film was heated at 100°C for 10 min and then allowed to cool to room temperature. TiO_2 was again spin coated on the already coated TiO_2 film and heated at 100°C for 10min and then allowed to cool to room temperature the spin coating, heating and cooling process was repeated to get desired thickness. The deposit films of thickness about 100 nm were slowly heated and then films were annealed at 500°C for 1 h using a heating rate of 2°C/min. Because of lack of heat-resistance of soda lime glass, the calcination temperature did not exceed 500^0C. About 120-150 nm thickness of both TiO_2 films irradiated Ag^+ ions by glycol reduction was measured by thickness instrument.

b) **Preparation of PEG-surfactant TiO_2 thin films:** Followed the above same procedure with the addition of PEG-2000 surfactant. The final composition of the solution in molar ratio was TIP: ethanol: acetyl acetone: PEG-2000 = 1:9:0.5:0.05. and it was heat treatment with the above procedure to get the desired thickness.

c) Loading of the TiO_2 thin Films with silver nanoparticals:

The prepared (1cm×1cm) TiO_2 thin film was kept in 10 mL of ethylene glycol (J.T. Baker, 99%) containing 0.1mM of $AgNO_3$ (Aldrich, 99%). The reaction mixture was irradiated under microwave irradiation frequency of 2.45 GHz, at power output of about 700W (to react for 2min at 218.4 °C) in domestic microwave oven model no- OM 18 MSP. During the microwave irradiation, the sample turned dark-gray due to surface Plasmon absorption of the deposited Ag nanoparticals.

The XRD diffraction studies were performed with Philips (model FW1710) diffractometer by using Cu Kα radiation (K= 0.15406 nm).Degradation of Mb using Philips TL 8W/08 BLB F8T5 Hg lamp, analyzed by UV-vis spectrophotometer (UV 1400, Shimadzu).

2.2.Measurements of photocatalytic activities:

The photocatalytic activity experiments on pure TiO_2 and Ag-TiO_2 thin film for the degradation of methylene blue under radiation of a 6×8W UV-A black light (spectral output 311–415 nm peaking at 368 nm; Philips TL 8W/08 F8 T5/BLB).The samples were immersed into the cell containing the MB solution (cell + solution + sample). Subsequently, the cells were exposed to UV-light at different exposure times (0.5, 1, 1.5, 2 and 2.5h). In a dark chamber by using methylene blue solution concentration of 2 mg/l. Sample of 5 ml was taken at every 1 h. The MB residual normalized concentration [MB] was determined indirectly from the absorbance spectra. Optical absorption spectra of MB after UV-light irradiation at different exposure times in the interval of 0–2.5 hours were performed in order to quantify the photocatalytic activity. The degradation MB was determined following the Beer–Lambert's law for absorption band with the maximum at 664 nm in the UV-visible spectra of MB, using a UV-visible spectrophotometer (UV 1400, Shimadzu).

RESULTS AND DISCUSSION

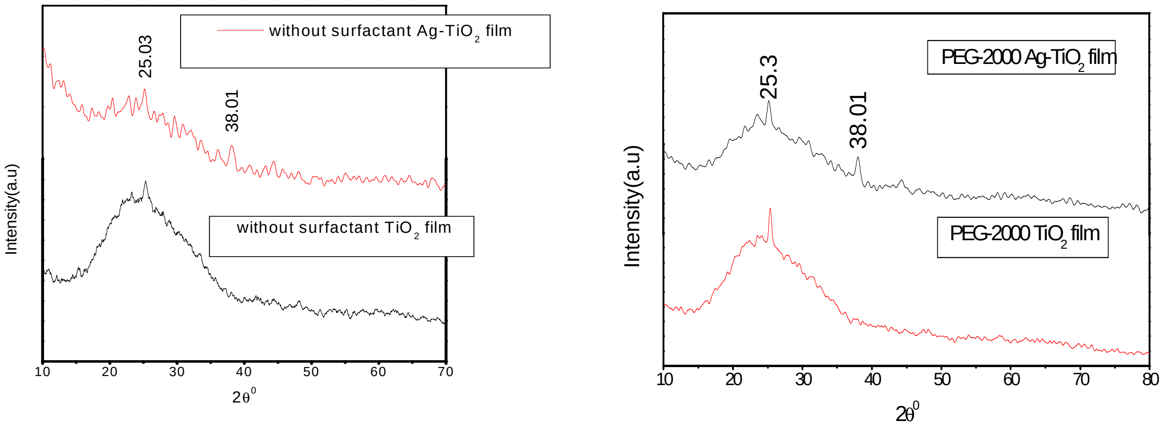
3.1.XRD studies

The X-ray diffraction (XRD) measurements, which were used to characterize the crystalline phase and crystallite size of the films, were carried out on an X-ray diffractometer (model FW1710) using Cu K α radiation at a scan rate of 0.05° 2θ s^{-1}. The accelerating voltage and applied current were 40 kV and 80mA, respectively. The crystallite size of the films was calculated using Scherer formula (d = 0.9λ/B cos θ, where d λ, B and θ are crystallite size, Cu Kα wavelength (0.15418 nm), full width at half maximum intensity (FWHM) of anatase (1 0 1) peak in radians and Bragg's diffraction angle, respectively). From the figure 1 shows that both TiO_2 films exists anatase phase pattern which is exactly matches with the JCPDS card NO.89-4921 and a very small peak belonging to Ag which exactly matches with the JCPDS Card No. 00-004-0783, which suggests that the average crystallite size of the films as given in Table 1

Table.1

catalyst	TiO_2 films Grain size(nm)	Ag-TiO_2 films Grain size(nm)
PEG-2000 surfactant	21.5	9.8
Without surfactant	25	23.75

While from the above table.1 the grain size of the TiO_2 films were decreased and the crystallite size increases for using PEG 2000, where as the seeds are agglomeration without using surfactants [16,17] thus the grain size of the films increases. Were as the grain size of the Ag-TiO_2 films decreases correspondingly surfactant and without surfactant TiO_2 films as shown in Table 1.

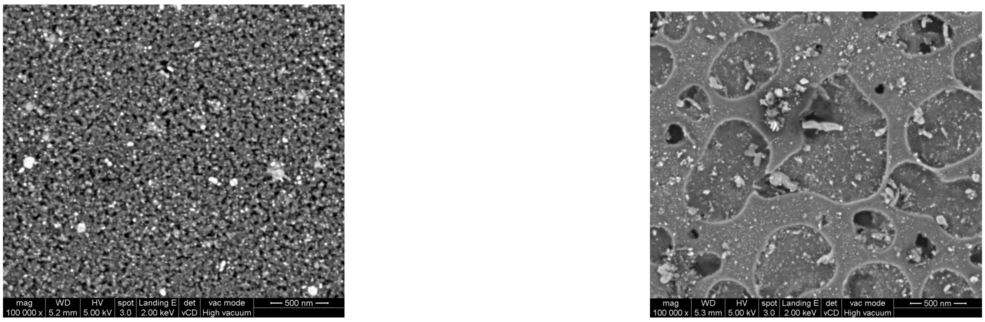


(a) (b)

Figure .1.XRD of (a) without surfactant TiO_2 and Ag-TiO_2 thin films (b) PEG-2000 surfactant TiO_2 and Ag-TiO_2 thin films.

3.2. SEM and EDX elemental analysis of Ag–TiO_2 nano thin films

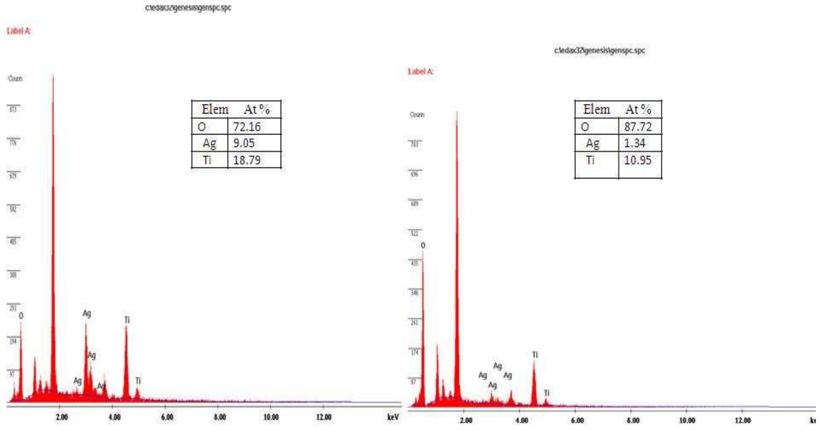
The sizes and dispersion of Ag–TiO_2 nano thin films without and with surfactants were adopted. It was observed that without surfactant the particles were agglomerated as shown in fig [2a]were as PEG-2000 was used as a dispersant, the low aggregation could be explained by steric hindrance because the dispersant kept the sol particles separated in the solution due to polymeric dispersant as long chain molecule[18]this as shown in SEM Fig [2b].



(a) (b)

Figure 2. SEM of (a) without surfactant Ag-TiO_2 thin films (b) PEG-2000 surfactant Ag-TiO_2 thin films.

The EDX results of Ag-TiO_2 film are shown in figure 3. The atomic ratios of Ag, Ti, and O are also listed in figure 2. The content of Ag was higher than the nominal value maybe because Ag was mainly on the surface of TiO_2 .The at wt% content of Ag was higher in surfactant Ag-TiO_2 film was about 9.05, were as the at wt% content of Ag in without surfactant film was 1.34% which is essential for photocatalytic analysis.



(a) (b)

Figure 3. EDX of (a) without surfactant TiO_2 and Ag-TiO_2 thin films (b) PEG-2000 surfactant TiO_2 and Ag-TiO_2 thin films.

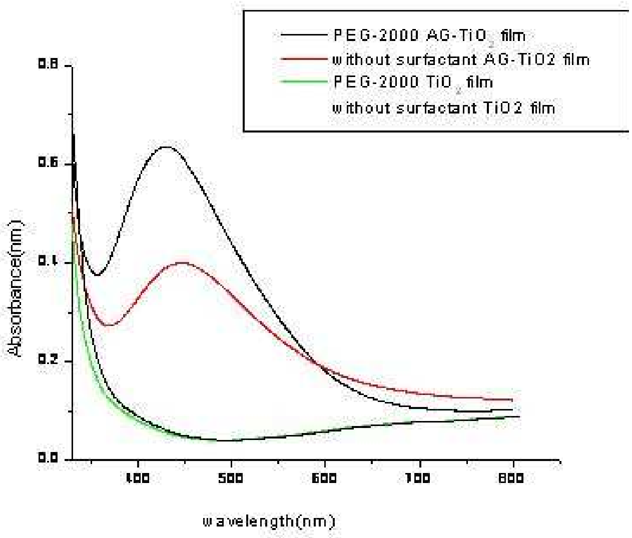


Figure 4a. Absorbance spectra of without and with surfactant TiO_2 and Ag-TiO_2 thin films

3.3. Absorbance spectra and optical band gap determination

UV-Vis spectra of TiO_2 and Ag-TiO_2 nano film was deposited on a soda lime glass substrate. One of the major objectives of the incorporation of Ag nanoparticals into TiO_2 nanoparticals is to increase the wavelength response range in order to enhance the photo excitation efficiency of TiO_2. But with the experimental result Plasmon peak moves to lower wavelengths on doping of TiO_2 thin films. This may indicate that the particle size decreases with doping of Ag content. Therefore, the optical properties such as the band gap of Ag-TiO_2 and TiO_2 nano film were determined by using the UV-Visible absorbance spectra shown in figure 4. From the Tauc's plot [19], the indirect band gap value reported in literature for bulk and film anatase is estimated at 3.20 and 3.39 eV, respectively. The larger band gap of the film in comparison to their bulk values is presumably due to the lattice deformation by an axial strain. [20] The evaluated band gap for the undoped TiO_2 has given in table 2, which is comparable to the values (3.7eV) cited in the literature for the quantum dot anatase TiO_2 thin films [21].correspondingly, the absorbance edge of Ag-TiO_2 nano thin films shifts significantly to the lower wavelength, compared to that of TiO_2 nano thin films this as shown in figure 4a, it is interesting to note here that while there is no significant absorption in the undoped TiO_2 for energies below its band gap, there is considerable absorption in the Ag-doped samples in the lower energy region (2.1–3.66 eV), increasing almost linearly with the increasing energy. As shown in figure 4b [22].

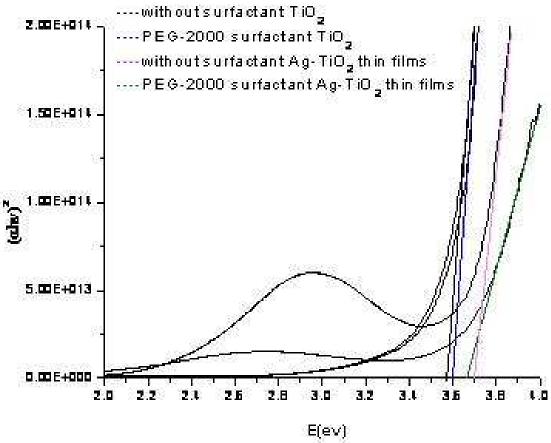


Figure. 4b. band gap of without and with surfactant TiO_2 and Ag-TiO_2 thin films

Films	Thickness (nm)		Band gap(eV) With surfactant	Band gap(eV) Without surfactant
	With surfactant	Without surfactant		
Ag-TiO_2	148.5	122.5	3.7	3.68
TiO_2	130	100	3.6	3.58

3.4.Photocatalytic activities:

Figure 6a,6b shows photo-catalytic activities of the 500^0 C calcinated TiO_2 films and Ag-TiO_2 films prepared by surfactant and without surfactant, which exists that very small percentage of methylene blue decomposes in the absence of TiO_2 films and Ag-TiO_2 films. It is seen that about 51% of methylene blue was decomposed after UV illumination for 2.5 h in the case of without surfactant TiO_2 films, whereas 77% methylene blue was decomposed after 2.5 h for the PEG-2000 TiO_2 films. Due to the low aggregation could be explained by steric hindrance because the dispersant kept the sol particles separated in the solution due to polymeric dispersant as long chain molecule [18]. Thereby it can be asserted that PEG 2000 would be the best surfactant for preparing uniform nanoparticles and high crystallinity was observed [16] this as shown in SEM and XRD. For The possibility reason for increasing the photocatalytic activity due to, Ti^{3+} ions are formed during calcination as a result of the reduction of Ti^{4+} to Ti^{3+} by organic residues such as alcohol and unhydrolyzed alkoxide group. Organic residuals draw oxygen atoms from surrounding TiO_2 network. Ti^{3+} ions on the surface of the TiO_2 films may trap the photogenerated electrons, which are transferred from Ti^{3+} surface states to O_2 adsorbed on active sites of Ti^{3+}. This results in the reduction of recombination of Photogenerated electrons and holes. The formation of a larger amount of Ti^{3+} ions contributes largely to the enhancement of the photoactivity of the TiO_2 films [21]. Therefore surfactant PEG-2000 TiO_2 nanofilms shows good photocatalytic activity then without surfactant TiO_2 nanofilms due to it exist both Ti^{+3} ions and more surface active sites then without surfactant TiO_2 films.

Silver nanoparticals plays important role for the deposited TiO_2 surface could act as electron–hole separation centers [22–24]. The photo-generated electrons were transferred from the TiO_2 conduction band to metallic silver particles on the surface of TiO_2. This process was thermodynamically possible because the Fermi level of TiO_2 was higher than that of silver metals [25]. The Schottky barrier was formed at the Ag–TiO_2 contact region, which improved the charge separation and thus retarded the recombination of the photo-generated electrons and photo-generated holes. The photo-generated electrons accumulated on the surface of Ag had good fluidity and could be transferred to oxygen molecules, which were adsorbed on the surface of Ag. As shown in Figure.5 the oxygen molecules could easily obtain the electrons to form H_2O_2, HO_2^-, and O_2^- [26]. These active species significantly promoted the photocatalytic oxidation process. Furthermore, the holes were accumulated at the valence band. The water molecules adsorbed on the surface of TiO_2 could interact with the holes, leading to the production of surface hydroxyl radical $^{\cdot}OH$, which was responsible for the oxidation decomposition of MB. About 74.5% percentage of methylene blue decompose in the absence of surfactant Ag-TiO_2 films were as 64 % of methylene blue decomposed after UV illumination for 2.5 h by using PEG-2000 surfactant Ag-TiO_2 films due to the surfactant films are more porous and more active surface area which deposits excess amount of silver nanoparticles then without surfactant films, therefore photocatalytic activity decreases that the surfactant Ag-TiO_2 films will also act as a trapping site by accepting the photo excited electrons from the TiO_2 valence band.

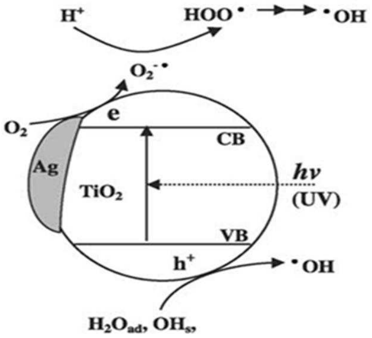


Figure 5.Photocatalytic mechanism of Ag-TiO_2 film

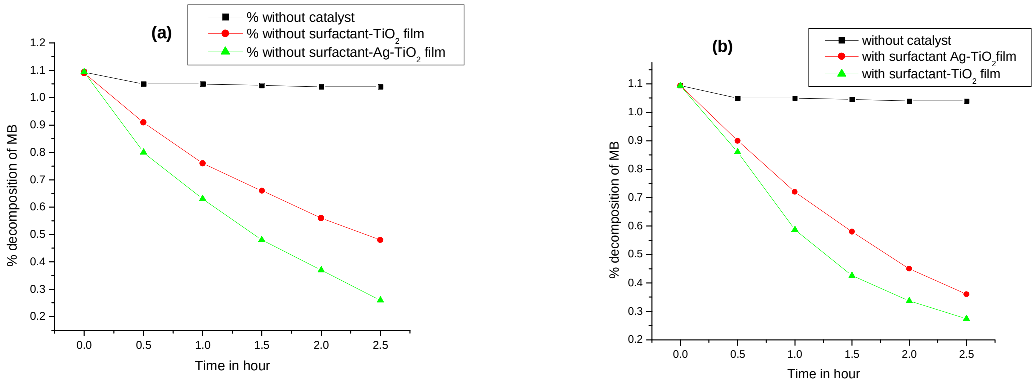


Fig. 6(a) **Fig. 6(b)**

Figure 6(a) Photocatalytic degradation of methylene blue using without surfactant TiO_2 and Ag-TiO_2 thin films 6(b) PEG-2000 surfactant TiO_2 and Ag-TiO_2 thin films

CONCLUSION

In this work, anatase TiO_2 thin films were prepared with surfactant and without surfactant sol-gel spin coating method. Both Ag-doped TiO_2 films prepared from simple glycol reduction by microwave irradiation technique. The deposited silver nano composites were confirmed by XRD pattern and % composition were analysed by EDX spectra's. For surfactants Ag-TiO_2 samples demonstrate lower photocatalytic activity then without surfactant films due to excess of silver content i.e. will also act as a trapping site by accepting the photo excited electrons from the TiO_2 valence band. Were as in comparison with surfactant TiO_2 films photocatalytic activity increases due to dispersant, low agglomeration and specific active sites on catalyst surface then without surfactant TiO_2 films.

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