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SYNTHESIS OF Ag-MODIFIED TiO_2 SOL-GEL FILMS AND ITS APPLICATION AS PHOTOCATALYSTS FOR METHYLENE BLUE DEGRADATION

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ABSTRACT

In the study, the photocatalytic activity of TiO_2 films that are created by dip-coating from a sol that contained titanium (IV) isopropoxide, monoethanolamine, and 2-methoxyethanol is demonstrated. Through photo-fixation of Ag (I) ions with varied concentration (10^{-2} - 10^{-4} M) in the water phase under UV illumination, the films are subsequently surface-modified with Ag co-catalyst layers. Scanning Electron Microscopy (SEM), X-Ray Photoelectron Spectroscopy (XPS), Ultraviolet-Visible (UV) Spectroscopy, and Electron Paramagnetic Resonance (EPR) techniques are used to physically characterize the samples. Results reveal that the modification of the co-catalyst had no impact on the thickness and porosity of the films. In addition, the study show that the modified TiO_2 films had increased photocatalytic activity. All the characterization methods used have shown the formation of surface - bound Ag (I) species and metallic silver nanoclusters. By measuring the Methylene Blue (MB) dye degradation under UV light illumination, as - prepared and Ag -modified TiO_2 films are evaluated for their photocatalytic activity, and the impact of the silver precursor concentration during photo-fixation is investigated. The highest catalytic activity is seen for films that have been modified at a concentration of Ag (I) of 10^{-2} M. Ordered from highest to lowest, the MB photodegradation rate constants are $TiO_2 < TiO_2/Ag,\ 10^{-4} < TiO_2/Ag,\ 10^{-3} < TiO_2/Ag,\ 10^{-2}$.

Keywords: TiO_2 sol-gel films, silver co - catalytic modification, photocatalysis, methylene blue.

INTRODUCTION

Titanium dioxide's intriguing properties, including photoactivity, stability, and affordability, have made it a material with significant potential for eliminating organic pollutants from wastewater [1 - 3]. During the catalytic process, the absorption of a photon by TiO_2, electron excitation from the valence band to the conduction band occurs, leading to the creation of positively charged holes and the photodegradation of various pollutants. To produce highly reactive oxygen species, the electron-hole pairs migrate independently to the surface of TiO_2 where they take part in a sequence of oxidation/reduction reactions with adsorbed species like water and oxygen [4, 5]. These reactive oxidizing species react with the contaminants that have been adsorbed on the surface, causing them to break down into toxic compounds. However, because of their brief lifetime, the photogenerated electrons and holes can quickly recombine in the bulk or on the surface of TiO_2, which lowers the material's photocatalytic performance. Consequently, modifying the semiconductor is required to improve its photocatalytic properties. To create an active photocatalyst and lower e^-/h^+ pair recombination, doping TiO_2 with noble metals is a good idea [6]. Tauster et al. report was the first to discuss TiO_2 doping with noble metals [7]. Numerous studies on the alteration of TiO_2 by noble metals, including Au, Ag, Pt, Pd, and many others, have been published since then [8 - 11]. Because a Schottky barrier forms between the TiO_2/metal junctions, encouraging interfacial charge transfer and delaying the recombination of e^-/h^+ pairs, the addition of these noble metals to the semiconductor surface boosts its photocatalytic efficiency. The field of wastewater treatment benefits from all of this. After a thorough analysis of the literature, more than 520 publications mentioning "TiO_2/Ag nanomaterials" and "Ag modified titanium dioxide" have been published. Since the start of the twenty-first century, the majority of these articles have been published, and their quantity has continued to rise. Given the enhanced photocatalytic capabilities of Ag/TiO_2-based photocatalysts, these results are not shocking. As a result, we think that an investigation of TiO_2/Ag photocatalysis is required to demonstrate the benefits of modified TiO_2 semiconductors for the degradation of organic pollutants from wastewater. A method for improving the photocatalytic efficiency of TiO_2 sol-gel films by Ag ions (10^{-2} -10^{-4} M) photo-fixed with UV illumination to degrade Methylene Blue more effectively is suggested here.

EXPERIMENTAL

Titanium (IV) isopropoxide (> 97.0 %) were from Sigma Aldrich Monoethanolamine and 2 methoxyethanol (> 99.9 %) were from Fluka. All chemicals were of analytical reagent grade and without further purification. The glass substrates (ca. 76 mm × 26 mm, ISO-LAB,) used as substrates were subsequently cleaned with distilled water for 20 min, respectively. Then, the substrates were dried in air.

The preparation of the TiO_2 sol-gel films involves a precursor solution of titanium (IV) isopropoxide (5 mL) mixed with monoethanolamine (20 mL) and 2-methoxyethanol (5 mL). The precursor sol was kept under magnetic stirring for 1 h at 60^{o}C to obtain a homogenous yellow solution. After 24 h of aging, the solution was deposited over glass substrates, using dip-coating technique. At room temperature, the withdrew at a rate of 0.9 cm per minute. The substrates were dried at 100°C for 10 min after deposition to remove any remaining organic material. The procedure was carried out five times. The films were then produced with five layers and thermally annealed in the oven for one hour at 500°C. Chemical photo-deposition was used to create the silver co-catalytic modified TiO_2 films. After being submerged in aqueous silver nitrate solutions of varying concentrations (10^{-2} - 10^{-4} M) for 20 minutes, the TiO_2/Ag films were photo-fixed with and without UV illumination and then washed with water before being dried at 100^{o}C for 10 min.

The surface morphology of the unmodified and Ag^+ co-catalyst modified TiO_2 sol-gel films were analyzed by Scanning Electron Microscope (SEM, A Hitachi TM4000, Krefeld, Germany), which used an accelerating voltage of 15 kV to produce the images. Before observation, the tested samples were coated with a thin layer of gold using a fine coater (JFC-1200 JEOL).

Measurements were performed on an ESCALAB MkII (VG Scientific, now Thermo Scientific, Manchester, UK) electron spectrometer with a base pressure in the analysis chamber of 5 x 10^{-10} mbar and a twin-anode MgK/AlK non - monochromated X-ray source using excitation energies of 1253.6 and 1486.6 eV, respectively, X-ray photoelectron (XPS). About 1 eV was the instrumental resolution. The energy scale was calibrated by setting the Ti2p line for the titanium-containing sample to 458.5 eV due to electrostatic sample charging. The X-ray satellites and a Shirley - type background were subtracted from the measured spectra as part of the processing [12]. Based on the normalization of the peak areas to the photoionization cross-sections of the various chemical species, as calculated by Scofield, the relative concentrations of the various chemical species were established [13].

At room temperature, TiO_2's Electron Paramagnetic Resonance (EPR) spectra were captured. With a JEOL JES-FA 100 EPR spectrometer operating in the

X-band with a typical TE011 cylindrical resonator, TiO_2/Ag films were recorded at 298 K. EPR spectra were captured at low temperatures using the Varied Temperature Controller ES-DVT4. Sending liquid nitrogen-cooled gas to the sample area allows for the achievement of the desired temperature. The following parameters were used to detect the EPR spectra - 100 kHz modulation frequency, 3 mW of microwave power, 0.2 mT of modulation amplitude, 0.3 s of time constant, and 2 min of sweep time.

The photocatalytic tests were carried out in a glass reactor that was furnished with a magnetic stirrer and an 18 W Sylvania BLB UV lamp with an emission range of 315 to 400 nm. The tests were conducted at room temperature with 500 rpm of constant stirring.

The photocatalytic efficiency of pure and silver co-catalytic modified TiO_2 films was compared in mineralization of Methylene Blue. The volume of organic dye solution was 150 mL with initial concentration of 5 ppm. The degradation process of the pollutant was measured by UV-vis absorbance spectroscopy (spectrophotometer Evolution 300 Thermo Scientific, wavelength range from 400 to 800 nm) after aliquot sampling at regular time intervals (1, 2, 3, 4 h).

Methylene Blue as a model compound for degradation was chosen. The dye concentration during the photocatalytic test is determined by spectrophotometry at $\lambda = 667$ nm using a calibration curve (correlation coefficient, R = 0.998).

The degree (D %) of photocatalytic mineralization of the dye was calculated using the equation:

$$D\% = (C_{in} - C_t)/C_{in} . 100 \quad (1)$$

where C_{in} represents the initial concentration, C_t represents the dye concentration after t min of photocatalysis.

RESULTS AND DISCUSSION

The structural morphology of the catalysts is investigated by SEM. Fig. 1 shows the surface of TiO_2/Ag, 10^{-2} sol-gel films. The morphology of the sample is homogeneous and consists of micro aggregates. The silver nanoparticles are distributed over the entire surface of the film, homogeneously (with dimensions of the order of 100 nm). They are located over the entire surface.

The elements that are present on the surface of titanium dioxide films are examined, as well as their oxidation states, using X-ray photoelectron spectroscopy. In particular, the oxidation state of Ag before and after the photocatalytic process is examined. Silver is present on the surface of TiO_2 as Ag^0 and Ag^+, as shown by the shape of the photoelectron and the Auger line (Fig. 2).

The Ag0 peak has a binding energy (BE) of 368.8 eV, according to the curve fitting procedure for the Ag3d line, while the Ag^+ peak has a BE of 367.8 eV. Additionally, two characteristics of the Auger peak can be clearly seen, indicating that Ag^0 has a kinetic energy of 357.2 eV and Ag^+ has a kinetic energy of 355.8 eV. Using the outcome of the curve fitting procedure, the concentration of Ag^+ clusters is three times higher than that predicted for Ag^0 particles. The relative concentrations of the listed elements on the surface of the TiO_2/Ag film can also be used to infer the presence of oxidized silver. The ratio Ti : O : Ag = 68: 24: 8 at. % that we calculated is different from the ratio Ti : O : Ag that was actually observed in our case, which is 1 : 2. This technique thus demonstrates that silver ions are photo-fixed on a semiconductor's surface. The oxygen is more abundant on the sample's surface. Hydroxide groups or Ag - O bonds may be to blame for the excess of oxygen. EPR measurements have also verified the existence of Ag^+ clusters.

The signal, which is narrow-band T1 with g values

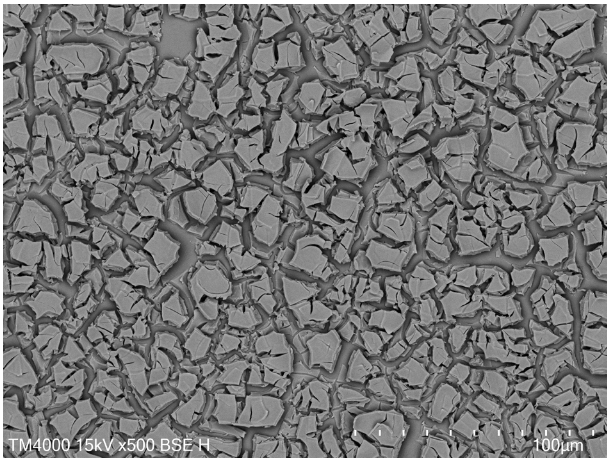

Fig. 1. SEM images of TiO_2/Ag, 10^{-2} sol-gel films.

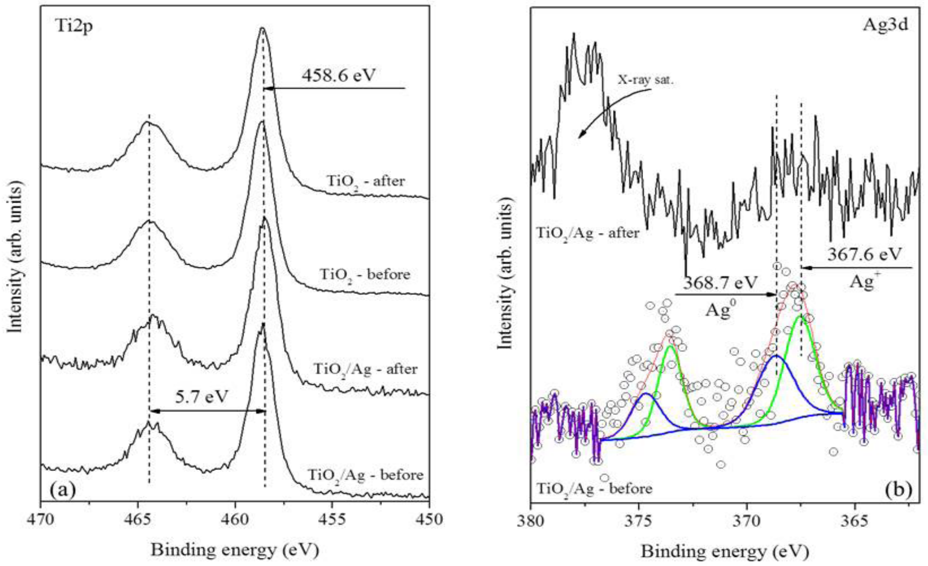

Fig. 2. XPS spectra of pure and TiO_2/Ag thin films (a) Ti2p and (b) Ag3d.

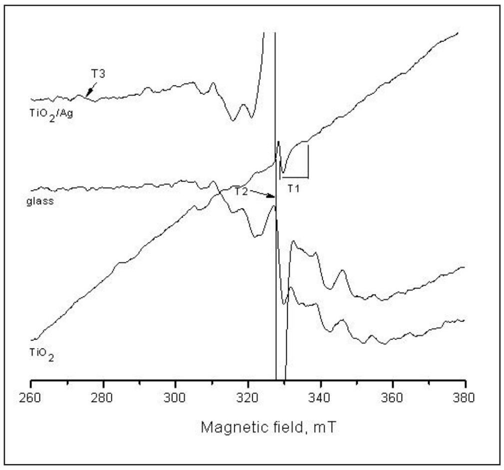

Fig. 3. EPR spectra of pure and TiO_2/Ag films.

of 1.99 and 1.96, was captured in TiO_2 films (Fig. 3). The substitution Ti^{3+} in hydrated anatase was identified as the cause of this signal, which has also been seen in colloidal TiO_2 anatase [14]. Silver ions are used to modify, and the intense signal T_2 at g = 2.0038 is then captured. Oxygen vacancies are responsible for the EPR peak at g = 2.001 - 2.004.

In the presence of pure and silver-modified TiO_2 thin films for a period of four hours, Methylene Blue degradation is depicted in Fig. 4 as a function of time under UV illumination. When it comes to the photocatalytic breakdown of different dyes, the effectiveness of semiconductor catalysts is comparable to that of other materials. According to earlier research, the Langmuir - Hinshelwood (L - H) equation governs how quickly textile dyes mineralize in heterogeneous systems when ultraviolet light is present [15]. To understand the kinetics of heterogeneous catalytic processes, the (L - H) equation is frequently used. In some studies, the effect of various experimental conditions has been described using the pseudo-first order kinetics assumption [15]. According to Fig. 4, the amount of Methylene Blue is reduced by about 40 % when the dye is subjected to photocatalytic degradation in the presence of UV light and TiO_2 thin films. Due to the typical behavior of titanium dioxide and the well - known band gap value, these results are expected.

In addition, Fig. 4(a) demonstrates how the photocatalytic activity of TiO_2/Ag thin films photo-fixed with ultraviolet light was significantly increased (nearly 62 %, calculated by equation 1) for the degradation of Methylene Blue.

Due to the presence of silver particles on the surface of TiO_2, these results were obtained. Due to the ability of the silver particles to store charge and accept electrons, carrier recombination is decreased, and the production of reactive oxygen species is increased. Thus, a collective oscillation known as a localized surface plasmon resonance can be produced by a

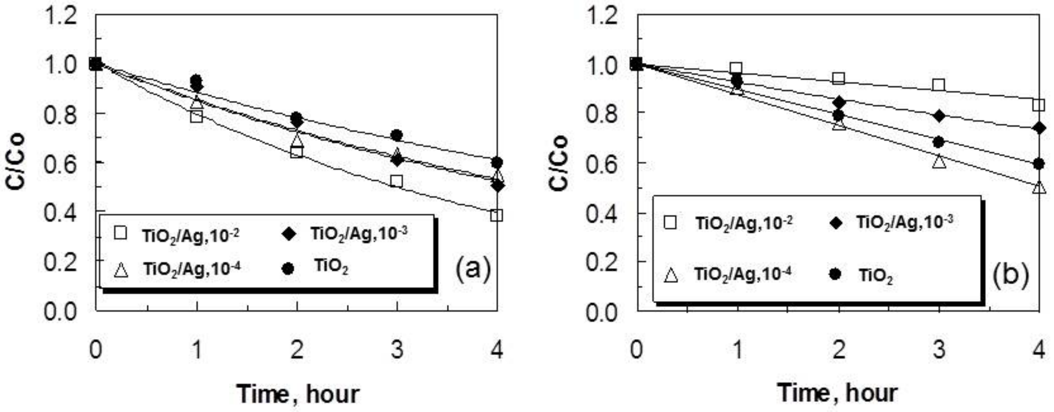

Fig. 4. Decrease of the Methylene Blue concentration versus time of illumination with pure and Ag-modified TiO_2 films with (a) and without (b) UV light photo-fixation.

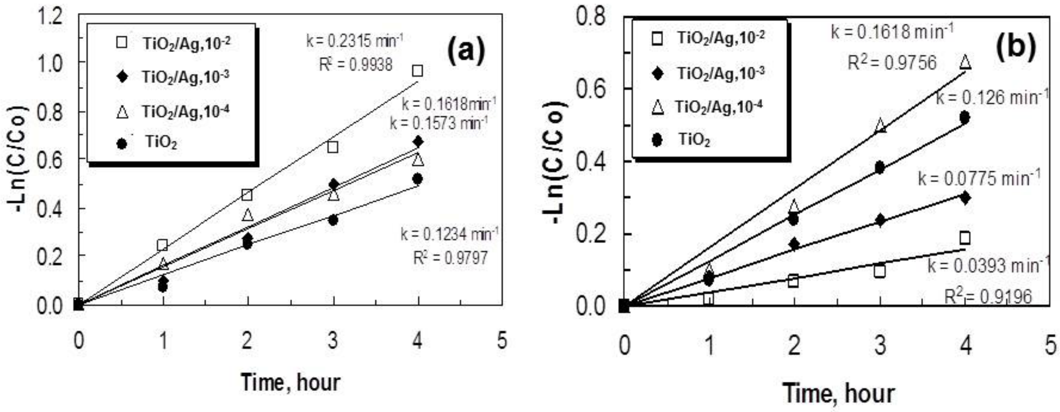

Fig. 5. Kinetic study on the photocatalytic degradation of Methylene Blue, using pure and Ag-modified TiO_2 films with (a) and without (b) UV light photo-fixation.

silver co-catalyst [15]. Other literature sources claim that silver particles have their electrons collectively oscillate in the conduction band, increasing the TiO_2 semiconductor's photocatalytic effectiveness [16]. According to experimental findings, silver co-catalytic modification of TiO_2 films in the presence of ultraviolet light significantly improves the efficiency of dye degradation compared to that of films fixed in the dark (Fig. 4(b)).

This result is probably due to the stronger interaction and charge transfer caused by photo-fixation with UV light. As a result, there is less e^- / h^+ pair recombination. As a result, UV-photofixed silver co-catalytically modified TiO_2 films have higher photocatalytic efficiency than UV-photofixed TiO_2 films.

The kinetic data in Fig. 4 are subjected to the pseudo-first order model. The slope of the linear fitting of $Ln(C_t/C_{in})$ vs. time (Fig. 5) was used to calculate the values of the rate constants for each test. The films modified with silver at a concentration of 10^{-2} M (Fig. 5(a)) have the highest photocatalytic activity, as can be seen from the figure ($k = 0.2315$ min^{-1}). This value is 1.87 times higher than the TiO_2 sol-gel films' value of 0.1234 min^{-1}. The rate of degradation of the organic dye provides evidence for the values of the rate constants, k. Eq. 1 is used to calculate the degradation.

In comparison to pure semiconductors, nanostructured silver co-catalytist modification TiO_2 films have a higher photocatalytic efficiency (D % = 40.57 %). In increasing order, TiO_2 < TiO_2/Ag, 10^{-4} < TiO_2/Ag,10^{-3} < TiO_2/Ag10^{-2}, the degree of MB - photodegradation. The kinetic values (r and D %) demonstrated that this combination could be used as an alternative to upping the photocatalytic activity of TiO_2 and confirmed the efficacy of this modification process and photo-fixation with UV light illumination.

CONCLUSIONS

TiO_2 thin films on glass substrates are deposited by simple and economical method starting from titanium (IV) isopropoxide dissolved in 2-methoxyethanol and monoethanoamine. Ag^+ is added to the nanostructures (from 10^{-2} to 10^{-4} M) through photo-fixation when ultraviolet light is present. The TiO_2/Ag sample has a sandwich structures surface, on which silver particles are evenly distributed. The XPS spectra confirm the presence of silver in the modified films. Compared to pure sol-gel films, modified samples exhibit higher photocatalytic efficiency. The results of the photocatalytic experiments showed that is 1.87 times higher in comparison with pure films. Our investigation shows that the modification of TiO_2 with silver ions by photo-fixation plays a significant role in the photocatalytic process.

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