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PHOTO-FIXATION OF Ag ONTO TiO_2 POWDER FILMS FOR IMPROVED PHOTOCATALYTIC ACTIVITY AND ATOMIC-ABSORPTION DETERMINATION OF RESIDUAL NOBLE METAL IN DYES SOLUTION

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Abstract

For the first time, we photo-fixed silver ions (10^{-2}, 10^{-3}, and 10^{-4} M) onto films prepared from commercial TiO_2 powder via ultraviolet illumination. The synthesis process is straightforward and environmentally friendly. The nanostructures are characterized by SEM, XRD, FAAS, and UV/Vis spectroscopy for the photocatalytic properties. The X-ray diffraction pattern demonstrated the phase of the anatase TiO_2 structure. Flame Atomic Absorption Spectrometry is used as a simple way to determine the Ag^+ content in solutions from the heterogeneous photocatalysis under UV illumination. The research shows that at the end of the degradation process, no silver ions are observed for both dyes – malachite green and methylene blue. The formation of stable intermediates by the reaction of OH with the triarylmethane dye during the photocatalysis resulted in faster degradation of malachite green than methylene blue. In comparison to pure TiO_2, the TiO_2/Ag films have higher photocatalytic efficiency. The reason is the presence of silver, which leads to a decrease in the recombination of pairs of charges.

Key words: TiO_2 powder films, silver co-catalytic modified, dyes

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Introduction. Heterogeneous photocatalysis is one of the advanced oxidation technologies being researched as a new method to decontaminate wastewater by mineralizing organic pollutants. Due to its stability, high surface area, nontoxicity, and low price, TiO_2 is the most popular photocatalyst among all others [1]. Optimizing the photocatalytic response is hampered by the massive charge carriers' rapid recombination rate. Different tactics are intended to regulate the stability and photocatalytic activity of titanium. By reducing the band gap energy and facilitating charge transportation, the modification of TiO_2 improves the photocatalytic performance. Pt, Ag, or Au are suitable noble metals to encourage the interfacial electron transfer process and speed up the separation of the massive charge carriers [2–4]. The deposition of small amounts on titanium surfaces is crucial to the understanding of noble metals. This low concentration improves titanium's photocatalytic performance without changing the surface properties or crystalline structure. Due to its high chemical stability and reactivity in the field of heterogeneous photocatalysis, Ag is a preferred material [5–8]. Ag is photodeposited on semiconductor surfaces for a variety of photocatalytic processes for degradation of organic pollutants [8–11]. The recombination rate of the charge carriers is slowed and the lifetime of the reactive species for redox reactions is lengthened by photo-deposition of metallic Ag nanoparticles on the titanium surface. This enhances the electron transition from the conduction band of TiO_2 to the Fermi level of silver. Recent years have seen increased research into the impact of silver deposition on titanium's ability for photocatalysis. Many different synthetic techniques have been developed to produce a wide variety of materials with different frameworks, chemical compositions, and pore structures.

In the present paper, we modify silver ion films prepared from commercial TiO_2 powder for the first time. The first objective of this study is to look into how photo-fixation (deposition) of Ag^+ affects titanium's structural, crystalline, and photocatalytic properties for the degradation of malachite green and methylene blue dyes as model pollutants. Second, for the first time, residual silver is determined using flame atomic absorption spectrometry.

Experimental. ***Substrates.*** Titanium dioxide commercial powder ($\geq$ 99.0%), polyethylene glycol 2000 (PEG 2000), ethanol (C_2H_5OH, $\geq$ 99.0%), nitric acid (HNO_3, $\geq$ 99.0%), and silver nitrate ($AgNO_3$) were received from Fluka. The glass slide substrates (ca. 76 mm $\times$ 26 mm) were delivered from ISO-LAB. Malachite green (MG, $C_{52}H_{54}N_4O_{12}$, λ_{max} = 615 nm, Croma-Gesellschaft mbH & Co.) oxalate and Methylene blue (MB, $C_{16}H_{18}ClN_3S$, λ_{max} = 660 nm, Fluka) were model pollutants for the photocatalytic tests.

Synthesis of TiO_2 and TiO_2/Ag powder films. The process used to create the powder catalysts is straightforward, a lot faster, less expensive, well-controlled, and ensures minimal energy use. First, C_2H_5OH (solvent, 50 ml) was added to PEG 2000 (stabilizer, 7 g). After stirring and heating the mixture for 30 min at a constant temperature of 70 °C, a clear-coloured solution was produced.

Second step, in 60 ml of ethanol, 7 g of commercially available TiO_2 powder was dissolved over the course of 15 min at room temperature. The PEG 2000 solution was combined with the resulting dispersion before being stirred for an additional 15 min and sonicated (15 kHz) for 30 min. TiO_2 films were created using the white suspension in its prepared form. At room temperature, the glass substrate was dipped into the precursor solution and then removed at a rate of 0.9 cm/min. After each subsequent dip, the films were dried at 100 °C for 10 min. The final powder films underwent a 60 min preheating and sintering process at 500 °C.

TiO_2 powder films that have been co-catalytically modified with silver were produced through chemical photo-deposition. The TiO_2/Ag films were photo-fixed with UV illumination after being submerged in an aqueous $AgNO_3$ solution for 20 min, and then they were washed with H_2O. To get rid of nitrate ions, the modified films were dried at 100 °C for 10 min. The modified titanium dioxide film (TiO_2/Ag, 10^{-2}) has better properties than pure titanium dioxide, according to photocatalytic results. This enabled us to produce and examine the photocatalytic properties of two more films – TiO_2/Ag, 10^{-3} M and TiO_2/Ag, 10^{-4} M.

In order to determine the elemental composition of the sample, the surface morphology of the produced powder films was examined using a scanning electron microscope (Hitachi TM4000 – accelerating voltage 15 kV) fitted with an energy dispersive X-ray analysis equipment (Bruker AXS Microanalysis GmbH) was performed, employing a Bruker AXS detector. X-ray diffraction studies were performed for phase and structure identification. The X-ray diffractograms of the synthesized nanocomposites were obtained using Siemens D500 with Cu-Kα radiation within 2θ range of $20°-70°$ at step of $0.05°2\theta$ and counting time 1 s/step. The BET surface area of pure and TiO_2/Ag powder films was estimated from the N_2 adsorption. For the BET analysis, the samples were degassed at 70 °C for 17 h in vacuum before the N_2 adsorption.

The photocatalytic degradation of Malachite green (MG) and Methylene blue (MB) dyes in aqueous solution (150 ml) with initial concentrations of 5 ppm was used to evaluate the photocatalytic efficacies of TiO_2 and TiO_2/Ag powder films. A glass photoreactor outfitted with a magnetic stirrer spinning at 500 rpm and a 36 W UV lamp with a 315–400 nm emission range was used to conduct the photocatalytic reaction. Before the illumination was turned on, the sample was allowed to acclimate in the dark for about 5 min. Using an Ealing Electro-optics, Inc. Research Radiometer, the light power density at the sample position was found to be 0.66 mW/cm^2. A UV-visible spectrophotometer (the Evolution 300 from Thermo Scientific) was used to measure the absorbance spectra. In the presence of UV illumination, all catalytic tests were carried out at room temperature (23 ± 2 °C).

The silver content was assessed in the solution after the photocatalytic tests and calibration with water solutions. A flame atomic-absorption spectrometer, model number Perkin Elmer A Analyst 400, was employed for the instrumental

measurements. The manufacturer-recommended instrumental parameters were used. The light source was a silver hollow cathode lamp. Daily preparations of Millipore water calibration standards at concentrations of 0.1, 0.5 and 1 mg/l Ag^+ were made. Three replicates of an instrumental measurement yielded the RSD 2–4%.

The Silver content that would appear in the solution during photocatalysis was determined at the 1st, 2nd, 3rd, and 4th hour from the photocatalysis beginning after its 5-fold concentration. The Ag concentration was provided according to the following analytical procedure: 5 ml of photocatalysis solution was placed in a small Beaker and one drop of concentrated HNO_3 was added. The solution was carefully heated near to dryness. After cooling 1 ml 0.5 mol/l HNO_3 was added.

Results and discussion. The surface of the TiO_2 and TiO_2/Ag films exhibits a homogeneous morphology with particles of various sizes, according to measurements made with a SEM (Fig. 1). This is a result of the agglomeration that is unavoidably brought on by the high temperature (500 °C) used to prepare the films. The morphology of the initial TiO_2 films is not significantly changed by the Ag co-catalytic modification. It is evident that the modification ions caused a slight reduction in crystal size, which is consistent with the results of the XRD analysis.

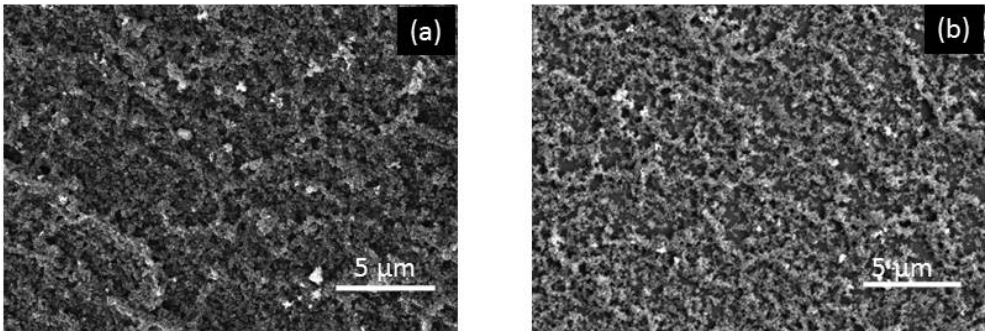


Fig. 1. SEM image of pure (a) and silver (10^{-2} M) co-catalytic modified (b) TiO_2 powder films

The presence of Ti, O, and Ag chemical elements in a co-catalytically modified TiO_2 film with the highest (10^{-2} M) silver content is estimated using energy dispersive X-ray spectroscopy (Fig. 2). The spectrum displays peaks of various intensities that represent the atoms of titanium, oxygen, and silver, respectively. Ag has a weight percentage of 7.58 wt %. The purity of the powder films produced is demonstrated by the lack of impurity peaks in the EDS spectrum. This outcome shows that it is possible to successfully produce high-purity Ag co-catalytically modified TiO_2 material that is photo-fixed under UV illumination. The glass substrates on which the nanostructured materials are deposited are likely to blame

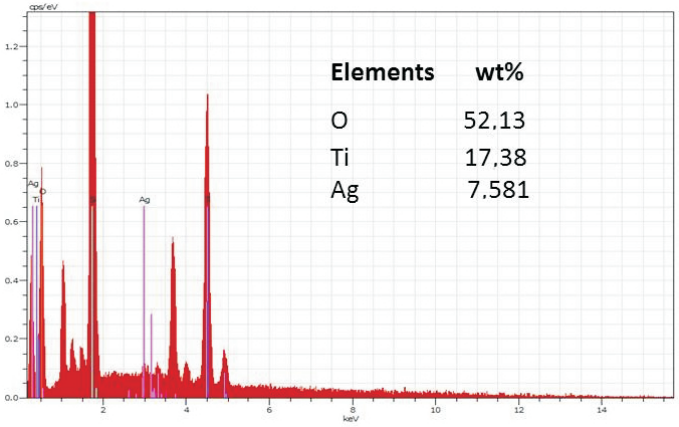


Fig. 2. Energy dispersive X-ray spectroscopy of silver (10^{-2} M) co-catalytic modified TiO_2 powder film

for the presence of Si.

By using XRD analysis, the prepared pure semiconductor and silver (10^{-2} M) co-catalytic modified films crystal structure is determined (Fig. 3). According to the information on the standard JCPDS card (96-500-0224), the recorded peaks show that the anatase phase is the primary phase of the TiO_2 powder film. The crystal planes (101), (004), (200), (105), (211), and (204) are represented by the intense diffraction peaks at 25.45, 38.35, 48.35, 53.91, 55.07, and 63.2°, respectively. Pure TiO_2 exhibits crystalline film with no impurities or other phases in its structure thanks to well-defined peaks. The anatase structure of the TiO_2/Ag film is unaltered by the addition of silver. The modified TiO_2 film does not exhibit any additional peaks as a result. However, additional peaks at 38.46, 45.86, and 64.72° appear when Ag is present at a concentration of 10^{-2} M. The planes 111, 200, and 220 of the metallic form of Ag (JCPDS 96-901-3048) correspond to these peaks. TiO_2 co-catalytically modified with silver ions has been reported to exhibit patterns similar to these [12]. According to the XRD results, the addition of silver ions had no discernible impact on the crystal size. However, the intensity of the TiO_2 peaks decreases when the film is co-catalytically modified. According to Scherrer equation, the average crystallite size (d(TiO_2) = 38.3 nm, d(TiO_2/Ag) = 32.5 nm) slightly decreases with silver concentration, showing that the crystalline lattice is nearly constant.

The surface area of TiO_2/Ag (38 m^2/g) is greater than that of pure TiO_2 (11 m^2/g) films. The effect of this parameter is determined in the photocatalytic experiments.

By observing MG and MB degradation under UV light, the photocatalytic efficiencies of the pure and co-catalytic silver modified films are calculated. We developed an economical process for the TiO_2 powder catalyst preparation in or-

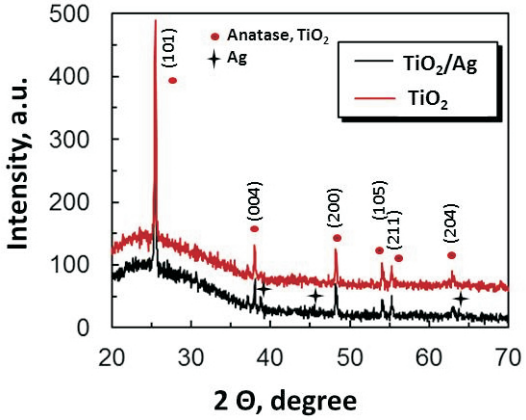


Fig. 3. XRD patterns of pure and silver co-catalytic modified TiO_2 powder films

der to investigate the impact of the co-catalytic modification. When silver ions are added, the catalyst's efficiency increases (from 10^{-4} to 10^{-2} M). In the presence of ultraviolet illumination, the degradation rate increases from 0.1684 to 0.3134 h^{-1} for MG degradation (Fig. 4a) and from 0.0847 to 0.1331 h^{-1} for MB degradation (Fig. 4b). According to the results displayed in Fig. 4, the photocatalytic reaction had pseudo-first-order kinetics. A linear regression is used to assess the apparent first-order reaction rate constants based on the experimental data. It is widely known that a variety of factors, including the synthesis, surface area, light illumination, and crystallite size, affect the photocatalytic efficiency of co-catalytically modified TiO_2. Silver is obviously helpful to the samples' photocatalytic behaviour under UV irradiation in our photocatalytic experiments. The dye solutions do not bleach when the pure and co-catalytically modified semiconductor films are not present.

Figure 4 demonstrates that the MG and MB are more successfully decoloured by the silver-modified samples than by the pure TiO_2 films. At the illuminated surface, the photocatalysts UV irradiation produced e^-/h^+ pairs. The rate of photocatalysis is lowered by the recombination of these charge carriers. The capacity of silver to trap electrons may account for the beneficial impact of the co-catalytic modification with silver ions on the efficiency of the TiO_2 for the photodegradation of the dyes. As a result, compared to pure semiconductors, a more efficient electron transfer happened through adsorption onto the surface molecules. Superoxide anions are created when oxygen that has been adsorbed onto the photocatalyst surface traps the electrons. However, the adsorbed water or hydroxide ions could be oxidized by the holes at the semiconductor surface, producing hydroxyl radicals. Bárdos et al. [13] demonstrated that electron transfer to silver ions is more effective than oxygen scavenging of electrons at the surface of excited

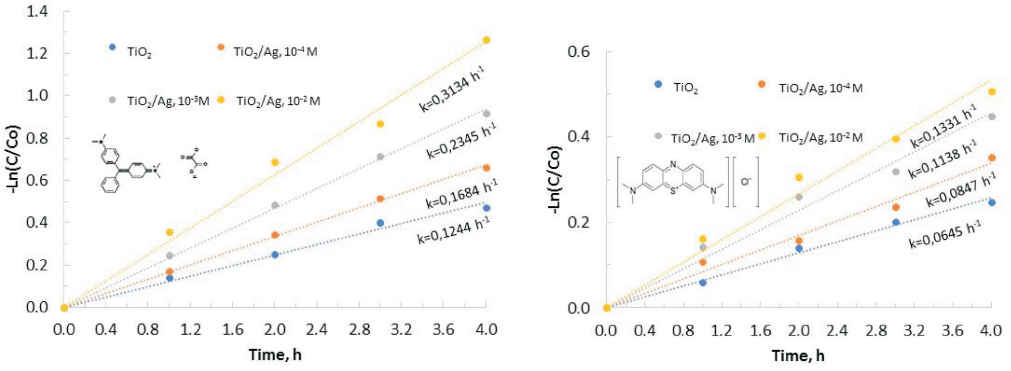


Fig. 4. The pseudo-first-order kinetics of degradation of malachite green (a) and methylene blue (b) dyes under UV light illumination using pure and silver co-catalytic modified powder films

semiconductor particles. As a result, less O_2^- is formed because electrons transfer to silver ions occurs more quickly than they do to oxygen molecules. However, the loading of Ag metal on the TiO_2 surfaces in the co-catalytic silver-modified semiconductors (TiO_2/Ag) may speed up the transport of photogenerated electrons to the external systems. Deposits that were partially negatively charged were produced when electrons were transferred to the metal deposits. By quickening the electron transfer to the dissolved oxygen molecules, the silver ion deposits on the surface increased photoactivity. Consequently, the release of trapped electrons from the Ag metal to the oxygen during oxygen reduction resulted in the formation of superoxide anion radicals.

The rate at which the organic dyes degrade provides evidence for the values k of the rate constants. Additionally, under UV light illumination, Fig. 4 compares the photocatalytic activity of TiO_2 with regard to the degradation of MG and MB at various silver concentrations. When compared to MB (D% = 67.43% for four hours, nanostructured films containing Ag, 10^{-3} M exhibit superior photocatalytic activity and faster degradation MG (D% = 72.11% for four hours). Films photofixed with 10^{-2} M silver ions exhibit the highest photocatalytic activity, whereas samples modified with 10^{-4} M silver exhibit the lowest activity ($D\%_{MG} = 58.04\%$ and $D\%_{MB} = 50.84\%$).

Malachite green degraded more quickly in the silver co-catalytically modified powder films than in methylene blue because stable intermediates were formed during the photocatalytic process when OH reacted with triarylmethane dye (C=C bond). The literature has reported on the likely mechanisms of methylene blue and malachite green degradation, which is caused by a reaction with OH [14, 15]. According to Houas et al. [14], the OH first cleaves the S+=C bond, which causes the central heterocyclic part to undergo a ring-opening reaction. The MB solution

degrades as a result of this. Ju et al. [15] demonstrated that, with regard to MG, the first stage of dye decolourization involves a radical attack on the central C atom, which changes it into a malachite green carbinol base and once more causes the pollutant to degrade.

Based on the aforementioned logic, it can be deduced that the accelerated degradation of malachite green observed in this study may be related to the hydroxyl radical's facilitated attack on the S atom. The higher electron density was the cause of this.

In all studied solutions of Methylene blue photocatalysis the Ag content is below the detection limit (0.0071 mg/l). Any Ag concentration (from 0.0076 ± 0.0005 to 0.014 ± 0.001 mg/l) is measured in solutions from Malachite green photocatalysis using TiO_2 powder films modified with 10^{-2} mol/l Ag^+. In all the rest cases of Malachite green photocatalysis the Ag content is below the detection limit of the analytical procedure for this dye (0.0014 mg/l). This is probably due to the fact that silver ions were not released during the photocatalytic process. The surface of the modified films was preserved and remained unchanged.

Conclusions. TiO_2/Ag photocatalysts are used for the photocatalytic degradation of MG and MB dyes in wastewater effluent. They are synthesized using an easy, economical, and well-controlled method. The UV-visible spectrophotometer, EDS, XRD, and SEM are used to characterize the photocatalysts. The photocatalytic efficiency of TiO_2 is increased and its rate constant is three times higher than that of bare TiO_2 due to the photo-fixation of Ag on TiO_2. The photocatalytic degradation of MG and MB represented well with the pseudo-first order kinetic model. The experimental results showed that the TiO_2/Ag, 10^{-2} possesses the highest photocatalytic properties of 96.39% and 68.83% for MG and MB, respectively. TiO_2's increased efficiency can be attributed to the synergistic effect of Ag and improved charge transfer between the two materials. According to the likely mechanism, the primary removal process for the breakdown of MG and MB is the OH pathway. The flame atomic absorption spectroscopy for the determination of residual noble metal in the dye solution found the silver to be below the detection limit. This is most likely because the photocatalytic process did not release any silver ions. The altered films' surface was kept intact and did not change. These results suggest that the synthesized TiO_2/Ag photocatalyst is effective when exposed to UV light and can be used in a practical manner to remove organic pollutants.

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