



# Visible light responsive photocatalytic ZnO:Al films decorated with Ag nanoparticles

M. Bizarro\*, E. Martínez-Padilla

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, A. P. 70-360, Coyoacán, C.P. 04510, D.F., México

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## ABSTRACT

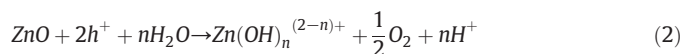
The spray pyrolysis technique was used to grow ZnO:Al films decorated with silver nanoparticles in their surface, in order to increase and stabilize the photocatalytic activity of ZnO. The appropriate amount of Ag nanoparticles was determined varying the concentration of an AgNO<sub>3</sub> solution and the spraying time. The films were characterized by X-ray diffraction, scanning electron microscopy and energy dispersed spectroscopy. The photocatalytic activity of the films was evaluated by the degradation of a methyl orange dye solution. The stability of the photocatalytic activity was studied along five degradation cycles while exposed to simulated sunlight, white light and UV light. We found that a spraying time of 8 min of the AgNO<sub>3</sub> solution gives nearly 3 at% of Ag in the ZnO:Al films. This amount of Ag nanoparticles stabilized the photoactivity under UV and sunlight along five degradation cycles, showing a synergistic effect between Al and Ag that greatly improved the photocatalytic performance of ZnO films.

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## 1. Introduction

Heterogeneous photocatalysis is already being applied to environmental remediation processes due to the reduction of organic pollutants in water and air and the inactivation of bacteria which are responsible of diseases [1,2]. Zinc oxide has attracted attention for this purpose due to its good photocatalytic efficiency, low production cost and availability [3,4]. It is a semiconductor with a band-gap about 3.2 eV, which means that it can only absorb UV light; but the position of its valence band confers the electron–hole pairs the sufficient oxidant power to decompose several organic molecules, such as dyes in dissolution [5–9]. The electron–hole recombination rate is also low, favoring the formation of highly oxidant species such as OH<sup>•</sup>, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub><sup>•-</sup>, which also contribute to the degradation of the pollutant [10].

One of the main drawbacks of ZnO is the photo-instability in aqueous solution when it is exposed to UV irradiation, which decreases its photocatalytic activity [11–14]. This photo-induced instability is known as photocorrosion, which occurs through the following reactions [12,15]:



where  $h^+$  are the positive holes created when the semiconductor is irradiated with UV light. Photocorrosion of ZnO is a crucial factor that may discourage its use in water treatment applications. Different efforts have been carried out in order to reduce the instability of ZnO, among which may be mentioned the passivation with inert layers –such as TiO<sub>2</sub>–, metal doping, polymeric coatings –such as polydimethylsiloxane [16] and polyaniline [14]–, more crystalline structures and even the hybridization with C<sub>60</sub> [17] and graphite-like structures [13]. Not all of these have been prosperous in a long term period [18]. Among these alternatives, the modification of ZnO with Ag has shown the improvement in the photocatalytic degradation of organic pollutants and also prevents the photocorrosion under UV light [11,19,20]. The role of Ag, on one hand, is to occupy the surface vacant sites of the ZnO lattice, suppressing the activation of surface oxygen atoms which in turn inhibits the photocorrosion [15]. On the other hand, it can act as electron sinks to enhance the separation of photoexcited electrons from holes that also favor the photocatalytic activity [20].

Recently, nanostructured Al-doped ZnO –widely used as a transparent conducting oxide [21–23]– have recently attracted attention as a photocatalyst due to its superior photocatalytic efficiency [24–27]. Moreover, in our previous work we found that doping ZnO with a proper amount of aluminum not only highly improves the photocatalytic activity of ZnO but also makes it sensitive to visible light [28,29]. However, the photocorrosion of the Al-doped ZnO films came out when the films were reused. Even though Al-doped ZnO and Ag-doped ZnO have been studied separately, the photocatalytic properties and photostability of

\* Corresponding author at: Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, A. P. 70-360, Coyoacán 04510, D. F., México. Tel.: +52 55 56224599; fax: +52 55 56161251.

E-mail address: [monserrat@iim.unam.mx](mailto:monserrat@iim.unam.mx) (M. Bizarro).

ZnO doped with both Al and Ag has not yet been reported. In this work we produced ZnO:Al films decorated with Ag nanoparticles in order to achieve a synergistic effect of both impurities that increase the photocatalytic activity and the photostability of ZnO films under sunlight.

## 2. Experimental setup

The spray pyrolysis technique was used to deposit ZnO:Al films on glass substrates, using zinc acetate dehydrate (Sigma–Aldrich, 98%) in a 0.2 molar concentration and aluminum chloride hexahydrate (Sigma–Aldrich, 99%) at an atomic ratio of Al/Zn = 0.25, as previously determined [28]. Both precursors were dissolved in deionized water. The films were deposited at a substrate temperature of 450 °C with gas and solution flow rates of 8 L/min and 8 mL/min, respectively. The films were annealed at 450 °C for 10 min in order to complete the decomposition of the metal-organic salts. The films were decorated with silver nanoparticles on their surface by spraying an AgNO<sub>3</sub> aqueous solution in different concentrations (1, 2, 5 and 10 at%). Once determined the best Ag concentration, the deposition time of the AgNO<sub>3</sub> solution was varied to optimize the silver nanoparticles loaded to the ZnO:Al films surface. The films were characterized by profilometry (Sloan Dektak 2A), X-ray diffraction (XRD Bruker D8) with the Cu K<sub>α1</sub> wavelength (1.54056 Å) starting at an angle of 10° to 80° in steps of 0.025°, and scanning electron microscopy (SEM JEOL7600F) with energy dispersed spectroscopy device (EDS) for chemical composition analysis using an operating voltage of 10kV with a current of 1 nA and a working distance of 5.8 mm.

The photocatalytic activity of the films was studied by the degradation of a methyl orange solution in a concentration of 10<sup>-5</sup> M. The samples were immersed in 10 mL of the dye solution and irradiated with a 9 W UV lamp with its maximum centered at 380 nm, in the first stage. The absorbance spectra were measured each 30 min in a Perkin Elmer Lambda 35 UV–vis spectrophotometer, to evaluate the degradation of the dye solution. After the selection of the proper amount of silver loaded on the surface of the photocatalysts, new identical samples were produced in order to test their photocatalytic stability after 5 degradation cycles under different light sources: UV, white light (9 W lamp with no UV contribution) and simulated sunlight (Oriel 96000, 150 W).

## 3. Results

### 3.1. Optimization of Ag loading and photocatalytic tests

The silver concentration in the spraying solution was selected taking into account the preliminary photocatalytic degradation tests. The rate of reaction was obtained following the Langmuir–Hinshelwood model in the low concentrations regime, stated in Eqs. (1) and (2) [30]:

$$r = \frac{dC}{dt} = k_r KC \quad (1)$$

$$\ln\left(\frac{C_0}{C}\right) = k_r K \cdot t = k_{app} \cdot t \quad (2)$$

Where  $C$  and  $C_0$  are the initial and final concentrations, respectively;  $k_r$  is the specific reaction rate constant for the oxidation of the dye,  $K$  is the equilibrium constant of the reaction and  $k_{app}$  is the apparent rate of reaction. The degradation efficiency was estimated using the expression in Eq. (3):

$$\text{Degradation \%} = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (3)$$

The apparent rate of reaction was plotted as a function of the silver content in the solution, as shown in Fig. 1. We observed a good increase in the rate of reaction with the silver concentration from 1 to 5%, and

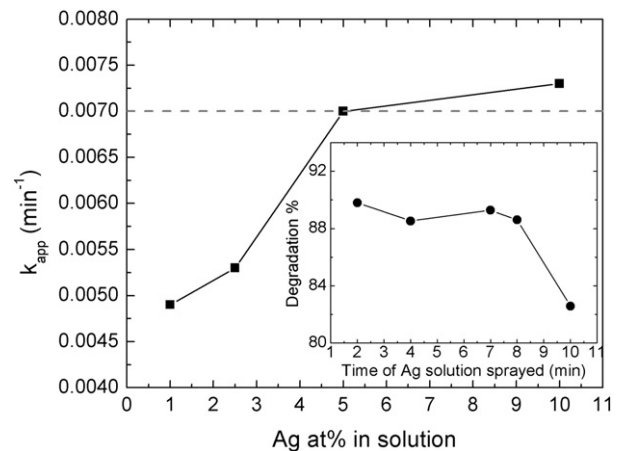


Fig. 1. Change in the degradation percentage of Ag doped ZnO films as a function of the Ag concentration in the spraying solution. Inset: Degradation efficiency of the ZnO:Al films with different spraying times of the Ag solution.

then it became practically constant from 5 to 10%. Then we selected a silver concentration of 5 at% for the rest of the samples.

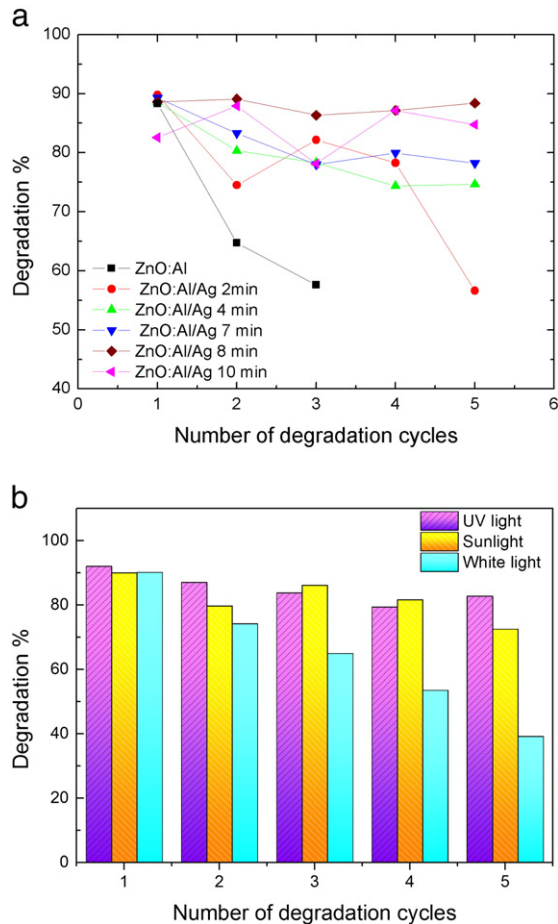
Further samples were prepared spraying the AgNO<sub>3</sub> 5 at% solution to the ZnO:Al films to form nanoparticles in their surface. The deposition time of the silver solution varied between 2 and 10 min. The thickness of the ZnO:Al films was around 550 nm; the presence of the silver nanoparticles did not give an important change in their thickness, as they were dispersed on the surface and did not form a layer. The degradation percentage was calculated and we found a similar degradation rate for the samples sprayed with 2, 4, 7 and 8 min, giving values of (89.15 ± 0.65)% of the dye decomposition. However, spraying the films during 10 min with the AgNO<sub>3</sub> solution diminished the photocatalytic activity giving an 82.6% degradation of the dye, as can be seen in the inset of Fig. 1. This behavior is explained by the large amount of silver loaded to the film, that was enough to cover many active sites of the ZnO:Al films blocking the light needed for the reactions. This was evident even with the naked eye because the sample acquired a dark color due to the silver loaded on its surface.

The stability of the photocatalytic activity of these films was studied after five degradation cycles. As it is observed in Fig. 2a, the photocatalytic activity of the ZnO:Al film drops after each reuse achieving less than 60% degradation in the third cycle. The films that were sprayed with the Ag solution made the ZnO:Al films more stable, getting the greatest stability for a spraying time of 8 min. The shortest Ag spraying time showed a slightly betterment of the ZnO:Al but the efficiency dropped again in the fifth cycle. Moreover, the sample with 10 min of sprayed Ag showed variations along the different cycles. An increase of its activity was observed for the fourth and fifth cycles, which can be due to a loss of Ag particles that allowed a better light absorption on the surface of the film. Thereby, as the film with 8 min of Ag presented the best performance after several reuses, this spraying time was selected to grow a new set of samples in order to evaluate their performance under visible light.

Ag decorated ZnO:Al films effectively responded both to sunlight and to white light, degrading 90% of the dye solution in the first stage. These samples were exposed again to five degradation cycles, after which it was observed that the efficiency is maintained when the samples are illuminated with UV or sunlight; however the samples that were irradiated with white light gradually decreased their activity after each reuse, as can be seen in Fig. 2b.

### 3.2. Microstructural characterization

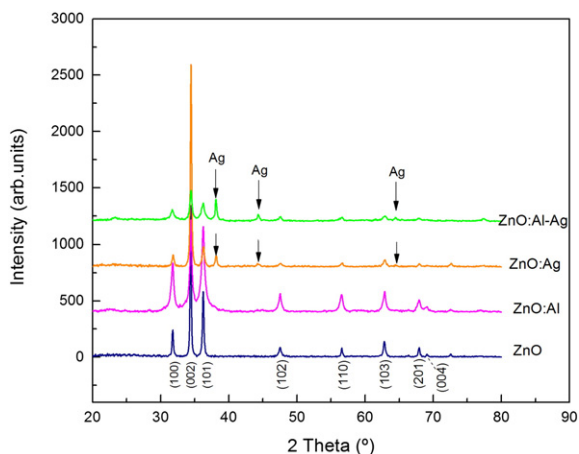
X-ray diffraction patterns were recorded for the undoped ZnO film as well as for each combination of doping elements: ZnO:Al, ZnO:Ag,



**Fig. 2.** (a) Stability of the photocatalytic activity of the films with different amount of Ag nanoparticles along 5 degradation cycles. (b) Photocatalytic performance of ZnO:Al/Ag films under different light sources during 5 cycles.

and ZnO:Al/Ag, as it can be seen in Fig. 3. The Al doping maintains the hexagonal wurzite structure of ZnO (according to the ICDD database file 01-036-1451), with no other phases present. Those samples spayed with Ag showed the corresponding Ag diffraction peaks, with no other Ag compounds, so we can discard the presence of silver oxide on the film.

In addition, Fig. 4 shows the SEM images of the ZnO:Al/Ag films, in which is possible to observe a wide size dispersion of the Ag particles, from very large particles around 500 nm to minuscule nanoparticles



**Fig. 3.** XRD patterns of un-doped and doped ZnO films.

less than 10 nm in diameter. These can be distinguished as bright particles dots in Fig. 4b. The EDS analysis revealed that the amount of silver loaded to the film was  $2.86 \pm 0.90$  at%, giving an Ag/Zn atomic ratio of 0.082. Even though this quantity is low, it has a great effect in the overall properties of the material.

### 3.3. Discussion

The enhancement of the photocatalytic activity of the films in more than 10% is mainly due to Al doping, as previously reported [29]. In this case the Ag nanoparticles on the surface of the films do not provide an extra increase of the activity, as it can be seen in Fig. 2a, where the samples with and without Ag nanoparticles have the same initial degradation efficiency. Nonetheless, the Ag nanoparticles indeed help to maintain the initial activity after several reuses. This improvement makes the photocatalyst be more effective for water treatment applications.

Studies about ZnO and its photocatalytic activity have proved that ZnO suffers photoinduced dissolution that greatly decreases its photocatalytic activity. This is still the case for ZnO:Al films. It has been identified that the photocorrosion process strongly depends on the orientation of the crystals but also occurs on the surface defect sites of ZnO [31]. Some of these defects may be due to dangling bonds in the surface layer of ZnO, which are ions ( $Zn^{2+}$  and  $O^{2-}$ ) on the surface that are incompletely coordinated and possess unpaired electron orbitals [32]. If Ag nanoparticles are placed on the surface of the ZnO:Al film, some of these defects are passivated or blocked, suppressing the reaction with surface oxygen [33]. As a result, the photocorrosion of ZnO:Al is inhibited. Ag nanoparticles also act as electron sinks that trap the photogenerated electrons in the conduction band, reducing the recombination of electrons and holes [34,35]. Moreover, Al doping favors the oxygen diffusion into the ZnO lattice and neutralizes some of the intrinsic oxygen vacancies [36], helping to reduce the electron-hole recombination too. Besides, the extra electron provided by Al atoms contributes to the reduction of the  $O_2$  dissolved in the aqueous medium and form the superoxide radical  $O_2^{\cdot-}$ . This highly reactive radical contributes to the formation of  $H_2O_2$  which accelerates the discoloration of the dye. This process is illustrated in Fig. 5, where is shown the photo-excitation of an electron from the valence band (VB) to the conduction band (CB) leaving a positive hole in the VB. The photogenerated electrons migrate to the Ag nanoparticles because the Fermi energy level of the system is lower than the CB of ZnO:Al, and the holes remain in the semiconductor surfaces, this charge separation reduces the electron-hole recombination. Furthermore, Al impurities are known to introduce shallow donors in ZnO, forming an n-type semiconductor [37]. This donor levels (marked with *d* in the diagram) – as well as the electrons trapped in the Ag nanoparticles – contribute to the formation of the reactive  $O_2^{\cdot-}$  species; whereas the holes in the VB react with the adsorbed water molecules to form hydroxyl radicals and  $H^+$ .

It was previously reported the discoloration of the dye using ZnO:Al films in the absence of light [29]. This also happened for the Ag decorated ZnO:Al films, as can be seen in Fig. 6. Here two possible mechanisms may occur: (i) the Al doping produces a high concentration of free carriers with high mobility, that can migrate to the surface of the ZnO film without the need of light and start the formation of  $O_2^{\cdot-}$  radicals. Kislov et al. also observed a contribution to the photocatalytic process by the “dark side” of a ZnO crystal, explained by charges drifting across the crystal [31]. (ii) the  $Al^{3+}$  attracts the electrons from the oxygen of water molecules, so that the bond between hydrogen and oxygen atoms weakens and facilitates the separation of one or more  $H^+$ . The higher the ions charge the greater the attraction and the easier it is for the  $H^+$  to dissociate. In this way, hydroxyl radicals ( $\cdot OH$ ) created from water hydrolysis are capable of initiating the degradation reactions without the need of light to activate the material. Xie et al., detected the presence of hydroxyl radical on Ag/ZnO powder under UV irradiation using PL technique, indicating the easiness of  $\cdot OH$  formation [11]. They also found that  $O_2$  is chemisorbed on Ag in the Ag/ZnO

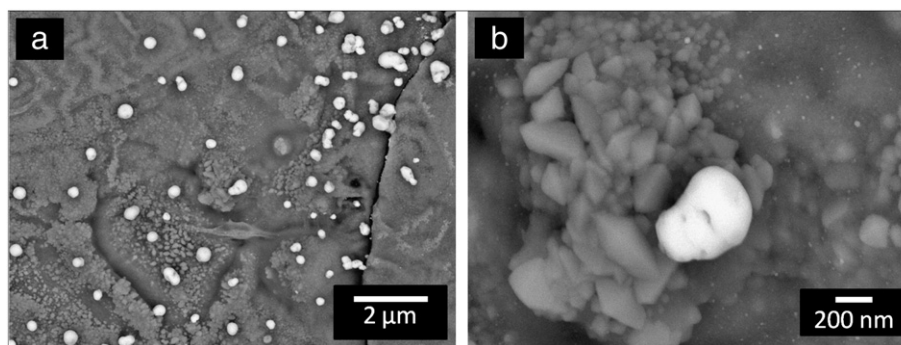


Fig. 4. SEM images of ZnO:Al/Ag film. (a) The bright dots or clusters were identified as elemental silver. (b) Zoom in of the image, where very small nanoparticles can be observed in the background.

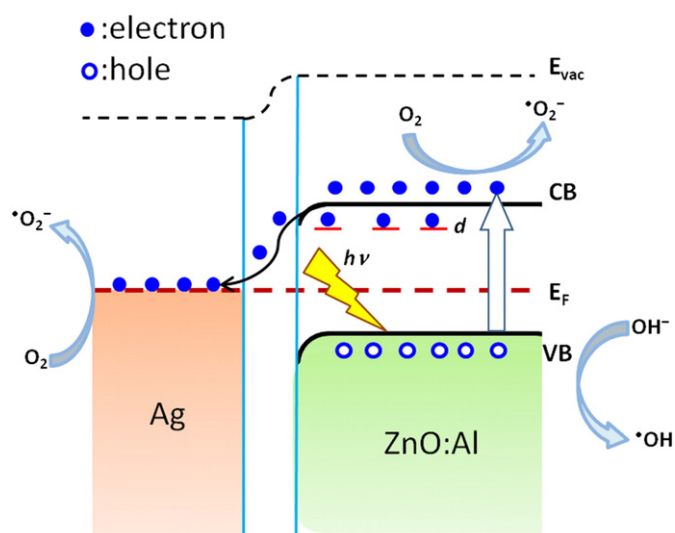


Fig. 5. Band diagram of the ZnO:Al/Ag films illustrating the charge transfer and photocatalytic process upon illumination.

photocatalyst and reacts with the photogenerated electrons to form active oxygen species. This process could be favored in our ZnO:Al/Ag films by the presence of the mobile charge carriers generated by Al doping. This means that both Al and Ag impurities have a synergistic effect which improves the photocatalytic efficiency of ZnO films and their stability after several reuses.

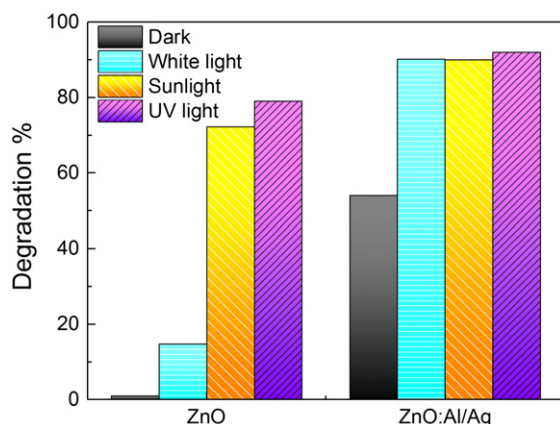


Fig. 6. Comparison of the photocatalytic efficiency of ZnO and ZnO:Al/Ag films under different illumination sources.

#### 4. Conclusions

Visible light responsive ZnO:Al/Ag films were deposited by spray pyrolysis. The addition of Ag nanoparticles conferred a high photostability to the ZnO:Al films after several reuses specially when they are illuminated with UV or sunlight. The enhancement of the photocatalytic activity is mainly due to the incorporation of Al atoms into the ZnO matrix, which provide mobile charge carriers that contribute to the formation of  $O_2^{\cdot-}$  radicals; this also favors the dissociation of water, producing  $\cdot OH$  radicals that accelerate the degradation reactions even in the absence of light. Ag nanoparticles occupy surface defect sites suppressing the reaction with surface oxygen and hence inhibiting the photocorrosion of ZnO:Al. Additionally, the photogenerated electrons trapped by the Ag nanoparticles react with the adsorbed  $O_2$  on Ag and form active oxygen species that contribute to the photocatalytic reactions. Combination of Al doping and Ag nanoparticles gives a synergistic effect that greatly improves the ZnO photocatalytic performance, making this material suitable for water treatment applications.

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