Using Ag/Ag₂O/SnO₂ Nanocomposites to Remove Malachite Green by a Photocatalytic Process

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Abstract. Silver/silver oxide/tin oxide nanocomposites of various weight ratios were synthesized using a microwave-assisted method. The Ag/Ag₂O/SnO₂ nanoparticle weight ratios used were 25:75, 50:50, and 75:25. All samples were characterized using X-ray diffraction, UV-Vis spectroscopy, Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA). The Ag/Ag₂O/SnO₂ nanocomposites contained cubic structures provided by the Ag and Ag₂O and tetragonal structures provided by the SnO₂. The silver resulted in surface plasmon resonance (SPR) at a wavelength of about 435 nm. The silver oxide material was transformed into pure Ag at a temperature of about 370 °C. The photocatalytic activity was tested on the degradation of malachite green (MG) from an aqueous solution. The results showed that Ag/Ag₂O/SnO₂ at a ratio of 50:50 exhibited the best photocatalytic performance for degrading MG under visible-light irradiation. The degradation of MG using Ag/Ag₂O/SnO₂ nanocomposites followed pseudo-first-order kinetic reactions, and electron holes were found to be the main species acting on the degradation process.

1. Introduction
Semiconductor photocatalysis is a potential application for solving energy and pollution problems [1]. One of these candidates is SnO₂ nanoparticles, which are n-type semiconductors having a wide band gap (3.6 eV), good photosensitivity and transparency, lower cost and no toxicity [1-4]. However, in practical applications, SnO₂ nanoparticles still have several limitations, including a high recombination rate of electrons and holes and the ability to be activated only under UV light irradiation.

To enhance the photocatalytic efficiency of SnO₂ nanoparticles, previous studies have applied several techniques, including doping with transition metal, coupling with other semiconductors, deposition of noble metals, and others [1, 5, 6]. Recently, silver and its oxide have been considered as promising materials to support photocatalysts. Ag₂O is a visible-light driven photocatalyst with a band gap of about (1.3–15 eV) [7, 8]. In addition, silver nanoparticles, Ag, can use the surface plasmon resonance (SPR) effect to enhance optical absorption and improve photocatalytic activity [9]. When silver nanoparticles interact with a semiconductor, it creates a metal-semiconductor Mott-Schottky (MS) heterojunction, which promotes charge transfer from the SnO₂ to the Ag; this, in turn, leads to the concentration of electrons into the Ag in built-in electric fields [7]. In addition, the coexistence of SnO₂, Ag₂O, and Ag maintains the photocatalytic stability of the Ag₂O.
As one of organic pollutant, Malachite green has been widely used in various industries such as a dye in silk; as a food colouring additive; and as a dye in wool, leather, cotton, jute, and paper [10]. Therefore, in this research investigate the formation of Ag/Ag2O/SnO2 nanocomposites as visible-light photocatalysts for removing Malachite Green (MG), a model organic pollutant. The research also proposed and investigated a photocatalytic mechanism.

2. Experimental

2.1. Materials
Tin Chloride (SnCl2), Silver Nitrate (AgNO3), Sodium Hydroxide (NaOH), and Sodium Dodecyl Sulphate (SDS) were purchased from Merk and used without further purification.

2.2. Synthesizing SnO2 nanoparticles
SnO2 nanoparticles were synthesized using the sol-gel method, in which SnCl2 was dissolved in 40 mL of deionized (DI) water and 15 mL of ethanol by magnetic stirring until a homogenous solution was obtained. Then, a NaOH solution was added to the above solution slowly and stirred for 30 min. Next, the mixture solution was heated at 180 °C for 3 h. After heat treatment, the mixture solution was cooled to room temperature naturally. The precipitates were collected by centrifugation, washed with deionized water and ethanol several times each, and dried in a vacuum drying oven at 80 °C for 8 h. Finally, the powder was calcinated in a furnace at 700 °C for 3 h to obtain the SnO2 nanoparticles.

2.3. Synthesizing Ag/Ag2O/SnO2
AgNO3 was dissolved in DI water to which SnO2 nanoparticles were then added. An amount of SDS solution was added to the above mixture and stirred for 5 min. Then, 10 mM NaOH was added to the solution and stirred for 10 min. The solution was irradiated by 800 W of microwaves for 2 min and then stirred for 30 min. The precipitated samples were collected using centrifugation and washed in ethanol and DI water several times. The final product was dried at 120 °C for 5 h. The molar ratios of Ag/Ag2O:SnO2 were 25:75, 50:50, and 75:25.

2.4. Photocatalytic measurement
A photocatalytic experiment was used to test the degradation of MG, a model organic pollutant. Typically, 20 mg/L of MG was poured into a 100-mL glass beaker. Then, 0.03 g of Ag/Ag2O/SnO2 nanocomposite was added to the solution and kept in the dark for 30 min to reach adsorption/desorption equilibrium. When this was achieved, the solution was irradiated for 2 h using a 40-W Xe lamp. The MG solution was collected every 15 min and analyzed using UV-Vis spectroscopy to investigate the MG degradation process. The decolorization and percent degradation of MG were calculated using the following equations.

\[ \text{Decolorization: } \frac{C_t}{C_0} \]  
\[ \text{% Degradation: } \frac{C_0 - C_t}{C_0} \times 100\% \]  

where \( C_0 \) is the initial dye concentration and \( C_t \) is the dye concentration after time \( t \).

To investigate the role of the photocatalytic mechanism, various scavengers were added, including Sodium Sulfate, Di-Ammonium Oxalate, and Tert-Butyl alcohol as electron, hole, and OH radicals, respectively.

3. Result and Discussion
Figure 1 shows the XRD spectra of Ag/Ag2O/SnO2 with various weight percentages. For comparison, the figure also plots the XRD spectra of pure SnO2. The Ag/Ag2O/SnO2 XRD results included several peaks corresponding to the combined cubic structures of the Ag and Ag2O and the tetragonal structures of the SnO2. As Figure 1 shows, increased SnO2 loading resulted in greater peak intensity of the
tetragonal structures of the SnO$_2$, which indicated increased SnO$_2$ quantities in the samples. The grain size and lattice parameters of the samples were investigated using Debye-Scherrer equations and the Rietveld refinement method. Table 2 shows the grain-size and lattice-parameter results, which indicated that the lattice parameters of the Ag/Ag$_2$O/SnO$_2$ did not change significantly. The results also indicated that formation of the Ag/Ag$_2$O/SnO$_2$ nanocomposites did not change the corresponding Ag, Ag$_2$O, and SnO$_2$ crystal structures.

To analyze the surface plasmon resonance (SPR) spectra of the silver nanoparticles, the optical properties of the samples were investigated using various weight ratios. The results showed that the SnO$_2$ nanoparticles did not exhibit the typical absorbance of the SPR spectra. However, after incorporating Ag/Ag$_2$O, the typical SPR spectra of Ag nanoparticles appeared at the 435 nm wavelength [9], and higher SnO$_2$ loads resulted in higher SPR peaks. This suggested that SnO$_2$ could be used in Ag$_2$O materials into Ag nanoparticles.

Figure 2 shows the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) measurement of the Ag/Ag$_2$O/SnO$_2$ with a weight ratio of Ag/Ag$_2$O/SnO$_2$ of 75:25. The figure shows that the TGA measurement indicated a loss of weight of about 0.3% from 100–200 °C due to the removal of adsorbed water from the samples. An interesting feature of the DTA/TGA measurements of the Ag/Ag$_2$O/SnO$_2$ nanocomposites was the exothermic process from 336–379 °C, which was due to the transformation of Ag$_2$O to Ag nanoparticles and the release of oxygen into the atmosphere [11].

![Figure 1](image1.png)

**Figure 1.** (a) XRD spectra of Ag/Ag$_2$O/SnO$_2$ with different weight ratio (black (SnO$_2$), red (25:75), blue (50:50), and green (75:25)). (b) UV-vis absorbance spectra of Ag/Ag$_2$O/SnO$_2$. Blue (SnO$_2$), red (75:25), green (50:50), dark cyan (25:75).

**Table 1.** Lattice parameters and grain size of Ag/Ag$_2$O/TiO$_2$ with different weight ratio.

| Sample                  | Lattice Parameter | Grain size (nm) |
|-------------------------|-------------------|-----------------|
|                         | a=b=c             | a=b=c           | a=b=c | Ag | Ag$_2$O | SnO$_2$ |
| SnO$_2$                 | 4.090             | 4.731           | 4.736 | 3.189 | 20       | 19       | 44       |
| Ag/Ag$_2$O:SnO$_2$ (25:75) | 4.088             | 4.727           | 4.734 | 3.186 | 22       | 17       | 44       |
| Ag/Ag$_2$O:SnO$_2$ (50:50) | 4.083             | 4.712           | 4.710 | 3.182 | 24       | 14       | 44       |
| Ag/Ag$_2$O:SnO$_2$ (75:25) | 4.083             | 4.712           | 4.710 | 3.182 | 24       | 14       | 44       |
Figure 2. DTA-TGA measurement of Ag/Ag₂O/SnO₂ (75:25) nanocomposites.

Figure 3. Malachite green absorbance spectra after and before photocatalytic reactions.

Figure 3 shows the MG absorbance spectra before and after the photocatalytic performance of Ag/Ag₂O/SnO₂ nanocomposites with various weight percentages. The results indicated that the absorbance spectra of the MG showed a maximum intensity at 600 nm. After the photocatalytic reaction, the absorbance spectra of the MG gradually decreased. This indicated
that the concentration of MG was reduced due to the photocatalytic experiments using Ag/Ag₂O/SnO₂ nanocomposites.

Figure 4(a) shows the decolorization process by which the Ag/Ag₂O/SnO₂ nanocomposites removed the MG from the aqueous solution. The results showed that as the weight ratio of the Ag/Ag₂O:SnO₂ increased from 25:75 to 50:50, the decolorization of the MG increased. However, as the weight ratio increased to 75:25, the decolorization decreased, indicating that the 50:50 weight ratio exhibited the optimum conditions for removing MG from the aqueous solution using photocatalytic activity under visible-light irradiation. Table 2 shows the percentages of degradation of the MG.

The kinetic reactions of the photocatalytic process of Ag/Ag₂O/SnO₂ nanocomposites on the degradation of MG were calculated using pseudo first-order kinetic reactions.

\[ K_{app}t = -\ln \frac{C_t}{C_0} \]  

where \( K_{app} \) is the rate constant of the photocatalytic reactions. Table 2 shows the apparent rate constants of all samples. The results showed that the apparent rate constant of the Ag/Ag₂O/SnO₂ nanocomposite increased from 0.01327 min⁻¹ at a weight ratio of 25:75 to 0.03521 min⁻¹ at a weight ratio of 50:50, and then decreased to 0.01984 min⁻¹ at a weight ratio of 75:25.

Figure 4(b) shows the influence of various radical scavengers on the photocatalytic activity of the Ag/Ag₂O/SnO₂ nanocomposite. The results showed that after adding any radical

| Sample            | % Degradation | Rate constant (min⁻¹) |
|-------------------|---------------|-----------------------|
| SnO₂              | 18            | 0.00157               |
| Ag/Ag₂O:SnO₂ (25:75) | 80            | 0.01327               |
| Ag/Ag₂O:SnO₂ (50:50) | 99            | 0.03521               |
| Ag/Ag₂O:SnO₂ (75:25) | 92            | 0.01984               |

Table 2. % degradation and rate constant of malachite green degradation using Ag/Ag₂O/SnO₂ photocatalyst.
scavenger, the photocatalytic activity of the Ag/Ag$_2$O/SnO$_2$ nanocomposite decreased due to the elimination of active species from the photocatalytic process. As the figure shows, adding Di-Ammonium Oxalate produced the lowest photocatalytic activity, indicating that it was the most active free radical species, and meaning that electron holes were the species having the most effect on the degradation process.

The proposed photocatalytic mechanism can be described as follows (see Figure 5): under visible-light irradiation, only Ag$_2$O can create electron hole pairs, due to its suitable band-gap energy [7, 12]. The electrons are transferred into the conduction band, leaving holes in the valence band. The electrons in the conduction band tend to recombine with the electron holes; however, the addition of another trapping state, including SnO$_2$ and Ag, can reduce the recombination of electrons and holes because the electrons from the conduction band of the Ag$_2$O may be transferred into the conduction band of the SnO$_2$. Furthermore, added Ag nanoparticles, which have lower conduction-band positions, can accept electrons from the SnO$_2$. Thus, the electron-transfer process leaves electron holes to react with water molecules, producing OH radicals and attacking the organic dye.

4. Conclusions

Ag/Ag$_2$O/SnO$_2$ with various weight ratios was synthesized using a microwave-assisted method. The existence of Ag in the samples was proved by XRD and UV-Vis absorbance spectroscopy. The thermal behavior of the samples revealed that all Ag$_2$O nanoparticles were transformed into Ag material. The samples with the Ag/Ag$_2$O:SnO$_2$ weight ratio of 50:50 exhibited the highest photocatalytic performance of the Ag/Ag$_2$O/SnO$_2$. The higher photocatalytic performance of Ag/Ag$_2$O/SnO$_2$ nanocomposites compare to SnO$_2$ nanoparticles is due to the
inhibition of recombination of electron and holes. For further study Ag/Ag$_2$O/SnO$_2$ nanocomposites will be combined with graphene for enhance the photocatalytic performance.

Reference

[1] X. Wang, H. Fan, P. Ren 2013 *Colloids Surf., A*, 419 140–146.
[2] R. Yang, Y.G. Gu, Y.Q. Li, J. Zheng, X.J. Li 2010 *Acta Mater.* 58 866–874.
[3] W.C. Zhou, R.B. Liu, Q. Wan, Q.L. Zhang, A.L. Pan, L. Guo, B.S. Zou 2009 *J. Phys. Chem. C* 113 1719–1726.
[4] H. Yuan, J.Q. Xu 2010 *Int. J. Eng. Appl. Chem.* 1 241–246.
[5] Z. Lin, N. Li, Z. Chen, P. Fu 2017 *Sensors and Actuator B* 239 501–510.
[6] S.G. Ghugal, S.S. Umare, R. Sasikala 2015 *Appl. Catal., A*, 496 25–31.
[7] H. Yang, J. Tian, T. Li, H. Cui 2016 *Catal. Commun.* 87 82–85.
[8] X. Wang, S. Li, H. Yu, J. Yu, S. Liu 2011 *Chem. Eur. J.* 17 7777–7780.
[9] R.A. Rather, S. Singh, B. Pal 2017 *Sol. Energy Mater. Sol. Cells* 160 463–469.
[10] E.S. Baeissa 2016 *J. Alloys Compd.* 672 564–570.
[11] A. Sakulkalavek, R. Sakdanuphab 2016 *Mater. Sci. Semicond. Process.* 56 313–323.
[12] Q. Luo, L. Wang, D. Wang, R. Yin, X. Li, J. An, X. Yang 2015 *Journal of Environmental Chemical Engineering* 3 622–629.