Ag/Ag₂O/TiO₂ nanocomposites: microwave-assisted synthesis, characterization, and photosonocatalytic activities

S P Prakoso¹, A Taufik¹,² and Rosari Saleh¹,²

¹Integrated Laboratory of Energy and Environment, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia
²Department of Physics, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Corresponding author’s e-mail: rosari.saleh@gmail.com

Abstract. Nanocomposites of Ag/Ag₂O/TiO₂ were synthesized using a microwave-assisted method. As-prepared samples were systematically characterized by X-ray diffraction, electron spin resonance, and diffuse reflectance spectroscopy. The photosonocatalytic performance was investigated under both UV and visible light and ultrasonic irradiation in terms of degradation of methylene blue (MB) dye in aqueous solution. Compared with the pure TiO₂ nanoparticles and Ag/Ag₂O nanocomposites, the Ag/Ag₂O/TiO₂ nanocomposites presented more responsive photosonocatalytic activity in the wide range of light wavelengths. It is believed that defect states in TiO₂ nanoparticles, which were observed by ESR measurements, played an important role in trapping the charge carrier in the photosonocatalytic process. In addition, the degradation process was studied in terms of the influence of several experimental parameters, and a reasonable mechanism of photosonocatalysis with Ag/Ag₂O/TiO₂ nanocomposites was proposed by correlating the active radical species involved with the physical properties of the as-synthesized samples.

1. Introduction

In recent years, photocatalytic technology has greatly aided the environment by its use in wastewater treatment [1, 2]. The efficiency of solar conversion in the photocatalytic process depends on several factors, including light absorption, charge separation and migration, and surface reactions [3, 4]. Along with low cost and high catalytic efficiency, physical and chemical stability are the primary reasons that titanium dioxide is chosen. However, it also has limitations, including that it works only with ultraviolet light [5] and, therefore, cannot be used with visible light. These limitations, along with its high rate of charge recombination and separation difficulties [6], make large-scale application impossible.

The presence of a metal element can provide efficient charge separation and migration, thus helping to facilitate photocatalytic activity and stability. Several studies have exhibited metal-semiconductor properties for capturing, storing, and discharging photo-generated electrons [7, 8]. One widely used material, Ag₂O, exhibits active photocatalysts and good stability while forming Ag-Ag₂O during photocatalytic reaction [9]. Deposition of silver nanoparticles to TiO₂ has attracted growing interest because this process can extend titanium dioxide excitation under visible irradiation [10-12]. This effect is due to suppressing recombination by trapping electrons using a Schottky barrier at the interface.

However, photocatalytic activity has several limitations due to its low ability to penetrate a nontransparent medium, including highly concentrated dye in wastewater. Therefore, it is important to find a new method that effectively treat highly concentrated dye. Sonocatalytic process is an alternative
method for degrading highly concentrated organic pollutant in wastewater because its ultrasonic wave has the ability to penetrate any water medium [13]. Therefore, the present study used a microwave-assisted method to synthesize a photosonocatalytic process that synthesized Ag/Ag\(_2\)O/TiO\(_2\) as a catalyst for removing organic dye from an aqueous solution.

2. Materials and methods

2.1. Materials
Both AgNO\(_3\) and TiO\(_2\) were obtained from Merck Millipore. AgNO\(_3\) was used as a precursor to synthesize Ag/Ag\(_2\)O. TiO\(_2\) was used to obtain the composite material. All chemicals were used without further purification.

2.2. Ag/Ag\(_2\)O synthesis
The synthesis step included producing the Ag/Ag\(_2\)O nanoparticles and adding the TiO\(_2\) nanoparticles. The Ag/Ag\(_2\)O nanoparticles were synthesized using the developed microwave-assisted method.

First, the silver nitrate precursor was mixed with sodium hydroxide by constant stirring at room temperature for 30 min. This mixture was heated in a microwave oven (Electrolux). Because beaker glass was used, the microwave heating was accomplished in power steps to avoid drying out the inside of the mixture. Total time inside the microwave oven was about 5 min.

The mixture was removed from the microwave oven and allowed to cool slowly in the open air for 30 min. Then, it was stirred for 1 h to ensure better particle growth. The resulting precipitate was washed with deionized (DI) water and alcohol to ensure there were no impurities in the sample and then dried in a 120°C furnace to yield Ag/Ag\(_2\)O nanoparticles.

2.3. Ag/Ag\(_2\)O/TiO\(_2\) formation
Commercially available TiO\(_2\) (Merck) was added to Ag/Ag\(_2\)O at ratios of 0.25:1 (25%), 0.5:1 (50%), and 0.75:1 (75%). Silver nanoparticles were immersed in DI water, and titanium dioxide was dissolved in sodium hydroxide. The mixing process was conducted under constant stirring and temperatures (80°C) for 1 h. Precipitate washing and drying were applied, resulting in the Ag/Ag\(_2\)O/TiO\(_2\) composite. The Ag/Ag\(_2\)O/TiO\(_2\) with 25%, 50%, and 75% Ag/Ag\(_2\)O were denoted as A 25-TiO\(_2\), A 50-TiO\(_2\), and A 75-TiO\(_2\), respectively.

2.4. Characterization
X-ray diffraction (XRD) analysis was performed using a Rigaku Miniflex 600. The patterns were recorded from 10°-90° at 30 kV with an intensity of 15 mA. The samples’ UV-Vis diffuse reflectance spectra (DRS) were obtained using a Shimadzu Spectrophotometer. Electron spin resonance (ESR) was performed using an X-band spectrometer equipped with a 9.1-GHz field modulation unit and an X-band JEOL JES-RE1X at room temperature.

2.5. Photosonocatalytic experiment
Photosonocatalytic activity was tested for its ability to remove methylene blue as a model organic pollutant. Using the typical process, 0.03 g of catalyst was immersed in 100 mL of methylene blue solution with a concentration of 40 mg/L and placed in a dark place for 30 min to reach adsorption-desorption equilibrium. Then, the solution was placed in an ultrasonic bath operated at 150 W and 40 kHz frequency and irradiated with a UV-C lamp and a Xenon (visible-light source) lamp separately. Every 15 min, the samples were investigated using UV-Vis spectroscopy to analyze the decolorization of the methylene blue.

3. Results and discussion
Figure 1 shows the XRD spectra of the Ag/Ag\(_2\)O/TiO\(_2\) with various Ag/Ag\(_2\)O wt.%. For comparison, the figure also shows the XRD spectra of TiO\(_2\) and Ag/Ag\(_2\)O. The peak at 2θ = 25.24° was attributed to the anatase structure of the TiO\(_2\), and the peak at 2θ = 44.12° was attributed the presence of the silver nanoparticles. In addition, cubic structures from the Ag\(_2\)O were detected at 2θ = 25.24°, 32.57°, 37.88°.
and 54.91°. No undesired peaks were detected, which would indicate the existence of impurity structures. The lattice parameter and grain size of the samples were calculated using the Rietveld refinement method and Debye Scherrer equations, and table 1 shows the results. As can be seen, the value of the sample’s lattice parameters differed slightly from those of its single materials. This was attributed to the intra-granular coupling of the composites, which provided intimate contact between the two oxide phases and improved the efficiency of the semiconductor-coupling effects of the crystal structures [14]. The TiO₂ grain size did not differ significantly from that of its single materials.

Figure 2 shows the UV-Vis DRS of the Ag/Ag₂O/TiO₂ composite for each TiO₂ concentration. All samples had broad absorption in the 400-700 nm range. A comparison was made with pure TiO₂, which had similar absorption characteristics. This broad absorption was attributed to the SPR effect of the sample’s Ag nanoparticles [15]. The absorption edge of the Ag/Ag₂O/TiO₂ was slightly red-shifted and had enhanced photoactivity under visible radiation. Less absorption was seen at higher concentrations of TiO₂, and absorption dropped even lower with pure TiO₂. The samples’ band-gap energies were calculated using the Kubelka-Munk equation, and the results are shown in table 1. The band-gap energy shifted slightly lower with increased Ag/Ag₂O.

![Figure 1](image)

**Figure. 1** XRD spectra of TiO₂ nanoparticles, Ag/Ag₂O, and Ag/Ag₂O/TiO₂ with different Ag/Ag₂O loading.

**Table 1.** Lattice parameter, grain size and band gap energy of TiO₂ nanoparticles, Ag/Ag₂O, and Ag/Ag₂O/TiO₂ with different Ag/Ag₂O loading.

| Sample          | Lattice Parameter (Å) | Grain Size (nm) | Energy Gap (eV) |
|-----------------|-----------------------|-----------------|-----------------|
|                 | Ag a=b=c              | Ag₂O a=b=c      | TiO₂ c         | Ag a=b | Ag₂O c | TiO₂ c |
| Ag/Ag₂O        | 4.088                 | 4.733           | -              | 22     | 21     | -      | -      |
| A 25 - TiO₂    | 4.094                 | 4.736           | 3.791          | 9.529  | 20     | 19     | 31     | 2.87   |
| A 50 - TiO₂    | 4.090                 | 4.734           | 3.788          | 9.524  | 21     | 19     | 29     | 2.71   |
| A 75 - TiO₂    | 4.071                 | 4.734           | 3.762          | 9.526  | 21     | 20     | 27     | 2.51   |
| TiO₂           | -                     | -               | 3.791          | 9.529  | -      | -      | 45     | 3.32   |
Figure 2. UV Vis Absorbance spectra of Ag/Ag$_2$O/TiO$_2$ with different Ag/Ag$_2$O loading.

Figure 3. ESR spectra of Ag/Ag$_2$O/TiO$_2$ with different Ag/Ag$_2$O loading.

Figure 3 shows the ESR spectra of Ag/Ag$_2$O/TiO$_2$ with various Ag/Ag$_2$O loadings. As can be seen, there were two main signals, in the ranges of 3361 and 3465 gauss, which were attributed to the Ti$^{3+}$ and oxygen-vacancy signals and which had $g$ values of 1.95 and 2.04, respectively [16]. The intensity of both signals increased gradually as Ag/Ag$_2$O decreased. Both the Ti$^{3+}$ and the oxygen vacancy acted as charge carrier traps that enhanced the samples’ catalytic performance.

Figure 4 shows the photosonocatalytic activity of Ag/Ag$_2$O/TiO$_2$ with various Ag/Ag$_2$O loadings under UV and visible-light irradiation. As can be seen, under both UV and visible light, the samples’ photosonocatalytic activity gradually increased with decreased Ag/Ag$_2$O. In addition, to understand the role of the photosonocatalytic process, the samples’ photocatalytic and sonocatalytic activities were investigated. Figure 5 shows the comparison of photocatalytic, sonocatalytic, and photosonocatalytic activities under both UV and visible-light irradiation. As can be seen, the samples’ degradation ability was enhanced by using simultaneous photocatalytic and sonocatalytic activity. This might be due to the existence of ultrasound irradiation that enhanced the production of OH radicals used to decompose the methylene blue in the aqueous solution. Ultrasound irradiation also has the ability to create spontaneous light, called sonoluminescence, which has a wide range of wavelengths. Therefore, formation of electron and hole pairs may increase with the addition of ultrasound irradiation [13]. Both photocatalytic and photosonocatalytic activities were higher in the Ag/Ag$_2$O/TiO$_2$ nanocomposites than in the TiO$_2$ nanoparticles. This may have been due to a retardation of electron-hole recombination caused by formation of heterojunctions among Ag, Ag$_2$O, and TiO$_2$.

Figure 6 shows the effects of scavenger addition on the photosonocatalytic activity of Ag/Ag$_2$O/TiO$_2$ nanocomposites. The addition of scavengers was tested to identify the main active species involved in the photocatalytic process. Three type of scavengers were used: ammonium oxalate, sodium sulfate, and tert-butyl ethanol, which detected hole, electron, and OH radical main active species. The addition of scavengers reduced the photocatalytic activity because these main active species in the photosonocatalytic process were captured by the scavengers. As can be seen, under both UV and visible-light irradiation, the addition of hole scavengers caused the lowest photosonocatalytic activity, indicating that holes are the main active species in the degradation process.

The possible mechanisms of both photocatalytic and photosonocatalytic activity can be described as follows: Under visible-light irradiation, TiO$_2$ cannot create electron and hole pairs due to insufficient visible-light energy. However, Ag$_2$O with a narrow band gap can create electron and hole pairs due to its suitable energy [17]. Electrons from the Ag$_2$O valence band were excited into the conduction band and left holes in the valence band. These electrons did not readily recombine with holes in the valence band but were captured by Ag and trapping state from TiO$_2$, including Ti$^{3+}$ and oxygen vacancy.
Figure 4. Photosonocatalytic activity of Ag/Ag₂O/TiO₂ under UV and visible light irradiation.

Figure 5. Photocatalytic, sonocatalytic, and photosonocatalytic activity of Ag/Ag₂O/TiO₂ nano-composites under visible and UV light irradiation.

Therefore, the recombination of electrons and holes was prevented, and photocatalytic activity under visible-light irradiation increased. Under UV light irradiation, only TiO₂ electrons and holes. The addition of ultrasound irradiation to the photocatalytic process (photosonocatalytic) created acoustic cavitation, which emitted light (i.e., sonoluminescences), which has a wide wavelength range (from UV to visible-light irradiation). Under these conditions of local high temperature and pressure, water molecules can be thermally dissociated into hydroxyl radicals (OH) to some extent [13, 18]. The sonoluminescence from ultrasound irradiation could create electron and hole pairs neither for TiO₂ nor for Ag₂O at the same time. Electrons from the conduction band of TiO₂ migrated into the conduction bands of Ag₂O and metallic Ag, while electrons from the conduction band of Ag₂O were captured by native defects, including Ti³⁺ and oxygen vacancy. Based on the ESR results, the Ti³⁺ and oxygen-vacancy signals increased with decreased Ag₂O/Ag content, indicating that decreased Ag₂O/Ag content resulted in higher oxygen vacancy and Ti³⁺ in the samples. Therefore, the highest photosonocatalytic activity was achieved by 25% Ag₂O/Ag. When electrons migrated from one state to another, holes
reacted with water molecules to form OH radicals and decompose the methylene blue in the aqueous solution. This result was confirmed by a scavenger experiment showing that holes and OH radicals were the main active species in the degradation process.

4. Conclusions
Ag/Ag2O/TiO2 composite was successfully synthesized using a microwave-assisted method. Composition of the composite was confirmed by XRD measurement. Adding silver to the TiO2 enhanced absorption into the visible region and extended usability for photosonocatalytic applications. The existence of native defects, including Ti3+ and oxygen vacancy, improved the photosonocatalytic experiment. Photosonocatalytic activity exhibits faster degrading activity than the photocatalytic or sonocatalytic processes.

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