Enhanced optical and photocatalytic properties of Ag NPs decorated-ZnO composites

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Received: 21 September 2024, Revised: 25 December 2024, Accepted: 26 December 2024

Abstract

The goal of this work is to synthesize and study composites of silver and zinc oxide nanoparticles for improved ZnO light absorption by the aggregation of Ag nanoparticles prepared by a simple process. Starting with the synthesis of silver nanoparticles from silver nitrate (Silver Nitrate; $AgNO_3$), the concentration of the synthesis of silver nanoparticles and zinc oxide composites was changed to 0.2%, 0.6%, and 1.0%. Initially, the amount of silver nanoparticles of 0.2%, 0.6%, and 1.0 % per 3 g of zinc oxide was carried out to determine the amount of silver nanoparticles suitable for important properties. Morphological analysis was performed using scanning electron microscopy (SEM). The crystal structure was analyzed by X-ray diffraction. The study on absorbance using the diffuse reflectance UV-visible spectroscopy technique and the photocatalytic efficiency was assessed by the decomposition of organic dyes under visible light. The analysis revealed that the silver nanoparticles and zinc oxide composites were morphologically cuboid and rod-shaped. As for the crystal structure, it was found to be hexagonal. The absorbance of composite materials is lower than that of pure zinc oxide in the 405–600 nm range. Silver nanoparticles will enhance light absorption in composite materials due to their favorable surface plasmon resonance characteristics. This enhances composite materials' optical absorption. The breakdown of organic dyes under visible light was used to measure the photocatalytic efficiency, and it was discovered that the best photocatalytic properties were obtained with Ag NPs 0.2% per 3 g of ZnO.

Keywords: Composite material, Silver nanoparticles, Zinc oxide

1. Introduction

Unique optical and electrical properties of silver nanoparticles have been intensively investigated due to their nanoscale particle size [1]. It has been applied in bio-sensor applications, and various close-up optical microscopy applications. Colloidal silver exhibits different colors due to light absorption and scattering in the region seen through the reflection of the plasmon. This is the frequency at which conduction electrons vibrate in response to the alternating electric field of incident electromagnetic radiation and is used as a catalyst in reactions such as the oxidation of styrene [2]-[3].

Zinc oxide is an inorganic compound in the form of a white insoluble powder, in nature it is usually found in the form of zinc sites, most of the widely used zinc oxide is produced synthetically [4]. Zinc oxide is used as an additive in materials and products, because of its wide and diverse properties such as environmental friendliness, a good semiconductor with a wide band gap (3.37 eV), large exciton binding energy (60 meV) as the oxygen or zinc interstitial n-type vacancies, good transparency, high electron mobility, and photochemical stability. As previously stated, it is an interesting optical catalyst due to its high sensitivity to light transparency to visible light and the ability to absorb UV light [5]-[7]. Therefore, it has been applied to improve the properties of other materials as shown in the following example: Additives to adjust the microstructure level to have the desired energy band structure, catalyst, sensor, transparent electrode in liquid crystal display, and electronic equipment, etc. [8]. A study by

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Ziashahabi et al. (2023) reported that silver is the best choice among the metal family that improves the photocatalytic activity efficiency of zinc oxide due to its high solubility, larger ionic size and the lowest orbital energy and silver ions have two characteristics and can be used to represent positions and interstitial objects [9].

Hence, in this research, we have presented the enhanced light absorption capacity of ZnO by the incorporation of Ag nanoparticles prepared by a simple process to improve the surface area of zinc oxide.

2. Experimental

2.1 Materials

Silver nitrate ($AgNO_3$), trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$), sodium borohydride ($NaBH_4$), potassium bromide (KBr), hydrogen peroxide (H_2O_2), and zinc oxide (ZnO) were used without further purification. Deionized water was utilized throughout the experiment. Rhodamine B (RhB) dye was employed as the organic dye for photocatalytic studies.

2.2 Preparation of Solutions

Trisodium citrate dihydrate was prepared at a concentration of 1.25×10^{-3} M, silver nitrate at 7.5×10^{-5} M, sodium borohydride at 2.0×10^{-4} M, and potassium bromide at 1.0×10^{-3} M. The required quantities of the compounds were: 0.367 g of trisodium citrate dihydrate, 0.0128 g of silver nitrate, 0.0076 g of sodium borohydride, and 0.119 g of potassium bromide. Hydrogen peroxide (H_2O_2) was prepared at a concentration of 5.0×10^{-2} M by diluting 0.1 ml of H_2O_2 in 100 ml of deionized water. Each compound was dissolved in deionized water using a magnetic stirrer at room temperature for 15 minutes at a constant speed until a clear solution was obtained. These solutions were subsequently used for the synthesis of silver nanoparticles (Ag NPs).

2.3 Synthesis of Silver Nanoparticles (Ag NPs)

Silver nanoparticles were synthesized via a simple chemical reduction process. Initially, 20 ml of trisodium citrate dihydrate solution was mixed with 70 ml of silver nitrate solution, and the mixture was stirred using a magnetic stirrer at a constant speed. Subsequently, 20 ml of hydrogen peroxide solution was added, followed by the addition of 0.4 ml of potassium bromide solution and 25 ml of sodium borohydride solution. The mixture was stirred continuously for 15 minutes at room temperature. The formation of silver nanoparticles was confirmed by a color change from colorless to dark yellow. These silver nanoparticles were further used for the synthesis of composite materials.

2.4 Preparation of Ag NPs/ZnO Composite Materials

Ag NPs/ZnO composite materials were prepared as follows: 3 g of zinc oxide (ZnO) was combined with silver nanoparticles in concentrations of 0.2%, 0.6%, and 1.0% (v/v). The mixtures were stirred using a magnetic stirrer at room temperature for 15 minutes. After stirring, the samples were transferred to an oven and dried at 100 °C for 24 hours. The dried composites were then finely ground into a powder for subsequent analyses.

2.5 Photocatalytic Measurements

The photocatalytic activity of the prepared Ag NPs/ZnO composites was evaluated by monitoring the degradation of Rhodamine B (RhB) dye. For each test, 0.01 g of ZnO or Ag NPs/ZnO composite was dispersed in 50 ml of RhB dye solution with vigorous stirring using a magnetic stirrer for 30 minutes. The suspensions were then irradiated under visible light in a photocatalytic chamber at room temperature. Changes in absorbance were recorded at 5-minute intervals to assess the degradation of RhB. The percentage degradation of RhB was calculated using Beer–Lambert's law [10], following Equation (1).

$$\%Degradation = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

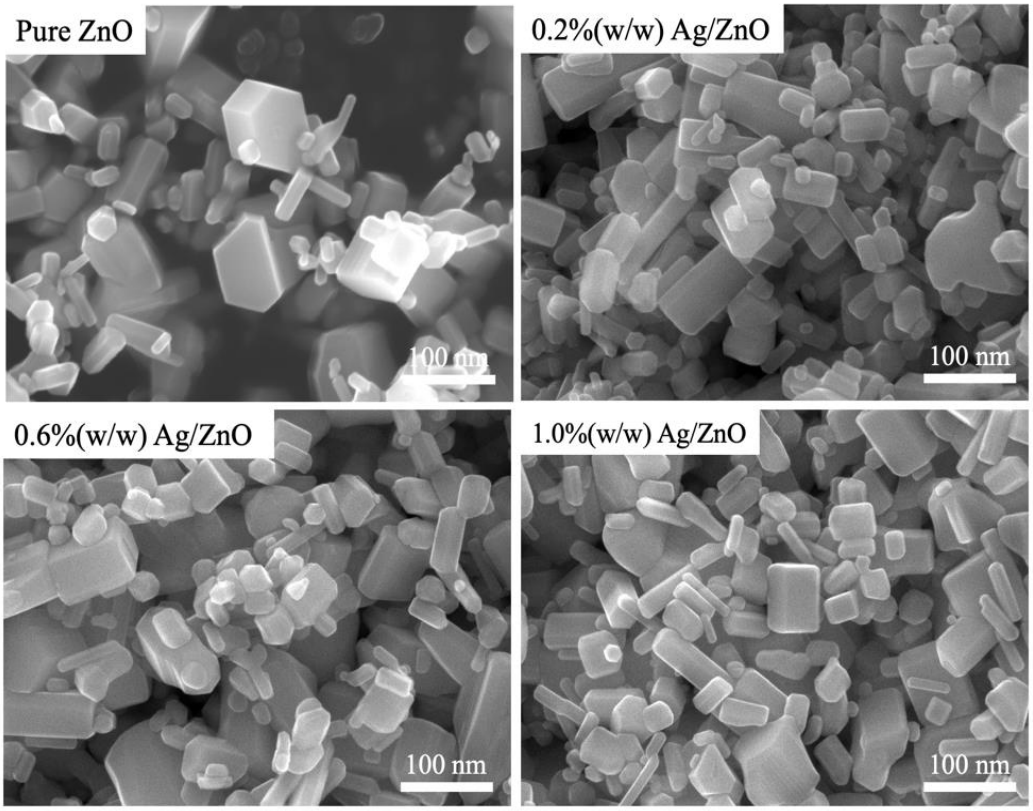
C_0 and **C** denote the initial dye concentration and the dye concentration at irradiation time **t**, respectively. Similarly, **A_0** and **A** represent the initial absorbance and the absorbance at reaction time **t**, respectively.

The kinetics of RhB dye photodegradation were evaluated using the Langmuir–Hinshelwood model [11], which is applicable to both gas–solid and liquid–solid interactions [12], as expressed in Equation (2).

$$ln\ \frac{C_0}{C} = k_{app}t \tag{2}$$

In this equation, $\mathbf{k_{app}}$ represents the apparent first-order rate constant, while **C** and $\mathbf{C_0}$ denote the concentrations of the dye at time **t** and time zero, respectively, during the photocatalytic reaction. The apparent rate constant ($\mathbf{k_{app}}$) is determined as the slope of the graph plotting $\mathbf{ln(C_0/C)}$ against time (**t**).

(a)



(b)

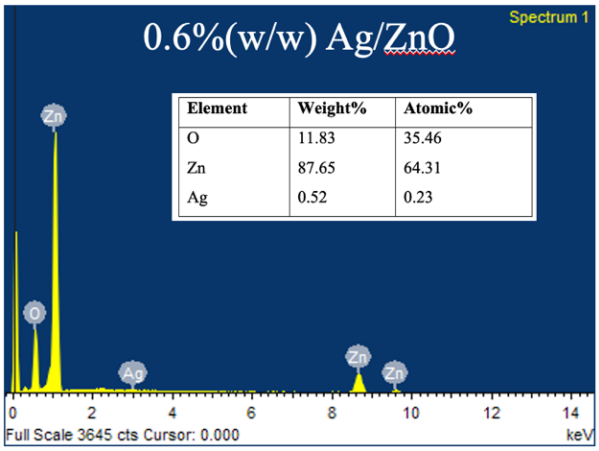


Fig. 1. (a) FE-SEM image of pristine ZnO and Ag NPs/ZnO composites showing the morphologies under various Ag NPs solution volumes. (b) EDX histogram of Ag NPs/ZnO composites displaying the elemental composition of the synthesized composites.

2.6 Characterization of Pristine ZnO and Ag NPs/ZnO Composites

Morphological analysis of the samples was performed using field emission scanning electron microscopy (FE-SEM) (JSM-7001F, JEOL, Japan). The crystal structures were characterized using X-ray diffraction (XRD) (SmartLab, Rigaku, Japan). Absorbance studies were conducted using diffuse reflectance UV-visible spectroscopy (UH4150, Hitachi, Japan), while the size of the silver nanoparticles was confirmed using a double-beam UV-VIS spectrophotometer (T92+ Spectrophotometer, PG Instruments, UK). The photocatalytic efficiency of the materials was evaluated by monitoring the decomposition of organic dyes under visible light irradiation using a single-beam UV-VIS spectrophotometer (UVG 123304, Thermo, UK).

3. Result and discussion

3.1 Morphological Studies

The morphology of pristine ZnO and Ag NPs/ZnO composites synthesized under different conditions 3 g ZnO with 0.2%, 0.6%, and 1.0% Ag NPs was analyzed using scanning electron microscopy (SEM). Figure 1a presents the typical SEM images of ZnO and Ag NPs/ZnO composites synthesized under various conditions at a magnification of 50,000×. The particles displayed a disorganized morphology, comprising cuboid and rod-like structures of varying sizes. Small and large particles were observed to be scattered throughout the samples, indicating the heterogeneous nature of the composites produced by this simple synthesis method.

The synthesized particles exhibited grain-like structures with average particle sizes ranging from 430 to 470 nm, as determined by histogram analysis. To confirm the incorporation of silver nanoparticles into the ZnO matrix, energy-dispersive X-ray spectroscopy (EDX) analysis was performed. The EDX spectra of the Ag NPs/ZnO composites, shown in Figure 1b, revealed the presence of zinc (Zn), silver (Ag), and oxygen (O), thereby confirming the successful synthesis of Ag NPs/ZnO composites. The distinct peaks corresponding to Zn, Ag, and O in the EDX spectrum provide clear evidence of these elements' incorporation into the composite materials.

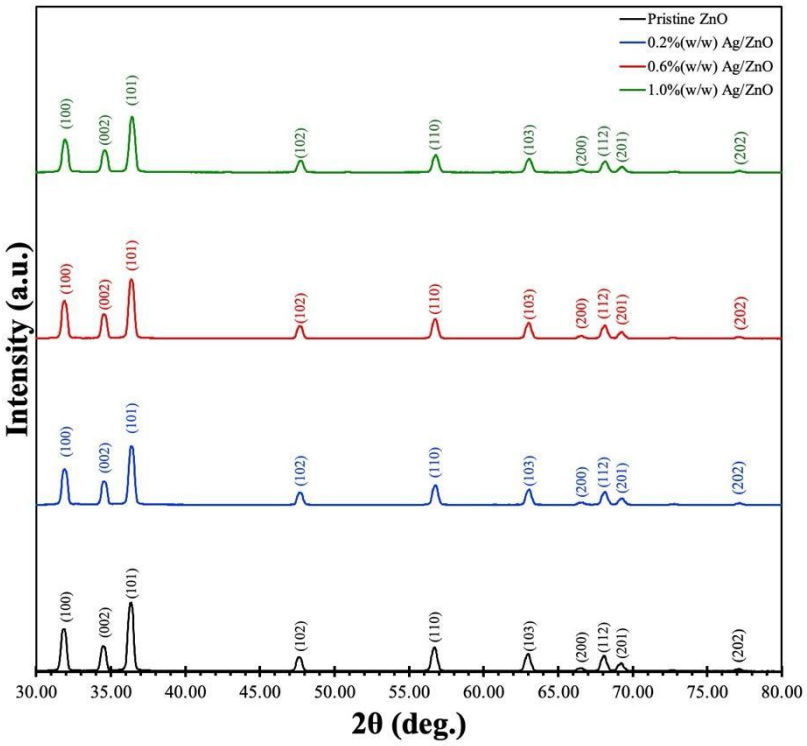


Fig. 2. X-ray diffraction patterns of Ag NPs/ZnO composites with varying Ag NP solution volumes: 0.2%, 0.6%, and 1.0%.

3.2 Structural Studies

The phase and crystal structure of pristine zinc oxide (ZnO) and Ag NPs/ZnO composites were characterized using X-ray diffraction (XRD). Figure 2 presents the XRD patterns of pure ZnO, with characteristic diffraction peaks observed at 2θ = 31.74°, 34.39°, 36.22°, 47.49°, 56.54°, and 62.79°, corresponding to the (100), (002), (101), (102), (110), and (103) planes, respectively (JCPDS card No. 36-1451).

The XRD patterns of the Ag NPs/ZnO composites exhibit peaks consistent with those of pure ZnO, indicating that the incorporation of Ag nanoparticles does not significantly affect the crystallinity of the composite. The results suggest that the synthesis process involves the surface deposition or incorporation of Ag NPs onto the ZnO particles without substantial disruption of the ZnO lattice structure. This finding aligns with previous studies [13], which reported that ZnO retains its highly stable wurtzite crystal structure, a thermodynamically favoured configuration that is challenging to alter under the conditions typically used for Ag NP deposition. Furthermore, Ag NPs are generally deposited on the surface of ZnO particles rather than substituting Zn or O atoms within the lattice [14]-[15]. Consequently, the core crystal structure of ZnO remains intact despite the surface modification by Ag NPs.

3.3 Optical Studies

The optical properties of the synthesized materials were investigated to analyze vibratory lattice behavior, energy band structure, impurity levels, activating agents, and magnetic excitation. The composite materials exhibited lower absorbance in the 405–600 nm range compared to pristine ZnO, which can be attributed to the reflectance properties of the silver nanoparticle (Ag NP) crystals. The reduced absorbance in the 400–600 nm range is primarily due to the wide intrinsic bandgap of ZnO, which restricts absorption to the UV region. While the incorporation of Ag nanoparticles induces plasmonic effects, enhancing light interaction, the improvement is insufficient to significantly increase absorbance within this range [16]-[17]. This finding strongly suggests the presence of Ag nanoparticles in the composite material. Diffuse Reflectance UV-Vis Spectroscopy (DRS) was used to further confirm the presence of Ag nanoparticles, as Ag NPs exhibit excellent surface plasmon resonance properties. The incorporation of Ag nanoparticles enhances light absorption, particularly in the visible region. Figure 3 illustrates the reflectance spectra of Ag NPs/ZnO composite materials with varying Ag loading levels, confirming the influence of Ag NPs on the optical properties of the composites.

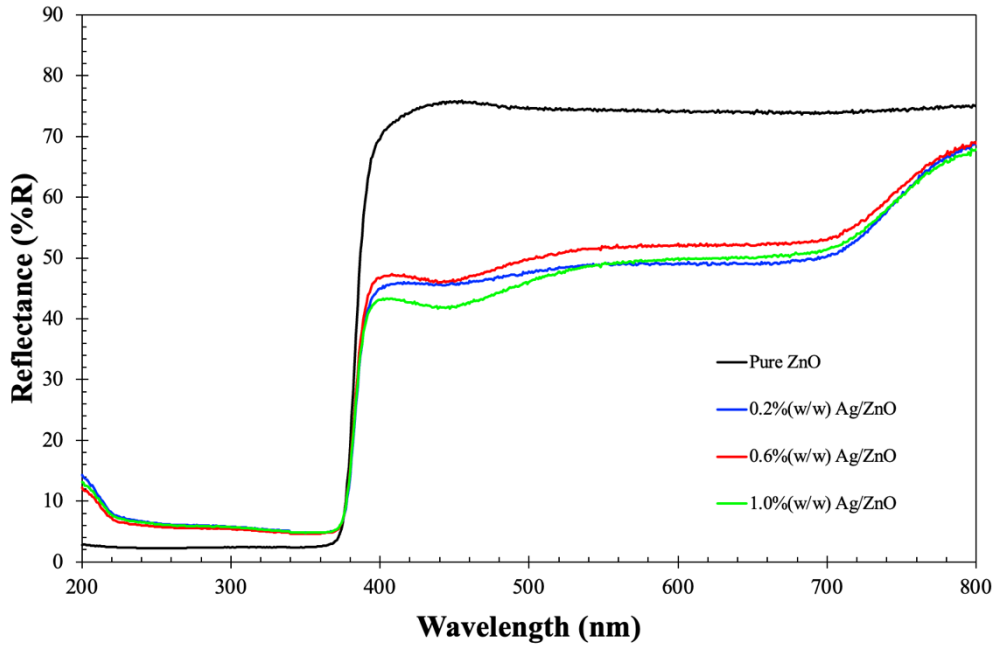


Fig. 3. Reflectance spectra of Ag NPs/ZnO composites with varying Ag loading contents.

Another critical aspect is the size estimation of silver nanoparticles at different concentrations using the empirical relationship between peak position and size for spherical Ag NPs. Particles smaller than 20 nm typically exhibit surface plasmon resonance (SPR) peaks near 400–410 nm, while an increase in particle size shifts the SPR peak toward longer wavelengths (~420–450 nm). Broader peaks indicate a larger particle size distribution or potential aggregation [18]-[20]. Consequently, the SPR peak observed near 430 nm suggests that the Ag NPs are within the size range of 30–50 nm, depending on the exact synthesis conditions. Figure 4 displays the absorption spectra of Ag NPs with varying Ag loading contents, confirming the size of the silver nanoparticles using a double-beam UV-Vis spectroscopy technique.

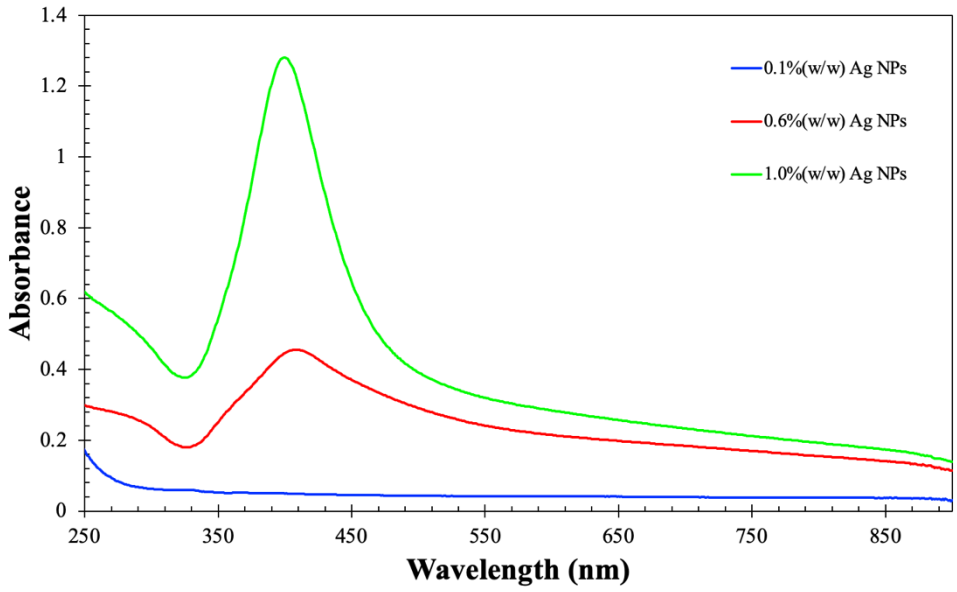


Fig. 4. Absorption spectra of Ag NPs with varying Ag loading contents.

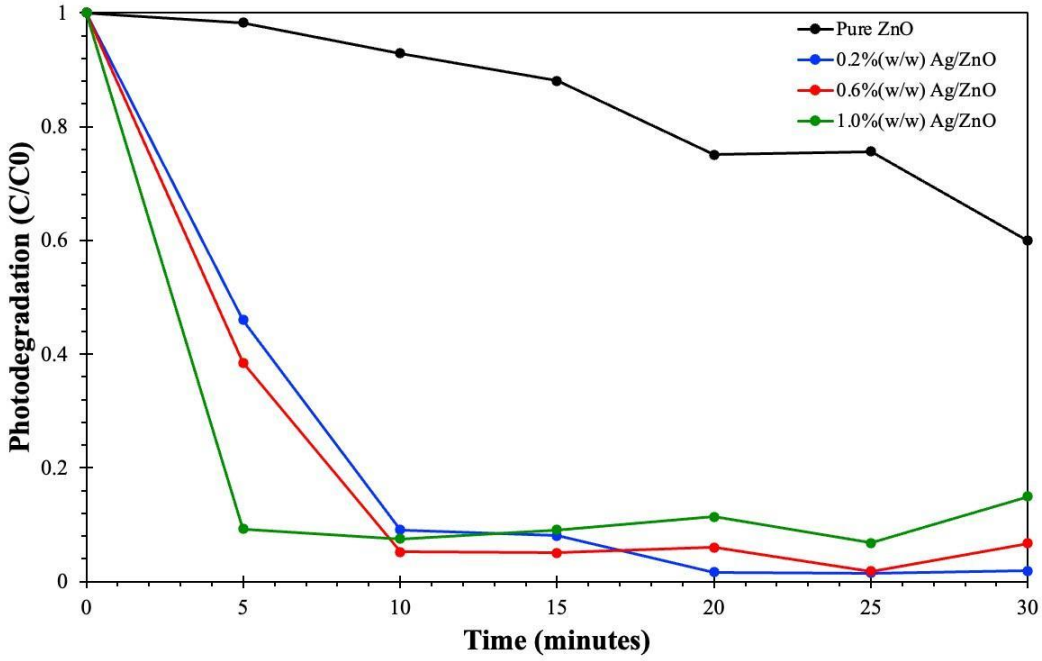


Fig. 5. Photodegradation of RhB solution under visible light irradiation using pristine ZnO and Ag NPs/ZnO composites with varying Ag loading levels.

Table 1. Rate constants for pristine ZnO and Ag NPs/ZnO composites at varying Ag loading contents under UV and visible light irradiation.

Sample Code	Times (minute)	Rate constant
Pristine ZnO	0	1
	5	0.983
	10	0.929
	15	0.880
	20	0.751
	25	0.756
	30	0.599
0.2%. Ag NPs: 3 g ZnO	0	1
	5	0.460
	10	0.091
	15	0.081
	20	0.017
	25	0.015
	30	0.019
0.6%. Ag NPs: 3 g ZnO	0	1
	5	0.385
	10	0.052
	15	0.050
	20	0.061
	25	0.018
	30	0.067
1.0%. Ag NPs: 3 g ZnO	0	1
	5	0.093
	10	0.075
	15	0.091
	20	0.114
	25	0.068
	30	0.150

3.4 Photocatalytic Degradation of organic Dyes

The incorporation of Ag ions into ZnO slightly altered particle sizes while maintaining the crystalline structure, resulting in significant variations in photocatalytic activity. Ag NPs/ZnO composites with varying Ag loading exhibited efficient photocatalytic activity, achieving substantial degradation of RhB dye within 10 minutes under visible light (Fig. 5.). Compared to pristine ZnO and Ag NPs, the ZnO/Ag NCs demonstrated enhanced visible-light-driven dye degradation and decolorization rates (Fig. 6.). This highlights the effectiveness of Ag doping in improving photocatalytic performance.

3.5 Surface Plasmon Resonance (SPR):

The surface plasmon resonance (SPR)-mediated electron transfer from Ag nanoparticles to the ZnO conduction band leads to the formation of positively charged Ag particles. These particles

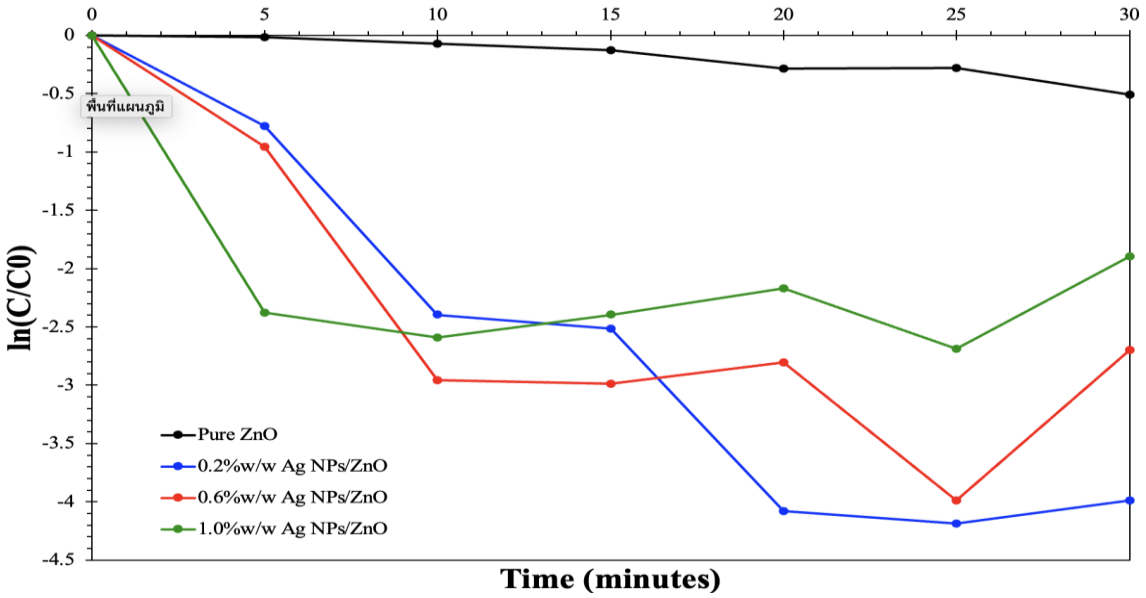


Fig. 6. Degradation rate of RhB for pristine ZnO and Ag NPs/ZnO composites under visible light irradiation at varying Ag loading contents.

interact with adsorbed oxygen, generating reactive oxygen species (e.g., O_2^{-}• and •OH), which play a crucial role in facilitating efficient dye degradation [21]. The deposition of Ag nanoparticles on ZnO significantly enhances charge separation, suppresses electron-hole recombination, and prolongs the lifetime of photogenerated carriers, thereby improving photocatalytic activity [22]-[23].

The photocatalytic efficiency was further analyzed by estimating the first-order reaction rate constant for dye degradation and comparing it across samples. Table 1 summarizes the rate constants for pristine ZnO and Ag NP/ZnO composites under UV and visible light irradiation. Additionally, Figure 6 depicts the degradation rate of RhB for the composite materials as a function of Ag nanoparticle concentration and irradiation time.

4. Conclusion

Ag/ZnO composites were successfully synthesized using a simple chemical process. The morphological, optical, and photocatalytic properties of the synthesized materials were thoroughly investigated. Among the composites, the sample with 0.2% Ag NPs: 3 g ZnO exhibited the highest photocatalytic activity, achieving efficient decolorization and degradation of organic dyes. The incorporation of Ag nanoparticles enhanced the visible-light absorptivity of ZnO due to the natural surface plasmon resonance properties of Ag. These results demonstrate the potential of Ag/ZnO composites for advanced optical and photocatalytic applications.

Acknowledgments

This work was supported by the Nano Materials Research Laboratory (NMRL). The authors extend their gratitude to the College of Materials Innovation and Technology, King Mongkut's Institute of Technology Ladkrabang, and the Department of Applied Physics, Faculty of Science and Technology, Rajabhat Rajanagarindra University, Chachoengsao, for their financial support. The authors acknowledge the facilities, and technical assistance from Nanotechnology and Materials Analytical Instrument Service Unit (NMIS) of College of Materials Innovation and Technology, King Mongkut Institute of Technology Ladkrabang.

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