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Biogenic Synthesis, Photocatalytic, and Photoelectrochemical Performance of Ag–ZnO Nanocomposite

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ABSTRACT: The development of coupled photoactive materials (metal/semiconductor) has resulted in significant advancements in heterogeneous visible light photocatalysis. This work reports the novel biogenic synthesis of visible light active Ag–ZnO nanocomposite for photocatalysis and photoelectrode using an electrochemically active biofilm (EAB). The results showed that the EAB functioned as a biogenic reducing tool for the reduction of Ag+, thereby eliminating the need for conventional reducing agents. The as-prepared Ag–ZnO nanocomposite was characterized by X-ray diffraction, transmission electron microscopy, diffuse reflectance spectroscopy, photoluminescence spectroscopy, and X-ray photoelectron spectroscopy. The photocatalytic experiments showed that the Ag–ZnO nanocomposite possessed excellent visible light photocatalytic activity for the degradation of methyl orange, methylene blue, and 4-nitrophenol. Electrochemical impedance spectroscopy and linear scan voltammetry under dark and visible light irradiation confirmed the enhanced visible light activity of the Ag–ZnO as photocatalyst and photoelectrode. These results suggest that Ag nanoparticles induced visible light photocatalytic degradation and enhanced the visible light activity of the photoelectrodes by minimizing the recombination of photogenerated electrons and holes, thereby extending the response of pure ZnO to visible light.

INTRODUCTION

Since Fujishima and Honda first reported photocatalysis by the splitting of water under UV irradiation in 1972, research in this field has expanded considerably.1 Photocatalysis has been attracting more attention as it finds use in a variety of products across the broad range of research areas, particularly environmental and energy related fields. Until recently, metal oxides, such as TiO2,2 ZnO,3 SnO2,4 etc., have been the prime choice for most studies in basic research and practical applications because of their high activity, low cost, high stability, nontoxicity, and chemical inertness, which makes them suitable for applications in water and air purification, sterilization, hydrogen evolution, and so forth.5,6

Among the metal oxides, TiO2 has been studied widely owing to its superior photocatalytic properties, whereas other metal oxides have received less attention. Zinc oxide has a similar band gap (∼3.27 eV at room temperature) to TiO2 and has been used as an environmental photocatalyst under UV light irradiation.7 However, the major drawback with ZnO is its wide band gap, resulting in its limited activity under visible light due mainly to the rapid recombination of photogenerated electrons/holes, which limit the photodegradation reaction under normal conditions.8 The fabrication of a photocatalyst that works under visible light, which covers 43% of sunlight, has been a challenging problem.9 Therefore, the development of a photocatalytic system that could utilize visible light irradiation is important for practical applications toward fulfilling the future energy demands.

Metals anchored on ZnO nanostructures have recently been used to extend the spectral response of ZnO toward visible light. Georgekutty et al.10 used a nonaqueous route, whereas Chen et al.11 used the photochemical deposition of Ag on ZnO for Ag/ZnO composite synthesis and further tested their photocatalytic activity. Deng et al.7 reported that the Schottky barrier in the regions between Ag and ZnO improves charge separation and enhances the efficiency of the degradation process. Ag can trap photogenerated electrons from the semiconductor, which allows holes to form hydroxyl radicals.

ABSTRACT: The development of coupled photoactive materials (metal/semiconductor) has resulted in significant advancements in heterogeneous visible light photocatalysis. This work reports the novel biogenic synthesis of visible light active Ag–ZnO nanocomposite for photocatalysis and photoelectrode using an electrochemically active biofilm (EAB). The results showed that the EAB functioned as a biogenic reducing tool for the reduction of Ag+, thereby eliminating the need for conventional reducing agents. The as-prepared Ag–ZnO nanocomposite was characterized by X-ray diffraction, transmission electron microscopy, diffuse reflectance spectroscopy, photoluminescence spectroscopy, and X-ray photoelectron spectroscopy. The photocatalytic experiments showed that the Ag–ZnO nanocomposite possessed excellent visible light photocatalytic activity for the degradation of methyl orange, methylene blue, and 4-nitrophenol. Electrochemical impedance spectroscopy and linear scan voltammetry under dark and visible light irradiation confirmed the enhanced visible light activity of the Ag–ZnO as photocatalyst and photoelectrode. These results suggest that Ag nanoparticles induced visible light photocatalytic degradation and enhanced the visible light activity of the photoelectrodes by minimizing the recombination of photogenerated electrons and holes, thereby extending the response of pure ZnO to visible light.
that can then react with the organic species, resulting in their degradation. 12–14 However, most reported methods use harmful chemicals, whose discharge into the environment is a major issue of concern. Therefore, there is increasing need for a novel route for metal–metal oxide nanocomposite synthesis. 15

Electrochemically active microorganisms form electrochemically active biofilms (EABs) on solid surfaces and have potential applications in bioenergy and chemical production. 15 EABs have attracted considerable attention in bio electrochemical systems (BESSs), such as microbial fuel cells, where they act as a living bioanode and produce excess electrons and protons by biologically oxidizing a range of substrates. The flow of these electrons produces a considerable amount of electricity. 16 Recently, it was reported that EABs could be used to reduce the band gap of metal oxide,17,18 synthesize noble metal nanoparticles, 19,20 hydrogen energy, 21 and metal–semiconductor nanocomposites with higher efficiency than other synthetic methods. 22

As part of an ongoing study of EABs, this work focused on the use of EABs for the decoration of pure ZnO nanostructures (p-ZnO) by silver nanoparticles (AgNPs). This work reports a very simple, biogenic, and facile method for the fabrication of Ag−ZnO nanocomposite (Ag−ZnO) by EAB as a reducing tool, which is far superior and fast compared to other microbial synthesis. 22 The enhancement in photocatalytic activity was attributed to the presence of AgNPs at the surface of p-ZnO and used for the degradation of methyl orange (MO), methylene blue (MB), and 4-nitrophenol (4-NP) in an aqueous solution under visible light irradiation. A possible charge transfer mechanism for the Ag−ZnO nanocomposite to degrade dyes, such as MO, MB, and 4-NP, is suggested. The EIS experiment under dark and visible light irradiation further supported the visible light activity of the Ag−ZnO nanocomposite, suggesting that Ag−ZnO is a good candidate for visible light photocatalysis and photoelectrodes. Ag−ZnO showed significantly high photocatalytic activity compared to p-ZnO. The method reported in this work, which does not involve the use of hazardous chemicals, capping agents and reducing agent etc., is simple and has great potential for commercialization.

**EXPERIMENTAL SECTION**

**Materials.** Nanosized zinc oxide (nano ZnO), silver nitrate (AgNO₃, 99% pure), and methylene blue (MB) were purchased from Sigma− Aldrich. Sodium acetate, methyl orange (MO), p-nitrophenol (4-NP) and sodium sulfate (Na₂SO₄) were obtained from Duksan Pure Chemicals Co. Ltd. South Korea and were used as received. Ethyl cellulose and α-terpineol were purchased from KANTO Chemical Co. Japan and fluorinated-doped transparent conducting oxide glass (FTO; F-doped SnO₂ glass; 7 Ω/sq) was purchased from Pilkington, U.S. Carbon paper (without wet proof, Fuel Cell Earth LLC) with a size of 2.5 × 4.5 cm² was dipped into a mineral salt medium containing sodium acetate (1 g L⁻¹) as the substrate and carbon source in a 250 mL bottle. Ten mL of anaerobic sludge (from a biogas plant in Paju, Korea) was added under strict anaerobic conditions by sparging N₂ gas for 5 min to remove the environmental oxygen. All media, including the bacterial inoculum, were changed every two days under strict anaerobic conditions. This process was repeated for two weeks, and a living EAB formed on the surface of the carbon paper.

**Synthesis of Ag−ZnO Nanocomposite.** The as-prepared EABs were used to synthesize the Ag−ZnO nanocomposite, as shown in Scheme 1. To obtain the Ag−ZnO colloids, 10 mM ZnO and 3 mM of AgNO₃ were added to 200 mL of distilled water with constant stirring. The solution was stirred for an additional 5 min to allow the complete adsorption of Ag⁺ ions on the p-ZnO surface. Silver ions at the ZnO surface were then reduced by the electrons produced by the EAB under anaerobic conditions, resulting in the anchoring of the AgNPs to the ZnO surface. A color change after 5 h indicated the formation of Ag−ZnO in the solution, which was then centrifuged to isolate Ag−ZnO. The isolated Ag−ZnO was dried in an air oven at 100 °C for 12 h, and stored in a desiccator until needed.

To further confirm the activity of the EAB, two controlled experiments were performed to check the role of the EAB and acetate. Of the two controlled experiments, one was performed in the absence of an electron donor (sodium acetate), in which only the prepared EAB was suspended in a 10 mM ZnO and 3 mM AgNO₃ solution under anaerobic conditions, whereas the other was performed in the absence of the EAB by adding only an electron donor (sodium acetate) in a 10 mM ZnO and 3 mM AgNO₃ solution under anaerobic conditions. In both controlled experiments, there was no color change, even after

photoelectrochemical spectroscopy (XPS, ESCALAB 250) was performed using a monochromatized Al Kα X-ray source (hν = 1486.6 eV) with a 500 μm spot size. The binding energy of Cls at 284.8 eV was used to calibrate the other binding energies. X-ray diffraction (XRD, PANalytical, X'pert PRO- MPD, Netherland) was carried out using Cu Kα radiation (λ = 0.15405 nm). The XRD peaks of the crystalline phases were compared with those of the standard compounds reported in the JCPDS data file. The size and distribution of the Ag−ZnO and p-ZnO nanoparticles were observed by field emission transmission electron microscopy (FE-TEM, Tecnai G2 F20, FEI, U.S.) with an accelerating voltage of 200 kV combined with energy dispersive spectrometry (EDS). The photoelectrochemical and photocatalytic experiments were performed using a 400 W lamp with irradiating intensity of 31.0 mW cm⁻² (λ > 500 nm, 3M, U.S.). Electrochemical impedance spectroscopy (EIS) was performed in a three electrode cell with a 0.2 M Na₂SO₄ aqueous solution as the electrolyte using a potentiosstat (VersaSTAT 3, Princeton Research, U.S.). The working electrodes were prepared as follows: 100 mg of p-ZnO and Ag−ZnO were suspended thoroughly using a conditioning mixer by adding ethyl cellulose as a binder and α-terpineol as a solvent for the paste, and then coated on FTO glass electrode using the doctor-blade method. The p-ZnO and Ag−ZnO-coated (FTO) glass substrates were used as the working electrode. Ag/AgCl (saturated with KCl) and a Pt gauge were used as the reference and counter electrodes.

**Electrochemically Active Biofilm (EAB) Preparation.** The EABs were developed on plain carbon paper according to previous reports. 15–24 In a typical procedure, carbon paper (without wet proof, Fuel Cell Earth LLC) with a size of 2.5 × 4.5 cm² was dipped into a mineral salt medium containing sodium acetate (1 g L⁻¹) as the substrate and carbon source in a 250 mL bottle. Ten mL of anaerobic sludge (from a biogas plant in Paju, Korea) was added under strict anaerobic conditions by sparging N₂ gas for 5 min to remove the environmental oxygen. All media, including the bacterial inoculum, were changed every two days under strict anaerobic conditions. This process was repeated for two weeks, and a living EAB formed on the surface of the carbon paper.

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24 h. These experiments confirmed the role of EAB and acetate in the synthesis of the Ag−ZnO nanocomposite.

**Evaluation of Dye Degradation.** The photocatalytic activity of Ag−ZnO nanocomposite was evaluated by the degradation of MO, MB, and 4-NP under visible light irradiation (λ > 500 nm). In a typical process, 2 mg of each p-ZnO and Ag−ZnO photocatalyst were added to three different 20 mL MO (10 mg L\(^{-1}\)), 20 mL MB (10 mg L\(^{-1}\)), and 20 mL of 4-NP (5 mg L\(^{-1}\)) solutions, and agitated for 30 min in the dark to achieve the adsorption−desorption equilibrium. The above suspension were irradiated with visible light and after a certain time interval (1 h), 2 mL of the solution was taken, and the catalyst was separated from the solution by centrifugation to obtain a clear liquid from which UV−vis spectra was measured. The decolorization efficiency of the photocatalyst was determined using the formula reported elsewhere.\(^{18,22}\)

**Photoelectrochemical Studies (EIS and LSV).** To examine the photoelectrochemical response of the p-ZnO and as-synthesized Ag−ZnO, EIS and LSV experiments were carried out under ambient conditions in the dark and under visible light irradiation in 50 mL of a 0.2 M Na\(_2\)SO\(_4\) aqueous solution at room temperature. For each electrode, EIS was first performed in the dark and later under visible light irradiation (λ > 500 nm) at 0.0 V and with a frequency ranging from 1 to 10\(^6\) Hz. The photocurrent response was obtained by LSV under dark and visible light irradiation at a scan rate of 50 mV/s over a potential range of −0.7 to 1.0 V.

**RESULTS AND DISCUSSION**

**Proposed Reaction Mechanism and Its Confirmation.**

EABs function as a reducing tool and provide an excess of electrons and protons by biologically decomposing sodium acetate.\(^{15−24}\) These electrons help in anchoring the metal nanoparticles to the surface of the ZnO nanostructure, as shown in Scheme 1. The advantage of this protocol is that it does not involve any external energy input, which makes this synthesis highly useful and efficient in the field of nanocomposite syntheses.\(^{15−24}\) Another exciting feature of this synthesis is that it occurs in water at room temperature and does not involve harmful chemicals, capping/reducing agents or severe treatments.

\[
\text{AgNO}_3(\text{aq}) \rightarrow \text{Ag}^+ + \text{NO}_3^- (\text{aq}) \quad (1)
\]

\[
\text{Ag}^+ (\text{aq}) + \hat{e}(\text{from EAB}) \rightarrow \text{Ag}\quad (2)
\]

\[
\text{NO}_3^- (\text{aq}) + \text{H}^+ (\text{from EAB}) \rightarrow \text{HNO}_3 \quad (3)
\]

To confirm the proposed mechanism and reaction steps involved in the synthesis of Ag−ZnO, the pH of the solution was measured before and after completion of the reaction. The pH of the reaction media decreased during the course of the reaction, and after 5 h, the pH changed from 7.9 to 6.8 due to the formation of acid (HNO\(_3\)) according to eqs 1, 2, and 3. Therefore, Ag\(^+\) was reduced by the EAB generated electrons and the formation of acid (HNO\(_3\)) occurred by the EAB generated protons.

**X-ray Diffraction.** Figure 1 shows the XRD patterns of the p-ZnO and as-synthesized Ag−ZnO, in which two sets of XRD peaks are observed. The peaks marked with (●) represent the signals of Ag and the remaining peaks represent the signals from p-ZnO. The inset shows the broadening of the Ag peak.
patterns are obtained: those unmarked were indexed to the well crystalline hexagonal wurtzite ZnO structure corresponding to JCPDS (36-1451), whereas the other peaks marked with "*" were assigned to face centered cubic (fcc) silver corresponding to JCPDS (04-0783). \(^{10,11}\) Compared to p-ZnO, the XRD pattern of ZnO after Ag anchoring was similar, suggesting that silver was not incorporated into the ZnO lattice. This can be attributed to the significantly larger ionic radius of Ag\(^+\) (126 pm) than Zn\(^2+\) (74 pm). Therefore, a silver metallic phase was attributed to the significantly larger ionic radius of Ag\(^+\) (126 pm) than Zn\(^2+\) (74 pm). Therefore, a silver metallic phase was attributed to Ag\(^+\) (74 pm). Therefore, a silver metallic phase was attributed to the significantly larger ionic radius of Ag\(^+\) (126 pm) than Zn\(^2+\) (74 pm).

The increase in the crystallite size of Ag–ZnO might be due to the anchoring of very small AgNPs at the surface of p-ZnO. The Ag (111) XRD peak is relatively weak and broad, as shown in the inset in Figure 1, indicating a small size and well dispersed Ag at the surface of p-ZnO, which is also consistent with the HR-TEM image.

**Transmission Electron Microscope.** Supporting Information, SI, Figure S1 and Figure 2 shows low and high-resolution TEM images of p-ZnO and as prepared Ag–ZnO, respectively. Figure 2c shows that the AgNPs are anchored to the ZnO surface with a particle size of \(\sim 7\)–12 nm. HRTEM (Figure 2d) reveals an interface and the continuity of lattice fringes between the AgNPs and ZnO. The lattice fringes of \(d = 0.26\) nm matched those of the (002) crystallographic plane of ZnO. The fringe spacing at 0.24 nm corresponds to the (111) plane of the face-centered cubic phase of AgNPs. HAADF-STEM of p-ZnO and Ag–ZnO are shown in SI Figures S2 and S3, respectively, whereas SI Figures S4 and S5 show the EDX spectra of the p-ZnO and Ag–ZnO, corresponding to the Ag (K), Zn (K), and O (K) lines. The EDX-elemental spectra were also supported by the elemental composition, as shown in SI Tables S1 and S2 for p-ZnO and Ag–ZnO, respectively. This further confirms the presence of the AgNPs in Ag–ZnO nanocomposite. EDX (SI Figure S5) also indicates the presence of the AgNPs in Ag–ZnO nanocomposite. The HRTEM results were in good agreement with the XRD result. These results show that Ag–ZnO has highly crystalline structure with a small and relatively uniform distribution of AgNPs at the ZnO surface, which is useful for the photocatalytic activities.

**Optical Properties.** The UV–visible diffuse reflectance (SI Figure S6) and absorbance spectra of p-ZnO and as-prepared Ag–ZnO were measured to determine their light absorption characteristics, as shown in the Figure 3a. The wavelength distribution of the absorbed light is an important property of photocatalysts, irrespective of the quantum yield. Therefore, the high photocactivity of Ag–ZnO was attributed to the higher visible light absorbance, as indicated by UV–visible diffuse reflectance spectroscopy. Ag–ZnO showed a typical absorption due to a band gap transition in the range, 400–550 nm, in the visible region caused by the surface plasmon band characteristics of silver, which further confirms that silver had been deposited successfully at the surface of p-ZnO. \(^{11}\) The extended absorbance of the Ag–ZnO in the visible region, which is the typical surface plasmon band exhibited by the AgNPs, confirmed that Ag–ZnO have considerable practical importance due to the efficient utilization of sunlight or visible light. The red-shifted absorption spectra provide some evidence of the interaction between Ag and ZnO, which is also in accordance with the XRD patterns. \(^{11}\)

The PL measurements were performed to determine the charge recombination and migration efficiency of the p-ZnO and Ag–ZnO because the photocatalytic activity is related closely to the PL intensity and the recombination rate of photo
excited electrons and holes. Figure 3b shows the PL spectra of 
p-ZnO and Ag−ZnO measured at an excitation wavelength of 
325 nm. The emission intensity of the PL spectrum of Ag− 
ZnO was lower than that of p-ZnO suggesting that the 
anchoring of AgNPs could quench the fluorescence from the 
ZnO nanoparticles and prolong electron−hole pair lifetime.
In general, the efficient charge separation and inhibited electron− 
hole recombination by AgNPs are favorable for enhancing the photocatalytic activity 
of p-ZnO. The PL spectra showed that anchoring AgNPs to the 
surface of ZnO could effectively inhibit electrons and holes 
recombination during the photocatalytic reaction under visible 
light irradiation.

XPS Analysis. The surface chemical composition and 
chemical states of p-ZnO and Ag−ZnO were investigated by 
XPS. Figure 4a presents the XPS survey spectra of p-ZnO and 
Ag−ZnO, showing that the material contains only Zn, Ag, O, 
and C. No other impurity elements were observed. The carbon 
peak shown in SI Figure S7 (C 1s = 284.8 eV) was assigned to 
residual carbon from the sample and hydrocarbons from the 
XPS instrument. However, high-resolution XPS of Zn 2p, O 1s, 
and Ag 3d (Figure 4b−d) showed that the binding energies of 
these electrons in the case of Ag−ZnO were slightly different, 
suggesting a strong interaction between the Ag and ZnO 
nanoparticles.7,11 Figure 4b shows the high resolution Zn 2p 
spectrum with specific peaks at 1021.5 ± 0.02 eV for 2p3/2 and 
1044.2 ± 0.03 eV for 2p1/2, indicating the oxidation state of 
Zn2+ in the form of ZnO in the materials.7,11
SI Figure S8 and Figure 4c shows the XPS spectra of O 1s of 
p-ZnO and Ag−ZnO. In Figure 4c and SI Figure S8, the peak at 
~528.7−530.16 ± 0.05 eV was assigned to lattice oxygen 
present in ZnO, whereas the peak at 531.60 ± 0.03 eV could be 
assigned to surface hydroxyl groups within the matrix of 
ZnO.14,18,26 The presence of surface hydroxyl groups facilitates 
the trapping of photoinduced electrons and holes, thereby 
enhancing the photocatalytic degradation process.14,27,28

Figure 4d presents the core level Ag 3d spectrum of the 
AgNPs in Ag−ZnO, showing of two individual peaks at 367.5 ± 
0.02 eV for Ag 3d3/2 and at 373.5 ± 0.02 eV for Ag 3d5/2 with 6 
eV splitting between the two peaks, which is evidence of the 
reduction of Ag ions by EAB to produce metallic silver.7,11,14 
Moreover, the binding energy (BE) of Ag 3d3/2 for the 
Ag−ZnO shifted remarkably to a lower binding energy compared to 
the corresponding value of the synthesized pure metallic Ag 
(BE value of Ag0 is approximately 368.2 ± 0.03 eV), possibly 
indicating a decrease in the electron density of Ag. Once the 
AgNPs are deposited on the surface of ZnO, electron transfer 
occurs from Ag to the conduction band (CB) of ZnO because 
the work function of silver is smaller than that of ZnO.7,14,28 
Therefore, a new Fermi energy level in Ag−ZnO is formed, 
resulting in the higher valence of Ag, indicating a strong 
interaction between Ag and the ZnO nanoparticles.7,14

Photocatalytic Performance. The photocatalytic performance of p-ZnO and Ag−ZnO for the degradation of MO, 
MB and 4-NP under visible light irradiation as a model reaction 
were investigated, as shown in Figure 5. The kinetic curves of 
photodegradation showed that compared to p-ZnO, Ag−ZnO 
promotes the photodegradation of MO, MB, and 4-NP under visible 
light irradiation due to the charge separation and visible 
light harvesting properties of the AgNPs. MO, MB, and 4-NP 
were degraded almost completely after 5, 4, and 6 h, 
respectively, under visible light irradiation in the presence of 
the Ag−ZnO photocatalyst. The higher observed photocatalytic 
activity of Ag−ZnO compared to p-ZnO indicates that the
AgNPs anchored at the surface of $p$-$ZnO$ behave like an electron sink, which could increase significantly the separation of the photogenerated electron–hole pairs and inhibit their recombination.\textsuperscript{7,12,26,28} This suggests that the AgNPs at the surface of $p$-$ZnO$ enhanced the photocatalytic activity of $p$-$ZnO$ for the effective degradation of dyes and organic compounds under visible light irradiation.

Mechanism of Degradation. Figure 6 illustrates the mechanistic profile of the photoinduced charge separation, migration and degradation process under visible light irradiation. The observed differences in the photocatalytic activities of $p$-$ZnO$ and Ag–$ZnO$ can be explained based on the difference in work function between $p$-$ZnO$ (5.2 eV) and Ag (4.2 eV).\textsuperscript{11,14,28} Generally, when two materials with different work functions are combined, a Schottky barrier will form and electrons will transfer from the materials with a low work function to the materials with a high work function.\textsuperscript{28,29} The Fermi energy of Ag is higher than that of ZnO due to the larger work function of ZnO. This leads to the transfer of electrons from the Fermi level of Ag to Fermi level of ZnO, until the two levels reach equilibrium and form a new Fermi energy level.\textsuperscript{30} The Fermi levels of Ag and ZnO were adjusted to the same value during the formation of the Ag–ZnO and formed a new Fermi energy level.\textsuperscript{14,29,30} During visible light irradiation, the equilibrated Fermi level electrons were injected rapidly into the ZnO conduction band via a surface phonon resonance (SPR) mechanism, and the injected electrons were trapped by dissolved oxygen molecules in water to yield high oxidative species, such as superoxide radical anions (\textsuperscript{•}$O_2$) and hydroxyl radicals (HO\textsuperscript{•}).\textsuperscript{13} The AgNPs in contact with $p$-$ZnO$ facilitates electron–hole separation, and subsequently helps in the formation of hydroxyl radicals. The superoxide radical anions (\textsuperscript{•}$O_2$) and hydroxyl radicals (HO\textsuperscript{•}) produced under visible light irradiation might be responsible for mineralization of the organic pollutants.\textsuperscript{12,28} Charge separation was also revealed by the decrease in the PL intensity of Ag–ZnO compared to $p$-$ZnO$. In general, photogenerated electrons can react with oxygen molecules adsorbed on the surface of the Ag–ZnO photocatalyst to yield \textsuperscript{•}$O_2$. Therefore, Ag–ZnO exhibits enhanced visible light photocatalytic activity compared to $p$-$ZnO$. Hence, the photocatalytic activity has a positive correlation with the formation rate of reactive radicals, i.e., faster formation radicals leading to a higher photocatalytic activity of the catalyst.\textsuperscript{15,26} Overall, these results suggest that AgNPs at the surface of ZnO will help increase the rate of formation of \textsuperscript{•}$O_2$ and HO\textsuperscript{•} reactive radicals, and simultaneously facilitate the degradation of organic pollutants.
that the AgNPs on ZnO could effectively improve the photocatalytic activity of Ag−ZnO by photoluminescence (PL) measurements (Figure 3b). This result clearly reveals that the AgNPs can effectively suppress the recombination of photogenerated electrons−hole pairs and enhance the photocatalytic activity of Ag−ZnO.33 On the basis of these results, we concluded that the Ag−ZnO could serve as effective materials for the enhancement of photocurrent.

Stability and Reusability of the Ag−ZnO. The stability of Ag−ZnO nanocomposite was evaluated by irradiation of a suspension of the Ag−ZnO in water with visible light and sonicated for one hour. Later, analyzing the solution for leached Ag−ZnO with UV−vis spectrophotometer (SI Figure S9). SI Figure S9 does not show any absorbance peak for silver. The reusability of Ag−ZnO was tested by centrifuging the catalyst from the dye solution, later washing with DI water and drying in an air oven at 100 °C. The reused catalyst showed a similar response to that of the fresh catalyst, highlighting the stability and reusability of Ag−ZnO.

**CONCLUSIONS**

This work reported a novel biogenic method to prepare a visible light active Ag−ZnO nanocomposite in water at room temperature using an EAB without using toxic chemicals, surfactant, and organic solvents. The formation mechanism of the Ag−ZnO nanocomposite shows that EAB appears to be a fascinating tool for nanocomposite synthesis because it does not involve any energy input. The as-prepared Ag−ZnO nanocomposite exhibited enhanced catalytic activity for the photodecomposition of MO, MB, and 4-NP by visible light. The enhanced photocatalytic activities of Ag−ZnO were attributed mainly to the reduced recombination rate of photogenerated electrons and holes pairs induced by the anchoring of AgNPs. EIS and LSV further confirmed that the as-prepared Ag−ZnO could be used as effective materials for photoelectrodes. In this study, a simple and biogenic method for preparing highly visible light active Ag−ZnO nanocomposite materials for possible applications in industrial effluent treatment and photoelectrodes was established. This environmentally friendly synthesis is expected to provide a new means of synthesizing a series of metal−metal oxide photocatalysts for use in photoassisted catalytic reactions.

**ASSOCIATED CONTENT**

Supporting Information

Further additional information [TEM, HAADF, and EDX of P-ZnO and Ag-ZnO, DRS spectra of P-ZnO and Ag-ZnO, C1s spectra of P-ZnO and Ag-ZnO, O 1s spectra of P-ZnO and UV−vis spectra of Ag-ZnO]. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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