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ARTICLE

Visible light-driven photocatalytic properties of polyphosphodiester-protected silver nanocomposites

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Silver nanocomposites are used to develop photocatalysts for various environmental, energy, and biomedical applications. However, the stability, biocompatibility, and performance of these colloids for practical applications need further improvement. Herein, silver nanocomposites protected with polyphosphodiester (PPDEs) were successfully synthesized. A conjugate was prepared by varying the ratio of phosphodiester to silver acetate, which were then exposed to visible light to form the silver nanocomposites, known as PEP- $\text{Na}_a\text{Ag}_b\text{-I}$ (a and b correspond to the ratio of Na^+ and Ag^+ in the feed). Then, the stability, photocatalytic activity, and recyclability of the colloids were evaluated. The spectral changes observed before and after irradiation confirmed the formation of photogenerated nanocomposites. The morphology of PEP- $\text{Na}_a\text{Ag}_b\text{-I}$ was characterized by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and X-ray photoelectron spectroscopy (XPS). The silver nanocomposites efficiently degraded Rhodamine B (RhB) under visible light, with the degradation efficiency of PEP- $\text{Na}_a\text{Ag}_b\text{-I}$ reaching 89% ($k = 5.12 \times 10^{-2} \text{ min}^{-1}$), indicating their photocatalytic performance. These nanocomposites achieved over 87% degradation of RhB even after six cycles, demonstrating their recyclability. The stability and recyclability of the colloids were reinforced by the polyphosphodiester. The role of specific reactive oxygen species (ROS) was explored by the conventional scavenger approach. The silver nanocomposites play a crucial role in the heterojunction, enhancing not only light harvesting but also increasing the capacity for electron acceptance and suppressing electron-hole recombination.

1. Introduction

Numerous studies have explored the design and synthesis of highly efficient photocatalysts for several applications, such as environmental purification,^{1–3} sustainable energy utilization,^{4,5} and medical engineering.^{6–9} In the 1970s, Fujishima and Honda discovered the ability of titanium dioxide (TiO_2) to drive photoelectrochemical water splitting under ultraviolet light,¹⁰ which revolutionized the photocatalytic industry. The unique properties of TiO_2 , including its chemical stability, electronic structure, and low cost¹¹ make it an excellent photocatalyst. However, its applications are constrained by its wide band gap energy (3.0–3.2 eV), which could utilize ~5% of the solar energy.^{12,13} To promote the efficiency of solar energy utilization, selecting materials with an absorption range that extends into the visible-light spectrum is a practical solution.

Recently, silver-based materials have garnered attention.^{14–16} Typically, silver (II) oxide (AgO), a p-type semiconductor with an optical band gap of 0.93–1.2 eV,^{17,18} displays superior light absorption. Silver (I) oxide (Ag_2O) is another outstanding photocatalyst, which can degrade persistent organic pollutants.^{19,20} Nevertheless, the practical applications of single-component photocatalysts are limited by rapid electron-hole recombination and poor stability.^{21,22} Modifying their physicochemical and optical characteristics via heterojunction construction and cocatalyst integration²³ can help overcome these issues. Metal nanocomposites incorporating gold, platinum, and silver are being increasingly explored due to their electron trapping and optical properties, which facilitate efficient charge separation. Particularly, silver nanocomposites exhibit a strong surface plasmon resonance effect, which enhances their photocatalytic performance under visible light.^{24,25} Silver nanocomposites can also trigger the recombination of electron-hole pairs, acting as electron sinks due to the Schottky barrier.^{26,27} Recent studies have demonstrated the remarkable photocatalytic performance of silver cocatalysts, including silver nanocomposites such as $\text{Ag}/\text{Ag}_2\text{O}$,^{28,29} Ag/AgCl ,^{30,31} $\text{Ag}/\text{Ag}_3\text{PO}_4$,³² and $\text{Ag}/\text{AgO}/\text{Ag}_2\text{O}$,³³ due to their narrow bandgap and excellent electrical conductivity.^{34,35}

Poly(ethylene sodium phosphate) (PEP- Na) is a polyphosphodiester (PPDE) that exhibits excellent water solubility (>200 mg/ml). A PPDE is formed through a reaction

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between a polyphosphotriester (PPTE) and trimethylamine, resulting in a polysalt, which was then treated with cation-exchange resin and neutralization.³⁶ The modification of PPTE's side chains into PPDE allows precise tuning of the polymer's properties.³⁷ Studies have explored the role of PEP-Na in various applications, including drug delivery,^{38,39} osteoporosis prevention,⁴⁰ and protein conjugation.⁴¹ However, the effect of exchanging Na⁺ ions with other ions on the photocatalytic performance of these compounds remains unexplored, which might lead to novel applications.

Herein, we aimed to synthesize silver nanocomposites protected with PPDEs via visible-light irradiation. The structural, morphological, and optical properties of the synthesized material were thoroughly investigated. The results showed that these nanocomposites exhibited effective photocatalytic activity for Rhodamine B (RhB) degradation under visible light and enhanced dispersibility due to the properties of PPDEs. Furthermore, the silver nanocomposites retained over 87% efficiency in dye degradation even after six cycles, highlighting their recyclability.

2. Experimental Section

2.1. Materials

2-Chloro-2-oxo-1,3,2-dioxaphosphalane (COP) was obtained from NOF Co., Ltd. (Tokyo, Japan). 2-Methoxy-2-oxo-1,3,2-dioxaphosphalane (MP) was distilled under reduced pressure and stored under argon at 4°C until further use.⁴² The cation-exchange resin Amberlite IR120 was supplied by Merck KGaA (Darmstadt, Germany). A 30% aqueous solution of trimethylamine was purchased from Nacalai Tesque, Inc. (Osaka, Japan). 1,8-Diazabicyclo[5,4,0]-undec-7-ene (DBU) was purchased from Sigma-Aldrich (Saint Louis, USA). Methanol, 2,6-dimethylpyridine (2,6-lutidine), toluene, chloroform-d 99.8% (contains 0.05 vol% TMS), benzyl alcohol, acetic acid, diethyl ether, sodium hydroxide (NaOH), fuming nitric acid, and silver acetate (CH₃COOAg) were purchased from FUJIFILM Wako Pure Chemical Inc. (Osaka, Japan).

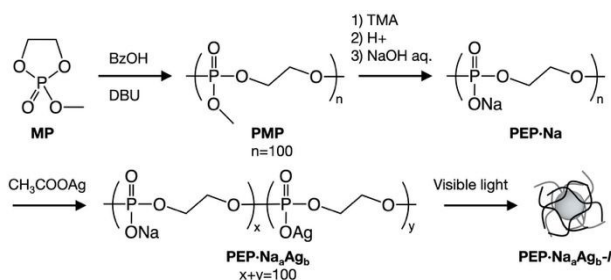


Figure 1. Synthesis of PEP-Na₃Ag₆-1

2.2. Preparation of silver nanocomposites protected with PPDEs

First, we synthesized PEP-Na (Figure 1). Briefly, 45 mmol of MP was mixed with 0.45 mmol of benzyl alcohol to facilitate polymerization. Then, DBU was added under an argon gas atmosphere. After stirring the mixture in an ice bath at 0°C,

methanol was added to reduce viscosity. After quenching DBU with acetic acid, the product was purified and reprecipitated from diethyl ether. Trimethylamine was used for quaternization, followed by a reaction with cation-exchange resin. Subsequently, the solution was filtered to remove the cation-exchange resin, and sodium hydroxide was added as a neutralizing agent. Then, the polymer solution was dialyzed for three days using a membrane with a molecular weight cut-off of 1000 (Spectra/Por®, Spectrum Laboratories, Inc., Rancho Dominguez, CA, USA), immersed in ultrapure water. The dialyzed solution was freeze-dried, yielding PEP-Na as a colorless solid.

Then, 200 mg of PEP-Na was mixed with CH₃COOAg at room temperature for 60 minutes. The mol ratio of phosphodiester unit (EP-Na) to CH₃COOAg was adjusted to 1:1, 2:1, and 5:1. In PEP-Na_aAg_b, a/b corresponds to the feeding ratio of EP-Na and CH₃COOAg. So, the PEP-Na₁Ag₁, PEP-Na₂Ag₁, and PEP-Na₅Ag₁ represent samples before exposure to the visible light. After dialysis for two days and freeze-drying, a gray colored solid was obtained. The ¹H-NMR spectra of each sample were obtained using a JNM-ECZ400 instrument (JEOL Ltd., Tokyo, Japan). The weight-average molecular weight (*M_w*) and molecular weight distribution were determined by JASCO gel-permeation chromatography (GPC; JASCO Corporation, Tokyo, Japan) using a calibration curve based on linear polyethylene glycol (PEG) standards. The elemental composition was precisely quantified using inductively coupled plasma-optical emission spectrometry (ICP-OES; Shimadzu Corporation, Kyoto, Japan), ensuring the accuracy of the silver content conjugated with PPDEs.

In the final step, we irradiated each sample with visible light at 83 mW/cm² for 60 minutes to form silver nanocomposites. Subsequently, the sample was freeze-dried to keep it in a solid state. After exposure to visible light, each sample is labeled as "light." Therefore, PEP-Na₁Ag₁-l, PEP-Na₂Ag₁-l, and PEP-Na₅Ag₁-l represent samples already exposed to the light.

2.3. Characterization of silver nanocomposites protected with PPDEs

The absorbance was measured using a JASCO V-650 and V-730 UV-Vis spectrophotometers (JASCO Corporation, Tokyo, Japan) in the range of 200–600 nm and 200–1100 nm, respectively. The wavelength accuracy of both the JASCO V-650 and JASCO V-730 instruments was ±0.2 nm, and the spectral bandwidth used for all measurements was 1.0 nm. Detailed morphological and crystallographic analyses were performed using transmission electron microscopy (TEM; JEM-1400, JEOL Ltd., Tokyo, Japan), operated at an accelerating voltage of 100 kV. TEM images of the synthesized material were used to determine the size and shape. A drop of the diluted sample was placed onto a carbon-coated copper grid. After leaving it for 10 minutes, the liquid fraction was carefully removed using filter paper. Particle sizes were determined from TEM images using ImageJ. The images were calibrated using the scale bar, and the diameter of 100 individual particles was manually measured. The lattice parameter was analyzed using selected area electron diffraction



(SAED) and a high-resolution transmission electron microscope (HRTEM; ARM 200F, JEOL Ltd., Tokyo, Japan), operated at 200 kV. The result was then used to identify the crystalline structure using ReciPro software.⁴³ A Zetasizer (Malvern Instruments, Worcestershire, U.K.) was employed to determine the average size and zeta potential, with particle size measurements better than $\pm 2\%$ on NIST traceable latex standards. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AMICUS/ESCA 3400 spectrometer (Kratos Analytical Ltd., Manchester, UK), equipped with a Mg anode X-ray source (1253.6 eV), which enabled detailed analysis of surface chemical states. The XPS binding energies were accurately calibrated using the phosphorus ($P_{2p} = 133.0$ eV), ensuring reliability in the characterization of the silver nanocomposites protected with PPDEs.

2.4. Photocatalytic activity

The photocatalytic activity was examined using 0.25 mg/ml (250 ppm) of the silver nanocomposites protected with PPDEs, combined with 6.9×10^{-6} M of RhB (3.3 ppm). The RhB concentration was adjusted to ensure reliable linearity in the measurements. Then, the mixture was exposed to visible light at 83 mW/cm². To calculate the C/C_0 ratio and first-order kinetics, the solution was collected at various intervals, and the supernatant was separated via centrifugation at 15000 rpm for 5 minutes before analysis. The degradation of RhB was quantitatively analyzed by measuring the decreased maximum absorption peak at 554 nm using a UV-Vis spectrophotometer. A RhB solution without the silver nanocomposites was used as the control to negate the influence of light on the dye. The degradation of RhB follows a pseudo-first-order kinetic model with respect to the reaction time:

$$-\ln(C_t/C_0) = k \times t \quad (1)$$

Here, C_0 and C_t represent the initial concentrations of RhB and those at various time intervals, respectively. k (min⁻¹) represents the apparent rate constant of the reaction.

2.5. Free radical scavenging experiment

The reactive species, such as h^+ , $\cdot OH$, and $O_2^{\cdot -}$ radicals, were identified using free radical scavenging agents specific to each species, including triethanolamine (TEOA), 2-propanol, and p-benzoquinone (p-BQ), respectively. The RhB degradation efficiency was compared with that of the sample with no scavenger.

2.6. Stability of silver nanocomposites protected with PPDEs

A 0.25 mg/ml sample was mixed with ultrapure water, and RhB was added to achieve a final concentration of 3.3 ppm in a total volume of 200 μ l. After exposure to visible light for 90 minutes, the supernatant was separated by centrifuging at 15000 rpm for 15 minutes. The RhB degradation efficiency (%) is calculated as $(A_0 - A_t)/A_0 \times 100$, where A_0 represents the initial absorbance and A_t represents the absorbance after decomposition.

3. Results and discussion

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3.1. Preparation of silver nanocomposites protected with PPDEs.

The ring-opening polymerization of MP resulted in PMP, which was demethylated to yield PEP-Na.^{44,45} The average polymerization degree of both PMP and PEP-Na was 100, and their molecular weights (M_w), measured using GPC, were 11.0×10^3 and 13.5×10^3 , respectively. The yield of PEP-Na, calculated from the integration of ¹H NMR spectra, was determined to be 96.5%. Both PMP and PEP-Na exhibited high water solubility and the capacity to function as electron acceptors, making them efficient supporting materials in metal-containing catalysts.

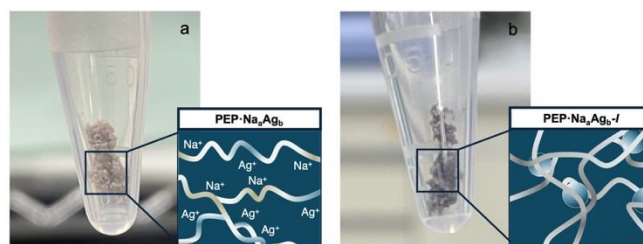
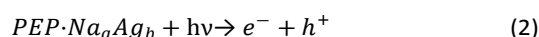


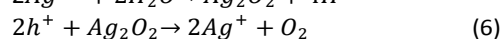
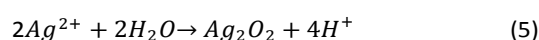
Figure 2. Schematic of PEP-NaAgb (a) and PEP-NaAgb-I (b)

The samples were synthesized by adjusting the ratio of [PEP-Na]: [CH₃COOAg] to 1:1 (PEP-Na₁Ag₁), 2:1 (PEP-Na₂Ag₁), and 5:1 (PEP-Na₅Ag₁), in which CH₃COOAg was the precursor of Ag⁺. The characteristics of PEP-Na_aAg_b are presented in Table 1. The ICP results show that the Ag concentrations of PEP-Na₁Ag₁, PEP-Na₂Ag₁, and PEP-Na₅Ag₁ were 0.96, 0.79, and 0.36 ppm, respectively. Accordingly, the actual molar ratios of [EP-Na]: [EP-Ag] for the aforementioned samples were 0.28:1, 0.50:1, and 2.72:1, respectively.

During ion exchange, Na⁺ ions were replaced with Ag⁺ ions to yield PEP-Na_aAg_b (Figure 2a). Upon exposure to visible light, the Ag⁺ ions produced may react with oxygen embedded in the polymer, forming stable oxides, such as AgO and Ag₂O. Since the formation of these oxides is non-selective, a mixture of AgO and Ag₂O might be present⁴⁶ (Figure 2b). Simultaneously, the absorbed photons provide energy to excite electrons from the valence band (VB) to the conduction band (CB).^{47,48} This process generates an electron-hole pair, where the excited electrons in the CB can reduce Ag⁺ ions to form silver nanocomposites. Along with its primary role as an electron acceptor, Ag⁺ can also interact with holes (h^+) left in VB to produce high-valent silver species, as shown in Eq.(2)–(4).⁴⁹



As Ag²⁺ can easily form peroxides in aqueous solutions (Eq.(5)), the photocatalytic oxidation of these peroxides might lead to the formation of O₂ Eq.(6)).⁵⁰



The formation of Ag_2O could occur when Ag^+ reacts with oxygen species on the surface, as represented in Eq.(7)–(8), and could be reduced to silver nanocomposites.⁵¹



Nevertheless, the effect of visible-light exposure on the structure of the nanocomposites was evaluated using filtration through centrifuge membranes with different pore sizes (Figure S1a). The results confirm that the PEP- Na_3Ag_1 can pass through the 50 kDa NMWL membrane (Amicon® Ultra centrifugal filter, Millipore, Billerica, MA, USA). No peaks were observed in the UV-Vis spectra in the visible region (Figure S1b), suggesting the presence of Ag^+ ions. In contrast, the silver nanocomposites protected with PPDEs, which were already exposed to visible light, exhibit a peak in the visible region. Furthermore, the residue that could pass through the membrane showed the same peak region as shown in Figure S1c, providing evidence that the light exposure causes the structural changes occurring in the silver nanocomposites.

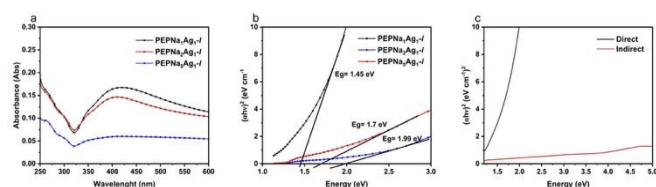


Figure 3. UV-Vis spectra (a) and Tauc plot (b) of the PEP- Na_1Ag_1 -I, PEP- Na_2Ag_1 -I, and PEP- Na_5Ag_1 -I nanocomposites. Direct and indirect band gap of the PEP- Na_1Ag_1 -I (c).

After visible-light irradiation, the UV-Vis spectra of PEP- Na_1Ag_1 -I, PEP- Na_2Ag_1 -I, and PEP- Na_5Ag_1 -I were analyzed to investigate their photophysical properties (Figure 3a–c). The color of the reaction changed from light yellow to gray/black, confirming the reduction.^{52,53} All samples were checked by a V-650 UV-Vis spectrophotometer, which exhibited an absorption peak in the visible region (Figure 3a), especially in the absorption region of silver in the composite, at 407–420 nm.⁵⁴ Heterogeneity of silver nanocomposites can significantly enhance visible-light absorption and separate electron–hole pairs, thereby improving photocatalytic activity.⁵⁵ The absorbance increased with an increase in Ag concentration, indicating that a higher number of particles were generated as more Ag^+ ions were reduced and transformed into silver nanocomposites.

The energy band gaps (E_g) for each sample were estimated by the Tauc plot:

$$\text{Direct:} \quad (\alpha h\nu)^2 = K(h\nu - E_g) \quad (9)$$

$$\text{Indirect:} \quad (\alpha h\nu)^{1/2} = K(h\nu - E_g) \quad (10)$$

Where α , $h\nu$, K , and E_g are the absorption coefficient, photon energy, energy-independent constant, and bandgap energy, respectively.

Figure 3b shows the optical direct bandgap determined by the Tauc plot using Eq. (9), where the absorbance was obtained from a V-730 UV–vis spectrophotometer. The bandgap energy (E_g) values of PEP- Na_1Ag_1 -I, PEP- Na_2Ag_1 -I, and PEP- Na_5Ag_1 -I were calculated to be 1.45 eV, 1.7 eV, and 1.99 eV, respectively.⁵⁶ These values correspond to the ratio of the PPDEs, with the highest ratio resulting in the least agglomeration. The silver nanocomposites exhibited a bandgap widening due to the quantum confinement effect.⁵⁷ As shown in Figure 3c, the curve plot compares the direct and indirect band gaps of PEP- Na_1Ag_1 -I obtained from Eqs. 9 and 10, respectively. The distinct work functions of the silver nanocomposites facilitated strong interactions among these components, resulting in broad and tightly bonded interfaces. Schottky barriers and band bending were generated at these interfaces due to the silver nanocomposites, eventually achieving equilibrium at their Fermi levels.^{58,59} Thus, the silver nanocomposites are expected to exhibit high photocatalytic abilities.

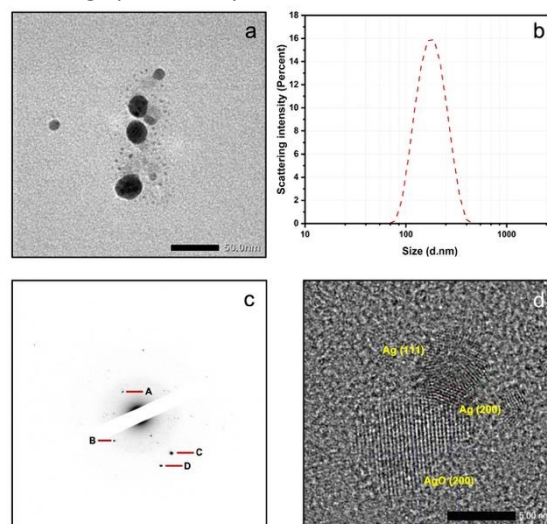


Figure 4. Transmission electron microscopy images (a), dynamic light scattering measurement (b), selected area electron diffraction patterns(c), and high-resolution TEM images (d) of PEP- Na_5Ag_1 -I.

The micrographs of the synthesized samples are shown in Figure 4a–d. The TEM images of the PEP- Na_5Ag_1 -I show regular spherical-shaped particles with an average size of 10–20 nm (Figure 4a). Based on the dynamic light scattering data shown in Figure 4b, the average diameter (Z_{ave}) was estimated to be 176 nm, which is more than that observed using TEM. This difference may be due to the surface functionalization of the polymer layer surrounding the silver nanocomposites, which is detected by DLS.⁶⁰ The corresponding polydispersity index (PDI) was 0.27. The crystalline structure of the silver nanocomposites was analyzed based on SAED patterns and HRTEM images (Figures 4c and 4d, respectively). The TEM image and corresponding SAED pattern are shown in Figure 4a and Figure 4c. The SAED pattern (Figure 4c) consists of diffraction spots and the halo pattern, suggesting that an amorphous structure was not observed. According to the standard lattice parameter in bulk Ag^{61} , AgO^{62} , and Ag_2O^{63} , the diffraction spot A was indexed as AgO {200}, while the spot B was indexed as Ag {111}. On the other hand, diffraction spot C cannot be determined because



the interplanar spacing of Ag_2O {220} (1.6829 Å), AgO (31-1) (1.6993 Å), and AgO (202) (1.6753 Å) are similar. Similarly, diffraction spot D cannot be distinguished because Ag {220} (1.4447 Å) and AgO (220) (1.4759 Å) are very close. Electron diffraction revealed that the silver-based nanocomposite consists of crystalline metallic silver and silver oxide. Figure 4d shows the HRTEM image of a silver-based nanocomposite particle with a complex shape. The upper area shows the multiple twin particle (MTP) structure, which is the typical characteristic structure of noble metal nanoparticles, with interplanar spacings matching those of Ag (111) and (200) planes. In contrast, the lattice fringes observed in the lower areas were indexed as AgO (200) from the spacing.

The surface chemical composition and valence state of the elements of silver nanocomposites were characterized by XPS (Figure 5a–d). The complete XPS spectrum reveals the presence of Ag , O , C , Na , and P elements (Figure 5a). The peak of the P_{2p} spectrum is at 133.0 eV, which directly corresponds to the phosphorus (Figure 5b).⁶⁴ The deconvoluted XPS spectrum of P_{2p} reveals that the peak at 133 eV constitutes 75–80% of the P_{2p} signal, which can be attributed to the presence of PO_4^{3-} within the polyphosphodiester molecule.⁶⁵

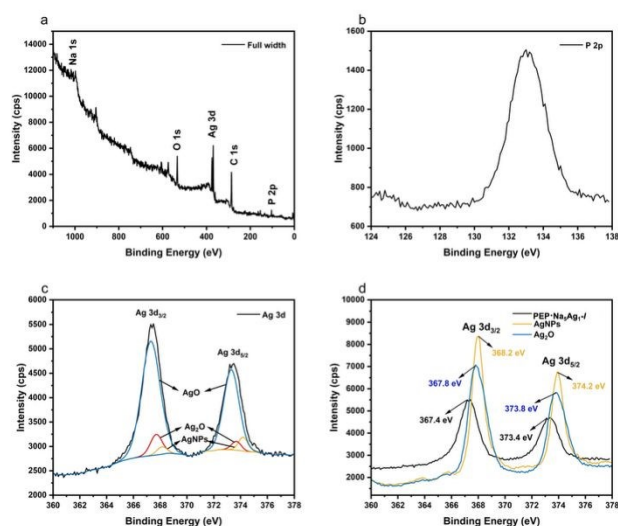


Figure 5. X-ray photoelectron spectroscopy full spectrum (a), P_{2p} (b), Ag_{3d} (c). The Ag_{3d} comparison of the PEP- $\text{Na}_5\text{Ag}_1\text{-I}$, AgNPs , and Ag_2O (d).

The XPS spectra of Ag_{3d} reveal two distinct peaks, displaying the spin-orbit split lines of $\text{Ag}3d_{3/2}$ and $\text{Ag}3d_{5/2}$ (Figure 5c). PEP- $\text{Na}_5\text{Ag}_1\text{-I}$ displayed peaks at 367.4 eV and 373.4 eV, which can be assigned to the standard Ag_{3d} binding energies of AgO at 367.3 eV and 373.3 eV.⁶⁶ The additional peaks observed at 367.8 eV and 373.8 eV can be attributed to Ag ions in the +1 oxidation state of Ag_2O .⁶⁷ Furthermore, the peaks at 368.2 eV and 374.2 eV indicate the presence of Ag .⁶⁸ The atomic percentages of AgO , Ag_2O , and Ag are 79.2%, 12%, and 8.8%, respectively. Metal oxidation typically results in a shift of binding energy (BE) to higher values due to a reduction in valence electron density. However, in the case of silver, the BE of oxides is lower than that of metallic Ag because of dominant effects such as the Hartree potential.⁶⁹ Figure 5d shows the chemical shift of the PEP- $\text{Na}_5\text{Ag}_1\text{-I}$ with the AgNPs and Ag_2O . The results indicate shifts of 0.8 eV and 0.4 eV, which correspond to those observed

for AgO with AgNPs and Ag_2O , respectively. These results confirm the presence of the dominant silver state of AgO .

The dispersibility properties of the silver nanocomposites were analyzed (Figure 6a–b). As shown in Figure 6a, these nanocomposites showed distinct differences in behavior. The commercial AgNPs and Ag_2O powders exhibited significant agglomeration even at low concentrations, while the PEP- $\text{Na}_5\text{Ag}_1\text{-I}$ dispersed more readily. The limited dispersibility of the commercial AgNPs and Ag_2O weakens their photocatalytic efficiency due to reduced interaction with aqueous environments. A comparison of the transmittance (%T) of the PEP- $\text{Na}_1\text{Ag}_1\text{-I}$, PEP- $\text{Na}_2\text{Ag}_1\text{-I}$, and PEP- $\text{Na}_5\text{Ag}_1\text{-I}$ revealed a notable trend (Figure 6b). PEP- $\text{Na}_5\text{Ag}_1\text{-I}$ achieved the highest %T, surpassing PEP- $\text{Na}_2\text{Ag}_1\text{-I}$ and PEP- $\text{Na}_1\text{Ag}_1\text{-I}$, indicating significantly improved dispersibility and transparency. The adsorption of high-molecular-weight charged polymers can induce electrosteric stabilization through a combination of steric hindrance and electrostatic repulsion.⁷⁰ These findings underscore that the enhanced dispersibility of the silver nanocomposites arises from the hydrophilic polymer coating layer of PPDEs, which imparts a negative surface charge with a zeta potential of -45.7 mV

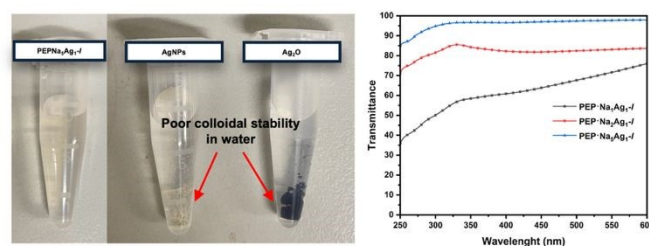


Figure 6. Photographs of the PEP- $\text{Na}_5\text{Ag}_1\text{-I}$, AgNPs , and Ag_2O (a). Transmittance (%T) spectra of the PEP- $\text{Na}_1\text{Ag}_1\text{-I}$, PEP- $\text{Na}_2\text{Ag}_1\text{-I}$, and PEP- $\text{Na}_5\text{Ag}_1\text{-I}$ (b).

3.2. Photocatalytic activity

Under visible-light irradiation, the photocatalytic performance of silver nanocomposites protected with PPDEs was evaluated at various time points under identical conditions by measuring the degradation efficiency of RhB (Figures 7a–f). The maximum absorption at 554 nm, these absorption bands may be attributed to the $\pi\text{-}\pi^*$ transitions of the conjugated molecules.⁷¹ After irradiation, PEP- $\text{Na}_1\text{Ag}_1\text{-I}$ displayed excellent photocatalytic activity at $t = 10$ minutes (Figure 7a). The absorption at 554 nm immediately decreased with an increase in irradiation time, as indicated by the reddish-violet color and absorption of the RhB solution.⁷² Furthermore, the intensity of a new peak at ~ 440 nm also increased, which is a characteristic of the absorption of silver nanocomposites. After irradiation for 45 minutes, the absorbance peak shifts to a higher wavelength at 447 nm. The blueshift of the absorbance peak occurs during irradiation time, accompanied by an increase in the particle's size.⁷³ The degradation of RhB was also evaluated under dark conditions, and no decrease in the 554 nm peak was observed (Figure 7b). PEP- $\text{Na}_2\text{Ag}_1\text{-I}$ followed a similar trend, with a slight reduction in the 554 nm peak, while a new peak around 407–434 nm appeared (Figure 7c). The results show the absorbance peak shifted to a higher wavelength of 434 nm after irradiation for 360 minutes. The lack of the RhB degradation under dark



conditions is consistent with PEP- Na_1Ag_1 -I (Figure 7d). Furthermore, as shown in Figure 7e, the photocatalytic activity of PEP- Na_5Ag_1 -I, represented by the peak at 554 nm, decreased slightly compared to that of PEP- Na_1Ag_1 -I and PEP- Na_2Ag_1 -I. However, the absorbance peak also indicated a blueshift according to irradiation time, as evidenced by a shift to 431 nm after 360 minutes of irradiation. No RhB degradation was observed under dark conditions (Figure 7f). The heterojunctions between silver nanocomposites are critical for photocatalysis, as they enhance visible-light absorption, adjust the geometry and electron structures of the nanocomposites, and reduce recombination of photo-induced electron-hole pairs.⁷⁴

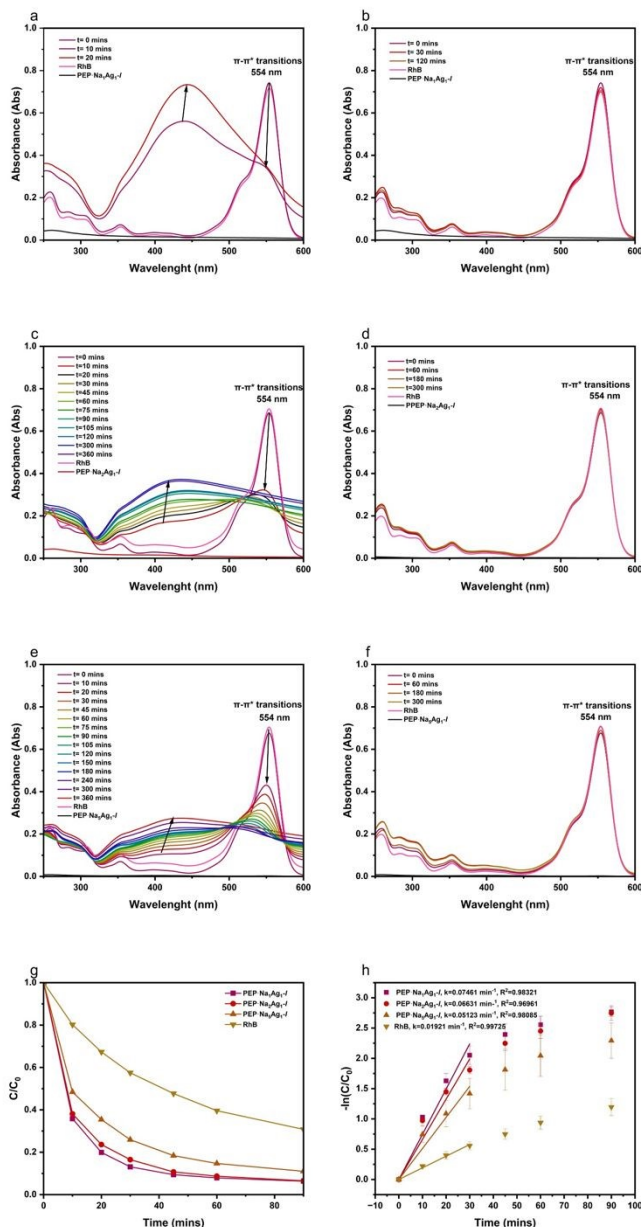


Figure 7. UV-Vis spectra showing RhB degradation by PEP- Na_1Ag_1 -I (a-b), PEP- Na_2Ag_1 -I (c-d), and PEP- Na_5Ag_1 -I (e-f) under visible light and dark conditions, respectively. The C/C_0 ratio (g), and first-order kinetics of PEP- Na_1Ag_1 -I, PEP- Na_2Ag_1 -I, PEP- Na_3Ag_1 -I, and the control sample are also shown (h).

At low dye concentrations, the degradation kinetics of the RhB can be described using the first-order Langmuir equation. A

comparison of the initial and final concentrations of each sample is shown in Figure 7g. All the samples exhibited higher photocatalytic activity than RhB irradiated by visible light. The PEP- Na_1Ag_1 -I demonstrated the highest photocatalytic activity, capable of removing approximately 94% of RhB after 90 minutes. The PEP- Na_2Ag_1 -I and PEP- Na_5Ag_1 -I samples also demonstrated high activity, removing 93.5% and 89% of RhB, respectively. The apparent reaction rate constant (k) was determined from the initial linear region (0–30 min) of the $-\ln(C/C_0)$ versus time plot (Figure 7h). After 30 minutes of irradiation, the RhB concentration becomes sufficiently low, leading to deviations from ideal pseudo-first-order linearity as shown in Figure S2. Therefore, the kinetic reaction rate was determined using data from the initial stage (0–30 min), where the reaction is described by a pseudo-first-order model. As the error bars represent the standard error of mean ($n=3$). The calculated k values ($t=0$ to 30 mins) obtained 7.46×10^{-2} , 6.63×10^{-2} , and $5.12 \times 10^{-2} \text{ min}^{-1}$ for PEP- Na_1Ag_1 -I, PEP- Na_2Ag_1 -I, and PEP- Na_5Ag_1 -I, respectively. The reaction rate constant of PEP- Na_1Ag_1 -I was more than three times that of the control sample, indicating that the presence of silver nanocomposites in PPDEs enables photocatalytic activity under visible light. The photocatalytic reaction rate constants under visible light of the silver-based photocatalyst were compared to those previously reported, as shown in Table S1. Obviously, our study exhibits an exceptional reaction rate constant compared with previous reports. Thus, the photocatalytic performance of the silver nanocomposites protected with PPDEs is remarkably under visible light, even without coupling with conventional semiconductor-based photocatalysts (e.g., TiO_2 , ZnO).

The proposed photocatalytic mechanism for RhB degradation by silver nanocomposites is explained using a schematic (Figure 8). Under visible-light exposure, electrons in the valence band (VB) of the silver nanocomposites are excited to the conduction band (CB), leaving behind holes in the VB. The CB potentials of Ag_2O (−0.31 eV) and AgO (0.72 eV) are well-aligned to facilitate electron transfer.⁷⁵ As the CB potential of AgO is more positive than that of Ag_2O , photogenerated electrons from Ag_2O can transfer to the CB of AgO and then to the Fermi level of Ag (0.99 eV), which acts as an electron sink. Photogenerated holes can migrate due to the more negative VB potential of Ag_2O (0.54 eV) compared to AgO (1.84 eV), creating a gradient that facilitates the accumulation of holes in Ag_2O , which are highly active in oxidation reactions.⁷⁶

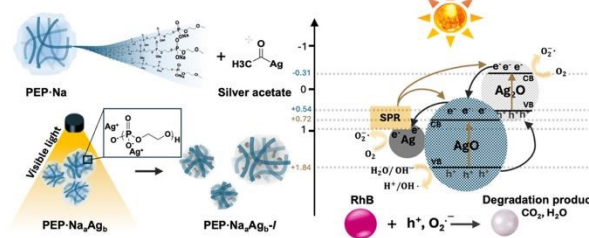


Figure 8. Schematic representation of the photocatalytic mechanism of silver nanocomposites.

The heterojunction structure of silver nanocomposites enabled the efficient transfer of electrons and holes across



different components, creating a multichannel charge transfer pathway. This mechanism effectively prevents charge recombination, prolongs the lifetime of reactive charges, and enhances photocatalytic activity. The Ag in the nanocomposite acts as a plasmonic center, enabling the absorption of visible light through localized surface plasmon resonance. This increases the generation of photogenerated carriers as well as facilitates their transfer within the heterojunction network.

In this study, the predominance of h^+ and $O_2^{\cdot-}$ radicals causes the stepwise degradation of RhB into CO_2 , H_2O , and other byproducts, as shown in Eq.(11)–(14). Further studies should focus on optimizing the content and distribution of silver nanocomposites to enhance charge separation in the multichannel.

The reactive oxygen species (ROS), such as holes (h^+), hydroxyl free radicals (OH^{\cdot}), and superoxide anion free radicals ($O_2^{\cdot-}$), are generated during optical excitation. During photocatalytic tests, specific scavengers were added to the RhB solutions under visible light to help identify the main ROS species responsible for degradation. The scavengers used for h^+ , OH^{\cdot} , and $O_2^{\cdot-}$ radicals were triethanolamine (TEOA), 2-propanol, and p-benzoquinone (p-BQ), respectively.

Figure 9 shows the photodegradation efficiency of the PEP- Na_5Ag_1-I with different scavengers and a control sample without any scavenger. The photodegradation efficiency of the PEP- Na_5Ag_1-I in RhB dye removal after 90 minutes of visible light exposure, with the addition of TEOA, 2-propanol, p-BQ, and no scavenger, was 31.7%, 91.5%, 35.5%, and 91.6%, respectively. Introducing these scavengers decreased both degradation rate and photocatalytic activity, indicating that two ROS contribute significantly to degradation (h^+ and $O_2^{\cdot-}$). The result shows that holes (h^+) have the greatest impact on this process, highlighting their predominant role in driving photocatalytic efficiency.

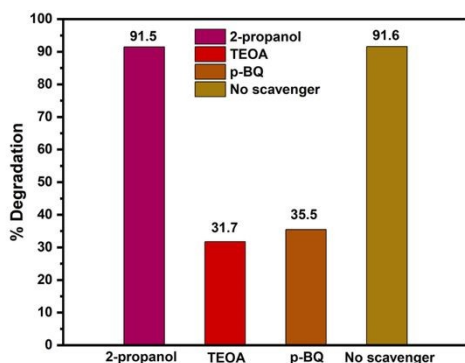
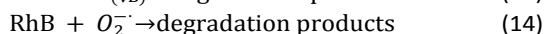
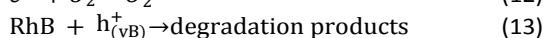
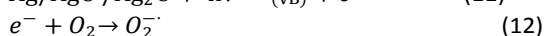
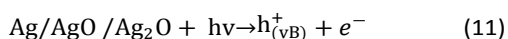


Figure 9. Free radical scavenger test of PEP- Na_5Ag_1-I . The h^+ , OH^{\cdot} , and $O_2^{\cdot-}$ radicals were removed using triethanolamine (TEOA), 2-propanol, and p-benzoquinone (p-BQ), respectively. The control sample did not have any scavengers.

The potential reactions involved in the photocatalytic degradation of the samples are outlined below.⁷⁷



Understanding the role of the silver nanocomposites as stable and efficient photocatalysts under visible light irradiation is essential for advancing photocatalytic applications. Figure 10 shows the photocatalytic performance of PEP- Na_5Ag_1-I , which degraded over 87% of the RhB dye after six cycles. As the ratio of the PPDEs influences the dispersibility, it also impacts the recyclability. Therefore, the PEP- Na_5Ag_1-I , which has a high ratio of PPDEs, exhibits consistent photocatalytic performance over repeated cycles by maintaining an active interface for ongoing ROS generation.

4. Conclusions

In this study, we designed and synthesized silver nanocomposites protected with PPDEs from unsaturated silver salts of PPDEs. The silver nanocomposites were formed via visible-light irradiation. The coexistence of PPDEs and silver nanocomposites was confirmed by different characterization techniques. The TEM/HRTEM images, SAED patterns, and XPS spectra revealed that the silver nanocomposites consist of Ag, AgO, and Ag_2O . Furthermore, these PEP- Na_1Ag_1-I , PEP- Na_2Ag_1-I , and PEP- Na_5Ag_1-I nanocomposites exhibited exceptional photocatalytic performance under visible light irradiation, achieving 94%, 93.5%, and 89% RhB degradation efficiency, respectively, within 90 minutes. Their reaction rate constants (k values) of 7.46×10^{-2} , 6.63×10^{-2} , and $5.12 \times 10^{-2} \text{ min}^{-1}$, respectively, represent a significant enhancement over the control sample. PEP- Na_5Ag_1-I showed the highest dispersibility, colloidal stability, and recyclability due to its elevated PPDE content. This nanocomposite retained over 87% RhB degradation efficiency even after six cycles, showing its high recyclability. The high photocatalytic efficiency of this system was driven by specific (h^+ and $O_2^{\cdot-}$), with the heterojunction structure enhancing charge transfer and suppressing electron-hole recombination.

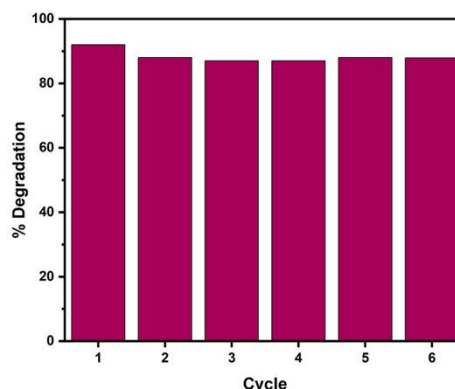


Figure 10. Recyclability of the PEP- Na_5Ag_1-I .

Author contributions

Thanaporn Jullabuth: methodology, formal analysis, investigation, writing – original draft, writing – review and editing. Yota Okuno: investigation, formal analysis. Hideya Kawasaki: methodology, data curation. Satoshi Ichikawa: investigation, writing – review & editing.



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Yasuhiko Iwasaki: conceptualization, formal analysis, funding acquisition, resources, supervision, writing – original draft, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article has been included as part of the supplementary information (SI). Supplementary information is available. See

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Data availability statement

The data supporting this article have been included as part of the Supplementary Information.

