



Article Synthesis of Au–Ag Alloy Nanoparticle-Incorporated AgBr Crystals

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Abstract: Nanoscale composites consisting of silver and silver halide (Ag–AgX, X = Cl, Br, I) have attracted much attention as a novel type of visible-light photocatalyst (the so-called plasmonic photocatalysts), for solar-to-chemical transformations. Support-free Au–Ag alloy nanoparticle-incorporated AgBr crystals (Au–Ag@AgBr) were synthesized by a photochemical method. At the initial step, Au ion-doped AgBr particles were prepared by adding an aqueous solution of AgNO₃ to a mixed aqueous solution of KBr and HAuBr₄. At the next step, UV-light illumination ($\lambda = 365$ nm) of a methanol suspension of the resulting solids yielded Au–Ag alloy nanoparticles with a mean size of approximately 5 nm in the micrometer-sized AgBr crystals. The mole percent of Au to all the Ag in Au–Ag@AgBr was controlled below < 0.16 mol% by the HAuBr₄ concentration in the first step. Finite-difference time-domain calculations indicated that the local electric field enhancement factor for the alloy nanoparticle drastically decreases with an increase in the Au content. Also, the peak of the localized surface plasmon resonance shifts towards longer wavelengths with increasing Au content. Au–Ag@AgBr is a highly promising plasmonic photocatalyst for sunlight-driven chemical transformations due to the compatibility of the high local electric field enhancement and sunlight harvesting efficiency.

Keywords: silver halide; silver–gold alloy nanoparticle; local electric field enhancement; plasmonic photocatalyst

1. Introduction

In view of energy and environmental issues, solar energy utilization for the production of useful chemicals and for the decomposition of harmful environmental pollutants has become increasingly important. Nanoparticles (NPs) made from Ag and Au have high absorption due to the localized surface plasmon resonance (LSPR). The LSPR excitation-driven photocatalysts represented by Au NP-loaded TiO₂ (Au/TiO₂) have emerged as a new type of visible-light photocatalysts [1,2]. Among the plasmonic photocatalysts, silver–silver halides (Ag–AgX, X = Cl, Br, I) also exhibit visible-light activity for important chemical reactions including hydrogen evolution [3,4] and CO₂ reduction [5–7]. Recently, Ag NP-incorporated AgBr crystals on TiO₂ have been shown to work as a plasmonic photocatalyst via the local electric field enhancement (LEFE) mechanism [8]. In this case, the key to improving the solar-to-chemical conversion efficiency is the compatibility of high LEFE and sunlight harvesting efficiency (LHE) [9]. Figure 1a shows the absorption spectra of spherical Au–Ag alloy NPs in water calculated as a function of the Au mole fraction (*x*) by the finite-difference time-domain (FDTD) method. Most LSPR absorption of Ag NPs is located at a wavelength region below 400 nm, while the absorption spectrum for Au NPs matches well with the solar spectrum. In the Au_x–Ag_{1–x} alloy system, the LSPR peak redshifts from 390 nm at x = 0 to 530 nm at x = 1. The light absorption or the generation rate of

the photocharge carriers is proportional to the electric field squared $|E|^2$ [10]. To indicate the plasmonic enhancement, the maximum local electric field enhancement factor (EF_{max}) is defined by Equation (1):

$$\mathrm{EF}_{\mathrm{max}} = (E_{\mathrm{max}}/E_0)^2 \tag{1}$$

where E_0 is the amplitude of incident electric field.

Figure 1b shows the EF_{max} calculated for various *x* values. Ag NPs (*x* = 0) possess much more intense EF_{max} than Au NPs (*x* = 1), and in the alloy system, the EF_{max} drastically decreases with an increase in *x*. Thus, precise control of the alloy composition would enhance the photocatalytic activity through the fulfilment of the optical requirements. Although the control of the Au–Ag alloy composition is generally difficult because of the large difference in the reduction potentials of Ag⁺ and Au³⁺ ions [11], Au–Ag alloy NPs have been synthesized by co-reduction of HAuCl₄ and AgNO₃ with NaBH₄ [12,13], citric acid [14], starch [15] or wolfberry fruit extract [16], and by γ -ray irradiation [17]. We have recently reported a photochemical method for preparing Au–Ag alloy NP-incorporated AgBr crystals on TiO₂ (Au–Ag@AgBr/TiO₂) [18].

In this study, a method has been developed to synthesize support-free Au–Ag@AgBr crystals with varying alloy compositions. The characterization of the samples and FDTD calculations for the model system indicate that Au–Ag@AgBr crystals are a promising material for plasmonic photocatalysis.



Figure 1. (a) Finite-difference time-domain (FDTD)-calculated absorption spectra of $Au_x - Ag_{1-x}$ alloy nanoparticles (*x*, mole fraction of Au) with a diameter of 5 nm in water. The absorption intensity is normalized with respect to the peak. (b) Maximum local electric field enhancement factor (EF_{max}) as a function of *x*. This data was cited from reference [18].

2. Results and Discussion

2.1. Synthesis of Au–Ag@AgBr

The Cl⁻ ligands of HAuCl₄ were substituted to Br⁻ ligands by the addition of KBr aqueous solution. The resulting HAuBr₄ is further reduced to HAuBr₂ by water in the presence of AgNO₃ (Equation (2)) [18] due to the negative standard Gibbs energy of the reaction ($\Delta_r G_0 = -57.6$ kJ mol⁻¹).

$$AuBr_4^- + 2Ag^+ + H_2O \rightarrow AuBr_2^- + 2AgBr + 2H^+ + 1/2O_2,$$
 (2)

Then, the slow addition of AgNO₃ aqueous solution to KBr aqueous solution containing HAuBr₄ at varying concentrations (C_{sol}) yields Au⁺ ion-doped AgBr particles (AgBr:Au⁺). The mole percent of Au to Ag in AgBr:Au⁺ ($y = ((Au \text{ mole/Ag mole}) \times 100)$) was determined by inductively coupled plasma spectroscopy. Figure 2a shows the relationship between y and C_{sol} . The y value monotonically increases with an increase in C_{sol} , and thus the Au-doping amount can be precisely controlled by the Au-complex concentration. X-ray diffraction (XRD) measurements were carried out for AgBr:Au⁺ with varying Au⁺ ion-doping amounts. As shown in Figure 2b, diffraction peaks at $2\theta = 26.8^{\circ}$, 31.0° , 44.4° ,

55.1°, 64.5°, 73.2° were indexed as the diffraction from the (111), (200), (220), (222), (400), and (331) crystal planes of AgBr, respectively, and are observed in every sample.



Figure 2. (a) Plots of Au doping amount (*y*) as a function of the added HAuCl₄ concentration (C_{sol}). (b) X-ray diffraction (XRD) patterns for AgBr:Au⁺ and AgBr reference pattern of the international center for diffraction data (ICDD).

Next, a methanol suspension of AgBr:Au⁺ was illuminated by ultraviolet light emitting diode (UV-LED) (λ = 365 nm). Figure 3a shows the scanning electron microscopy (SEM) image of the sample (y = 0.159 mol%) obtained after UV-light irradiation. Micrometer-sized particles are observed, and the other samples with different Au-doping amounts had a similar size and shape. In order to directly confirm the formation of metal NPs in AgBr, the surrounding AgBr was selectively dissolved by an aqueous solution of 7.5 M NaCl and 40 mM octadecyltrimetylammonium chloride. Figure 3b shows a high resolution transmission electron microscopy (HR-TEM) image for a metal NP obtained after dissolving the AgBr matrix of irradiated Au–Ag@AgBr (y = 0.041 mol%). The particle size is approximately 5 nm, and the observed d-spacing is in agreement with the values of Au (111) and Ag (111) planes (Au(111) = 0.236 nm (the international center for diffraction data (ICDD) No. 00-004-0784), Ag(111) = 0.237 nm (ICDD No. 01-071-3752)). Figure 3c shows energy dispersive X-ray spectroscopy (EDX) line-elemental analysis for the metal NP. While the intensity of Au is smaller compared with that of Ag due to the small doping amount of Au (y = 0.041 mol%), Ag and Au co-exist homogeneously in the metal NP in contrast to the core-shell structure [19]. Evidently, the Au–Ag alloy NP-incorporated AgBr crystals are formed by this solid-phase photochemical reaction. No change in the XRD patterns of AgBr:Au⁺ was observed before and after irradiation, most likely due to the small amounts of the metal NPs generated.



Figure 3. (a) Scanning electron microscopy (SEM) image of Au–Ag@AgBr (y = 0.159 mol%). High resolution transmission electron microscopy (HR-TEM) image (b) and energy dispersive X-ray spectroscopy (EDX) analysis (c) of metal nanoparticles obtained from Au–Ag@AgBr (y = 0.041 mol%) by dissolving AgBr.

Figure 4a,b compares the UV-Vis absorption spectra of AgBr:Au⁺ with varying *y* before (Figure 4a) and after (Figure 4b) irradiation by UV-LED. Before irradiation, all samples possess strong absorption below 470 nm due to the interband transition of AgBr with a very weak LSPR absorption. After irradiation, the LSPR greatly intensifies around 500–600 nm, which also indicates the growth of Ag and/or Au NPs in AgBr by irradiation.



Figure 4. (a) UV-visible absorption spectra for AgBr:Au⁺ with varying *y* before (a) and after (b) irradiation with UV light.

Figure 5a shows the UV-Vis absorption spectra of the Au–Ag colloids obtained by dissolving the AgBr matrix of Au–Ag@AgBr. At y = 0, the LSPR peak is located at 414 nm, and the increase in y causes the redshift in the LSPR peak and its significant broadening. A similar trend was observed for the Au–Ag colloids obtained from Au–Ag@AgBr/mesoporous-TiO₂ in the previous report, although the alloy composition could not be determined [18]. Figure 5b shows the LSPR peak position (λ_{max}) for the Au–Ag colloids as a function of y. In each case, the λ_{max} monotonically increases with an increase in y. Thus, Au–Ag alloy NP-incorporated AgBr crystals can be formed by the solid-phase photochemical reaction, and the alloy composition can be simply controlled by the Au doping amount.



Figure 5. (a) UV-visible absorption spectra for Au–Ag aqueous colloids prepared from Au–Ag@AgBr by dissolving AgBr. (b) Plots of λ_{max} of localized surface plasmon resonance (LSPR) as a function of Au-doping amount (*y*).

2.3. Mechanism on the Formation of Au-Ag@AgBr

We propose a reaction mechanism on the solid-state photochemical formation of Au–Ag alloy NP-incorporated AgBr crystals by taking the results of the previous density functional theory calculations [18] (Scheme 1). The Au⁺ ions doped into AgBr substitute the interstitial Ag ions (Ag_i^+) to occupy the interstitial sites (Au_i^+) . The rise in C_{sol} increases the mole ratio of the Au_i⁺ ions (*m*) to Ag_i⁺ ions (*n*). Irradiation of AgBr by photons with more energy (*hv*) than the band gap

excites the electrons from the valence band (VB) to the conduction band (CB) (Equation (3)). Methanol works as a sacrificial electron donor for the VB-holes (h^+_{VB}) (Equation (4)). On the other hand, the CB-electrons (e^-_{CB}) can be trapped by the levels of the interstitial ions Ag_i⁺ or Au_i⁺ (M_i⁺) (Equation (5)). Due to the large electronegativity, the resulting metal atom (M) collects e^-_{CB} to generate a metal anion (Equation (6)) [20]. Ag⁺ ions can easily migrate in an AgBr lattice with a low activation energy (~4 kJ mol⁻¹) [21]. Thus, the Ag_i⁺ and Au_i⁺ ions can migrate to the Ag and Au metal anions to generate a diatomic metal cluster (Equation (7)). Through repetition of these processes, Au_x-Ag_{1-x} alloy NPs grow in AgBr crystals, and the mole ratio of Au (x = m/(m + n)) can be changed by C_{sol} or the amount of doped Au⁺ ions (y) (Equation (8)).

$$AgBr + h\nu \to e^{-}_{CB} + h^{+}_{VB}, \qquad (3)$$

$$h^+_{VB} + CH_3OH \rightarrow OP,$$
 (4)

where OP denotes the oxidized product.

$$M_i^+ + e^-_{CB} \to M, \tag{5}$$

where the Au or Ag metal atom is abbreviated as M.

$$M + e^-_{CB} \to M^-, \tag{6}$$

$$M^- + M_i^+ \to M^- M, \tag{7}$$

$$M - M + M_i^+ + e^-_{CB} \to \dots \to Au_m - Ag_n,$$
(8)



Scheme 1. Proposed mechanism for the synthesis of Au–Ag alloy nanoparticle-incorporated AgBr crystals.

3. Experimental Section

3.1. Catalyst Preparation and Characterization

An aqueous solution of KBr (0.1 M, 80 mL) containing $HAuBr_4$ (0–1 mM) was prepared by dissolution of $HAuCl_4$ and KBr in distilled water. AgNO₃ aqueous solution (0.1 M, 40 mL) was added dropwise slowly to the solution at 0.5 mL min⁻¹ using a Perista pump. The resulting suspension was

stirred at room temperature for 1 h. The particles collected by centrifugation were washed with distilled water three times and dried in vacuo to obtain AgBr:Au⁺. The amounts of Ag and Au in the reaction solutions before and after the formation of AgBr particles were determined by inductively coupled plasma spectroscopy (ICPS-7000, Shimadzu). From the difference in each amount, the mole numbers of Ag and Au contained in AgBr:Au⁺ were calculated. The particles (100 mg) were re-dispersed into methanol (20 mL), and illuminated by UV-light (λ = 365 nm, the light intensity integrated from 310 to 420 nm $(I_{310-420}) = 4.0 \text{ mW cm}^{-2}$) at room temperature for 15 min. The particles collected by centrifugation were washed with distilled water three times and dried in vacuo to obtain Au-Ag@AgBr. The sample morphology was characterized by scanning electron microscopy (SEM, Hitachi S-800) at an acceleration voltage of 10 kV. Further, the samples were observed by transmission electron microscopy (TEM) at an applied voltage of 200 kV (JEM-2100F, JEOL). X-ray diffraction (XRD) was measured by a Mini Flex X-ray diffractometer (Rigaku) operating at 40 kV and 100 mA. The scans were collected in the range from 20° to 90° (2 θ) by the use of Cu K α radiation ($\lambda = 1.545$ Å). Diffuse reflectance UV-Vis-NIR spectra of the samples were recorded on a UV-2600 spectrometer (Shimadzu) with an integrating sphere unit (Shimadzu, ISR-2600Plus) by using a quartz cell at room temperature. The reflectance (R_{∞}) was recorded with respect to a reference of BaSO₄, and the Kubelka–Munk function [$F(R_{\infty})$] expressing the relative absorption coefficient was calculated by the equation $F(R_{\infty}) = (1 - R_{\infty})^2/2R_{\infty}$.

3.2. FDTD Calculaitons

According to the method previously reported [17], the local electric field of $Au_x - Ag_{1-x}$ alloy NPs was analyzed by the three-dimensional (3D) finite-difference time-domain (FDTD) method using FDTD Solutions (Lumerical Solutions, Inc. Vancouver, BC, Canada). For the models constructed by fixing the metal particle size at 5 nm, the calculations were performed in a water medium using the optical constants (refractive index and extinction coefficient) previously reported [22].

4. Conclusions

The optical property and local electric field enhancement of Au–Ag alloy NPs strongly depends on the alloy composition. This study has presented a photochemical method for synthesizing support-free Au–Ag alloy NP-incorporeated AgBr crystals (Au–Ag@AgBr) with the alloy composition controlled. We anticipate that the present Au–Ag@AgBr can be a promising plasmonic photocatalyst for efficient solar-to-chemical transformations through fine-tuning of the alloy composition.

Author Contributions: S.N. prepared the catalysts, and conducted characterization. M.F. performed FDTD calculation. H.T. supervised the experimental work and data analysis.

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