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Photochemical formation of silver–gold (Ag–Au) composite colloids in solutions containing sodium alginate

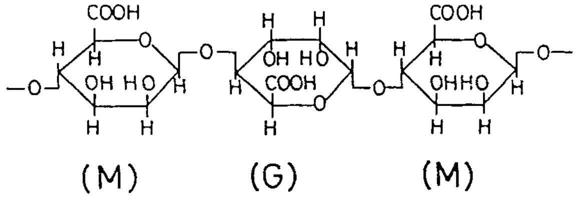
Tomoo Sato,* Shigeru Kuroda, Akinori Takami, Yoshiro Yonezawa and Hiroshi Hada
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan

Photochemical formation of colloidal silver, colloidal gold and silver–gold (Ag–Au) composite colloids under mild conditions has been studied. Irradiation of either aqueous $AgClO_4$ or $HAuCl_4$ solution in the presence of sodium alginate (SA) with 253.7 nm light yielded colloidal silver or gold, whose particle diameter was 10–30 nm or 40–60 nm, respectively. The Ag–Au composite colloids consisting of mixtures of silver and gold domains (particle diameter 30–150 nm) have been prepared and their extinction spectra have been examined on the basis of a conventional Mie theory in combination with an effective medium theory to estimate the optical constants of these colloids. It has been shown that the extinction spectra of the Ag–Au composite colloids are completely different from those of Ag–Au alloy colloids, in that the former have two extinction maxima close to the colloidal extinction bands of pure silver and gold, in contrast to a single extinction maximum of the latter. The importance of natural, high-molecular carboxylic acids such as alginic acid in the photochemical formation of metal colloids and thin films has been stressed.

Keywords: Photochemistry, silver alginate, Ag–Au composite colloids, metal particles, extinction spectrum, Mie scattering, surface plasmon, polyelectrolyte, protective agent

INTRODUCTION

Preparation of colloidal metals in solutions by chemical reduction methods has long been known.[1-3] We have studied photochemical formation of metal particles and thin films under fairly mild conditions.[4-7] In a previous paper,[5] we reported that colloidal silver, gold and platinum were formed by irradiation of $AgClO_4$, $HAuCl_4$ and Na_2PtCl_6 solutions, respectively, with UV light (wavelength $\lambda = 253.7$ nm) in the presence of protective agents such as sodium alginate (SA), sodium dodecylsulphate (SDS) and colloidal silica (SiO_2). We have obtained thin films of silver salts of alginic acid by ion exchange between sodium alginate and silver nitrate ($AgNO_3$).[7] When silver alginate films were photolyzed by UV light, colloidal silver particles (10–50 nm diameter) were formed in an early stage. After prolonged irradiation, they aggregated at the illuminated side of the films, giving rise[6] to clear silver mirrors whose sheet resistance were *ca* 10^{-8} times smaller than the original films. Recently, it has been reported that ion exchange and gelation of sodium alginate is useful for fabrication of high-Tc superconducting oxide ceramic fibers.[8] An interesting aspect of the photochemistry of metallic ions in the presence of sodium alginate would lie in the fact that alginic acid, $(C_5H_7O_4COOH)_x$, a block heteropolymer of D-mannuronic acid and L-guluronic acid (Scheme 1),[9,10] forms silver salts that are precursors of silver particles and thin films. Moreover, polyelectrolytes such as sodium alginate could play a role as a protective agent in solutions to prevent the colloidal metal particles from coalescing by enclosing them firmly in the network structure.



Scheme 1

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* Author to whom correspondence should be addressed.

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Colloidal silver and gold exhibit characteristic extinction bands in the visible region of the extinction spectra due to surface plasmon resonance.[11-14] Photophysical processes, e.g. nonlinear optical effects[15] and surface-enhanced Raman effects[16,17] of colloidal silver and gold particles in solutions, polymer matrices and glasses, have attracted considerable attention relevant to their potential application in optoelectronics. Optical properties of bulk and thin films of Ag–Au alloys have been studied extensively.[18,19] However, studies that examine the preparation and physicochemical properties of colloidal particles composed of both gold and silver have not received as much attention.[20-22] In this study, we have tried to prepare 'composite colloids' of gold and silver in solutions by a photochemical method. Here, we shall define the 'Ag–Au composite colloid' as those colloidal particles consisting of mixtures of Ag domains and Au domains whose domain sizes are considerably smaller than the particle diameter. We could expect some novel features in the optical properties of Ag–Au composite colloids compared with Ag–Au alloy colloids, which may be relevant to many future applications in optoelectronics and related fields.

EXPERIMENTAL

Sodium alginate used in this work was newly purchased from Nacalai Tesque, and purified by the method of Konishi *et al.*[23,24] $AgClO_4$, $HAuCl_4$, HNO_3, HCl and NH_4OH were used as received. All aqueous solutions were prepared in the dark, before use, using distilled water. Photolysis of the solutions and quantitative analysis of deposited silver and gold were carried out as described in previous paper.[5] The light source (a 200 W low-pressure mercury lamp) and the reaction cell (a rectangular quartz vessel of 1 cm × 1 cm × 4 cm in size) were as before. The cell was set up in a dark box and 3.5 cm^3 of aqueous sodium alginate solution (0.2 wt %) containing $AgClO_4$ and/or $HAuCl_4$ was placed in it for photolysis. The incident intensity of UV light ($\lambda = 253{\cdot}7$ nm) on the cell, as measured using ferrioxalate actinometry,[25,26] was $1.2 \times 10^{16}\ cm^{-2}\ s^{-1}$. Irradiation of the solution was carried out in air, at room temperature.

After irradiation, deposited metals in the solution were purified by dialysis with a semipermeable membrane, Visking tube 20/32 (Visking Co.). The sample was collected and transferred into a dialysis tube. Dialysis was carried out with 0.1% NH_4OH solution for 4 h. Afterwards, dialysis was continued with a large excess of water for 20 h. After dialysis at room temperature, in the dark, the sample was carefully transferred to the vessel. The sample containing colloidal silver only was dissolved in hot conc. HNO_3. The sample containing colloidal gold and/or silver was dissolved in aqua regia (conc. HCl/conc. HNO_3 3:1). Solutions were then diluted to 100 cm^3 and submitted for quantitative metal analysis by means of atomic absorption spectrometry using a Jarrel–Ash AA-8200 spectrophotometer. Special attention was paid to the solution that contained $HAuCl_4$ and was not subjected to irradiation.

If the solution did not contain colloidal silver at all, dialysis was performed for 4 h with 0.01 mol dm^{-3} HNO_3 solution and then for 20 h with a large excess of water. On the other hand, when colloidal silver was present in the solution, silver and gold were analyzed separately using 0.1% NH_4OH and 0.01 mol dm^{-3} HNO_3 solutions, respectively, to avoid dissolution of colloidal silver during dialysis. The quantum yield for metal deposition, Φ_M (M = Ag, Au), was evaluated by use of Eqn [1]:

$$\Phi_M = \frac{1}{\alpha I} \times \frac{d[M]}{dt} \qquad [1]$$

where d[M]/d*t* is the initial rate of formation of the reduced metal (atom s^{-1}), *I* the number of photons incident on the solution (photon s^{-1}) and α the percentage absorption.

Extinction spectra of metallic ions and colloids in solutions were measured with a Shimadzu UV-260 spectrophotometer. The absorbance was expressed in terms of optical density per cm lightpath length, although the actual lightpath length of the quartz cell was either 0.2 or 1 cm. Samples for transmission electron microscopy (TEM) were prepared by placing a small drop of the colloidal solution on a copper grid coated with a thin amorphous carbon film. The individual sample was then allowed to dry for a few hours before it was placed in the specimen holder. TEM characterization was carried out using a JEOL JEM-1200EX electron microscope operating at 80 kV.

RESULTS AND DISCUSSION

Photochemical formation of colloidal silver, colloidal gold and composite colloids

We have photolyzed 10^{-3} mol dm^{-3} solutions of $AgClO_4$ (System I) and $HAuCl_4$ (System II) with UV light. The change of extinction spectra with irradiation is shown in Fig. 1. Characteristic extinction bands due to surface plasmon resonance of colloidal silver and gold were observed. The distinct peak of colloidal silver was located at $\lambda = 390$–400 nm in System I. In System II, the extinction maximum of colloidal gold appeared initially at $\lambda = 545$ nm until 40 min irradiation and then shifted to 535 nm. The dependence of the amount of reduced metals on the irradiation time is given in Fig. 2. The amount of reduced silver, ΔN_{Ag}, increased monotonically with irradiation and leveled off at 80–85% of the initial $[Ag^+]$ after 120 min. The Φ_{Ag} value was found to be 0.035–0.038 ($\alpha = 0.20$). The amount of reduced gold, ΔN_{Au}, reached a saturation value after 40 min of irradiation. The conversion efficiency was *ca* 75% and Φ_{Au} was estimated to be 0.041 ($\alpha = 1.0$). TEM images of colloidal metals in Systems I and II are shown in Fig. 3. The colloidal silver formed after 60 min of irradiation was spherical in shape with a range of diameters, $d = 10$–30 nm. The colloidal gold particles formed after 90 min irradiation were ellipsoidal ranging

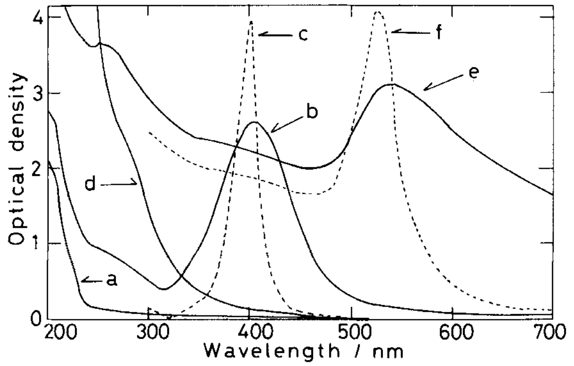


Figure 1 Extinction spectra of reaction mixtures containing 0.2 wt % SA in water before (a, d) and after (b, e) photolysis and calculated extinction spectra of colloidal silver (c) and gold (f) in water. a (0 min), b (20 min): 10^{-3} mol dm^{-3} $AgClO_4$ (System I). d (0 min), e (60 min): 10^{-3} mol dm^{-3} $HAuCl_4$ (System II). c: diameter 20 nm, $[Ag] = 8.6 \times 10^{-5}$ mol dm^{-3}. f: diameter 50 nm, $[Au] = 7.5 \times 10^{-4}$ mol dm^{-3}.

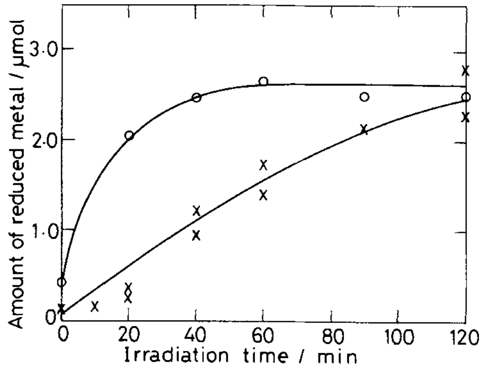


Figure 2 Growth of the amount of reduced metals in 0.2 wt % SA solution with irradiation time. ×, Silver from 10^{-3} mol dm^{-3} $AgClO_4$ (System I); ○, gold from 10^{-3} mol dm^{-3} $HAuCl_4$ (System II). Volume of the reaction mixture 3.5 cm^3.

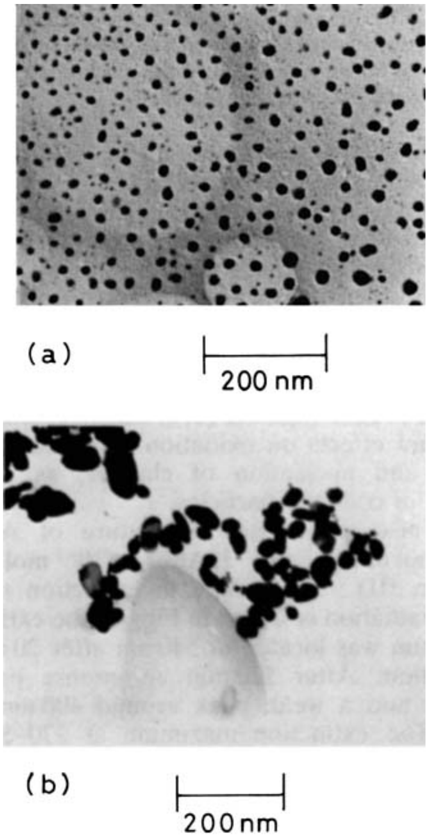


Figure 3 Transmission electron micrograph (TEM) of colloidal silver (a) and gold (b) formed by photolysis of System I and System II, respectively. (a) Irradiation time 60 min; (b) irradiation time 90 min. The bar corresponds to 200 nm.

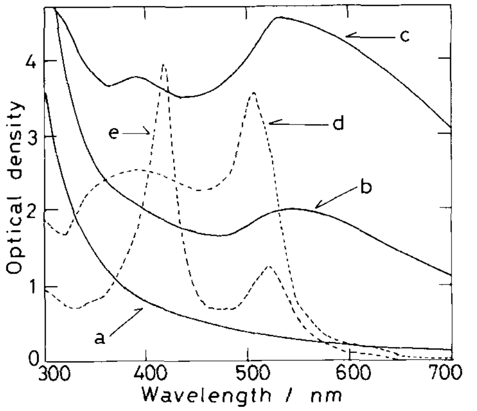


Figure 4 Variation of extinction spectra of reaction mixtures containing 0.2 wt % SA in water with irradiation (a, b, c) and calculated extinction spectra of Ag–Au composite colloid (d) and a simple mixture of pure colloidal silver and gold (e) in water. The solution contained 10^{-3} mol dm^{-3} $AgClO_4$ and 10^{-3} mol dm^{-3} $HAuCl_4$ (System III). a, 0 min; b, 20 min; c, 120 min. d: Diameter of the composite colloid 40 nm, [Ag] = 4.3×10^{-4} mol dm^{-3}, [Au] = 8.8×10^{-4} mol dm^{-3}. e: A superposition of the extinction spectrum of pure colloidal silver and gold, the diameters of each of which are 40 nm. [Ag], [Au] are the same as for curve d. Note that the optical density of d and e is reduced by 1/2 and 1/4, respectively.

over 20–40 nm along the minor axis and 40–60 nm along the major axis.

The measured extinction maxima for both the colloidal silver and gold in the present study were found to be at shorter wavelengths (10–20 nm) than those in our previous work.[5] In addition, ΔN_{Ag} was *ca* three times larger than before, which resulted in larger optical densities. Such discrepancies could reflect the different protective actions of sodium alginate (SA) which should cause profound effects on oxidation of reduced metal atoms and nucleation of clusters, as well as growth of colloidal particles.

We next photolyzed a mixture of $AgClO_4$ (10^{-3} mol dm^{-3}) and $HAuCl_4$ (10^{-3} mol dm^{-3}) (System III). The change in extinction spectra with irradiation is shown in Fig. 4. The extinction maximum was located at 540 nm after 20 min of irradiation. After 120 min an intense peak at 530 nm and a weak peak around 400 nm were seen. The extinction maximum at 520–540 nm increased monotonically with irradiation until 90–120 min. The dependence of ΔN_{Ag} and ΔN_{Au} on irradiation time is given in Fig. 5. ΔN_{Au} increased more rapidly than ΔN_{Ag} and attained a saturation value after *ca* 60 min of irradiation. The conversion efficiency at this stage was *ca* 90 %. On the other hand, the conversion efficiency of Ag^+ was 40 %, even after 120 min irradiation. Values of ϕ_M were 0.0076–0.0080 ($\alpha = 1.0$) for colloidal silver and 0.040 ($\alpha = 1.0$) for colloidal gold. Of note is the fact that the colloidal extinction band for silver did not appear in System III, in spite of the presence of reduced silver, before 120 min. TEM images of the colloidal particles from System III are shown in Fig. 6. The TEM image of the sample after 20 min of irradiation (a) showed collections of large ($d = 30$–50 nm) and small ($d = 5$–10 nm) particles. It is likely that some of the smaller particles stuck to the surface of larger ones. After 120 min of irradiation (b), the number of larger particles with smooth surfaces increased.

We have photolyzed 10^{-3} mol dm^{-3} solution of $HAuCl_4$ in the presence of colloidal silver. To this end, a 2.5 cm^3 solution of System I was first irradiated with UV light and then a 0.5 cm^3 solution of System II was added to it to prepare the reactant solution (System IV). It appears, from Fig. 2, that an equal amount of reduced silver and Ag^+ (1.25 μmol), together with 0.5 μmol of $AuCl_4$- were present in System IV at the beginning. The change in extinction spectra with irradiation is shown in Fig. 7. Before irradiation, a broad extinction band with a small peak around 440–460 nm appeared. The peak position changed gradually from around 430–440 nm (30 min of irradiation) to 440–460 nm (60 min) to 460–480 nm (90 min). The extinction spectrum did not change much without irradiation. The dependence of ΔN_{Ag} and ΔN_{Au} on irradiation times is given in Fig. 8. Before UV irradiation, the observed ΔN_{Ag} of 0.5 μmol was far smaller than the expected value of 1.25 μmol. On the

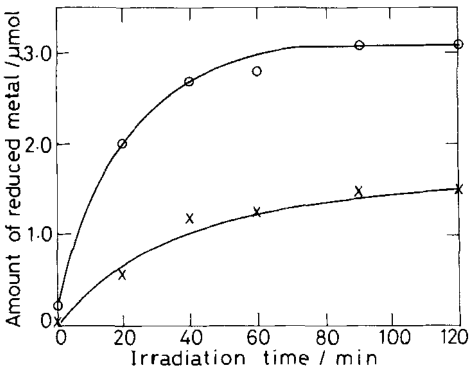


Figure 5 Growth of the amount of reduced metals in 0.2 wt % SA solution with irradiation time. The solution contained 10^{-3} mol dm^{-3} $AgClO_4$ and 10^{-3} mol dm^{-3} $HAuCl_4$ (System III). ×, Silver from System III; ○, gold from System III. Volume of the reaction mixture 3.5 cm^3.

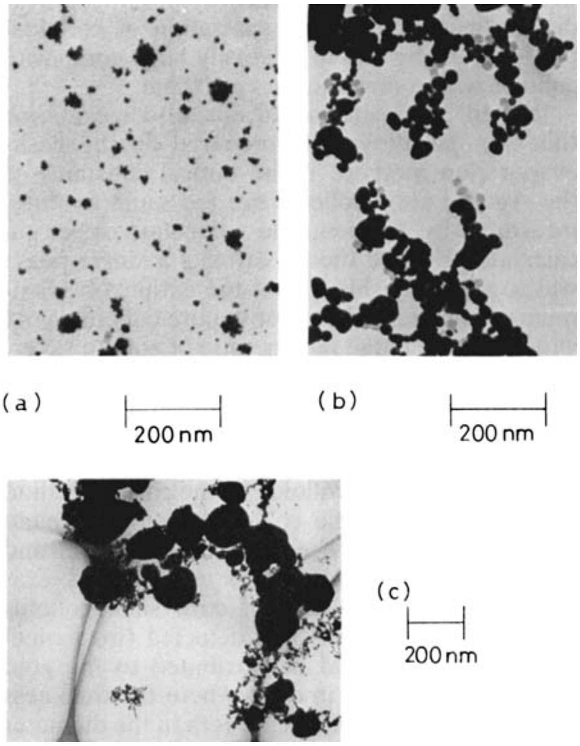


Figure 6 Transmission electron micrograph of Ag–Au composite colloids formed by photolysis of System III (a, b) and System IV (c). (a) Irradiation time 20 min; (b) irradiation time 120 min; (c) irradiation time 150 min. The bar corresponds to 200 nm.

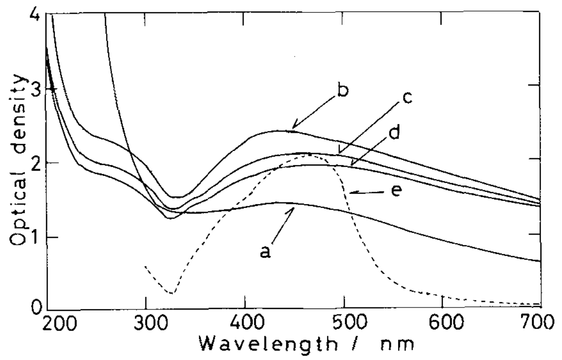


Figure 7 Variation of extinction spectra of reaction mixtures containing 0.2 wt % SA in water with irradiation (a, b, c, d) and calculated extinction spectra of Ag–Au composite colloid (e) in water. The solution contained colloidal silver, $AgClO_4$ and $HAuCl_4$ at the beginning (System IV). Total concentrations of silver and gold are 8.3×10^{-4} mol dm^{-3} and 1.7×10^{-4} mol dm^{-3}, respectively. a, 0 min; b, 30 min; c, 60 min; d, 90 min. e: Diameter 65 nm, [Ag] = 5.7×10^{-4} mol dm^{-3}, [Au] = 1.5×10^{-4} mol dm^{-3}. Note that the optical density of e is reduced by 2/5.

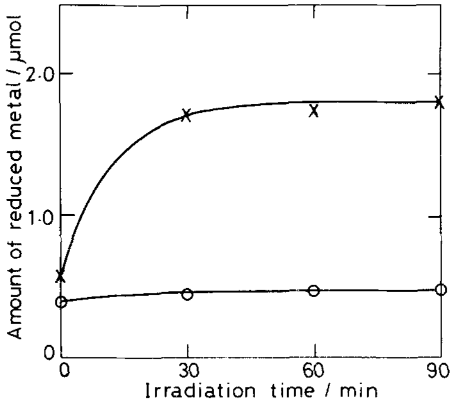


Figure 8 Growth of the amount of reduced metals in 0.2 wt % SA solution with irradiation time. The solution contained colloidal silver, $AgClO_4$ and $HAuCl_4$ at the beginning (System IV). Total concentrations of silver and gold are 8.3×10^{-4} mol dm^{-3} and 1.7×10^{-4} mol dm^{-3} respectively. ×, Silver from System IV; ○, gold from System IV. Volume of the reaction mixture 3.0 cm^3.

contrary, ΔN_{Au} of about 0.5 μmol was almost equal to the amount of $AuCl_4^-$ that existed at the beginning. Such observations indicate that $AuCl_4^-$ is reduced by colloidal silver in System IV, before irradiation, due to the difference in the standard electrode potentials of $E^0(Ag^+/Ag)$ and $E^0(AuCl_4^-/Au)$. Although ΔN_{Au} remained almost constant under UV irradiation, ΔN_{Ag} increased and reached the saturation value of 1.75 μmol (conversion efficiency *ca* 70 %) after 30 min of irradiation. The Φ_{Ag} value was 0.043 ($\alpha = 1.0$). The TEM image of the sample, before irradiation, showed a spherical shape with $d = 40$ nm, just the same as the colloidal silver in Fig. 3. After 150 min of irradiation, relatively large spherical particles ($d = 100$–150 nm) were the major products, together with a small amount of particles with $d = 20$–40 nm (Fig. 6(c)).

Optical properties and structure of composite colloids

We have evaluated the extinction coefficients of colloidal silver and gold by Mie theory.[6,12-14,27] The resultant Mie curves are given in Fig. 1. The particle diameters of colloidal silver and gold were assumed to be $d = 20$ nm and 50 nm, respectively. The concentration of colloidal solutions employed corresponds to those obtained by 20 min irradiation of System I (0.086 mmol dm^{-3}) and 90 min irradiation of System II

(0.75 mmol dm^{-3}), respectively. The Mie curves were moderately close to the observed colloidal extinction spectra.

We next examined the optical properties of the Ag–Au composite colloids by introducing an effective medium approximation[6,28,29] to estimate the optical constants. Effective dielectric constants of the composite colloids, ε_S, were determined by Eqn [2]:

$$V_{Ag}\times\frac{\varepsilon_{Ag}-\varepsilon_S}{\varepsilon_{Ag}+2\varepsilon_S}+V_{Au}\times\frac{\varepsilon_{Au}-\varepsilon_S}{\varepsilon_{Au}+2\varepsilon_S}=0 \qquad [2]$$

Here, ε_{Ag} and ε_{Au} denote the complex dielectric constants of bulk silver and gold, and V_{Ag} and V_{Au} the volume fraction of silver and gold domains in the Ag–Au composite colloid, respectively. The Mie curves of the Ag–Au composite colloids are given in Figs 4 and 7. Particle diameter ($d = 40$ nm) and the concentration of silver and gold domains ($[Ag^0] = 0.43$ mmol dm^{-3} $[Au^0] = 0.88$ mmol dm^{-3}) were chosen with reference to System III after 120 min of irradiation. The existence of two extinction maxima near the colloidal peaks of silver and gold was evident. The intensity of the extinction maximum at 500–510 nm appeared to be *ca* 1.5 times larger than that of the pure colloidal gold. On the other hand, the extinction maximum around 420 nm was reduced to less than one-tenth of that of pure colloidal silver. It is obvious that the Mie curve in Fig. 4 is different from a superposition of the curves of pure colloidal silver and gold. The Mie curve in Fig. 7 was obtained by using parameters corresponding to System IV after 90 min of irradiation: $d = 65$ nm, $[Ag^0] = 0.57$ mmol dm^{-3}, $[Au^0] = 0.15$ mmol dm^{-3}. The general feature of the Mie curve in Fig. 7 was not so far from the observed spectrum. If $d = 50$ nm was employed instead of 65 nm, an extinction spectrum having a peak at 425 nm and a shoulder near 470 nm developed. Furthermore, a choice of $d = 100$ nm resulted in a broad extinction spectrum with a peak at 515 nm. We could thus assume that a single peak at 430–520 nm, characteristic of System IV, results from silver domains in the composite colloid whose extinction maximum has been much red-shifted due to an increase in the average particle diameter. In reality, as the amount of reduced silver and gold did not change much after 30 min of irradiation, the red shift of the extinction maximum by *ca* 50 nm and the decrease of the peak intensity by prolonged irradiation would imply reorganization of colloidal particles, giving rise to relatively large composite colloids with a diameter of *ca* 100 nm.

Ripken[19] has determined optical constants for thin Ag–Au alloy films prepared by the flash-evaporation method. If the optical constants of the Ag–Au alloy colloids are the same as those measured by Ripken, the extinction spectrum calculated by Mie theory exhibits a single peak, which gradually shifts from the extinction maximum of pure colloidal silver to pure colloidal gold with variation in the mixing ratio of gold to silver. Mie prediction has been confirmed by Papavassiliou for the Ag–Au alloy colloids obtained from Ag–Au bulk alloy by the Svedberg method.[21] Recently, Teo and co-workers[22] prepared Ag–Au alloy colloids by the citrate method and observed a single colloidal extinction band that was located between the colloidal silver and gold extinction bands. Morris and Collins[20] examined optical properties of core–shell colloids (gold core/silver shell) and detected two extinction bands that could be attributed to the gold core and silver shell in cases where the thickness of the silver shell was much less than the diameter of the gold core. We observe a similar core–shell colloid analogy using the photochemical method. We first photolyzed system II with UV light, after which the reaction mixture was added to System I and further photolyzed. The colloidal solution obtained in this way showed a similar extinction spectrum to those reported by Morris and Collins. These observations strongly suggest that colloidal particles having a composite structure made of silver and gold domains of a size smaller than the wavelength of the incident light could show two extinction bands representing both domains. In this sense, Ag–Au composite colloids from Systems III and IV may or can be distinguished from the Ag–Au alloy colloids and also from the simple mixture of pure silver colloid and gold colloid.

To obtain more insight into the structure of the Ag–Au composite colloids, we have carried out a preliminary examination by X-ray photoelectron spectroscopy using Shimadzu ESCA 750 spectrometer with radiation from the Mg Kα line. Colloidal solutions were dropped onto one side of a Pyrex glass plate and dried under a nitrogen atmosphere. The $Ag_{3d5/2}$ and $Au_{4s7/2}$ lines were recorded before and after sputtering for 5 min with argon at 1.5 kV and the ratio of the signal intensity of the $Au_{4s7/2}$ line to the $Ag_{3d5/2}$ line (R)

was evaluated. It is reasonable to assume that different R values before and after argon sputtering reflect the difference of composition between the inside and outside of the colloidal particles. From such a viewpoint, the compositions inside and outside the Ag–Au composite colloids from System IV are almost the same, since the R value (0.25) was not changed by sputtering. In the case of the sample taken from System III after 120 min of irradiation, the R value varied from *ca* 1/3 (before sputtering) to 1.0 (after sputtering). Moreover, the difference in binding energies, $I = E_{Ag} - E_{Au}$, of the composite colloids was increased from 284.26 eV† to 284.44 eV by sputtering. On the other hand, the difference in the binding energies of pure colloidal silver and gold was 284.15 eV (before sputtering) and 284.23 eV (after sputtering). I value, that of sample from System IV (284.44 eV), was not changed by sputtering. It is likely that the inside of the composite colloid from System III consists of a Ag–Au composite layer, while the outside is composed of a silver-rich layer. These observations indicate that the detailed structure of the composite colloids can be controlled by changing conditions in our photochemical reaction process.

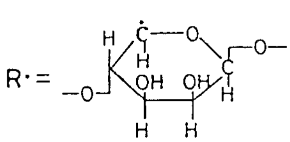
Conditions controlling the formation of composite colloids

A primary photochemical process for photolysis of silver perchlorate ($AgClO_4$) in solutions containing sodium alginate is assumed to be one-electron transfer from the carboxylate ion to the bound Ag^+, giving rise to a silver atom (Ag^0):[5,7,23,24]

$$RCOO^-Ag^+ \xrightarrow{h\nu} Ag^0 + RCOO^{\bullet} \qquad [3]$$

The carboxyl radical ($RCOO^{\bullet}$) could either decompose into secondary radicals ($R^{\bullet}$) and CO_2, or convert to a carboxylic acid (RCOOH) by hydrogen abstraction from the C–H bond of the polymer chain (Eqn [4])

$$\begin{tikzcd} RCOO^{\bullet} \arrow[r] \arrow[dr, "+H^{\bullet}"'] & R^{\bullet} + CO_2 \\ & RCOOH \end{tikzcd} \qquad [4]$$



Subsequent agglomeration processes of Ag^0 produce colloidal silver, $(Ag^0)_n$, and bulk silver, Ag^M:

$$n\,Ag^0 \rightarrow (Ag^0)_n,\ Ag^M \qquad [5]$$

In case of $HAuCl_4$ solutions, photochemical reactions seem to proceed in a manner similar to that proposed by Kurihara *et al.*,[30,31] giving rise to gold atoms (Au^0) irrespective of the presence of sodium alginate:

$$AuCl_4^- \xrightarrow{h\nu} AuCl_3^- + Cl^{\bullet} \qquad [6]$$

$$2AuCl_3^- \rightarrow AuCl_4^- + AuCl_2^- \qquad [7]$$

$$AuCl_2^- \xrightarrow{h\nu} Au^0 + Cl^{\bullet} + Cl^- \qquad [8]$$

Gold atoms accrete or agglomerate to form colloidal gold, $(Au^0)_n$, and bulk gold, Au^M:

$$n\,Au^0 \rightarrow (Au^0)_n, Au^M \qquad [9]$$

The rate of silver reduction in System III was rather small in the early stage. It seems that some of the Ag^0 formed by the photochemical reaction is oxidized by $AuCl_4^-$, giving rise to Au^0. As the concentration of $HAuCl_4$ becomes much smaller than $AgClO_4$ in the final stage, preferential deposition of colloidal silver at the surface of Ag–Au composite colloids might occur. In contrast, nearly equal amounts of reduced silver and gold were present even before irradiation in System IV. Formation of Ag–Au composite colloids with UV irradiation proceeds in a somewhat different manner in this case, resulting in almost the same composition in the interior as at the exterior of the colloids.

The Ag–Au composite colloids in this work can be distinguished from the alloy colloids. The Ag–Au alloys are usually manufactured under severe conditions, e.g. high temperature,[18] vacuum evaporation[19] and electric discharge.[21]

On the other hand, photochemical formation of composite colloids proceeds in solution at room temperature. This seems to be even milder than several chemical reduction methods such as the citrate method which uses a boiling solution and which has been employed to prepare Ag–Au

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† $1\ eV = 96.4853\ kJ\ mol^{-1}$.

alloy colloids by Teo *et al.*[22] It would be reasonable to assume that Ag^0 and Au^0 generated by photolysis at room temperature are not mixed at once just as they are, but aggregate after first forming monometallic clusters and domains under the influence of sodium alginate (SA). Although full understanding of the interaction of SA with metallic ions, atoms, clusters and colloids is needed for elucidation of the details of the protective effects of sodium alginate, these influences require further study. Furthermore, comparison with other protective agents—surfactants like sodium dodecylsulphate (SDS), colloidal silica, as well as high-molecular-weight carboxylic acids like pectic acid and polyacrylic acid—is interesting. Research along this line is now in progress.

CONCLUSION

Irradiation of either $AgClO_4$ or $HAuCl_4$ solution in the presence of sodium alginate with UV ($\lambda = 253.7$ nm) light gave colloidal silver or gold, characterized by a distinct extinction peak originating from surface plasmon resonance. Ag–Au composite colloids were formed by photolysis of a mixed solution of $AgClO_4$ and $HAuCl_4$. Indeed, thin films and small particles made of Ag–Au alloys have been prepared by a number of methods, e.g. flash-evaporation, arc discharge, and the citrate method. The photochemical method proposed in this work has a unique feature in that it preferentially affords Ag–Au composite colloids. We could reproduce two peaks in the extinction spectra of the composite colloids by introducing an effective medium approximation to evaluate the optical constants and combine them with the calculation based on the Mie theory. Alginic acid, a typical high-molecular-weight carboxylic acid in nature, seems to be useful for preparation of metal particles and thin films under mild conditions due to an ability to form metallic salts with various cations and its sensitivity to UV–visible light, as well as the protective action of metal particles.

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