

## 광화학적 방법을 이용한 금속입자의 합성과 광학적 특성 연구

高敏鎭\* · Joel Plawsky†

LG화학기술원 신소재연구소

†RPI 공과대학 화학공학과

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## Surface Plasmon Resonances of Metal Colloidal Particles Synthesized by a Photo-Chemical Process

Min-Jin Ko\* and Joel Plawsky†

LG Chemical Ltd/Research Park, Advanced Materials Research Institute  
Science Town, Taejeon 305-380, Korea

†Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180

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**요약.** 이 논문에서는 광화학적 방법을 이용하여 금속 콜로이드 입자를 반도체 나노입자를 함유한 수용액 내에서 제조하여 그 광학적 특성을 관찰하였다. 형성된 금속입자는 사용된 반도체 입자에 따라 다른 경향을 나타낸다. Au 금속 입자를 CdS 입자를 함유한 수용액에서 제조한 경우 일반적인 금속 입자의 Plasmon Resonance의 특성을 보이는 반면 Ag 금속 입자를 AgBr 입자를 함유한 용액에서 제조한 경우 Red-Shift 현상을 보였고, 그 정도는 UV 조사량에 따라 달라졌다. 이러한 금속 Plasmon Resonance의 Red-Shift 현상을 Effective Medium 이론을 이용하여 이론적으로 설명하였다.

**ABSTRACT.** Metal colloidal particles have been prepared by a photo-chemical process in an aqueous solution containing semiconductor nanocrystallites. Metal colloidal particles produced in CdS and AgBr exhibit different absorption spectra. Au particles produced in solution with CdS show typical Au plasmon resonance absorption spectra. On the other hand Ag particles in solution with AgBr shows surface plasmon resonance absorption spectra which are red-shifted, as compared to that of a dispersion of homogeneous Ag colloidal particles in the same host. The extent of red-shift depends on the UV illumination time. This phenomenon is interpreted within the context of effective medium theory for small volume fractions. From the theory, a metal coated particle predicts Ag plasmon resonance, red shifted with respect to 400 nm that would be associated with a silver particle in solution. The absorption peak position is very sensitive to the coating thickness.

## INTRODUCTION

Nanometer-sized particles of metals and semiconductors have been intensively investigated in recent years because of their novel electrical, optical, magnetic, and chemical properties.<sup>1</sup> For semiconductor particles with a diameter less than a critical size (the *deBroglie* wavelength of the carriers), photoexcited carriers can be three-dimensionally confined, and the electronic state and

optical behavior are expected to show zero-dimensional features. This effect causes a quantization of their energy levels, leading a shift in the position of the optical absorption edge, thus allowing wavelength tunability. It is also known that the enhancements in nonlinear optics and photoluminescences result from such quantizations. The optical and electronic properties of semiconductor nanocrystallites, as a function of size, have been

studied by several researchers.<sup>2</sup>

On the other hand ultrafine metal particles have several interesting properties compared with bulk materials. It is known that the intensity of Raman scattering of organic molecules adsorbed on a metal surface increases up to  $10^5$ - $10^6$  times more than that in the solution. This phenomenon is known as surface-enhanced Raman scattering (SERS). Silver and gold are particularly interesting metals to study because its dielectric properties are such that they show large plasmon resonances in small particle form. The strong surface mediated plasmon resonance in the metals is also utilized for increasing the nonlinear optical properties in metal-semiconductor hybrid particle form.<sup>3</sup> Other intriguing perspectives for the development of novel electronic devices,<sup>4</sup> electro-optical applications<sup>5</sup> and also catalysis<sup>6</sup> have been established.

Some of the techniques used for the formation of ultra-small crystallites are molecular beam epitaxy, chemical vapor deposition, and melting and recrystallization in glasses. However these methods are time consuming, costly, and not really applicable to large scale production. Various alternative approaches to prepare nanometer-size have been developed through colloidal chemistry.<sup>7</sup> These include colloidal precipitation from aqueous solution in micelles, vesicles, bilayer lipid membranes, Langmuir-Blodgett films, the channels of zeolites, and even in biological cells. In this article, we try to produce metal colloidal particle using a photochemical process through semiconductor nanocrystallites, where two kinds of particles could be hybridized in a nanoscopic scale, and see their optical behavior of the resulting colloidal particles.

## EXPERIMENTAL

Plausible mechanism for the photochemical reduction process of a metal on a semiconductor is schematically illustrated Fig. 1. Bandgap excitation produces electrons in the conduction band and holes in the valence band of the semiconductor particles. The excited electron is then transferred to a metal cation adsorbed near the semiconductor

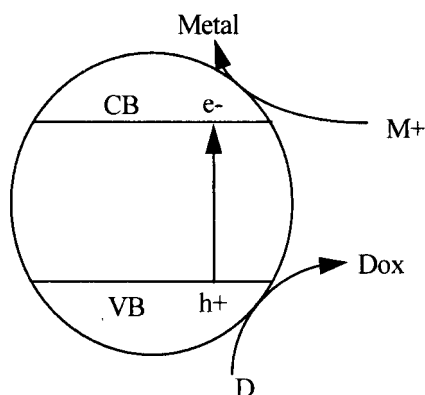


Fig. 1. Schematic of a photochemical reduction mechanism.

where the reduction occurs. The metal ions need to be at the surface during the exposure to light since the recombination of the electron and hole is very fast. In fact, it is known from aqueous colloidal experiments that inorganic and metal ions can chemisorb on semiconductor nanocrystallites and can have marked effects on luminescence.<sup>8</sup> The photo-reduction of the metal cation must also be accompanied by a corresponding oxidation. Generally, oxidizable additives (electron donors) are added to scavenge the holes in the semiconductor and thus to avoid the dissociation of the semiconductor.

**Materials.** All materials were used without further purification. Sodium sulfide( $\text{Na}_2\text{S}$ ), cadmium nitrate( $\text{Cd}(\text{NO}_3)_2$ ), sodium bromide( $\text{NaBr}$ ), ethylene diamine tetra acetic acid(EDTA), silver nitrate( $\text{AgNO}_3$ ), and potassium dicyanoaurate( $\text{KAu}(\text{CN})_2$ ) were provided by Aldrich. Dodecyl sodium sulfate (SDS) was from Matheson.

## Preparation

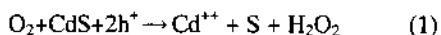
**Case I. Ag-CdS or Au-CdS system.** CdS semiconductor nanocrystallites are prepared by precipitation from an aqueous surfactant solution. This method, which is a slight variation of the method developed by R. Rossetti *et al.*,<sup>7</sup> incorporates the drop by drop addition of  $1.0 \times 10^{-2}$  M  $\text{Na}_2\text{S}$  solution to 50 ml of  $1.5 \times 10^{-3}$  M  $\text{Cd}(\text{NO}_3)_2$  solution containing  $1.5 \times 10^{-3}$  M SDS or polyphosphate as a stabilizing agent while constantly

stirring. The concentration of CdS nanocrystallites is varied by changing the total volume of the  $\text{Na}_2\text{S}$  solution added into the  $\text{Cd}(\text{NO}_3)_2$  solution. A faint yellow appearance begins to form upon the addition of the first several drops of  $\text{Na}_2\text{S}$  solution due to the formation of CdS crystallites, and this color becomes more intense as additional sulfur ions are added. For metal reduction on the CdS nanocrystallites, an electron donor(EDTA) and metal salts( $\text{AgNO}_3$ ), or  $\text{KAu}(\text{CN})_2$ , are added into the CdS solution. Typically the final concentration of metal salt and the electron donor are  $1.0 \times 10^{-3}$  M and  $1.5 \times 10^{-3}$  M, respectively. After 5 min. of ultrasonic stirring, the obtained solution is exposed to light from a 100 watt Hg lamp for periods from a few minutes to two hours. The reduction of metal ions is monitored by an absorption spectrophotometer (Cary05 dual-beam spectrophotometer).

**Case II. Ag-AgBr system.** This procedure is similar to that used in Ag-CdS or Au-CdS system. AgBr nanocrystallites are again made by injecting and stirring a bromide ion( $\text{Br}^-$ ) aqueous solution into a  $\text{Ag}^+$  ion aqueous solution containing SDS as a stabilizer. The  $\text{Br}^-$  ion aqueous solution is prepared by dissolving sodium bromide into deionized water. The solution is then irradiated with 100 watt Hg lamp after the injection of the electron donor, EDTA.

## RESULTS AND DISCUSSION

An attempt was made to produce Ag colloidal particles on the surface of CdS nanocrystallites in aqueous solution through a photochemical reduction mechanism. However, a serious problem associated with the use of CdS as a photosensitizer for the metal reduction is its inherent chemical instability under illumination. The CdS nanocrystallites would be photo-dissolved in the presence of oxygen; Holes produced in the valence band by UV light migrate to the surface of the particles where rapid oxidation of sulfide ions to sulfur occurs. The main photochemical reaction is known as follows



In our experiments, we observed that the color of CdS solution changed from yellow to bright-yellow or greenish-yellow after UV illumination and the intensity of absorption also decreased with a little blue shift of the absorption onset, indicating that the colloidal CdS particles became smaller during their photo-dissolution. Such a photo-dissolution process can be blocked either by deoxygenating the solution or by trapping the holes,  $h^+$ , formed during the irradiation of the particles. Here we used EDTA serving as sacrificial electron donors to scavenge the hole produced in the valence band under the illumination. There was no significant change of absorption after the UV exposure for an hour.

The absorption spectra of the CdS solution containing an excess of  $\text{Cd}^{2+}$  ions before and after the addition of  $\text{Ag}^+$  ions are shown in Fig. 2. It can be seen that the introduction of small concentration of silver ions into the CdS solution obviously increases the absorption in the visible range of the spectrum, and the absorption onset shifts toward longer wavelengths. The color of the solution changed immediately from yellow to brown after the injection of the  $\text{Ag}^+$  ions into the CdS colloidal solution. We can understand this results as being due to a solvation effect. As  $\text{Ag}_2\text{S}$  ( $6.69 \times 10^{-50}$ ) has a lower solubility product than CdS( $1.40 \times 10^{-29}$ ), Ag ions might etch Cd ions in

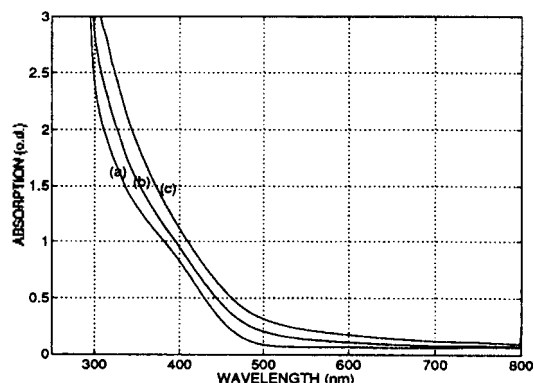


Fig. 2. Absorption spectra of CdS solution (a) before addition of  $\text{AgNO}_3$  and (b), (c) after addition of  $\text{AgNO}_3$ .  $[\text{CdS}] = 6.0 \times 10^{-4}$  M, and  $[\text{AgNO}_3] = 1.0 \times 10^{-4}$  M (b) or  $[\text{AgNO}_3] = 2.0 \times 10^{-4}$  M (c), respectively.

solution. It should be stressed that because of the absence of excess  $S^{2-}$  ions in the solution, the separated  $Ag_2S$  single nanocrystallites would not be formed directly. At first,  $Ag^+$  ions are adsorbed to the surface of CdS particles, and then the  $Ag^+$  ions displace Cd in the Cd-S bond to form a Ag-S bond on the surface of CdS particles, resulting in the formation of  $Ag_2S$  particles. Thus, metallic silver particles could not be formed in aqueous solution.

The absorption spectrum of the CdS solution containing Au ions is shown in Fig. 3(a). It can be seen that unlike a Ag ions case, the introduction of Au ions into the CdS solution does not change the absorption spectrum, indicating that the Au ions do not etch the Cd ions to form  $Au_2S$ . After illumination of the solution, the color changes from yellow to red, and the absorption peak appears at approximately 535 nm, as shown in Fig. 3(b) and (c). This peak is a characteristic of reduced Au atoms. No Au plasmon peak is observed without CdS nanocrystallites. Thus, indeed, the electrons produced by the bandgap excitation are responsible for the reduction of Au ions adsorbed on the surface of CdS nanocrystallites. It is important, however, to note that increasing the illumination time does not significantly alter the absorption spectrum, but only increases the intensity of the Au plasmon absorption. If Au metal particles are layered on the

surface of CdS nanocrystallites, the position of Au plasmon peak is expected to be changed. This result implies that the excited electrons are captured by the Au cations adsorbed on the surface of CdS, but reduced metallic Au atoms are not laden on the semiconductor nanocrystallites. Separate nucleation and growth can be explained the following way. Bulk CdS semiconductor has a zinc-blende structure with a lattice constant 5.46 Å, while bulk Au metal has a cubic lattice constant of 4.0786 Å. This difference in lattice constants implies that the solid state Cd-S bond length for zinc-blende structure is 25% longer than the Au-Au bond length. Thus, Au layer on CdS nanocrystallites would be expected to be strained as in a heterostructured epitaxial growth system.

The absorption spectra of AgBr colloidal solution containing excess  $Ag^+$  ions before and after UV illumination are shown in Fig. 4. It can be seen that the spectrum is almost flat at the region of visible wavelengths due to the high bandgap of AgBr colloidal particles. After the illumination of the solution, the color changed from colorless to blue, then dark yellow. Fig. 4 shows that a considerably broad absorption band ranging from 400 nm to 700 nm appeared shortly after UV exposure and the broad peak gradually shifted to a shorter wavelength as the illumination time increased. The red shift phenomena after UV illumination indicate that the Ag particles are

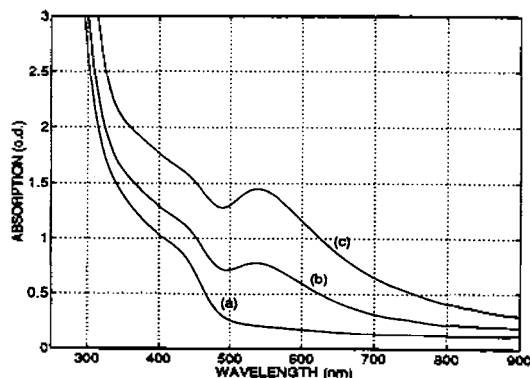


Fig. 3. Absorption spectra of CdS solution (a) before UV illumination and (b), (c) after UV illumination.  $[CdS]=7.5 \times 10^{-4}$  M,  $[KAu(CN)_2]=1.5 \times 10^{-3}$  M.

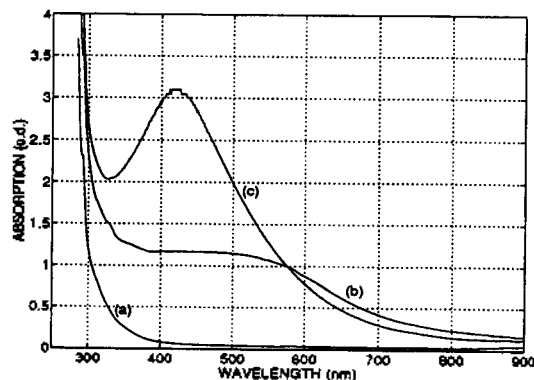


Fig. 4. Absorption spectra of AgBr solution (a) before UV illumination and (b), (c) after UV illumination.  $[AgBr]=0.5 \times 10^{-4}$  M,  $[AgNO_3]=2.0 \times 10^{-3}$ .

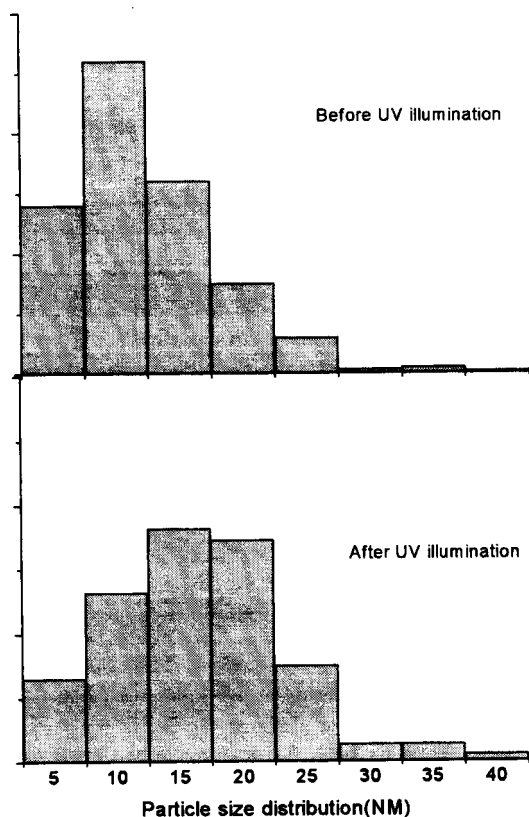


Fig. 5. Particle size distribution of colloidal particles before and after UV illumination in Fig. 4(c).

modified by the higher refractive index environment compared to aqueous solution, in this case, AgBr. The particle size distribution before and after UV exposure measured using the quasi-elastic light scattering technique(QELS) is shown in Fig. 5. It is seen that average particle size increases after UV illumination with broad distribution.

In order to describe the unique optical phenomena in Fig. 4, the optical absorption of Ag-AgBr hybrid system has been calculated. The scattering and absorption from layered spherical particles have been treated by several research.<sup>3,9</sup> In this case we assume that the particle consists of a core(region I) of radius  $r_1$  with a uniform spherical shell(region II), giving a total particle radius  $r_2$ , and is surrounded by a dielectric medium (region III). The dielectric constitutive

equation for the inhomogeneous composite of core, shell and host medium can be represented as an equivalent homogeneous medium of dielectric permittivity,  $\tilde{\epsilon}$ . Since, in our case, the volume fraction of the particles is very small, interparticle effects can be neglected. This leads to an expression of the Maxwell-Garnett form, which to the first order in particle volume fraction  $\rho$ , is

$$\tilde{\epsilon} = \epsilon_3 + 3\rho\epsilon_3 \frac{\epsilon_2\epsilon_a - \epsilon_3\epsilon_b}{\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b} \quad (2)$$

where  $\epsilon_a = \epsilon_1[3-2P] + 2\epsilon_2P$ ,  $\epsilon_b = \epsilon_1P + \epsilon_2[3-P]$ ,  $P = 1 - (r_1/r_2)^3$ .  $\epsilon_1$  is the dielectric constant of core material,  $\epsilon_2$ , the dielectric constant of shell material,  $\epsilon_3$ , the dielectric constant of the glass host, and  $P$  the ratio of shell volume to total particle volume. Total extinction of the composite will have a loss contribution from intrinsic molecular absorption and a loss contribution from particle scattering. Optical absorption characteristics of this model were calculated in the Rayleigh approximation since the dimensions of the particles of our samples are much smaller than the wavelengths of the visible light, and, thus, scattering loss is negligible. The extinction coefficient,  $\alpha$ , is given by

$$\alpha = (2\pi/\lambda_0 \tilde{n}) \tilde{\epsilon}''/\epsilon_0, \quad (3)$$

where  $\lambda_0$  is the vacuo wavelength,  $\tilde{n}$  is effective refractive index at the vacuo wavelength and is  $(\epsilon_3/\epsilon_0)^{1/2}$ , and  $\tilde{\epsilon}''$  is the imaginary part of the effective dielectric constant and is obtained from equation (2). At the plasmon resonance absorption coefficient becomes

$$\begin{aligned} \alpha &= (6\pi\tilde{n}/\lambda_0)\rho \frac{\text{Re}[\epsilon_2\epsilon_a - \epsilon_3\epsilon_b]}{\text{Im}[\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b]} \\ &= (6\pi\tilde{n}/\lambda_0)\rho \\ &\quad \frac{(\epsilon_1' - \epsilon_2' - \epsilon_1'' - \epsilon_2'')(3-2P) + 2(\epsilon_2' - \epsilon_2'')^2P - \epsilon_3[\epsilon_1'P + \epsilon_2'(3-P)]}{\epsilon_1''[\epsilon_2'(3-2P) + 2\epsilon_3P] + \epsilon_2''[\epsilon_1'(3-2P) + 4\epsilon_2'P + 2\epsilon_3(3-P)]} \end{aligned} \quad (4)$$

Absorption spectra calculated using this colloidal model are shown in Fig. 6 for Ag layered AgBr particles at various  $P$  (volume ratio of shell) values. The dielectric constants of AgBr and Ag were obtained from the experimental data<sup>10</sup> and a cubic spline routine was used for interpolation. The

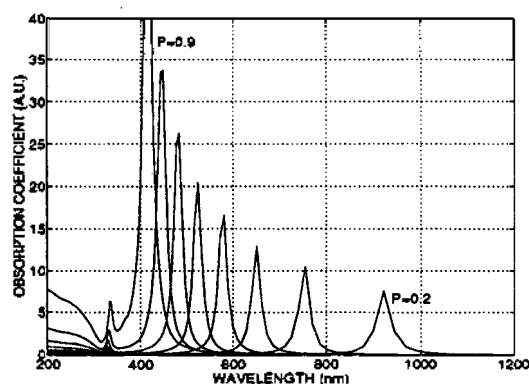


Fig. 6. Calculated absorption spectra of Ag laden AgBr particles with various  $P$  values.  $P$  is a volume ratio of metallic shell.

calculations at variable  $P$  show that as the metallic shell radius decrease, the red shift becomes progressively larger. At  $P=1$  corresponding to infinite shell thickness, the maximum absorption shift to around 400 nm is reached, which is the plasmon resonance of a dispersion of homogeneous Ag colloidal particles in the same host. Our experimental results in Fig. 4 are consistent with this theory in that the layered thickness of the metallic Ag increases with UV illumination time. The broadening of the absorption peak in the measured spectrum of Fig. 4(b) would result from a distribution of layered thickness.

## CONCLUSIONS

We have shown in this study that metal colloidal particles can be produced by a photochemical process in aqueous solution containing semiconductor nanocrystallites. Semiconductor particles here acts as a photosensitizer. On preparing Ag metal colloidal particles in aqueous solution containing CdS nanocrystallites, it was found that the silver ions dissociate CdS to form  $\text{Ag}_2\text{S}$  due to the solvation effect. On the other hand Au and Ag metal colloidal particles are successful produced in solution containing CdS and AgBr, respectively. In particular Ag colloidal particles formed in AgBr solution are interesting in that its plasmon resonances show the shifts to

longer wavelengths, depending on the UV illumination time. These plasmon shifts were described using the effective medium theory for small volume fractions. The calculated absorption spectra of Ag-AgBr hybrid structured particles found to be in good agreement with the experimental results. Further studies are targeted toward understanding the effect of semiconductor structure on the formation of hybrid particles, and improve the size and layered thickness of the particles. A novel optical response of metal-semiconductor hybrid aggregates would attract much interest in a fundamental physical point of view and applications. Hybridized properties open a wide interest of material design and their studies are underway.

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