

The Effect of Applied Potential on Plasmon Resonance Bands of Nanoscopic Silver Particles Adsorbed on Transparent Electrodes

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Abstract

The plasmon resonance spectra of nanoscopic silver particles adsorbed on transparent semiconductor electrodes in contact with eight aqueous electrolytes (KCl, KBr, KI, NaCl, NaBr, NaI, NaClO₄, and KPF₆) have been examined. In all electrolytes, the plasmon resonance bands are red-shifted and decreased in intensity as the applied potential is made more positive. The degree of the potential-induced spectral changes depends on the electrolyte type and concentration. The change in plasmon absorption band is largest for the higher concentration. At constant concentration, the potential-induced spectral changes are largest in the presence of I⁻, Cl⁻ and Br⁻ anions and smallest in the presence of PF₆⁻ and ClO₄⁻ anions. The largest effects for particles in contact with I⁻, Cl⁻ and Br⁻ anions may arise from more severe reduction in electron mean free lifetime and/or the formation of a metal-adsorbate complex which is highly absorbing in the spectral region of the plasmon resonance band.

Keywords: Surface plasmon spectroscopy; Nanoscopic silver particles; Semiconductor electrodes.

Introduction

Previous studies of nanoscopic metal particles in bulk solution have demonstrated that surface chemistry can induce changes in the optical properties of the particles most notably in the region of the plasmon resonance band.^[1-4] This band can be red- or blue-shifted depending on whether the adsorbing species are electron donating or withdrawing, or if their presence changes the refractive index of the layer immediately adjacent to the metal surface.^[5-8]

In the experiments of Henglein, et al.,^[9,10] the intensity, wavelength and bandwidth of the plasmon band were observed to change with density of free electrons in the metal particles. They found that when electrons are extracted from colloidal silver in aqueous solution by OH radicals the band is red-shifted, its intensity decreases and its bandwidth increases. Opposite effects were observed when electrons were added to the colloid by the reducing radicals. In addition to, the shape and position of the plasmon absorption band changes with absorption of nucleophiles. These changes were explained qualitatively by Henglein, et al. via a Mie scattering

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equation for the absorption coefficient of a collection of uniform spheres very small compared to the wavelength of light. According to their study, the spectral changes can be attributed mainly to changes in electron density in the surface of the colloid as a result of adsorption. Whereas, for the anion to bind to the surface lattice, it pushes the electrons of the surface atoms to the interior of the metal and causes a red-shift as a result of depletion of the electron density in the surface, or by creating a surface dipole structure that decreases the mean free path of the electron. However, recently Mulvaney^[1] suggested that the chemisorption spectral effects are mainly due to the “demetalization” of the surface atoms accompanied by oxidation of the adsorbed anion (with proton or oxygen production).

Underwood and Mulvaney^[7] have shown that the plasmon band is red-shifted, broadened and increased in intensity as the refractive index at the optical frequency of the surrounding medium increases. They found that optical changes associated with the transfer of colloidal gold particles into organic solvents with different refractive indices were in good quantitative agreement with the prediction of Mie theory.

In a similar experiment, Henglein and coworkers^[11] found that the addition of I⁻ up to 20 times more than needed for one monolayer coverage on colloidal silver films causes a decrease in intensity and broadening of the plasmon band without a change in position of the peak. The damping of the peak was attributed to changes in resonance boundary conditions at the surface as a consequence of electron donation within a thin surface layer as well as adsorption. Moreover, Cotton and coworkers^[12,13] reported the reduction of cytochrom by bromide and iodide modified laser-ablated silver colloid, the reaction was monitored by surface-enhanced resonance Raman scattering and absorption spectroscopies.

In most previous studies, redox- or anion adsorption-induced spectral changes of nanoscopic metal particles have been considered for particles in bulk solution. In bulk solution, altering the potential of the metal phase, which in turn leads to some spectral effect, requires addition of chemical reagents to the solution,^[11,14] or generating reducing radicals *in-situ* by means of γ -irradiation.^[5] Using an optically transparent thin layer electrode, Mulvaney and coworkers have shown that the optical properties of silver particles in bulk solution can also be altered electrochemically.^[4] Their spectroelectrochemical approach is most significant because it offers a means for determining the number of electrons transferred to the particles, and the particle diffusion coefficient.

One problem with aqueous metal colloids is that they are sensitive to the ionic strength of the solution. It is well known that increasing the ionic strength induces colloidal aggregation, which in turn results in a red-shift and decreased intensity of the plasmon absorption band. In the work of Henglein and Mulvaney,^[14] the ionic strength was limited to 50 μM to avoid aggregation. For electrochemical studies, Mulvaney et al. show that it was required to employ surfactants to prevent particle aggregation at the

higher ionic strengths.^[4] Cotton and coworkers,^[12] have recently demonstrated that the plasmon resonance band of surface-bound silver colloids (ca. 10 nm radius) is only slightly affected by iodide additives, thus suggesting that the large spectral shifts seen in bulk solution arise primarily from particle aggregation.

In this study, we describe a simple set of experiments, *similar to that used by Foss et al.*^[15] in which colloidal silver particles are adsorbed on optically transparent antimony-doped tin oxide electrodes. In these experiments, it is possible to examine the optical properties of nanoscopic metal particles using a simple spectroelectrochemical cell in an optical transmittance configuration.^[15] The metal phase electron density and extent of anion adsorption can thus be altered in a straightforward manner via the applied potential, and the resulting changes in optical properties can be monitored *in-situ*. Furthermore, since the particles are immobilized on the SnO₂ electrodes, they are not subject to the salting-out effects associated with bulk colloids. Thus, one can examine electrochemically-induced spectral effects at higher ionic strengths without the need for surfactant species which can complicate the interpretation of the spectra.^[15]

Experimental

Materials

Sodium perchlorate NaClO₄ (Fluka), potassium iodide KI (JANSSEN CHIMICA), potassium chloride KCl (BDH), potassium hexafluorophosphate KPF₆ (UORSICH, MERCH), sodium chloride NaCl (BDH), sodium iodide NaI (GCC), potassium bromide KBr (MERCH), sodium bromide NaBr (MERCH) were doubly recrystallized from triply distilled water. Sodium citrate and silver nitrate (Fisher) were used as received.

All glassware were thoroughly cleaned in aqua-regia and rinsed copiously with triply distilled water. All solutions of the salts were prepared in triply distilled water.

Silver Colloid Preparation

Colloidal silver solutions were prepared according to Graber, et al^[16] with some modification in the quantity of sodium citrate and silver nitrate. Approximately 90 mg of AgNO₃ was dissolved in 500 mg of triply distilled water and brought to boiling while being vigorously stirred. Reduction of the silver salt was accomplished by adding in a single step a 10 mL of 1% (w/v) sodium citrate. The solution was kept on boiling for about one hour, after the end of reaction, the color of the colloid was greenish-yellow. The UV/Visible spectra of the bulk silver colloids collected with a Unicam Helios- α spectrometer revealed extinction maxima of 426 nm (Figure 1), based on Henglein's study^[17] the expected radius of the silver particles is ca. 10 \pm 2 nm.

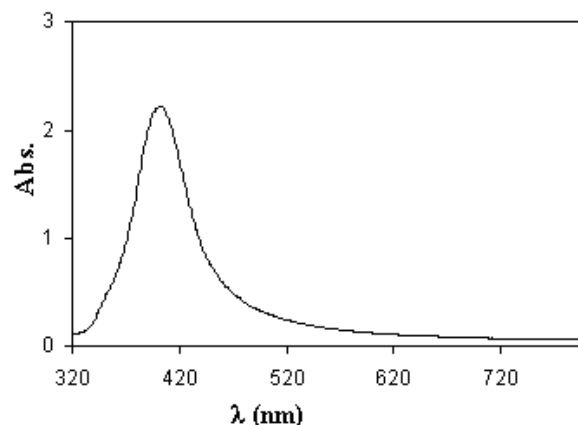


Figure 1. Absorption spectra of silver colloids in bulk solution.

Spectroelectrochemical Setup

The spectroelectrochemical set-up is shown in Figure 2. All glass components (including the windows) are Pyrex.^[15] The reference electrode in all studies was a silver chloride coated silver wire immersed in 4 M KCl (this configuration henceforth referred to as SSCE). The counter electrode in all cases was a strip of Pt foil. To avoid problems associated with reduction of the SnO₂ electrode and silver oxide formation, the applied potential during spectroelectrochemical investigations was limited to the range 0.05-0.65 V vs SSCE.^[15] Potentials were controlled with Princeton Applied Research Co. (PARC) model 264A potentiation/galvanostat. All spectra were obtained using Unicam Heλios-α UV/ visible spectrophotometer.

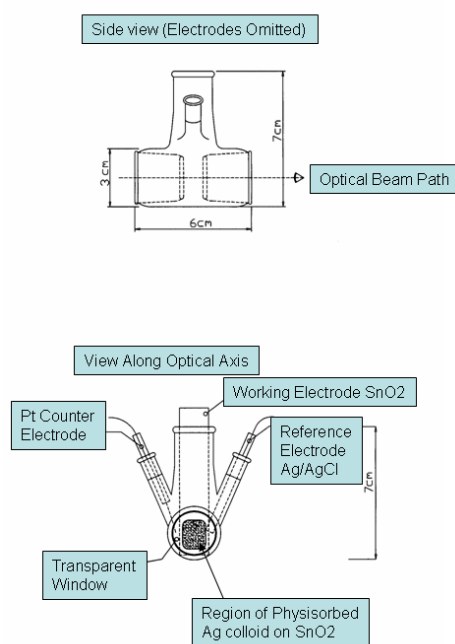


Figure 2. Spectroelectrochemical cell: side-view and view along light path, (adapted from ref. 15).

The working electrode was a 20x75x3 mm transparent glass slide coated with antimony doped tin oxide (Delta Technologies, Limited). Silver colloid solution was evaporated on the working electrode at room temperature for few hours and the dried physisorbed colloid was rinsed with triply distilled water. Then, the working electrode was kept in contact with triply distilled water for 5-15 minutes before being introduced into the electrochemical cell. Once the deposited Ag layer was rinsed with triply distilled water, it was not allowed to dry prior to the experiment.

In a typical experiment, the first spectrum was collected at an applied potential of 0.05 V vs SSCE. The applied potential was then changed to the most positive value (0.65 V) and another spectrum was recorded. To check for reproducibility, the applied potential was then returned to 0.05 V for a second spectral collection at that potential. Spectra were then collected at intermediate potentials 0.55 V vs SSCE. In all cases, the cell potential was applied for two minutes before the spectral scan was initiated.

Results and discussion

Figure 3 shows spectra of silver particles adsorbed on SnO₂ electrode in contact with 0.075 M KI. Curve 1 (*solid line*) is the plasmon resonance band when the applied potential is +0.05 V vs Ag/AgCl. Curve 2 (*dot line*) is the plasmon resonance band when the applied potential is +0.65 V vs Ag/AgCl. The application of a more positive potential causes a red-shift and a damping in absorbance intensity. The potential-induced red-shift and damping are more pronounced in the presence of NaX and KX (where, X= I⁻, Cl⁻, Br⁻), while in the presence of NaClO₄ and KPF₆ the red-shift and damping are smallest. Figure 4 shows the plasmon resonance bands at applied potentials of 0.05, 0.45, 0.55 and 0.65 V in contact with 0.075 M KCl. For these spectra, the broadening of the plasmon resonance band as the applied potential is made more positive is quite evident. The subtle changes in λ_{max} were determined by fitting the spectra in the peak regions to a polynomial function.

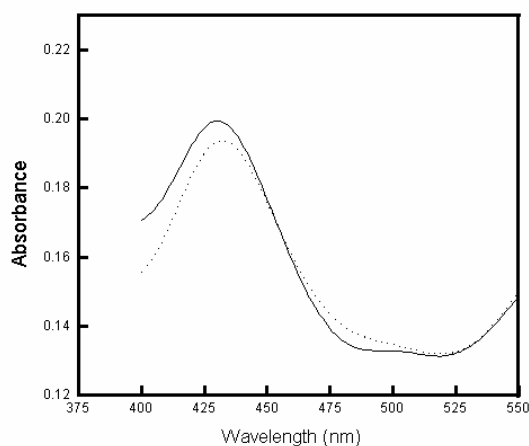


Figure 3. Absorption spectra of colloidal silver particles on SnO₂ electrode in contact with 0.075 M KI solution. (—) spectrum at +0.05 V vs SSCE. (----): spectrum at +0.65 V vs SSCE.

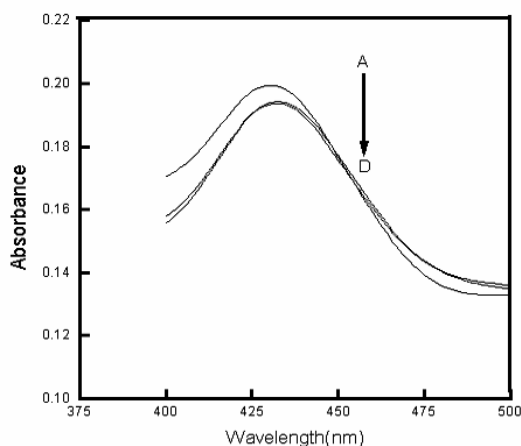


Figure 4. Absorption spectra of colloidal silver particles on SnO₂ electrode in contact with 0.075 M KCl solution. (A) spectrum at +0.05 V vs SSCE. (B): spectrum at +0.45 V vs SSCE. (C): spectrum at +0.55 V vs SSCE. (D): spectrum at +0.65 V vs SSCE.

To compare extinction damping as a function of applied potential, we chose the quantity $A_{\max}(E)/A_{\max}(0.05)$, which is the measured maximum extinction at a given potential normalized to the maximum extinction at the lowest applied potential (0.05 V vs SSCE). Figures 5 and 6 show plots of $A_{\max}(E)/A_{\max}(0.05)$ versus the applied potential for the eight electrolytes examined in this study. In all cases, the spectral damping is more evident in the presence of NaX and KX (where, X = I⁻, Cl⁻, Br⁻) than in the presence of NaClO₄ and KPF₆ electrolytes.

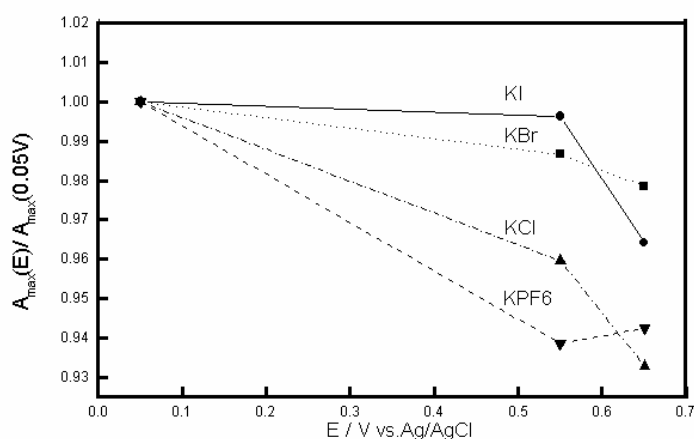


Figure 5. Changes in silver particle plasmon resonance band relative intensity as a function of applied potential for KX electrolytes (X= I⁻, Cl⁻, Br⁻, and PF₆⁻).

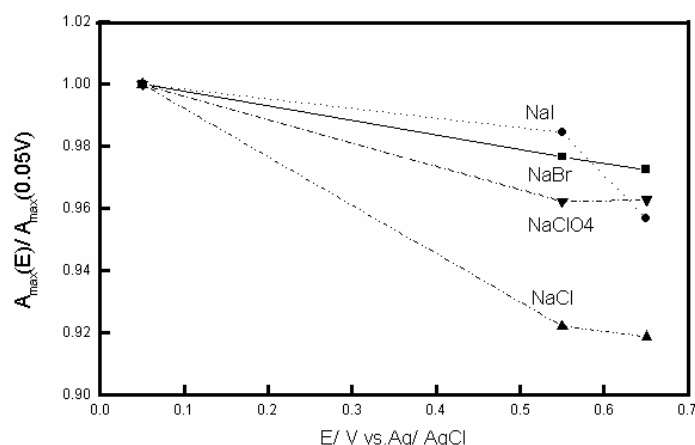


Figure 6. Changes in silver particle plasmon resonance band relative intensity as a function of applied potential for NaX electrolytes (X= I⁻, Cl⁻, Br⁻, and ClO₄⁻).

The most obvious results concern the electrolyte identity. Potential-induced red-shifts and damping are most pronounced for NaBr, NaI, NaCl, KCl, KBr, KI, whereas spectral changes are weaker in the cases of NaClO₄ and KPF₆ solutions. These differences in electro-optical effects are not unexpected, given that ClO₄⁻ and PF₆⁻ are considered to be weakly- or non-specifically adsorbed at the Ag surface.^[18] The anions I⁻, Cl⁻ and Br⁻, on the other hand, are known to be specifically adsorbed on Ag (that is, to form chemical bonds with Ag).^[19] However, the exact relationships between nanoscopic metal particle optical spectra and either electrostatic or specific adsorption are not well known.

The adsorption of anions such as I⁻, Cl⁻ and Br⁻ is envisioned to have two effects. First, because these halides are large and polarizable, their concentration at the particle surface increases the local refractive index, thus redefining the plasmon resonance condition. Secondly, the adsorption of anions can be expected to alter the surface lattice structure of the metal, and therefore the effective free electron relaxation time τ_{eff} . In order to consider the combined effects of boundary refractive index and free electron relaxation time changes, it is necessary to employ the multiple shell model of particle polarizability.

The multiple shell model of particle polarizability assumes a spherical core structure with radius a_1 , and dielectric constant ϵ_1 coated with a shell layer of dielectric constant ϵ_2 . Thus, the polarizability (α) of this layered coated sphere structure that embedded in a host medium with dielectric constant (ϵ_h) can be calculated using Eq. 1.^[20,21]

$$\alpha = 4\pi a_2^3 \left[\frac{[(\varepsilon_2 - \varepsilon_h)(\varepsilon_1 + 2\varepsilon_2) + f^3(\varepsilon_1 - \varepsilon_2)(\varepsilon_h + 2\varepsilon_2)]}{[(\varepsilon_2 + 2\varepsilon_h)(\varepsilon_1 + 2\varepsilon_2) + f^3(\varepsilon_1 - \varepsilon_2)(2\varepsilon_2 + 2\varepsilon_h)]} \right] \quad (1)$$

Where, f is the fraction of the total particle volume occupied by inner sphere ($f = a_1/a_2$, a_2 = radius of a shell layer).

The contribution of the polarizability from equation 1 to the calculated spectrum can be obtained by considering the scattered theory expression for the transmittance through a medium containing spherical particles, Eq. 2. ^[22]

$$T = \exp(-N\pi a_1^2 Q_{ext} d) \quad (2)$$

Where N is the number of spheres per unit volume, a_1 is the sphere radius and d is the path length. The extinction coefficient Q_{ext} represents the sum of radiation removed from the incident light beam by scattering and absorption for spherical particle of radius embedded in a medium of refractive index n_o . The cross extinction coefficient is given by ^[20,22,23]

$$Q_{ext} = (2/X^2) \sum_1^{\infty} (2n+1) \text{Re}(a_n + b_n) \quad (3)$$

where the summation is from $n=1$ to $n=\infty$, $X = 2\pi n_o a_1 / \lambda$ (λ is the wavelength of the incident light) and b_n and a_n are the Mie scattering coefficients which are functions of a and λ in terms of Bessel functions, ^[20] Q_{ext} is (usually) normalized to the cross-sectional area of the sphere (πa^2) to obtain a normalized extinction cross section:

$$C_{ext} = \pi a^2 Q_{ext} = C_{sca} + C_{abs} \quad (4)$$

where C_{sca} and C_{abs} are the scattering and absorption cross section, respectively.

The radiation scattered (of the particle) originates from oscillating electric and magnetic dipoles and higher-order multi poles. In the Rayleigh limit ($a \ll \lambda$), the scattering and absorption cross sections are related to the particle polarizability via Eq. 5. ^[22]

$$C_{sca} = \left(\frac{8}{3}\right) \pi K^4 |\alpha|^2 \quad (5a)$$

$$C_{abs} = 4\pi K \text{Im}(\alpha) \quad (5b)$$

Where $K=2\pi n_o/\lambda$, the vertical lines “|” in equation (5a) denote the square modules of the complex function (α). The operator “ Im ” in equation (5b) signifies that only the imaginary component of α should be considered.

Equations 2, 4 and 5 allow the calculation of the spectra of small particle system. Whereas considering only the real part of ε_f and ε_h allows semi-quantitative production about shifts in λ_{max} . Real and imaginary components of ε_f , ε_h and α are needed in order to calculate full spectra, and observe changes in intensity and bandwidths.

For a virtually infinite medium, the relaxation time τ_b , is the period in which the electron is effectively 'free'. τ_b decreases as the frequency of collisions between the

electrons and the lattice atoms increases.^[24] If a metal particle is very small, then mean free electrons also scatter off the wall of the particle; this reduces their mean free lifetime. The particle size-corrected mean effective lifetime (τ_{eff}) is determined from via Eq. 6: ^[24c-e]

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{v_f}{a} \quad (6)$$

Where, v_f the Fermi velocity of the metal and a is the metal particle radius.

To "correct" experimental ϵ_1 for particle size effects, the following procedure is employed:

- 1) The real metal is assumed to have Drude-type free electrons properties as well as quantum mechanical properties of the core electrons. Furthermore, these two types of properties are assumed to be additive, via Eq. 7: ^[25,26]

$$\epsilon_{1,exp} = \epsilon_{core} + \epsilon_{free} \quad (7)$$

- 2) The small particle size effect on the free electron relaxation time is assumed to affect only the second term in Eq. 7.
- 3) The size-adjusted experimental dielectric ϵ_2 calculated by subtracting the bulk free electron term ϵ_{free} from $\epsilon_{m,exp}$, and replacing it with a size-adjusted term, according to

$$\epsilon_2 = \epsilon_{1,exp} - \epsilon_{free} + \epsilon_{free,adj} \quad (8a)$$

Or, more explicitly

$$\epsilon_2 = \epsilon_{1,exp} + \frac{\omega_{p,b}^2}{\omega(\omega + i/\tau_b)} - \frac{\omega_{adj}^2}{\omega(\omega + i/\tau_{eff})} \quad (8b)$$

Where $\omega_{p,b}$ and τ_b are taken from experiment for the bulk silver frequency and electron mean free lifetime, ^[7,25a,26,27] and τ_{eff} is the adjusted or effective lifetime that calculated from equation (6). The plasma frequency (ω_{adj}) is adjusted according to the relation: ^[20]

$$\omega_{adj}^2 = \frac{N_{e,adj} e^2}{\epsilon^o m_e} \quad (9)$$

Where $N_{e,adj}$ is the adjusted concentration of free electrons, ϵ^o is the permittivity of vacuum, and e and m_e are the charge and the rest mass of an electron, respectively.

According to Foss's study^[15] on gold particles, they found that the larger the refractive index of the adsorbed layer, the greater the red-shift and intensity increase. It is apparent then, that the increase in the adsorbed layer refractive index overwhelms the tendency of the electron depletion to decrease the extinction intensity. Clearly, the combined effects of an increase in the boundary refractive index and a decrease in electron concentration do not explain these results which have been seen in the KC1 and KBr electrolytes studies. In their study they assumed that the only effect associated with anion adsorption was an increase in the refractive index of the layer immediately outside the metal particle.^[15] However, if the chemical interaction between

the anions and the metal surface atoms is strong, it is reasonable to expect that anion adsorption will induce lattice strain, or even lattice disruption inside the metal particle.^[1]

To calculate the extinction cross-section C_{ext} for 9.0 nm radius silver spheres in water, we used the silver ϵ_1 data of Johnson and Christy.^[28] The plasmon resonance frequency $\omega_{p,b}$ ($=1.4 \times 10^{16} \text{ sec}^{-1}$), the relaxation time τ_b ($=1.945 \times 10^{-13} \text{ sec}$), and the Fermi velocity ($v_f = 1.4 \times 10^6 \text{ m} \cdot \text{sec}^{-1}$) for silver. We assumed a host dielectric constant ϵ_h of 1.77, which corresponds to the square of the optical refractive index of water ($n_o = 1.33$). Except that the relaxation time is reduced an additional 45% and 50% (after the size-correction drops the relaxation time by 90% relative to the bulk value). The silver particle radius ($a = 9.0 \text{ nm}$), the host dielectric ϵ_h and the *size-adjusted* ϵ_2 were inserted into the equation 1. The resulting complex polarizability parameters were in turn used to calculate C_{ext} via equations 4 and 5 for the $0.2\text{-}1.2 \mu\text{m}$ wavelength range, and then T calculated via Eq. 2. The result is shown in Figure 7. The red-shift, intensity decrease, and band broadening are consistent with the experimental NaX and KX studies.

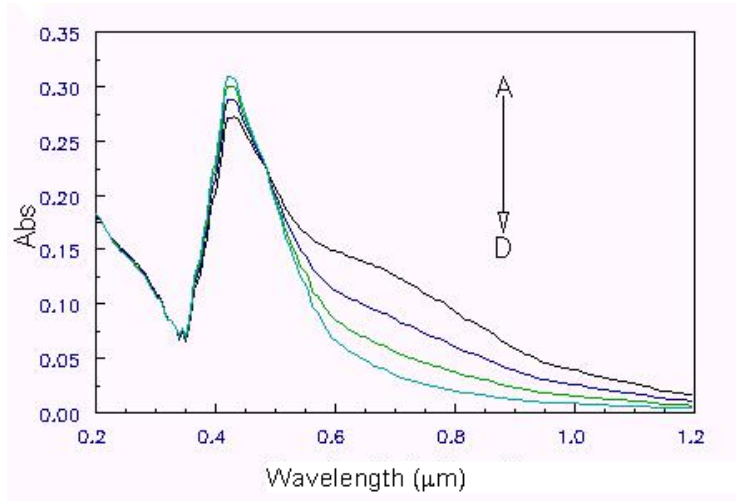


Figure 7. Calculated extinction spectra of unperturbed 9.0 nm radius colloidal silver (curve-A), and the same colloid when electron density is decreased by 27.5% ($\sigma = 40 \mu\text{C}/\text{cm}^2$) within a thickness of 1.5 \AA in the surface layer of Ag particle and relaxation time is decreased by 40%, 45% and 50% in the entire particle's volume curves **B-D**, respectively. The refractive index in an adsorbed layer of thickness 3.0 \AA is 1.55.

To simulate the spectral changes as a function of electrolyte concentration, the relaxation time τ_{eff} and the adsorbed layer refractive index (n_2) are decreased and increased, respectively, such that they represent the effect of increasing the number of adsorbed anions. For simplicity, we hold ω_p in the depletion layer constant at $1.19 \times 10^{16} \text{ sec}^{-1}$. In Figure 8, curve-C is the unperturbed silver particle spectrum. The curve-B corresponds to $n_2 = 1.4$ and $\tau = 4.5 \times 10^{-15} \text{ sec}$. The curve-A corresponds to $n_2 = 1.55$ and $\tau = 3.5 \times 10^{-15} \text{ sec}$.

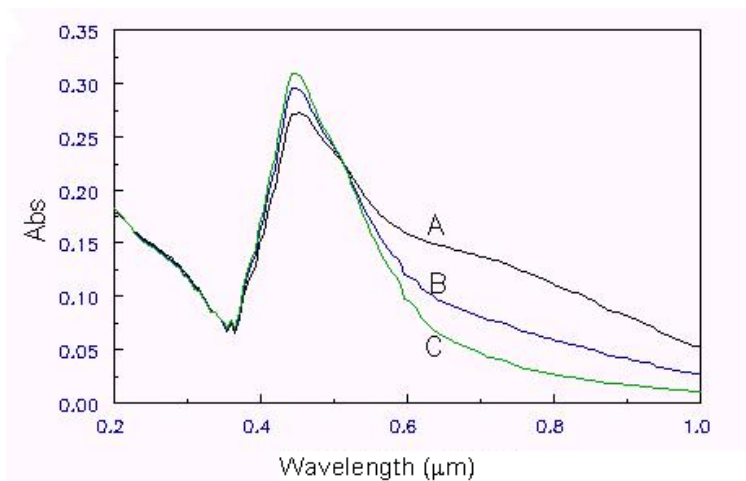


Figure 8. Calculated extinction spectra of unperturbed 9.0nm radius colloidal as in Figure 7 for different variations in electron density (N), relaxation time (τ) and refractive index (n). *Curve C*: unperturbed silver solloid; *Curve B*: N decreased by 27.5%, τ decreased by 22% and $n = 1.4$; *Curve A*: N decreased by 27.5%, (τ) decreased by 40% and $n = 1.55$.

The spectral effect of a concerted change in τ and n are consistent with the concentration-dependent changes observed in the halide electrolyte studies. Figures 7 and 8 show that a reduction in τ arising from potential-induced anion adsorption may be the major mechanism in the damping of the plasmon resonance peak. Furthermore, the reduction in τ overcomes any increase in the refractive index of the adsorbed layer. However, we also note that the increase in the adsorbed layer refractive refractive index increases the magnitude of the concentration-induced red-shift.

The trend in spectral changes with applied potential (at constant electrolyte concentration) can be explained in a similar way. The more positive the applied potential, the greater the reduction in the electron density in the metal, and the greater the adsorption of anions. As more anions are adsorbed, the relaxation time τ is further reduced.

Conclusion

In this study, it has been shown that the plasmon resonance band of nanoscopic silver particles adsorbed onto transparent electrodes can be altered by means of an external potential, similar to the results that have been obtained by Foss et al.^[15] for gold particles. Increasing the applied potential in the positive direction induces red-shifts and intensity damping of the plasmon resonance band. These shifts are subtle, and not as large as those observed for metal colloids in bulk solution. Nonetheless, potential-induced effects are measurable for silver particles in contact with specifically adsorbing anions (I^- , Cl^- and Br^-) and weakly adsorbing species (ClO_4^- and PF_6^-).

Since intensity damping is observed for silver particles in contact with the weakly adsorbing species PF_6^- , we conclude that reduction in the electron mean free

lifetime τ is a general consequence of anodic interfacial polarization and specific anion adsorption. The more conspicuous intensity damping seen in for silver particles with Γ^- , Cl^- and Br^- solutions may arise from more extensive reductions in τ and/or the formation of a silver-halide compound layer which is itself highly absorbing in the region of the plasmon resonance band.

The theory-experiment comparison is quite satisfactory; the λ_{max} 's differ by only ca. 1 nm, and the overall profiles are very similar. The broader width of the experimental spectrum is due to the dispersion in silver particle size in the colloidal sample.

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