Electrochemical Effects on Spectral properties of Silver Nano Particles Adsorbed on Transparent Cd-TiO₂ Electrodes

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ABSTRACT

In this study, optical measurements are used to monitor electrochemical changes on the surface of silver nanoparticles. The potential dependence of the plasmon resonance spectra of these metal nanoparticles immobilized on transparent electrodes surface in contact with three aqueous solutions of (KSCN, NaBr, NaI), and ammonia solution, have been studied. In all these solutions, the plasmon resonance bands and their intensities were found to depend on the applied potential, where when it is made positive, the bands are red-shifted and decreased in intensity. The degree of spectral changes was found to depend on the dielectric properties of the electrolyte, electrolyte identity and its concentration. The change in plasmon absorption band is largest for the lower concentration. At constant concentration, the potential-induced spectral changes are largest in the presence SCN⁻ for silver and in the presence of ammonia solution for copper. These effects may arise from more 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: plasmon resonance; metal nanoparticles; silver; transmission electron microscope (TEM); applied potential; transparent electrodes.

INTRODUCTION

Recently intensive research work have been carried out to synthesize functional noble metal nanoparticles due to their unique optical properties related with their plasmon resonance and because of their remarkable wide range of potential applications in electronics, optics, sensors, biosensors, medical and biological application(1-4). One of the remarkable optical property of noble metal nanoparticle is that the position of the peak maxima as well as the absorbance of the plasmon resonance spectra which are highly sensitive to nanoparticle size, shape, the change of partial charge, the dielectric properties of the surrounding environment, density of electrons, molecular absorption/desorption and inter-particle interaction(5-8).

Studies on metal nanoparticles in bulk solution have shown that interactions on the surface of these particles, can induce notable changes in the region of the plasmon resonance band[9-12]. This band can be red- or blue-shifted depending on the previous factors[13-16]. Several reports have described the potential dependence of the Plasmon resonance band of metal nanoparticles in an aqueous solution;(17,18). The shift and damping of plasmon resonance band and intensity changes were found to depend on the applied potential, accordingly metal nanoparticles showed different plasmon resonance absorption behavior as a result of change of dielectric property of the surrounding media, absorption and/or desorption and charging/discharging of the particles.

The effect of the applied potential on the spectral behavior of silver nanoparticles was studied by Daniels and Chumanov(19), using a spectr﻿//electrochemical approach in different electrolytes. Spectral changes were observed and presented as difference spectra measured between applied potentials and the potential of zero charge. The changes were attributed to potential-induced changes of the local dielectric environment around the nanoparticles.

Toyota et al(20) characterized the potential dependent behavior of absorption bands of gold nanoparticles immobilized on a monolayer of amine-terminated siloxane coated on an indium-tin oxide electrode, by combined use of electrochemical and UV–Vis transmission–absorption spectroelectrochemical methods. The gold nanoparticles showed a potential dependent shift of the plasmon absorption band due to charging–discharging of the particles; at more negative potentials, a sharper and greater absorption peak was observed at a shorter wavelength. The potential step coulometry measurement estimated that the transferred amount of charge as being approximately 1500 electrons V⁻¹ per particle, which is in good agreement with the spectral shift.

The work of Henglein, et al.[21,22] showed that wavelength bandwidth, and the intensity, of the plasmon band was found to depend on the change of free electrons density in the metal particles. They found that the band is red-shifted, its intensity decreases and its bandwidth increases as electrons in colloidal silver in aqueous solution decreases by oxidizing radicals. Opposite effects were observed when electrons were increased in the colloid by the reducing radicals. In addition to
that, the shape and position of the plasmon absorption band changes with absorption of nucleophiles. These changes were found to be in good quantitative agreement with the prediction of Mie scattering equation for the absorption of metal nanoparticles. 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, the nucleophiles which bind to the surface of the particles, causes a red-shift as a result of decreasing the electron density on the surface, or decreasing the mean free path of the electron due to a surface dipole structure created on the surface. Mulvaney[11] reported that the spectral changes due to absorption of nucleophiles are mainly due to the “demetalization” of the surface atoms accompanied by oxidation of the adsorbed anions. Underwood and Mulvaney[15] have shown that the plasmon band is red-shifted, broadened and increased in intensity as the refractive index of 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[23] found that the addition of 1 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. 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[24]. 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[24]. Cotton and coworkers,[25,26] 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 suggestion 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.[27] and Al-Rawashdehet al.[28], in which colloidal silver particles are adsorbed on optically transparent cadmium-doped tin oxide electrodes. In these experiments, it is possible to examine the optical properties of metal nanoparticles using a simple spectroelectrochemical cell in an optical transmittance configuration[27]. 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 surfactants species which can complicate the interpretation of the spectra.[27] 

**EXPERIMENTAL**

**Materials**

Sodium Iodide, NaI (BDH), Sodium bromide, NaBr (BDH), Potassium thiocynate, KSCN (MERCH). Tri- sodium citrate (Scharlu,AR) silver nitrate (BDH), Ammonia solution (Scharlu, AR). All chemicals were used as received and the solutions of the salts were prepared in a double distilled water.

All glassware were thoroughly cleaned in an alcoholic KOH, and rinsed copiously with double distilled water.

**Silver Colloid Preparation**

Several methods which are used for the synthesis of silver nanoparticles have been reported which includes chemical reduction [29], thermal decomposition [30], laser ablation [31], and sonochemical synthesis [32]. Among these, chemical reduction method and laser ablation method are the most commonly employed synthetic routes. The chemical reduction method involves the reduction of metal salt like silver nitrate in an appropriate medium using various reducing agents like citrate, borohydride, etc. to produce colloidal suspensions integrated by nanoparticles [33]. In the citrate reduction method described by Lee and Meisel, silver nitrate is dissolved in distilled water and brought to boiling. A solution of sodium citrate is added and the solution is kept on boiling. The resulting colloid was greenish yellow and had absorption maximum at 420 nm [29].

Colloidal silver solutions were prepared according to Graber, et al[34] and Solomon et.al [35]. Approximately 90 mg of AgNO₃ was added to a clean dry 125-mL Erlenmeyer flask, dissolved in 500 mg of doubly distilled water and the solution was boiled. Sodium citrate solution 1.0% w/v (10 mL) was added to the silver solution all at once with vigorous stirring. The solution was kept on boiling for one hour, at the end of reaction, the color of the silver colloidal sol was greenish-yellow and has absorption maximum of 431.1 nm (Figure.1). The UV/Visible spectra of the silver colloids were carried out using 1 cm quartz cuvette with a Varian Carry- 50 UV/ visible spectrometer.
Size determination by TEM method

Transmission electron microscopy (TEM) were used to determine the particle size [35-39]. Samples were prepared by placing a drop of colloidal solution containing nanoparticles on a carbon-coated copper grid. TEM measurements were carried out at 80 KV using JEOL Model JEM 1011, transmission electron microscope. The result presented in figure 2.
Transparent Electrodes preparation

The transparent electrodes(T.E), 90x10x3 mm in dimension, were a transparent microscope glass slide coated with cadmium doped tin oxide prepared in physics department, Taif university, by sputtering method[40] using sputtering UNIT model UNIVEX 350 with a rate thickness monitor model INFICON AQM-160

Spectroelectrochemical measurements

Spectroelectrochemical studies based on the work of Foss, et al.[27].

To avoid problems associated with reduction of the SnO₂ electrode and metal oxide formation, the applied potential during spectroelectrochemical investigations was limited to the range 0.10-0.60 V. Potentials were applied using DC-Power supply Peaktech model 6070. The spectra were obtained using Varian Carry 50 UV/ visible spectrophotometer.

Metal colloid solution was evaporated on the transparent Cd-TiO₂ electrode(T.E.) at room temperature for 3 hours and the dry colloid was rinsed with double distilled water. Then, the (T.E.) was kept in contact with double distilled water for few minutes before being introduced into the spectrophotometric cell. Potentials were applied using the power supply which connected to the (T.E.)

The spectra were recorded at applied potentials of 0.0, 0.1, 0.4, 0.5, 0.6 Volts.

RESULTS AND DISCUSSION

To study the effects of anion identity and their concentration on the plasmon resonance absorption spectra, each metal nanoparticles was brought in contact with NaI, NaBr, KSCN, or NH₃ solutions separately. For a given solution, the spectroscopic measurements were carried out at three different concentrations(1.0x10⁻¹, 1.0x10⁻², 1.0x10⁻³ M).

Figure(3):Silver nanoparticles(size 50 nm) in contact with NaI at different concentrations
Figure(4): Silver nanoparticles (size 50 nm) in contact with NaBr at different concentrations

Figure(5): Silver nanoparticles (size 50 nm) in contact with KSCN at different concentrations
Figure (6): Silver nanoparticles (size 50 nm) in contact with NH$_3$ at different concentrations

Figures (3-6) show the absorption spectra of silver nanoparticles (size 50 nm) in contact with different electrolytes (NaI, NaBr, KSCN, and NH$_3$), at the three different concentrations. The results concerning the anion identity reveal that the plasmon resonance band of silver nanoparticles, in general, is red-shifted and decreased in intensity and the largest changes in the plasmon spectra are observed at concentration of (0.001M), when the NP’s come in contact with iodide and thiocyanate ions[24,25]. This may be attributed to the formation of either simple salts or complexes with these anions when strongly adsorbed on the surface of silver particles or/and to the change in the refractive index of the media as well as the change in the dielectric properties of the surrounding environment[8,15,41]. The decrease in intensity and increase in band width i.e. damping of the spectra is due to surface scattering in these sols[42,43] to silver sol results in formation of layer(s) coverage on the colloidal silver upon addition of electrolytes result in changes in the resonance condition at the metal surfaces. This changes is due increase in the refractive index at the metal surface as a consequence of anion adsorption on the other hand, adsorption of anions is also expected to alter free electron relaxation time [6]. Ammonia solution results in an increase in the band width and decrease in intensity as well, but no change in the position of the bands are observed and this may be due to its weak adsorption on the metal surface. Changes in silver particle plasmon resonance band relative intensity as a function of electrolytes concentration are presented in Figure (7) and Figure (9).
To study the effect of applied potentials on the plasmon resonance absorption spectra of silver nanoparticles, the colloidal sol adsorbed on SnO$_2$ electrode was brought in contact with $1.0\times10^{-3}$ M NaI, in the electrochemical cell and the absorption spectra measured against applied potentials.

The application of a more positive potential causes a red-shift and damping in absorbance intensity. The potential-induced red-shift and damping are more pronounced in the presence of NaI and NaBr, while in the presence of NH$_3$ and KSCN the red-shift and damping are the smallest[24]. Figure(8) shows the Plasmon resonance bands at applied potentials of 0.1, 0.4, 0.5 and 0.6 V in contact with 0.001 M NaI.

![Figure(8):Silver nanoparticles(size 50 nm) adsorbed on SnO$_2$ electrode in contact with NaI at different potentials](image)

For these spectra, the broadening of the plasmon resonance band as the applied potential is made more positive is quite evident.

**Size-dependent Adsorption Effects**

In general, resonance position shift to lower energies and damping of the spectral bands are observed for larger particles, where surface scattering play a big role in silver due to the larger mean-free path of the surface electron[5]. The spectral changes in the plasmon resonance band of silver particles(size 65 nm) in contact with NaBr at different concentrations are presented in Figures(9).
Figure (9): Silver nanoparticles (size 65nm) adsorbed on SnO$_2$ electrode in contact with NaBr at different concentrations

In the same manner as discussed for the particles size 50 nm, if one considers figure (4) and figure (9), it is clear that the degree of anion concentration-induced red-shifting, and damping increases as the size of silver particles increase figure (10).

Figure (10): Silver NP's (size 65) in contact with NaBr solution at different concentration

Figure (11): Silver nanoparticles (size 65nm) adsorbed on SnO$_2$ electrode in contact with NaI at different potentials
Figure (8) shows the results of the potential-induced effects on the plasmon resonance bands of silver nanoparticles size 50 nm. Compare to that of silver nanoparticles size 65 nm Figure(11), one can see that the degree of red-shifting and damping diminish as the particle radius increases, Figure(12).

![Graph showing absorbance vs concentration for different sizes of silver nanoparticles](image)

**Figure 12:** Silver NP's (different sizes) in contact with NaI(0.001M) at different Potential

The anions I⁻, Br⁻, and SCN⁻ are known to be adsorbed on Ag to form chemical bonds, and NH₃ is known to form coordinate bonds [44-50]. The adsorption of such anions and electron pair donor, is expected to increase the electron density at the particle surface, thus changing the equilibrium state of the metals, altering their surface lattice structure, and increasing the local refractive index, and hence changes free electron relaxation time[15,51]

Since silver atoms on the surface are coordinatively unsaturated and vacant orbitals on the surface can accept electron pairs from nucleophilic entities, it is quite possible chemisorption of these nucleophiles on the silver nanoparticle surface result in the damping of the surface plasmon band due to increase of the concentration of the free electrons on the metal surface and the absorption peak maximum of 431.5 nm indicates pronounced change in the electron density distribution of the donating nucleophiles[52].

The surface plasmon resonance peaks of noble metal nanoparticles generally red-shift as the refractive index of the surrounding environment is increased. According to Foss’s study[27] on gold particles, it is found that the larger the refractive index of the adsorbed layer, the greater the red-shift and intensity increase. The combined effects of an increase in the refractive index of the surrounding environment and a decrease in electron concentration explain these results for the NaI and NaBr electrolytes. In their study they assumed that the only effect associated with anion adsorption was an increase in the refractive index of the surrounding media.[45] 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]

The spectral effect of a concerted change in free electron relaxation time are consistent with the concentration-dependent changes observed in the halide electrolyte studies. Furthermore, the reduction in free electron relaxation time overcomes any increase in the refractive index of the adsorbed layer. However, according to Al-Rawashdehet. al. it has been noted that the increase in the adsorbed layer 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 is further reduced.

**CONCLUSION**

In this study, it has been shown that the plasmon resonance band of silver nanoparticles adsorbed onto transparent electrodes can be altered by means of changing the concentration of the reacting nucleophiles and by means of an external potential, similar to the results that have been obtained by Foss et al.[27] for gold particles. Increasing the applied potential in the positive direction induces red-shifts and intensity damping of the Plasmon resonance band for silver nanoparticles. These shifts, in some cases are larger than those observed for metal colloids in bulk solution. Nonetheless, potential-induced effects are measurable for metal particles in contact with specifically adsorbing anions (I⁻, Br⁻, and SCN⁻).
The more conspicuous intensity damping seen for silver nanoparticles with I- and this may arise from (increasing the local refractive index) more extensive reductions in the free electron relaxation time and/or the formation of a silver-halide compound layer which are themselves highly absorbing in the region of the plasmon resonance band.

The overall curves are very similar. The broader width of the experimental spectrum is due to the dispersion in metal particle size in the colloidal samples[28].

REFERENCES


