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Effect of bromide and chloride ions for the dissolution of colloidal gold

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Abstract

Gold organosol has been synthesized in toluene employing two-phase (water–toluene) extraction of $AuCl_4^-$ followed by its reduction with sodium borohydride in presence of cationic surfactants with variable counter ions. The influence of the counterions of the phase transfer reagent and stabilizing ligand on the photochemical stability of the gold colloids in toluene has been investigated. The counterions of the surfactants, i.e. bromide or chloride ions at times generate the corresponding radicals under UV-irradiation, which oxidize the gold clusters. It is explored that photodiscoloration process is faster for bromide system as compared to chloride. The slower discoloration in presence of only chloride system has been explained in the light of electron affinity of chlorine and stability of chlorocomplex. The photodiscoloration is facilitated in chloroform. It has further been observed that HCl oxidizes the gold nanoparticles under ambient condition. Finally the thermal activation facilitates the oxidation process in presence of bromide ions.

Keywords: Gold nanoparticles; Chloride and bromide counterions; Free radicals; UV-irradiation

1. Introduction

Dissolution of coinage metal nanoparticles has already proven to be useful for the realization in many aspects of nanoscience. The evolution of metal ions as a consequence of dissolution of metal nanoparticles in ambient conditions has got impetus in studying the underlying electric-field-assisted properties of metal clusters [1,2]. Regardless of the nature and characteristic of metal nanoparticles, chemical methods are mostly used to dissolve them to form the corresponding metal ions. Generally, a nucleophile (ligand) is used along with an oxidizing agent for dissolving the metals in both aqueous and non-aqueous [3,4] medium. These systems include mineral acid/aqua regia, cyanide/O_2, I_2/I^- or I_2/SCN^-, elemental halogen, halide, organic solvent, etc. It is well known that the redox potential of a particular metal depends on the value of aggregation number (n) and more precisely, decreases with decreasing particle size [5]. On the other hand, the redox potential decreases further by adsorption of nucleophile to the surface of the particles. Previously, we have reported the nucleophile-induced dissolution of silver nanoparticles in presence of oxygen [6]. In that case, the adsorption of BH_4^- ions to the surface of the nanoparticles resulted out a lowering in the reduction potential value of silver from positive to negative. The large negative shift in reduction potential value makes the nanoparticles susceptible towards oxidation by oxygen.

Recently the mild oxidation of gold nanoparticles has been studied in great detail for resizing the particles after growth. A few reports have been renowned in this decade, pertaining to the dissolution of metal nanoclustures in solution, where most of the approaches primarily involve thermal/laser heating and cyanide dissolution [7,8]. Tsung et al. reported that the size of Au nanorods decreases by length and become spheres by dissolution in presence HCl at a certain temperature [9]. Furthermore, it was reported that single crystalline cubes and tetrahedrons of silver with truncated corners/edges could be prepared in high yields through the selective etching and dissolution of twinned seeds by chloride ions in presence of oxygen (from air). It is also reported that sonochemical reduction of Cu^{2+} in presence of CTAB produces CuBr instead of copper cluster [10]. Noble

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metals in bulk are photoactive only to a small extent whereas in the nanoregime they exhibit increased photochemical activity because of their high surface-to-volume ratio and unusual electronic properties. Silver and gold nanoparticles show significant photoactivity and undergo several photophysical phase transformations. In this context, Henglein and co-workers reported the photochemical dissolution of Ag colloids when photoejected electrons were scavenged away by species such as N_2O [11]. Kawahara et al. reported photoinduced sintering of Au nanoparticles on supported TiO_2 in aqueous solutions containing halogen ions [12]. All the reactions mentioned above, were studied in aqueous medium. It is well known that an organic solvent system consists of elemental halogen (chlorine, bromine and iodine), a halide dissolve the noble metals. Nakao reported the conversion of a gold hydrosol stabilized by cetylpyridinium chloride (CPC), to gold organosol in chloroform and investigated the spontaneous oxidation of gold and palladium nanoparticles in organic solvent system under UV-irradiation [13].

In this article, we report the bromide ion assisted ready dissolution of gold nanoparticles in toluene under UV. The comparative study for the photochemical stability of gold nanoparticles between the bromide and chloride counterions of the stabilizing ligand has been investigated. Bromide shows higher photochemical activity than chlorides for the dissolution of the gold colloids and the results have been substantiated through the electron affinity and stability constant values of the corresponding gold complexes under consideration. The effect of thermal energy for the dissolution of gold nanoparticles in presence of bromide has been studied in detail. Finally, the oxidation of gold organosol has been studied in hydrochoric acid. The dissolution process in presence of chloroform has also been studied.

2. Experimental section

2.1. Reagents and instruments

All the reagents used were of AR grade. Chloroauric acid ($HAuCl_4 \cdot 3H_2O$), cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC) and sodium borohydride were purchased from Aldrich. Phase transfer agents *viz.* tetraethylammonium chloride (TEAC) and tetraoctylammonium bromide (TOAB) were used as received from Aldrich. Hydrogen chloride (HCl) was purchase from Aldrich. Toluene and chloroform were purchased from Merck and were dried before use.

The absorption spectrum of each solution was recorded in a Spectrascan UV 2600 digital spectrophotometer (Chemito, India) in a 1-cm well-stoppered quartz cuvette and the solvent background was subtracted each time. Photoirradiations were carried out with a photoreactor fitted with germicidal lamps of wavelength ~365 nm (Sankyo, Denki, Japan) of UVC G8 T5. The photoreactor can produce a flux of 850 lux (1 lumen flux of photon/(cm^2 s)). The UV flux was measured using a Digital Lux Meter (model LX-101, Taiwan). Photochemical reactions were carried out under ambient condition, air in 1 cm well-stoppered quartz cuvette. The cell was kept in an upright position and 3 cm apart from the light source. Electron micrographs of the metal colloids were measured with a Hitachi H-9000NAR transmission electron microscope, operating at 200 kV. The samples were prepared by mounting a drop of the solution on a carbon-coated copper grid and allowing it to dry under vacuum.

2.2. Synthesis of gold organosol stabilized by cationic surfactants

The synthesis of cationic surfactant-stabilized gold nanoparticles was carried out in a two-step procedure [14]. In a typical preparation, $AuCl_4^-$ was first transferred from an aqueous solution to toluene using tetraoctylammonium bromide as the phase transfer reagent and was, then, reduced with sodium borohydride in the presence of cationic surfactants, CTAC or CTAB as stabilizing agent. Upon the addition of the reducing agent, the toluenic solution changed color from light yellow to characteristic color of gold colloid within a few minutes.

The preparation technique is as follows. To an aqueous solution of $HAuCl_4$ (1 mL, 10 mM), 20 mg of TOAB was added and toluene (20 mL) was introduced above the aqueous layer. Upon shaking, $AuCl_4^-$ ions were transferred from aqueous phase to the organic layer. The organic phase was separated and divided into two parts: to one part CTAC was added and to the other CTAB. Each part was mixed well so that the final concentration of stabilizers in all the sets was maintained to 5 mM. Finally, 1 mg of sodium borohydride was introduced to each solution and all the reaction mixtures were shaken vigorously. During shaking, at first, the yellow color due to $AuCl_4^-$ disappeared and the solution became colorless within a few minutes. The solution turned into characteristic color of gold colloids on further shaking. The method is reproducible and the final concentration of gold in this experiment was 0.5 mM. The same procedure was carried out with the phase transfer reagent tetraethylammonium chloride and stabilized by CTAC. The as synthesized organosol was diluted to 0.05 mM and irradiated under UV light to study the effect of the counter ions of the phase transfer reagent on the photochemical stability of the gold colloids.

3. Results and discussion

Fig. 1 shows the absorption spectral features for the evolution of gold nanoparticles in toluene. The toluenic dispersion of CTAB shows no characteristic absorption maximum in the range of 300–700 nm (trace a). Conversely, the $[TOA]^+[AuBr_4]^-$ ion-pair in toluene exhibits an absorption maximum at 348 nm (trace b), relating to metal-to-ligand charge transfer (MLCT) band of $AuBr_4^-$ complexes [15]. Addition of CTAC or CTAB to the toluenic solution of Au(III) caused no change in the absorption spectra. Upon the addition of $NaBH_4$ into the reaction mixture, the yellow color of the solution gradually disappears and after a certain time, the solution becomes completely colorless indicating the formation of AuO_2^- species in the alkaline condition [16]. On further shaking, the appearance of the pinkish tinge

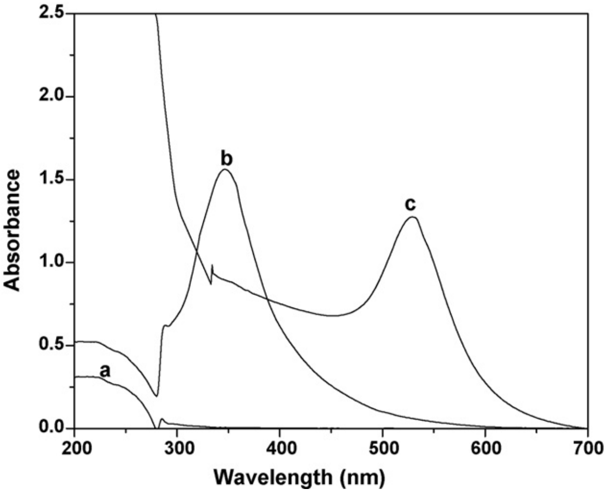

Fig. 1. Absorption spectra of toluenic dispersion of (a) CTAB and (b) $[\mathrm{TOA}]^+[\mathrm{AuBr}_4]^-$, (c) CTAB-capped Au nanoparticles. Condition: $[\mathrm{HAuCl}_4] = 0.5$ mM; $[\mathrm{C}_{16}\mathrm{TAB}] = 5$ mM; [TOAB] = 1 mM. The volume of the solution was 20 mL with toluene.

within the solution indicates the onset of the evolution of gold particles. The color of the solution gradually changes from light pink to red to wine red upon completion of the reduction reaction. Absorption measurement of this resulting solution shows a new absorption band with a maximum intensity at 530 nm (trace c), which corresponds to a typical plasmon band of gold nanoparticles.

Following the elucidation of Brust protocol for the synthesis and capping of gold colloids, George Thomas et al. [17] reported the preparation of tetraoctylammonium bromide (TOAB) capped gold nanoparticles. In an attempt to adopt a similar synthetic procedure, we employed TOAB as the phase transfer reagent and CTAC or CTAB (surfactant containing chloride or bromide respectively as the counterion) as the stabilizing agents in two different sets. The color of the organosol faded in both the cases under UV-irradiation. It is seen that the gold organosol synthesized in the presence of cetyltrimethylammonium bromide in toluene is decolorized within a few minutes time. When 2 mL of the gold sol stabilized by CTAB was subjected to UV-irradiation in a well-stoppered quartz cuvette, it has been found that the color of the sol faded gradually from bottom to the top of the cuvette and finally, become colorless. The changes in the absorption spectra during photodiscoloration of gold nanoparticles are shown in Fig. 2. The spectral profile shows a gradual decrease in the optical density of ∼530 nm peak, assigned to the surface plasmon absorption of colloidal gold. These results indicate that discoloration of the gold colloids occur at the expense of the dissolution of the gold particles. Oxidation of the metal particles occurs within 30 min to yield a complete colorless solution in case of Br^- ions. The same trend has been observed for the gold particles stabilized by CTAC. But the discoloration becomes slower compared to the above case while all the conditions are kept unaltered. To investigate the role of Br^- ion in the photodiscoloration process we repeated the Au sol preparation using TEAC and CTAC to obtain a colloidal gold system devoid of Br^-. Although the photodiscoloration process is found to be active in the present case, it has been noticed that the absence of bromide ion retarded the rate of the reaction to a noticeable extent. Fig. 3 shows the absorption spectral profile of gold nanoparticles in presence of only Br^-, a mixture of Cl^- and Br^- systems and only Cl^-. Traces a–c are the surface plasmon absorption of gold nanoparticles in only Br^-, the mixture of Cl^- and Br^- and only Cl^- system, respectively. Traces d–f are the alteration in the absorption spectra a–c, respectively, after 30 min of irradiation. In Br^- system, the gold particles are completely oxidized within 30 min of irradiation under the experimental condition. But the oxidation of Au(0) is slower for a mixture of Cl^- and Br^- system and slowest for only Cl^- system. Fig. 4 shows the photodecolorization after 2 h of irradiation. Trace c shows the complete oxidation of gold nanoparticles in mixed chloride–bromide system after 2 h of irradiation, whereas, there is no complete oxidation of gold nanoparticles after a long time of irradiation for only chloride system (trace d). The TEM imaging has been carried out to investigate the oxidation process in bromide system under UV irradiation. TEM imag-

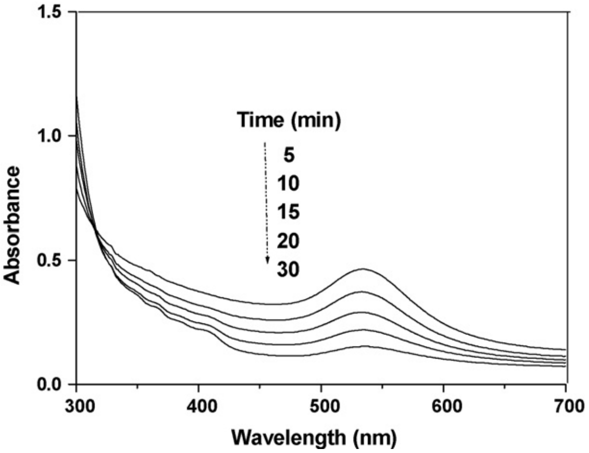

Fig. 2. Absorption spectra for the successive dissolution of gold nanoparticles (0.05 mM) stabilized by CTAB.

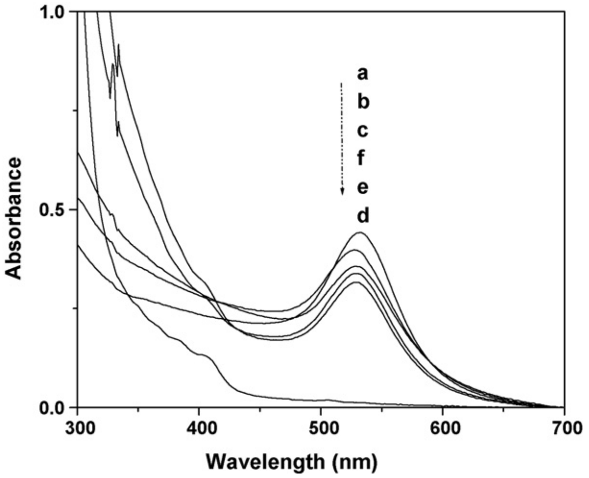

Fig. 3. Absorption spectra of gold nanoparticles (a–c) before and (d–f) after 30 min of UV-irradiation, respectively, in the systems consist of (a, d) bromide, (b, e) bromide–chloride mixture and (c, f) chloride.

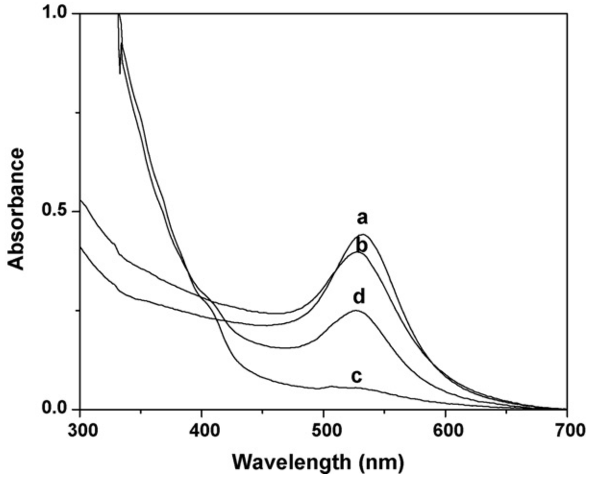

Fig. 4. Absorption spectra of gold nanoparticles (a, b) before and (c, d) after 2 h of irradiation in a system consist of (a, c) mixture of chloride and bromide and (b, d) only chloride ions.

ing shows the size of gold nanoparticles after there preparation was 10 ± 3 nm stabilized by CTAB (Fig. 5A). Fig. 5B shows that the particle size decreases to ~5 nm after 15 min irradiation. After 30 min of irradiation no particles were observed under transmission electron microscope showing complete oxidation.

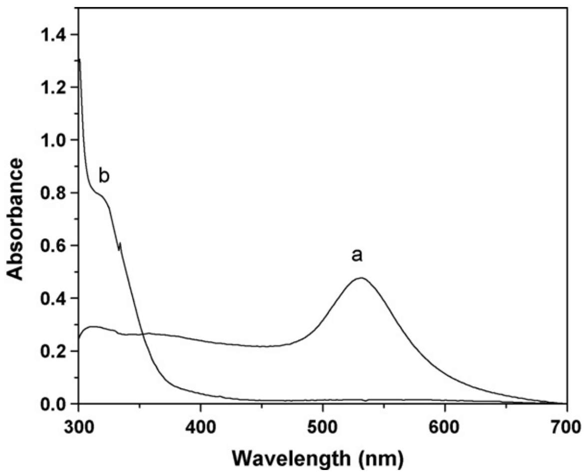

Fig. 6. Absorption spectra of CTAB-stabilized gold nanoparticles (0.05 mM) in chloroform (a) before and (b) after 5 min UV-irradiation.

To have an insight into the mechanism of photodiscoloration process 0.3 mL of 0.5 mM gold sol-containing chloride–bromide ions was introduced into 2.7 mL of chloroform and it has been observed that the color is faded within 5 min of irradiation. Fig. 6a (trace a) shows the surface plasmon peak of gold clusters at 532 nm. After irradiation under UV light for 5 min the plasmon peak of gold vanished completely and a new peak at 325 nm was engendered (trace b) corresponding to complex $[AuCl_4]^-[CTA]^+$ [18]. The color fading is caused by dissolution of gold clusters as a consequence of reaction with chlorine radical, generated by the photodegradation of chloroform and the Cl^- ions of the stabilizing ligand form the complex with Au(III). It has been found that gold clusters are dissolved in chloform forming ion-pair *viz.* tetrachloroaurate(III)–CTA^+. Although, the photoproduced halide radicals have transient existence, these ($X^\bullet$) are generated continuously under UV. Thus the faster discoloration is due to the production of more chlorine radicals from chloroform under UV.

Therefore, a plausible mechanism for the dissolution of colloidal gold may be formulated as follows. The photoirradiation of gold particles in bromide system results bromine radicals, which oxidizes the gold preferentially. In chloride–bromide system photoirradiation results in the formation of chlorine radical ($Cl^\bullet$) and solvated electrons from the adsorbed Cl^- ions on the gold surface [19]. The $Cl^\bullet$ presumably, then, generates $Br^\bullet$, which oxidizes the colloidal gold [11]. The Au(I) ion thus formed combines with two Br^- to give colorless $AuBr_2^-$ which do not absorb in UV region [20] dissolves in toluene by forming a soluble ion-pair with the cetyltrimethylammonium ion.

$$Cl^- \xrightarrow{h\gamma} Cl^\bullet + e^- \ \text{(solv.)}$$

$$Cl^\bullet + Br^- \rightarrow Cl^- + Br^\bullet$$

$$Au + Br^\bullet + [CTA]^+Br^- \rightarrow [CTA]^+[AuBr_2]^-$$

But the Au(I) ions are neither reduced further nor they readily disproportionate because the redox potential of $E^0_{Au(1)/Au(0)}$ is quite negative [18].

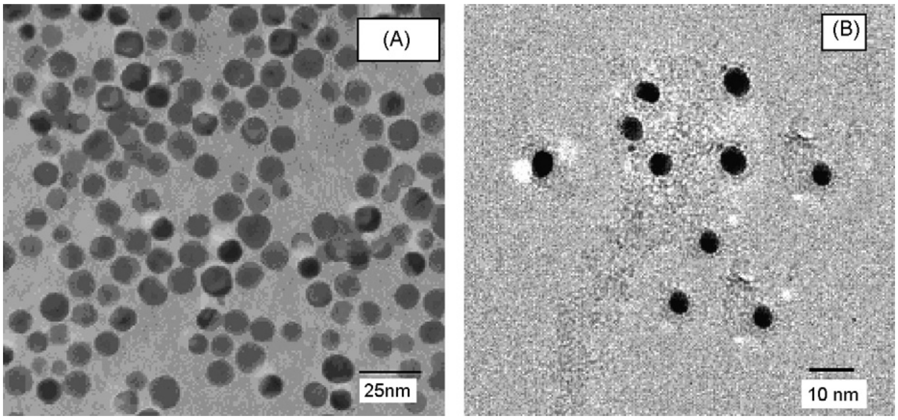

Fig. 5. TEM images of CTAB-stabilized organosol (A) before (B) after 15 min UV-irradiation.

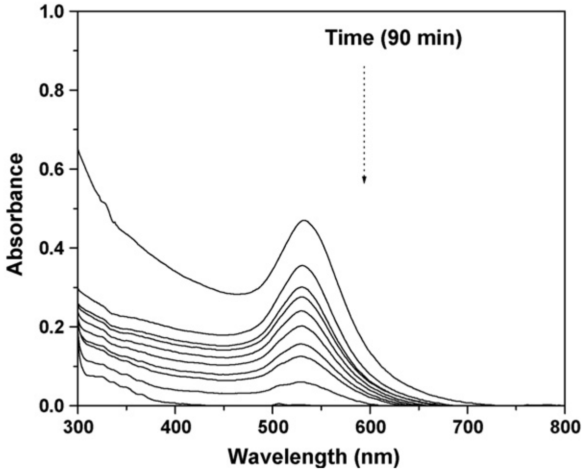

Fig. 7. Absorption spectra for the successive dissolution of CTAB-stabilized gold nanoparticles heating at ∼70° C.

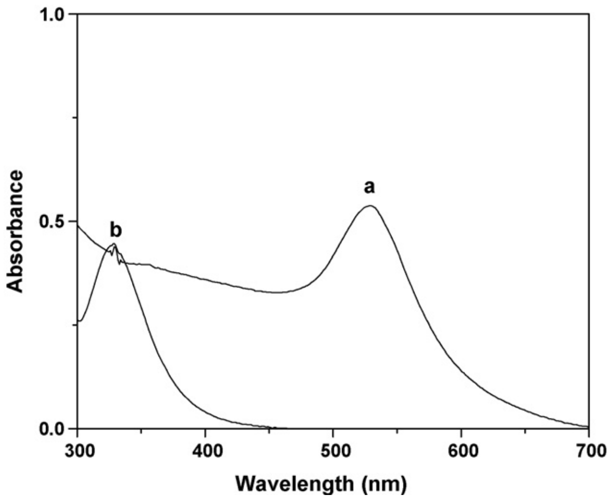

Fig. 8. Absorption spectra of CTAC-stabilized gold nanoparticles in toluene (a) before and (b) after reaction with concentrated HCl.

The slower dissolution of Au sol in a system containing only $\mathrm{Cl}^{\bullet}$ can be elucidated as follows. Chlorine has higher electron affinity than bromine. Therefore, $\mathrm{Cl}^{\bullet}$ and the solvated electrons recombine preferentially in the absence of any bromide ion. However, the presence of bromide ions in toluene, in turn, generates $\mathrm{Br}^{\bullet}$ along with $\mathrm{Br}^{\bullet}$, which oxidizes colloidal gold. The probability of recombination of $\mathrm{Cl}^{\bullet}$ with solvated electron and stability constant for the formation of chlorocomplex make the oxidation of gold slower in comparison to the corresponding bromocomplex [21,22].

It was observed that mild oxidation of gold occurs at 70 °C at pH around 3 in aqueous medium in presence of dilute HCl [9]. Enthrallingly, in toluene these naoparticles show unusual behavior when all the three systems (bromide, chloride and bromide–chloride mixture) were heated at 70 °C on a water bath. Fig. 7 shows the oxidation of gold nanoparticles at ∼70° C in presence of Br^- ions. It was observed that the gold nanoparticles were oxidized completely in bromide but neither in chloride nor in bromide–chloride system. This confirms the active role of Br^- ions for the oxidation and consequently the dissolution of gold nanoparticles in toluene. Since the bromocomplex of gold is more stable than chlorocomplex the colorless solution after oxidation is $[\mathrm{AuBr}_2]^-$. Presumably due to the easier formation of bromocomplex than chlorocomplex, bromide ions are more active for dissolution of gold complex [12].

Interestingly, upon the addition of concentrated HCl solution to the organosol the characteristics color of the gold cluster fades away slowly. Upon the addition of HCl, a biphasic system is evinced where the gold organosol lies over the concentrated HCl. On standing the organic layer turns slight yellow showing the UV–vis absorption spectra at 327 nm (Fig. 8). The fading of gold organosol is due to the oxidation of Au(0) to Au(III) forming $\mathrm{AuCl}_4{}^-$. As the concentration of HCl decreases more time takes for the oxidation process. An increase in acid concentration enhances the oxidation rate because the addition of H^+ increases the reduction potential of half reaction involving O_2 [9]. This shows that the oxidation of gold in toluene medium takes place in presence of HCl.

4. Conclusion

In conclusion, we have reported that organosol system consist of bromide ions readily oxidize gold nanoparticles in presence of UV light and thermal activation. Under photoirradiation, these ions are converted to the corresponding chlorine and bromine radicals, which oxidize the gold clusters. The oxidation was observed faster in presence of bromide than chloride ions of the system. The slower rate of photodiscoloration in presence of chloride counter ions has been authenticated to higher electron affinity of chlorine than bromine and the higher stability constant of bromocomplex than the corresponding chlorocomplex. The oxidation in presence of bromide ions might provide a new avenue to the size selective synthesis of the nanoparticles in organic medium.

Acknowledgements

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