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Photochemical dissolution of gold nanoparticles by bromine containing trihalomethanes (THMs) in an aqueous triton X-100 medium and its analytical application

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Abstract

Gold sol, photo chemically prepared in aqueous Triton X-100 (TX-100) medium is discolored by photo irradiation in presence of $KBrO_3$ and any one of the following bromine containing trihalomethanes (THMs), such as bromoform ($CHBr_3$), chlorodibromomethane ($CHClBr_2$), bromodichloromethane ($CHCl_2Br$) owing to the dissolution of colloidal gold nanoparticles. Upon dissolution of gold, $HAuBr_4$ is formed whose absorption maximum is at 400 nm. The absorbance at this wavelength gives a measure of the concentration of THM. The dissolution of gold nanoparticles can also be monitored at the plasmon absorption of gold viz. 523 nm to relate the concentration of THM.

Keywords: Trihalomethane; Gold nanoparticles; Nucleophile

1. Introduction

Metal dissolution is an important step in metal recovery. Noble and coinage metals viz. Au, Ag and Cu are of special interest in this aspect. To dissolve metals as metal ions, mostly chemical methods are used. Starting from aqua regia, various types of aqueous and non-aqueous systems have been used so far for this purpose. Only a few reports those involve photochemical method for dissolution have appeared in the literature. A critical review of these systems shows that in all cases an appropriate oxidative treatment is required. It has been observed that a nucleophile (ligand) has been used along with an oxidizing agent irrespective of the medium whether aqueous [1] or non-aqueous [2,3]. 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 high positive reduction potential is the root cause of nobility of noble metals. Recent studies [4] indicate that the reduction potential of a metal can be varied by the presence of a nucleophile and with the variation in size of the metal particles as well. A decrease in the particle size results in the lowering of the reduction potential value (E^o) [5] making them more susceptible towards oxidation (i.e. dissolution). This is quite clear from the high reactivity of nanoscale metal particles [6]. Further, adsorption of a nucleophile onto the surface of the metal particle would be expected to shift the Fermi potential level in a negative direction [4], i.e. a further decrease in reduction potential. The more the nucleophilicity of the ligand, the more is the lowering of the Fermi potential. An analogy can be drawn from the comparison of E^o values shown in the earlier literature [7]. The ligand plays another role simultaneously. It stabilizes the oxidized metal ion by the formation of complex or insoluble salt that in turn leads to further lowering of reduction potential. The E^o value is the total of the nucleophile and salt formation effects. However, the former effect becomes more important in case of metal particles having large surface area due to the availability of more adsorption sites for the nucleophile.

In this report, we describe the dissolution of a photo chemically prepared gold hydrosol in TX-100 medium, by bromine containing trihalomethanes (THMs), such as bromoform ($CHBr_3$), chlorodibromomethane ($CHClBr_2$), bromodichloromethane ($CHCl_2Br$) in presence of $KBrO_3$ and light. Such a procedure for gold dissolution is totally new and has applications in the quantification of $CHBr_3$, $CHClBr_2$, and $CHCl_2Br$.

THMs are listed as priority pollutants by the Environmental Protection Agency of the United States, due to their tumerogenic properties and deleterious effects to the nervous system of test animals [8]. The bromine containing

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THMs are produced in drinking water system during disinfection if the disinfecting material is HOBr. If the bromide content present in water is high, then also they are produced during chlorination. Hence finding out a procedure for the quantification of these THMs is important. In that regard also, the new procedure for gold dissolution, described here is important.

2. Experimental section

2.1. Materials and methods

All absorbance measurements were carried out in UV-visible spectrophotometer (model: Shimadzu UV-160). Photochemical reactions were carried out in 1 cm well-stoppered quartz cuvettes. Photo irradiation was carried out with an ordinary germicidal lamp (Sankyo Denki, Japan; 15 W). The cells were kept at a distance of 3 cm from the light source. Gilson micropipette with micro tips was used for sample addition.

All reagents were of AR grade. A stock solution of gold (III) chloride was prepared by dissolving 1.0 g of chloroauric acid (Johnson Matthey, Royston, Hertfordshire, UK) in 500 ml double distilled water and it was standardized by the quinol method and was found to be of 5×10^{-3} M gold concentration. TX-100 solutions were prepared by dissolving appropriate volume of this in known volume of distilled water. THMs, such as $CHBr_3$, $CHClBr_2$ and $CHCl_2Br$ were from Aldrich. Carbon tetrachloride and other solvents, such as methanol, acetonitrile, chloroform, were of high purity and purchased from Merck. Chemicals, such as $CHCl_3$, $KBrO_3$, KI, I_2, NaBr, monochloroacetic acid (MCA), dichloroacetic acid (DCA) and trichloroacetic acid (TCA) were from BDH. An aqueous solution of $KBrO_3$ (0.5 M), an aqueous solution containing KI (2.5×10^{-2} M)/I_2 (2.5×10^{-3} M), and methanolic solutions of $CHBr_3$ (1.14×10^{-1} M), $CHClBr_2$ (1.22×10^{-1} M) and $CHCl_2Br$ (9.03×10^{-2} M) were prepared as stock.

2.2. Preparation of gold hydrosol in a photochemical way

Gold hydrosol having beautiful pink color and containing 3.33×10^{-4} to 5.00×10^{-4} M gold in 10^{-2} M TX-100 was prepared from $HAuCl_4$ photo chemically following a procedure reported earlier [9–11]. During the preparation, TX-100 acted both as a reducing agent and a stabilizer. The plasmon absorption for gold sol was at 523 nm.

2.3. Photochemical dissolution of gold

Gold hydrosol, prepared according to the above said procedure, was taken in a cuvette. To it were then added, aqueous solutions of $KBrO_3$ (final concentration remained in the range of $\sim 10^{-2}$ M) and any one of the three THMs viz. $CHBr_3$ (final concentration was in the range of 1.1×10^{-4} to 2.7×10^{-3} M), $CHClBr_2$ (final concentration remained in the range of 2.9×10^{-4} to 3.4×10^{-3} M) or $CHCl_2Br$ (final concentration was in the range of 4.3×10^{-4} to 2.9×10^{-3} M). The mixture was then irradiated for 20 min. The pink color of the gold sol faded gradually and yellow color developed. The absorbance measurement at $\lambda_{max} = 400$ nm could be done either immediately or after some time. The waiting time could be varied from 0 to 24 h. Dissolution of gold by the above mentioned THMs could also be monitored at the plasmon band of gold nanoparticles, i.e. at 523 nm. The decrease in the absorbance at 523 nm with the increase in THM concentration was noticed. Measurement in this case also could be done with varying waiting time. In either case linear calibration curves were obtained with good correlation coefficients.

3. Results and discussion

3.1. Absorbance studies on the dissolution of gold

Instantaneous dissolution of the gold sol took place when $KBrO_3$ and either of $CHBr_3$ or $CHClBr_2$ or $CHCl_2Br$ were added to it in appropriate amounts and was photo irradiated. Without the irradiation, no color change was noticed even in 24 h time when kept in the dark. The irradiation was carried out using ordinary germicidal lamp. The pink gold sol having λ_{max} at 523 nm (Fig. 1, curve A), faded gradually and finally changed to light yellow. A distinct peak thus now appeared at $\lambda_{max} = 400$ nm and the intensity of the peak at 523 nm due to Au (0) decreased. Curves B and C of Fig. 1 show the absorption spectra of the sol after its dissolution in presence of 1.70×10^{-3} M and 1.13×10^{-3} M of $CHBr_3$, respectively, when 20 min photo irradiation was done and the measurement was carried out after 17 h. With higher concentrations of $CHBr_3$ the solution became hazy on long

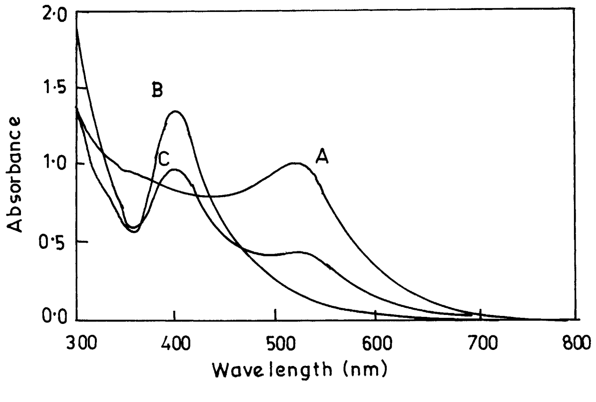


Fig. 1. Curve A shows the absorption spectrum of gold sol (3.33×10^{-4} M) before photo irradiation. Curves B and C show the absorption spectra after the dissolution of gold sol (on 20 min photo irradiation and 17 h wait) in the presence of $KBrO_3$ (10^{-2} M), and $CHBr_3$ (1.70×10^{-3} and 1.13×10^{-3} M, respectively) in TX-100 (10^{-2} M) medium. Reference used was the blank in all cases.

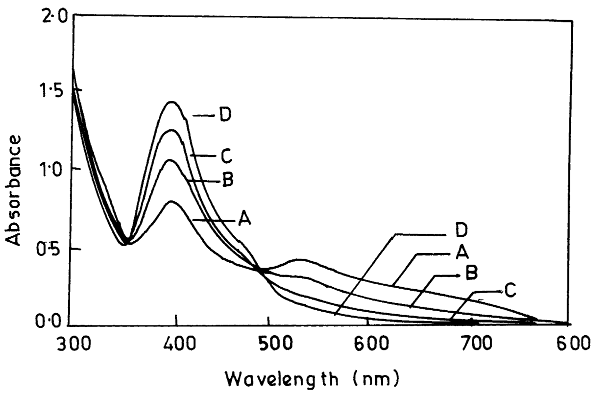


Fig. 2. Absorption spectra after gold sol (5.0×10^{-4} M) dissolution in the presence of $CHBr_3$ (1.70×10^{-3} M) and $KBrO_3$ ($\sim 10^{-2}$ M), in TX-100 (10^{-2} M) on 20 min photo irradiation and waiting for various time intervals: curve (A) 2; (B) 5; (C) 8; (D) 22 h. Reference used was air.

standing. Addition of methanol at this stage brought about the dissolution and the solution turned to a transparent liquid.

When measurement was done immediately, the peak at 400 nm was not that intense. On keeping the solution in the dark up to 24 h, the intensity of the peak at 400 nm gradually increased. Fig. 2 shows, how with the variation of waiting time, the intensity of the peak at 400 nm-peak increases and the peak intensity at 523 nm peak due to gold plasmon absorption decreases.

Similar phenomenon occurs for the other brominated THMs viz. $CHClBr_2$ and $CHCl_2Br$ also. THM that does not contain bromine (for example, $CHCl_3$) did not produce any peak at 400 nm.

The peak appeared at 400 nm after dissolution, is due to the formation of $HAuBr_4$ [12]. This can also be evidenced from the infrared (IR) spectrum obtained after thorough drying of the sample. The peak obtained at $263\,cm^{-1}$ in the infrared spectrum could be assigned to the vibrational frequency of $AuBr_4^-$ [13]. The pH of the solution after the dissolution of gold sol remained at ~3–4 which also speaks in favor of the formation of $HAuBr_4$.The pink gold sol can again be quantitatively regenerated by the addition of $NaBH_4$ into the solution. The 400 nm peak disappeared totally thereby and quantitative regeneration of the peak at 523 nm took place. After dissolution, the precipitation of gold from the solution could also be brought about by the addition of Zn dust into the solution. This caused a concomitant disappearance of the yellow color.

Ordinary incandescent bulb could not bring about the dissolution, instead caused the formation of lot of precipitate. The peak at 400 nm due to the formation of $AuBr_4^-$ was also not seen in this case. UV light (7.5 W) of long range emission (~365 nm), on the other hand, when used for irradiation could cause the appearance of the peak at 400 nm although the absorbance, under similar conditions, is much less. Also, in this case the solution turned little bluish.

To see the effect of O_2 on the dissolution of gold, a simple experiment was performed. When the reaction was carried out in N_2 atmosphere after purging out the dissolved oxygen, the reaction did occur and the peak at 400 nm also appeared. But in this case, when N_2 gas was passed for 2–3 min, precipitation of blue gold was noticed and hence absorbance at 523 nm due to gold plasmon absorption was decreased even before the photo irradiation. As a result, after dissolution also, the absorbance at 400 nm peak was much less, in this case, in comparison to that obtained under similar condition but in the presence of O_2. This could be rationalized as due to the initial precipitation of some amount of gold.

To see the effect of other halogenated organic compounds, such as TCA, DCA, MCA, carbon tetrachloride (CCl_4), chloroform ($CHCl_3$) (which is an important chlorinated THM), etc. on the dissolution of gold, the same reaction was studied keeping the conditions same. It has been noticed that none of the above mentioned chloroorganics brings about the dissolution of gold. However, dissolution of gold nanoparticles can be carried out using $CHClBr_2$ and $CHCl_2Br$ under similar conditions as described earlier.

3.2. Reaction of gold sol with different brominated THMs

The photochemical dissolution of gold sol by $CHBr_3$ can nicely be exploited for analytical purpose for the quantification of $CHBr_3$. The absorbance values (at $\lambda_{max} = 400$ nm) obtained after the dissolution of gold sol with different concentrations of $CHBr_3$ were plotted against $CHBr_3$ concentration. An irradiation time of 20 min was used for dissolution. Either air or blank could be used as the reference. After the dissolution, the absorbance could be measured immediately or after some time. Variation in waiting time led to different absorbance values for a particular set. When waiting time was up to 3 h, linear calibration was obtained in the range of 0–2.84×10^{-3} M. But the correlation coefficient was not very good. But as the waiting time is increased linear calibration was obtained with good correlation coefficient. Calibration curves could also be made for $CHClBr_2$ in a similar way but not for $CHCl_2Br$. When the waiting time used was 24 h, the equation for the curve for $CHBr_3$ was $OD = 240.4 \times C\ (M) + 0.973$. The correlation coefficient was 0.985 and linear dynamic range (LDR) was 0–2.7×10^{-3} M. Similarly for $CHClBr_2$ the equation obtained for the linear curve was $OD = 220.5 \times C\ (M) + 0.912$ (correlation coefficient = 0.980). LDR in this case was 0–3.4×10^{-3} M. References used for all measurements were air and waiting time was 24 h. The standard deviation in all cases was $< \pm 7\%$. The limit of detection for $CHBr_3$ and $CHClBr_2$ were 6.0×10^{-5} and 1.4×10^{-4} M, respectively. In case of $CHCl_2Br$, the formation of $HAuBr_4$ occurred (as evidenced by the yellow color produced and the peak appearing at 400 nm) but the absorbance values could not give a linear relation with the concentration of $CHCl_2Br$.

Calibration of brominated THMs as evidenced from gold dissolution could also be made. As gold dissolution takes place during its photochemical reaction with brominated THMs in presence of $KBrO_3$, the intensity of the plasmon

Table 1

THM	LDR (M)	Waiting time (h)	Slope	Intercept	S.D.	Correlation coefficient
$CHBr_3$	0–2.2 × 10^{-3}	6	−449.2	1.55	0.030	−0.998
		24	−624.8	1.51	0.059	−0.995
$CHClBr_2$	0–3.4 × 10^{-3}	6	−324.8	1.45	0.094	−0.979
		24	−341.2	1.26	0.050	−0.995
$CHCl_2Br$	0–2.9 × 10^{-3}	6	−346.2	1.63	0.072	−0.979
		24	−438.7	1.52	0.052	−0.994

absorption band at 523 nm decreases. It is also interesting to note that the intensity at 523 nm is a measure of THM concentration. The measurement can be done with varying waiting time. The statistical data are shown in Table 1. Linear calibration curves for $CHBr_3$, $CHClBr_2$ and $CHCl_2Br$ (using a waiting time of 24 h) are shown in Fig. 3.

3.3. Kinetic studies for obtaining optimum time for irradiation

Since, the dissolution of gold depends on the kinetic action of the UV light on the gold sol in presence of brominated THMs and $KBrO_3$, studies were carried out to find out the optimum time of irradiation required for the complete dissolution. It has been noticed that an irradiation for 15 min is required to get maximum dissolution. Fig. 4 shows how the time of irradiation affects the development of the peak at 400 nm using $CHBr_3$. The study was made on the absorbance measured immediately after the irradiation. Once the absorbance reaches a maximum, further irradiation up to 35 min caused no change in the absorbance value. Waiting time thereafter, however, could cause significant increases in the absorbance values and in ~24 h time it reached at a maximum.

Dissolution of gold using other systems, such as CN^-/O_2 or I_2/I^- which are already known to be good reagents for gold dissolution [14] was studied and compared with the system described here. The same gold sol which was photo chemically prepared in TX-100 (10^{-2} M) medium, could be dissolved by CN^-/O_2. The dissolution could be evidenced by the gradual decrease of the gold plasmon band. In this case concomitant gradual shift of the gold plasmon absorption band towards red was also noticed during the dissolution. But if the gold sol is prepared in TX-100 medium having concentration in the range of 10^{-1} M, the red shift of the plasmon band did not occur. Instead, only gradual decrease in the absorbance with the addition of CN^- occurred due to the dissolution of gold. This occurred almost immediately after the addition of CN^-. More elaborate studies regarding this dissolution and its use in cyanide determination have been reported elsewhere [15].

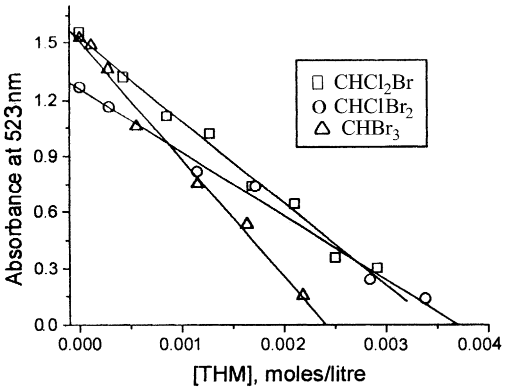


Fig. 3. Calibration curves for $CHBr_3$, $CHClBr_2$ and $CHCl_2Br$. Measurements were carried out at 523 nm after 24 h wait. Air was used as reference blank.

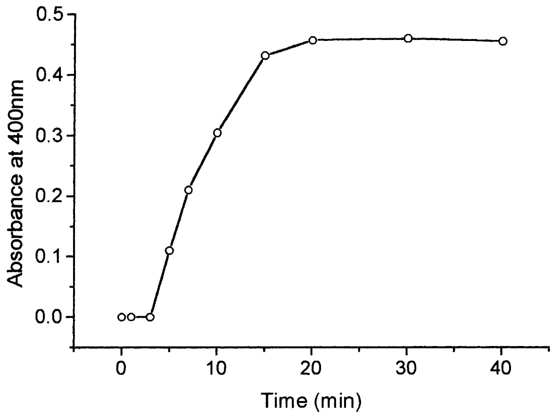


Fig. 4. Effect of irradiation time on the dissolution of gold (5.0×10^{-4} M) in TX-100 (10^{-2} M) by $CHBr_3$ (1.70×10^{-3} M) and $KBrO_3$ (1.2×10^{-2} M) on photoirradiation. Immediate measurements of the absorbance values (at λ_{max} = 400 nm) were taken.

Dissolution of gold by I_2/I^- system (where final $[I_2] = 2.5 \times 10^{-4}$ and $[I^-] = 2.5 \times 10^{-3}$ M) took place at room temperature and without $h\nu$. The absorbance at 523 nm due to gold plasmon absorption diminished immediately, and with time further lowering of absorbance was noticed. A weak peak at 360 nm appeared immediately.

3.4. Effect of $KBrO_3$ on the dissolution of gold

The presence of both $KBrO_3$ and brominated THM is essential for the formation of $AuBr_4^-$ shown by the

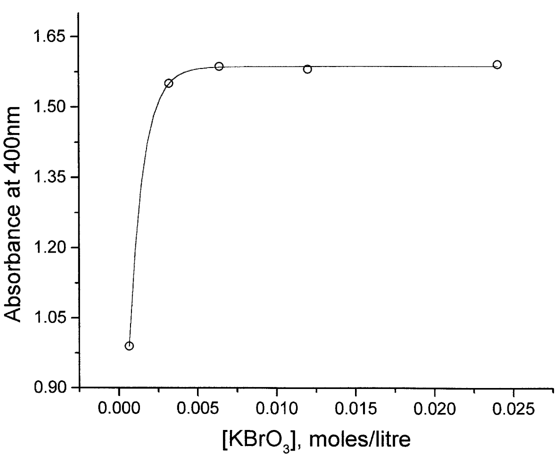


Fig. 5. Effect of $KBrO_3$ on the formation of $HAuBr_4$ due to the dissolution of gold nano-particles by $CHBr_3$ (1.70×10^{-3} M).

appearance of the 400 nm-peak after gold sol dissolution. In the absence of any one of these two, the peak did not appear. In no case the peak at 400 nm did appear when no irradiation was done. In the absence of brominated THM, if photo irradiation of a mixture containing gold sol and $KBrO_3$ is carried out, the peak due to gold sol shifted a little towards red. If a mixture containing gold sol and $CHBr_3$ was irradiated, the solution turned little blue, and no peak at 400 nm did appear. When a mixture of $KBrO_3$ and brominated THM in TX-100 (10^{-2} M) was irradiated in the absence of gold sol no coloration was noticed.

To know the optimum concentration range of $KBrO_3$, a systematic study was undertaken, in which the concentration of $KBrO_3$ was varied keeping the concentration of $CHBr_3$ fixed at 1.7×10^{-3} M, and other conditions same. The absorbance at 400 nm was monitored after 20 h wait. A plot of absorbance versus concentration of $KBrO_3$ was made (Fig. 5). It showed that final concentration of $KBrO_3$ in the range of 3.2×10^{-3} to 2.4×10^{-2} M is optimum to get efficient gold dissolution.

3.5. Effect of TX-100 concentration

TX-100 being a primary hydroxyl group-bearing compound can bring about the photochemical reduction of Au (III) to Au (0) [9]. It was thus felt pertinent to see the effect of TX-100 concentration on the formation of gold particles and its dissolution by $CHBr_3$ and $KBrO_3$ by photo irradiation. During this study the TX-100 concentration was varied from 10^{-1} to 10^{-4} M. It has been noticed that formation of Au (0) was very slow in TX-100 with a concentration $\sim 10^{-4}$ M, i.e. below the critical micellar concentration (CMC). After the dissolution of gold, however, in this case, the peak for $HAuBr_4$ appeared at 383 nm. In 10^{-3} M TX-100, the formation of Au (0) was as usual. But after the dissolution the peak for $HAuBr_4$ was noticed to be little blue shifted as compared to that appeared in the case of TX-100 in the range of 10^{-1} to 10^{-2} M. The peak intensities, however, were almost same for all, as observed after 24 h.

3.6. Dissolution of gold nanoparticles aged (i.e. after keeping for long time) and freshly prepared

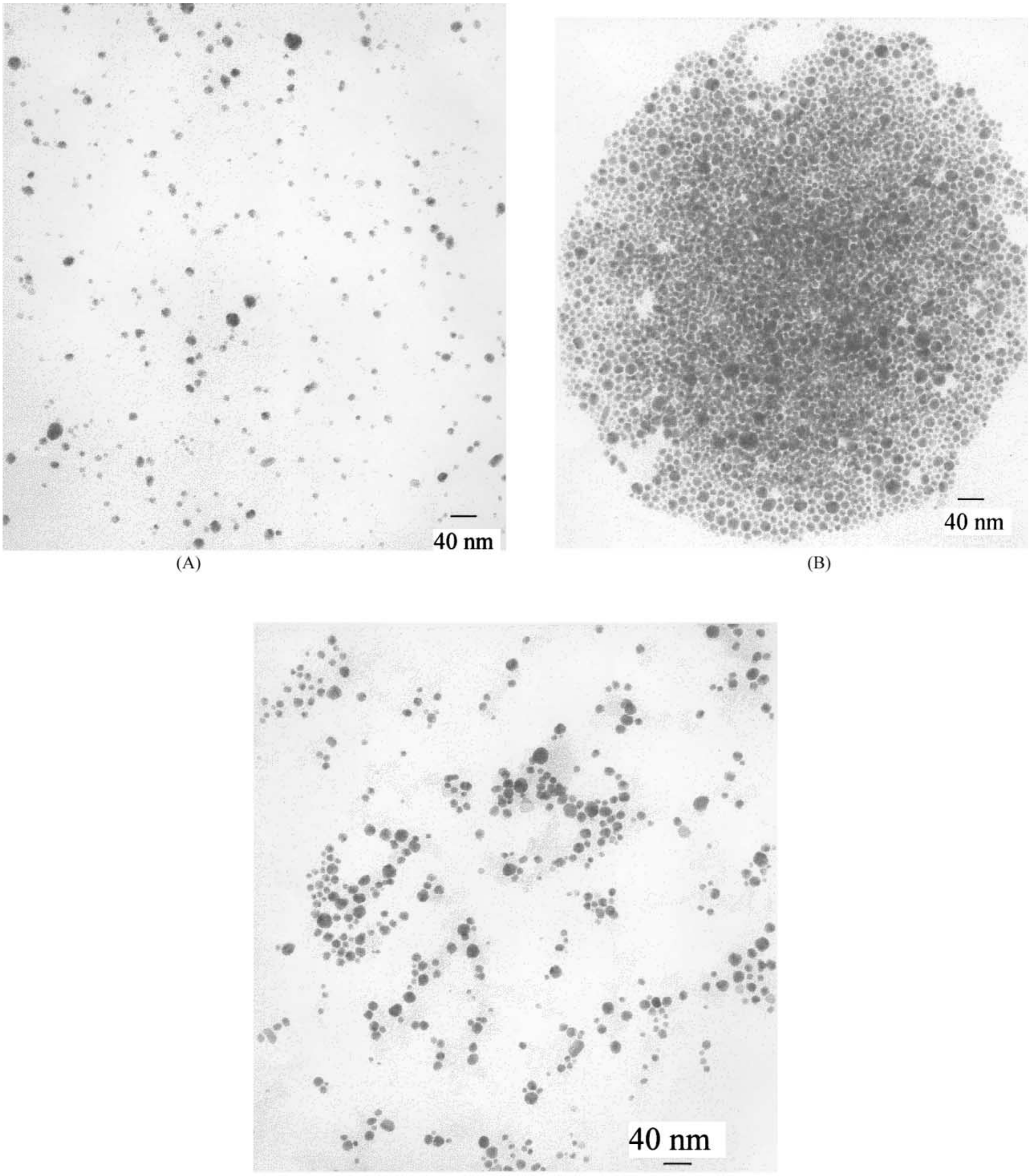
If aged (i.e. after keeping long time the already prepared gold) gold nanoparticles are used for dissolution in TX-100 then the dissolution do not occur immediately. That means the pink gold sol slowly turned to blue and then to yellow. This phenomenon is possibly due to the surface oxidation of gold particles, which makes them little inactive initially. After the oxide layer is removed, however, the dissociation occurs. On the other hand, if a freshly prepared gold sol is used then photochemical dissolution of the gold sol using $CHBr_3$ leading to $HAuBr_4$ takes place in a much quicker way.

Transmission electron microscopy (TEM) photograph of the freshly prepared gold sol (Fig. 6) (A) the aggregated sol after 5 min irradiation and immediate measurement (B) and the same aggregated sol but after a 15 min waiting time (C) are shown. From the TEM photographs it is noticed that the gold sol at the start (A) contains more number of smaller particles than that contained in the sol after 5 min irradiation and 15 min wait, i.e. after dissolution starts (C). This indicates that smaller particles dissolve fast. The TEM photograph of the aggregated sol (B) shows the intermediate stage where the nanoparticles of gold club together. This stage is followed by the quick dissolution of the particles in a short time.

Analytical results were not very reproducible, if freshly prepared gold sol was used. All analytical studies, therefore, were done with aged particles.

It is well known that photo irradiation of $CHBr_3$ results in the formation of bromine radicals ($Br^\bullet$). Solar promoted photo reductive dehalogenation of $CHBr_3/CHClBr_2/CHCl_2$ Br with the formation of lower homologues in the absence or presence of catalyst with the evolution of HBr is also possible [16]. Therefore, the first step possibly is a photo conversion of these molecules to $Br^\bullet$ free radicals. These free radicals generated in the aqueous solvent may diffuse to the colloidal gold particles and transfer an electron onto them [17]. One colloidal particle may accommodate a large number of electrons. The Fermi level in the metal thus is shifted to a more negative potential by electron pick up from the radicals. The electrode potential of bromate, depending upon the electrode reaction may vary. The bromate ion is a good oxidizing agent and probably now act as an oxidizing agent to oxidize Au (0) to Au (III).

To have further support that the reaction proceeds via a free radical mechanism, the reaction was performed under the same conditions with the additional presence of a radical inhibitor, hydroquinone (HQ). It is seen that under the same conditions, when the blank (i.e. sample without HQ) causes significant dissolution of gold (in ~6 h time), a little bluish solution is obtained in presence of HQ. However, in the presence of benzoyl peroxide (BP) which is known to be



(A) (B) (C)

Fig. 6. TEM photographs of: (A) Freshly prepared gold sol in TX-100 (10^{-2} M) medium; (B) Freshly prepared gold sol aggregated due to 5 min photo irradiation in the presence of $KBrO_3$ (1.2×10^{-2} M), $CHBr_3$ (2.7×10^{-3} M) and TX-100 (10^{-2} M); (C) After 15 min wait of the same aggregated gold sol as represented in B.

a radical initiator, the dissolution occurred in a faster rate. This also speaks in favor of the radical mechanism for the reaction.

The photo bleaching of gold sol, however, has a resemblance with the dissolution of gold in an organic medium, such as chloroform, which has been performed [13] in the presence of Br^-, cetylpyridinium chloride (CPC) and light. This caused the formation of the yellow colored ion-pair $[CP^+]$ $[AuBr_4{}^-]$. In that case bromine radical acted as an oxidizing agent in the presence of Br^-. The same ion pair could also be prepared by the dissolution of gold in the presence of bromine-cetylpyridinium bromide-benzene system. In the process described here, however, bromine radical possibly is not the oxidizing agent. Because, in that case Br^- in lieu of BrO_3^-, should also cause the dissolution of gold. The dissolution of gold with the evolution of the 400 nm-peak, on photo irradiation, however, could not be possible when replacement of BrO_3^- ion by Br^-, was done. In this case, the sol, although turned blue, yet no discoloration or yellow color formation took place.

4. Conclusions

Here has been described a photochemical procedure for the dissolution of gold nanoparticles prepared in TX-100 photo chemically, using BrO_3^- and either of $CHBr_3$, $CHClBr_2$, $CHCl_2Br$. The dissolution procedure described here is new and simple. In one step the dissolution could be done without applying any harsh condition. The gold forms $HAuBr_4$ after dissolution with the evolution of an absorption band at 400 nm. The peak intensity increases as the waiting time increases. With the evolution of the band at 400 nm, the plasmon band due to the gold nanoparticles is also decreased. The absorbance at either 400 or 523 nm has linear relation to the THM concentration. Thus quantification of THM is possible in very low range.

Acknowledgements

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