Effect of radiation dose on the size of bismuth particles produced by radiolysis

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Abstract. Colloidal bismuth is formed in γ-irradiated solutions , containing BiO^+, 0.2 M propanol-2 and 2×10^{-2} M of polyacrylic acid. Radiolytic reduction of these solutions produces long-lived bismuth clusters which are stabilized on the polymer chains. The clusters have a distinct absorption band at 350 nm with a tentatively assigned to Bi_n^0 or Bi_n^{x+} structures. With continued irradiation, the clusters coalesce into colloidal particles of 5 nm diameter. The absorption spectra of Bi oligomers and colloidal particles are reported as well as the optical changes accompanying their formation.

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1 Introduction

Nano materials are of great scientific interest for their unique properties and their potential for various applications, in electronics, catalysis, and biology. One of the underlying reasons is that the optical, electrical and redox properties of a metal or semiconductor can be tuned and manipulated in fascinating ways by controlling dimension rather than just composition [1,2]. Nanocrystallinebismuth has not received much attention although confinement or size reduction should lead to drastic modifications of its physical properties [3–6] as evidenced by Bi nanowires [7]. Indeed, bismuth is a metal which is slightly noble ($E^\circ(Bi^{3+}/Bi) = 0.215$ V) and is classified as a semimetal due to its small band gap $\sim$0.015 eV. Among other effects of confinement, a huge increase in magnetoresistance has been observed and it is expected that nano-Bi will behave as a semiconductor [8].

Radiolysis technique has proven to be an appropriate method of preparing size-controlled colloids [9]. Bi colloids were produced for the first time by Henglein *et al.* by radiolysis of BiO^+ aqueous solution in the presence of polyethyleneimine and were used to study reduction and catalytic reactions [10]. In the present work, we revisit the same system and investigate the influence of radiation dose on the size of the Bi colloids.

2 Experimental procedure

All chemicals were of the highest available purity from Aldrich or Acros. The materials used were $BiOClO_4$, 2-propanol (scavenger), polyacrylamide carboxyl – high modified – (PAAC) and polyacrylic acid (PAA). The solution contained $BiOClO_4$ (3×10^{-4} M), PAAC (2×10^{-3} M), PAA (2×10^{-2} M) and scavenger (0.2 M). Under these conditions the pH is naturally acid (pH $= 4$). Solutions were prepared in glass vessels with a rubber plastic septum to prevent exposure to air. Air was removed from the vessels by flushing with argon for 30 min before irradiation. The pH was adjusted with sulphuric acid and sodium hydroxide. Radiolysis was carried out using a cobalt source (2 kGy h^{-1}). The samples were characterized directly after irradiation by UV-visible spectroscopic analysis on a Varian Cary instrument and transmission electron microscopy on a JEOL instrument (200 kV).

It is well known that radiolysis of water produces the following molecular and radical species in solution [9,10]
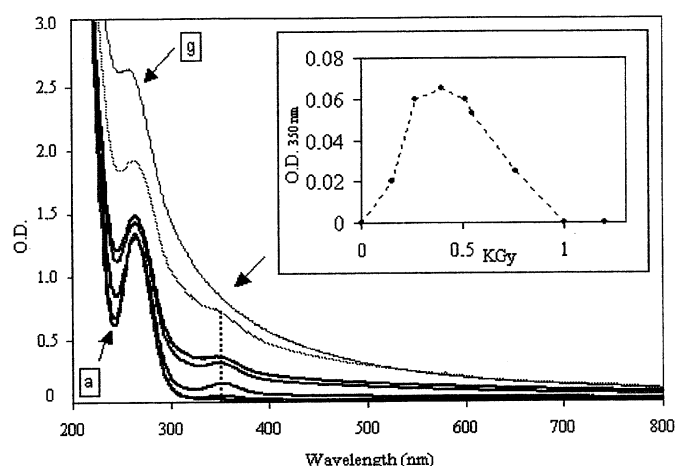
$$H_2O \xrightarrow{\gamma} e_s^-, \ OH^\cdot, \ H^\cdot, \ H_2, \ H_2O_2.$$
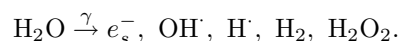
The oxidizing radicals are scavenged by 2-propanol forming $(CH_3)_2C^\cdot OH$. Both the hydrated electron and the organic radicals contribute to the reduction of the solute:

$$BiO^+ + e_s^- \rightarrow BiO$$
$$BiO^+ + (CH_3)_2C^\cdot OH \rightarrow (CH_3)_2CO + BiO + H^+.$$
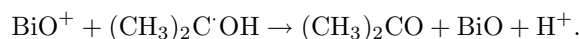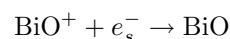
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Fig. 1. Absorption spectra of Bi colloids produced by γ-irradiation of solution containing 3×10^{-4} M of BiOClO$_4$ and 2×10^{-2} M polymer, pH = 4. Curves a–g correspond to 0, 0.05, 0.16, 0.3, 0.5, 0.6, 1 kGy respectively. Inset: evolution of the optical density at 350 nm of the same solutions irradiated as a function of the dose; optical path: 1 cm.

Then the colloid forms by coalescence *via* a multistep process or disproportionating reaction.

$$n \, \mathrm{Bi}^\circ \rightarrow \mathrm{Bi}_n.$$
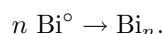
3 Results and discussion

The pure solutions containing 3×10^{-4} M of BiO$^+$ and 2×10^{-2} M of polyacrylic acid show absorption bands at 240 nm and 210 nm, respectively. However, the mixed solution displays, before γ-irradiation, an absorption band around 260 nm (Fig. 1a). This absorption band obviously arises from the complex formed from the BiO$^+$ ion and the PAA polymer. The BiO$^+$ ions are not free in polyacryl acid solution, but are present as a complex with the polymer, which is also a stabilizer of the Bi clusters. The ion BiO is coordinatively unsaturated and interacts with the lone electron pair of the nucleophilic carboxyl group on the polymer. Because this interaction is quite strong, it should have an influence on the growth of Bi clusters. Since the BiO$^+$/PAA complex has been found to be unstable in highly acidic or basic media our experiments were carried out in solutions with a pH = 4−7.

The absorption spectra of solutions after γ-irradiation with different doses are shown in Figures 1b–1g. Air was removed from the solution by evacuation before the measurements. The absorption intensity at 260 nm due to the BiO$^+$ complex decreases slightly with increasing dose, while a new absorption band at 350 nm and an increased intensity in the UV region are observed. Higher doses produce a significant increase in the absorption at longer wavelengths. After complete reduction, the spectrum has an absorption maximum at 250 nm with a long tail extending across the whole visible part of the spectrum. This final spectrum resembles the surface plasmon absorption of colloidal semi-metallic Bi, which has been previously
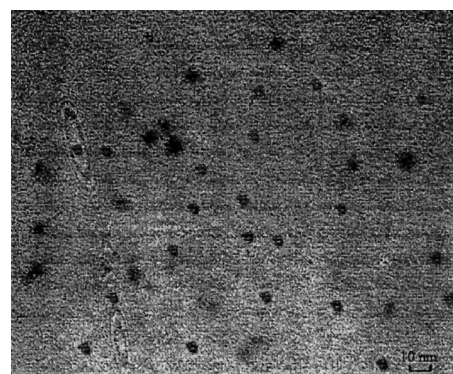
Fig. 2. Electron micrograph of irradiated sample containing 3×10^{-4} M of BiOClO$_4$ and 2×10^{-2} M polymer, pH = 4.
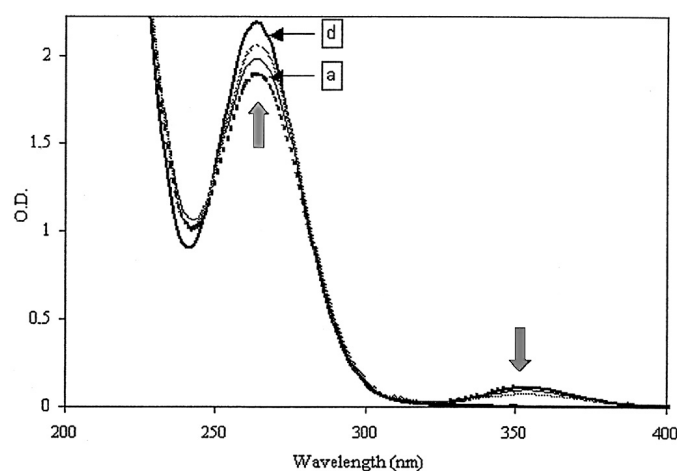
Fig. 3. Time evolution of absorption spectra of Bi clusters for the sample containing 3×10^{-4} M of BiOClO$_4$ and 2×10^{-2} M polymer, irradiated at a dose of 0.2 kGy. Curves a–d exposures to the air of: 0, 6 min; 25, and 30 min; optical path: 1 cm.

reported [10]. Assuming that all BiO$^+$ are reduced, the absorption coefficient per Bi atom is 8800 mol^{-1} l cm^{-1} at 253 nm. In Figure 2, electron micrograph of the colloidal particles are shown after complete reduction. The mean particle diameter of the sol was 5 nm.

We believe that the 350 nm band corresponds to a Bi cluster of non semi metal nature, which is a precursor of Bi colloidal particles. In the inset of the Figure 1, the 350 nm absorption intensity is plotted as a function of irradiation time. The absorption was corrected for the contribution of colloidal Bi. It can be seen that the absorbance at 350 nm first increases with the dose in the range 0−0.2 kGy and then decreases above 0.2 kGy. We conclude that, under these conditions, the Bi clusters are destroyed and yield to the formation of colloidal particles of larger size.

A cluster consisting of a small number of Bi atoms should be reactive toward oxygen. Figure 3 shows the time evolution of the absorption spectra of the sol irradiated with a dose of 0.2 kGy after exposure to air. At this dose, 15% of the BiO$^+$ is transformed into oligomer clusters. The oxidation was carried out very slowly: the vessel containing the oligomer solution was exposed to air

without shaking the solution. Under these conditions, it can be seen that the absorbance at 350 nm decreases as a function of time after the end of irradiation while the absorbance at 260 nm increases. During this evolution, an isosbestic point is observed at 280 nm between the two maxima, indicating that the Bi clusters are replaced stoichiometrically by BiO^+ complexes in presence of air. The final spectrum corresponds to the spectrum of the solution before irradiation (Fig. 1a). Further investigations are in progress in order to calculate the yield of reduced equivalents in the cluster and to determine whether the cluster consists of $(Bi°)_n$ or $Bi_x(BiO)_n^{y+}$, n being a small number. The existence of BiO is excluded since this species has previously been tabulated in the literature [10] with a maximum at 270 nm.

The formation of metal colloidal particles *via* an intermediate cluster, containing a small number of metal atoms, has previously been encountered in the literature [11,12]. In the case of silver, in the early stages of reduction, the stable clusters Ag_4^{2+} and Ag_9^+ and larger clusters, characterized by rather distinct absorption bands, are formed and accumulated in the solution before the coalescence reaction takes place. The case of palladium resembles the growth process observed here for bismuth [12]. A rather small early reduction product (Pd_2^{2+}) is stabilized, and there is no stabilization of the larger clusters which are certainly formed during the formation of the colloidal metal particles. The existence of the long-lived intermediate clusters is due to the presence of the polymer in the solution, the clusters are immobilized on the polymer chains. The high stability of the clusters towards the polymer is explained by the high coordinative unsaturation of the bismuth atoms with the O containing ligands of the polymer. A clear distinction between charged and uncharged bismuth clusters cannot be made. We favor the charged species clusters because of the stability of the cluster in the presence of excess bismuth ions in the solution. The exact size of the long-lived bismuth clusters is not known. A size determination by physical methods would be desirable.

4 Conclusion

Radiolysis of solutions containing metal ions makes it possible to regulate the generation of clusters consisting of a small number of atoms. In this work, we were able to synthesize and characterize bismuth clusters, precursor of the bismuth colloids. Further investigations are in progress in order to determine the nature and oxidation state of the bismuth in the small early reduction products observed and measure their electronic properties.

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