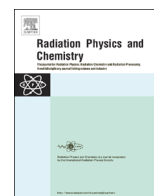




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## Controlling the size and distribution of copper nanoparticles in double and triple polymer metal complexes by X-ray irradiation

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## HIGHLIGHTS

- Cu nanoparticles were synthesized by radiation-induced reduction of Cu(II) complexed with charged polymers.
- Double complexes of Cu(II) and poly(allylamine) yielded particles with wide size distribution.
- Irradiation of triple complexes of Cu(II), PAIAm and poly(acrylic acid) resulted with very small and narrow size distribution.
- Complexation of Cu(II) with polyelectrolytes has a strong effect on the size and size distribution of Cu nanoparticles.

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## ABSTRACT

Copper nanoparticles were synthesized in double and triple polymer/metal ion complexes of poly(allylamine) (PAIAm)-copper(II), poly(allylamine)-poly(acrylic acid) (PAA)-copper(II) in aqueous solution in the presence of alcohol by irradiation with X-rays. Structural characterization of synthesized PAIAm-Cu, and PAIAm-PAA-Cu nanocomposites was carried out by transmission electron microscopy (TEM) and the radiation-induced reduction was monitored by UV–vis spectroscopy. The electron microscopy studies have demonstrated that the size of Cu nanoclusters is 2–4 nm in triple polymer metal complexes, whereas the double system yields copper nanoparticles with a very wide size distribution. The metal nature of nanoparticles was confirmed by microdiffraction measurements.

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## 1. Introduction

For more than three decades, metal nanoclusters have received increasing interest due to their unique electronic, magnetic, optical, catalytic properties and novel applications compared to their bulk forms. Noble metal nanoclusters, such as gold and silver, have been extensively studied because of their high conductivity and excellent non-oxidizing properties. Alternatively, high conductivity as much as gold and silver and low cost of copper makes it favorable for some applications. The nanoscale properties of copper significantly increase its potential application as catalyst, sensors, anti-bacterial products, etc. While extremely large surface area of copper nanoclusters provides high catalytic and chemical activity to these species, due to high surface energy of copper nanoclusters, they are not stable and can be oxidized easily. Synthesis of copper nanoclusters with controlled size, shape, and uniform dispersion in a matrix and stability has therefore been a

major challenge. Solving these problems can lead to increased varieties of the use of copper nanoclusters and maybe replacing some noble metal nanoclusters in many fields of nanotechnology (Yi Zhong et al., 2011). Prevention of coagulation as well as improvement of stability of metal nanoclusters can be achieved by using proper polymers. In particular, polyelectrolytes are convenient for this purpose (Zezin et al., 2010; Dey, 2011). Such combination allows designing advanced functional materials (Ramesh et al., 2009).

Many methods are available for the reduction of metal ions, i.e., chemical, thermal, photochemical and ionizing radiation. Among these methods ionizing radiation is the most versatile and environmentally friendly technique for the preparation of nanoclusters with adjustable size and narrow size distribution (Belloni, 2006; Joshi et al., 1998; Marignier et al., 1985). In aqueous systems, by using the radiolysis products of water namely, hydrated electrons  $e_{aq}^-$  and  $H\cdot$  radicals which are the strongest reducing agents, metal ions can be reduced easily at room temperature [ $E^0(H_2O/e_{aq}^-) = -2.87$  V and  $E^0(H\cdot/H) = -2.3$  V] Spinks and Woods, 1964. On the other hand, other major radiolysis product  $\bullet OH$  radical which is the strongest reducing agent in aqueous systems, can

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oxidize metal atoms back to metal ions. To prevent this oxidation, alcohols are generally used as scavengers of  $\cdot\text{OH}$  radicals. The resulting hydroxyalkyl radicals from alcohols have reducing properties.

In this paper, we report the synthesis of Cu nanoparticles in double and triple systems by X-ray irradiation. Double system was prepared from solutions of poly(allylamine) (PAIAm) and copper ions, and triple system was prepared from solutions of PAIAm, poly(acrylic acid) (PAA) and copper ions. The main purpose is to show the effect of polymer/Cu complexation on the size and distribution of copper nanoclusters formed in these systems.

## 2. Experimental

### 2.1. Materials

Poly (allylamine), PAIAm was obtained by deacidification of poly(allylamine hydrochloride) which has an average  $M_w$  of 15 000 and purchased from Aldrich. Poly(acrylic acid) (PAA) with  $M_w$  of 230 000, 25 wt% in  $\text{H}_2\text{O}$  and copper (II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) (99.995%) was purchased from BDH and Aldrich respectively. As a scavenging agent ethanol ( $\geq 99.8\%$ ) and for adjusting pH of the suspension formic acid (Sigma-Aldrich, 98–100%) was used. All the solutions were prepared with deionized water with a maximum conductivity 0.05  $\mu\text{S}$ .

### 2.2. Method

Polymer/metal ion double complex was prepared from the aqueous solutions of 0.3 M PAIAm and 0.15 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  by adding a few drops of formic acid to reduce pH of the solution to 4.32. Physical appearance of double complex solution is homogeneous. Molarity of polymer solutions is based on the concentration of repeating units.

To prepare polymer/metal ion triple complex, first 0.3 M PAIAm and 0.3 M PAA solutions were mixed in equimolar ratio to prepare stoichiometric interpolyelectrolyte complex (IPEC). In order to prevent the formation of large complex agglomerates, formic acid is used as a shielding solvent and pH is reduced to 3.2. Then, IPEC was mixed with 0.15 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  which formed a suspension with a pH of 3.55.

After addition of ethanol (10% by volume), double and triple systems were bubbled with pure argon and irradiated with X-rays using a 5-BKhV-6(W) tube with a tungsten anode (30 kV, 70 mA). The solutions and suspensions were irradiated in plastic cells with wall thickness of ca. 5 mm. Taking into account that half-attenuation length for the 30 keV X-rays in water is ca. 20 mm, the effect of inhomogeneous dose distribution should be relatively small. Since the absorption of X-rays in this range of photon energy is determined mainly by photoeffect, the mass absorption coefficient of copper is, at least, 50 times higher than those of light elements (Hubbel and Settler, 1996), which results in significant enhancement of the dose rate in the presence of copper ions even in relatively low concentrations. This effect was taken into account in the calculation of the absorbed dose based on ferrosulfate dosimetry carried out in the same geometry (the dose was corrected to the ratio of mass absorption coefficients of the studied system and dosimetric solution). The estimated total absorbed dose was ca. 140 kGy after 2 h of irradiation. More detailed discussion of the peculiarities of the X-ray induced radiation-chemical processes of reduction of metal ions can be found elsewhere (Feldman et al., 2013).

### 2.3. Characterization

Structural characterization of synthesized PAIAm-Cu, and PAIAm-PAA-Cu nanocomposites was carried out using Leo-912 AB OMEGA transmission electron microscopy (TEM) at a resolution of 0.3 nm. Perkin-Elmer Lambda 9 UV-visible spectrometer was used to monitor the radiation-induced transformations.

## 3. Results and discussions

$\text{Cu}^{+2}$  ions can be reduced to atoms with  $e_{\text{aq}}^-$ ,  $\text{H}\cdot$  atoms and  $\text{CH}_3\cdot\text{CHOH}$  radicals resulting from ethanol due to reactions with  $\cdot\text{OH}$  radicals (and partially with  $\text{H}\cdot$  atoms). This is a two-stage process yielding first  $\text{Cu}^+$  and then neutral Cu atoms (more details of the mechanism were presented by Ershov (1994)). Fast reactions between copper atoms and copper ions result in formation of metastable copper nanoclusters  $\text{Cu}_n^{m+}$  ( $m < n$ ). These clusters are charged species and consequently polymers containing ionogenic groups in polar media are effective stabilizers for the metal nanoparticles and charged species (Zezin et al., 2010). Chain structure and properties of functional groups of polymers affect size and distribution of metal nanoclusters in polymers. Most commonly, metal nanoclusters are stabilized with one kind of polymer and form double polymer metal complex between polymer and metal nanoclusters, Poly(vinyl alcohol) (PVA) (Rozra et al., 2012); poly(ethylene imine) (PEI) (Kislenko and Oliylyk, 2002) and poly(acrylic acid) (PAA) (Xu et al., 1998) are some of the polymers used for this purpose. Furthermore, IPEC prepared by two oppositely charged polymers can be also used as a chelating ligand such as PAA-PEI (Zezin et al., 2007); Poly(1-vinylimidazole)-poly(methylmethacrylate) (Andersson et al., 2011). In this work, we prepared double polymer/metal ion complex system from the solution of PAIAm-Cu(II) and triple polymer/metal ion complex system from a mixture of solutions of PAIAm-PAA-Cu(II) and then irradiated in aqueous-alcohol mixture by X-rays at room temperature. PAIAm was used for the first time in this work as a chelating ligand which has a primary amine functional group in the side chain.

In the case of double systems, Cu ions are complexed due to interaction with the lone pairs of nitrogen atoms of PAIAm. The stable configuration of the complexes includes four nitrogen atoms (four amino groups) coordinated with one  $\text{Cu}^{2+}$  ion. Binding of copper ions is confirmed by optical absorption measurements, which demonstrate a characteristic intense absorption band with maximum at ca. 780 nm (note that aqua complex of  $\text{Cu}^{2+}$  have much weaker absorption shifted to the red). The optical absorption remains virtually unchanged under different ratios of copper ions and amino groups (1:2 and 1:4), which indicates similar nature of the complex. Meanwhile, at relatively high content of  $\text{Cu}^{2+}$  ions used in this work ( $[\text{Cu}^{2+}]/[-\text{NH}_2]=1:2$ ), one should expect that a considerable part of copper ions exists in a “free” form (that is, in the form of aqua complexes). On the other hand, triple complex ligand environment includes functional groups of both polymers, as shown in Scheme resulting in a stronger binding and more compact structure. Scheme 1

For both double and triple systems irradiation leads to effective reduction of copper ions as evidenced by dramatic change in the sample color from blue to red and decay of absorption at 780 nm. TEM pictures taken from the double and triple complexes irradiated to 140 kGy are shown in Figs.1 and 2, respectively. The TEM image obtained for double system (Fig. 1) demonstrates formation of both small and large nanoparticles. Furthermore, other fragments of the same sample revealed even larger particles ( $> 100$  nm). Thus, for this system we have a very wide size distribution of nanoparticles (from 1–2 nm to colloidal metal).

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