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Spatial organization of a metal–polymer nanocomposite obtained by the radiation-induced reduction of copper ions in the poly(allylamine)–poly(acrylic acid)–Cu^{2+} system

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The X-ray-induced reduction of Cu^{2+} ions in aqueous–alcoholic suspensions containing poly(allylamine) and poly(acrylic acid) leads to a specific microheterogeneous structure with microdomains (100–200 nm) enriched by small copper nanoparticles (2 to 4 nm), which are dispersed in a continuous matrix.

The design of nanocomposites with tunable size and spatial distribution of nanoparticles is of key importance for functional properties of such materials. The radiation-chemical reduction of metal ions is a powerful tool for the preparation of metal nanoparticles and functional nanocomposites for various prospective applications.[1–7] Recently,[6,8] we have introduced a novel approach to a single-stage fabrication of metal–polymer nanocomposites by radiation-chemical technique, starting from films of triple interpolyelectrolyte complexes of poly(acrylic acid) (PAA)–poly(ethylene imine) (PEI)–metal ion, which are swellable in aqueous solution. Further investigations revealed wide opportunities for obtaining metal–polymer nanocomposites with various spatial distributions of nanoparticles from such systems using X-ray irradiation.[8–10]

Here we present the preliminary results of studies of the X-ray induced reduction of copper ions in solutions of poly(allylamine) (PAlAm) and mixed triple systems PAlAm–PAA–Cu^{2+}, which demonstrated the formation and specific organization of copper nanoparticles in microheterogeneous systems. Note that the triple systems were found to form relatively stable suspensions under weakly acidic conditions, when cooperative interaction between polyanion and polycation are suppressed. In this case, the samples contain labile complexes between certain amino groups and acrylate groups (partial ‘zipping’), which is somewhat different from completely zipped polyelectrolyte films used previously.[6,8–10]

The experimental approaches were described in detail elsewhere.[6] The solutions of 0.3 M PAlAm [obtained by deacidification of poly(allylamine hydrochloride) having average M_w of 15000] containing 0.15 M Cu^{2+} (pH 7.9) ions in aqueous–alcohol mixture (10% ethanol) and suspensions of triple systems (0.3 M PAlAm–0.3 M PAA–0.15 M Cu^{2+}, pH 3.55) 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). Molarity of polymer solutions is based on the concentration of repeating units. The solution and suspensions were irradiated in plastic cells with thin walls and a layer thickness was ~5 mm (note that a half-attenuation length for the 30-keV X-rays in water is ~20 mm, that is, the effect of inhomogeneous dose distribution should be relatively small). The irradiation time varied from 1 to 120 min. The reduction of copper ions and formation of nanoparticles after irradiation were monitored by optical absorption spectroscopy and transmission electron microscopy (TEM).

The basic mechanism of reduction of copper ions and formation of nanoparticles upon irradiation of PEI solutions was described previously.[2,7] Generally speaking, irradiation of aqueous solutions in the absence of oxygen leads to formation of both reducing species (hydrated electrons e^-_aq and H atoms) and a strong oxidizer (OH radicals). In the presence of alcohol, OH radicals are converted to hydroxyalkyl radicals with reducing properties ($\text{CH}_3^\bullet\text{CHOH}$ in the case of ethanol) due to hydrogen abstraction reaction. All the reducing radicals (e^-_aq, H and $\text{CH}_3^\bullet\text{CHOH}$) can react with Cu^{2+} to yield Cu$^+$ ions. The crucial step in preparation of metal copper nanoparticles is the formation of neutral copper atoms (Cu^0) from Cu$^+$ in a bulk solution, which occurs only due to reaction with the strongest reductant (e^-_aq).[2] Further processes include formation of clusters Cu_n^{m+} and, finally, metal nanoparticles with surface charge stabilized by interaction with polyelectrolytes (the nucleation and particle growth in interpolyelectrolyte complexes were considered previously[6,9,10]). In line with results reported for dilute solutions of PEI–Cu^{2+},[2] the present optical absorption studies demonstrate reduction of Cu^{2+} ions (decrease of strong absorption with maximum at ~260 nm) at early stages of the process (1–3 min). Prolonged irradiation (up to 1–2 h) of solutions containing PAlAm leads to formation of nanoparticles (an intense band at ~570 nm with a shoulder in the range of 400–450 nm, similar to those observed previously[2]). It is difficult to obtain quantitative optical absorption data for the triple systems (suspensions) because of very strong scattering of the samples; however, the radiation-induced color change is similar to that observed for solutions. The formation of relatively small nanoparticles was determined by TEM in the samples irradiated for 2 h, both for solutions (PAlAm only, nanoparticle diameter of 2 to 6 nm) and suspensions (PAlAm + PAA, nanoparticle diameter of 2–4 nm). The microdiffraction data show reflexes of metal copper (broadened due to lattice imperfection), which confirms the identity of nanoparticles.

Meanwhile, the most striking result (which is the focus of this communication) is concerned with specific spatial organization of nanoparticles observed in the irradiated triple system. As demonstrated in Figure 1, in addition to formation of small

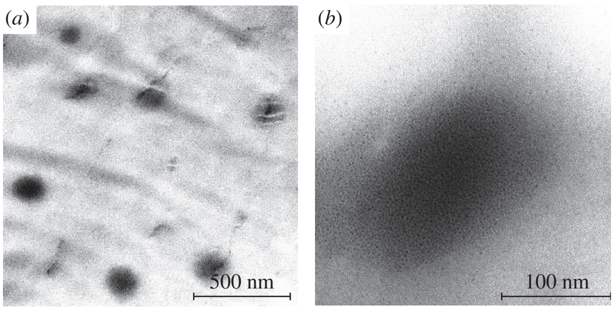

Figure 1 (*a*) TEM images of the nanocomposite obtained after irradiation of aqueous–alcoholic suspension containing PAlAm, PAA and copper ions by X-rays for 120 min (see text for details); (*b*) enlarged view of a copper-rich microphase.

primary particles, the irradiated sample also reveals a secondary microdomain structure with a domain size of 100–200 nm, so it can be described as a double-phase microheterogeneous system. The dispersed microphase is densely filled with small metal nanoparticles, while the second microphase forming a continuous matrix [Figure 1(*a*)] is almost free of these inclusions. The reason for this behavior may be explained by the effect of specific interaction of PAA anions with positively charged surface of copper nanoparticles demonstrated in our recent IR-spectroscopic studies of nanoparticles stabilized in interpolyelectrolyte films.[10] In this case, we may suggest that the microphase enriched by nanoparticles is actually formed mainly by PAA molecules bound to copper nanoparticles owing to ionic interactions. On the other hand, it is logical to assume that the domains with low content of nanoparticles are formed mainly by PAlAm macromolecules. The macroscopic phase separation is prevented by existence of partial zipping between PAlAm and PAA macromolecules due to ionic interactions.

Thus, in the case of triple system (PAlAm–PAA–Cu^{2+}), we have obtained a sort of hierarchic nanocomposite with a two-level organization. This type of structure can be compared with that obtained using amphiphilic block copolymers as templates for synthesis of nanoparticles,[11–13] and it may present a considerable interest for various potential applications.

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