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A one-pot radiation-chemical synthesis of metal-polymeric nanohybrides in solutions of vinyltriazole containing gold ions

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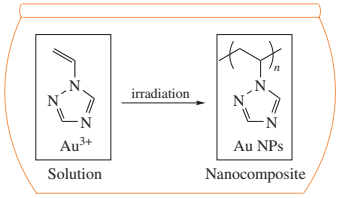
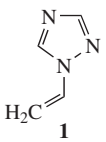
The X-ray irradiation of aqueous solutions containing 1-vinyl-1,2,4-triazole (monomer) and gold ions results in simultaneous polymerization and formation of nanoparticles, which provides a single-step preparation of metal-polymeric nanohybrids.



Metal-polymeric nanohybrids are promising materials for the design of functional devices. A major challenge in the synthesis of nanocomposites with tailor-made properties is to control the size and spatial distribution of nanoparticles. Attention has been focused on the development of methods for obtaining functional nanocomposites with desired structures.[1–5]

Recently, different techniques for the reduction of metal ions in polymer systems were actively developed for one-stage preparation of composites with metal nanostructures.[6–8] The radiation-initiated reduction of metal ions is an environmentally friendly and universal approach to the synthesis of nanoparticles with controlled sizes.[9,10] On the other hand, ionizing radiation is widely used to initiate polymerization. Thus, in principle, it is possible to prepare metal-polymeric nanohybrids by a radiation-chemical method *via* simultaneous polymerization and reduction in systems containing monomers and metal ions. However, to the best of our knowledge, this approach has not been implemented so far.

Here, we report preliminary results of a single-stage radiation-chemical synthesis of metal-polymeric nanocomposites in solutions containing a 1-vinyl-1,2,4-triazole monomer **1** and metal ions (Au^{3+}).



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Gold nanoparticles possess prominent optical, conductive, bactericidal and catalytic properties. Radiation-chemical approaches are extensively used to synthesize gold nanoparticles.[10] Poly-1-vinyl-1,2,4-triazole is a nontoxic polymer, resistant to aggressive media. This polymer is prepared by the radical polymerization of compound **1** using azobis(isobutyronitrile) as an initiator.[11]

The size of nanoparticles formed during the reduction of metal ions is determined by the interaction of functional groups of polymers with their surface.[12] An increase in the interaction energy between macromolecules and nanoparticle surfaces leads to the formation of smaller nanoparticles. The conditions of the interactions with nanoparticle surfaces can be varied by changing the pH of the medium.[5]

The metal-polymeric nanohybrides were synthesized in a 0.01 M solution of **1** at a 25 : 1 molar ratio between compound **1** and chloroauric acid ($HAuCl_4 \cdot 3H_2O$). The samples were irradiated in a 10% ethanol–water mixture using an X-ray irradiator with a 5-BKhV-6 tube with a tungsten anode (30 kV, 70 mA) in plastic cells with thin walls 5 mm in diameter. Such conditions ensured an essentially uniform generation of radiolysis products in the irradiated sample volume. This irradiation technique has been successfully used for the synthesis of nanoparticles in aqueous solutions and polymer dispersions.[13–15]

Radiation-chemical transformations in aqueous solutions are mainly due to the indirect effect of irradiation on the solvent, which implies the reactions of reactive solvent radiolysis products initiating the polymerization and reduction of metal ions. The major intermediates of water radiolysis are reducing active species (hydrated electrons and H atoms) and OH radicals, which are strong oxidants. The introduction of alcohol additives ensures the complete scavenging of OH radicals to generate hydroxyalkyl radicals (MeCHOH in the case of ethanol), which are reducing agents that can initiate radical polymerization.[16] The mechanism of the radiation-initiated formation of gold nanoparticles at various pH values has been discussed in detail previously.[17]

The UV-VIS optical spectroscopy data demonstrated that an increase in the irradiation dose at pH 6.0 and 3.6 for 1-vinyl-1,2,4-triazole **1** solutions containing gold ions led to a gradual decrease in an absorption band at 226 nm due to the double bond in the monomer molecules. In the sample irradiated to a dose of 5 kGy, this band was not observed because of the completion of 1-vinyl-1,2,4-triazole polymerization [Figure 1(*a*)]. In addition, the spectra of samples irradiated to 1 kGy revealed a plasmonic absorption band of gold nanoparticles with a maximum at 534 nm [Figure 1(*b*)]. The X-ray diffraction patterns of the irradiated

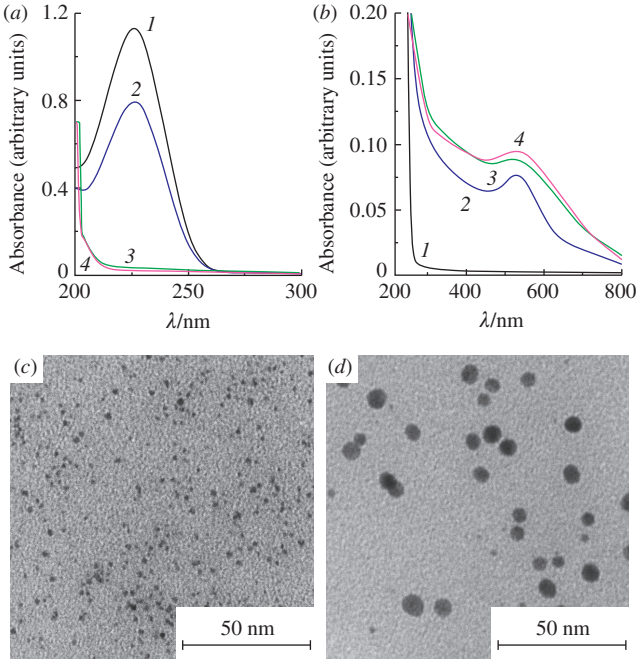

Figure 1 (*a*) Optical absorption spectrum of the Au^{3+}/**1** solution irradiated to different doses and diluted by a factor of 500: (*1*) initial sample, (*2*) 1 kGy, (*3*) 5 kGy, and (*4*) 10 kGy demonstrating conversion of monomer under irradiation; (*b*) spectrum of the undiluted sample with the formation of gold nanoparticles; (*c*) TEM image of the sample irradiated to 10 kGy at pH 3.6; and (*d*) TEM image of the sample irradiated to 10 kGy at pH 6.0.

samples exhibited reflections corresponding to interplanar distances of 2.35, 2.00, 1.44 and 1.22 Å due to the formation of particles with a crystal lattice of metallic gold. The optical signal intensity of the gold nanoparticles reached a maximum in the samples irradiated to a dose of 10 kGy.

The interaction of nitrogen-containing functional groups of macromolecules with the surface of clusters and nanoparticles in the course of their formation made it possible to control the size of the latter. Micrographs of the samples irradiated to a dose of 10 kGy at pH 3.6 and 6.0 demonstrated the presence of nanoparticles with sizes 1–4 and 2–12 nm, respectively [Figure 1(*c*),(*d*)].

It is well known that, when chloroauric acid is used as a precursor for the synthesis of nanoparticles, they acquire a negative charge due to the sorption of chloride ions on the surface.[18] To evaluate the degree of protonation, we have carried out comparative measurements of pH in aqueous solutions containing only sulfuric acid and in solutions containing both sulfuric acid and polyvinyltriazole over a wide range of acid concentrations. The degrees of protonation of the functional groups of polyvinyltriazole at pH 6.0 and 3.6 were about 0 and 40%, respectively. At pH 3.6, the average diameter of nanoparticles was 2 nm, whereas larger particles with an average diameter of 7 nm were formed at pH 6.0.

Thus, an increase in the positive charge density on a macromolecular chain resulted in a higher efficiency of the interaction with the surface of nanoparticles and led to their stabilization at earlier stages of nanoparticle formation. The experimental results showed the possibility of the one-stage synthesis of metal-polymeric nanohybrids in irradiated solutions of 1-vinyl-1,2,4-triazole–gold ions. The effective interaction of the monomer and the functional groups of resulting macromolecules with gold nanoparticles makes it possible to control their sizes and to obtain a uniform distribution of nanoparticles in the bulk of the polymer matrix.

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