Synthesis of Chitosan-Stabilized Au Nanoparticles with Controllable Sizes

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Abstract—Au nanoparticles stabilized by chitosan have been prepared under the combined action of ultraviolet radiation and thermal exposure of its solutions doped with HAuCl\textsubscript{4}. With the use of absorption spectrophotometry and small-angle X-ray scattering, it has been shown that the use of chitosan of different molecular masses allows one to control both the sizes of Au particles and their aggregative stability in nanodispersions.

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INTRODUCTION

The manufacture of composite materials based on polymers containing nanosized particles of noble metals, particularly gold, is an urgent present-day task. The increased interest in the formation of nanosized particles embedded into a polymer matrix is associated with their unusual chemical and physical properties, namely, catalytic, electric, optical, and magnetic. This circumstance makes it possible to employ these particles in a great variety of application areas [1]. The most widely used methods of preparing such composites include the introduction of metal-containing precursors into a polymer solution or the addition of these precursors in the course of polymerization accompanied by reduction as well as the polymerization of monomer blends with metal nanoparticles preformed therein. The reduction is usually performed by heating metal compounds or introducing chemical reducing agents, such as sodium tetrahydroborate, citric acid, or other organic compounds [2].

As is known, the size and dispersity of nanoparticles and the time stability of the structure and properties of the related composites may be governed by varying the nature of a stabilizer, i.e., by a polymer matrix [3–5]. Considerable recent attention has been focused on the synthesis of composites containing nanoparticles of metals, such as Au, Ag, Pt, and Pd, stabilized by dendrimers [6, 7]. From the viewpoint of feasible practical applications, the synthesis of nanocomposites with the use of the natural polysaccharide—poly(1,4-2-amino-desoxy-\(\beta\,D\)-glucose)—seems to be prospective. Glucosamine, the repeating unit of chitosan, functions as a reducing agent. This allows one to synthesize nanosized metal particles, particularly noble metals, in the absence of additional reducing agents [8–10]. The presence of hydroxyl, amino, and ester groups, which determine high chelate-forming properties, ensures the stabilization of the particles being formed. The absence of toxicity, hypoallergeny, and biocompatibility in this polymer make it possible to use composites on its basis in biotechnology, whereas resistance to laser radiation offers prospects for photonic applications. In addition, the reactive groups of chitosan allow (with the structure of the backbone being preserved) preparation of various chitosan derivatives via modification either through polymer-analogous transformations or through depolymerization giving rise to oligomers.

The purpose of this study is to gain insight into the effect of the molecular mass chitosan on the size distribution and aggregative stability of gold nanoparticles in nanodispersions prepared under UV irradiation of chitosan solutions doped with HAuCl\textsubscript{4}. Small-angle X-ray scattering and absorption spectrophotometry were used as investigation techniques.

EXPERIMENTAL

Two series of experiments were performed in this study. First, the effect of chitosan molecular mass on the size of the formed nanosized particles was examined and, second, the effect of the polymer-to-dopant ratio was investigated. In the first series, the formation of nanoparticles was carried out in aqueous solutions of...
chitosan and its oligomer doped with hydrogen tetrachloroaurate (HAuCl₄, 1 wt %), as well as in a solution containing the aliquot mixture of chitosan and its oligomer solutions. Chitosan and its oligomer with \( M_n = 7.8 \times 10^4 \) and \( 4 \times 10^3 \), respectively, were used; the deacetylation degrees were equal and comprised 80%. In the second series of experiments, the solutions of high-molecular-mass chitosan of the constant concentration (3 wt %) doped with HAuCl₄ with a concentration of 0.125–2.0 wt % with respect to chitosan were prepared.

Nanoparticles of gold were obtained under UV irradiation with subsequent thermal treatment of solutions doped with HAuCl₄ at 80°C. The nucleation and growth of gold nanoparticles were monitored by measuring a change in the extinction of the samples in UV and visible spectral regions. The spectra were taken on a UV-1650 (Shimadzu) spectrophotometer operating in UV and visible regions.

The size and polydispersity of the nanosized particles were estimated by the method of small-angle X-ray scattering. This method is used to study the structure of highly dispersed systems of different natures when the sizes of scattering heterogeneities fall in the range of \( \sim 2–100 \) nm \([11, 12]\). To register X-ray patterns, a KRM-1 setup was employed with the collimation of the primary beam according to the Kratky scheme; \( \text{CuK}_\alpha \) radiation (\( \lambda = 1.54 \) Å) monochromated by an Ni filter was used and the intensity of the scattered radiation was measured within the angular range \( \theta = 5'–160' \). Because it is nondestructive, the method of small-angle X-ray scattering allows one to examine samples in the form of films, thin plates, or solutions. The well-developed theory of small-angle X-ray scattering \([11, 12]\) allows one to calculate the structural characteristics of highly dispersed systems and, in particular, the factor of shape of scattering heterogeneities \( f \) that characterizes the shape of particles and the size distribution function \( p(l) \) \([13, 14]\). For a particle of an arbitrary shape, \( f \) is the ratio of the radius of gyration to the radius of gyration of a sphere with the same volume. The greater the degree of anisometry of particles (at a constant volume), the larger the radius of gyration and the more pronounced the deviation of \( f \) from unity. For polydisperse systems in which the shape of particles is close to spherical, the values of the shape factor are in the range 0.5–1.0. The shape factor and the distribution function were estimated according to the following formulas (1) and (2), respectively:

\[
f = \frac{\pi AE}{16Q}, \tag{1}
\]

where \( E = 2\pi \int_0^\infty s i(s)ds, \ Q = \int_0^\infty s^2 i(s)ds, \ A = \lim_{s \to \infty} s^4 i(s), \ s = 4\pi \sin \theta/\lambda \) is the modulus of the vector of reciprocal space; and \( i(s) \) is the intensity of the scattered radiation;

\[
p(l) = \int_0^\infty K(s, l) i(s)ds \tag{2}
\]

where \( K(s, l) \) is an operator containing the Fourier transform.

RESULTS AND DISCUSSION

The kinetics of the formation of gold nanosize particles was monitored from the appearance of the absorption band in the visible spectral region that corresponds to the plasma resonance of the nanoparticles being formed \([15]\); this band is absent in the spectra of initial chitosan solutions doped with HAuCl₄. Figure 1 demonstrates the absorption spectra of nanocomposite solutions. As is seen, on passage from the oligomer solution (520.5 nm) to the solution of a high-molecular-mass chitosan (523.5 nm), the absorption maximum shifts toward the long-wave region. It is known \([15, 16]\) that the position of the absorption maximum shifts to longer wavelengths with an increase in the average size of particles. This effect allows one to infer that coarser nanoparticles formed in the solution of the high-molecular-mass chitosan as compared with those prepared from the oligomer solution.

Furthermore, we studied the influence of the polymer-to-dopant (HAuCl₄) ratios on the size of gold nanoparticles. The solutions of nanocomposites were characterized by the appearance of the absorption band in the visible spectral region. The wavelengths of the absorption maxima and the corresponding average