



Synthesis and Study of PNIPAM Nanogels Incorporated with Colloidal Silver

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(Received 08 May 2013; published online 30 August 2013)

Composite nanoparticles consisting of polymer gels with incorporated silver nanoparticles have been synthesized. The synthesis comprises two main stages. Initially, monodisperse hydrogel particles with a controlled diameter of approximately 500 nm are obtained by N-isopropylacrylamide polymerization. Then, silver ions are reduced on the surface of the polymer network. Variations in the concentration ratio between reductants and silver nitrate make it possible to produce silver nanoparticles with sizes in a range of 10-30 nm and different packing densities on the gel particle surface. The resultant nanocomposites have been studied by transmission electron microscopy, spectrophotometry, and dynamic light scattering. Depending on the size and packing density of the silver nanoparticles on the polymer particle surface, the plasmon resonance of the nanocomposites varies in a range of 420-750 nm, which determines variations in the color of the colloid from yellow, orange, and red to blue and blue-green. After the inclusion of silver nanoparticles, nanogels of poly(N-isopropylacrylamide) retain their capability for thermosensitive phase transition with a lower critical mixing temperature of 31 °C.

Keywords: Nanogels, Silver nanoparticles, Swelling

PACS numbers: 62.23.St, 42.70.Jk

1. INTRODUCTION

Polymer hydrogels are porous materials that are swelling but insoluble in water [1]. When gel particles in colloids have micron or submicron sizes, the gels are commonly referred to as microgels [2] or nanogels [3]. At present, particular interest is focused on nanogels formed from so-called smart polymers [4, 5], which can change their swelling index with changes in ambient parameters, such as temperature, pH, or chemical composition [1, 5-7]. Such colloids are widely used as the platforms for target drug delivery [2, 8-10], as well as for the production of biosensors [11, 12] and composite nanomaterials [13, 14]. There are many polymers, primarily substituted derivatives of polyacrylamide, the lower critical temperature of which lies in a temperature range of 9-85 °C [15, 16, 17]. One of the most extensively studied thermosensitive polymers is poly(N-isopropylacrylamide) (PNIPAM), the phase transition temperature of which is 31-32 °C. Composite nanostructures representing metal nanoparticle containing polymer gels occupy a special place among modified nanogels. This nano technological approach enables one to combine the unique optical properties of metal based colloids and the physicochemical features of nanogels in the same structure. For example, in [18], silver nanoparticles were coated with a poly(N-isopropylacrylamide) shells containing incorporated insulin. The resonance scattering of silver nanoparticles served for determining glucose concentration, while conformational transformation of nanogel macromolecules was used for controlled release of insulin. Another significant group of studies deals with the photothermal properties of metal nanoparticles that are used as ingredients of composites [20-25]. Usually, the studied composites consist of gold nanorods exhibiting plasmon resonance

in the region in which biological tissues and thermosensitive nanogels are transparent. The combination of photothermal heating of gold nanorods and the thermosensitive phase transition of a nanogel makes such structures efficient for laser photolysis [20-22] and photosensitive delivery of drugs [25] or nanoparticles themselves [23]. Finally, studies [26, 27] have been recently published in which such nanocomposites were used to capture targeted molecules in the course of their investigation by giant Raman scattering (amplification on gold nanoparticles inside a gel).

There are three basic laboratory approaches to obtaining composite materials consisting of metal particles and PNIPAM. The first one is based on radical precipitation polymerization on the surface of plasmon resonant nanoparticles. A much simpler method of nanocomposite production was proposed in [20]. Since PNIPAM particles are charged negatively at pH 3-10, they can adsorb any positively charged nanoparticles, e.g., gold nanorods, due to electrostatic interactions. Finally, the third method entails chemical synthesis of metal nanoparticles in a preformed gel. At present, this method is, as a rule, used for the synthesis of bulky samples [21, 28], and there are few publications concerning the production of nanocomposites containing gold nanoparticles in this way [29]. This study is devoted to the development of a methodology for synthesis of PNIPAM nanogels containing silver nanoparticles of different sizes and investigation of the optical properties of such nanocomposites in relation to their composition and temperature.

2. MATERIALS AND METHODS

The following reagents and materials were used in this study: silver nitrate (> 99.9%), isopropylacrylamide

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(NIPAM), NN-methylenebisacrylamide (MBA), acrylic acid, isoascorbic acid, sodium borohydride, ammonium persulfate (all produced by Sigma-Aldrich and used as received), compressed argon (99.99 %), and MilliQ water. Poly(N-isopropylacrylamide) gel particles were synthesized as was described in detail in our recent publication [30]. In a typical synthesis protocol, water (50 mL) was placed into the flask and NIPAM (0.5 g), MBA (0.04 g), and acrylic acid (30 mL) were added. The flask was thermostated at 70 °C, while the reaction mixture was stirred (300 rpm) for 30 min. Then, an aqueous 0.074 M ammonium persulfate solution (2 mL) was added in order to initiate polymerization. The reaction was performed at 70 °C under argon for 4 h, during which the colorless solution became milk-white, which evidenced the formation of colloidal particles of PNIPAM. In order to obtain nanogels containing silver particles of different sizes, a 10 mg/mL AgNO₃ solution (0.05, 0.1, 0.2, 0.5, 1, or 2 mL) was added to the nanogel (4 mL). A reaction mixture was incubated for 30 min at room temperature; then, a 100 mM ascorbic acid solution (10 mL) was added, and the mixture was incubated for 20 min until it acquired a yellowish tint.

At the final stage of the synthesis, water (20 mL) and a 25 mM sodium borohydride solution (50 mL) were added to the colloid under intense stirring. During subsequent 5-10 min, the colloid acquired a yellow, orange, red, blue, or blue-green color, depending on the amount of silver nitrate added to the system. The resultant composite nanogels were centrifuged at 4000 rpm for 5 min and redispersed in water (10 mL). This procedure was repeated five times to completely remove unbound particles.

The samples were studied by transmission electron microscopy (TEM) using a Libra 120 microscope (Carl Zeiss). The geometrical parameters of the nanocomposites and the temperature dependence of the diameter of swollen gel particles were determined using a Malvern Zetasizer Nano ZS system for dynamic light scattering under standard conditions of signal accumulation and processing. Absorbance spectra of the samples were measured in 2-mm quartz cells using a Specord 250 spectrophotometer (Analytik Jena) in a wavelength range of 320-1000 nm.

3. RESULTS AND DISCUSSION

3.1 Nanocomposite Synthesis

The protocol of the synthesis of PNIPAM gel particles based on N-isopropylacrylamide polymerization is well known and has been described in many publications [10, 16, 31, 32]. According to [20], the concentrations of the monomers and polymerization initiator used in this study ensure the formation of a monodisperse colloid with a particle size of about 500 nm and their number concentration of about $7.5 \times 10^8 \text{ mL}^{-1}$. Fig. 1 shows the TEM images of the synthesized PNIPAM nanogel. The analysis of the images has shown that the gel particle size is $360 \pm 20 \text{ nm}$. It should be noted that this size value refers to the sample dried in vacuum, and it can be significantly different from the gel particle size in an aqueous medium.

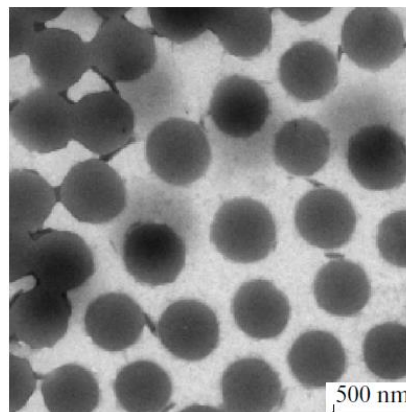


Fig. 1 – TEM image of PNIPAM gels particles

The second stage of the composite nanogel synthesis is the targeted reduction of silver ions on the surface of the polymer network. The key moment of this procedure is the creation of the conditions for preferable silver reduction inside or on the surface of polymer gel particles rather than in the free bulk (dispersion medium). A similar problem is relevant to the synthesis of metal nanoshells on dielectric cores [33, 34].

Positively charged silver ions are adsorbed due to their electrostatic interaction with the dissociated carboxyl groups of acrylic acid added as a comonomer into the reaction mixture in the course of nanogel synthesis. The yellowish tint, which the AgNO₃ containing dispersion acquires in a time after the addition of ascorbic acid, is associated with the reduction of Ag⁺ ions; the nucleation of metal nanoparticles starts already during the 20 min incubation of the dispersion containing gel particles, silver nitrate, and ascorbic acid. The subsequent addition of sodium borohydride leads to more complete and rapid reduction of silver ions observed as the formation of larger metal particles (as large as 30 nm). In addition, we have experimentally revealed that the system dilution before the addition of sodium borohydride yields colloids with different colors.

The formation of silver particles on the surface of gel particles (confirmed by TEM analysis) evidences that silver ions do remain on the surface and, possibly, inside the gel particles for, at least, several seconds, which are necessary for the addition of the reductant.

The subsequent washing of the composite nanogel by centrifugation at a low acceleration and redispersion in water almost completely removes free silver particles. According to the ratios between the optical densities of supernatants and redispersed sediments of particles, the fraction of the precursor adsorbed by gel particles varies from 10 to 70 % for different samples.

Fig. 2 depicts the survey and magnified TEM images of composite nanogels synthesized by the reduction of silver ions at AgNO₃/gel ratios of (a) 0.125, (b) 0.5, and (c) 2.5 mg/mL. Obviously, silver particles formed on the polymer network have different sizes and packing densities depending on the amount of silver nitrate added to the gel.

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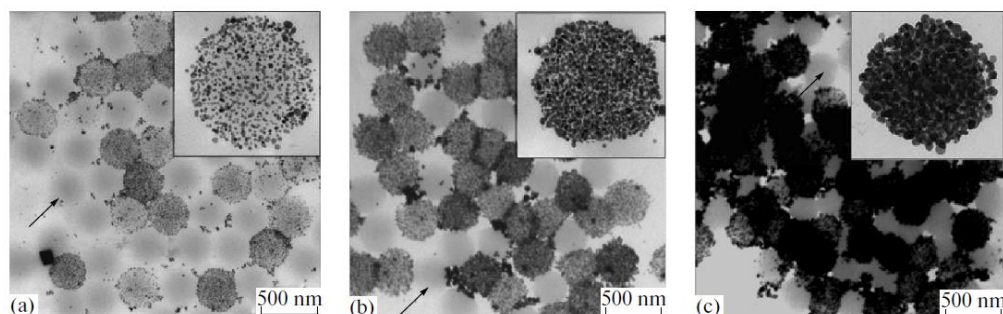


Fig. 2 – Survey and (insets) magnified TEM images of composite nanogels obtained by the reduction of silver ions on the surface of PNIPAM nanogel at AgNO_3 / nanogel ratios of (a) 0.125, (b) 0.5, and (c) 2.5 mg / mL

gel. In particular, at the lowest concentration of silver nitrate (Fig. 2a; 10 mg/mL AgNO_3 solution (0.05 mL) and nanogel, (4 mL), the average particle size is 10 nm, while the interparticle distance is much larger. A densely packed array of silver particles with an average size of 30 nm is formed at the highest concentration of silver nitrate (Fig. 2c).

3.2 Extinction Spectra of the Composite Nanogels

Fig. 3 illustrates the experimental extinction spectra of the composite nanogels containing different amounts of silver nanoparticles with different sizes. At the lowest amount of the reduced silver, the spectrum has a maximum at 420 nm (Fig. 3, curve 1). The shape of the spectrum and the half-width of the band with the maximum at 420 nm somewhat differ from those observed for typical silver colloids and correspond to the superposition of the absorbance spectra of small silver nanoparticles and submicron particles of the PNIPAM gel. The situation changes with an increase in the size and packing density of silver nanoparticles

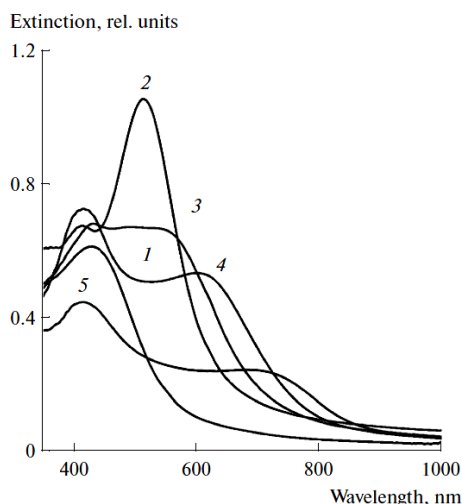


Fig. 3 – Extinction spectra of composite nanogels obtained by the reduction of a 10 mg/mL AgNO_3 solution ((1) 0.05, (2) 0.1, (3) 0.2, (4) 0.5, and (5) 1 mL) in the presence of PNIPAM nanogel (4 mL)

occurring on the polymer network (Fig. 3, curves 2-5). The growth of the amount of reduced silver nitrate leads to the appearance of a second maximum (or an inflection) in the composite gel spectrum in addition to

the short wavelength maximum at approximately 420 nm, with the new maximum corresponding to the optically interfering particles and collective electron oscillation. The position of this maximum shifts from 520 to 750 nm with the growth of the packing density of silver nano particles.

3.3 Temperature Dependent Phase Transition in the Nanogels

Temperature dependence of the diameter of swollen gel particles was investigated by dynamic light scattering. Fig. 4 exhibits the temperature dependences of the diameters of swollen particles for a PNIPAM gel and a composite nanogel in a range of 20-45 °C. It can be seen (curve 1) that the average hydrodynamic size of PNIPAM particles is 520 nm at 20-25 °C and 270 nm at 35-45 °C. These data confirm the above assumption that the size of the gel particles (about 400 nm) determined by TEM is “intermediate” or, to be more precise, somewhat underestimated, because dried particles have been examined with the microscope. The critical temperature of the polymer nanogel shrinkage is 31 °C.

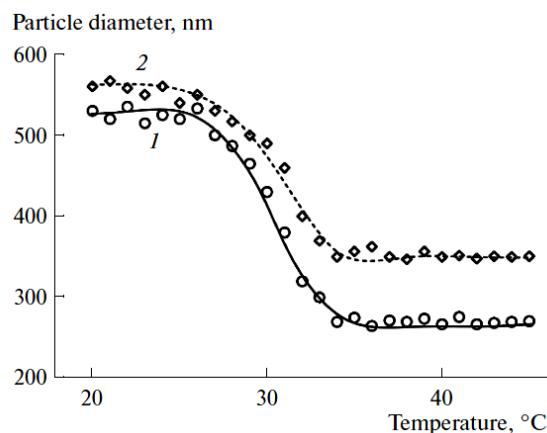


Fig. 4 – Temperature dependences of hydrodynamic particle diameters of (1) PNIPAM nanogel and (2) composite nanogel containing silver nanoparticles

Fig. 4 also shows a similar temperature dependence of the particle diameter of a composite nanogel containing silver nanoparticles with a diameter of 10 nm (TEM images of this sample are depicted in Fig. 2a, while the spectral characteristic is shown in Fig. 3, curve 1). In this case, we also observe a

conformational transformation of the polymer macromolecule with temperature; however, the average particle diameter is somewhat larger, with the difference being more pronounced for the hydrophobic shrunk form. We assume that this difference is associated with the incorporated silver nanoparticles which hinder the free shrinkage of the polymer network. It should be noted that, in the case of silver nanoparticles densely packed on the gel particle surface (TEM data are given in Fig. 2a and the spectral characteristic is shown in Fig. 3, curve 5), we have not revealed a significant shrinkage of the particles, and this fact additionally supports our assumption. In order to verify the stability of the dispersion composite particles upon the phase transition in the polymer, we measured the hydrodynamic radii of the particles during 5 swelling / shrinkage cycles (Fig. 5).

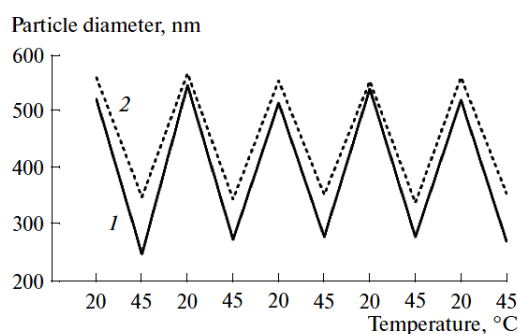


Fig. 5 – Change in the hydrodynamic diameter of particles of (1) PNIPAM nanogel and (2) composite PNIPAM / Ag nanogel during five cycles of heating to 45°C followed by cooling to 20°C

It can be seen that the five passages through the

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4. CONCLUSIONS

In this study, composite particles consisting of polyisopropylacrylamide gel particles with a diameter of about 500 nm and incorporated colloidal silver have been synthesized. Variations in reagent concentrations make it possible to produce silver nanoparticles with different sizes and packing densities on the surface of the polymer particles. Concerning the optical properties of the composite nanogels, it should be noted that, when the silver nanoparticles are not densely packed on the surface, the colloid has one maximum of plasmon resonance near 420 nm, which is typical of silver nanoparticles. The optical interaction between more densely packed silver particles leads to a split of plasmon resonance into two bands and a shift of the collective plasmon resonance to the near IR region. Composite nanogels containing silver nanoparticles exhibit a thermosensitive phase transition with the critical temperature of polymer network shrinkage of ; their dispersions remain stable for at least five cycles of polymer network swelling / shrinkage.

ACKNOWLEDGEMENTS

This study was supported by the Russian Foundation for Basic Research (projects nos. 11_02_00128a and 12_02_00397a), Programs of Presidium of Russian Academy of Sciences "Basic Sciences for Medicine" and "Basic Foundations of Technologies of Nanostructures and Nanomaterials."