Di-(2-ethylhexyl) dithiophosphoric acid surface protected gold nanoparticles: micellar synthesis, stabilization, isolation, and properties

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Abstract Gold nanoparticles (AuNPs) were synthesized in the organic solution by means of the reduction of HAuCl₄ by hydrazine in reverse micelles of oxyethylated surfactant Triton N-42, with decane as the dispersion medium. To isolate the powder of particles, the micelles were destroyed with chloroform in the presence of di-(2-ethylhexyl) dithiophosphoric acid as a surface protecting agent. According to the results of several experiments, the yield is within the limits of 90–98%, calculated for gold. The obtained preparations are dark blue hydrophobic powders containing aggregated but not agglomerated gold nanoparticles, as well as microcrystals (∼0.08–0.2 μm) of NaCl. The powders get re-dispersed in weakly polar organic solvents with the formation of colloidal solutions. The shape of the nanoparticles is spherical. Their nuclei are gold single crystals with a narrow size distribution; their diameter (d_{Au}) is about two times as large as the diameter of the aqueous nucleus (d_{c}) of initial micelles: d_{Au}=7.7±1.4 nm (d_{c}=3.6 nm) and 8.8±1.5 nm (4.6 nm). The preparations were studied by means of dynamic light scattering, atomic force microscopy, transmission electron microscopy, UV–vis spectroscopy, IR spectroscopy, X-ray powder diffraction, and thermogravimetric and elemental analyses. In the case of the particles with d_{Au}=8.8 nm, the product is a mixture of AuNPs and the salt with the molar ratio Au/NaCl≈1:4.54, while the gross composition of AuNPs per one gold atom is estimated as Au(C₁₆H₃₄O₂P₂Na₂N₂H₄)^0.16 with the number of gold atoms in one particle ∼21,000.

Keywords Gold nanoparticles · Reverse micelles · Triton N-42 surfactant · Di-(2-ethylhexyl) dithiophosphoric acid

Introduction

Gold nanoparticles (AuNPs) are very important for advanced materials and nanotechnology first of all due to their electron, optical, and catalytic properties [1–5]. Among a number of the methods of their preparation, rather widespread one is chemical reduction of gold species in solutions including homogeneous [6, 7], heterogeneous [8–10], and colloidal [11, 12] systems. Synthesis in reverse micelles is one of the efficient methods of obtaining nanoparticles with a narrow size distribution due to the possibility of purposeful adjustment of micelle structure through dosed solubilization of the disperse aqueous phase (DAP) [12–15].

Previously, we studied the kinetics of growth and oxidative dissolution of gold and silver nanoparticles in the reverse micelles of surfactants [16–21]. The particle formation occurs inside the polar cavities of reverse micelles during the reduction of the ionic species of metals present in DAP. The isolation of particles from the colloidal solution in the form of the powdered solid phase is achieved due to the destruction of micelles with a polar
solvent. The problem of the conservation of the initial size of nanoparticles during the isolation process is a very urgent task, so the isolation of the particles is performed in the presence of a protective agent preventing their agglomeration. Different types of protective reagents for gold nanoparticles are known, in particular citrate ion [6, 7], alkylthiols [22–24], alkylthioacetates [25], organic amines [26, 27], and phosphines [28].

The goal of the present work was to develop a method of synthesis, stabilization, and isolation of AuNPs from micellar solutions of Triton N-42 with the conservation of initial size, as well as examination of some physiochemical characteristics of the resulting preparations. The protective reagents for stabilization were AOT (intermediate protective reagent) and di-(2-ethylhexyl) dithiophosphoric acid (major stabilizing agent). Di-(2-ethylhexyl) dithiophosphoric acid had not been used previously for particle stabilization, but it is well known as a selective extracting agent for nonferrous and noble metals [29–32].

**Experimental section**

The reagents used in the work were: metal gold (+99.95%); chemically pure grade, concentrated aqueous solutions of HCl and hydrazine; pure grade di-(2-ethylhexyl) dithiophosphate (C₁₀H₃₄O₂PS₂H, DTPA), n-decane, n-heptane, chloroform, and toluene; Triton N-42 (TN-42) and sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) surfactants by Sigma.

Crystalline HAuCl₄⋅3H₂O was synthesized from metal Au according to the conventional procedure [33].

Standard solutions 0.23 M HAuCl₄, 2 M DTPA, 0.25 M TN-42, and 0.25 M AOT were prepared by dissolving the weighed portions of reagents in the aqueous solution of 3 M HCl, toluene, decane, and chloroform, respectively.

**Synthesis of AuNPs** Nanoparticles were synthesized through the reduction of tetrachloroauric acid by hydrazine in TN-42 reverse micelles at the solubilization capacity of micellar solution Vₖ/Vₒ=0.005 and 0.02 (Vₖ/Vₒ—the volume ratio of dispersed aqueous and organic phases). The micellar solutions of HAuCl₄ (A) and N₂H₄ (B) were made by means of injection solubilization of 20 μL (or 80 μL) of the aqueous solution of 0.23 M HAuCl₄ or concentrated N₂H₄ (~20 M) into 4 mL solution of 0.25 M TN-42 in decane. To synthesize AuNPs, the solutions A and B having equal Vₖ/Vₒ were mixed at room temperature in the volume ratio of 1:1. The color of the reaction mixture changed from yellow to deep red indicating the formation of AuNPs. The micellar solutions of synthesized AuNPs were stable for 6 months and had the conventional SPR band at 525 nm.

**Isolation of NPs from micellar solution** To precipitate AuNPs from the TN-42 solution, micelles were destroyed by chloroform in the presence of stabilizing agents. In typical experiment, 8 mL of AuNPs micellar solution in decane was mixed with the 8 mL solution of 0.25 M AOT in chloroform and 0.46 mL solution of 2 M DTPA in toluene. There was an instant color change to blue after mixing the solutions. The resulting dark blue powder of nanoparticles was separated from the colorless solution of the surfactant by centrifuging, washed by decantation with chloroform and heptane, and dried in the air to the constant mass.

**Instrumentation and measurements** The hydrodynamic diameters of the micelles of the surfactant (dₘₘ), AuNPs in micellar solutions during synthesis (dₘₚ), and in colloidal solutions prepared through re-dispersion of the preparation of particles in toluene (dₐₜₜ) were measured by dynamic light scattering (DLS) method at an angle of 90° in a quartz cell with a section of 1×1 cm² at a temperature of T=20°C with 90Plus spectrometer (Brookhaven Inst). The solutions were de-dusted preliminarily by passing them many times through a glass filter with the pores 0.5 μm in diameter. The standard deviation of the determined average values of the hydrodynamic diameters, with the number of measurements more than 20, did not exceed 0.2 nm. In the synthesis of AuNPs, the initial size of reverse micelles of TN-42 was governed by changing the solubilization capacity Vₖ/Vₒ of the micellar solution in agreement with the known dependence dₘₘ= dₒ+bVₖ/Vₒ [34, 35], where Vₖ and Vₒ are the volumes of solubilized DAP and micellar solution, b is an empirical constant, dₒ is the hydrodynamic diameter of “dry” micelles in the absence of DAP (Vₖ=0). In fact, dₒ=5.6 nm, measured by means of DLS for the solution of 0.25 M TN-42 in decane, is close to the doubled length of TN-42 molecule [36]. The diameters of the water nuclei of micelles (dₜ) and the gold nuclei of nanoparticles (dₐₜₜ) were determined as dₜ=dₘₘ−dₒ and dₚ=dₘₜ−dₒ assuming the spherical shape of micelles. At Vₖ/Vₒ=0.005 and 0.02, the initial micelles of TN-42 have the size of the water nuclei dₜ=3.6 and 4.6 nm (Table 1).

| Vₖ/Vₒ | a | b |
|---|---|---|
| dₘₘ (nm) | dₜ (nm) | dₘₚ (nm) | dₐₜₜ (nm) (DLS) | dₐₜₜ (nm) (TEM) |
| 0.005 | 9.2 | 3.6 | 13.5 | 7.9 | 7.7±1.4 |
| 0.02 | 10.2 | 4.6 | 14.1 | 8.5 | 8.8±1.5 |

a initial micelles of TN-42, b AuNPs synthesized in initial micelles of TN-42

*Confidence interval for probability P=0.95
Examination of the nanoparticle preparation by means of atomic force microscopy (AFM) was performed in the semi-contact mode with the scanning probe microscope Solver Pro (NT-MDT) in the air. The samples were prepared by depositing a drop of the colloidal solution of the preparation in toluene on the substrate made of mica and by subsequent evaporation of the solvent.

The morphology and size of individual nanoparticles in preparations were studied with the transmission electron microscope JEM-2010 (JEOL) with the accelerating voltage of 200 kV. To prepare the sample, a drop of the solution of particle preparation in toluene treated with ultrasound was dried on the substrate made of 200-mesh copper grid covered with a “holey” carbon film. Local energy-dispersive X-ray spectroscopy (EDX) analysis of the preparations was performed with EDAX spectrometer (EDAX Co) with Si-Li detector.

X-ray powder diffraction (XRD) data were obtained with a DRON-3M diffractometer ($R=192$ mm, Cu$K_{\alpha}$ radiation, Ni-filter, scintillation point detector with amplitude discrimination) at the room temperature over the range $5^\circ$–$60^\circ$ 2$\theta$ with step 0.03$^\circ$ in 2$\theta$ and 1 s counting time per step. The samples were prepared by grinding the powder in agate mortar with heptane and further deposition of this suspension on the polished side of a standard sample holder. Coherent scattering region for AuNPs was estimated using the Scherrer equation. The calculation was performed for the diffraction peak (111) of gold taking into account FWHM of the reference sample—Si.

The UV-visible spectra of the solutions were recorded with SHIMADZU UV-1700 spectrophotometer.

The IR absorption spectra within the range 4,000–400 cm$^{-1}$ were recorded with a Fourier transform spectrometer SCIMITAR FTS 2000 in a thin layer between KBr glass plates for the liquid reagent C$_{16}$H$_{34}$O$_2$PS$_2$H and in KBr tablets for the nanoparticle preparation.

Chemical CHN analysis of the preparations was made with the EURO EA 3000 instrument. Analysis for gold and sodium after the dissolution of the weighed portion of preparation in aqua regia, evaporation, and transfer into the solution of 2 M HCl were carried out by means of atomic absorption in air-acetylene flame using Hitachi Z-8000 instrument.

Thermogravimetric examination of the preparation was carried out using with thermobalance TG 2009 F1 Iris (NETZSCH) in a corundum crucible under the atmosphere of helium at the gas flow rate of 35 mL/min and heating rate of 10°C/min.

Results and discussion

Isolation of nanoparticles by means of double sequential stabilization

Destruction of micelles by chloroform without adding AOT causes rapid agglomeration of AuNPs even before DTPA is introduced. In the presence of chloroform, adsorption on particle surface is likely to be much weaker for nonionic TN-42 than for anionic surfactant AOT that provides intermediate stabilization of particles during micelle destruction and then is replaced by DTPA, which is a stronger protective reagent for chalcophilic gold (Fig. 1).

It was established by means of non-aqueous electrophoresis that, during the reduction of gold by hydrazine in TN-42 micelles, the nanoparticles have a positive surface charge increasing linearly with an increase in the concentration of the reducing agent [37]. During the reduction of Au$^{III}$ and Ag$^+$ by hydrazine in AOT micelles, the charge of Au and Ag NPs is positive, too, and it increases with the dilution of AOT solution in decane by chloroform [14, 38]. On the basis of the results reported in the present work and those obtained previously, we can propose the following hypothetical mechanism of double sequential stabilization. Chloroform is a known reagent destroying the micelles of oxyethylated surfactants in alkanes even in insignificant concentrations; it is used for concentrating precious metals in the form of salt solutions [39] and NPs [40]. In the case of NPs, chloroform desorbs a part of the molecules of nonionic TN-42 from the surface of AuNPs, which causes a decrease in the osmic and steric components of disjoining pressure and causes subsequent coagulation and agglomeration of NPs [37]. The presence of AOT in chloroform
causes more rapid diffusion of the surface-active anion to the positively charged nanoparticle and subsequent adsorption due to the electrostatic attraction. The protective surface layer of surfactant on a nanoparticle is partially recovered, and coagulation is suppressed. Diffusion of uncharged DTPA molecules is slower, and adsorption at the initial stage is due only to Van der Waals attraction. However, with time, DTPA molecules start to form strong, preferably donor–acceptor bonds with AuNPs due to sulfur atoms possessing high affinity to chalcophilic gold [33], and displace AOT from the surface layer. Thus, AOT provides intermediate stabilization of AuNPs. The surface DTPA layer in the organic environment containing chloroform protects nanoparticles only from agglomeration but does not protect them from coagulation, so as time goes by, large aggregates (flocs) of NPs undergo sedimentation and get isolated as the powder. The presence of chemisorbed surface layer of DTPA (with the hydrophobic layer of hydrocarbon groups turned outward) creates the possibility for gold nanoparticle to get peptized in nonpolar solvents.

Note that our considerations have a hypothetical character; a more extensive investigation of the mechanism of double sequential stabilization is a part of our future work.

Properties of the preparation

The AuNPs powder is hydrophobic and gets re-dispersed in weakly polar organic solvents, in particular in toluene, with the formation of blue colloidal solutions. The color and absorption spectrum of the solution exhibiting a broad band with the maximum at about 650 nm (Fig. 2) provide evidence of particle aggregation [41]. During re-dispersion through manual agitation, aggregates with a size up to $d_{ha}=600\pm50$ nm are detected by means of DLS in the colloidal solution of the preparation; under the ultrasonic treatment of the solution with moderate intensity the size decreases to $d_{ua}=240\pm20$ nm. A similar trend is observed also by means of AFM. The images of the films (Fig. 3a, b) obtained as a result of the evaporation of toluene solution of the preparation on mica surface before ultrasonic treatment display the aggregates of ellipsoid shape; their major and minor axes are estimated as $d_1=225\pm15$ and $d_2=200\pm18$ nm, respectively, for the number of measurements $N=102$ (Fig. 3c, d). After ultrasonic treatment of the solution, the size of aggregates decreased to 40–50 nm. Thus, aggregation of particles in the preparation does not lead to their agglomeration and merging.

The IR spectra of DTPA and the AuNPs preparation are presented in Fig. 4. The spectra contain the bands characteristic of dialkylthio phosphoric acids [42–44]: the bands of asymmetric bending vibrations of CH$_3$ and CH$_2$ groups, 1,463 cm$^{-1}$ AuNPs (1,463 cm$^{-1}$ DTPA); symmetric vibrations of CH$_3$ and CH$_2$ groups, 1,381 cm$^{-1}$ (1,380 cm$^{-1}$); vibrations of the (P)–O–C fragment, 1,018 cm$^{-1}$ (1,019 cm$^{-1}$); and stretching vibrations of thiophosphoryl group $P=S$, 671 cm$^{-1}$ (669 cm$^{-1}$). The difference is the presence of a broad band of stretching vibrations of (P)–S–H bond in the region of 2,550–2,650 cm$^{-1}$ in the spectrum of DTPA, while this band does not appear in the spectrum of AuNPs. This means that the protective coating of AuNPs is composed of C$_{16}$H$_{34}$O$_2$PS$_2$ anions adsorbed on the surface of particle nuclei, which explains the hydrophobic character of the formed nanoparticles.

The XRD data show that two crystal phases are present in the preparations: metal Au and NaCl (Fig. 5). The source of Cl$^-$ ions is the initial form AuCl$_4^-$, while the source of Na$^+$ is AOT during the isolation of AuNPs. Judging from broadening of diffraction peaks, the gold phase is ultrafine. The coherent scattering region for AuNPs in the preparation obtained at $V/V_0=0.02$ was estimated to be at a level of 3–4 nm.

For the preparation of AuNPs obtained at $V/V_0=0.02$, elemental analysis was carried out. The results are presented in Table 2. According to the gold content of the preparation 37%, the yield of the product calculated for the metal is estimated on the basis of several experiments to be within the range 90–98%. The presence of nitrogen in the preparation is explained by the use of hydrazine as the reducing agent in the synthesis of AuNPs. Because of a large excess of the reducing agent, it is assumed that the major form of nitrogen in the preparation is directly N$_2$H$_4$.

The TGA data are in satisfactory agreement with the elemental analysis. Three steps of thermolysis of AuNPs are observed during heating the sample of the preparation in helium atmosphere (Fig. 6a). The first step relates to the temperature range of 90–210°C, and the weight loss of

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**Fig. 2** UV–vis spectra of (1) AuNPs in micellar solution of TN-42 during synthesis and (2) AuNPs powder re-dispersed in toluene.
2.1% is observed, which corresponds to the detachment of hydrazine. Its calculated content is equal to 1.9% (Table 2). At the second stage (210–430°C) and the third one (430–735°C), the weight losses are 3.1% and 7.1%, respectively. The total weight loss at the second and the third stages (10.2%) can be related to the detachment of the protective reagent; its mass fraction in the preparation is estimated to be 10.6% as suggested by the data of elemental analysis. Therefore, the whole DTPA of the AuNPs sample is completely desorbed at 210–735°C. According to XRD data, the product of thermal decomposition at 735°C is a mixture of the phases of metal Au and NaCl (Fig. 6b). When heated above 735°C weight loss is observed due to sublimation of NaCl. The residual mass is 35.1%, which roughly corresponds to the Au content in the product (37%).

Characterization of AuNPs One can clearly see the chain structure of the aggregates in the TEM micrograph (Fig. 7a, b), which is a characteristic of the ensembles of nano-

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**Fig. 3** a 2D and b 3D AFM images of ellipsoid aggregates of AuNPs obtained at \( V_s/V_o=0.02 \), and the size distribution for their c major and d minor axes.

**Fig. 4** IR spectra of (1) DTPA and (2) AuNPs powder.

**Fig. 5** Diffraction patterns of AuNPs powder prepared at \( V_s/V_o=0.02 \).
particles and conforms with the UV–vis spectra of colloidal solutions of AuNPs powder re-dispersed in toluene. The gold nuclei of the particles have spherical shape and a narrow size distribution (Table 1). The EDX spectrum of individual AuNPs (Fig. 7c), in addition to the signals from C and Cu, which are due to the substrate, exhibits intense signals of Au (lines Au Mα and Au Lα), as well as the elements present in the protective reagent C16H34O2PS2H: O (OKα line), P (PKα line), and S (SKα line). In addition to AuNPs, the TEM micrograph contains separate cubic microcrystals of the salt, with the edges 80–150 nm long (Fig. 7g). Their EDX spectrum (Fig. 7h) contains the signals of Na (NaKα line) and Cl (ClKα line). The salt crystals create a strong background, so the signals of Na and Cl manifest themselves in the EDX spectrum of gold particles (Fig. 7c). Thus, the results of TEM and EDX analysis confirm the XRD data concerning the presence of the dispersed NaCl phase in the preparations of AuNPs.

One can see in the high-resolution TEM (HRTEM) micrograph that the nuclei of nanoparticles are single crystals (Fig. 7d). Interplanar spacings are equal to 2.35 Å and relate to the distance d111 of metal gold (Fig. 7e, f). The absence of twinning structures in AuNPs, as well as the narrow size distribution of the particles (17–18%), confirms our idea of the kinetic mechanism according to which the growth of AuNPs occurs in separate micelles independently and synchronously as a result of the addition of new gold atoms to the particles but not due to the addition of particles from neighboring micelles [45].

The average values of AuNPs nucleus diameter, determined by means of DLS in the micellar solution of TN-42 during synthesis, are in good agreement with TEM data for individual particles in the preparations (Table 1). So, the change of the protective reagent for the particles from TN-42 sequentially for AOT and then for DTPA during the isolation of the powder allows one to conserve the size of AuNPs nucleus, obtained during the micellar synthesis. At the same time, under the chosen synthesis conditions, the size of AuNPs is almost two times as large as the size of the water nuclei of initial micelles. A similar phenomenon was observed previously by other researchers [46]. Therefore, the micelles of oxyethylated surfactants like TN-42 are not rigid templates but undergo structural rearrangements while the particles get formed.

On the basis of the results of XRD, IR, ED and elemental analysis, stoichiometry of the molecules of protective reagent, and the principle of electric neutrality, it may be concluded that the preparation is a mixture of AuNPs and the salt with the molar ratio Au/NaCl ≈ 1:4.54, and the gross composition of AuNPs per one gold atom is estimated as Au(C16H34O2PS2Na 2N2H4)0.16; the number of gold atoms in one particle is ∼21,000 in the case when the metal nucleus has a diameter dAu=8.8 nm. The total number of gold atoms in a particle was determined as Nt=VAu/Va, where VAu=(1/6)·π·dAu3=357 nm3 is the volume of gold nanoparticle and Va=0.016962 nm 3 is the atomic volume of gold. The resulting value Nt=21,036 agrees with the calculated value of Ntcalc for the “magic” particle with completely filled 18 atomic layers having the fcc structure.

Table 2 Results of the analysis of AuNPs powder (dAu=8.8±1.5 nm) and calculated element content for [Au(C16H34O2PS2Na 2N2H4)0.16+ 4.54NaCl] (FW=532)

| Element     | Found (wt.%)* | Calculated (wt.%) |
|-------------|---------------|------------------|
| Au          | 37±1          | 37.02            |
| C           | 6.1±0.2       | 5.78             |
| H           | 1.0±0.2       | 1.27             |
| N           | 1.7±0.2       | 1.68             |
| Na          | 23.2±0.7      | 20.31            |

*Variation range is used as the error value

Fig. 6 a Thermogravimetric data for AuNPs powder prepared at Vs/Vo=0.02, and b diffraction patterns of thermolysis product at 735°C

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Fig. 7 TEM images and the size distribution for AuNPs prepared at a $V_s/V_o=0.005$ and b 0.02; c, d HRTEM, e FFT, and f EDX for AuNPs prepared at $V_s/V_o=0.02$; g TEM and h EDX of NaCl microcrystals.
For such a particle, the number of surface atoms and the total number of gold atoms are \( N_s^{\text{calc}} = 10n^2 + 2 = 3,242 \) and \( N_s^{\text{calc}} = 1 + \Sigma(10n^2 + 2) = 21,127 \), where \( n = 18 \) is the number of a layer [47]. The ratio \( N_s^{\text{calc}}/N_s^{\text{calc}} = 0.15 \) is close to the stoichiometric value \( \text{C}_{16}\text{H}_{34}\text{O}_2\text{PS}_2^-/\text{Au} = 0.16 \) in the preparation. Assuming the monolayer adsorption of the protective reagent, this means that there is approximately one \( \text{C}_{16}\text{H}_{34}\text{O}_2\text{PS}_2^- \) anion per one surface gold atom; the negative charge of the anion is compensated by \( \text{Na}^+ \) cation. In addition, we assume that two \( \text{N}_2\text{H}_4 \) molecules form hydrogen bonds with two oxygen atoms in \( \text{C}_{16}\text{H}_{34}\text{O}_2\text{PS}_2^- \).

Conclusions

We present the synthesis method for AuNPs in reverse micelles of nonionic oxyethylated surfactant TN-42 with the subsequent isolation of nanoparticles as powder. To isolate nanoparticles from the micellar solution, the micelles were destroyed with a polar solvent, chloroform, in the presence of a surfactant, AOT (intermediate stabilizing agent), and a protective reagent, DTPA (the final surface stabilizing agent), which possesses high affinity to gold due to S-containing functional groups. The developed method of double sequential stabilization allows one to isolate AuNPs from micelles without changing the size of particle nuclei. The yield of the product with respect to gold is 90–98%.

The resulting preparations contain AuNPs and NaCl microcrystals. The NPs consist of the metal nucleus and the protective shell. The nuclei are gold single crystals having the spherical shape and a narrow size distribution with the average diameters \( 7.7 \pm 1.4 \) and \( 8.8 \pm 1.4 \) nm, which are two times as large as the diameters of aqueous nuclei of initial TN-42 micelles 3.6 and 4.6 nm. The shell is composed of chemisorbed \( \text{C}_{16}\text{H}_{34}\text{O}_2\text{PS}_2^- \) anions that have \( \text{Na}^+ \) cations as the counter-ions; in addition, due to their oxygen atoms, they participate in hydrogen bonding with two \( \text{N}_2\text{H}_4 \) molecules. Assuming monolayer adsorption, there is approximately one \( \text{C}_{16}\text{H}_{34}\text{O}_2\text{PS}_2^- \) anion per one surface gold atom.

The preparation is a hydrophobic powder of aggregated but not agglomerated AuNPs peptizing in weakly polar organic solvents with the formation of colloid solutions. These solutions can be used to deposit the layers of AuNPs on various substrates and to impregnate porous matrices.

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