Microstructure and Rheological Behavior of Stabilized Gold Nanoparticles Hydrosol

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Received September 19, 2020; revised September 19, 2020; accepted October 9, 2020

Abstract—A comprehensive analysis of an aqueous solution of gold nanoparticles with an average size of 6 nm in a citrate buffer has been carried out, with investigation of the solution rheology and structure by electron and atomic force microscopy. A deviation of the rheological behavior of hydrosol from the Newtonian properties is found even at low gold nanoparticle concentrations. The specific features of the rheological behavior of hydrosol are explained based on the transmission electron microscopy (TEM) data.

DOI: 10.1134/S106377452104009X

INTRODUCTION

The interest in the research and developments in the field of functional materials and devices containing ordered micro- and nanostructured coatings as key elements is due to their high technological potential. A promising line of research in electron vacuum systems is the formation of homogeneous ordered layers of carbon, semiconductor, or metallic nanoparticles (NPs) on different substrates [1–3].

According to [4], the deposition of thin films from a solution by the spin coating technique in a correctly chosen mode allows one to obtain disaggregated detonation nanodiamond (DND) single crystallites on highly oriented Ni–W alloy substrates. However, at high rates of film deposition or formation from a solution, which cause high shear stresses, the laminar solution flow can be disrupted. In this case, the consideration of the non-Newtonian properties of colloidal solutions (the dependence of effective viscosity on the shear rate and the presence of yield point) may be of significant importance for optimizing the properties of coatings formed.

To understand the origin of the non-Newtonian properties of a solution, it is necessary to investigate its structure not only based on data on the solution composition indicated by manufacturer. The most complete information can be obtained by microscopy, with the solvent effect taken into account.

Colloidal gold solutions are used not only in catalysis, formation of coatings in optics, and in the field of functional materials, but also in biotechnology and as carriers for targeted drug delivery [5, 6]. Therefore, the study of the structural organization of Au particles in a hydrosol and specific features of their rheological behavior is a scientific task of both theoretical and practical importance. The application range and physicochemical properties of gold NP hydrosols depend strongly on the stability (in particular, aggregation) of solutions and on the particle size. Currently, the classical method of Au reduction from chlorine-containing complexes or salts in a citrate buffer is widely used [7]. Such solutions remain stable for several weeks [8], and the structure of the citrate layers of stabilized particles has been studied well [9]. However, to increase the period of aggregation stability, different stabilizers (often surfactants) are introduced into Au NP solutions. In commercial products, the chemical nature of additives is not disclosed, being protected by patent laws. The rheological characteristics and structural organization of such solutions become fundamentally important, especially for electron vacuum systems.

EXPERIMENTAL

The object of study was a stabilized hydrosol of Au NPs in a citrate buffer (Sigma Aldrich, USA). The core size declared by the manufacturer is 4–7 nm, with an average hydrodynamic diameter of 14–25 nm. The NP content in the solution is no less than $4.92\times10^{13}$ mL, which corresponds to a concentration of ~0.01 wt % (assuming the gold density to be 19.32 g/mL).
The particle size distribution was measured by dynamic light scattering (DLS) on a Zetasizer Nano ZSP analyzer (Malvern Instruments Ltd, USA). The analyzer is equipped with a 632.8-nm He–Ne laser; the photodetector is oriented at an angle of 173°. The distributions of Au NP hydrodynamic diameters in suspensions were calculated from the autocorrelation functions of light scattering intensity using the Zetasizer software. The suspensions were placed in a 10-mm-thick quartz cuvette. The measurements were performed at 20°C.

The spectrophotometric measurements were carried out on a Shimadzu UV-3600 spectrophotometer (Japan) in the wavelength range of 830–310 nm; the optical path length was 10 mm.

The rheological behavior of the sample in comparison with the buffer (distilled water) was studied using a Physica MCR 501 rotational viscometer (Anton Paar, Germany) in the double gap measuring geometry at a controlled shear rate; the flow and viscosity curves were found in a wide range of shear rates from 1 to 1000 s⁻¹. The measurement time per point was varied from 300 to 1 s according to the logarithmic law with an increase in the shear rate.

To perform atomic force microscopy (AFM) and transmission electron microscopy (TEM) investigations, an Au hydrosol was deposited onto highly oriented Ni–W alloy substrates and/or copper electron microscopy grids with a carbon film by spin coating in a Chemat Technology Spin Coater KW-4A system. The Ni–W substrates were prepared in the form of square fragments 5 × 5 mm in size. Before applying the solution, they were washed with alcohol and fixed on a glass substrate. The Au NP solution (20 μL) was deposited onto a stationary substrate of spin coating apparatus without preliminary distribution at 4000 rpm. The induction time from the instant of deposition to the spin coating onset was 30 s and the rotation was performed for 1 min.

Images of the metal substrate surface were obtained with a Helios NanoLab 660 ion-beam scanning electron microscope (ThermoFisher Scientific, USA). Particles were examined with an Osiris transmission electron microscope (ThermoFisher Scientific, USA) at an accelerating voltage of 200 kV.

AFM images were obtained with a MultiMode 8 microscope (Veeco Instruments, USA).

RESULTS AND DISCUSSION

To confirm the parameters of particles in hydrosol, declared by the manufacturer, and establish the effect of shear stress on the structural organization of particles, distributions of particle hydrodynamic radii were obtained by the DLS method before and after the rheological tests. The size distribution as a function of light scattering intensity (Fig. 1a) contains two maxima with sizes of 15 ± 3 and 185 ± 92 nm, which is indicative of the presence of two fractions of particles. The smaller size fraction corresponds to the individual Au NPs declared by the manufacturer, while the second fraction is obviously related to the formation of aggregates. Nevertheless, it is well-known that the scattering intensity of large objects is much higher than that of small ones [10]. Therefore, the number of such aggregates is small, and the only maximum at 12 ± 2 nm is observed upon rearrangement of the size distribution over the number of particles (Fig. 1b). Note that the hydrodynamic radius determined in the solution by the DLS method is usually somewhat larger than the actual particle size, which is related to the presence of solvation shells, which are instrumentally perceived as a single whole with the particle. The size distributions measured before and after the rheological measurements are identical, which points out the absence of irreversible structural changes under shear stresses.

A comparison of the results of spectrophotometric measurements (Fig. 2) with the data of [11] also con-
firms the particle size indicated by the manufacturer. The absorption maximum is observed at a wavelength of 520 nm, which is typical of solutions of Au NPs 13.3 ± 0.6 nm in size.

The TEM study (Fig. 3) demonstrates monodispersity of Au NPs 3–6 nm in size, which corresponds to manufacturer’s documentation.

When transferred to a substrate, particles form separate groups (islands) consisting of several tens of particles. The contrast variations show that particles form not one layer on the grid but two (Fig. 3a, inset) or even three layers, which is unambiguously evidenced by the mass thickness contrast in Fig. 3a. The high-resolution TEM study (Fig. 3b) yielded conventional images of particles with zone axes close to the [011] and [001] directions. Twins and stacking faults, typical of gold particles, are observed.

When studying the particle distribution formed during spin coating of solutions, the morphology of the initial substrate becomes important. The presence of significant inhomogeneities may lead to undesirable aggregation and nonuniformity of the particle distribution over the surface. Therefore, the morphology of the Ni–W substrates used in this study was preliminarily investigated by scanning electron microscopy (SEM). Figure 4 shows the Ni95W5 substrate surface at different magnifications. In the low-magnification image, one can distinguish individual grains with different contrasts related to different grain orientations. The grain sizes are about 20–100 μm. The examination of the surface at a high magnification beyond the grain boundaries revealed no roughness or other defects. The effect of grain boundaries on the substrates will be apparently local and should not affect much the Au NP distribution on the substrate.

The AFM data obtained at a lower magnification show that particles on the Ni–W substrate with atomic ordering are also arranged into island clusters (Fig. 5).

The accuracy of rheological measurements, especially at low shear rates, depends strongly, among other factors, on the measurement time. Therefore, to select the appropriate measurement mode, preliminary tests were made. After the measurement mode optimization, the curves of flow (Fig. 6a) and viscosity (Fig. 6b) of the Au NP hydrosol in comparison with the dispersion medium (distilled water) were obtained.

Note that low-viscosity substances are difficult to investigate, especially at low shear rates (there is a spread of points in the plots). Water is known to be a Newtonian liquid, whose viscosity during flowing is independent of the shear rate and the shear stress increases linearly with an increase in the shear rate (Newton’s equation):

\[
\tau = \eta \dot{\gamma},
\]

where \(\tau\) is the shear stress, \(\dot{\gamma}\) is the shear rate, and \(\eta\) is the viscosity. The dependences obtained for water are approximated by the Newton’s equation. The model and experimental data are in good agreement. The resulting viscosity is 0.00098 Pa s, which is close to the value reported in the literature: 0.001 Pa s. The approximation reliability \(R^2\) was 0.9995.

At the transition to the Au NP sol, the character of the sample flow changes: in the low-rate region, a deviation from the Newtonian behavior is observed, which may be due to the occurrence of a weak elastic component. The viscosity curve descends and then forms a plateau. Note that the decrement is small and, at a rate of 1 s\(^{-1}\), the viscosity of the hydrosol is higher than that of water by a factor of only 4. The flow curve, in turn, exhibits a slight deviation from the linear dependence toward larger values. This behavior is typical of viscoelastic fluids and can be approximated by different rheological models [12]. The results were approximated by the Bingham model

\[
\tau = \tau_0 + \eta \dot{\gamma}
\]
and the Herschel–Bulkley model

\[ \tau = \tau_0 + \eta \dot{\gamma}^n, \]  

(3)

where \( \tau_0 \) is the parameter of the limit shear stress (yield point) and \( n \) is an exponent. Obviously, the Herschel–Bulkley model is more flexible and passes to the Bingham model at \( n = 1 \). It can be seen in Fig. 6 that both models adequately describe the experimental data with extremely high approximation reliability \( R^2 \). Note that the Herschel–Bulkley equation approximates more accurately the viscosity in the range of high shear rates. The calculated equation parameters are given in Table 1.

It is interesting to compare the obtained parameters with the results of previous measurements on DND nanoparticles with a positive potential \( \zeta \) and a size of 4–5 nm (Fig. 7) [13]. The presented data show that all samples exhibit non-Newtonian properties, and their viscosity decreases with an increase in the shear rate. The figure shows the viscosity values obtained by the approximation using the Bingham equation. In addition, the deviation from the Newtonian behavior for DND particles increases with an increase in concentration, which is most pronounced at a low shear rate of 1 s\(^{-1}\) (Fig. 7).

A comparison of the rheological data on the solutions of particles of both types shows that the viscosity of the nanodiamond hydrosol at low shear rates and a concentration of \( \sim 0.01 \) wt % turns out to be higher than the viscosity of the DND hydrosol at a concentration of 0.74 wt % and amounts to \( 3.31 \times 10^{-3} \) Pa s (compare with \( 2.12 \times 10^{-3} \) Pa s). The diamond and gold mass concentrations differ by a factor of more than 70; taking into account the similar particle sizes and a significant difference in density (3.51 and 19.32 g/cm\(^3\) for diamond and gold, respectively), it appears that the difference between volumetric concentrations will be even larger by a factor of about 5. For DND, the deviation from the Newtonian behavior at low (less than 1 wt %) concentrations was explained by the interaction between particles and the formation of chains and a weak percolation network, which was confirmed later by cryogenic electron microscopy [14].

Table 1. Parameters of gold nanoparticle suspension

| Parameter                  | \( \tau_0, \) Pa | \( \eta, \) Pa s | \( n \)  | \( R^2 \)   |
|----------------------------|-----------------|-----------------|--------|-----------|
| Herschel–Bulkley model     | 0.00217         | 0.00107         | 0.9865 | 0.9999    |
| Bingham model              | 0.00230         | 0.00100         |        | 0.9992    |

Fig. 4. Secondary-electron SEM image of the Ni–W substrate surface: (a) individual grains are distinguished, (b) boundaries between grains with a pronounced wedge-shaped dip, and (c) surface appearing smooth at a high magnification.

Fig. 5. AFM images demonstrating the island-like distribution of gold nanoparticles on the Ni–W substrate.
However, for the Au NP hydrosol, the particle concentration is much lower and the formation of a percolation network is highly improbable, if possible at all. As was mentioned above, Au NPs in buffer solutions are often additionally stabilized by different surfactants. In this case, the concentration of additives is much higher than the Au concentration. As is known, surfactants can change the rheological behavior of dispersed systems; then, if a gold hydrosol contains surfactants, its deviation from the rheological behavior is not surprising.

It can be suggested that specifically the presence of a large amount of an organic component in the solution is responsible for the strong manifestation of non-Newtonian properties of liquid at a relatively small amount of Au NPs. At the same time, the TEM and AFM data show a possibility of forming Au particle clusters, which can also change the properties of the Au hydrosol. Such dependences can only be identified using additional techniques and require separate investigations.

**CONCLUSIONS**

The classical TEM and AFM methods allow one to establish the structure of gold nanoparticle films obtained by spin coating on a substrate (islands) and can indicate indirectly the structural organization of the hydrosol. The observed deviations of the rheological behavior of gold nanoparticle hydrosol with a concentration of about 0.01 wt % may be related to the formation of clusters and chains of interacting gold particles, as well as the presence of stabilizing high-molecular substances. We emphasize that solution structure may be characteristic of other colloidal solutions of metallic NPs, including stabilized surfactants.

**ACKNOWLEDGMENTS**

We are grateful to E.V. Razuvaeva, S.N. Malakhov, and D.R. Streletssov, National Research Centre “Kurchatov Institute,” for the help in carrying out dynamic light scattering, spectrophotometry, and atomic force microscopy investigations, respectively, and to A.A. Korovin for the help in optimizing the spin coating technique.

**FUNDING**

This study was supported in part by the Ministry of Science and Higher Education of the Russian Federation within a State assignment to the Federal Research Center “Crystallography and Photonics” of the Russian Academy of Sciences and by the Russian Foundation for Basic Research, project no. 19-02-00937.

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Translated by E. Bondareva