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Noble metal nanoparticles functionalized by natural asphaltenes as model phases for geochemical research

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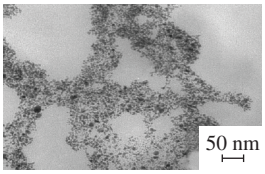
The nanosized particles of noble metals were stabilized by asphaltenes in order to explore the migration of the elements in natural organic media. Data on the sizes of particles and their stability in hydrocarbon solutions were obtained.



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To understand the accumulation of rare elements in ore deposits, it is important to study the speciation of the elements and their transport under natural conditions. The formation of noble metal deposits is related to the transfer of metals with natural inorganic and organic solutions and fluids containing their dissolved molecular (complex) compounds. However, their transport in the form of particles is more effective for the accumulation.[1,2] In particular, the transport of nanosized gold in liquid media under natural conditions was reported.[3]

The identification of factors controlling the ability of a substance to migrate in geological systems in micro- and nanodispersed states is important for modern nanogeochemistry.[2,4] The synthesis and characterization of nanoparticles (NPs) and nanofluids necessary for modeling natural interactions are promising.[5,6]

The role of nanosized organomineral complexes in the transport of platinum group elements and gold in aqueous (*e.g.*, oceanic[7] and anthropogenic[8]) systems was experimentally studied. Much less is known on the transfer of metals by hydrocarbon gases and liquids in the mantle fluids[9,10] involved in the formation of endogenous ore occurrences and deposits. This transportation of minerals and complex compounds was studied in model experiments.[11] It is important to consider the formation and behavior of nanosized noble metals (in particular, particles associated with asphaltenes as natural metal concentrators) in relation to hydrocarbon-containing systems.

Previously, we considered nanosized model substances and sorption materials intended for various purposes, in particular, the microwave synthesis of nanoparticles.[12–14] The gold, palladium, and platinum NPs stabilized by fulvic acids were used to study the transfer and migration of metals in a natural aquatic environment.[8] The behavior of these NPs in contact with geochemical barriers allowed us to establish that nanosized gold and palladium stabilized by fulvic acids are more sorption-active than the dissolved (ionic) forms of these metals, and their transfer as so-called pseudocolloids (for example, sorbed on iron hydroxides) can be efficient.

Only a few of publications were devoted to the dispersions of NPs that are stable in organic, especially nonpolar, media.[15,16] In this work, the two-phase synthesis of nanosized noble metals in hydrocarbons was performed as described elsewhere.[17,18] We used cetyltrimethylammonium bromide (CTAB)[†] and natural asphaltenes (extracted from oil by standard techniques) as surface modifiers to obtain nanosized gold and palladium according to a ligand substitution method including the synthesis of NPs with a hydrophobic surface and the subsequent functionalization.

The basic synthesis conditions were tested using gold NPs (AuNPs), which can be easily identified by plasmon resonance spectra in the visible region.[‡] The AuNPs were obtained in a concentration range of 0.4–4 mM by the reduction of a complex gold chloride added to a solution of CTAB in toluene with $NaBH_4$ in a NaOH solution. The AuNPs were formed in a wide range of CTAB concentrations (0.77–2.8 mg ml^{-1}) with a maximum yield at a CTAB concentration of 1.4 mg ml^{-1}. The synthesized particles were characterized by a maximum in the absorption spectra at 540–542 nm [Figure 1(*a*)], which indicated their narrow size distribution. The linear dependence of the optical density (at λ = 542 nm) of the solutions on the concentration of gold made

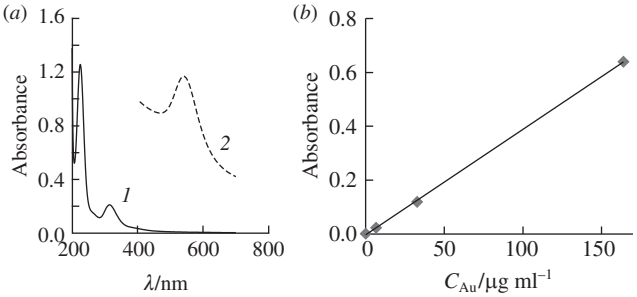

Figure 1 (*a*) Absorption spectra of (*1*) a gold chloride solution and (*2*) a dispersion of AuNPs@CTAB in toluene and (*b*) the optical density of AuNPs@CTAB (in toluene) as a function of gold concentration.

[†] Mass of 364.5, Merck, ⩾ 97%.

[‡] Optical density was measured on a UV-1800 spectrophotometer (Shimadzu, Japan). The gold content of solutions was determined by ETAAS (Solaar MQZ, Thermo Elemental, USA). Particle images were measured using a JEM-100CX electron microscope (Jeol, Japan) at the UNIQEM Collection Center for Biotechnology, Russian Academy of Sciences. The size distribution of particles in solutions was studied by dynamic light scattering (DLS) using an ARN-2 particle size analyzer (Russia).

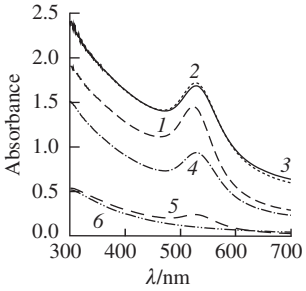

Figure 2 Spectra of AuNPs (24.6 μg ml^{-1}) (*1*) on the day of synthesis and after (*2*) 2, (*3*) 3, (*4*) 6, (*5*) 9 and (*6*) 13 days.

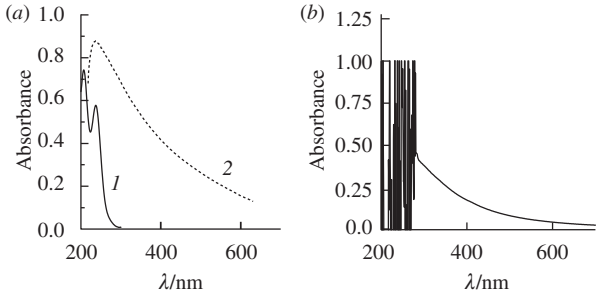

Figure 4 Absorption spectra of (*a*) (*1*) a palladium chloride solution and (*2*) a dispersion of PdNPs and (*b*) a solution of asphaltenes in toluene.

it possible to determine gold concentrations in organic systems [Figure 1(*b*)].

The factors affecting the yield and stability of the materials were studied. The AuNPs were formed at $NaBH_4$ concentrations of 0.1–10% (0.026–2.6 mol dm^{-3}); the particle size distribution was independent of the concentration of $NaBH_4$. In accordance with published data on the dependence of the absorption maximum on the diameter of AuNPs,[19,20] the size of the resulting particles was 20–40 nm.

The synthesis was carried out at room temperature. It was suggested[21,22] to use a cooled solution of $NaBH_4$, but we did not notice any differences. We found that the stability of sols depended on the $NaBH_4$ content and reached a maximum at a minimum concentration of the reducing agent; therefore, it is necessary to separate an organic phase from an aqueous phase. The organic phase influenced the stability of sol. In a concentration range of 80–800 μg ml^{-1}, AuNPs were most stable (for at least a month) in a mixture of toluene and hexane (1 : 1). This mixture was also convenient for the subsequent preparation of AuNPs@Asp since asphaltenes are readily soluble in toluene.

When CTAB was replaced with asphaltenes in the shell of AuNPs, a sol was obtained, which was stable for no more than a day. Sols stable for 7–14 days were prepared by replacing toluene with its mixture with dichloromethane (1 : 1). A decrease in the volume of an aqueous gold solution to 60 μl eliminated the stage of phase separation. A particle size of 25–40 nm (spectrophotometric, TEM and DLS data) corresponded to an absorption wavelength of 528.5 nm. Figure 2 shows the absorption spectra of AuNPs@Asp, and Figure 3 depicts the TEM images of AuNPs@Asp and PdNPs@Asp.

Palladium particles (PdNPs) are more difficult to prepare and identify, although the existence of these natural[23] and model[24] nanosized forms was reported. This is due to the coincidence of the optical characteristics of the initial palladium complexes (222–234 nm), PdNPs (230 nm) [Figure 4(*a*)] and asphaltenes (190–280 nm) [Figure 4(*b*)] in the UV region.

PdNPs were synthesized as described above for AuNPs using CTAB as a primary modifying agent in a mixture of toluene and dichloromethane (1 : 1). This agent on the surface of particles was then replaced with asphaltenes from a solution in toluene. Upon the addition of $NaBH_4$ in 1 M NaOH, the solution color changed from light brown to dark brown. The final intensely colored colloidal solution contained 18 μg ml^{-1} (0.17 mmol) of Pd, 12 μg ml^{-1} (0.013 mmol) of asphaltenes and 3.5 mg ml^{-1} (0.01 mol) of CTAB.

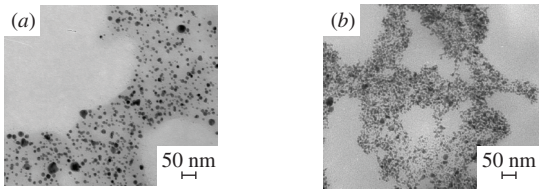

Figure 3 TEM images of asphaltene-stabilized (*a*) AuNPs and (*b*) PdNPs.

According to the TEM data [Figure 3(*b*)], the size of PdNPs was 5–10 nm. The stability of particles in the system was evaluated based on the optical density of the suspension. The PdNPs were stable for at least three weeks.

Thus, stable nanosized noble metal particles were obtained and characterized. The stability of dispersions confirmed the possibility of the occurrence of noble metal NPs under natural conditions and the experimental modeling of the transfer of these elements by hydrocarbon fluids during the formation of ore deposits.

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