Mendeleev Commun., 2001, 11(4), 147–148

Silver nanoparticles stabilised with heteropoly anions in an aqueous solution: optical properties and electronic polarisation

Boris G. Ershov* and Andrei V. Gordeev

Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow. Fax: +7 095 335 1778; e-mail: ershov@ipc.rssi.ru

10.1070/MC2001v011n04ABEH001462

The optical absorption spectra and electronic polarisation of silver nanoparticles prepared by the radiation-chemical reduction of silver ions in an aqueous solution in the presence of the heteropoly anions $PW_{11}O_{39}^{7-}$ and $P_2W_{17}O_{61}^{10-}$ were studied.

Nanosized metal particles exhibit lyophobic properties, and various organic compounds (such as polymers, polyelectrolytes and surfactants) are primarily used to stabilise them in water (see, for example, ref. 1 and references therein). Here, we report on the possibility of using the nanosized heteropoly anions $PW_{11}O_{39}^{7-}$ and $P_2W_{17}O_{61}^{10-}$ for this purpose by the example of the preparation of silver sols. The heteropoly anions have been used earlier to stabilize Rh and Ir nanoparticles.[2] The distinctive property of these anions is that they can add electrons (undergo reduction) to form so-called blues with the retention of their structures.[3] Therefore, it would be expected that the application of heteropoly compounds to stabilise metal nanoparticles will make it possible to affect purposefully their electronic characteristics. Thus, the reduction of the stabilising layer of a heteropoly compound in nanosized aggregates can induce its electronic polarization, that is, affect the charge of a metal nucleus. Previously,[4] electrons were pumped into silver sols by the discharge of alcohol radicals generated by a microsecond pulse of accelerated electrons in an alcohol-containing solution. A process of this kind was more clearly demonstrated by the direct charging of silver sols at a cathode.[5] In both of the above cases, the electronic polarisation of silver particles was accompanied by a shift of the absorption band due to surface plasmons towards the UV region (blue shift).

Chemically pure $(NH_4)_7PW_{11}O_{39}$ and $K_{10}P_2W_{17}O_{61}$, as well as $AgClO_4$ from Aldrich, were used. Solutions were prepared using triply distilled water and deaerated by pumping to a high vacuum before irradiation. Samples in special glass vessels equipped with quartz cells for optical measurements were γ-irradiated using a ^{60}Co source. The absorbed dose rate was 25 Gy s^{-1}, as measured with the ferrous sulfate dosimeter. The absorption spectra were recorded on Specord UV-VIS or Shimadzu UV-3100 instruments at ambient temperature. Samples for electron-microscopic studies were prepared by applying a drop of the test solution to a carbon–copper grid followed by drying in an argon atmosphere. A Phillips EM-30 electron microscope was used.

Figure 1 shows the optical absorption spectra of an evacuated aqueous 10^{-4} M $AgClO_4$ solution containing isopropanol (0.1 mol dm^{-3}) and a $P_2W_{17}O_{62}^{10-}$ additive before (curve *1*) and after γ-irradiation (curve *2*). The action of γ-radiation on isopropanol-containing solutions results in the formation of hydrated electrons, which are powerful reducing agents (reduction potential of –2.7 V), and $Me_2C^{\cdot}OH$ radicals (–1.5 V).[6] The latter species appear in the reactions of H atoms and OH radicals (water radiolysis products) with isopropanol. It can be seen that irradiation resulted in the appearance of optical absorption with a maximum at 392 nm, which is typical of silver sols, and a band with a maximum at 650 nm, which is due to the reduction product of $P_2W_{17}O_{62}^{10-}$ (blue).[3,7] The subsequent γ-irradiation of the solution caused no detectable changes in the spectra. Therefore, the radiation dose in use (0.75 kGy) was sufficient for the radiation-chemical reduction of all of the silver ions and $P_2W_{17}O_{61}^{10-}$ heteropoly anions. Note that the molar absorption coefficient of silver clusters is high, namely, $\varepsilon = 1.9\times10^4$ dm^3 mol^{-1} cm^{-1}. Electron-microscopic data (Figure 2) demonstrated that the resulting silver particles are spherical in shape and the particle size is 10–20 nm. The admission of air (Figure 1, curve *3*) resulted in the oxidation of the blue and in the disappearance of the relevant absorption band at 650 nm. In this case, the intensity of the band due to silver nanoparticles dramatically decreased, and this band was shifted to the long-wavelength region (λ_{max} = 410 nm). The repeated γ-irradiation of the solution under a vacuum restored the initial absorption spectrum (Figure 1, curve *4*). The above oxidation–reduction procedure can be repeated several times with the same optical effects. Silver nanoparticles stabilised with the heteropoly compound or its reduction product (blue) in an aqueous solution were found to be stable for a very long time (in a matter of months). A similar behaviour towards optical changes in silver sols was observed with the use of the $PW_{11}O_{39}^{7-}$ heteropoly anion (10^{-5}–10^{-4} M) as a stabilising agent.

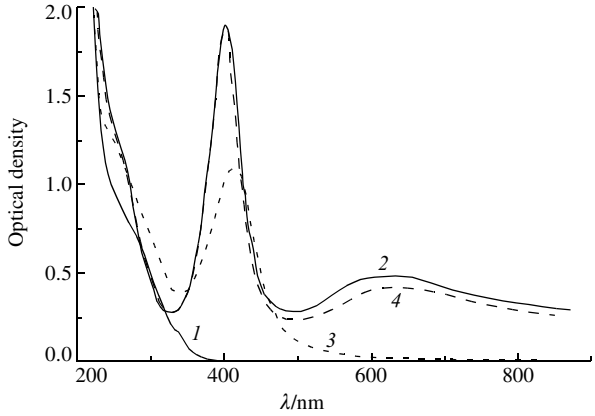

Figure 1 Absorption spectra of a deaerated solution containing $AgClO_4$ (1×10^{-4} mol dm^{-3}), Me_2CHOH (0.1 mol dm^{-3}), and $P_2W_{17}O_{61}^{10-}$ (2×10^{-4} mol dm^{-3}) (*1*) before irradiation, (*2*) after γ-irradiation for 30 min, (*3*) after the admission of air and (*4*) after repeated irradiation for 30 min. Absorbed dose rate: 1.5 kGy h^{-1}. Approximately 6.6×10^{-6} mol dm^{-3} of hydrated electrons and 8.4×10^{-6} mol dm^{-3} of Me_2COH radicals per minute of irradiation were formed.

The observed reversible changes in the absorption of silver nanoparticles are due to reversible changes in their electronic states in the cyclic reduction–oxidation of the heteropoly anion. The electronic polarisation of silver nanoparticles is attained by discharging powerful reducing species (hydrated electrons and Me_2COH alcohol radicals) on these particles. The reduction of the heteropoly compound, which forms a stabilising layer of nanoparticles, is also responsible for an increase in the electron density on a metal nucleus. This resulted in an increase in the absorption band intensity and in a blue shift relative to the case of clusters with oxidized heteropoly compounds (410 nm). According to the Mie–Drude theory,[8,9] the position of the absorption band maximum of the surface plasmon in the metal is determined by the equation

$$\lambda_{max}^2 = (2\pi c)^2 m(\varepsilon_0 + 2n)/4\pi N_e e^2, \quad (1)$$

where c is the velocity of light, m is the effective electron mass, e is the electron charge, ε_0 is the permittivity of silver, n is the refractive index of the medium, and N_e is the density of free electrons in the metal. It can be seen that an increase in N_e results in a shift of the plasmon absorption band of the metal towards the UV region and a decrease in N_e results in a shift

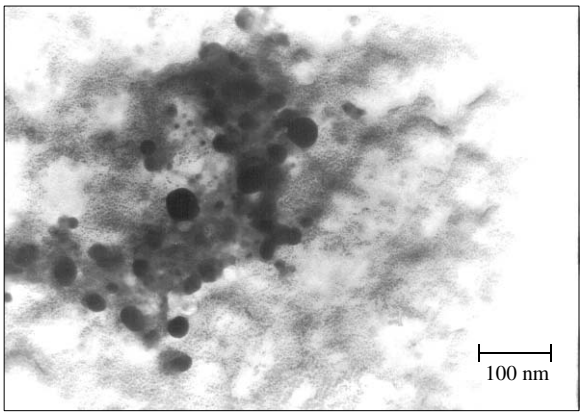

Figure 2 Electron micrograph of silver particles prepared by γ-irradiation of a solution containing $AgClO_4$ (1×10^{-4} mol dm^{-3}), Me_2CHOH (0.1 mol dm^{-3}), and $P_2W_{17}O_{61}^{10-}$ (2×10^{-5} mol dm^{-3}). The irradiation conditions are specified in Figure 1.

towards the visible region. It also follows from equation (1) that the positions of the absorption bands are related to the relative concentrations of electrons on the metal nuclei by the expression

$$\lambda_i^2/\lambda_f^2 = N_f/N_i \qquad (2)$$

where the subscripts 'i' and 'f' refer to the initial and final states, respectively. As well as Henglein *et al.*[4] and Mulvaney *et al.*,[5] we cannot establish a direct correlation of the position of the absorption band of silver nanoparticles with the charge of particles. The charge cannot be calculated from the positions of λ_i and λ_f with a required accuracy because of the uncertainty of the values of ε_0 and n, which results, in particular, from the uncertain composition of the nearest environment of nanoparticles. However, we found, using equation (2), that the reduction of the heteropoly compound and the formation of the blue increase the electron density on silver sols by 9.4%. This value is somewhat higher than that attained in the electrochemical charging of a silver sol, when the absorption band was shifted from 404 to 392 nm. This shift corresponds to a change in the sol charge by 6.2%.[5] The standard reduction potential of the pair HPC^{n-}/HPC (HPC is a heteropoly compound) is approximately equal to –0.3 V.[3] We found that the position of an absorption band due to surface plasmons in silver at 392 nm corresponds to an equilibrium charge of silver sols at the above potential. Note that it is most likely that the relationship between the charge of metal nanoparticles and the properties of the medium found for silver will also manifest itself in reactions catalysed by other transition metal nanoparticles.

This work was supported in part by the Russian Foundation for Basic Research (grant no. 00-03-32107).

References

1 A. D. Pomogailo, *Usp. Khim*., 1997, **66**, 750 (*Russ. Chem. Rev*., 1997, **66**, 679).
2 J. D. Aiken and R. G. Finke, *J. Am. Chem. Soc*., 1998, **120**, 9545.
3 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, New York, 1983.
4 A. Henglein, P. Mulvaney and T. Linnert, *Faraday Discuss. Chem. Soc*., 1991, **92**, 31.
5 T. Ung, M. Giersig, D. Dunstan and P. Mulvaney, *Langmuir*, 1997, **13**, 1773.
6 B. G. Ershov, *Usp. Khim*., 1997, **66**, 103 (*Russ. Chem. Rev*., 1997, **66**, 93).
7 A. V. Gordeev and B. G. Ershov, *Khim. Vys. Energ*., 1999, **33**, 258 [*High Energy Chem*. (*Engl. Transl*.), 1999, **33**, 218].
8 W. T. Doyle, *Phys. Rev*., 1958, **111**, 1067.
9 R. H. Doremus, *J. Chem. Phys*., 1965, **42**, 414.

Received: 19th April 2001; Com. 01/1788