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Procedure for Controlling Size of Silver Particles Deposited Photochemically on Quartz

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Abstract—The results of studying optical properties of silver films deposited photochemically on a quartz surface are presented. The films consist of isolated silver particles of 5–50 nm in size and of agglomerates of several micrometers in size and contain up to 7 wt % of Ag_2O. Treatment of the films with dimethylformamide solution of $[Pden_2](BPh_4)_2$ results in a decrease in the average particle size due to dissolution of small particles (5–15 nm) and destruction of greater agglomerates.

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Films consisting of silver nanoparticles deposited on solid carriers have physicochemical properties essentially differing from those of the bulk metal. It is caused by the size effects from electronic and structural changes in small particles and resulting in specific changes in their surface and bulk properties. In particular, such films have characteristic plasmon absorption bands in UV and/or visible spectral region [1]. The character of the absorption, i.e. the intensity and shape of the plasmon band, is determined by the shape and size of metal particles and by homogeneity of their size distribution [2]. This property finds application in optics when producing light filters allowing separating light of a necessary narrow wavelength range [3]. As it was found, the less particle size deviates from an average size, the narrower is the absorption band of a film, and it is the more selective in relation to the absorbed light.

The preparation of equidimensional silver colloidal particles is based on a chemical [4–6] or radiation-chemical [7, 8] reduction of silver ions in rigid polymeric matrices or in porous materials where particle growth is limited by a pore size. It seems promising to modify a solid carrier surface on which metal nanoparticles are precipitated photochemically, by metal oxides with semiconductor properties, for example, by TiO_2 [9, 10]. In this case the modifying agent promotes the formation of small particles owing to a low quantum yield of the reduction of metal ions. The control over optical properties of systems based on metal nanoparticles is also achieved by a variation of donor-acceptor properties of a surface layer of atoms due to the modification of particles by polymers [11] containing electrophilic or nucleophilic functional groups. Cations of other metals, deposited on a nanoparticle surface to form nucleus-shell structures [12], and also anions [13] can be considered as electron-donor or acceptor surface-modifying agents of a peculiar kind. Spectrophotometry is a convenient method for controlling the size and dispersity of silver particles possessing characteristic plasmon absorption bands in the visible spectral region.

The aim of this work was to develop a method for controlling optical properties of materials based on silver nanoparticles.

The irradiation of 0.01 M $AgNO_3$ solutions in N,N-dimethylformamide (DMF) in contact with a quartz slide surface by a monochromatic light with the excitation wavelength of 254 nm results in the precipitation of silver films on a quartz surface. The film color varies from brown to gray-brown in the course of the irradiation. The absorption spectra of the films taken during the photolysis are presented in Fig. 1. The film formation is accompanied by increasing absorption at 500 nm (a plasmon band). The band is widened in the course of the irradiation that points to the deposition of particles with a wide size distribution

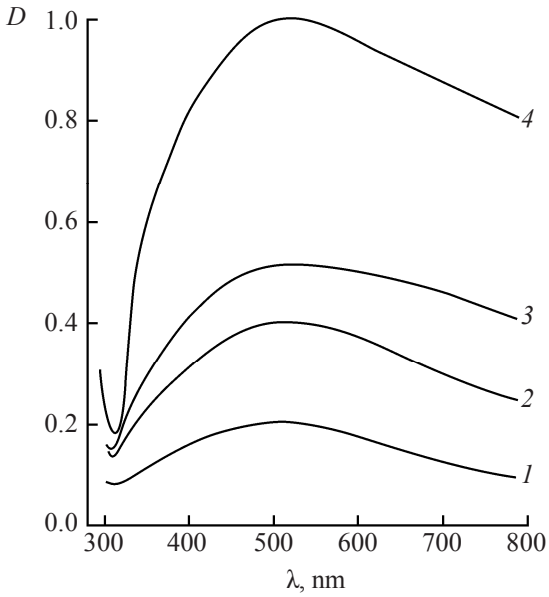

Fig. 1. Absorption spectra of silver films obtained on the irradiation of 0.01 M $AgNO_3$ solution in DMF by UV light within: (*1*) 1.5; (*2*) 3; (*3*) 6; and (*4*) 15 min.

and to the formation of larger agglomerates of particles. According to the electronic microscopy data (Fig. 2a), the films with optical density of 0.2–0.4 relative units consist of particles of 5–50 nm in size. The particles are of irregular shapes and are randomly located on a carrier surface. The films with optical density of 0.5–0.7 units consist of both individual particles (40–50 nm) and agglomerates of several micrometers in size (Fig. 2b). In the case of films with $D > 1$ a quartz surface is almost completely coated with silver. The presence of silver in the films (0.2 *D* units) is proved by the X-ray photoelectron spectroscopy (XRPES). The intensive Ag $3d_{5/2}$ signal at 368.15 eV points to the fact that the films consist of silver particles. The signal of O 1*s* at 535.3 eV corresponding to the Ag–O bond points to the formation of oxide on the surface of particles. The oxide content reaches 7 wt %.

The exposure of a quartz plate with a deposited silver film to a 0.005 M DMF solution of bisethylendiaminepalladium(II) tetraphenylborate, $[Pden_2]\cdot(BPh_4)_2$, within 30 s results in essential changes in the film structure. After 30 s of the contact with the solution of the palladium complex the optical density in the long-wavelength part of the film spectrum decreases and the maximum is displaced to the shortwave region from 480 up to 440 nm, therewith the plasmon absorption intensity increases: the optical density in the region of the maximum increases from 0.15 up to 0.175 relative units (Fig. 3). On keeping a film in darkness at room temperature within 2 h a blue shift of the absorption band up to 410 nm and further increase in its intensity are observed; the optical density reaches 0.2 units. The film color becomes bright yellow.

The increase in the absorption band intensity points to the formation of particles with a narrow size distribution, and the blue shift, to a decrease in the average particle size after contacting with the palladium compound. As it is seen from the table, the ratio (δ) of the half-height of the plasmon absorption band to its half-width, which is a criterion of the "monodispersity" of the resulting systems, also points to the increase in size homogeneity of particles. After 2 h of storage of the samples the optical density in the entire wavelength range decreases, and the absorption maximum is shifted to 400 nm.

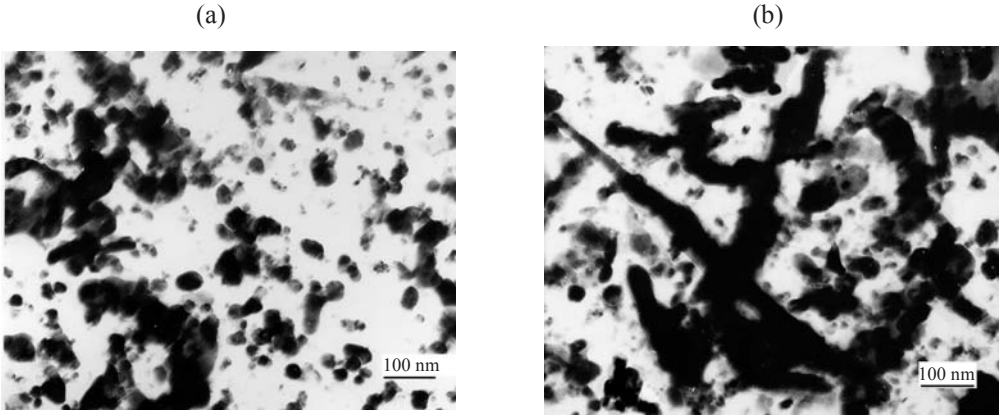

Fig. 2. Microphotographs of silver films obtained on the irradiation of 0.01 M $AgNO_3$ solution within: (a) 1.5 and (b) 15 min.

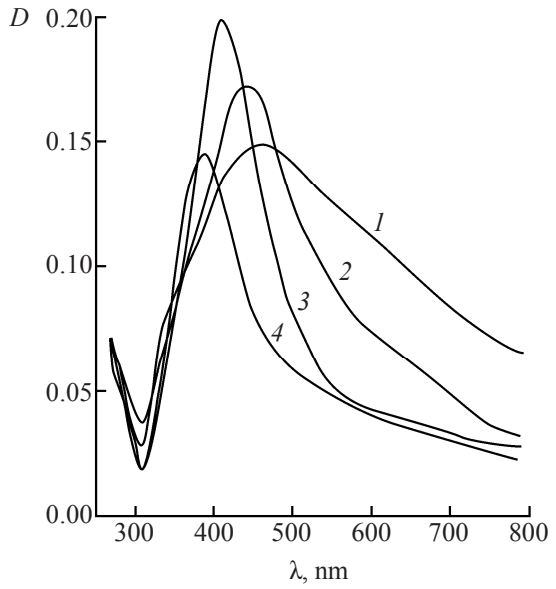

Fig. 3. Variations in the absorption spectrum of a silver film (*1*) of 0.15 *D* unit contacted with 0.005 M $[Pden_2]\cdot(BPh_4)_2$ solution in DMF on keeping in darkness within : (*2*) 0, (*3*) 2, and (*4*) 24 h.

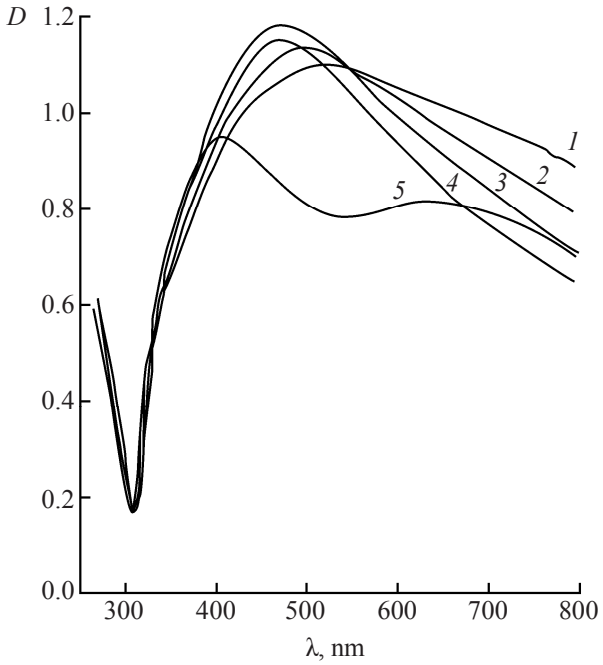

Fig. 4. Variations in the absorption spectrum of a silver film (*1*) of 1.1 *D* unit contacted with 0.005 M $[Pden_2]\cdot(BPh_4)_2$ solution in DMF on keeping in darkness within: (*2*) 0, (*3*) 4, (*4*) 6, and (*5*) 24 h.

The films characterized by high optical densities (*D* 1.1 units) (Fig. 4) undergo similar conversions after the contact with the $[Pden_2](BPh_4)_2$ solution. At the same time we can distinguish the following regularities: (1) the intensity of the plasmon absorption band increases within 4 h of dark storage and exceeds that for the films consisting of a lesser amount of particles (the table), and the band maximum is shifted from 520 to 480 nm; (2) a decrease in the optical density is observed after 4 h of storage, and after 24 h a band with a maximum at 420 nm and a wide shoulder at 640 nm is formed in the spectrum. Such a spectrum is characteristic for chain structures of particles [1].

The observed spectral variations are attributable to the influence of $[Pden_2]^{2+}$ ions on silver particles. When silver atoms in a surface layer of a particle are contacted with $[Pden_2]^{2+}$ ions a redox reaction can proceed to form smaller particles stable under existing conditions.

$$[Pden_2]^{2+} + Ag_n^0 \rightarrow [Pden_2]^{+} + Ag_{n-1} + Ag^{+}.$$

The dissolution of the surface layer of particles making agglomerates results in the formation of isolated silver particles on the carrier. The oxidation promotes the increase in the fraction of smaller particles and, as a consequence, the increase in the plasmon absorption intensity in the spectrum.

The decrease in the optical density by ~25% after storage within 2–4 h is caused by further oxidation of particles present in the film by $[Pden_2]^{2+}$ ions and air oxygen. The experiments have shown that it is not possible to avoid the oxidation even if a film is carefully washed out with DMF after the contact with a $[Pden_2](BPh_4)_2$ solution. However washing out the film with DMF and its subsequent irradiation by UV light within 2–3 min allow spectral characteristics to be stabilized. According to XRPES, the intensive signal of Ag $3d_{5/2}$ at 368.3 eV corresponding to silver metallic particles is present in the spectra of the films thus obtained together with the signal of O 1*s* at

Variations in the ratio ($\delta\times10^4$) of the half-height of the plasmon absorption (*D* units) to its half-width (λ, nm) for silver films with various initial optical density after a contact with $[Pden_2](BPh_4)_2$ within 0–24 h

D, rel. units	Initial Ag film, $\delta\times10^4$	0	1	2	4	6	24
0.15	3.5	7.6	–	15.2	14.3	–	12.0
1.1	11.0	12.0	16.4	20.3	34.5	21.0	12.8

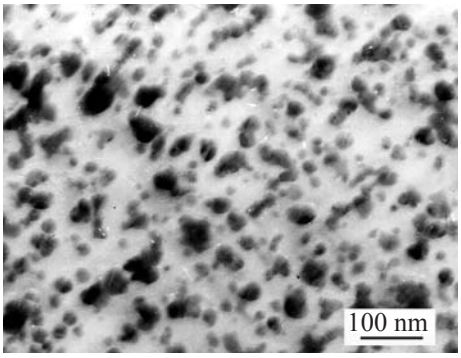

Fig. 5. Microphotograph of a silver film (0.15 *D* units) after treatment with a 0.005 M $[Pden_2](BPh_4)_2$ solution in DMF, dark drying within 2 h, and the subsequent irradiation by light with λ_{exc} 254 nm within 2 min.

534.0 eV corresponding to the Ag–O bond. The content of the Ag_2O oxide is 3.5 wt %. The decrease in the oxide content in the film also points to its dissolution upon the interaction with $[Pden_2](BPh_4)_2$. Furthermore, weak signals of C 1*s* electrons were detected at 286.4 eV in the C–N bond in amines (5.9 wt %), at 287.7 eV in the C=O bond, and N 1*s* signals at 400.1 eV in the C–N bond in amines (1.8 wt %) [15]. As these signals were absent from the initial samples deposited from DMF solutions, the result obtained can be assigned to ethylenediamine and products of its oxidation by UV light. Using XRPES, we have found neither pure palladium nor its compounds in the film.

The electron microscopy data (Fig. 5) have shown the decrease in the silver particle size up to 25 nm and the complete absence of agglomerates of particles in the film. The dissolution of the fraction with particle size 5–15 nm was observed. The method allows obtaining silver particles with a narrow size distribution in the absence of polymeric stabilizers. The resulting samples are stable and conserve their optical properties for 2 years.

EXPERIMENTAL

Colloidal silver films were prepared according to the procedure [14] by the photochemical reduction of 0.01 M $AgNO_3$ solutions in DMF contacting with a quartz glass. The thickness of the photolyte layer was 1–5 mm. The solutions were irradiated by monochromatic UV light of a Philips TUV 4W/G4 T5 lamp with a 254 nm wave length of excitation; the light intensity was 4.8×10^{16} quant cm^{-2} s^{-1}. The wavelength choice is caused by the DMF characteristic absorption at 268 nm. The concentration of silver particles deposited on a quartz surface was varied by changing the duration of photolyte irradiation. The resulting films were washed by DMF and dried under dark conditions at room temperature in air. Then the films were kept within 30 s in 0.005 M DMF solutions of bis-ethylendiaminepalladium(II) tetraphenylborate, $[Pden_2]\cdot(BPh_4)_2$.

Changes in the structure of films were detected by spectrophotometry (SF-2000) by an increase or a decrease in the characteristic absorption in the range of 350–450 nm and by transmission electronic microscopy (a Hitachi HU-11 instrument, resolution of 0.3 nm). The X-ray photoelectron spectra were recorded on an AXIS Ultra electronic spectrometer of Kratos Analytical corporation at the excitation by AlK_α (1486.6 eV) monochromatic radiation. The spectra processing was carried out with the use of a Kratos Analytical corporation software. Atomic concentrations were determined from the areas of photoelectric lines in view of the transmission function of the spectrometer after subtracting the noise (Shirley or linear), using the corresponding susceptibility factors (ionization cross sections).

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