Changes in the Morphology and Optical Absorption of Colloidal Silver Reduced with Formic Acid in the Polymer Matrix under UV Irradiation

Andrey L. Rogach, Gvidona P. Shevchenko,* Zinaida M. Afanas'eva, and Vadim V. Sviridov

Physico-Chemical Research Institute, Belarus State University, 220080 Minsk, Belarus

The influence of the UV irradiation on the morphology and optical properties of nanosize colloidal silver particles formed in the poly(vinyl alcohol) matrix containing Ag^+ and formic acid was investigated. Formation of both filament and ultrafine silver particles accompanied by a strong blue shift of the silver plasmon absorption band from 425 to 385 nm was observed under UV irradiation. The mechanism of the electron accumulation on silver particles is proposed to explain the observed morphological and spectral changes.

Introduction

Colloidal Ag particles in polymer matrices and their optical properties have been under extensive investigation as the subjects of photographic science.[1−4] The spectral position of the silver plasmon absorption band as a function of the particle size[1−3] and shape,[2,3] surface composition of the particles,[2,4] and dielectric constants of the matrix[1] has been determined. Photographic processing procedures have been developed[5−8] which permit one to control the size, shape, and surface composition of silver particles and thus to affect the spectral characteristics of the silver particles forming the photographic image. This enabled the obtainment of colored "polychrome" photographic images on the conventional black-and-white photographic emulsions comprising no traditional color components−dyes.

In the recent works of Henglein's school of thought,[9−16] nanosize Ag particles in aqueous solutions have been considered as an intermediate state between the single atoms and the bulk material, with a series of surprising properties. It was shown that not only the size, the shape, and the chemical surface modification but also the electron density increase in silver particles significantly alters the optical properties of Ag sols. A blue shift of the silver plasmon absorption band resulting from the electronic polarization of Ag particles was observed for aqueous Ag sols in the case of electron transfer from the free radicals generated radiolytically[9−14] or photolytically,[12,13] due to the chemisorption of the nucleophilic agents (e.g. phosphine[16]), and as the result of the underpotential deposition of cadmium and lead on the silver particles.[14,15] Even a mere addition of sodium borohydride into the aqueous Ag sol prepared using citrate as a reducing agent increased the electron density on the particles and caused the blue shift of the silver plasmon absorption band.[17] The electrons accumulated on Ag particles can take part in the redox reactions, i.e. Ag particles play the role of the nanoelectrodes which are "not charged by an outer potential source, but internally by chemical electron transfer reaction".[14] The excess free energy storage has been observed on Ag nanostructures generated on nonmetallic conductive substrates (SnO$_2$, glassy carbon) under high cathodic polarization.[18−20] Ag particles formed under these conditions showed the extreme dependence of the catalytic activity on the potential and catalyzed the anodic oxidation of small organic molecules in the oscillatory mode.[21]

In this paper the results of the investigation of the UV irradiation effect on the morphology and optical absorption of the nanosize colloidal Ag particles formed in the poly(vinyl alcohol) (PVA) matrix by Ag^+ reduction with formic acid are presented.

Experimental Section

In order to produce PVA films containing colloidal Ag particles the mixture was prepared according to the following method.[22] One hundred milligrams (0.6 mmol) of AgNO$_3$ was dissolved in 10 mL of 5% aqueous ammonia. The solution was then mixed with 10 mL of 5% aqueous solution of PVA, and 0.25 mL (6.6 mmol) of formic acid was added dropwise under vigorous stirring (the standard procedure of the mixture preparation). The mixture was diluted 1:4 with 5% PVA aqueous solution, casted onto glass substrates, and allowed to dry for 10 h at room temperature in the dark.

In addition to the samples prepared as described above, samples were also investigated in which (a) ammonia was absent in the mixture, i.e. 100 mg (0.6 mmol) of AgNO$_3$ was dissolved in 10 mL of aqueous solution, and (b) 1 mL of 6 M NaBH$_4$ aqueous solution was used instead of formic acid as a reducing agent; the other conditions remained the same.

Absorption spectra of the films were measured with the Specord M-40 UV−vis double-beam spectrophotometer. Transmission electron microscopy (TEM) was performed using the H-800 (Hitachi) microscope operating at 200 kV. Samples for electron microscopy were prepared by diluting the mixture 1:4 with water and dropping the solution onto a collodium-coated copper mesh grid, followed by carbon sputtering and drying in the dark. UV irradiation of the samples was carried out with a whole spectrum of the mercury lamp.

Results

Ag^+ ions in the aqueous solution prepared by the standard procedure described above are not reduced in colloidal silver over a fortnight if the solution is kept in the dark. During the drying of the viscous mixture on the glass substrate in the dark a yellow coloring of the layer is observed, suggesting the colloidal silver formation. In the absence of ammonia in the mixture or on using NaBH$_4$ instead of formic acid, the Ag^+ reduction occurs in the solution immediately after the addition of the reducing agent.

According to TEM observations, the individual, nearly spherical Ag particles about 40 nm in diameter are formed in the PVA film dried in the dark (Figure 1a). The localization of the plasmon absorption band of these particles at 425 nm (Figure 2, spectrum 1) correlates with the data on the light

Figure 1. Electron micrographs of Ag particles in the unexposed PVA film (a) and in the PVA film after 5 min (b) and 30 min (c) of the UV irradiation. The filament Ag growth during the chemical development of the silver halide photographic layer is also shown (d).
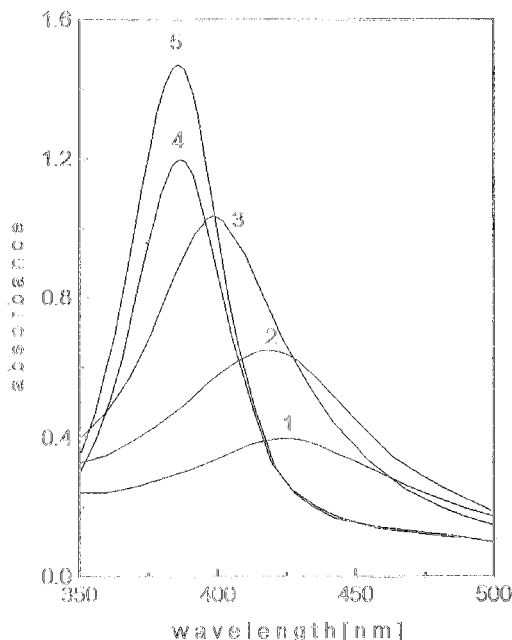

Figure 2. Absorption spectra of Ag particles in the PVA film: unexposed sample (1) and the samples after 5 min (2), 10 min (3), 30 min (4), and 1 h (5) of the UV irradiation.

absorption for the colloidal spherical Ag particles of similar size in the polymer gelatine layers.[1,2,23] The UV irradiation of the sample stimulates the additional Ag^+ reduction in the polymer layer. In the initial stages of the UV irradiation the Ag^+ reduction takes place mainly on the surface of Ag particles formed in the dark and results in the formation of filament Ag structures (Figure 1b). In some cases more than one filament

grows from the previously formed center. The filament width is the same or a little smaller than the size of the growth centers (20−40 nm). Further UV irradiation leads to the formation of a large number of small Ag particles (spherical in shape or in the form of short filament) less than 5 nm in diameter independent of the previously formed centers (Figure 1c).

The effect of the UV irradiation on the light absorption by the Ag particles in the PVA film is shown in Figure 2. The UV irradiation causes an asymmetric change of the silver plasmon absorption band with bleaching at longer wavelengths and an increase of the absorbance at shorter wavelengths. The full widths at half-maximum of the absorption band decreases during the irradiation. The blue shift of the silver plasmon absorption band takes place persistently during the UV irradiation; the maximum reaches 385 nm in 30 min of the UV irradiation. Further UV irradiation leads to an increase of the absorbance at the spectral peak position only, without any blue shift. The intensity of the silver plasmon absorption band increases approximately by a factor of 5 in comparison with the initial optical density. After 1 h of the UV irradiation the absorption spectrum of the sample remains unchanged, probably due to the complete reduction of Ag^+ in the polymer layer. The position of the maximum of the silver plasmon absorption band of the irradiated samples at 385 nm remains constant over months.

Neither morphological nor spectral changes have been observed during the UV irradiation of the PVA films containing colloidal silver, which were produced using $NaBH_4$ instead of formic acid as a reducing agent.

Discussion

It seems necessary to mention two phenomena found in the framework of this investigation: (i) formation of the filament Ag structures in the polymer film and (ii) an unusually strong blue shift of the silver plasmon absorption band during UV irradiation of the samples. Note, that in ref 22, from where the sample preparation procedure has been taken (except of the UV irradiation of the samples), the filament Ag structures were not formed.

The filament growth of Ag particles formed by Ag^+ reduction is to be expected if the following two conditions are fulfilled: (i) factors promoting growth of Ag particles in a particular direction, i.e. the Ag^+ reduction at a definite spot on the growing silver particle, and (ii) diffusion limitations on Ag^+ ions in the system. The filament Ag growth is well known for the reduction of the silver halide photographic layers[24−31] (Figure 1d). Small Ag nuclei formed on the surface of the silver halide microcrystals upon exposure of the photographic layer catalyze the reduction of Ag^+ ions provided by the developing solution or silver halide microcrystals. Filament silver growth takes place when the discharge rate of the reducing agent on the surface of the Ag centers exceeds the rate of Ag^+ transport toward the reaction site, which leads also to the accumulation of the electrons on the silver growth centers.[31] Filament shape is dictated by the uneven Ag^+ reduction due to the "microroughness" of the particles. The electric field just next to the point of the local surface curvature is higher, which causes an increased flux of Ag^+ ions to that point and an enhanced filament growth.

Another possible reason for the filament shape of Ag particles is known from the dendritic growth during the electrodeposition of metals.[32] The concentration overpotential is less at the tip of the grown whiskers than that on the planar surface.[33] The tip tends, therefore, to grow faster than the rest of the particle.

The following mechanism of the electron accumulation on Ag particles and reduction of Ag^+ ions can be proposed. UV

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irradiation stimulates the photolysis of formic acid, which occurs in aqueous solution under UV irradiation through the free radical mechanism and leads to the formation of the reducing organic and oxidizing OH radicals.[34,35] Oxidizing OH radicals can be converted into the reducing organic radicals in the presence of the alcohol groups[12,13] of PVA. The generation of a reducing agent during photochemical oxidation of formic acid has been shown for TiO_2−PVA thin layers.[36] The reduction by a free radical mechanism may proceed in our system too, due to the presence of moisture in the polymer layer.

In our samples the photooxidation of formic acid occurs mainly at the surface of Ag particles formed in the polymer layer in the dark, which collect photogenerated electrons according to the reaction:

$$Ag_n + xHCOOH \xrightarrow{h\nu} Ag_n^{x-} + xCO_2 + 2xH^+ \qquad (1)$$
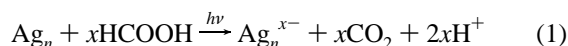
The Ag^+ reduction occurs at the surface of the cathodically polarized Ag particles, and the particles are growing:

$$Ag_n^{x-} + Ag^+ \rightarrow Ag_{n+1}^{x-1} \qquad (2)$$
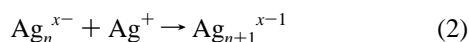
Thus, Ag particles play the role of microelectrodes which collect electrons from formic acid; the nonuniform localization of the Ag^+ reduction on the particle surface leads to the silver filament formation (Figure 1b) as described above for the reduction of the silver halide photographic layers. The accumulation of the electron density on the silver particles under UV irradiation is due to the high formic acid concentration in the polymer layer. Photolytic reduction of Ag^+ ions, independent of the silver centers formed in the dark, proceeds under UV irradiation along with the filament Ag growth and becomes dominant (Figure 1c) upon prolonged UV irradiation because the concentration of silver ions in the polymer layer is decreased.

Now let us consider the spectral changes which could be expected because of the morphological changes of the silver particles during UV irradiation of the samples. The changeover from the spherical shape of the Ag particles to the ellipsoidal one (model of an ideal filament) causes a splitting of the original single absorption band of the spherical particles into two absorption bands which move to shorter and to longer wavelengths concurrently with the increase of the axial ratio of the ellipsoid.[37] In the actual system which contains filament Ag structures of different sizes and orientations (e.g. the reduced photographic layer), the overlap of the absorption bands results in a broadening of the absorption bands and in an unstructured "gray" absorption in the whole visible spectral region.[2] For our samples, however, some increase of the silver particle absorbance in the long-wavelength spectral region (Figure 2, spectrum 2) was observed only as a background of the persistent blue shift of the silver plasmon absorption band accompanied by the decrease of the full widths at half-maximum of the absorption band in spite of the filament particle growth in the early stages of the UV irradiation. The formation of a large number of small Ag particles less than 5 nm in diameter under continuous UV irradiation can lead, according to the references,[37,38] to a change in the absorption band shape only, but it does not cause any shift of the absorption maximum. In our samples these small Ag particles contributed mainly to the enhancement of the already shifted silver absorption band at 385 nm (Figure 2, spectra 4,5).

The persistent blue shift of the single silver plasmon absorption band taking place at all the stages of the UV irradiation of our samples could be due to the electron accumulation on Ag particles—the mechanism presented above for the explanation of the filament silver growth. The electron

accumulation on the Ag particles alters the position of the Fermi level in the particles and affects their spectral characteristics.[9−15] According to the theory of the light absorption by small metal particles,[37] the wavelength of maximum absorption is inversely proportional to the square root of the density of free electrons in the particles. Thus, electron accumulation on Ag particles causes the blue shift of the surface plasmon absorption band. An estimation of the electron density enhancement that causes the observed shift of the plasmon absorption band from 425 to 385 nm using model equations[15] of the light absorption by colloidal Ag particles gives a value of about 20%.

The observed fact that the position of the absorption maximum of the irradiated samples remains at 385 nm for a long time makes it necessary to explain the negative charge "preservation" on Ag particles. In the above cited references[9−14] the localization of the shifted absorption band of aqueous nanosize Ag sols in the short-wavelength area was observed under inert atmosphere only. The electronic density donation into silver particles via underpotential deposition of Cd and Pb on their surfaces[14,15] allowed observation of a "blue-shifted" silver plasmon absorption band for an indefinitely long time. Chemisorption of the polymer layer components on the surface of Ag particles, which provides the formation of a protective dielectric layer, as well as the stabilizing action of the PVA matrix as a whole could be the probable factors protecting the excess electrons in Ag particles long enough.

Conclusion

The strong blue shift of the silver plasmon absorption band from 425 to 385 nm was observed for nanosize colloidal silver particles formed by Ag^+ reduction with formic acid in the poly-(vinyl alcohol) matrix upon UV irradiation. The electron accumulation on silver particles that influenced their optical properties seems to be responsible for the observed morphological and spectral changes. The formation of the silver filament structures in the polymer matrix upon UV irradiation is compared with the silver filament growth taking place during the reduction of the silver halide photographic layer.

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