ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 7, pp. 1421–1424. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.N. Brazhnikova, Yu.Yu. Gavronskaya, V.N. Pak, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 7, pp. 1065–1068.

# Photoreduction of $Ag^+$ Cations in a Perfluorosulfonic Membrane

**E. N. Brazhnikova, Yu. Yu. Gavronskaya, and V. N. Pak**

*Hertzen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia*
*e-mail: pakviacheslav@mail.ru*

Received December 16, 2008

**Abstract**—The two-stage synthesis of nanosize silver in the pore space of a perfluorosulfonic membrane by ion-exchange fixation of $Ag^+$ cations with the subsequent photoreduction in formaldehyde vapor was fulfilled. The study of the obtained composites shows that they contain silver "near-wall" form and nanoparticles weakly connected with the membrane surface.

**DOI:** 10.1134/S1070363209070020

During the last years much attention has been given to the preparation and study of nanoparticles encapsulated in polymers [1, 2]. Despite the durable previous history of the problem, works devoted to the synthesis and stabilization of silver nanosize forms still provide a considerable part of publications (from the large array of the publications we refer here to the works [1–6]). Nanoporous perfluorosulfonic membranes (PFSM) were considered among polymeric matrixes for silver incapsulation [6]. The configuration of PFSM internal space was not yet completely determined, however the presence of hollows with average diameter of ~4 nm connected by narrow canals of ~1 nm diameter was considered to be most probable [7, 8]. Thus, the formation of "guest" compound particles is limited by the parameters of the membrane porous structure stable due to the rigidity of the fluorocarbon frame of the polymer. The sulfo groups fixed on the walls of the membrane hollows provide a possibility to use ion exchange as the first stage of the encapsulation. Thus, in [6] silver nanoparticles were synthesized in PFSM by ion-exchange fixation of $Ag^+$ cations with the subsequent insertion of a $NaBH_4$ aqueous solution in a pore space that provided their fast reduction. In the optical spectrum of thus modified membrane one wide symmetric band with a maximum at 400 nm was observed. According to common notions [1–6, 9], this band was assigned to the surface plasmon resonance of metal nanoparticles. It is necessary to note that the shape of the band and the position of its maximum recorded in [6] did not depend on the amount of silver in the membrane.

To study the stages of metal nanoparticles formation in a membrane in the mode of gradual soft reduction, in the present work we studied additionally the character of the $Ag^+$ ion-exchange sorption in PFSM, using subsequntly the photoreduction of the fixed cations by formaldehyde vapor.

The concentration of accessible sulfo groups in an MF-4SK membrane determined by the titration with alkali is 0.84 mmol $g^{-1}$. The value of $Ag^+$ sorption from nitrate solutions was persistently reproduced at the level of 0.38±0.05 mmol $g^{-1}$ in all cases when the complete content of cations in a solution exceeds the membrane sorption capacity. The fixed form of silver appears hydrolytically stable and is retained completely under conditions of washing membranes from a porous solution. Thus, the sorption of $Ag^+$ cations in PFSM [$-SO_3H + Ag^+ \rightarrow (-SO_3^-)Ag^+ + H^+$] in some sense has irreversible character that was found earlier in the cases of two- and three-charged cations [10–12]. The use of only ~46% of sulfo groups (of the amount determined by the titration) should be assigned both to the nonuniformity of their distribution on the walls of hollows and to the difficulty in the ion-exchange sorption in narrow membrane canals.

The membrane modified by silver retains a high transparence over a wide range of 250–800 nm not only during its durable storage in air, but also on the irradiation by the full spectrum of a mercury lamp that confirms additionally the stability of the fixed form of cations. A gradual $Ag^+ \rightarrow Ag^0$ photoreduction can be realized by lighting samples in a quartz ampoule in the presence of formaldehyde vapor. In a series of spectra (Fig. 1) reflecting metallic silver formation in membrane hollows, the intensity of two main absorption

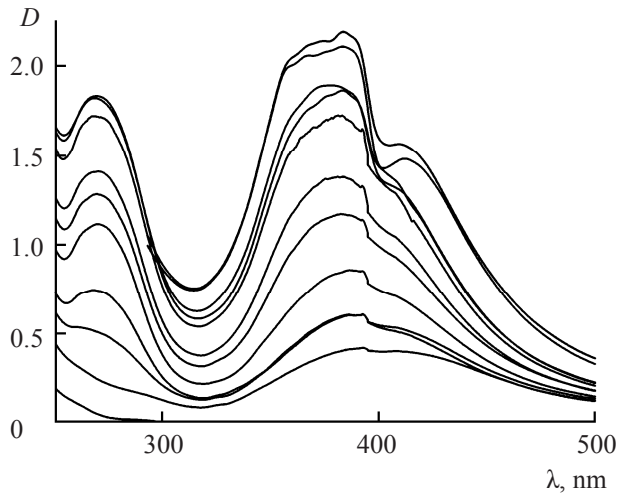


**Fig. 1.** Spectral characteristic of photoreduction of the membrane containing 0.38 mmol $g^{-1}$ of fixed silver cations. Electronic spectra were taken every 5 min of irradiation.

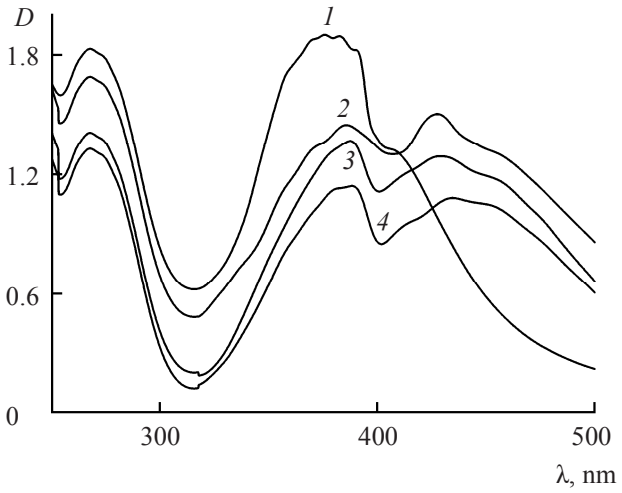


**Fig. 2.** Variation of electron absorption spectra of a membrane containing 0.38 mmol $g^{-1}$ of metallic silver as a result of its heating in nitrogen atmosphere at 80°C within, min: (*1*) 5, (*2*) 10, (*3*) 15, and (*4*) 20.

bands with maxima at 270 and 380 nm increases, the second band being asymmetric, and a clear maximum at 410 nm appears against the background of its long-wave shoulder during the reduction. Therefore the facts suggest that as a result of the gradual photoreduction at least three forms of encapsulated silver appear. The first information on their nature can be obtained on heating the modified membranes in a nitrogen atmosphere. The selected low temperature of 80°C dictated by the thermal instability of PFSM porous structure [7, 8, 10], nevertheless, gives rise to serious variations in the spectra (Fig. 2): the central absorption band with a maximum at 380 nm noticeably weakens, while the long-wave absorption adjoining it becomes more intensive, extends, and is displaced into the visible region. It is important to note that the state of silver characterized by the maximum at 270 nm appears to be heat-resistant. The results obtained suggest that under conditions of the gradual photoreduction might form a "near-wall" silver species rather strongly kept due to polarization by the membrane. Long-wave absorption bands most likely belong to metastable encapsulated silver nanoparticles weakly bound to the carrying agent and consequently capable of integrating at the thermal activation of their mobility. The upper (hardly being realized) limit of the size of integrated particles is the size of the carrying agent hollows (~4 nm [7, 8]).

The photoreduction of cations begins and goes "from walls of hollows" keeping a part of silver atoms; however by virtue of structural and energy inhomogeneity of the membrane interior space, a certain part of metal is liberated in the form of separate nanoparticles weakly bound with the carrying agent. It is possible that the formation of such integrated nanoparticles will be hampered as the amount of cations fixed in PFSM decreases. When a membrane with the 0.15 mmol $g^{-1}$ concentration of $Ag^+$ cations is photoreduced with formaldehyde the preferential increase in the intensity of the short-wave band with a maximum at 270 nm is clearly observed (Fig. 3),

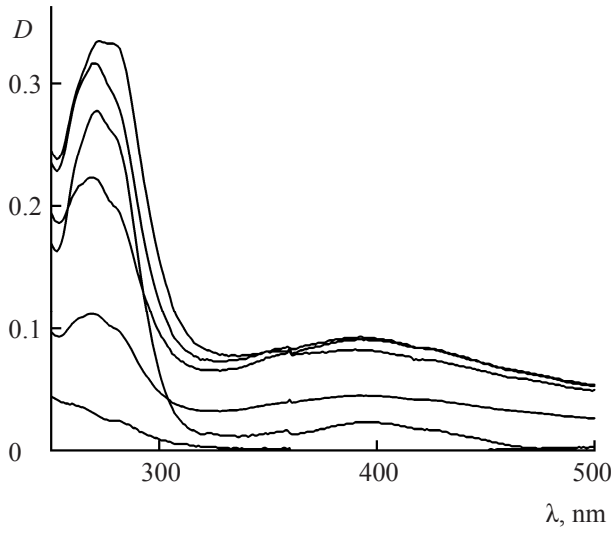


**Fig. 3.** Electronic spectra taken every 5 min during the photoreduction of a membrane with 0.15 mmol $g^{-1}$ $Ag^+$ concentration.

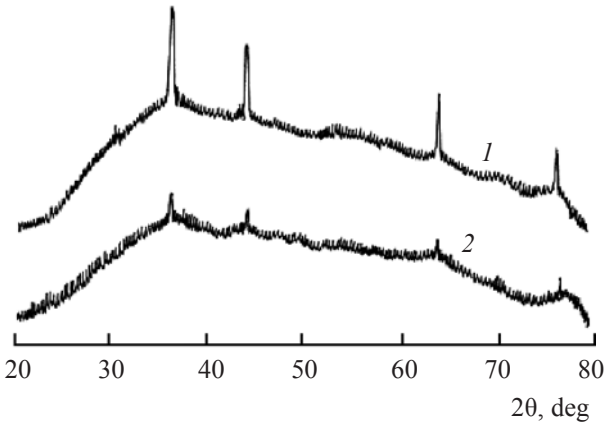


**Fig. 4.** X-ray patterns of membranes containing metal silver in an amount (mmol $g^{-1}$) of: (*1*) 0.38 and (*2*) 0.15.

which confirms the formation of "near-wall" silver, whereas the plasmon band of integrated metal nanoparticles weakly bound to a surface is only outlined.

The data of the X-ray phase analysis serve as the additional indication on the formation of various forms of silver encapsulated in PFSM (Fig. 4). In the X-ray pattern of the membrane containing 0.38 mmol $g^{-1}$ of silver, the main reflexes from the (111), (200), (220), and (311) metal planes are rather clearly recorded that corresponds to the known data on the possibility of reliable crystal-chemical identification of particles with a size of ~1−2 nm [1–6]. The reason for the decrease in the silver concentration in a membrane to 0.15 mmol $g^{-1}$ (Fig. 4) can be the domination of small particles forming a near-wall layer.

The X-ray electron spectra recorded in the ionization band of interior 3*d* states of encapsulated silver are presented in Fig. 5 in comparison to a bulk metal. The electron counting maxima with energies of 368 and 374 eV corresponding to the $3d_{5/2}$ and $3d_{3/2}$ states of silver, respectively, are present in all cases, whereas the special metal state in membranes appears as bands displaced by 1 eV to higher energies. In a sample with a reduced concentration of encapsulated silver the bands with the maxima 369 and 375 eV dominate, which points to a dominance of the metal "near-wall" form. The appreciable increase in the binding energy of silver inner electrons in this case is defined by the appearance of a positive effective charge on atoms, which, in turn, is a consequence of the polarizing action exerted on them by membrane walls. Taking into account the X-ray amorphous nature

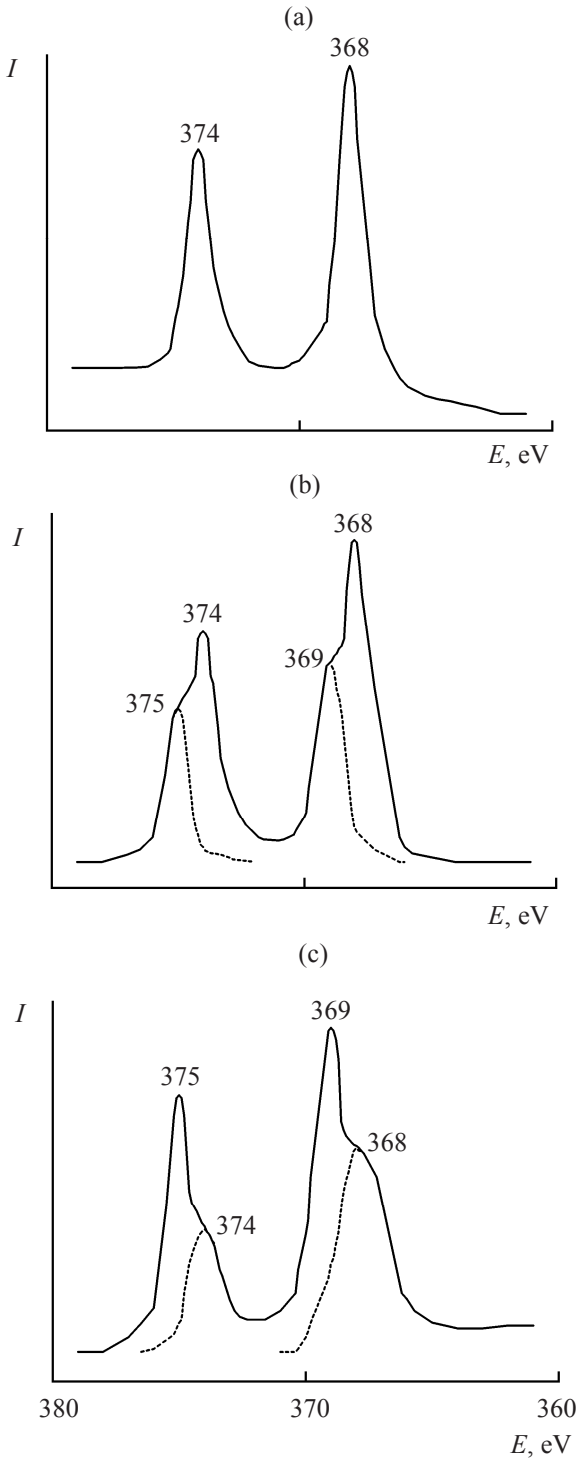


**Fig. 5.** X-ray electron spectra of (a) metal silver and membranes containing its nanosized forms (mmol $g^{-1}$), (b) 0.38 and (c) 0.15. *I* is counting rate of electrons, *E* is binding energy of electrons.

of the silver "near-wall" form, we can consider it to a first approximation as a combination of metal clusters consisting of several atoms. The main role in their fixation on the walls of PFSM hollows and in the determination of the silver charge state seems to belong to sulfo groups having strong electron-acceptor power.

## EXPERIMENTAL

In this work we used MF-4SK perfluorosulfonic membranes ~0.25 mm thick. The technique of their preliminary preparation, as well as the determination of the concentration of sulfo groups in them (0.84 mmol $g^{-1}$), were repeatedly described earlier [10–12]. Ion-exchange modification of membranes was carried out by holding within 1 h in $AgNO_3$ aqueous solutions with concentrations providing 2–5-fold excess of cations in relation to the amount of sulfo groups in the used samples. On the ion exchange termination the membranes were carefully washed out with water up to the complete removal of the working solution from the pore space. The value of $Ag^+$ irreversible sorption was determined gravimetrically, the weight increase being related to 1 g of a dry membrane. The results obtained fairly accurately coincided with the results of the gravimetric determination of silver in the form of AgCl after dissolving cations by boiling membranes in nitric acid. To carry out the photoreduction of samples, they were placed in a quartz ampoule above a saturated aqueous solution of formaldehyde and irradiated with unfiltered radiation of an SVD-120A mercury lamp. Absorption spectra of modified PFSM were recorded by a Shimadzu UV-2550 spectrometer. The X-ray patterns were taken on a "Dron-6" diffractometer with a copper anode. The X-ray electron spectra of samples were recorded on an ES-2401 instrument in the band of removal interior 3*d* electrons of silver (Mg$K_\alpha$ exciting radiation with the energy of 1253.6 eV).

## REFERENCES


1. Krutyakov, Yu.A., Kudrinskii, A.A., Olenin, A.Yu., and Lisichkin, G.V., *Usp. Khim*., 2008, vol. 77, no. 3, p. 242.
2. Bronshtein, L.M., Sidorov, S.I., and Valetskii, P.M., *Usp. Khim*., 2004, vol. 73, no. 5, p. 542.
3. Perkas, N., Shuster, M., Amirian, G., Koltypin, Yu., and Gedanken, A., *J. Polym. Sci., A: Polym. Chem*., 2008, vol. 46, no. 10, p. 1719.
4. Kim, J.H., Kim, C.K., Won, J., and Kang, Y.S., *J. Membr. Sci*., 2005, vol. 250, nos. 1–2, p. 207.
5. Li, X., Hao, X., and Na, H., *Mater. Lett*., 2007, vol. 61, no. 2, p. 421.
6. Sachdeva, A., Sodaye, S., Pandey, A.K., and Goswami, A., *Anal. Chem*., 2006, vol. 76, p. 7169.
7. Gierke, T.D., Munn, G.E., and Wilson, F.C.J., *J. Polym. Sci., B: Polym. Phys*., 1981, vol. 19, no. 11, p. 1687.
8. Xu, H., Wang, X., Shao, Z., and Hsing, I., *Appl. Electrochem*., 2002, vol. 32, no. 12, p. 1337.
9. Slistan-Grijalva, A., Herrera-Urbina, R., Rivas-Silva, J.F., Ava-los-Borja, M., Castillon-Barraza, F.F., and Posada-Amarillas, A., *Physica*, 2005, vol. 27, nos. 1–2, p. 104.
10. Petushkov, A.A., Shilov, S.M., and Pak, V.N., *J. Luminescence*, 2006, vol. 116, nos. 1–2, p. 127.
11. Brazhnikova, E.N. and Pak, V.N., *Zh. Prikl. Khim*., 2007, vol. 80, no. 2, p. 226.
12. Gavronskaya, Yu.Yu., Shilov, S.M., and Pak, V.N., *Zh. Obshch. Khim*., 2008, vol. 78, no. 2, p. 187.