

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230633965>

Surface modification of nanometer-scale silver particles by imidazole

ARTICLE *in* LANGMUIR · APRIL 1993

Impact Factor: 4.46 · DOI: 10.1021/la00028a017

CITATIONS

61

READS

49

2 AUTHORS:



[Vesna V Vodnik](#)

Vinča Institute of Nuclear Sciences

76 PUBLICATIONS 625 CITATIONS

SEE PROFILE



[Jovan M Nedeljković](#)

Vinča Institute of Nuclear Sciences

188 PUBLICATIONS 3,503 CITATIONS

SEE PROFILE

Surface Modification of Nanometer-Scale Silver Particles by Imidazole

Vesna V. Vuković and Jovan M. Nedeljković*

Institute of Nuclear Sciences, Vinča, P.O. Box 522, 11001 Belgrade, Yugoslavia

Received August 10, 1992. In Final Form: December 10, 1992

The effects of imidazole addition on the optical properties and reactivity of colloidal silver particles (40-Å diameter) were studied. Absorption spectra of surface-modified silver particles are significantly different from those of the primary silver sol. A decrease and broadening of the surface plasmon absorption band are accompanied by the formation of a distinct long-wavelength absorption band. The interaction of surface atoms with nucleophilic molecules leads to a partial oxidation of surface atoms, while the interior of colloidal particles receives a corresponding negative charge which can be picked up by the electron acceptors. This mechanism explains catalyzed oxidation of surface-modified silver particles in the absence of air by inorganic and organic electron acceptors (Cu^{2+} , nitrobenzene), as well as their high reactivity with oxygen. The Fermi potential of surface-modified silver particles by imidazole seems to lie close to -0.40 V, i.e., close to the standard one-electron transfer potential of nitrobenzene.

Introduction

During the past decade, the investigation of nanometer-scale semiconductors and metals in solution has attracted the attention of many researchers.^{1,2} These investigations have shown that the redox chemistry of such particles is enhanced and that they could be useful as photochemical sensitizers³ and catalysts for free radical processes.⁴ Recently, a number of reports on the properties of surface-modified particles have appeared, such as the one on the preparation of quantum-size CdS particles soluble in organic solvents carrying organic thiol groups on their surface.⁵⁻⁸ Similarly, in the case of metals, it has been shown that the presence of nucleophilic molecules in the colloidal solution of silver or in the solution of nonmetallic oligomeric silver clusters can drastically change the shape and the position of the absorption bands.⁹⁻¹⁷ The silver atoms on the surface are coordinatively unsaturated. One may expect that unoccupied orbitals exist on the surface into which a nucleophilic reagent can donate an electron pair. The consequence is not only a change in the optical

absorption of the colloidal particles but also a change in their reactivity.

In this paper we have focused on the surface modification of silver particles with imidazole, histidine, and alanine. Under certain conditions surface-modified silver particles have optical properties and reactivity completely different from those of the primary silver sol. The differences are due to the fact that the silver particles carry nucleophilic molecules on their surface.

Experimental Section

All reagents were commercial products of the highest purity available. Solutions were prepared with triply distilled water. Oxygen was removed by bubbling with argon.

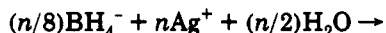
Spectrophotometric measurements of colloidal solutions were carried out on a Perkin-Elmer Lambda 5 UV-vis spectrophotometer.

Preparation of Silver Sols by Using NaBH_4 as a Reducing Agent. Primary silver sols were prepared by reduction of silver ions using NaBH_4 . A 10-mg sample of NaBH_4 was added to 100 mL of an Ar-saturated solution of 0.5×10^{-4} M Ag_2SO_4 ; mixed vigorously, they formed a clear yellow sol. The pH increased due to the hydrolysis of excess NaBH_4 and after several tens of minutes reached 9.8. The primary silver sol changed color upon addition of imidazole or histidine.

Photochemical Preparation of Surface-Modified Silver Particles. A solution which contained 0.5×10^{-4} M Ag_2SO_4 and $(2-8) \times 10^{-3}$ M imidazole (histidine, alanine) was purged with argon, sealed, and then illuminated by the light from an Osram XBO 150-W lamp. The absorbed light intensity was 7×10^{-7} einstein min^{-1} , as measured by potassium ferrioxalate actinometry.¹⁸

Results and Discussion

Optical Properties of Surface-Modified Silver Particles. The addition of sodium borohydride, NaBH_4 , to a deaerated solution of silver sulfate lead to the complete reduction of silver ions, and the yellow color of colloidal silver appeared (eq 1). The initial pH of the solution

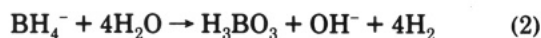


increased to 9.8 upon the addition of NaBH_4 due to the hydrolysis of excess NaBH_4 according to eq 2. The

* To whom correspondence should be addressed.

- (1) Henglein, A. *Top. Curr. Chem.* 1988, 143, 113.
- (2) Andres, R. P.; Averback, R. S.; Brown, W. L.; Brus, L. E.; Goddard, W. A.; Kaldor, A.; Louie, S. G.; Moskovits, M.; Percy, P. S.; Riley, S. J.; Siegel, R. W.; Spaepen, F.; Wang, Y. *J. Mater. Res.* 1989, 4, 704.
- (3) Nedeljkovic, J. M.; Nenadovic, M. T.; Micic, O. I.; Nozik, A. J. *J. Phys. Chem.* 1986, 90, 12.
- (4) Henglein, A. *J. Phys. Chem.* 1979, 83, 2209.
- (5) Nosaka, Y.; Yamaguchi, K.; Miyama, H.; Hagashi, A. *Chem. Lett.* 1988, 605.
- (6) Hayes, D.; Micic, O. I.; Nenadovic, M. T.; Swayambunathan, W.; Meisel, D. *J. Phys. Chem.* 1989, 93, 4603.
- (7) Fischer, Ch-H.; Henglein, A. *J. Phys. Chem.* 1989, 93, 5578.
- (8) Herron, N.; Wang, Y.; Eckert, H. *J. Am. Chem. Soc.* 1990, 112, 1322.
- (9) S. Sal'sedo, K. A.; Tsvetkov, V. V.; Yagodovskii, V. D. *Zh. Fiz. Khim.* 1989, 63, 3295.
- (10) S. Sal'sedo, K. A.; Tsvetkov, V. V.; Yagodovskii, V. D. *Zh. Fiz. Khim.* 1990, 64, 1858.
- (11) Mostafavi, M.; Keghouche, N.; Delcourt, M.-O.; Belloni, J. *Chem. Phys. Lett.* 1990, 167, 193.
- (12) Henglein, A.; Linnert, T.; Mulvaney, P. *Ber. Bunsen-Ges. Phys. Chem.* 1990, 94, 1449.
- (13) Fojtik, A.; Mulvaney, P.; Linnert, T.; Giersig, M.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* 1991, 95, 770.
- (14) Linnert, T.; Mulvaney, P.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* 1991, 95, 838.
- (15) Mulvaney, P.; Linnert, T.; Henglein, A. *J. Phys. Chem.* 1991, 95, 7843.
- (16) Subramanian, S.; Nedeljkovic, J. M.; Patel, R. C. *J. Colloid Interface Sci.* 1992, 150, 81.
- (17) Nedeljkovic, J. M.; Marjanovic, B. N. *J. Colloid Interface Sci.*, in press.

(18) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, A* 1956, 235, 518.



absorption spectrum contained the strong surface plasmon absorption band at 375 nm, caused by the excitation of the electron gas in the metallic silver particles (Figure 1, curve a). The particle distribution was narrow with a mean diameter of $D = 40 \text{ \AA}$ according to the electron microscopy data. Assuming that the density of the particles is the same as that of bulk silver, a mean agglomeration number of 1960 was calculated from the mean diameter. A significant decrease and broadening of the surface plasmon band followed by the development of a new band in the visible spectral region was observed upon addition of imidazole to the colloidal solution of silver. This new absorption band shifted to the red as a function of the aging time, and different colors as orange, red, and purple were observed (Figure 1, curves b–e). The appearance of different colors was also observed in the case of surface-modified nanometer-scale silver particles by ethylenediaminetetraacetic acid.¹⁷ It should be pointed out here that under our experimental conditions optical effects due to aggregation or enhanced growth of silver particles are highly improbable because of the fact that no increase in scattering of the solution upon addition of imidazole was observed. All colloidal solutions were stable and transparent and did not show any opalescence in a period of several hours. Similar optical effects were observed by Heard et al.¹⁹ after adsorption of pyridine and 4-(dimethylamino)pyridine onto the silver particles. However, these researchers suggested that a long-wavelength (>500 nm) absorption band arose from particles of the primary sol which had aggregated but not coalesced to form true solid particles.

The preparation of colloidal silver was also performed in the presence of surface-active reagents such as hexametaphosphate (HMP) and sodium dodecyl sulfate (SDS). The addition of HMP at low concentrations ($<1 \times 10^{-4} \text{ M}$) to the silver sol which contained imidazole did not affect the development of the long-wavelength absorption band. However, the disappearance of the long-wavelength absorption band and recovery of the surface plasmon absorption band were noticed when the concentration of HMP was higher than $1 \times 10^{-3} \text{ M}$ (Figure 2A). A similar effect was observed upon addition of imidazole to the primary silver sol prepared in the presence of SDS. Development of the long-wavelength absorption band was significantly retarded when the concentrations of SDS and imidazole were comparable (Figure 2B). These results can be understood in terms of the competition between imidazole and HMP or SDS for the silver surface, and the obviously stronger complexing capability of HMP and SDS molecules.

As expected, optical effects similar to those described for imidazole were observed upon addition of histidine to the colloidal solution of silver at temperatures higher than 35°C . In order to differentiate between the influence of the amino and carboxyl groups and that of the side chain of histidine (imidazole) on the optical properties of silver particles, the separate experiments with alanine were also performed. Addition of alanine to the primary silver sol at room temperature did not have any influence on the optical properties of silver particles. However, at elevated temperatures ($>75^\circ\text{C}$) a significant decrease and broadening of the surface plasmon band were observed as well as the presence of the featureless tail in the visible spectral

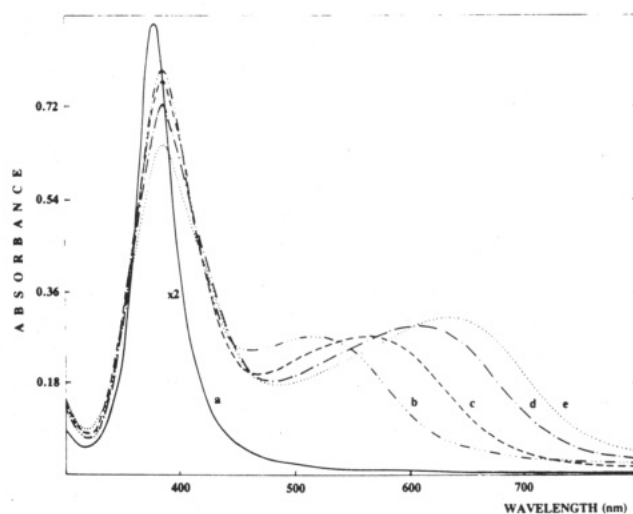


Figure 1. Absorption spectrum of $1 \times 10^{-4} \text{ M}$ primary silver colloid obtained after addition of NaBH_4 (10 mg/100 mL) into $0.5 \times 10^{-4} \text{ M}$ Ag_2SO_4 (a) and absorption spectra at various times after addition of 1.8 mL of $5 \times 10^{-2} \text{ M}$ imidazole into 20 mL of primary silver colloid: 1 min (b); 10 min (c); 35 min (d); 50 min (e).

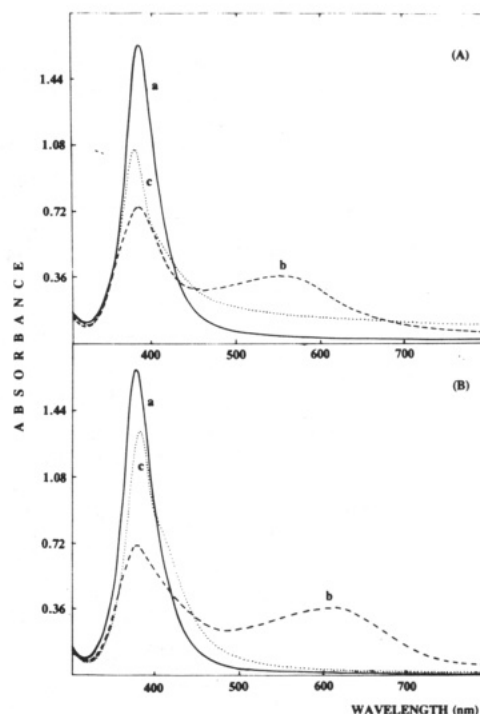


Figure 2. Absorption spectra of silver colloids: (A) $1 \times 10^{-4} \text{ M}$ primary silver colloid (a), 8 min after addition of 2 mL of $5 \times 10^{-2} \text{ M}$ imidazole into 20 mL of primary silver colloid (b), immediately after addition of 0.1 mL of 0.1 M HMP into solution b (c); (B) $1 \times 10^{-4} \text{ M}$ primary silver colloid (a), 10 min after addition of 0.9 mL of $5 \times 10^{-2} \text{ M}$ imidazole into 20 mL of solution which contained $1 \times 10^{-4} \text{ M}$ primary silver colloid and $5 \times 10^{-4} \text{ M}$ SDS (b) or $2 \times 10^{-3} \text{ M}$ SDS (c).

region. Similar effects upon addition of aromatic and aliphatic amino acids to the silver sol were reported by Chumanov et al.²⁰ We concluded that the appearance of the distinct long-wavelength absorption band is associated with adsorption of the aromatic molecules onto the silver surface. Addition of aliphatic amino acid (alanine), or NH_3 ,¹² or the presence of anions such as S^{2-} ,^{9,10,12,15} $\text{S}_2\text{O}_3^{2-}$,^{9,10} $\text{HSCH}_2\text{COO}^-$,¹³ $\text{HS}(\text{CH}_2)_2\text{COO}^-$,¹³ and CN^- ¹⁵

(19) Heard, S. M.; Grieser, F.; Barraclough, C. G.; Sanders, J. V. *J. Colloid Interface Sci.* 1983, 93, 545.

(20) Chumanov, G. D.; Efremov, R. G.; Nabiev, I. R. *J. Raman Spectrosc.* 1990, 21, 43.

lead only to an asymmetric broadening of the surface plasmon band into the long-wavelength region.

Surface-modified silver particles were also prepared photochemically. It is well-known that the initial process of photolysis of deaerated aqueous solutions of aromatic and aliphatic amino acids is photoionization.²¹ We took advantage of this process to produce small silver particles by reducing silver ions from the corresponding complexes with hydrated electrons. The characteristic absorption spectrum of photochemically prepared surface-modified silver particles by imidazole is shown in Figure 4 (curve a). It should be noted that the absorption spectrum shows a slight shift toward the red and significant broadening of the surface plasmon absorption band as well as the presence of a featureless tail in the visible spectral region. Similar absorption spectra were also observed in the cases of histidine and alanine.

Although the interaction between a nucleophilic reagent and metal surface has a local character, there is a possibility for electron delocalization of chemisorbed molecules and their participation in electron plasma. The decrease and asymmetric broadening of the surface plasmon band that were observed can be explained by the increase of the effective concentration of free conductive electrons and consequently by the change of the extinction cross section.²² The presence of the absorption bands in the region from 400 to 600 nm indicates important changes in the electron density distribution of the ligands.¹¹

Catalytic Oxidation of Surface-Modified Silver Particles. Henglein⁴ showed that colloidal particles can store several hundreds of electrons after injection of electrons by radiolytically generated reducing radicals. The position of the Fermi level is shifted toward more negative potentials, and stored electrons can initiate multielectron reduction processes such as reduction of water or reduction of many organic and inorganic solutes.

The position of the Fermi level of silver particles can also be drastically changed in the presence of a nucleophilic reagent that donates an electron pair to the unoccupied orbitals which exist on the surface. An example of the enhanced reactivity of surface-modified silver particles is their catalyzed oxidative corrosion. The fact that the oxidation of metal by oxygen is facilitated by a nucleophilic reagent is well-known, the extraction of gold from ores by cyanide in the presence of air being a typical example. In the present study, the addition of a complexing agent to the colloidal solution of silver and the subsequent exposure to air led to a significantly faster dissolution of silver as compared with experiments where the primary silver sol was used (Figure 3). Thermodynamically, this effect is understood in terms of the higher stability of the products of oxidation, i.e., formation of complex species instead of Ag^+ . The formation constants of the imidazole-silver(I) complexes are $\text{p}K_1 = 3.11$ and $\text{p}K_2 = 3.73$, and it is interesting that these values are close to the corresponding formation constants of the ammonia-silver(I) system.²³⁻²⁵ The mechanism for the catalyzed oxidative corrosion is based on partial oxidation of a surface atom after chemisorption of nucleophilic reagents, while the excess electron density is accepted by the interior of the silver particle. Only a certain number of molecules can be chemisorbed until an equilibrium is reached as the accumulated negative charge on the particle prevents

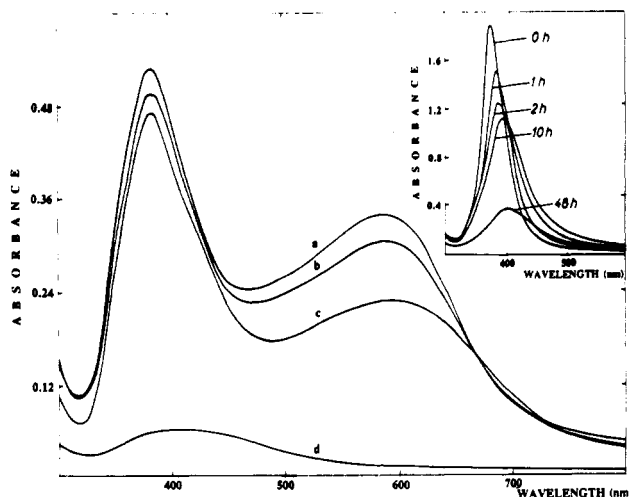


Figure 3. Absorption spectra of 1×10^{-4} M colloidal silver solution in the presence of 8.3×10^{-3} M imidazole before (a) and after the exposure to air: (b) 10 min; (c) 40 min; (d) 120 min. The inset is the absorption spectrum of 1×10^{-4} M colloidal silver solution before (0) and at various times after the exposure to air.

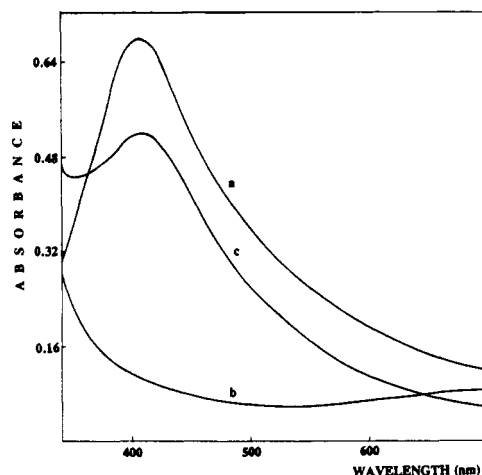


Figure 4. Absorption spectrum of 1×10^{-4} M photochemically prepared silver colloidal solution in the presence of 4.5×10^{-3} M imidazole (a), absorption spectrum immediately upon addition of 0.2 mL of 5×10^{-2} M CuCl_2 into 3.5 mL of solution a under an argon atmosphere (b), and absorption spectrum 30 min after addition of 0.4 mL of 5×10^{-2} M nitrobenzene into 3.5 mL of solution under an argon atmosphere (c).

further donation of charge. Henglein¹² termed this effect "preoxidation" of the surface atoms. Upon admission of oxygen into the solution, the electrons on the silver particles are picked up and further complexation can proceed until all the silver is dissolved.

The oxidation of the surface-modified silver particles by imidazole was also achieved by using organic and inorganic electron acceptors instead of oxygen. The electron acceptors (Cu^{2+} ions and nitrobenzene) have already been used to test the enhanced redox capability of the surface-modified silver particles.^{15,26} It should be emphasized that, in all cases, the addition of the electron acceptor to the silver sol in the absence of the nucleophilic molecules did not result in the oxidation of silver particles. In Figure 4 (curves a and b), the absorption spectra of the photochemically prepared silver particles modified by imidazole are shown before and after the addition of Cu^{2+} ions under an argon atmosphere. The broad absorption band of a silver sol faded away immediately. The solution

(21) Mossoba, M. M.; Makino, K.; Riesz, P. *J. Phys. Chem.* 1982, 86, 3478.

(22) Yagodovskii, V. D. *Zh. Fiz. Khim.* 1974, 48, 1093.

(23) Gold, D. H.; Gregor, H. P. *J. Phys. Chem.* 1960, 64, 1461.

(24) Banmen, J. E., Jr.; Wang, J. C. *Inorg. Chem.* 1964, 3, 368.

(25) Datta, S. P.; Grzybowski, A. K. *J. Chem. Soc. A* 1966, 1059.

(26) Henglein, A.; Mulvaney, P.; Linnert, T. *Faraday Discuss. Chem. Soc.* 1991, 92, 34.

became blue, its absorption spectrum being identical with the well-known spectrum of the copper complexes of imidazole.²⁷ This result undoubtedly showed that the Fermi level of silver particles modified by imidazole was significantly shifted toward a negative potential, and is more negative than the standard redox potential of the $\text{Cu}^{2+}/\text{Cu}^+$ couple (0.153 V). The complete dissolution of photochemically prepared silver particles in the presence of histidine or alanine was also observed upon the addition of Cu^{2+} ions.

When nitrobenzene was used as an electron acceptor, slow and uncomplete disappearance of the silver absorption band was observed (Figure 4, curve c). The equilibrium was established 30 min after the addition of nitrobenzene. The Fermi potential of photochemically prepared silver particles complexed on its surface by imidazole seems to lie close to -0.40 V, i.e., close to the standard one-electron transfer potential of nitrobenzene. This result is in agreement with previously estimated positions of the Fermi level in the case of surface-modified silver particles by CN^- ions (-0.44 V),¹⁵ and ethylenediaminetetraacetic acid (<-0.35 V).¹⁷ Such results widely expand the field of fundamental as well as applied studies on electron transfer catalysis.

Conclusion

In the present study, surface modification of silver particles is achieved by using biologically important

nucleophilic molecules such as imidazole and histidine. Optical properties of surface-modified silver particles significantly differ from those of the primary silver sol. The formation of orange, red, and purple silver sols is not the consequence of aggregation or enhanced growth of silver particles, and is assigned to the interaction between silver particles and nucleophilic molecules. Also, the electronic properties of the surface-modified silver particles are changed because of the interaction between silver particles and nucleophilic molecules. As a consequence, the Fermi level is shifted toward more negative potentials (-0.40 V), and the reducing ability of surface-modified silver particles is enhanced. This is demonstrated by the catalyzed oxidation of surface-modified silver particles in the absence of air by inorganic and organic electron acceptors, as well as their high reactivity toward oxygen. The processes on the surface-modified silver particles resemble those in conventional electrochemistry. The only difference is that instead of observing the changes in electrode potential we follow the changes in optical absorption which indicate "cathodic polarization" of the surface-modified silver particles. The extension of this study to other noble metals is expected to be straightforward.

Acknowledgment. We thank Dr. Tijana Rajh and Dr. Slobodan Jovanović for many helpful discussions during the preparation of this paper.

(27) Edsall, J. T.; Felsenfeld, G.; Goodman, D. S.; Gurd, F. R. N. *J. Am. Chem. Soc.* 1954, 76, 3054.