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The role of oxygen in plasmon-driven transformation of silver nanoparticles

Jan Krajczewski, Karol Kołątaj, Sylwia Parzyszek, Heman Burhanalden Abdulrahman, Andrzej Kudelski*

Department of Chemistry, Warsaw University, Pasteur 1, PL-02-093 Warsaw, Poland

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ABSTRACT

Plasmon-driven transformation (PDTr) of silver nanoparticles is a very valuable tool for formation of various anisotropic silver nanostructures. PDTr involves two steps: slow surface dissolution of silver nanoparticles, and redeposition of dissolved silver by the photocatalytic reduction of Ag^+ cations. Photocatalytic reduction of Ag^+ occurs preferentially at such places of silver nanostructures, at which strong surface plasmons are excited (usually sharp edges, tips). Therefore, during PDTr the inhomogeneity of nanoparticles may increase. Up to now all synthesis of Ag nanoparticles utilizing PDTr have been carried out in the solution containing dissolved oxygen. In this contribution we have shown that when another oxidising agent (e.g., 1,4-benzoquinone) is present in the reaction mixture, the PDTr of silver nanoparticles can be carried out even in the deoxidised solution. Moreover, using oxidising agents other than oxygen allows for some modification of the PDTr process (especially synthesis of smaller Ag nanostructures). Explanation of the observed phenomenon is proposed (involving complete oxidation by the dissolved oxygen of some very small Ag clusters).

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1. Introduction

To date, the majority of nanomaterials, in which "active" parts are metal nanoclusters, contain spherical nanoparticles. Hence, many methods to synthesize isotropic metal nanoparticles have been developed with moderate to excellent control over their sizes. Anisotropic nanoparticles (e.g., wires, prisms) may be, however, significantly better for numerous photonic, plasmonic, electronic and photocatalytic applications than the isotropic ones [1]. One of the most promising methods of the synthesis of different types of anisotropic silver nanoparticles with relatively good control over their shapes and sizes is so-called plasmon-driven transformation (PDTr). Such conversion was observed by Jin et al. [2], who showed that upon irradiation with light "almost spherical" Ag nanoparticles are converted into triangular nanoprisms. Since the initial report of the PDTr reconstruction of Ag nanoparticles, there has been much interest in understanding the mechanism of this process. Briefly speaking, further investigations showed that the transformation process involves two steps: **(i)** partial surface dissolution of silver nanostructures, and then **(ii)** photocatalytic reduction of Ag^+ which causes preferential redeposition of silver at same places of silver nanoparticles [3,4]. The efficient photocatalytic reduction of Ag^+ occurs only at such places of the silver nanoclusters, at which strong surface plasmons are excited (usually sharp edges [5]). Therefore, during light-induced transformation the inhomogeneity of Ag nanoparticles may increase. If the surface plasmons on the silver nanoparticles are not excited – either due to the absence of photostimulation or a mismatch between the excitation frequency and the frequency of the surface plasmon resonance (SPR) of the silver nanoparticle – the deposition of silver does not occur [1]. The ratio of the reducing deposition of silver on the surface of plasmonic nanoparticles increases with the increase of the near field intensity enhancement. Due to SPR one can also control the size of formed nanoparticles: as the nanoparticles grow and their SPR shifts from the excitation frequency, the nanoparticles absorb less light and their growth slows. The other studies of the PDTr process have shown that the final geometry of obtained nanostructures also depends on the initial geometry of the photo-transferred nanoparticles and on the temperature at which PDTr has been carried out [6–9].

As far as we know up to now all PDTr synthesis of anisotropic silver nanoparticles have been always carried out in the presence of dissolved oxygen. In this work we present the first example of a photo-transformation process of silver nanoparticles in the O_2-free conditions. We proved that by using other oxidising agent

* Corresponding author at: Faculty of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland.
E-mail address: akudel@chem.uw.edu.pl (A. Kudelski).

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(1,4-benzoquinone) it is also possible to obtain required rate of the surface dissolution of silver, allowing for efficient enough second step of the PDTr (redeposition of silver). Controlling the rate of the surface dissolution of silver allows for some modification of the product of the PDTr process, for example, elimination of oxygen facilitates synthesis of very small anisotropic Ag nanostructures. Possible mechanism of the observed phenomenon is discussed.

2. Materials and methods

2.1. Materials

Silver nitrate and trisodium citrate dihydrate (NaCit) were purchased from POCH SA, Poland (both compounds were pure p.a.). L-Arginine, 1,4-benzoquinone, crystal violet and *p*-mercaptobenzoic acid were acquired from Sigma-Aldrich (Poland). Rhodamine 6G hydrochloride and sodium borohydride ($NaBH_4$) ≥99% were purchased from Fluka Analytical (Poland). All compounds were used as received without further purification or treatment. Argon (≥99.999%) was acquired from Air Products (Poland). Water used for all experiments was purified in Milli-pore Milli-Q system.

2.2. Chemical synthesis of silver nanoparticles

Silver nanoparticles, which have been further transformed in the PDTr process were prepared by the reduction of $AgNO_3$ with $NaBH_4$ in the presence of NaCit. Briefly, to 100 mL of aqueous solution containing $AgNO_3$ (0.1 mM) and NaCit (3 mM) freshly prepared ice-cold aqueous solution of $NaBH_4$ (0.8 mL, 0.01 M) was added while vigorously stirring. Immediately after addition of the solution of sodium borohydride the colour of the reaction mixture changed to yellow which indicates formation of silver nanoparticles.

2.3. Light-induced transformation

In a typical light-induced transformation about 9 mL of a chemically prepared silver sol (see above) was put into the cylindrical glass reactor (with diameter of 2 cm) and then illuminated for 24 h using 2 light-emitting diode (LED) clusters generating light beams with relative narrow spectral half-width ($\Delta\lambda < 20$ nm). Irradiation has been carried out using LED clusters emitting radiation of various wavelengths: $\lambda = 660$ nm (red), $\lambda = 520$ nm (green), $\lambda = 470$ nm (blue), $\lambda = 440$ nm (blue-violet) and $\lambda = 410$ nm (violet). Average luminous flux was 270 lumens. In the case of irradiation of deoxygenated sols, the reactor was filled with chemically prepared silver sol, the reaction mixture was deaerated by bubbling with argon for 1 h, and then the reactor was hermetically sealed under the argon atmosphere.

2.4. Characterization methods

UV–vis spectra were collected using a Thermo Scientific Evolution 201 spectrophotometer. The transmission electron microscopy (TEM) measurements were carried out using LIBRA 120 (Zeiss, Germany) electron microscope working at an accelerating voltage of 120 kV. The electron microscope was equipped with the in-column OMEGA filter and charge-coupled device (CCD) detector. Before TEM measurements the samples of silver sols were dropped onto Formvar-coated 400-mesh nickel grids (Agar Scientific) and allowed to dry. Raman spectra were recorded using a Horiba Jobin–Yvon Labram HR800 spectrometer equipped with Peltier-cooled (1024 × 256 pixel) CCD detector and 600 grooves/mm holographic grating. The Raman spectrometer was coupled with a BX40 Olympus confocal microscope equipped with a long distance

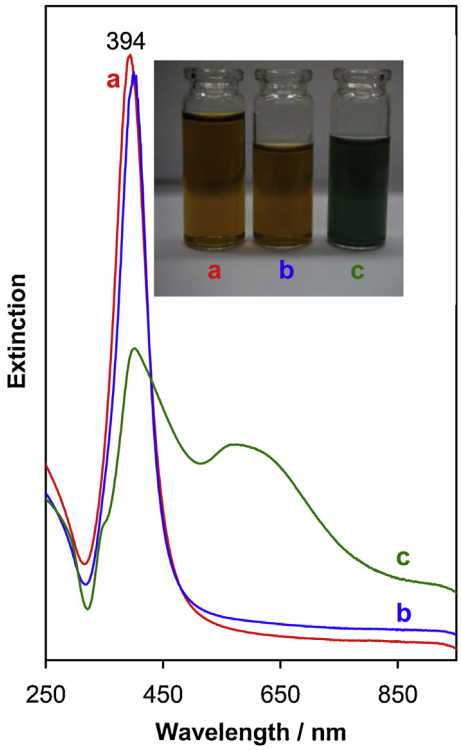

Fig. 1. Extinction spectra of Ag sols. (a) Freshly synthesised "precursor" silver sol, (b) deaerated silver sol irradiated for 3 days, (c) sol in contact with air irradiated for 24 h. Irradiation has been carried out using green excitation radiation ($\lambda = 520$ nm). Inset shows the visual appearance of sols a, b, and c. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

50× objective. A He–Ne laser provided the excitation radiation with the wavelength of 632.8 nm.

3. Results and discussion

The visual appearance and UV–vis extinction spectra of chemically prepared Ag sol before irradiation, irradiated after deoxygenation and irradiated in contact with air are shown in Fig. 1. As can be seen in this figure the chemically prepared sol is yellow and the position of the plasmon band for this colloid is 394 nm. Fig. 2a shows the TEM image of chemically synthesised nanoparticles. As can be seen in this micrograph formed Ag nanoparticles are very small and mostly spherical. On the basis of TEM measurements we calculated that the average diameter (from 300 randomly chosen objects) of chemically synthesised nanoparticles is 3.5 ± 0.7 nm.

If the silver sol is deaerated, it is very resistant to the irradiation with the visible light. We found that the optical properties of the sol does not change observably after irradiation lasting for a few days (see Fig. 1, spectrum and sample b). Also the TEM measurements do not reveal any significant change in the morphology of the silver nanoparticles after irradiation of the O_2-free Ag sol. However, when the silver sol is kept in contact with air (it means sol is saturated with oxygen at $p_{O2} = 0.2$ bar) the irradiation of the silver sol causes well visible changes of its colour from yellow to green (see Fig. 1, spectrum and sample c). TEM analysis of photochemically transformed nanoparticles showed that as have been already shown by other groups [1–4,6–9], irradiation of the Ag sol causes formation of some silver nanoprisms and the average length of the edge of formed nanoprisms increases with increasing wavelength of the excitation radiation (see Fig. 2b and c).

As mentioned in the Introduction, up to now all photochemical transformations of silver nanoparticles have been carried out in the presence of dissolved oxygen. Therefore, we decided to verify

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