Photochemical Metallization of DNA

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Upon UV irradiation of silver(I) ion solutions containing alcohol as reduction agents, metal nanoparticles are grown on a DNA polymer chain. This metallization is independent of the DNA double-helicity and is controlled by the chemical structure of alcohol as well as by the wavelength of the light source.

Heavy metal ions such as silver cations are known to form different types of complexes with DNA.[1] In solutions of reducing noble metal ions, macromolecules function as nanosized metal nucleation templates that have been successfully utilized for the preparation of metal nanowires.[2] On the other hand, it is known that photochemical reduction of noble metal ions results in the formation of metal nanoparticles (NPs),[3] which is particularly attractive to control metal nanostructure formation. The possibility to use DNA for photochemical silver deposition has been recently shown by Berti et al.,[4] who reported that the presence of DNA itself is sufficient to trigger metal deposition on DNA. In this report, we demonstrate that the presence of reduction agent is yet necessary condition for DNA photochemical metallization to proceed. To make clear the mechanism of silver metal growth on DNA we studied metallization of long T4 phage DNA (166 kDa, ca. 57 μm) molecules upon photoreduction of $AgNO_3$ in solutions prepared by dilution of commercially available T4 DNA in TE buffer solution[5] and in pure water[5] in the presence of different alcohols as reduction agents.

With the addition of 10 mM silver nitrate solution to 5 μM DNA solutions (in phosphates) in water or in buffer, no visual changes were observed in either case (Figure 1Aa), and the solutions remained transparent for several hours (Figure 1Ab). After the solutions were exposed to UV light of $\lambda = 254$ nm, in water solution of DNA no changes were recognized, while DNA buffer solution turned progressively to yellow, yellow-brown, and then red-brown within 10–15 min (Figure 1Ac). After irradiation, a broad peak at 450 nm was observed on UV spectra of DNA in buffer solution (Figure 1B, (1)), which corresponds to the plasmon resonance absorbance of silver nanoparticles (NPs), while no visible spectrum absorbance was found for DNA in pure water (Figure 1B, (2)). Formation of metal NPs in buffered DNA solutions was confirmed by transmission electron microscopy (TEM) observations. Figures 1C and 1D show a DNA chain decorated by silver NPs of approximately 20–30 nm in diameter, which are located primarily on the DNA chain. It is concluded that formation of silver NPs on a DNA chain occurs upon UV irradiation only in solutions containing small amounts of buffer components.

Indeed, when we added Tris into solution of DNA in pure water, formation of nanoparticles after irradiation was confirmed (Figure 2A). Although the peak of NPs was detected even at very low concentrations of Tris, formation of a significant amount of nanoparticles was observed at Tris concentrations higher than

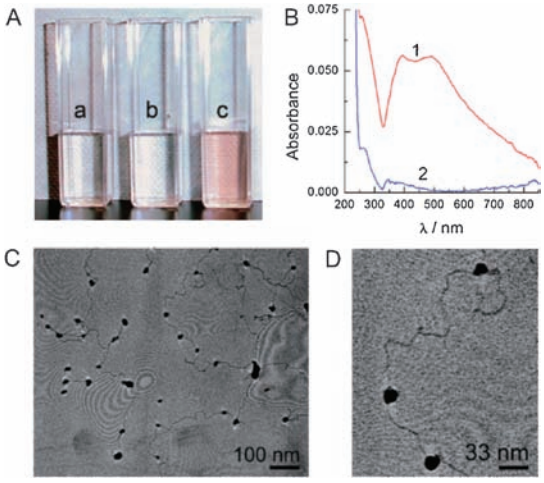


Figure 1. A. Aqueous T4 DNA solutions (5 μM) and 10 mM $AgNO_3$ after mixing (a), after 10 h in a dark place (b), and after an additional 15 min of irradiation by 254-nm UV light (c). **B**. UV–vis spectra of T4 DNA (2.5 μM) in buffer (ca. 25 μM of Tris and 2.5 μM EDTA in 2.5 μM DNA solution) after addition of 25 μM of $AgNO_3$ and 5 min irradiation by 254-nm light (1), and spectrum of the T4 DNA in pure water after the same treatment (2). **C**. Transmission electron microscope image of the T4 DNA chain decorated with silver NPs observed after T4 DNA (1 μM) mixing with $AgNO_3$ (10 mM) after 5 min of 254-nm irradiation. **D** Magnified area of Figure 1C.

25 μM (approximately 1/100 of the $AgNO_3$ concentration).

Spectra of either double- or single-stranded DNAs[6] after photochemical metallization were almost the same (data not shown), indicating that the templating effect of DNA is solely due to the DNA polymeric structure. Contrary to that, in the absence of DNA or even in a mixture of DNA monomers at the same concentrations, a very broad absorbance band at about 525 nm was observed, indicating formation of polydisperse NPs of larger size that in the presence of DNA.

To clarify the influence of the chemical nature of alcohol molecules on silver reduction, we compared photoreduction in the presence of various alcohols; ethanol, 1-propanol, glycerol, and Tris. Figure 2B shows UV–vis spectra of solutions containing these alcohols in the presence of $AgNO_3$ (2.5 mM) and DNA (25 μM) after 5 min irradiation. In the presence of each of these compounds, a peak at 450 nm was observed after irradiation. The effect of alcohols with one hydroxy group was the same, but in the case of glycerol, the 450-nm absorbance was approximately 3 times higher.

Finally, photoreduction experiments were performed under long-wave UV irradiation. Solutions of DNA containing 25 μM $AgNO_3$ and 25 μM Tris, were irradiated by 254-nm

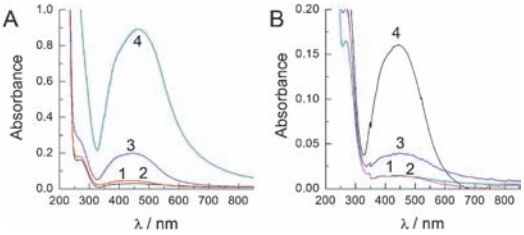
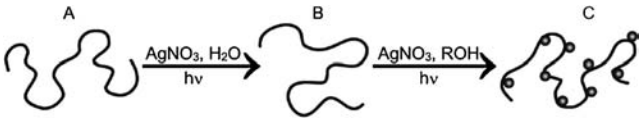


Figure 2. A. Spectra of DNA solutions (25 μM) in the presence of $AgNO_3$ (2.5 mM) and different concentrations of Tris: 250 nM (1), 2.5 μM (2), 25 μM (3), and 250 μM (4) after 5 min of irradiation by 254-nm light. **B**. Spectra of DNA solutions (25 μM) in the presence of $AgNO_3$ (2.5 mM) and different hydroxy-containing reagents: ethanol (1), propanol (2), glycerol (3), and Tris (4) at the same concentration of 125 μM after 5 min of irradiation by 254-nm light.



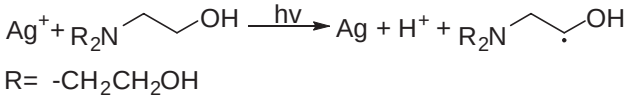
Scheme 1. Schematic illustration of DNA metallization.

or by 365-nm light, during the same time and the resulting spectra were compared. It is found that, in contrast to intensive plasmon absorbance of the sample after 254-nm light irradiation, the same time 365-nm light irradiation leads to a very weak NP plasmon absorbance. Nevertheless, kinetically slow formation of metal NPs takes place even upon weaker irradiation.

Our observations of DNA photochemical metallization show that in a pure aqueous solution, DNA is not metallized in the presence of silver ion upon irradiation (A → B), but in solutions with alcohols metallization of DNA chain, i.e., formation of silver NPs on DNA template, takes place (B → C) (Scheme 1). This photoreduction resembles a photographic process, in which the DNA chain functions as a nucleation template, similar to the clusters of silver formed upon lighting, which results in selective metallization of DNA or clusters.

The following four conditions are necessary for DNA metallization to occur: (i) the presence of DNA as a template, (ii) source of metal ion, (iii) alcohol as a reduction agent, and (iv) short-wave UV irradiation. Both DNA and alcohol molecules can be potentially involved in silver ion reduction; however, after a comparison of silver nanoparticle formation in water and in buffer solutions (Figure 1B), it becomes clear that only in the presence of alcohols does silver reduction on DNA proceed to a measurable extent. This finding is in disagreement with a model suggested by Berti et al.,[4] which assumed that DNA chains can simultaneously act as a sensitizer and as a template for metal deposition, thus leading to the formation of nanoparticles on DNA. Because Berti et al. did not take into consideration the presence of Tris buffer in the irradiated DNA sample, the reported metallization has been performed under conditions of reduction agent, i.e., Tris. According to our new findings, the presence of DNA in pure water is insufficient for successful photoreduction.

Photochemical reduction of silver ion in the presence of various alcohols was described a decade ago.[7] It was reported that reduction of silver ion proceeds through the formation of free radicals in alcohol molecules due to abstraction of α-hydrogen and a further reduction of silver cation, as shown in Scheme 2 in the example of Tris.



Scheme 2. Photochemical reduction of silver ion in solution of Tris.

The light-sensitive nature of silver ion, especially in alcohol solutions, has been documented, and it is suggested that upon silver ion irradiation an abstraction of hydrogen atoms from alcohols occurs.

The alteration in the efficacy of silver nanoparticle formation between different alcohols is suggested to be due to kinetics of silver reduction, which influences the rate of NP growth. In solutions of ethanol or 1-propanol with the same number of α-hydrogens, the observed spectra of NP are of the same intensity. In solutions of glycerol with three hydroxy groups, after the same irradiation time, the intensity of the NP peak is approximately three times higher. However, regardless of the same number of α-hydrogens in Tris and in glycerol, the effect of Tris on silver reduction is different (Figure 2B). We suggest that the efficacy of Tris is due to the presence of the amine group, which upon protonation acts as an electron acceptor and facilitates hydrogen abstraction.[8]

In conclusion, selective photochemical deposition of noble metals on a DNA chain template controlled by the presence of small amounts of alcohols can be utilized for preparation of DNA–metal nanocomposites and enrichment of metal on a DNA chain.

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.

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5 DNA sample prepared by dilution of commercial DNA in TE buffer contained Tris (2-amino-2-(hydroxymethyl)-1,3-propanediol, ca. 10-fold excess to DNA phosphates) and EDTA (ethylenedinitrilotetraacetic acid, ca. equivalent amount of DNA phosphates). DNA in pure water was obtained by dialysis of commercial DNA in Spectra/Por® dialysis tube (MWCO 25,000 D) against water.
6 Further experiments were performed with synthetic poly(guanylic) and poly(cytidylic) acids (single-stranded DNAs) or their equimolar mixture (double-stranded DNA).
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