

DNA as a basis for the reduction of silver and gold ions and for photo-induced processes in silver nanoparticles

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ABSTRACT

The unique structural features and powerful recognition capabilities of DNA allows us the assembling of artificial nanostructures on DNA molecules, including nanowire.

In this work we investigated the reduction of silver and gold ions on DNA in the solution by ascorbic acid as a reductant using UV-VIS spectroscopy. Due to the different interactions of Ag^+ and Au^{3+} ions with DNA, the reduction process is also different. Interaction of silver ions is characterized by inter-cross type of links with DNA, and the reduction of silver ions takes long time. In 4 days absorption spectra at the wavelength of silver nanoparticles can be observed. The absorption spectra have complex form, they remind absorption spectra of substances having specific resonance interactions. Gold ions interact with DNA through the phosphates, and their reduction happens fast (1-2 minutes). The absorption spectra are similar to the spectra of gold nanoparticles. An attention should be paid to the resistance of reduced silver and gold ions in the complex with DNA, as we observed, lifetimes are weeks and months.

Kinetic study of photo-irradiation of 10 nm size AgNPs, and AgNPs-DNA complexes has made it possible to determine rate constant and energy for the desorption of silver atoms from the surface of AgNPs that are equal respectively to $k_d \cong 2.2 \times 10^{-5} \text{ s}^{-1}$, $E_d \cong 84 \text{ kJ/M Ag}^0$ for AgNPs bound with DNA.

Keywords: DNA, Metal ions, silver nanoparticles, Spectrophotometry, Thermodynamics

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1. Introduction

Nanotechnology is an interdisciplinary field of fundamental and applied sciences, it is based on scientific and experimental foundations, and includes fields of science such as: organic chemistry, molecular biology, semiconductor physics, energy storage [1-2], engineering [3], microfabrication [4], and molecular engineering [5].

Study on the interaction of nanostructured materials with biomolecules leading to biological applications has been an active area in recent years [6-7]. In particular, nucleic acid sensing through interaction with nanoparticles can be used for the development of novel biosensor for clinical diagnosis [8-10], imaging [11], and drug delivery applications [12-13].

The sizes of most of the biological structures are determined by nanoscale, for example the radii of the deoxyribonucleic acid (DNA) double helix is 2 nm. DNA is well known as a blueprint of life, amazingly rich in information content, however, its unique structural features and powerful recognition capabilities can also be of interest for assembling artificial structures on DNA molecule for a variety of applications [14-18]. DNA is more stable than other biological molecules (proteins, RNA), it can be synthesized in different structures and is therefore often used as a base to create different nanostructures [19-23]. DNA has a high affinity to metal cation, and these localized cations can be reduced to form metallic nanoparticles that follow the contour of the DNA template. The processes for depositing metal nanostructures on DNA by the reduction of metal ions are known as DNA metallization.

The poor electrical properties of DNA [24] can be overcome by building metal nanowires in which the double stranded DNA acts as a template for the seed-mediated growth of silver, gold, or palladium [25-34] wires. DNA based metal nanowires are obtained through different methods. For example, the widespread method is the adsorption of nanoparticles on DNA surface, to obtain copper [35] and palladium [29] nanowires they add metal ions and after reductant to the DNA fixed on the surface.

Reduction processes of the metal ions on DNA depends on the interaction between DNA and metal ion. Soft ions in particular Cu^+ , Ag^+ , Pt^{2+} , Hg^{2+} ions are able to form the chelate complex with guanine (G-N7 and G-O6) or so-called inter-strand cross-links in DNA, and hard ions such as Mn^{2+} , Fe^{3+} , Al^{3+} , Co^{3+} , Au^{3+} ions interact with phosphate backbone of DNA [36-37].

In recent years, in our laboratory, along with other works, the study of reduction of silver ion by using spectroscopic methods has been done on various surfaces (DNA, G4-PAMAM dendrimer, membrane, hair, cotton) [38-41]. We studied the reduction process of silver ions under the influence of ascorbic acid.

The goal of the present investigation is to study reduction process of silver and gold ions on DNA and the interaction of AgNPs (10 nm) with thymus DNA by spectroscopic and thermodynamic methods in darkness and under photo-irradiation.

2. Materials and Method

2.1 Materials

DNA. - In our tests we used the Calf thymus DNA (40% GC), obtained from “Sigma-Aldrich”. The concentration of nucleic acids was determined by UV absorption using molar extinction coefficients ($\epsilon=6600 \text{ cm}^{-1} \text{ M}^{-1}$ at $\lambda=260 \text{ nm}$). The double helix structure of the polymers was proved by their hyperchromicity (~33%) and their typical thermal denaturation transition (0.01 M NaCl).

Ions. - Bidistillate water served as a solvent. In tests with Ag^+ ions chemically pure salts AgNO_3 were used and NaNO_3 served as background electrolytes, and with Au^{3+} salt HAuCl_4 were used and NaCl served as background electrolytes. For the reduction of silver ions ascorbic acid (AA) was used. All salts were purchased in “Sigma-Aldrich”. All experiments were performed in 10^{-2} M NaNO_3 or NaCl.

Silver dispersion nanoparticles (AgNPs) 10 nm particle size in aqua buffer containing citrate buffer as stabilizer was purchased in “Sigma-Aldrich”. Extinction coefficient, $\epsilon = 11800 \text{ M}^{-1} \text{ cm}^{-1}$, was calculated from the given concentration at $\lambda=396 \text{ nm}$.

G4(NH_2)₆₄ PAMAM dendrimer, with molecular sizes 4.5 nm, molecular weight 14215, was also purchased from “Sigma-Aldrich” ($\lambda = 280 \text{ nm}$). G4 PAMAM dendrimers were dissolved in a citrate buffer.

2.2 Methods

Registration of absorption spectra was carried out by compact, precessive, mobile, small power consumption optical fiber spectrometer AvaSpec ULS 2048-USB2 (200-1100 nm). The melting was performed from 25 to 95°C at 260 nm. Photo-irradiation was carried out in reactor with the fixed light beam in 1cm rectangular fluorescent quartz cell. In the same cell with the interval of 5 min absorption spectra of irradiated solutions were registered by AvaSpec spectrometer. Before each absorption registration the cell was shut to protect the solution from photo-irradiation. Registration time was 8 msec. As a source of radiation Hg (see Figure 1) arch high pressure discharge lamp with rating of 35 W in glass balloon was used. Radiation power in the cell was 600 mW.

3. Results and Discussions

We have studied the process of reduction of Ag^+ ions on the DNA induced by reductant ascorbic acid (AA), and interaction of DNA with silver nanoparticles. Figure 2 shows the absorption spectra of reduced silver ions in the complex with DNA. Ag^+ ions do not have the spectrum either in the near ultraviolet or in the visible regions, while the Ag^0 atoms have a spectrum in the visible region which allows us to monitor the ion reduction process.

The reduction of silver ion on DNA takes a long time, the spectrum appeared on the fourth day and reached a maximum on day 6 (Figure 2.). The absorption spectra have complex form, they remind absorption spectra of substances having specific resonance interactions. Silver ion Ag^+ is a soft metal ion, according to the Pearson's theory [42], and tends to form linear complexes, it interacts with bases and forms the so-called interstrand cross-link in DNA [41]. Comparing the areas under the absorption spectra of the reduced silver ions and silver

nanoparticles, we can assume that on the fourth day the amount of the reduced silver ions is 37% of added Ag^+ and in the equilibrium it is 71%.

For the comparison and better understanding we investigated the reduction process of Au^{3+} ions on DNA and Ag^+ on G4 PAMAM (polyamidoamine) dendrimer.

Figure 3 shows the absorption spectra of reduced gold ions (Au^{3+}) in the complex with DNA. The reduction of gold ions takes only couple of minutes. Unlike the silver ion, the trivalent gold ion is a hard metal ion, and it interacts with DNA phosphates. Such a difference in reduction time of silver and gold ions should be caused by the difference in the interaction with DNA and depend on the binding sites of the ions. As we mentioned earlier silver ions bind to the bases of DNA. We can assume that DNA-bound silver ions are not accessible for AA, during the dynamic process, the ion comes to the surface, is reduced, and, as a soft metal, again binds to the DNA base. In case of gold ions, they are bound to the phosphate backbone and the reduction is fast. Au^0 atom is a soft metal and probably it also binds to DNA bases.

Figure 4 shows the absorption spectra of reduced silver ions (Ag^+) in the complex with G4 PAMAM dendrimer. Polyamidoamine dendrimer polymers consist of an ethylenediamine core, a repetitive branching amidoamine internal structure and a primary amine terminal surface. The fourth generation of PAMAM has a spherical structure and 64 amino groups on the surface.

Figure 5 represents the Kinetic curves of silver ions reduction on DNA (a), gold ions reduction on DNA (b), and silver ions reduction on G4 PAMAM dendrimer (c) in M_t/M_e and $t^{1/2}$ coordinates,

where M_t is the number of ions absorbed at time t , M_e is the number of ions in equilibrium (saturation in optical absorption).

We can see that kinetic curves of the reduction of silver and gold ions on the DNA have S-shape, which means that DNA changes conformation during the reduction of ions. In case of G4 PAMAM dendrimer (Figure 3), kinetic curve is linear, which shows that simple diffusion takes place.

$$M_t/M_e = 2(Dt/\pi)^{1/2} [\text{cm/s}^{1/2}] \quad (1)$$

where D is diffusion coefficient. It also shows that G4 PAMAM dendrimer does not change conformation during the formation of a nanocomplex with silver atoms.

In order to investigate the interaction of DNA with silver nanoparticles the irradiation of the Hg arch discharge lamp was used (see Fig. 1). Figures 5 and 6 represents absorption spectra of free AgNPs, and AgNPs bound to DNA before and after photo-irradiation. The company nanoComposix [43] gives sample absorption spectra for spherical AgNPs with different particle sizes at the same mass concentration 0.02 mg/ml. We used silver nanoparticles of 10 nm diameter and its absorption spectrum is in good agreement with given data.

The photo-irradiation of both samples, AgNPs and AgNPs - DNA complex, were performed the same way, they were irradiated for 3 hours on the first day and 5 hours on the second day.

We should especially point out that in a nanoparticle, which consists of one kind of atoms, along with the mentioned dispersion interaction, the so-called resonance interaction should take place [44]. Such types of interactions are typical for molecular crystals, and they usually lead to exciton splitting of the principal absorption band. Inevitable condition for exciton splitting is the presence of a system consisting of identical groups and having a hard structure [45]. The absence of splitting can mean that AgNPs under investigation have a liquid structure resembling a drop, which under definite conditions such as temperature, photo-irradiation, variations in dielectric constant of the environment should be characterized by conformational transitions.

During photo-irradiation, as is known, a photon can be absorbed by any atom of AgNPs. If the atom is located on the surface of AgNPs, photo-irradiation can cause desorption of the atom, and

inside the nanoparticle, dissipation of excited atom energy into heat will occur, but photo-irradiation cannot cause noticeable heating of 10 nm AgNPs. The atom desorbed from the surface will either be adsorbed again or will move into the solution. The atom passing into the solution will be oxidized to silver ion which has no absorption. Analysis of Figures 6 and 7 shows that the area under the absorption spectrum does not change during photo-irradiation, which means that the number of atoms does not change, i.e. further adsorption of atoms takes place.

Figure 6 shows that photo-irradiation causes the redshift (~10 nm) of the maximum of the spectrum and after splitting of the band. The last spectrum is in very good agreement with the spectrum of silver nanorod [46]. We can conclude that the desorption and subsequent adsorption of the silver atom on the nanoparticle leads to a change in the shape of the nanoparticle and finally we get a silver nanorod.

Figure 7 shows absorption spectra of AgNPs-DNA complex before and after irradiation. In this case, we have a redshift of ~30 nm after 8 hours of photo-irradiation and we have no band splitting. The maximum (424 nm) of the last curve is the same as for reduced silver ions on DNA (Fig. 2), and it can be assumed that silver atoms desorbed from nanoparticles are adsorbed on DNA.

Let us consider the changes in absorption spectra for photo-irradiated AgNPs and AgNPs-DNA complexes given in Figure 6 and 7 versus the duration of irradiation in $\ln[C_0/(C_0 - C_t)]$ and t coordinates (Figure 8 and Figure 9), where C_0 is the concentration of silver atoms in the nanoparticles at the beginning C_t is the concentration of silver atoms desorbed by the time moment t , calculated from the difference between absorptions at $\lambda = 396$ nm.

The analysis of the curves shows that only the initial stage of the given curves of the desorption kinetics obey the linear law of Langmuir first-order equation:

$$\ln[C_0/(C_0 - C_t)] = kt \quad (2)$$

The constants of desorption rate for silver atoms from the surface of AgNPs has been evaluated from the slopes of the curves, and the data are, for free AgNPs - $k_d \cong 1.6 \times 10^{-5} \text{ s}^{-1}$, and for AgNPs bound with DNA, $k_d \cong 2.2 \times 10^{-5} \text{ s}^{-1}$. The values allow us to estimate the activation energy E_d for the desorption reaction using the equation

$$k_d = v^0 \exp(-E_d/RT) \quad (3)$$

where v^0 is the pre-exponential factor assumed as $v^0 \approx 10^{10} \text{ s}^{-1}$ (reciprocal quantity to silver atom oscillation time in nanoparticles) and E_d is the desorption energy in this case, we have acquired the value for $E_d \cong 85 \text{ kJ/mol}(\text{Ag}^0)$ for free AgNPs and $E_d \cong 84 \text{ kJ/mol}$ for AgNPs bound with DNA at $T = 300 \text{ K}$. We can see, that the difference between desorption energies for free AgNPs and for AgNPs bound with DNA are very similar, difference is in subsequent adsorptions. In case of free AgNP silver atoms adsorb on the nanoparticle, and in the case of DNA-AgNPs complex silver atoms adsorb on DNA.

Figure 10 shows melting curves of DNA, and complexes of DNA with silver ions and silver nanoparticles. As can be seen from the figure, in the case of the DNA- Ag^+ complex, the melting temperature of DNA increases from 65.3°C to 75.2°C , the hyperchromic effect does not change, the transition is less cooperative, silver ions prevent the rapid melting of the DNA molecule. When the DNA-AgNPs complex melts, the melting temperature increases to 76.8°C . It should be noted that during the melting of DNA-AgNPs, the real hyperchromic effect of DNA does not change, the change on Figure 10 is caused by a change in the spectrum of AgNPs, which has absorption in the ultraviolet region (Figure 11). It is interesting that neither DNA nor DNA- Ag^+ complex shows a transition in case of re-melting, which means that DNA renaturation does not occur during cooling. In the case of re-melting the DNA-AgNPs complex, we obtained a melt

with the same 76.8 °C melting temperature. This means that partial renaturation takes place and AgNPs keep DNA single strands together during the melting.

Figure 11 shows absorption spectra of AgNPs at 25 and 90 °C, absorbance is reduced by 24 %. The decrease in the intensity of the absorption band is due to the partial corrosion of AgNPs, caused by the oxidation of silver atoms to ions that do not have an absorption spectrum.

Figure 12 shows absorption spectra of DNA and DNA-AgNPs complexes at 25 and 90 °C, in this case the absorbance is reduced by 78%. As is known, with an increase in temperature, the concentration of hydrogen ions in water increases (by about two orders of magnitude with a change of 100 °C), which causes corrosion (Figure 11). In the case of the DNA-AgNP complex, DNA acts as a mediator, since it is a negatively charged helix, the concentration of positively charged hydrogen ions around it increases, which causes more severe corrosion of AgNP (Figure 12).

4. Conclusion

Using spectrophotometry and thermodynamic approaches, we have shown. that

- The reduction of silver and gold ions on DNA causes the conformational changes of DNA.
- During photoirradiation of silver nanoparticles and complexes of silver nanoparticles with DNA, desorption of silver atoms from the surface of AgNPs (diameter 10 nm) occurs. In the case of free AgNPs, the subsequent adsorption of a silver atom on a nanoparticle leads to a change in the shape of the nanoparticle, while in the case of AgNPs–DNA complexes, the atoms are adsorbed on the DNA surface.
- The kinetic study of photo-desorption makes it possible to determine the desorption rate constants k_d and desorption activation energy E_d that are equal to $k_d \cong 1.6 \times 10^{-5} \text{ s}^{-1}$; $E_d \cong 85 \text{ kJ/mol (Ag}^0\text{)}$ for AgNPs, and $k_d \cong 2.2 \times 10^{-5} \text{ s}^{-1}$; $E_d \cong 84 \text{ kJ/mol (Ag}^0\text{)}$ for AgNPs bound with DNA.
- The melting behavior of DNA-AgNPs complexes shows that the interaction of DNA with AgNPs increases the melting temperature of DNA, and at higher temperatures, DNA promotes corrosion of Ag.

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Figure captions:

Figure 1. The spectra of Hg high pressure discharge lamp at a wavelength of 350-1000 nm.

Figure 2. Spectra for silver ion reduction in complexes DNA-Ag⁺-AA. [DNA] – 5.3·10⁻⁴ M (P), [AgNO₃] – 1.7·10⁻³ M, [AA] – 1.7·10⁻³ M.

Figure 3. Spectra for gold ion reduction in complexes DNA-Au³⁺-AA. [DNA] – 0.5·10⁻⁴ M (P), [HAuCl₄] – 1.4·10⁻⁴ M, [AA] – 2.5·10⁻⁴ M.

Figure 4. Spectra for silver ion reduction in G4 PAMAM-Ag⁺-AA complex. [G4] - 1.4·10⁻⁴ M, [AgNO₃] - 1.2·10⁻⁴ M, [AA] - 2.4·10⁻⁴ M.

Figure 5. Kinetic curves of reductions in M_t /M_e and t^{1/2} coordinates for (a) silver ions on DNA, (b) gold ions on DNA, (c) silver ions on G4 PAMAM dendrimer.

Figure 6. Absorption spectra of AgNPs before and after irradiation. [AgNPs] – 5.6·10⁻⁵ M (Ag⁰).

Figure 7. Absorption spectra of AgNPs-DNA before and after irradiation. [AgNPs] – 5.6·10⁻⁵ M (Ag⁰), [DNA] – 1.2·10⁻⁴ M(P).

Figure 8. Kinetic curve of photo-desorption in ln[C₀ / (C₀-C_t)] and t coordinates for AgNPs.

Figure 9. Kinetic curve of photo-desorption in ln[C₀ / (C₀-C_t)] and t coordinates for AgNPs bound with DNA.

Figure 10. Normalized melting curves of DNA (1) and DNA complexes with Ag⁺ (2), AgNPs (3), AgNPs melted second times (4). [DNA] - 7.6 · 10⁻⁵ M(P), [AgNO₃] – 7.6 · 10⁻⁶M, [AgNPs] – 3.5 · 10⁻⁵ M(Ag⁰).

Figure 11. Absorption spectra of AgNPs at 25 and 90 °C. (1) AgNPs at 25 °C; (2) AgNPs at 90 °C; [AgNPs]–3.5x10⁻⁵M(Ag⁰).

Figure 12. Absorption spectra of DNA and DNA-AgNPs complexes at 25 and 90 °C. (1) DNA at 25 °C; (2) DNA at 90 °C; (3), DNA-AgNPs complex at 25 °C; and (4). DNA-AgNPs complex at 90 °C. [AgNPs]–3.5x10⁻⁵M(Ag⁰), [DNA]-7.6x10⁻⁵ M (P).