Photo-induced formation of Au-Ag nanowires complex on DNA support

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A UV-photoirradiation method has been proved for a novel, easy mode for the synthesis of semi-conducting Au-Ag nanowires complex on DNA. The nanowires have average diameters ranging from 2-50 nm in length. During Au-Ag alloy nanowire synthesis, the DNA acts as both as a reducing agent and as a non-specific capping agent for the metal nanoparticles. The Au-Ag alloy nanowires are important for the synthesis of composite nanowires for functional nanodevices, sensors, miniature computers or optoelectronics. In this article is presented the process of obtaining of DNA-gold nanoparticles, DNA-silver nanoparticles and DNA-Au-Ag nanoparticles which were prepared by chemical reduction of DNA- metal (Au and Ag) complex. The DNA-Au (III) was formed by reacting DNA with a 10^{-2} M of $HAuCl_4$ solution and the DNA-Ag was formed by reacting DNA with a 10^{-2} M of an $AgNO_3$ solution. The complex in solution reacted with EDTA reducing Au (III) and Ag (I) to Au and Ag. So, these solutions are responsible for creating nanodimensional aggregates. The particle distributions were obtained by transmission electron microscopy (TEM). This method, of metallic nanoparticles incorporated and stabilized by DNA, has resulted in a rather uniform dispersion of Ag, Au, Ag-Au nanoparticles of spherical shape and 2~50 nm in diameter.

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Keywords: DNA, Gold and silver nanowires complexes, Metallic nanoparticles

1. Introduction

The capacity to install nanoparticles into networks and circuits in a precise and controlled way is the key to produce a variety of nano-instruments. Arrays of nanometer–sized metal or semiconductors, or quantum dots, may show a variety of quantum phenomena, with applications in optical devices [1], nanometer-sized sensors [2], advanced computer architectures [3], ultradense memories [4] and quantum-information science and technology [5, 6].

The necessity to produce regular arrangements of nanoparticles led to the desire of using DNA as pattern for the assembly of nanoscale patterns [7,8].

DNA (deoxyribonucleic acid) is a natural polymer. Since the discovery of its double helical structure, the science of DNA has been the center of biological science and biotechnology research [9].

DNA has an important molecular characteristic which makes this polymer interesting and remarkable for designing a large variety of structures and systems which exist in its molecular and submolecular recognition properties [10, 11].

DNA may be used as a structural molecule, because it has a lot of advantages and can be readily synthesized in lengths between 5-100 nucleotides [8].

DNA can be linked together longer linear molecules or more complex shapes, and it can be changed at predetermined sites to permit the fixation of other molecules in a specific manner [8].

DNA has been used previously in other experiments, such as attaching of oligonucleotide derivatized nanoparticles to DNA using hybridization techniques [10,11].

The purpose of this study was to make new gold-silver nanowires using DNA, as promising devices for medical and biomedical applications, using an easy and low-cost method.

The synthesis was done in a mixed solution containing DNA, $HAuCl_4$ and $AgNO_3$ in the presence of UV-photoradiation.

2. Experimental part

2.1. Reagents

Silver nitrate ($AgNO_3$) was purchased from Merck. The chloroauric acid ($HAuCl_4$) was from Sigma-Aldrich. Ethylenediaminetetraacetic acid (EDTA) was purchased from Merck and a fresh 10^{-2} M solution was used in the experiment.

2.2. Synthesis of Au-Ag alloy nanowires on DNA

A stock solution of DNA (3 μg/ml) was prepared by mixing appropriate amounts of DNA with EDTA buffer

and stirred for 8 hours. In parallel were made solutions of $HAuCl_4$ and $AgNO_3$ at 10^{-2} M concentration.
For the first sample, $HAuCl_4$ solution was mixed with DNA solution. For the second one, $AgNO_3$ solution was used along with the DNA, and the third one consisted of the combination of $HAuCl_4$, $AgNO_3$ and DNA solutions.
The resulting solutions were analyzed by UV-visible spectroscopy before and after a UV-photoirradiated for 3 h. After UV-photoirradiation the color of solutions had changed. The DNA-Au-Ag complex was pink-purple, the DNA-Au solution was yellow, and the DNA-Ag solution was reddish-brown.

2.3. Characterization methods

UV-VIS spectroscopy analysis

The absorption spectra of the samples were recorded on a UV-VIS spectrophotometer (SPECORD M 42), with a 1 cm quartz cuvette for liquid samples, in the range of 200 and 800 nm wavelengths.

A sample of Au (III) and Ag (I) solution was mixed with DNA and held under UV light, resulting in the formation of metallic nanoparticles on the DNA support.

Maximum absorbance was measured between 400-500 nm, indicating the formation of silver nanoparticles. For DNA-AuNP complex, the maximum absorbance was measured at 600 nm; for DNA-AuNPs-AgNPs complex, it was measured between 450-540 nm.

Fourier transform infrared spectroscopy FTIR

FTIR is a technique for measuring infrared spectra. For the spectrum acquisition a Perkin-Elmer FTIR spectrometer in the range of 4000–700 cm^{-1} was used.

Infrared spectroscopy is currently used routinely for automatic identification of chemical species. Infrared absorption spectra (IR spectra) are mainly vibrational spectra of molecules. An IR spectrum is the absorption of radiant energy curve (in the IR) of the sample molecules, depending on the wavelength or frequency radiation.

Using the library spectra of the FTIR spectrometer, the information obtained from the samples was interpreted.

Transmission Electron Microscopy TEM

A high resolution transmission electron microscope (HR-TEM, Tecnai F30, G^2, STWIN) was used at an accelerating voltage of 200 kV for imaging of the resultant nanowires. The Energy Dispersive X-Ray Spectrum (EDAX) was recorded with the instrument connected with the HR-TEM during TEM experiments.

***Energy dispersive X-ray spectroscopy* EDAX**

EDAX is a technical method used for the elemental analysis and chemical characterization of different types of samples.

Fig. 1. Tecnai G² F30 HR-TEM S-TWIN.

3. Results

Characterization of Ag-DNA, Au-DNA and Ag-Au-DNA complexes by UV-VIS absorption spectroscopy

After mixing the $HAuCl_4$ 10^{-2} M solution with the $AgNO_3$ 10^{-2} M solution and the DNA one, a complex was formed which was confirmed by a shift in the UV-visible spectrum compared with the pure DNA solution. The resulting solution was continuously UV-photoirradiated for 3 h. After completion of the reaction, the solution became reddish-brown in color. The UV light exposure resulted in the formation of metallic seeds/nuclei on the DNA.
The colorless aqueous solution of $AgNO_3$ has no specific absorption band above 200 nm in the UV-VIS spectrum. (fig. 2). The color of $HAuCl_4$ solution was yellow and presented an intense absorption band at 295 nm due to metal-ligand charge transfer band from the $AuCl_4^-$ complex. The aqueous DNA solution had an absorption band at 275 nm (fig. 2).

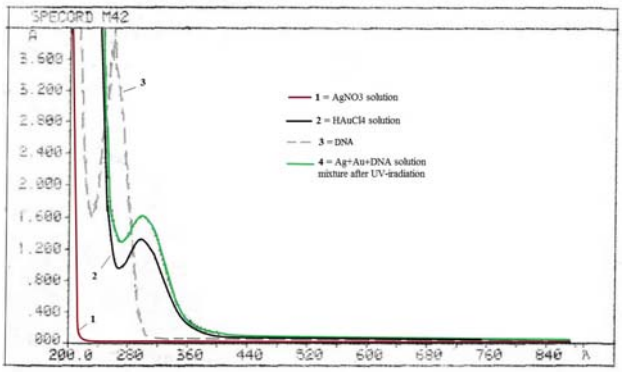

Fig.2. Absorption spectra of the $AgNO_3$, $HAuCl_4$ solutions and Au-Ag-DNA solution mixture after 30 min UV-irradiation (at UV lamp).

After the addition of Ag (I) and Au (III) solutions to the aqueous DNA solution, it was observed the change of color after UV-photoirradiation. The colour of this mixed solution became pink. The spectrum of DNA-Au-Ag complex presented an absorption peak at 500 nm due to initial formation of the complex of DNA with metal ions [13].

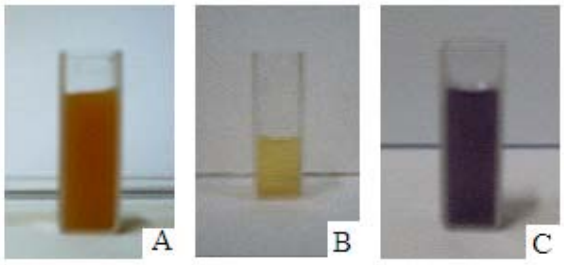

Fig. 3. The colors of the different solutions. A) DNA-Ag solution was reddish-brown; B) DNA-Au solution was yellow; C) DNA-Au-Ag complex was pink-purple.

The mixed Au (III) and DNA solutions, (8 hours), was exposed to UV light for 3 hours. It presented a band at 540 nm due to the formation of Au NPs on DNA (Fig. 4) [16].

The same process was accomplished for aqueous $AgNO_3$ solution mixed with the DNA one. It presented a weak band appeared at 448 nm due to the formation of Ag NPs on DNA as shown in figure 4 [17]. After completing the reduction process for 3 hours under UV-irradiation, the AuNP and AgNP solutions remained stable for more than 2 months in dark at -4°C.

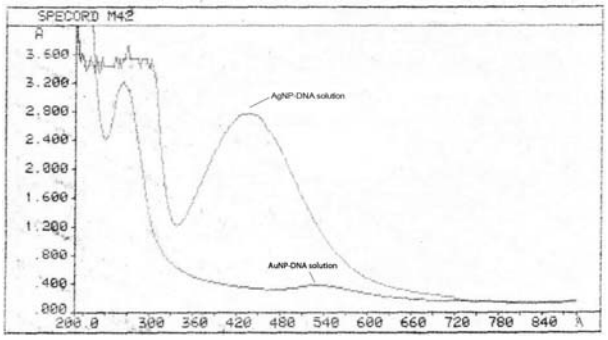

Fig.4. Absorption spectra of the $AgNO_3$, $HAuCl_4$ solutions after 3 hours of photoirradiation

Characterization of DNA-Au, DNA-Ag, DNA-Au-Ag complex by FTIR analysis

Perkin-Elmer spectrometer FTIR Spectrum in the range 4000–700 cm^{-1} was used. The sample was dried and then placed in Fourier Transform Infrared FTIR for the analysis of the nanoparticles. The FTIR spectra indicate various functional groups present at different positions.

The presence of the bands at 1223 cm^{-1} associated with the antisymmetric vibrations of phosphates and at 1012 cm^{-1} (deoxyribose band), confirmed that a sugar-phosphate chain of DNA exist [17].

The bands at 1223 cm^{-1}, 1058 and 1715 cm^{-1} are typical for DNA. In Ag-DNA sample are not found, but at 1385-1360 cm^{-1} regions (fig. 5) are observed characteristic bands specific for silver nitrate [17].

Fig. 6 compares the FTIR of DNA simple solution and the DNA-Au (III) complex. In the 1600 cm^{-1} region, in-plane base vibrations resulted in absorption bands particularly sensitive to base pairing and base stacking. Absorptions in the 1200-1400 cm^{-1} regions were caused by stretching bands from C-O groups in DNA sugars. The bands at 1465 cm^{-1} characterized the imidazolic ring vibration [9, 18]. Its intensity was decreased and a new band was observed at 1401 cm^{-1} (fig. 6), which again indicates that there is a binding between the $HAuCl_4$ and DNA. Sugar vibrations appear in the 1068 cm^{-1} region.

Gold/silver ions from Au-Ag-DNA nanoparticles sample present differential FTIR signal (fig. 7), which are reflected at 1633, 1465 cm^{-1} bands that corresponds to GT, ATGC, C, and AC (A, T, G and C are the four nucleotides found in DNA). The presence of these bands in the gold/silver plasmon region suggests formation of the chiral clustering specific for nanoparticles. Those data demonstrate that the helical structure of DNA is covered by nanosilver [19].

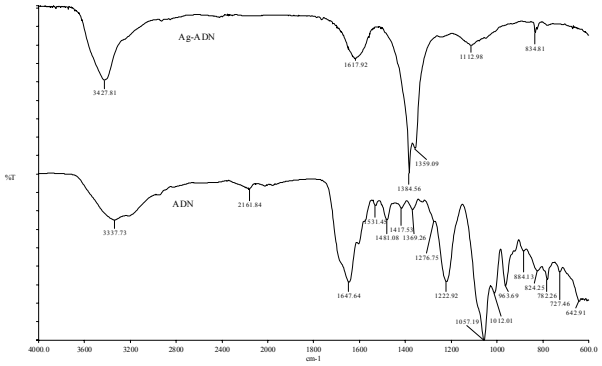

Fig. 5. FTIR spectra of DNA and Ag-DNA complex

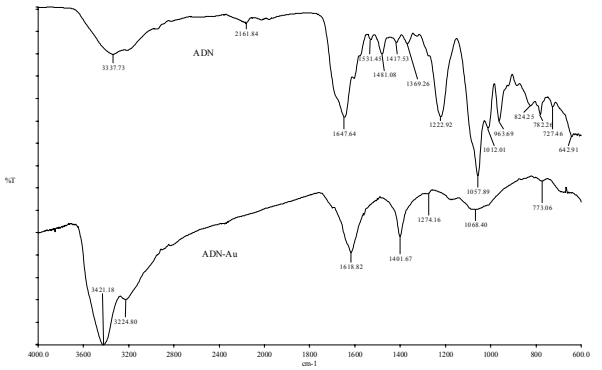

Fig. 6. FTIR spectra of DNA and Au-DNA complex

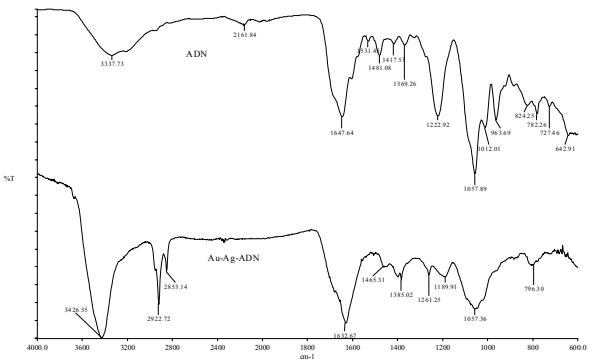

Fig. 7. FTIR spectra of DNA and Au-Ag-DNA complex

Characterization of metallic nanoparticles obtained using DNA support by TEM analysis

Figs. 8,9,10 show the TEM images of Au-DNA, Ag-DNA, and Au-Ag-DNA alloy nanowires. These figures represent the TEM image after 3 hours of UV-photoirradiation. The separate Au-Ag DNA alloy particles presented diameters between 2-50 nm.

It was clearly observed that the particles are aggregating together to form nanowires. In the DNA-silver solution, it was confirmed the fact that all the individual particles had aggregated together and had formed continuous wires. The diameters of the nanowires were shortened to 2-50 nm, through ultrasonication and centrifugation processes.

The TEM image shows that the nanowires are continuous and the alloy particles grow selectively on the DNA chains. There are a few nodules, which might be due to the aggregation of several particles or to inhomogeneous growth.

The same types of nodules were also observed in other studies [20] describing the synthesis of hybrid Au/Pt nanowires.

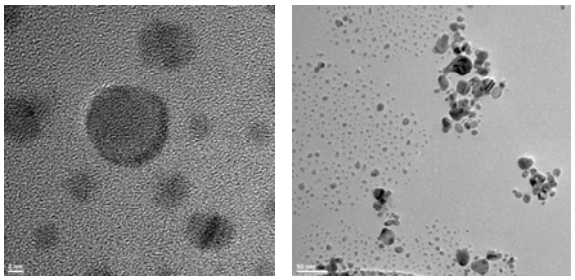

Fig. 8. TEM images of the Ag-DNA alloy particles after 3 hours of UV-photoirradiation

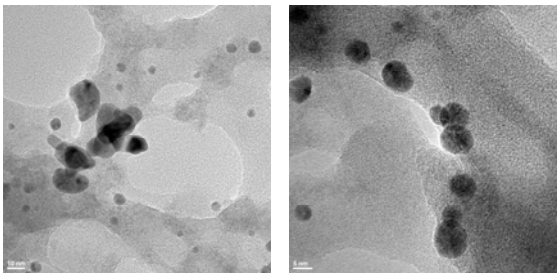

Fig. 9. TEM images of the Au-DNA alloy particles after 3 hours of UV-photoirradiation

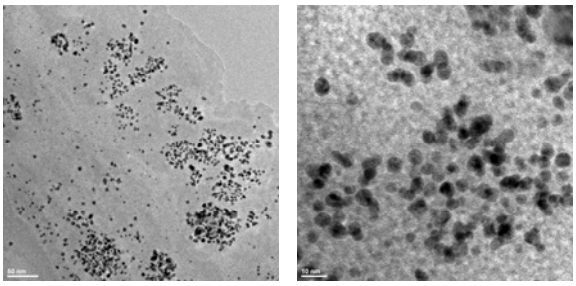

Fig. 10. TEM images of the Au-Ag-DNA alloy particles after 3 hours of UV-photoirradiation

EDX technique

Energy Dispersive X-ray Spectroscopy was used to present the chemical composition of the obtained nanoparticles. The EDX spectrum consists of different peaks for gold, silver, carbon, copper, and chromium. The silver and gold peaks originated from the nanoparticles using DNA support whilst the other ones were derived from the TEM grid and sample holder.

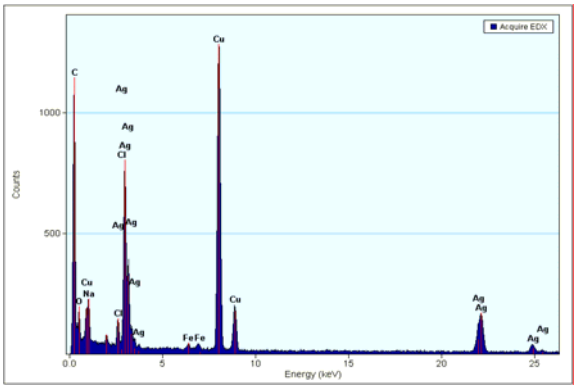

Fig. 11. EDX image of Ag-DNA nanoparticles

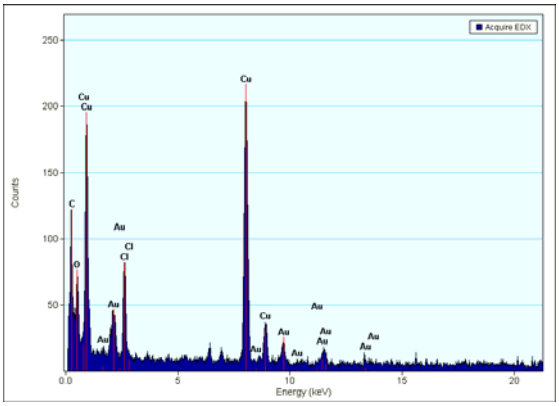

Fig. 12. EDX image of Au-DNA nanoparticles

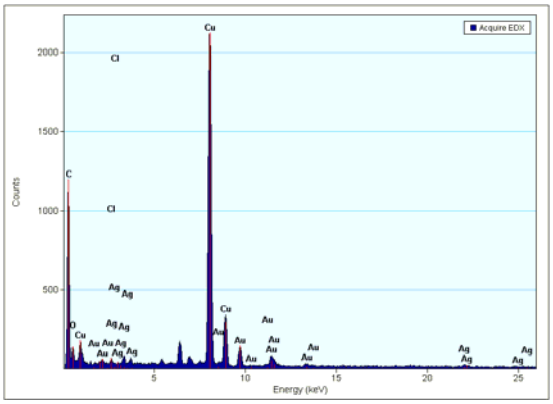

Fig. 13. EDX image of Au-Ag-DNA nanoparticles

4. Discussion

Fig. 2 shows the absorption spectra of the $AgNO_3$, $HAuCl_4$ solutions and Au-Ag-DNA solution mixture after 30 min UV-irradiation (at UV lamp).

Fig. 3 presents the change in color of the solutions after UV-photoirradiated.

Fig. 4 shows the images after 3 hours of UV-photoirradiation.

In Figs. 5,6,7 is observed the FTIR spectra of Au-DNA nanoparticles, Ag-DNA nanoparticles and Au-Ag-DNA nanoparticles.

The Figs. 8,9,10 show the TEM images of the Au-DNA nanoparticles, Ag-DNA nanoparticles and Au-Ag-DNA nanoparticles, after 3 hours of UV-photoirradiation.

In these images it is clearly observed that the particles are aggregated to form nanowires with 2-50 nanometers diameter.

The EDX analysis (Figs. 11,12,13) showed that the silver and gold peaks originate from the nanoparticles obtained using DNA support. Thus, both TEM and EDX techniques confirmed the formation of metal-DNA nanoparticles.

5. Conclusion

The present study demonstrated an easy and non expensive method for the synthesis of Au-Ag alloy nanowires on DNA using UV-photoirradiation for 3 hours. The synthesized alloy nanowires are nanometers in size, with a diameter between 2-50 nm in solution, stabilized on the DNA.

The present research could be extended to the fabrication of intricate circuitry using the DNA property to form complex shapes by hybridization. Using UV-photoirradiation the formation of metallic nanomaterials on DNA polymer support can be accomplished.

Such nanostructures could be applicable in nanomedicine. In the future, this process may lead to a quick synthesis method for hybrid and composite nanowires for functional nanodevices, miniature computers, optoelectronics and sensors.

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