Preparation of 1D nanostructures using biomolecules

Stela Pruneanu¹, Liliana Olenic¹, Lucian Barbu Tudoran², Irina Kacso¹, Said A Farha Al-Said³, Reda Hassanien³, Andrew Houlton³ and Benjamin R Horrocks³

¹ National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath, 400293 Cluj-Napoca, Romania

² Babes-Bolyai University, Electron Microscopy Center, 1 Mihail Kogălniceanu, 400006 Cluj-Napoca, Romania

³ School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK

E-mail: stela.pruneanu@itim-cj.ro

Abstract. In this paper we have shown that one-dimensional (1D) particle arrays can be obtained using biomolecules, like DNA or amino-acids. Nano-arrays of silver and gold were prepared in a single-step synthesis, by exploiting the binding abilities of λ-DNA and L-Arginine. The morphology and optical properties of these nanostructures were investigated using AFM, TEM and UV-Vis absorption spectroscopy.

1. Introduction

The controlled organization of metallic nanoparticles into one-dimensional (1D) arrays has attracted an increased interest due to their possible application in nanoelectronics, optoelectronics and biosensor devices [1]. Template synthesis (e.g. filling the pores of an alumina membrane with the desired material) has proved to be one of the most successful methods which can provide anisotropic nanostructures, such as nanorods and nanowires [2]. However, due to the inherent difficulties related with the selection and usage of a single nanowire, other methods have been developed, by employing supramolecular templates like DNA, peptide nanofibrils or phospholipids [3-5].

Besides these methods, particular attention has been given to preparation of ‘template-free’ 1D arrays. This new approach is based on coupling gold nanoparticles by using amino-acids or by partial removal of the organic stabilization layer which increases dipole-dipole interactions, leading to anisotropic orientation of nanoparticles [6].

In this work we report the preparation of extensive 1D arrays of metallic nanoparticles: (i) by using DNA as a template and (ii) by exploiting the binding ability of amino-acids (L-Arginine). The evolution in time of morphological and optical properties of metallic nanoparticles attached to biomolecules, were investigated using AFM, TEM and UV-Vis absorption spectroscopy.
2. Experimental

λ-DNA stock solution (500 µg/mL in 10 mM Tris-HCl pH 8 + 1 mM EDTA) was purchased from New England Biolabs, United Kingdom. Chloroauric acid (HAuCl₄), sodium citrate, sodium borohydride and L-arginine were obtained from Aldrich Chemicals and used as received. Colloidal gold (GNP) was prepared by reducing HAuCl₄ with sodium citrate and NaBH₄. Arginine-capped gold nanoparticles (Arg-GNP) were obtained by reducing HAuCl₄ with NaBH₄, in the presence of L-Arginine (L-Arg). Preparation of DNA templated silver nanostructures (Ag-DNA) is given in reference [7].

2.1. UV-Vis Spectroscopy

Optical properties of Ag-DNA solution, colloidal gold and arginine-capped gold nanoparticles were monitored using an UV-Vis spectrophotometer (JASCO V-570).

2.2. TEM measurements

For TEM analysis drops of colloidal gold or arginine-capped gold nanoparticles were placed on carbon-coated copper grids. The grids were allowed to dry prior to TEM measurements (JEOL-JEM 1010 instrument).

2.3. AFM

AFM imaging was performed in air on a Dimension Nanoscope V system (Veeco Inc., Metrology group) using Veeco NanoProbe tips. All of the AFM images are height images taken in tapping mode.

3. Results and discussion

3.1. Silver 1D nanostructures templated on DNA

DNA’s rich functionality (e.g. negatively charged phosphate groups and nucleobases) allows it to interact with different metals, forming 1D particle arrays or continuous wires (depending on the reaction time). We have investigated the interaction between silver and DNA because the high conductivity of silver makes it ideal for integration in electrical circuits. The templating reaction is efficient and after 24 hours, silver nano crystals can be visualized strongly attached to DNA. Figures 1 a, b shows typical examples of such 1D nanostructures (beads-on-a string appearance) along with randomly dispersed silver nanocrystals, on the SiO₂/Si surface. Some strands show DNA regions smoothly covered by silver (figure 1a) while others are densely packed with nanoparticles (figure 1b).

![Figure 1. a, b: AFM images of silver crystals arranged as 1D nanostructures along DNA strands; the grayscale corresponds to a height range of 30 respectively 35 nm.](image-url)
The mean diameter of silver nanoparticles attached to DNA is around 50 nm (measured as height by AFM tip). Besides these, one can notice randomly dispersed nanoparticles on SiO\textsubscript{2}/Si surface, having a mean diameter of 20 nm (figure 1a) respectively 10 nm (figure 1b). It is important to emphasize that nanoparticles attached to DNA are bigger than those randomly dispersed in solution, which can suggests that the reduction of silver ions is catalyzed by DNA.

In order to better understand the interaction between silver and DNA, we have also monitored the evolution of the Ag-DNA mixture by UV-Vis spectroscopy. Metallic nanostructures (nanoparticles, nanorods) can exhibit strong local resonances of light-induced electron plasma oscillations [8]. The electric field of an incoming light wave induces a polarization of the free electrons of metallic nanoparticle, with respect to its ionic core. A charge difference is created at the nanoparticle surface, which in turn acts as a restoring force (Coulomb attraction). In this way, a dipolar oscillation of the free electrons results, whose frequency is determined by the electron density, effective mass and particle shape. This electronic motion is specific for nanoparticles due to the geometrical confinement effects of free electrons. The resonance of the free electronic cloud with the incident light wave generates an absorption band, also known as surface plasmon resonance band (SPB). This band is observed in the UV-visible spectrum and its position is characteristic for each metal (silver, gold). This is the reason which supports the study of silver-DNA interaction, by UV-Vis spectroscopy (figure 2).

The first spectrum is that of stock DNA solution which exhibits the characteristic nucleic acid absorption band at 260 nm. The next spectrum was recorded after incubating DNA with silver’ reagent, for 15 minutes. A decrease of the 260 nm absorption peak was detected together with a shift towards higher wavelengths (271 nm). The evolution of the mixture was then closely monitored, but no further change was observed within 2 days. The spectrum recorded on the third day revealed a new maximum developed around 440 nm, due to surface plasmon bands of silver nanoparticles. The strong absorption band below 300 nm can be attributed to non-metallic silver clusters (Ag\textsuperscript{2+}) formed in the initial stage of silver reduction. This type of clusters can be stabilized by sodium dodecyl sulphate [9] or sodium poly(phosphate) [10]. In our case, the phosphate groups on DNA strands can act as stabilizing group, which explains the increase in band intensity with time. The transition from non-metallic to metallic particle is confirmed by the appearance of the 440 nm surface plasmon band. This takes place due to agglomeration of silver clusters which generates nanometer-sized metal particles.

3.2. One-dimensional nanostructures prepared from arginine-capped gold nanoparticles

Alternatively, 1D metallic nanostructures can be obtained in the absence of a template, by exploiting the binding ability of amino-acids (L-Arg). In order to show the influence of L-Arg on nanoparticles morphology, we have also prepared citrate-capped gold nanoparticles. Figure 3a shows a typical TEM image of citrate-capped gold nanoparticles, one hour after preparation. One can notice the sphere shape of particles as well as the uniform distribution of diameters (mean diameter 4 nm).

In contrast with this, arginine-capped gold nanoparticles agglomerate into larger spherical or elliptical aggregates (diameter around 20 nm, figure 3b). Within 3 hours since the reducing agent was
added to the solution, the appearance of Arg-GNP has radically changed and nanoparticles are no longer forming spherical aggregates. They have connected with each other, forming nanochains of various lengths, from tens to hundreds of nm (figure 4 a,b). In particular, figure 4b shows that the gold nanoparticles are well fused into each other (the length of the branch is around 450 nm). With time, the chain like nanostructures increases in length and develops additional branches and closed loops. These 1D structures remains stable in solution for weeks, although they can be destroyed by ultrasound.

Figure 3. TEM images: citrate-capped gold nanoparticles (a); Arg-GNP immediately after preparation (b).

Figure 4. a, b: TEM images of Arg-GNP, 3 hours after preparation.

The evolution of UV-Vis spectra (figure 5) is in good agreement with TEM images, confirming the change in time of nanoparticles morphology. This is clearly shown by the change in surface plasmon resonance band, which depends on the dielectric properties of metal and surrounding medium as well as on the dimension of nanoparticles [11]. For a small sphere, Mie theory shows that the light absorption is given by a single SPB, which is associated with a dipolar charge distribution on the surface (transverse surface plasmon resonance) [12]. As the particles become less symmetric (e.g. by assembling into nanowires) the charge distribution induced on the surface can result in dipolar modes with different resonant frequencies. Consequently, an additional SPB band is developed, generally red shifted (longitudinal surface plasmon resonance).
In the case of arginine-capped gold nanoparticles, the transition from dispersed nanoparticles to one-dimensional nanochains is clearly evidenced by the absorption spectra. After preparation (90 min.) the spectrum of Arg-GNP is that characteristic for dispersed nano spheres with a sharp peak at 530 nm (see also the TEM image, fig.3b). This is assigned to the dipole resonance, which gives rise to the transverse surface plasmon band. Within 3 hours, the plasmon peak broadened and decreased in intensity. A new broad peak developed around 750 nm, due to the linear arrangement of nanoparticles, which generates the longitudinal surface plasmon band. The linear self-assembly of nanoparticles is favored by arginine binding ability, which interacts not only with gold but also with adjacent molecules, forming 1D nanostructures.

4. Conclusions
In conclusion we have shown that 1D nanoparticles arrays can be obtained either by using DNA as a template or by spontaneously assembly of arginine-capped colloidal gold. AFM, TEM and UV-Vis spectroscopy have confirmed the transition from dispersed nanoparticles to linear assembled nanostructures (silver and gold).

References
[1] Tang Z Y and Kotov N A 2005 Adv. Mater 17 951
[2] Nagle L, Ryan D, Cobbe S and Fitzmaurice D 2003 Nano Lett. 3 51
[3] Braun E, Eichen Y, Sivan U and Ben-Yoseph G 1998 Nature 391 775
[4] Djalali R, Chen Y and Matsui H 2002 J. Am. Chem. Soc. 124 13660
[5] Zhang D B, Qi L M, Ma J M and Cheng H M 2001 Chem. Mater. 13 2753
[6] Lin S, Li M, Dujardin E, Girard C and Mann S 2005 Adv. Mater. 17 2553
[7] Farha Al-Said S A, Hassanien R, Hannant J, Galindo M A, Pruneau S, Pike A R, Houlton A and Horrocks B R 2009 Electrochem. Commun. 11 550
[8] Gonzalez A L and Noguez C 2007 Phys. Stat. Sol. (c) 4 11 4118
[9] Henglein A 1979 J. Phys. Chem. 83 2209
[10] Henglein A 1989 Chem. Phys. Lett. 154 473
[11] Moores A and Goettmann F 2006 New J. Chem. 30 1121
[12] Mie G 1908 Ann. Phys. Leipz. 25 377.