Communication

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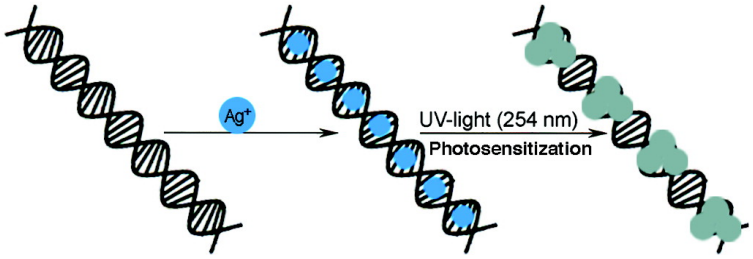

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DNA-Templated Photoinduced Silver Deposition

Lorenzo Berti,* Andrea Alessandrini, and Paolo Facci

National Research Center on nanoStructures and bioSystems at Surfaces S3, INFM-CNR, Via G. Campi 213/A, 41100 Modena, Italy

Received April 15, 2005; E-mail: berti.lorenzo@unimo.it

Thanks to its unique self-recognition properties, DNA is widely recognized as an ideal candidate for assisting the bottom-up assembling of nanostructures. Unfortunately, its lack of electrical conductivity currently limits its use as a structural scaffold. The challenge of creating self-assembling functional nanodevices will ultimately require nanocomponents to be precisely positioned and electrically addressable. It is therefore desirable to transform DNA into a better conductor, so it could act as a structural as well as an electrically conductive scaffold.[1] It has been recently demonstrated that metal nanoclusters[2] and nanowires can be formed through a DNA-templated process that uses the chemical reduction of a DNA-complexed metal ion. With this approach, DNA-templated nanowires of silver,[3] platinum,[4] palladium,[5] and copper[6] have been obtained. In this communication, we report a photography-derived methodology for forming silver nanoclusters, taking advantage of DNA's great affinity for Ag(I) ions, and using UV light for the in situ photoreduction of DNA-complexed silver ions.

The photoreduction rate of $AgNO_3$ to elemental silver in aqueous solution is very slow but can be significantly increased by adding an organic catalyst.[7] This catalyzed photoreduction process has been successfully employed in the polymer-templated synthesis of silver nanoparticles.[8,9] As DNA can form stable complexes with Ag(I) by embedding the ions inside the double helix,[10−12] we reasoned that it would be possible to grow chains of silver nanoparticles through photoreduction of silver-laden DNA. We also speculated that DNA itself would act as photosensitizer, as it is well-known that short-wavelength UV irradiation causes photooxidation of DNA bases.[13] To test our hypothesis, DNA−Ag^+ complexes of defined stoichiometry were formed by mixing λ-phage DNA and $AgNO_3$. On the basis of reported studies,[10] Ag^+:nucleotides molar ratios larger than 0.5 should guarantee saturation of all possible DNA binding sites. Upon mixing, the formation of a DNA−Ag^+ complex was instantaneous, witnessed from both a slight shift in the UV absorbance maximum and a dramatic increase in the absorbance intensity.[2] Exposing the DNA−Ag^+ complex to 254 nm UV light resulted in the appearance of a peak centered at around 420 nm (for experimental details see Supporting Information). Such a peak is attributable to the surface plasmon resonance of small silver nanoparticles forming under the experimental conditions.[14] Concomitantly, the DNA absorption peak at 260 nm showed a small decrease in intensity (Figure 1A). Because of the intimate nature of the DNA:Ag^+ complex, this effect could be attributable to decomplexation of the bases and to changes in the duplex structure. The photoreduction process was considered complete when extending the irradiation time did not cause any changes in the plasmon resonance peak intensity or shape. After silver photoreduction had taken place, the complexation/photoreduction cycle was repeated, resulting in stepwise silver nanoparticles growth. We repeated the cycle for a total of four times (G1−G4). After each cycle was completed, we observed that the surface plasmon resonance peak

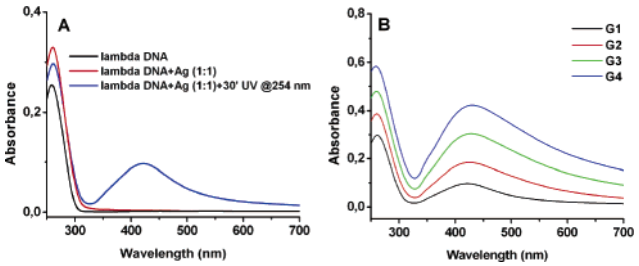

Figure 1. (A) UV−vis spectra showing the photoreduction sequence for a 1:1 DNA:Ag^+ complex. Upon addition of silver ions, the 260 nm λ-DNA absorbance (black line) experienced a large increase in intensity (red line). Following photoreduction, a peak formed at 420 nm, demonstrating the formation of silver nanoparticles (blue line). (B) UV−vis spectra showing the effect of four sequential cycles of silver complexation/photoreduction. G1−G4 correspond, respectively, to 1:1, 1:2, 1:3, and 1:4 nucleotides:Ag^+ ratios. Only the spectrum obtained at the end of each photoreduction cycle is shown. The absorbance at 260 nm at the end of every cycle is larger than that at the end of the previous one, but still experienced a decrease in intensity after each photoirradiation step.

increased and broadened (Figure 1B), indicating an increase in the number and polydispersity of nanoparticles.[15]

Interestingly, after the first photoreduction cycle, the irradiation time necessary to complete the subsequent Ag^+ photoreductions was significantly shorter, dropping from 30 to 5 min. This fact could be attributable to the catalytic effect given by the presence of the pre-existing metal seeds.

Tapping mode AFM images for G1−G4 on mica were obtained (see Supporting Information), showing how the DNA morphology changed dramatically. A "bumpy" structure was noticeable, and bigger clusters were present at tracts. We would like to point out at this stage that, by the proposed photochemical approach, the metal growth was observed only along the DNA, and very little or no background metal deposition was present. An undesired side effect to the sequential metal deposition procedure appears to be the photodegradation of DNA upon repeated exposure to UV light, as evidenced by the progressive shortening of DNA fragments.

To test the possibility of growing templated nanoparticles while minimizing the undesired DNA degradation, we attempted a single-step photoreduction process, where a DNA−Ag^+ complex was photoreduced in the presence of excess silver ions. Complex stoichiometries of 1:1, 1:5, 1:20, and 1:100 nucleotides:Ag^+ ratios were investigated. As the amount of Ag^+ in solution increased, an improvement in the homogeneity of the silver clusters' distribution and in the minimization of photodegradation was observed (Figure 2). For a nucleotides:Ag^+ ratio of 1:100, nonspecific silver deposition becomes significant (see Supporting Information), making the photoreduction impractical under those conditions.

As an alternative procedure to the photoreduction in solution, we attempted the photoreduction of mica-immobilized DNA. λ-DNA was immobilized on mica by an established procedure,[16]

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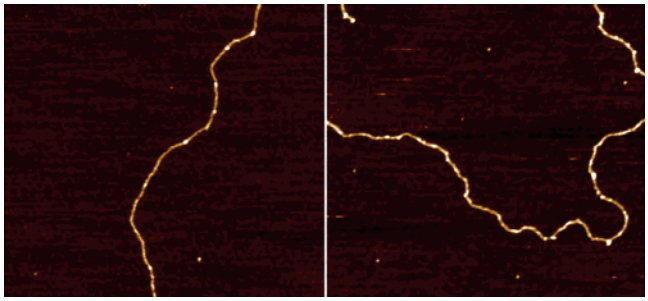

Figure 2. Tapping mode AFM images of photoreduced 1:5 (left) and 1:20 (right) nucleotides:Ag^+ complexes. The image on the right shows a larger amount of clusters present along the DNA chain, and no background metal deposition is observed (scan size = 1 μm × 1 μm, z scale = 5 nm).

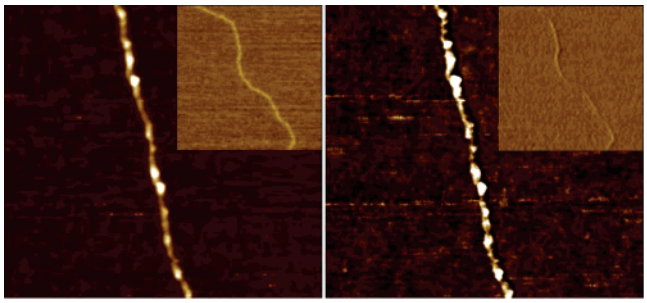

Figure 3. Tapping mode AFM height (left) and phase (right) images of a DNA−Ag^+ complex photoreduced on mica. This sample was obtained by first immobilizing λ-DNA and then exposing it to UV light for 5 min through a thin 10 mM $AgNO_3$ liquid film. For comparison, the insets in each figure show, respectively, a topographic (left) and phase (right) image of λ-DNA before the treatment (scan size = 500 nm × 500 nm, z scale = 5 nm).

exposed to UV light in the presence of an aqueous film of silver nitrate, and imaged by tapping mode AFM (Figure 3).

Experiments were conducted by varying the concentration of the silver solution and the exposure times. A silver nitrate concentration of 10 mM and an exposure time of 5 min yielded the best results in terms of improving the homogeneity of particle distribution and lowering the background of nonspecific silver reduction.

Although the formulation of a detailed mechanism is premature at this stage, it seems reasonable to assume that DNA bases act as photosensitizers, thanks to their strong absorption in the UV. DNA notoriously undertakes photooxidation when exposed to UV radiation, forming very reactive radical intermediates or generating singlet oxygen.[13] Both species might play a role in the reduction of the complexed silver ions, but further investigation will be necessary in order to prove it. Also, an involvement of the solvent in the photoreduction mechanism cannot be ruled out. However, its participation in the electron transfer would most likely follow the photosensitization step operated by the DNA. In fact, irradiating an aqueous silver nitrate solution under the same conditions does not result in silver nanoparticle formation, indicating that DNA plays an active role in the reduction process. To confirm the role of DNA in the photosensitization event, we formed a DNA:Ag^+ complex and attempted silver reduction by irradiating at 366 nm, a wavelength where DNA does not absorb. Under those conditions, we were not able to detect the formation of silver nanoparticles based on the absence of the characteristic plasmon resonance peak. Also, simply irradiating DNA with 254 nm UV light does not show any significant changes in the DNA morphology.

Independently of the procedure followed, one common aspect was silver nanoparticles size. On the basis of their height, a range between 1.5 and 3 nm was routinely observed, independent of the conditions employed.[17] Increasing the silver load or the photoreduction times resulted in a more homogeneous nanocluster coverage, rather than in the enlargement of individual clusters. It would seem that the growth process is self-limiting, a factor which would be consistent with the templating and catalytic effect provided by the DNA. In fact, as the silver nanoclusters grow, DNA might have a stabilizing effect preventing it from growing beyond a certain size through aggregation with other clusters. Furthermore, once the clusters have reached a critical size, they might stop UV light from reaching and photooxidizing the DNA, blocking the catalytic photoreductive cycle. More simply, silver reduction might stop as DNA becomes completely photooxidized.

In conclusion, we have reported three different strategies for achieving the DNA-templated photoreduction of silver ions and formed strings of silver nanoparticles in a very simple, rapid, and effective way. A mechanism hypothesis was formulated but will require more investigation to be confirmed. We are now hoping to exploit the silver nanoparticles as metallic seeds to catalyze further metal deposition with the goal of obtaining a conductive nanowire. Subsequent metal deposition on the seeds is most likely not limited to silver, but can be extended to other metals. To that extent, further efforts are currently being undertaken in our lab.

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Supporting Information Available: Methods and Materials, Experimental Procedures, AFM images, Grain size analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The particles' size and density were extrapolated from AFM images. See the Supporting Information for details on the procedure followed.

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