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Chirality of Silver Nanoparticles Synthesized on DNA

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Chiral imprinting in molecular and polymer films and enantio-separations using chiral substrates[1] as well as templating of inorganic nanostructures by biomolecules[2] have been frequently reported in recent years. In some cases binding of chiral molecules to a substrate lacking optical rotation has induced optical activity in the substrate. It has been demonstrated that the formation of small gold clusters (20−40 gold atoms) in the presence of chiral glutathione molecules results in the appearance of circular dichroism at wavelengths characteristic of the particle's electronic transition frequency.[3] Imprinting of chiral molecules in a silica matrix was also shown to induce circular dichroism in achiral dye molecules trapped at the same matrix.[4]

It has been shown that randomly aggregated silver nanoparticles possess giant local optical rotations at the plasmon excitation wavelengths,[5] which would average to zero on larger scales, while in the case of lithographically fabricated periodic chiral metal nanostructure arrays, the large optical activity occurred on a macroscopic scale.[6] Dickson and co-workers have reported on the formation of small (few atoms) silver clusters on a short *single-stranded* DNA template,[7] They used the circular dichroism (CD) observed at the silver cluster electronic transition wavelength to prove that the clusters were in proximity to the DNA, without discussing the origin of this phenomenon. Many other DNA metallization schemes were previously described.[8]

In this communication we report on a large CD response of silver nanoparticles grown on a chiral poly(dG)-poly(dC) *double stranded* (ds) scaffold at the silver particle surface plasmon frequency. It is suggested that the chiral DNA template has induced the growth of chiral nanoparticles.

The silver particles in the present work were produced by reduction of Ag^+ bound to 700 base pairs poly(dG)-poly(dC). This long homopolymer was synthesized by Klenow exo-fragment of DNA polymerase I.[9] The DNA was complexed with Ag^+ ions, resulting in a significant change of the CD spectrum of the DNA. The spectrum of poly(dG-)-poly(dC) is characterized by a positive band at 260 nm; the band became negative after the addition of Ag^+ (see Figure 1B). We have observed that the complex between the DNA and Ag^+ ions is stable and does not dissociate during size-exclusion HPLC (data not shown). Reduction of excess of Ag^+ in the presence of the DNA (Ag/base-pair ratio of 10) with $NaBH_4$ in anaerobiosis resulted in the appearance of a new band centered at 425 nm in the absorption and CD spectra of the complex (Figure 1A,B). This band is associated with the plasmon of the silver nanoparticles formed on the poly(dG-)-poly(dC) scaffold. The intensity of this CD band increased in time until it reached a maximum 15 min after the addition of $NaBH_4$. Similar CD spectra were observed for Ag particles grown on poly(dA)-poly(dT).

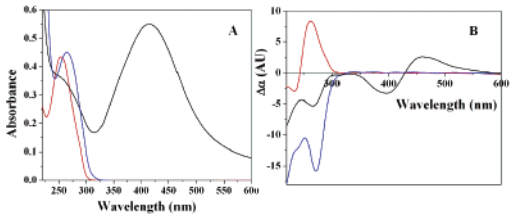

Figure 1. Absorption (A) and CD (B) spectra of bare DNA (red), DNA complexed with Ag^+ (blue) and with NaBH4 reduced Ag^+ (black).

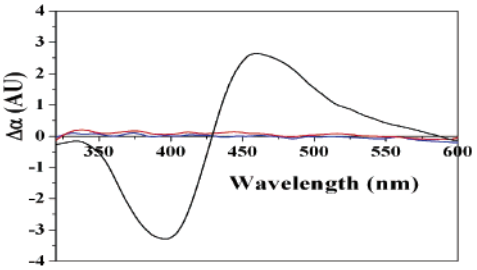

Figure 2. CD spectra measured on Ag nanoparticles grown directly on the DNA (black), Ag particles grown without DNA (red), and Ag particles adsorbed to the DNA (blue).

The band amplitude in the CD spectrum remained unchanged for hours, indicating relatively high stability of the nanoparticle−DNA complex. The nanoparticles did not dissociate from the DNA during chromatography of the complex. This indicates that the complex was kinetically stable and once formed the particles stay bound to the DNA. The stability of the complexes enabled us to deposit them on a carbon coated copper grid and observe them by transmission electron microscopy (TEM). Linear chains of silver particles bound to the DNA scaffold are seen in Figure 3C. To understand whether the chirality was induced in the particles during their growth in the helical DNA environment, silver nanocrystals were prepared separately and complexed with the DNA afterward. The latter particles were prepared by $NaBH_4$ reduction of Ag^+ with trisodium citrate as a negatively charged surface-stabilizing agent. This procedure resulted in the formation of silver nanocrystals, of about 5 nm average size, which did not exhibit any CD signal. Incubation of these particles with poly(dG)-poly(dC) resulted in the formation of a stable complex which was eluded as a single peak from the size-exclusion column. The particles not bound to the DNA were trapped within the column matrix; thus, only the particles bound to the DNA were eluted from the column. Apparently, the negative charges of the DNA backbone replaced the citrate anions adsorbed to the Ag nanocrystals in a ligand exchange process, and a DNA/Ag nanocrystal complex was formed. This complex was characterized by CD, absorption spectroscopy, and TEM and compared with the complex produced by reduction of Ag^+ bound to the DNA. Figure 2 shows CD spectra measured

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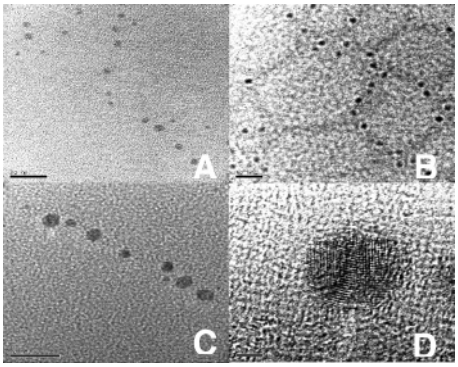

Figure 3. TEM images: A focused image (A) and a defocused image (B) of Ag nanocrystals complexed to the DNA; an image of Ag nanocrystals grown on the DNA template (C); a HRTEM image (D) of an Ag nanocrystal grown on the DNA template. Scale bars are 20 nm (A, C), 50 nm (B), and 2 nm (D).

on (1) the Ag nanoparticles grown directly on the DNA, (2) Ag particles grown without DNA, and (3) the latter Ag particles complexed with the DNA. It can be clearly seen that only the silver particles, which were grown on the DNA template, show a characteristic CD spectrum in the 350−550 nm region. Neither the Ag nanocrystals in solution nor the nanoparticles adsorbed to the DNA showed a CD response around 400 nm.

A typical DNA−Ag nanoparticle complex formed with the particles synthesized ex-situ is seen in Figure 3A as a linear chain of silver particles ordered by the DNA scaffold. Stripes of organic material, probably related to the DNA strands can be barely seen with a defocused electron beam (Figure 3B). Similar images were observed for the Ag nanoparticles grown on the DNA (as in Figure 3C). High-resolution TEM images of the nanocrystals grown on the DNA template revealed a large number of defects, mostly twins (Figure 3D).

The similarity of the TEM images of the two types of DNA−Ag samples and the large difference between the CD spectra of the two samples lead to the conclusion that the DNA has directed asymmetric growth of the particles from Ag clusters bound to this chiral template. The Ag nanocrystals produced in optically inactive aqueous environment and complexed with the DNA lack this handedness.

As suggested by Schaaf and Whetten thiol capped gold clusters may show chiroptical effects due to three possible reasons[3]: (1) formation of a chiral metal core due to the influence of chiral ligand molecules on the formation of the cluster, (2) electronic interaction between the chiral ligands and achiral metal core electrons, and (3) chiral arrangements of the ligands on an achiral metal core. It was recently calculated that the two latter mechanisms may produce significant CD at the electronic resonance of the metal core.[10] Nevertheless, it appears that in the present case, as also suggested by Schaaf and Whetten for the gluthathione−gold system, the first mechanism was in action.

There is a fundamental difference between the present case and the appearance of CD in the monodisperse gold or silver clusters synthesized with gluthathione[3] or single stranded DNA.[7] In ref 3 the samples, of 20−40 atom clusters, were separated to single size clusters which are characterized by a high probability to pack in low-symmetry chiral configurations. The silver particles observed in the present work were polydisperse with apparently random shapes. Hence, the mechanism by which the ds-DNA induced the growth of chiral silver particles of a particular handedness with an appreciable yield has to be different from the one acting on the small metal clusters and would probably be related to the helical DNA structure rather than the chiral building blocks.

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