

CHIRALITY OF SILVER NANOPARTICLES SYNTHESIZED ON DNA

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Chiral imprinting in molecular and polymer films and enantioseparations using chiral substrates are well known phenomena.¹ It has been found that the binding of chiral molecules to a substrate lacking optical rotation has induced optical activity in the substrate. Small metal clusters have been shown to exhibit optical activity depending on their arrangement² or growth template. These metallic nanoparticles have usually been grown through the reduction of metallic cations using various templates (e.g., various surfactants and peptides). DNA was found to be an excellent template for the growth of metallic nanoparticles.³ In this work we demonstrate that a DNA template induces chirality of silver nanoparticles grown in it. The silver particles were produced by reduction of Ag^+ bound to 700 base pairs poly(dG)-poly(dC). The complex between the DNA and Ag^+ ions is stable and does not dissociate during size-exclusion HPLC. Reduction of Ag^+ with NaBH_4 in anaerobiosis resulted in the appearance of a new band centered around 425 nm in the absorption and CD spectra of the complex. This band in the CD spectrum is associated with the plasmon of the silver nanoparticles formed on the poly(dG)-poly(dC) scaffold. In order to understand whether or not the chirality is induced in the particles during its formation in the optically active DNA environment we have prepared silver nanocrystals separately from the DNA and complexed them with the DNA afterwards. Only the silver particles, which were grown on the DNA template, show a characteristic CD spectrum in the 350-550 nm region. Neither Ag nanocrystals in solution nor the nanoparticles absorbed to the DNA (post-synthesis) showed CD response around 400 nm (see figure below). Based on the similarity of the TEM images of the two types of DNA-Ag samples and large difference between the CD spectra of the two samples we suggest that the DNA directed asymmetric assembly of the particles from Ag atoms bound to this chiral template. The Ag nanocrystals produced in optically inactive aqueous environment by reduction of Ag^+ atoms and further complexation of the particles with the DNA lack this chirality. The passivation of small gold clusters with chiral molecules gives rise to optical activity⁴. Several explanations for this optical activity were thought of, among them the formation of a chiral metal core due to the influence of the chiral ligand

molecules on the formation of the cluster or through chiral arrangements of the ligands on an achiral metal core. We believe that in our case of the former explanation is more plausible than the latter one.

References:

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Figures

