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Assembly of Au Nanoparticles with Anisotropic Optical Property Directed by 2'-Phosphorothioate Oligo-DNA

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Two complemental 2'-phosphorothioate oligo-DNA compounds were used as linker molecules to provide the necessary symmetry-breaking mechanism to direct the assembly of 13 nm Au nanoparticles into aggregates with anisotropic optical properties.

Keywords gold nanoparticle, oligo-DNA, assembly

The assembly of inorganic nanoparticles into ordered arrays yields materials with novel physical properties arising from interactions between the nanoparticles.[1,2] Recently, biomolecules have been widely employed as linker molecules to connect inorganic nanoparticles into extended meso- and macroscopic architectures.[3-5] Among the biomolecules concerned, DNA has received special attention due to their specific and selective reactivity. The most-studied DNA for assembly of nanoparticles is alkanethiol-capped DNA, in which the thiol group is modified at DNA termini of position 5' or 3'. Generally if spherical nanoparticles were used as building blocks, the resulting assembly directed by such alkanethiol-capped DNA are primarily two- and three-dimensional hexagonal close-packed aggregates showing isotropic optical properties.[6,7] When anisotropic nanoparticles such as nanorods were employed as building blocks, assemblies with anisotropic optical properties could be constructed,[8] and such assemblies were attractive due to their application potentials to light polarization of polarizers,[9] polarized luminescence,[10] and polarized light emitting diodes.[10,11] However, it is still a challenge to construct assembly with optical anisotropic properties from optically isotropic spherical nanoparticles by biomolecules such as DNA without the help of template technique. Phosphorothioate oligo-DNA is well known as antisense DNA, which was widely employed in manipulating expression of specific gene products[12,13] and as template to direct the formation of nanoparticles.[14] Herein, we report the using of two complemental 2'-phosphorothioate oligo-DNA (2'-PS oligo-DNA) (Figure 1) as linker molecules to provide the necessary symmetry-breaking mechanism to direct the assembly of 13 nm Au nanoparticles into aggregates with anisotropic optical properties.

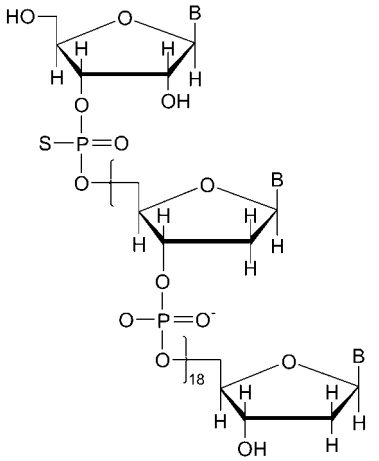

Figure 1 Chemical structure of 2'-PS oligo-DNA. B was used to represent guanine or cytimidine. Phosphorothioate oligo-DNA used here are 2'-phosphorothioate oligoguanine and oligocytosine containing 20 bases (2' PS oligo-G_{20} and 2'-PS oligo-C_{20}), in which the non-bridging oxygen atom between C^1 and C^2 of the phosphate backbone is replaced by a sulfur.

The UV-visible spectrum of the 13 nm gold nanoparticles coated by 2'-PS oligo-G_{20} or 2'-PS oligo-C_{20}, shows a plasma peak at 519 nm (Figure 2a), quite similar to that coated by citrate.[15] The shoulder peak at 260 nm indicates the presence of the oligonucleotides. After the gold nanoparticles modified by 2'-PS oligo-G_{20} and those coated by 2'-PS oligo-C_{20} were mixed at 1∶1, UV-visible spectrum of the Au nanoparticles showed a red-shifted plasma peak at 536 nm with decreased intensity due to the DNA renaturation and an additional broad peak appeared at 676 nm (Figure 2b). After DNA annealing treatment, the peak at 676 nm

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became weaker and experienced a red-shift to 727 nm (Figure 2c), suggesting the formation of larger aggregates of Au nanoparticles due to the further renaturation of the DNA, which was illustrated by the further decreased intensity of the absorbance at 260 nm.[16]

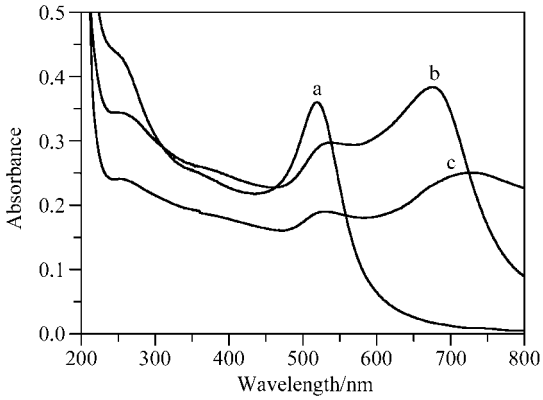


Figure 2 UV-visible spectra of the Au nanoparticles coated by 2'-PS oligo-C_{20} or 2'-PS oligo-G_{20} (a), the 1∶1 mixture of the Au nanoparticles coated by 2'-PS oligo-C_{20} and 2'-PS oligo-G_{20} (b), and the 1∶1 mixture after DNA annealing treatment (c).

TEM observations show that the gold nanoparticles modified by 2'-PS oligo-G_{20} or coated by 2'-PS oligo-C_{20} were isolated before mixing (Figure 3a), after DNA renaturation, they were assembled into relatively loosely-packed aggregates compared to these directed by alkanethiol-capped DNA (Figure 3b). In case of alkanethiol-capped DNA, the space between the nanoparticles in the assembly was determined by the length of the DNA duplex.[6] When the 2'-PS oligo-DNA was used as linker molecules, the space between the Au nanoparticles is about 2 nm, much smaller than the length of the 2'-PS oligo-DNA containing 20 bases (6.8 nm). After the annealing treatment, the Au nanoparticles are assembled into larger 3D aggregates (Figure 3c) and still no hexagonal closely packed arrangement of the Au nanoparticles as that of aggregates directed by alkanethiol-capped DNA could be observed. Such assemblies of Au nanoparticles directed by 2'-PS oligo-DNA and alkanethiol capped oligo-DNA were suggested to be different to some extent. When the 2'-PS oligo-DNA molecules were located on surface of the Au nanoparticles via the coordination between the thioate groups and the surface Au atoms, they should be oriented almost normally to the particle surface due to the introduction of the thioate group at the second phosphate from the 5' end. After DNA renaturation, the Au nanoparticles should also be almost perpendicular to the DNA duplex. At this time, the space between the Au nanoparticles of the assembly was primarily determined by diameter of the DNA duplex but not the length of DNA strand. This is in consistent with the TEM observation, which displays the interparticle space of about 2.0 nm (see Figure 3a), or 30 bases as linker molecules, and the resulting assembly exhibited almost the similar space between the gold nanoparticles. Such short interparticle spacing which is difficult to be acquired by the alkanethiol-capped DNA[17] might allow the strong interactions between the nanoparticles. In addition, the 2'-PS oligo-DNA would demand larger space to complete the renaturation. This is to say, during the renaturation, the compact symmetric hexagonal arrangement of the Au nanoparticles was sterically unfavorite. Therefore, in our experiment, the linker molecules, 2-PS oligo-DNA, could provide the necessary symmetry-breaking mechanism to direct the formation of Au nanoparticle assemblies with anisotropic optical properties. Scheme 1 illustrates the proposed mechanism for the formation of the Au nanoparticle assemblies directed by 2'-PS oligo-DNA.

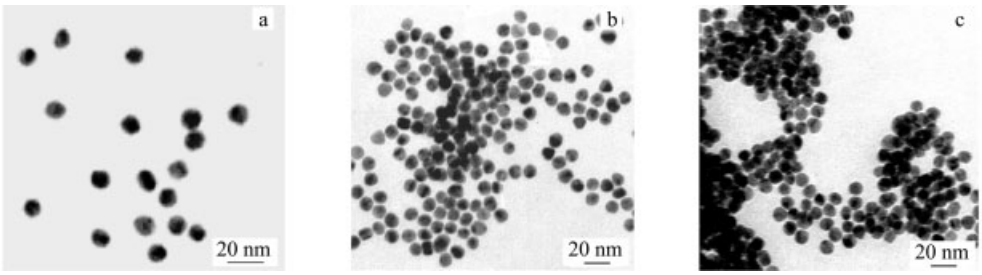
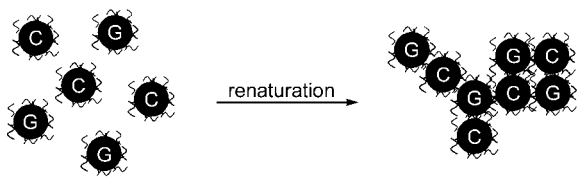


Figure 3 TEM images of (a) the Au nanoparticle modified by 2'-PS oligo-G_{20}, (b) the Au nanoparticle aggregates after DNA renaturation and (c) the aggregates after DNA annealing.

Scheme 1 Proposed mechanism for formation of the Au nanoparticle assemblies directed by the 2'-PS oligo-DNA. Spheres labeled with G represent Au nanoparticles coated by 2'-PS oligo-G_{20} and those labeled with C represent Au nanoparticles modified by 2'-PS oligo-C_{20}



The plasma resonance of Au colloids linked by alkanethiol-capped DNA has been known to shift to longer wavelength and become broader than that of the dispersed Au particles due to the collective electromagnetic response of the isotropic aggregate containing thousands of nanoparticles.[17] Appearance of the second peak at longer wavelength usually indicates the anisotropic optical properties of the Au nanoparticle aggregates. According to Mie scattering theory, short interparticle spacing between the nanoparticles of the aggregates is critical to the observation of the second peak at longer wavelength.[18] Co-existence of the two peaks in both the UV-visible spectra of the mixture before and after annealing (Figure 2b and 2c) indicates the anisotropic optical properties of the Au nanoparticle assemblies directed by the 2'-PS oligo DNA.

In summary, when 2'-phosphorothioate oligo-DNA was used as linker molecules, the space between the particles in the assemblies was primarily dominated by the diameter of the DNA duplex, allowing the strong interactions between the nanoparticles. In addition, the thioate group introduced at phosphate site of the DNA was unfavorite to the symmetric arrangement of the Au nanoparticles of the assemblies. The combination of strong interparticle interactions and symmetric-breaking mechanism endows the assemblies from optically isotropic spherical Au nanoparticles with anisotropic properties. Since one or more thioate groups can be modified at different sites of the phosphate groups of oligo DNA, the employment of phosphorothioate oligo-DNA as linker may provide new insight into the controllable assembly of inorganic nanoparticles.

Experimental

The 13 nm Au colloids were prepared by sodium citrate reduction of $HAuCl_4$ solution according to the literature.[14] 2'-Phosphorothioate oligo-DNA compounds used were 2'-phosphorothioate oligoguanine (2'-PS oligo-G_{20}) and 2'-phosphorothioate oligocytimidine (2'-PS oligo-C_{20}) from GENEMED SYNTHESIS. Water with a conductivity of 18 MΩ•cm was used in the experiment. 4 mL of Au colloids (1 nmol•L^{-1}) were treated with 8 μL of 2'-PS oligo-C_{20} (40 μmol•L^{-1}) and 8 μL of 2'-PS oligo-G_{20} (40 μmol•L^{-1}) respectively.[18] The solutions were stirred for 36 h under nitrogen flow at room temperature to ensure complete interaction between Au nanoparticles and the oligonucleotides. Then the two colloidal Au solutions were combined together. After the addition of NaCl at a concentration of 0.15 mol/L, immediately, the solution experienced a color change from red to purple. To make the DNA be further renatured, DNA annealing was carried out by heating the mixture at 90 ℃ for 2 min and then cooling it to room temperature slowly. UV-visible spectra were recorded on a Shimadzu UV-1602 spectrophotometer. Transmission electron microscopy (TEM) images were observed on a Hitachi H-8100 IV electron microscope by using carbon coated copper grid as substrates.

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19 In this experiment, on average, each Au nanoparticle was wrapped by about 80 oligonucleotides. When the nanoparticle was coated by more oligonucleotides, *i.e*., 200, similar results were observed. However, splitting of the two peaks became larger and aggregates containing more Au nanoparticles were observed under TEM.

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