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Surface Plasmon Coupled Circular Dichroism of Au Nanoparticles on Peptide Nanotubes

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Nature produces several macroscopic objects with chiral morphologies through biomineralization[1] and one of the most remarkable examples is the coiling of calcium carbonate shells.[1a,b] The macroscopic chiral shapes in natural systems mainly originate from the transfer of chiral information of various biomolecules present in the living organisms. Chirality transfer in these systems is complex and hence various laboratory models on the enantioselective interactions of inorganic and organic crystals with amino acids and biomarkers have been considered.[1,2] Chiral molecules can induce optical activity in achiral chromophores, and electronic circular dichroism (CD) has been used to investigate chirality transfer in biomolecular systems.[3] Recent studies have shown that the inorganic nanoparticles having chiral molecules in their vicinity show optical activity.[4−7] Various chiral nanosystems include (i) gold nanoclusters capped with L-glutathione,[4a,b] D- and L-penicillamines,[4c] D- and L-cysteine derivatives,[4d,e] calix[4]arenes;[5] (ii) CdS capped with D- and L-penicillamines;[6a] (iii) CdTe capped with D- and L-cysteine derivatives;[6b] and (iv) silver nanoparticles grown on double stranded DNA.[7] In all the above systems, except the latter one, nanoparticles are capped with chiral ligands. Even though significant progress has been made in the design and study of such chiral nanoclusters,[4−6] chirality transfer from surfaces with reduced elements of symmetry to nanomaterials is not well understood.[1b] Herein we report the in situ growth of Au nanoparticles on D- and L-isomers of diphenylalanine peptide nanotubes and their chiroptical properties.

Diphenylalanine peptide nanotubes (PNT) possess several unique properties:[8] (i) they are homogeneous with persistent length, (ii) biocompatible, and (iii) stable to thermal degradation (up to 150 °C). PNT were prepared by the self-assembly of D- and L-isomers of diphenylalanine by adopting a reported procedure;[8b] water was injected to a stock solution of dipeptide in 1,1,1,3,3,3-hexafluoro-2-propanol and kept for aging (24 h). Both the isomers of PNT possess strong absorption at 258 nm and shoulder at 220 nm (trace a_1; inset of Figure 1) and their CD profile showed symmetrical mirror images with an intense peak at 228 nm (trace a_1, a_2; Figure 1). Formation of PNT was confirmed by FTIR (see the Supporting Information) and HRTEM analysis (Figure 2A).

With the objective of investigating the chirality transfer to metal nanoparticles, ethylene glycol thiol protected Au nanoparticles[9] (EG-Au; 0.032 mM) having an average diameter of 4.5 nm were added to both D- and L-isomers of PNT (3.2 mM). All the experiments were carried out at pH 10. The plasmon band of Au nanoparticle bound on PNT got red-shifted (see the Supporting Information) and adsorption of nanoparticles was further confirmed through the TEM studies (Figure 2B). The CD peak corresponding to the PNT at 228 nm showed slight decrease in intensity (traces b_1 and b_2; Figure 1); however, no signal was observed at the gold surface plasmon frequency, ruling out the possibility of chirality transfer. It was reported that gold nanoparticles bound on the surface of PNT can act as nucleation sites for the reduction of gold ions.[8c] PNT seeded with EG-Au nanoparticles was further mixed with an aqueous solution of $HAuCl_4$ (1.06 mM) and the solution was irradiated at 300 nm in a Rayonet photochemical reactor for 3 h. A substantial increase in the intensity of the surface plasmon band was observed, indicating the reduction of gold ions to gold nanoparticles (trace c_1; inset of Figure 1). This observation was further confirmed through TEM analysis; well separated gold nanoparticle bunches were observed on PNT (Figure 2C). EG-Au nanoparticles seeded on the PNT can act as the nucleation site and the chiral molecules on their surface provide a restricted environment, which drives the selective growth of nanoparticles as bunches. The close proximity of Au nanoparticles in each of these bunches (inset of Figure 2C) on PNT induce coupling of their plasmon oscillations, resulting in a shift in the absorption band to 533 nm. The position of the new resonance band depends mainly on the interparticle distance and orientation.[10] However, further resolution of the organization of nanoparticle using HRTEM was difficult

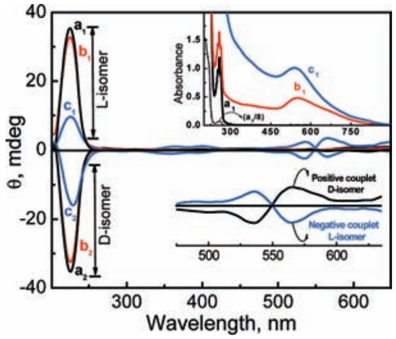

Figure 1. Absorption (inset) and CD spectra of (a) diphenylalanine peptide nanotubes (PNT; 3.2 mM) in water/HFP (99:1) at pH 10 on subsequent addition of (b) EG-Au nanoparticles (0.032 mM) and (c) $HAuCl_4$ (1.06 mM), followed by photochemical irradiation (3 h). Absorption spectrum of PNT up to 200 nm as dotted trace in top inset and CD spectra at the surface plasmon frequency as bottom inset. Subscripts 1 and 2 denote L- and D-isomers of PNT, respectively.

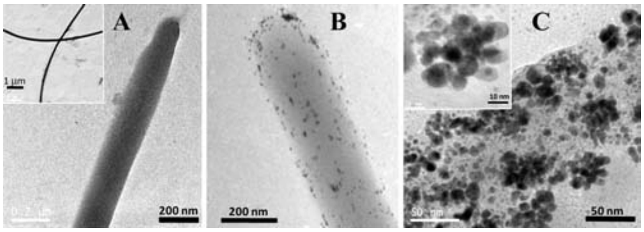

Figure 2. (A−C) TEM images of diphenylalanine peptide nanotubes (PNT) in the (A) absence and (B) presence of EG-Au nanoparticles; (C) after photochemical irradiation for 3 h. Inset of A shows low-resolution TEM image of PNT and that of C shows HRTEM image of one of the bunches.

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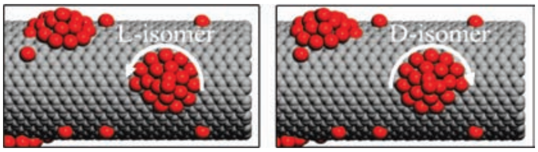
Scheme 1



because of the deformation of PNT on prolonged exposure to electron beam.

The assembly of gold nanoparticles on peptide nanotubes was further probed using CD spectroscopy, which can provide valuable information about the geometrical properties of these hybrid systems. Interestingly, gold nanoparticle bunches on D- and L-isomers of PNT showed bisignated CD signal with symmetrical mirror images at the gold surface plasmon frequency (traces c_1 and c_2; Figure 1). The D-isomers of PNT showed positive followed by negative cotton effects (positive couplet). In contrast, an inversion of CD signal was observed with negative followed by positive cotton effects for the L-isomer (negative couplet). Anisotropic factor (g-factor) of gold nanoparticle bunches on D- and L-isomers of PNT are in the range of $\pm 5 \times 10^{-5}$, comparable with earlier reports.[4]

The obvious question is how the bisignated CD signal with symmetrical mirror images was observed at the surface plasmon frequency of gold nanoparticles. It is well-established in the literature that the induction of chirality can occur when an achiral chromophore and a chiral component are in close contact.[11] It occurs mainly through the destruction of the symmetry of the former resulting from the structural perturbation of the latter. In the present case, the hybrid system consists of achiral gold nanoparticles and chiral peptide template as two components. Chiral molecules have been shown to reduce the symmetry of growing crystals.[1a−c] Adsorption of EG-Au nanoparticles on to the PNT surface results in the lowering of symmetry due to the fact that the surface does not allow some symmetry elements to occur. The adsorbed nanoparticles act as nucleation sites and the chiral molecules on the surface breaks the symmetry of the growing nanoparticles. It was reported earlier from our group and others that the closely packed linear organization of Au nanoparticles and nanorods can result in the coupling of surface plasmon resonance which depends on the particle size, array spacing, array symmetry, and polarization direction.[10] Interestingly, the mirror image relationship in the CD spectra, observed at the surface plasmon frequency, clearly indicates that the chiral molecules on the D- and L-isomers of PNT drive the organization of Au nanoparticles in two different ways, with opposite chirality (note the direction of arrows in Scheme 1). In the present case, we believe that the Au nanoparticles are asymmetrically organized as bunches on PNT (however, experimental data available do not rule out the possibility of the chiral arrangement of atoms in a nanoparticle). Thus the surface plasmon coupled circular dichroism originates from plasmon coupling between the asymmetrically organized Au nanoparticles. A similar mechanism of exciton coupled circular dichroism operates in various chromophoric systems and these aspects are well-established.[3,11]

Nanoclusters capped with chiral molecules show optical activity at their discrete electronic transition and three different mechanisms have been proposed:[4b,12] (i) formation of chiral core, (ii) chiral organization of the chiral adsorbate on an achiral core, and (iii) electronic interaction between the chiral molecules and the achiral metal core. More recently, CD active surface plasmon resonance bands were observed in gold nanoparticles capped with chiral calix[4]arenes[5] and silver nanoparticles adsorbed on DNA template.[7] We have adopted a different strategy for inducing chirality to Au nanoparticle assembly by growing them on chiral surface having reduced elements of symmetry. In the present case the surface plasmon coupled circular dichroism originates from the asymmetric organization of Au nanoparticles on surface resulting in bisignated CD signals. It is noteworthy that chiral information and asymmetry at the molecular level on the D- and L-isomers of PNT are transferred to gold nanoparticles.

In conclusion, Au nanoparticles grown on D- and L-isomers of diphenylalanine peptide nanotubes showed a bisignated CD signal at their surface plasmon frequency with positive and negative couplets. The concepts presented here can be further utilized for understanding the surface chirality in complex biological systems. Chiral surface plasmon resonance originating through the desymmetrization of the Au nanoparticle assembly may have potential application in optical devices.

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Supporting Information Available: Details on the assembly of nanoparticles on peptide nanotubes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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