DOCTORAL THESIS

Interaction of molecules and helical nanoparticles characterized by electronic circular dichroism

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Abstract

It is of fundamental significance to differentiate an enantiomer from its mirror image (i.e., enantiodifferentiation), through monitoring optical activity (OA) of enantiomers that is typically characterized by electronic circular dichroism (ECD or CD) in the UV-visible region. However, sub-wavelength molecular dimensions substantially prevent enantiomers from effectively perceiving the different circular polarization states, leading to low enantiomeric OA and weak enantiodifferentiation. Some approaches have been developed to amplify the enantiomeric OA; alternatively, on the basis of the emerging chiral metamaterials of metallic helical nanoparticles (HNPs) I devise two methods to enhance the enantiodifferentiation.

First, I employ glancing angle deposition (GLAD) to deposit Ag HNPs with a helical pitch (*P*) larger than wire diameter (*d*) of the helical, i.e., Ag nanohelices (AgNHs). AgNHs exhibit strong plasmonic CD composed of a broadband longitudinal mode (i.e., L-mode) in the visible region, a transverse mode (i.e., T-mode) at a wavelength of ~370 nm, and a dielectric mode in the deep UV region (at a wavelength shorter than 320 nm). Adsorption of alkyl ligands on the AgNHs markedly weakens the two plasmonic CD modes, and the T-mode is weakened more seriously than the L-mode. The deterioration of the plasmonic CD is exacerbated with increasing the bonding energy of the Ag-alkyl ligand contacts, attributed to the increase of the dielectric constant of the medium of the AgNHs (ε_r) and the electron withdrawal from the AgNHs towards the alkyl ligands. Derived from the ligand-induced weakening of the plasmonic CD, enantiodifferentiation of L-Glutathione (L-GSH) from D-GSH is dramatically enhanced. The chiroptical weakening sensitively varies with the absolute configuration of GSH, resulting in an enantiodifferentiation anisotropic *g* factor of ~0.5 that is independent on the AgNH helicity. The AgNH-induced anisotropy *g* factor is superior to those obtained by other methods, by 2 – 4 orders of magnitude. It is the largest achieved up-to-date, as high as one-fourth of the theoretical maximum.

Second, I operate GLAD with fast substrate rotation to reduce *P* less than *d*, to generate AgHNPs that exhibit negligible dielectric CD in the deep UV region, offering a helical substrate to directly amplify the OA of enantiomers grafted on the AgHNPs. The anchoring of enantiomers on AgHNPs with the sub-5 nm *P* leads to the enantioselective amplification of the enantiomeric OA in roughly

ten folds; the LH- and RH-AgHNPs give rise to amplify the OA of (*S*)- and (*R*)-enantiomers, respectively. It is ascribed to the change of the dihedral angle of an enantiomer adsorbed on AgHNPs. Such the enantioselective amplification tends not to occur as long as $P > 5$ nm.

Moreover, given the enantiodifferentiation of biomolecules that are typically dissolved in an aqueous solution, the effect of water on the plasmonic CD of AgHNPs is investigated and compared with that of AgNHs. Hydrophobic AgNHs with high structural porosity give rise to the irreversible water effect on the plasmonic CD; and hydrophilic AgHNPs with low structural porosity lead to the reversible water effect.

At the end, I devise a new methodology to generate plasmonic CD through chirality transfer from chiral host to achiral guest, owing to the helicity duplication of the achiral guest from the chiral host. It leads to inducing chiroptical activity of the achiral guest made of some plasmonic materials that aren't facilely sculptured in the helical. The new methodology effectively broadens the range of materials made from the chiral nanostructures, which is on demand to develop diverse chirality-related bioapplications.

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