HOTSPOT ENHANCED PLASMON-COUPLED CIRCULAR DICHROISM FOR SINGLE CHIRAL BIOMOLECULE SENSING

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Biomolecules crucial for life, such as proteins, peptides, DNA, and amino acids, exhibit chirality, impacting pharmaceuticals where opposite handed drug molecules interact differentially with the body. Detecting molecular chirality is vital in Chemistry, and is often done through Circular Dichroism (CD) spectroscopy, measuring differential extinction of circularly polarized light by analytes. CD spectroscopy also aids in discerning protein conformational changes. However, conventional CD spectroscopy faces limitations, including poor size match and specialized UV optics requirements. An emerging approach involves using plasmonic nanomaterials to enhance molecular sensitivity and shift CD responses into the visible spectrum. In this project, our aim was to leverage hotspot junctions to assess the feasibility of single molecule detection. Anisotropic nanoparticle assemblies with chiral molecules may incur directional misalignment, leading to residual structural chirality, often masking the molecular response. To mitigate this, we employed an achiral substrate composed of isotropic nanospheres with low inherent chirality. We chose Bovine Hemoglobin (BHb) as our molecule of interest because of its absorption spectral overlap with the gold nanospheres (AuNSs) in visible region. We exploited dipole-dipole interactions between BHb and AuNSs dimers, inducing chirality in the plasmonic dimer through BHb presence in the nanogap, known as plasmon-coupled CD (PCCD). Correlated single-particle dark-field circular differential scattering (CDS) measurements were conducted on BHb-assisted AuNSs dimers to detect PCCD, and negative CDS signals were obtained. As a control, we further employed NaCl-mediated AuNS dimers and got low CDS signals, clearly indicating the absence of BHb. Our results underscore the potential of plasmonic nanomaterials in enhancing the sensitivity and applicability of CDS for single analyte detection, advancing molecular analysis and pharmaceutical research. In addition, the ability to detect single biomolecule and its conformational changes could have far-reaching consequences for understanding neurodegenerative diseases, such as Alzheimer's and Parkinson's.