Chirality-driven interparticle interactions in plasmonic colloids revealed by optical spectroscopy

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Noble metal nanoparticles (NPs) are versatile colloidal building blocks whose stability and aggregation behavior are highly sensitive to surface chemistry. Their localized surface plasmon resonance, arising from the collective oscillation of free electrons, is strongly affected by both interfacial chemistry and interparticle coupling, providing a direct all-optical readout of colloidal assembly and phase behavior at the nanoscale. For this reason, in the last decades silver and gold NPs have been widely exploited as high-performance colorimetric [1] and spectroscopic [2] optical sensors.
Here, we explore chirality-driven interactions in suspensions of spherical citrate-capped gold NPs by combining UV-visible spectroscopy and surface-enhanced Raman scattering (SERS). We investigate the colloidal behavior of a single gold NP batch in the presence of different chiral organic analytes and observe a pronounced enantioselective response. This is evidenced by selective NP aggregation, detectable through changes in the optical response of the colloidal dispersion. Despite the nominally achiral geometry of the NPs, these results indicate the emergence of enantioselective interparticle interactions. While previous studies attributed this effect to structural asymmetries within the NP core [3], we instead identify the molecular stabilizing layer as the dominant source of chirality. SERS measurements reveal that citrate molecules bind asymmetrically to the gold surface, effectively generating a chiral interfacial environment.
To test this hypothesis, we systematically tailor the nanoparticle interface by replacing the citrate layer with achiral and chiral ligands and by varying NP size. We find that achiral interfaces suppress enantioselectivity, while chiral ligands enable a programmable and tunable enantioselective response.
These results demonstrate that chirality in plasmonic colloids is not an intrinsic nanoparticle property, but rather an emergent feature arising from interfacial molecular organization.

Keywords:
plasmonics, colloids, chirality, interparticle interactions.

References:

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