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UNVEILING THE MESOSCALE ASSEMBLY OF GOLD NANOPARTICLES ON SOFT TEMPLATES VIA NANOPLASMONIC ISOSBESTIC POINTS

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The controlled clustering of plasmonic nanoparticles (NPs) generates unique optical properties through the coupling of localized surface plasmon resonances (LSPR) of individual NPs. This phenomenon can be achieved with lower synthetic efforts, using spontaneous assembly onto soft templates in liquid media, such as liposomes [1], lipid NPs [2], polymeric NPs [3], and biological vesicles [4]. The structure of NPs assemblies originates from thermodynamic equilibrium, and the LSPR variation induced by clustering can yield information on the physicochemical properties of the templating agent, including concentration, nanomechanics, and purity from biological contaminants [4,5]. However, monitoring how the assembly mesostructure determines final optical properties remains a critical challenge to inform the design of advanced plasmonic materials [6,7]. Here, we introduce "nanoplasmonic isosbestic" as optical descriptors of the mesoscale organization of gold nanoparticles (AuNPs) on soft templates. Unlike isosbestic points in molecular spectroscopy, which describe chemical equilibria, our numerical simulations demonstrate that nanoplasmonic isosbestic emerge from the coexistence of individual AuNPs and AuNP clusters where the interparticle spacing controls the isosbestic wavelength. By templating AuNPs assembly onto synthetic free-standing lipid bilayers with tunable membrane rigidity, we experimentally achieve precise control over interparticle spacing and prove that it is mirrored by univocal modulation of the isosbestic wavelength. In addition, from an analytical perspective, we show that isosbestic points can fingerprint key template's properties, such as the stiffness of the free-standing bilayers, enabling non-invasive optical probing. As a proof-of-concept, we apply this approach to profile the stiffness of biologically relevant templates, i.e., Extracellular Vesicles (EVs). For the first time, we demonstrate a direct correlation between interparticle spacing and isosbestic behavior, providing fundamental understanding of structure-function relationship in plasmonic systems. These findings position plasmonic isosbestic points as descriptors to reveal mesoscale organization in nanoplasmonic structures and introduce a new strategy for optically characterizing soft materials.

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