Re-entrant plasmon coupling driven by phase behavior of microgel–nanoparticle systems

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The development of flexible photonic devices with adaptive optical properties has attracted increasing attention in recent years. A well-established strategy to integrate soft and photonic components relies on embedding plasmonic nanoparticles (NPs) within thermoresponsive microgels [1]. In these hybrid particles, the volume phase transition (VPT) of the polymeric microgel couples microscale structural changes to nanoscale plasmonic interactions, enabling external control over interparticle distances and, consequently, over plasmon coupling and optical response [2]. However, the role of colloidal stability in determining the optical response of such hybrid systems has been largely overlooked, despite its potential to give rise to a much broader range of optical behaviors.

We reveal a counter-intuitive re-entrant behavior in the optical response of electrostatically assembled microgel–NP complexes as a function of the NP-to-microgel number ratio: increasing NP loading initially enhances coupling, but beyond a critical threshold a it leads to a weakening of the optical response [3]. To rationalize this behavior, we combine optical spectroscopy with X-ray and dynamic light scattering techniques to establish a quantitative relationship between plasmonic coupling and interparticle distance, identifying two distinct coupling regimes. We then demonstrate that, beyond the VPT-driven gathering of NPs within individual complexes, plasmonic coupling is also governed by inter-complex interactions that emerge at intermediate NP loading, where loss of colloidal stability leads to the formation of large aggregates and to pronounced enhancement of the plasmonic response.

We rationalize the overall phenomenology within the framework of charge-patch interactions by constructing a NP-loading-temperature phase diagram that directly links colloidal stability to optical response. Our findings demonstrate that plasmonic coupling in soft colloidal systems is controlled not only by nanoscale structure but also by mesoscale phase behavior, thus establishing a general framework for harnessing colloidal interactions to program optical responses in soft photonic materials.

References:

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