2-4-4. Plasmon-Mediated Excitation

Overview

In the optical near-fields of localized surface plasmons (LSPs) generated by metallic nanostructures, the extreme spatial confinement of the electromagnetic field perturbs the conventional optical selection rules that are normally derived under the long-wavelength approximation, thereby giving rise to otherwise inaccessible excitation and polarization channels in adjacent material systems. This subwavelength localization of the LSP field also facilitates the establishment of strong light-matter coupling regimes, in which hybridized polaritonic states are formed. Molecular ensembles embedded in such strong coupling environments experience modified electromagnetic vacuum fluctuations, leading to substantial alterations in their intrinsic physical properties and chemical reactivity, even in the absence of external illumination. Nanostructured interfaces thus provide promising platforms for generating matter property-modulating fields.

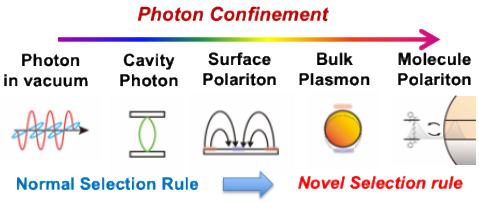

Figure 1. Localization of electromagnetic field.

Current Status and Frontiers

The optical properties of materials are generally governed by optical selection rules determined by the wavelength of the incident electromagnetic field. In the vicinity of the visible region, however, theoretical studies have predicted that the long-wavelength approximation can break down due to field localization, leading to a modulation of the selection rules for electronic excitations (Ishihara *et al.*). This prediction was later validated by the experimental demonstration that such modulation occurs in the electronic excitation of single-walled carbon nanotubes adsorbed on plasmon-active metallic nanostructures (Murakoshi *et al.*), as revealed through resonance Raman scattering spectroscopy (see Section 1-1-12. "Surface-Enhanced Raman Spectroscopy"). Subsequent theoretical analyses indicated that quadrupolar excitation modes within nanotube cross-sections of ~1 nm diameter could be involved in this phenomenon. This discovery highlights that plasmon-mediated excitations can endow material systems with optical responses, both in wavelength and polarization, that are inaccessible under conventional conditions (Schatz *et al.*).

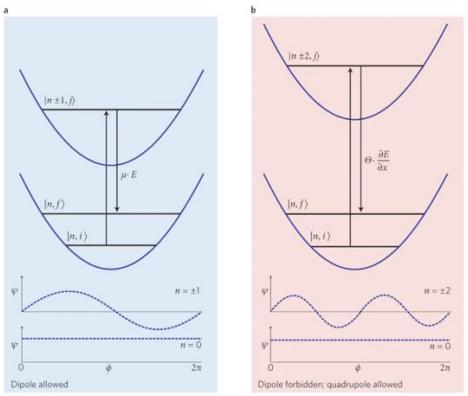

Figure 2. Higher order electronics excitation.[2b]

In free space, even in complete darkness, the vacuum fluctuations of the electromagnetic field give rise to the spontaneous creation and annihilation of

field quanta in energy, space, and time domains. These fluctuations are known to underlie intermolecular forces such as London dispersion interactions, as well as the autodissociation ability of water molecules etc. When matter enters a strong coupling regime, its intrinsic properties are modulated by the redefinition of these fluctuations. Since the pioneering work, which introduced the concept of many-body quantum systems where quasiparticles such as excitons, phonons, and magnons exist in quantum superposition (Hopfield *et al.*), considerable attention has been directed toward the formation and control of strong coupling states arising from the interaction of molecular ensembles with the controlled electromagnetic field (see Section 1-4-6. "Optical Microcavities"). Theoretically, it has been proposed that such light-matter strong coupling states can create novel reaction pathways of electron transfer processes in homogeneous systems, leading to enhanced electron transfer rates as well as the disappearance of the Marcus inverted region (Nitzan *et al.*). Extending the theoretical framework of electron transfer under strong coupling to electrochemical systems suggests that the formation of ultra-strong coupling states could accelerate electrochemical electron transfer rates by nearly an order of magnitude (Fukushima *et al.*). The principal mechanism is attributed to the narrowing of the optical density of states imposed by the field.

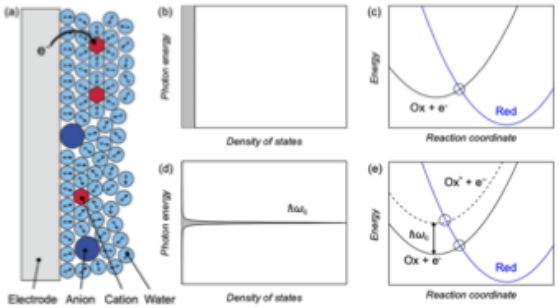

Figure 3. Electron transfer theory at electrified interfaces under strong coupling conditions.[5]

Thus, the spatial confinement of the electric field associated with localized surface plasmons (LSPs) on metallic nanostructure surfaces not only modulates the excitation and polarization modes of matter, but also serves as a powerful tool for constructing quantum superposition states in many-body systems. Notably, the formation of strong coupling states does not require external optical excitation; even under dark conditions, material systems can acquire photonic characteristics and exhibit modulated chemical reactivity.

References

1. T. Iida, et al., *Appl. Phys. Lett.,* **98**, 053108 (2011).
2. (a) M. Takase, et al., *Nat. Photo.*, **7**, 550–554 (2013); (b) C. M. Aikens, et al., *ibid*, **7**, 508–510 (2013).
3. J. J. Hopfield, *Phys. Rev.*, **112**, 1555–1567 (1958).
4. A. Semenov, et al., *J. Chem. Phys.,* **150**, 174122 (2019).
5. T. Hayashi, et al., *J. Chem. Phys.*, **161**, 181101 (2024).

Future Perspectives and Directions

Challenges to be addressed within the next decade: This research direction will emerge as a new paradigm in photochemistry, driving advances in the efficiency of energy, material, and information conversions. (Author: Kei Murakoshi)