1-4-5. Optical Microcavities

Overview

Optical microcavities are photonic structures that confine light within a subwavelength-scale volume, thereby enhancing the local electromagnetic field and influencing chemical reactivity. Fabry-Pérot cavities, toroidal cavities (whispering-gallery mode, WGM), and photonic crystal can provide high quality factors (Q) and small mode volumes, enabling strong coupling between light and matter. Such strong coupling can reconstruct reaction pathways, control reaction rates and selectivity, and modify electron transfer processes. Recent progress has highlighted the potential of vibrational strong coupling (VSC) and quantum coherence for photochemical control. Moreover, applications are expanding to include cooperative excitation of molecular ensembles, proton conductivity, and conductivity enhancement in polymers.

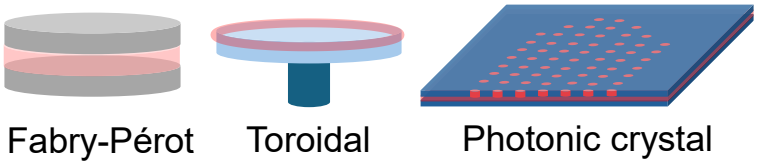

Figure 1. Optical Microcavities.

Current Status and Frontiers

Optical microcavities form resonant modes by confining light in a limited space under resonance conditions. Representative examples include Fabry-Pérot cavities that form standing waves between parallel mirrors, toroidal cavities with circulating modes sustained by total internal reflection, photonic crystals, and plasmonic nanocavities based on metallic nanostructures. Fabry-Pérot cavities have long been used in optical physics and photochemistry, offering high-Q and stable resonant modes. Toroidal and photonic crystal cavities can achieve extremely low scattering losses, with Q factors exceeding 10^8. Plasmonic nanocavities provide ultralow mode volumes, though their Q factors are relatively lower. In this report, we focus primarily on phenomena observed in Fabry-Pérot cavities from the viewpoint of photochemical applications.

Inside a cavity, the local electromagnetic field is enhanced, interacting with molecular electronic and vibrational states. In the strong coupling regime, molecular excitons hybridize with cavity photons to form polaritonic states. This reconstruction of excitonic energy landscapes is expected to alter both ground- and excited-state energy surfaces relevant to photochemical reactions. During the 1970s-1990s, cavity QED studies demonstrated strong coupling of atoms or single excitons with cavity photons, revealing vacuum Rabi splitting and coherent excitation exchange. In photochemistry, extending these concepts to molecular ensembles and reactions has opened pathways toward controlling reaction kinetics and selectivity.

Vibrational strong coupling (VSC), where molecular vibrational modes couple strongly with cavity modes, enables control over chemical reactivity and product

selectivity. The strong coupling of C=O stretching vibrations with Fabry-Pérot cavities was reported in 2015, followed by demonstrations of VSC effects in multiple chemical reactions. For example, VSC applied to molecules with two reactive sites modifies both reaction rates and product ratios, with changes in activation entropy and enthalpy confirming the reshaping of chemical energy landscapes (Ebbesen et al.). In Prins cyclization reactions of aldehydes and ketones, VSC was shown to decrease reaction rates and increase activation energies, while leaving the mechanistic pathway unchanged, suggesting that VSC is becoming an emerging tool in synthetic chemistry (Hirai et al.).

Furthermore, strong coupling between the O-H stretching vibration of water and cavity modes was shown to enhance proton conductivity by an order of magnitude at resonance, indicating that the design of vacuum electromagnetic field environments can modify ground-state physical properties of water (Fukushima and Murakoshi et al.). In amorphous, non-conducting polymers, VSC has also been shown to increase electrical conductivity by several orders of magnitude, suggesting that collective strong coupling facilitates charge and ion transport (Thomas et al.). Remarkably, these effects occur in the absence of external photoexcitation, directly demonstrating the impact of quantum light-matter interactions between cavities and chemical substances.

Hybrid structures combining optical microcavities with plasmonic nanostructures have revealed cooperative molecular excitations arising from quantum coherence. Strong coupling between localized surface plasmons and Fabry-Pérot modes broadens the spatial extent of plasmonic excitation, enabling multiple molecules to be excited in phase. This cooperative behavior improves hydrogen evolution efficiency in photocatalysis and homogenizes the spatial distribution of surface-enhanced Raman scattering (SERS) signals, enhancing reproducibility for sensing applications (Misawa et al.). These findings represent direct evidence that quantum coherence mediated by optical cavities can influence chemical reactivity in a quantifiable manner.

References

1. A. Thomas, E. Devaux, C. Genet, T. W. Ebbesen, et al., *Science*, **363**, 615–619 (2019).
2. K. Hirai, R. Takeda, J. A. Hutchison, H. Uji-i, *Angew. Chem. Int. Ed.*, **59**, 5332–5335 (2020).
3. T. Fukushima, S. Yoshimitsu, K. Murakoshi, *J. Am. Chem. Soc.*, **144**, 12177–12183 (2022).
4. S. Kumar, V. Kaliginedi, A. Thomas, et al., *J. Am. Chem. Soc.*, **146**, 18999–19008 (2024).
5. X. Zang, X. Shi, T. Oshikiri, K. Ueno, Y. Sunaba, K. Sasaki, H. Misawa, *J. Phys. Chem. C*, **125**, 19880–19886 (2021).

Future Perspectives and Directions

Challenges to be addressed within the next decade include: elucidating the mechanisms by which vibrational strong coupling modulates chemical processes; establishing theoretical models that incorporate electromagnetic field distributions and intermolecular interactions within cavities; developing cavity design principles for selective chemical reaction control; and creating highly efficient photochemical energy conversion systems that integrate field enhancement with quantum coherence effects.

(Author: Kosei Ueno)