2-4-2. Plasmon-induced chemical reactions

Overview

Plasmon-induced chemical reactions utilize the enhanced optical near-fields and hot carriers generated by localized surface plasmon resonance (LSPR) in metallic nanoparticles to control chemical processes. In the late 2000s, pioneering works by Misawa, Tsuboi, and collaborators demonstrated multiphoton reactions mediated by plasmonic near-field enhancement, leading to the rapid expansion of this field. More recently, applications have extended to photochromic switching and photocatalytic reactions, positioning plasmoic chemistry as a promising approach for environmental technologies, energy conversion, and the development of functional molecular materials.

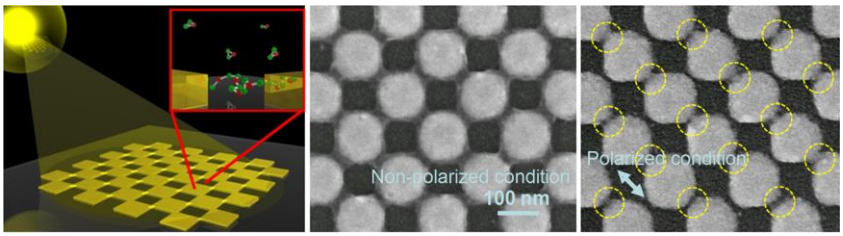

Figure 1. Two-photon-induced photopolymerization driven by an incoherent light source.

Current Status and Frontiers

LSPR originating from metallic nanoparticles has long been associated with chemistry, with early developments in surface-enhanced Raman scattering (SERS) and fluorescence enhancement for chemical sensing. Landmark contributions from Prof. Tawa (Kwansei Gakuin University) in fluorescence biosensing, as well as precise nanoparticle syntheses by Prof. Teranishi (Kyoto University) and Prof. Torimoto (Nagoya University), provided a strong foundation for the field. The 2007–2011 MEXT Grant-in-Aid for Scientific Research on Priority Areas Program "*Strong Photon-Molecule Coupling Fields for Chemical Reactions*" provided the platform on which Prof. Misawa (Hokkaido University) and collaborators introduced the concept of applying plasmonic enhancement to photochemical reactions, a milestone that established plasmonic chemistry as a distinct field of study.

Plasmon resonances can be understood as optical microcavities whose field intensity depends on the plasmon dephasing time and the degree of spatial confinement. In particular, gold nanoparticle dimers with nanogap structures concentrate local fields into single-nanometer volumes, achieving enhancements of up to 10^4 relative to the incident field. This enables extremely high photon flux densities, efficiently inducing photochemical reactions governed by multiphoton absorption. Such spatial confinement of optical near-fields is qualitatively distinct from Fabry-Pérot or photonic crystals,

defining the essential characteristics of plasmonic chemistry.

Research on plasmon-induced chemical reactions began with multiphoton processes driven by local field enhancement. Two-photon polymerization using nanogap structures without the need for pulsed lasers was demonstrated [Ueno and Misawa et al.], and two-photon photochromic switching with continuous-wave near-infrared light was subsequently achieved [Tsuboi et al.]. One-photon photochromic reactions were also found to be enhanced by plasmonic near-fields at gold nanoparticle surfaces [Nishi and Kobatake et al.]. Moreover, quantitative evaluation of two-photon photochromic efficiency in gold nanodimers revealed a clear correlation between local field distributions and reaction yields [Misawa et al.]. These localized near-field effects have further been extended to nanolithography, enabling sub-10-nm resolution patterning [Ueno et al.].

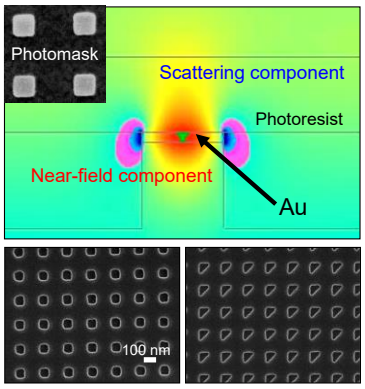

Figure 2. Nanolithography.

Building on these advances in multiphoton-driven processes, subsequent research expanded to photocatalytic reactions. Visible-light-driven organic reduction reactions on plasmonic nanostructures were reported [Tanaka and Kominami et al.], and plasmon-assisted water splitting mediated by strong light-matter coupling was demonstrated [Misawa et al.]. Collectively, these studies underscore the broad applicability of plasmon-induced chemical reactions, ranging from molecular switching to sustainable energy conversion.

References

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Future Perspectives and Directions

Key challenges to be addressed within the next decade include: establishing rational design principles for plasmonic nanostructures to achieve selective reaction control; quantitative evaluation of quantum yields in photochromic and photocatalytic processes; and the development of highly efficient energy conversion systems that synergistically integrate near-field enhancement with hot-carrier effects.

(Author: Kosei Ueno)