2-4. Plasmon Chemistry

Overview

When the localized surface plasmon resonance (LSPR) of metal nanoparticles is excited, a charge imbalance (polarization) arises on the nanoparticle surface and, as a result, a strong localized electromagnetic field (near field) is formed in the vicinity of the surface. The near field is confined within sub-diffraction spaces, and neighboring molecules are influenced by both steep electric-field gradients and high field intensity, to the extent that the long-wavelength approximation can break down. Furthermore, via Landau damping (the principal nonradiative relaxation channel), electron–hole pairs (hot carriers) are generated in the metal. This is understood to occur because the near field contains large wave-vector components that facilitate momentum conservation … These effects make LSPR an emerging reaction field that enables control over the selectivity and efficiency of photochemical reactions.

Current Status and Frontiers

Japanese researchers have played a major role in observing photocurrents that utilize hot carriers generated by LSPR. In 1996, Yoko (Kyoto University) and co-workers reported, for the first time, the generation of photocurrent based on LSPR excitation using TiO_2 electrodes loaded with gold nanoparticles (AuNP/TiO_2).[1] In 2007, Furube (AIST) and co-workers used femtosecond transient absorption spectroscopy to selectively excite the LSPR of AuNP/TiO_2 and verified that electrons are injected from AuNPs into the TiO_2 conduction band.[2] Subsequently, it was reported that hot holes generated with AuNP/TiO_2 electrodes oxidize water to evolve oxygen,[3] and Oshikiri (Hokkaido University) and co-workers reported selective ammonia synthesis via nitrogen fixation, indicating the potential of this approach for artificial photosynthesis. The mechanism of hot-carrier generation accompanying LSPR had long been debated; in 2014, Govorov and co-workers presented a theory in which Landau damping generates hot carriers, which is now widely accepted and continues to be experimentally tested.[4] In recent years, studies on plasmonic catalysis that exploit the near field induced by LSPR, hot-carrier chemistry, and local heating associated with carrier relaxation have progressed vigorously to suppress activation barriers and improve selectivity. These studies have expanded not only to solution reactions but also to gas-phase reactions, including propylene epoxidation and the selective hydrogenation of acetylene to ethylene. On the other hand, a single monolayer of gold nanoparticles on a substrate electrode such as AuNP/TiO_2 (Fig. 1(a)) cannot absorb visible light sufficiently, which has been a bottleneck for improving energy-conversion efficiency. A breakthrough has been achieved by fabricating functional TiO_2 nanoelectrodes with a cavity mode resonant at nearly the same wavelength as the LSPR of AuNPs and mounting AuNPs on them so that the LSPR

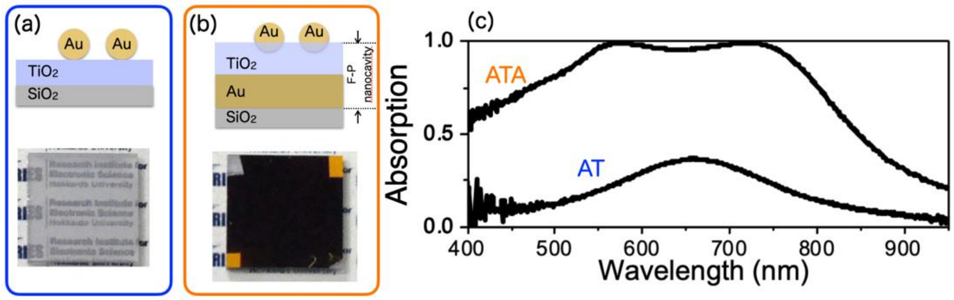

Figure 1. (a) Conventional LSPR electrode (AT); (b) strong-coupling electrode (ATA); (c) absorption spectra of AT and ATA.

mode and the cavity mode form modal strong coupling (Fig. 1(b)). Under strong coupling, the absorption spectrum exhibits two split peaks with large oscillator strength, enabling efficient absorption over a broad visible range (Fig. 1(c)) and improving the quantum yield of water photolysis compared with conventional plasmonic electrodes.[5] Recent studies further show that, in such strongly coupled electrodes, multiple AuNP LSPRs oscillate in-phase with quantum coherence through the nanocavity; the optical energy captured over the coherent area is distributed among AuNPs in the area but funnels into the nanoparticle with the fastest dephasing, thereby injecting hot electrons into TiO_2 with high efficiency.[6] Research is also advancing on what nanoparticle shapes within the coherent area optimize the quantum efficiency of electron injection, which is expected to contribute to the development of plasmonic catalysis.

References

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Future Perspectives and Directions

Challenges and goals desired to be addressed/achieved within the next ten years: While Landau damping is considered the principal mechanism for hot-carrier generation from LSPR, its full picture remains to be clarified. Progress in its elucidation, the realization of hot carriers with higher energies, and achieving higher selectivity and efficiency in plasmonic catalytic reactions are desired.

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