2-4-1. Plasmon-Induced Charge Separation

Overview

Plasmon-induced charge separation (PICS) refers to charge separation based on the electron transfer from metal nanoparticles (NPs) in a localized surface plasmon resonance (LSPR) state to the conduction band of a semiconductor (Fig. 1), or on the hole transfer to the valence band. It was first reported in the mid-2000s (Tatsuma *et al.*).[1] PICS enables the direct conversion of plasmons into an electron flow. It has been applied to photocatalysis under visible light and photovoltaics under visible–near-infrared light, and a variety of other applications are being explored.

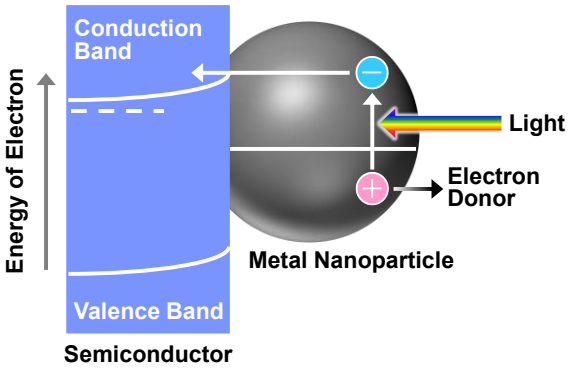

Figure 1. Plasmon-induced charge separation (PICS).

Current Status and Frontiers

So-called plasmon enhancement, which was reported before 2000, is based on the excitation of semiconductors or other substances by the optical near field generated around plasmonic NPs. In such cases, the absorption band of the semiconductor must overlap with that of the LSPR, and there exists an optimal distance between them. In contrast, in PICS, spectral overlap is not required, and it is preferable for the metal NP and semiconductor to form a Schottky junction. The mechanism is often explained by the external photoelectric effect, in which hot carriers (electrons[1] or holes[2]) generated during the relaxation process of plasmons migrate across the interface. However, in some systems, PICS is instead described by interfacial electron transfer transitions, in which electrons in the NP are directly excited into the semiconductor.

Since its discovery, the combination of Au NPs with TiO_2 has consistently been the most widely employed in PICS.[1] Nevertheless, if sufficient conductivity is ensured, compound nanomaterials can also be used in place of metallic NPs. A variety of semiconductors have been applied, including silicon,[3] while graphene, conductive compounds, and even insulators with surface defects have also been utilized.

Experimentally, the most straightforward and common approach is to coat an electrode with TiO_2, load Au NPs on the surface, and irradiate the electrode with light. Photocurrents can then be electrochemically observed, for instance as a result of ethanol

oxidation at the photoanode and O_2 reduction at the counter electrode.[1] PICS is typically identified by examining correlations between the shape of the photocurrent action spectrum and the absorption spectrum.

When employed as a photocatalyst (Fig. 2a), PICS enables visible-light-driven reactions such as water splitting[4] and CO_2 reduction. In terms of photoelectric conversion (Fig. 2b), not only visible light but also near-infrared light[3] can be utilized. In addition, applications have been explored in multicolor photochromism and photoresponsive gels.

If hot carriers can be harnessed for redox reactions before undergoing deactivation or delocalization, site-selective reactions become feasible, enabling nanofabrication based on dissolution and deposition processes. Attempts have also been made to fabricate chiral nanostructures using circularly polarized light[5] and to realize metamaterials.

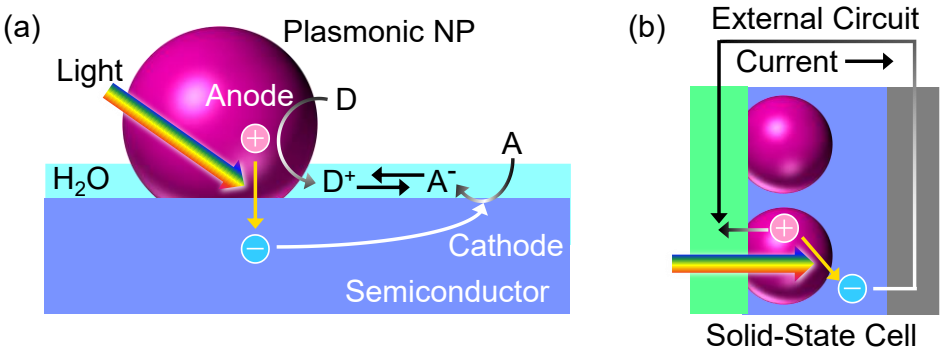

Figure 2. (a) Photocatalyst and (b) solid-state photovoltaic cell based on PICS

References

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Future Perspectives and Directions

Challenges and goals for the next decade: extending photocatalytic reactions to longer wavelengths; enhancing the practical applicability of various potential applications.

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