

Localized surface plasmon (LSP) resonance of metal nanostructures have various applications such as for biosensors, chemical sensors, near-field optical spectroscopies such as surface-enhanced Raman, fluorescence enhancement, photovoltaics, photocatalysts, and treatment of cancers. Fundamental understanding of the interaction between materials and the LSP is essential for their application. Furthermore, real-space experimental investigation is invaluable for understanding the basis of the interaction between the LSP and materials, because the LSP is confined to a nm-scale region near the metal surface. However, this kind of experiment has never been achieved. In this study, we have clarified the interaction between the LSP and molecules at the single-molecule level by real-space and real-time observations of a plasmon-induced chemical reaction for the first time.

Plasmon-induced chemical reactions of molecules adsorbed on metal nanostructures are attracting increased attention as novel photocatalytic reactions. Many previous papers explained that the reactions occur through the indirect hot-electron transfer mechanism. In the indirect mechanism, hot-electron transfer leads to a transient negative ion state of the adsorbed molecule and a vibrational mode is excited, resulting in dissociation of the chemical bond in molecules such as O<sub>2</sub> and H<sub>2</sub>. The proposed mechanism has been discussed on the basis of ensemble observations of the local reactions and is, therefore, still controversial.

In this study, we propose a novel reaction mechanism on the basis of real-time and real-space observation of single-molecule chemical reaction induced by a LSP for the first time. This is achieved by optically exciting the LSP in the gap between a plasmonic Ag tip and a metal substrate with a scanning tunneling microscope (STM). The target molecule is dimethyl disulfide, (CH<sub>3</sub>S)<sub>2</sub>. Visible-light-induced photodissociation of this molecule adsorbed on metal substrates occurs through direct photoexcitation of the frontier electronic states ( $n_s \rightarrow \sigma_{ss}^*$ ), as reported in our previous study [*J. Am. Chem. Soc.* 139, 3115 (2017)]. Dissociation of the S-S bond in (CH<sub>3</sub>S)<sub>2</sub> is induced by the LSP excited by light irradiation. Quantitative analysis of the dissociation reaction with STM combined with theoretical calculations reveals that the LSP induces efficient excitation of the molecule. Moreover, the elementary reaction pathway is clarified by the combination of real-time and real-space observations at the single-molecule level. The mechanistic knowledge obtained in this study provides deep insights into the interaction between LSPs and molecules at metal surfaces for designing efficient photocatalysis based on LSPs in a highly-controlled fashion.