Single-molecule spectroscopy using localized-surface plasmon

Yousoo Kim

Department of Applied Chemistry, The University of Tokyo Surface and Interface Science Laboratory, RIKEN

Irradiation of light to the metallic nanostructure causes collective vibration of free electrons (plasmon), followed by the creation of an electromagnetic field, i.e., localized surface plasmon (LSP). The LSP has a characteristic interaction with matter, especially a single molecule. The scanning tunneling microscope (STM) is a versatile and powerful tool for investigating and controlling the chemistry of individual molecules on solid surfaces. We have developed an optical STM technology that combines the STM with light irradiation and detection technologies for our own purpose [1], which allows us to apply the LSP to exploring novel chemical reactions and spectroscopy based on the interaction between the LSP and electronic/vibrational quantum states of a single molecule at the STM junction. We have developed single-molecule emission and absorption (Fig. 1(a)) spectroscopy [1] using the interaction between the LSP and a molecule, in which the LSP participates in the exciton formation in a target molecule [2,3]. Combining the emission and absorption spectroscopies, we visualized fluorescence resonance energy transfer between two different molecules [4]. We have also explored the detailed mechanism of single-molecule chemical dynamics induced by the LSP (Fig. 1(b)) [5]. We also applied the LSP to measure tip-enhanced resonance Raman spectra of a single molecule (Fig. 1(c)) [6]. Furthermore, we achieved an ultrahigh-energy resolution photoluminescence measurement of a single molecule using a tunable excitation laser (Fig. 1(d)) [7]. These optical setups enable a real-space measurement of photocurrent pathways at a single molecule (Fig. 1(e)) [8].

In this talk, I will discuss recent issues focusing on single-molecule spectroscopy based on the molecular excitation by localized surface plasmon at the STM junction, which has been applied to exploring the quantum states of a phthalocyanine and its derivatives.



Fig. 1 Single-molecule chemistry and spectroscopy using localized surface plasmon at the STM tip junction

REFERENCES

- [1] H. Imada et al., Physical Review Letters, 119 (2017) 013901
- [2] K. Miwa et al., Nano Letters, 19 (2019) 2803
- [3] K. Kimura et al., Nature, 570 (2019) 210
- [4] H. Imada et al., Nature, 538 (2016) 364
- [5] E. Kazuma et al., Science, 360 (2018) 521
- [6] R.B. Jaculbia et al., Nature Nanotechnology, 15 (2020) 105
- [7] H. Imada et al., Science, 373 (2021) 95
- [8] M. Imai-Imada et al., Nature 603 (2022) 829