1C5b Extraordinary Field Enhancement at TiO_2 Nanogap: Plasmon-free Enhancement up to 2000-fold and Its High Reproductivity

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Recently, semiconductor attracts much attention as another material to produce high field enhancement, which is given by high scattering efficiency due to both high electric- and magnetic-field enhancements[1]. As a wide gap semiconductor, titanium dioxide (TiO_2) has been known as a very important material for photocatalysts, the photoelectrode for hydrogen evolution reaction, and the porous layer of perovskite solar cells. Their properties as well as device performances such as photoconversion efficiencies are significantly enhanced if integration of TiO_2 providing a large field enhancement of light is made possible. In the previous study, we found extraordinary field enhancement of a porous TiO_2 layer[2]. Its enhancement factor (EF) of up to 500 was achieved, which corresponds to the largest EF for a semiconductor. This extraordinary EF was ascribed to the nanogap between TiO_2 particles. However, the detail mechanism of the nanogap effect has not been clarified. In addition, it was difficult to establish high reproductivity of the extraordinary EF. Here, we show further extraordinary EF (ca. 2000) and high reproductivity of EF using a TiO_2 porous plate. Extraordinary EFs of TiO_2 nanogaps with various particle size and morphology are evaluated using the finite-difference time-domain (FDTD) calculations.

The field enhancement was investigated with respect to the fluorescence intensity of a dye molecule of the crystal violet (CV). The fluorescence spectrum of CV was measured with a confocal microscope spectrometer at an excitation wavelength of 632.8 nm using a He–Ne laser. The EF was calculated as a ratio of the fluorescence intensities with and without TiO_2. The electric field distribution on the surface of the TiO_2 layer was calculated using the FDTD method.

Fig.1 shows the fluorescence spectra of a CV solution with (black solid and dotted lines) and without (gray line) the TiO_2. The fluorescence intensity is significantly increased in the presence of the TiO_2. The maximum EF is up to 2000. In addition, it was found that the EF depends on the size of TiO_2 particles, composing of the TiO_2 plate. Results of FDTD calculations revealed the size and morphology effects on the extraordinary EF. Furthermore, we demonstrated very high reproducibility of extraordinary EF, as shown in Fig. 1 (black solid lines). Namely, the TiO_2 plate with a flat surface shows a high EF and high reproductivity. To consider the property of TiO_2 and to design their size and morphology, both of which provide a large field enhancement of light, must be important to realize higher performances of photocatalyst, hydrogen evolution reaction, and perovskite solar cell.

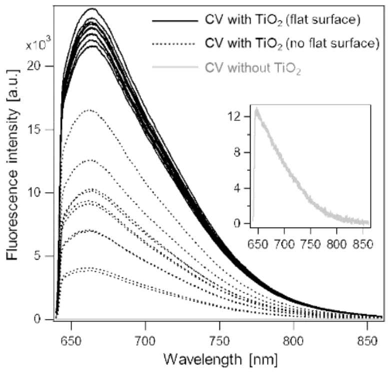

Fig.1. Fluorescence spectra of CV solution with (black solid and dotted lines) and without (gray solid line) TiO_2. The inset shows fluorescence spectra of CV solution without TiO_2.

References:1) A. I. Kuznetsov, A. E. Miroshnichenko, M. L. Brongersma, Y. S. Kivshar, B. Luk'yanchuk, *Science*, 354, 2472 (2016).

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