Supporting Information

Super-Resolution Mapping of Reactive Sites on Titania-Based Nanoparticles with Water-Soluble Fluorogenic Probes

Takashi Tachikawa, Tomoyuki Yonezawa, and Tetsuro Majima**

The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

tachi45@sanken.osaka-u.ac.jp (T.T.); majima@sanken.osaka-u.ac.jp (T.M.)

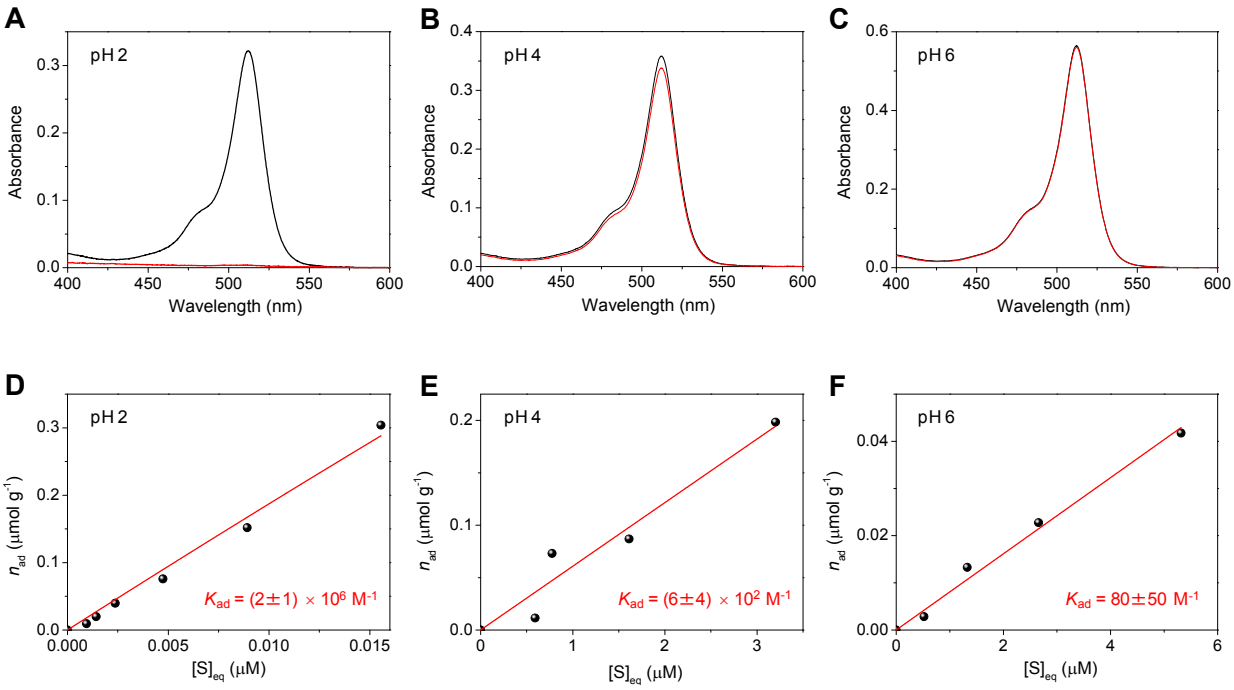

Figure S1. (A-C) UV-visible absorption spectra of DS-DN-BODIPY in aqueous methanol (black lines) and in aqueous methanol after reaching adsorption equilibrium with the surface of TiO_2 nanoparticles (Ishihara Sangyo, ST-01; pure anatase, 7 nm particle size) (red lines), respectively. The pH values of added water (10 vol%) are 2 (A), 4 (B), and 6 (C). (D-F)

Langmuir adsorption plots. According to the Langmuir adsorption model, n_{ad} can be expressed by the following equation,

$$n_{ad} = \frac{K_{ad}[S]_{eq}}{1 + K_{ad}[S]_{eq}} \times n_S \qquad \text{(S1)}$$

where n_S is the total number of adsorption sites and K_{ad} is the equilibrium constant of adsorption. See ref. S1 for experimental procedures. The red lines are the best fits obtained by the calculations based on eq S1.

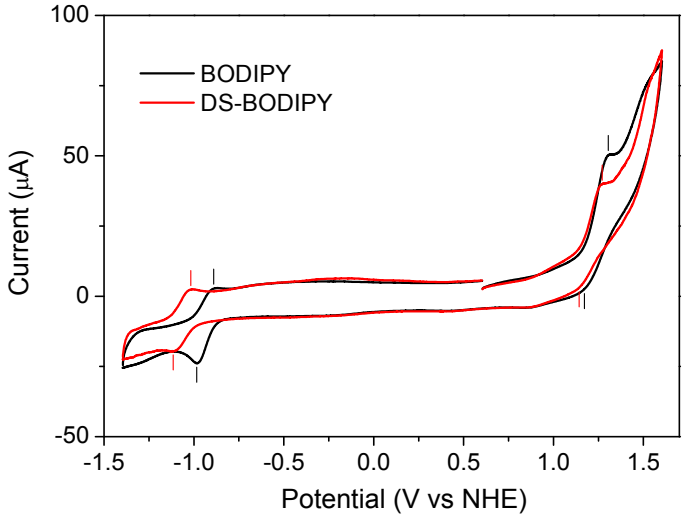

Figure S2. Cyclic voltammograms of electrolyte solutions (0.1 M TBATFB in DMF) containing 4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) (Invitrogen, D3921) (0.5 mM) and 4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene-2,6-disulfonic acid (DS-BODIPY) (Invitrogen, D-3238) (0.5 mM). Cyclic voltammetry experiments were carried out at room temperature using an electrochemical analyzer (ALS, model 660A) with a standard three-electrode configuration, which was composed of a Pt working electrode, a Pt wire counter electrode, and an Ag/Ag^+ non-aqueous reference electrode. Sample solutions were prepared by dissolving the substrates in *N*,*N*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as the electrolyte. All potentials were calibrated using ferrocene (Fc) (1.0 mM) as an internal standard (+0.677 V vs NHE for the Fc^+/Fc couple).[S2]

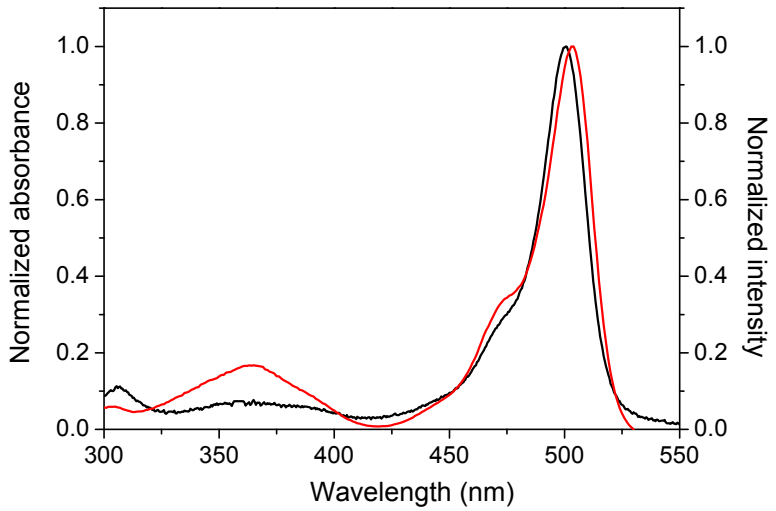

Figure S3. Excitation spectrum (red) of methanol solutions of DS-DN-BODIPY after UV irradiation of TiO_2 (emission collected at 540 nm) and UV–visible absorption spectrum (black) of the purified fluorescent product.

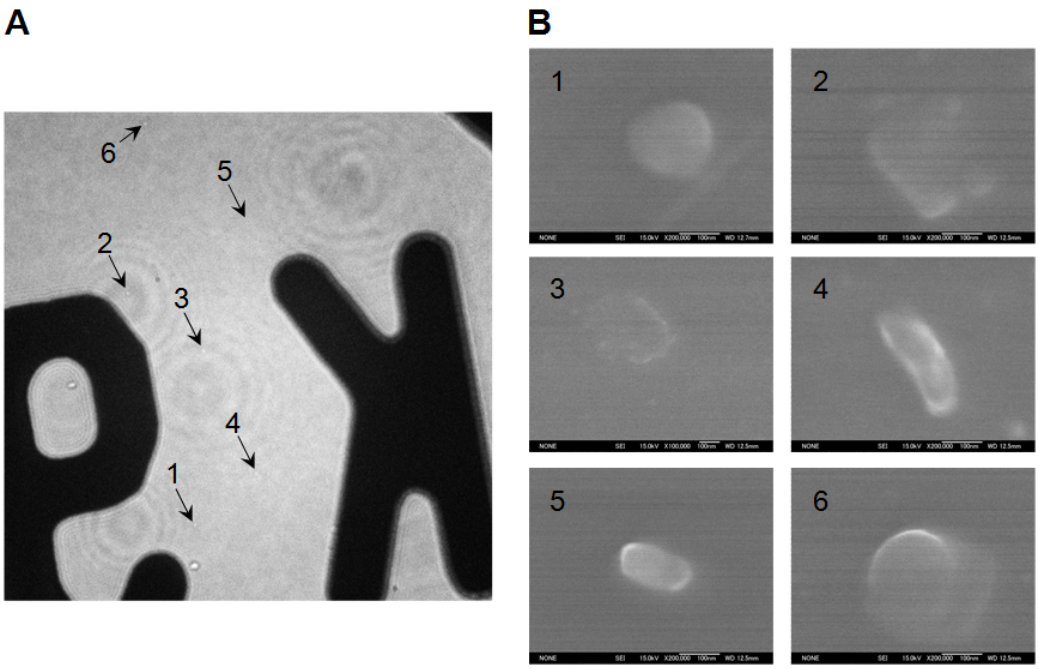

Figure S4. Comparison of optical transmission (A) and SEM (B) images of A-100 TiO_2 nanoparticles immobilized on the cover glass.

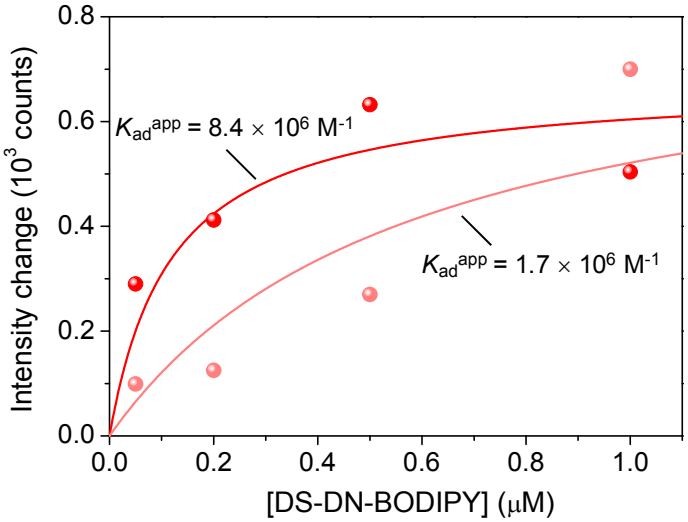

Figure S5. DS-DN-BODIPY concentration dependence of fluorescence intensity obtained for different Au/TiO_2 particles. The solid lines were obtained from eq 1 in the main text.

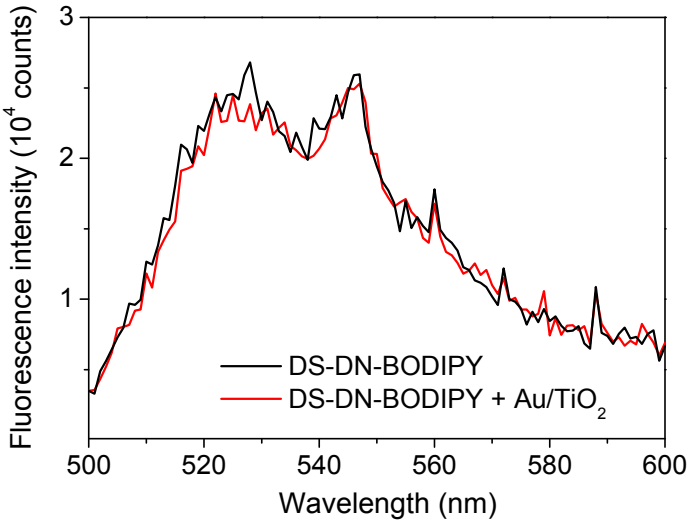

Figure S6. Fluorescence spectra of the DS-DN-BODIPY (1 μM) aqueous methanol solutions in the absence (black) and presence (red) of 8-nm Au/TiO_2. The emission peaks at around 545 nm are due to the light scattering from the samples.

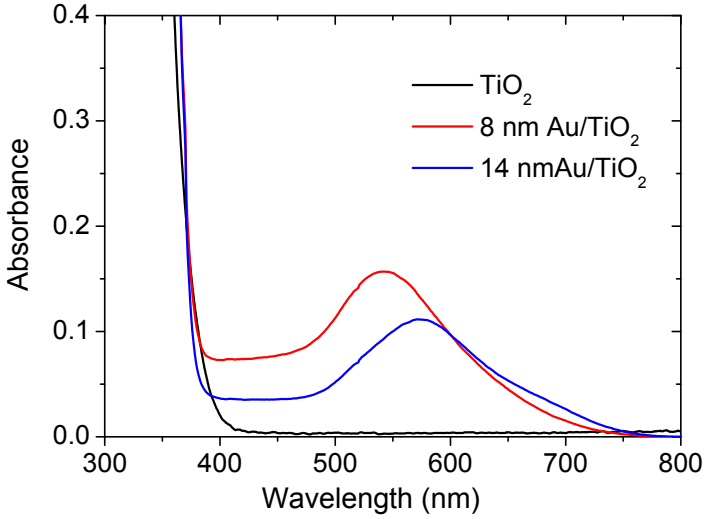

Figure S7. Diffuse reflectance spectra of TiO_2 (Ishihara Sangyo, A-100) and Au/TiO_2 measured with UV–visible–NIR spectrophotometer (Jasco V-570). The data are adapted from ref S3.

References.

S1. Tachikawa, T.; Tojo, S.; Fujitsuka, M.; Sekino, T.; Majima, T. Photoinduced Charge Separation in Titania Nanotubes. *J. Phys. Chem. B* **2006**, *110*, 14055–14059.

S2. Bao, D.; Millare, B.; Xia, W.; Steyer, B. G.; Gerasimenko, A. A.; Ferreira, A.; Contreras A.; Vullev, V. I. Electrochemical Oxidation of Ferrocene: A Strong Dependence on the Concentration of the Supporting Electrolyte for Nonpolar Solvents. *J. Phys. Chem. A* **2009**, *113*, 1259–1267.

S3. Wang, N.; Tachikawa, T.; Majima, T. Single-Molecule, Single-Particle Observation of Size-Dependent Photocatalytic Activity in Au/TiO_2 Nanocomposites. *Chem. Sci.* **2011**, *2*, 891–900.