

Supplementary information

Electrofluorescence Switching of Tetrazine-modified TiO₂

Seogjae Seo,^{a†} Clémence Allain,^{b†} Jongbeom Na,^a Sehwan Kim,^a Xu Yang,^a Chihyun Park,^a Jérémy Malinge,^b Pierre Audebert^b and Eunkyong Kim^{*a}

† These authors contributed equally to this work.

Experimental Details

Photoluminescence of triethoxysilane-appended chloroalkoxy tetrazine (ESTZ) modified TiO₂

With excitation light ($\lambda_{\text{exc}} = 330$ nm), the photoluminescence of ESTZ modified anatase TiO₂ was provided in Figure S1. Because 330 nm incident light induced a wide photoluminescence band of anatase TiO₂ at ~380 nm and ~480 nm, a second absorption band was selected to excite ESTZ exclusively.

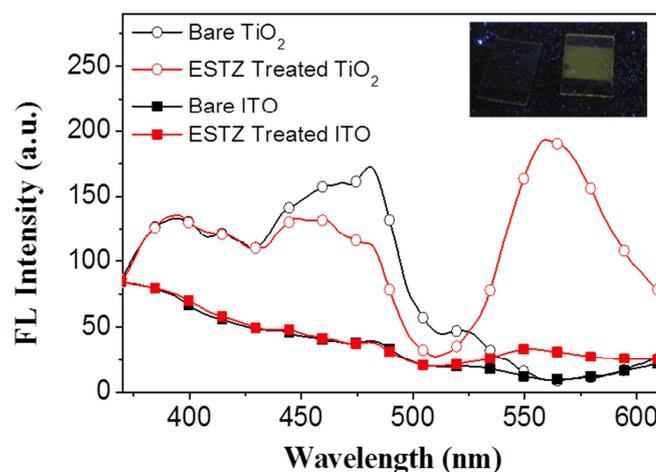


Figure S1. Fluorescence spectra of an ESTZ-treated TiO₂ electrode and an ESTZ-treated ITO electrode ($\lambda_{\text{exc}} = 330$ nm). The inset shows images of the bare TiO₂ electrode and the ESTZ-treated TiO₂ electrode under UV.

When ESTZ was anchored on the TiO₂ surface, an increase in fluorescence emission intensity was observed during the first 30 min of the anchoring reaction, after which the fluorescence emission intensity decreased slightly. This was likely because the high loading concentration of ESTZ on the TiO₂ nanostructure induced bimolecular processes that reduced the fluorescence quantum yield without changing the fluorescence emission spectrum (Figure S2).

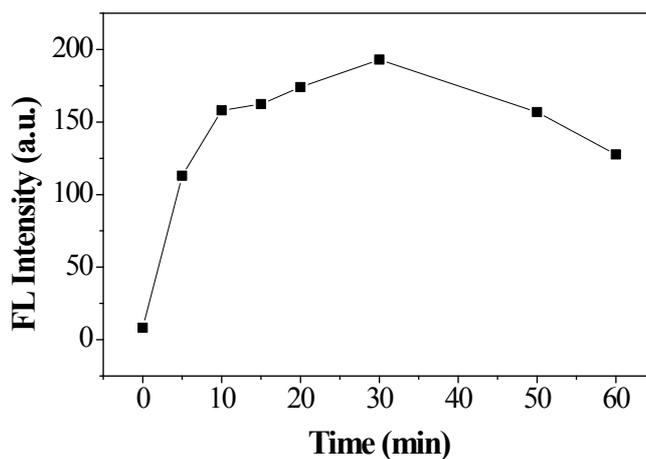


Figure S2. Fluorescence intensity evolution during the ESTZ reaction with the TiO₂-nanoparticle-layer electrode as monitored by tetrazine emission ($\lambda_{\text{emi}} = 566 \text{ nm}$)

Cyclic Voltammograms (CVs) of ESTZ-treated TiO₂

The CVs of ESTZ-treated TiO₂ revealed a large reduction peak and oxidation peak at -0.68V and -0.46V, respectively, which were consistent with the tetrazine unit potential ($E_{\text{red}}^0 = -0.50\text{V}$); however, these peaks disappeared after a few cycle. (Figure S3)

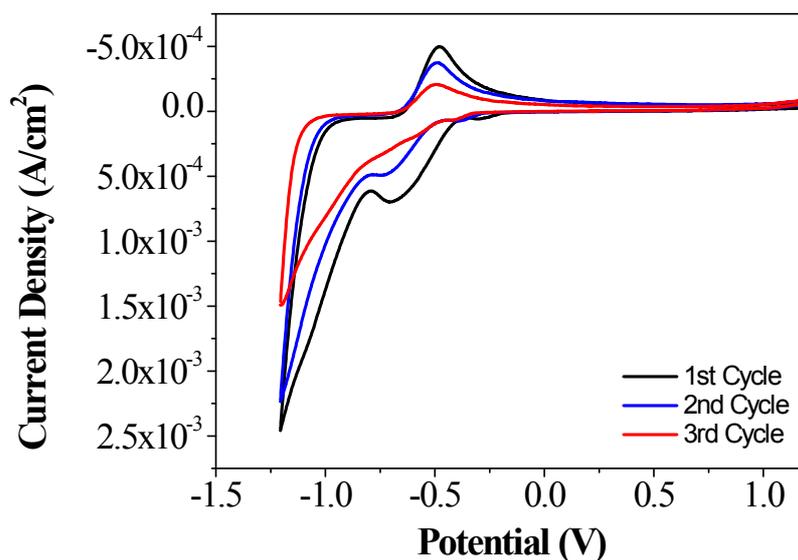


Figure S3. Cyclic voltammogram of an ESTZ-treated TiO₂-nanoparticle-layered ITO electrode recorded at a scan rate of 100 mV/s in a three-electrode cell with an Ag/AgCl reference, a TBAPF₆ 0.1 M acetonitrile solution as the electrolyte. The CV was performed in a glove box under a nitrogen atmosphere.

Figure S4 shows that the capacitive properties of TiO₂ nanoparticles decreased with an increasing amount of redox mediator.

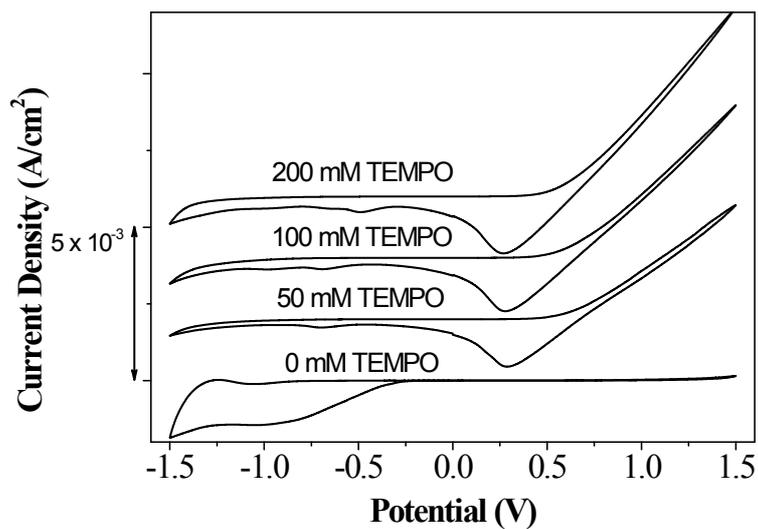


Figure S4. Cyclic voltammogram of a TiO₂ nanoparticle layer on ITO glass recorded at a scan rate of 100 mV/s in a three-electrode cell with an Ag/AgCl reference, TBAPF₆ 0.1 M acetonitrile solution as the electrolyte, and various concentrations of TEMPO.