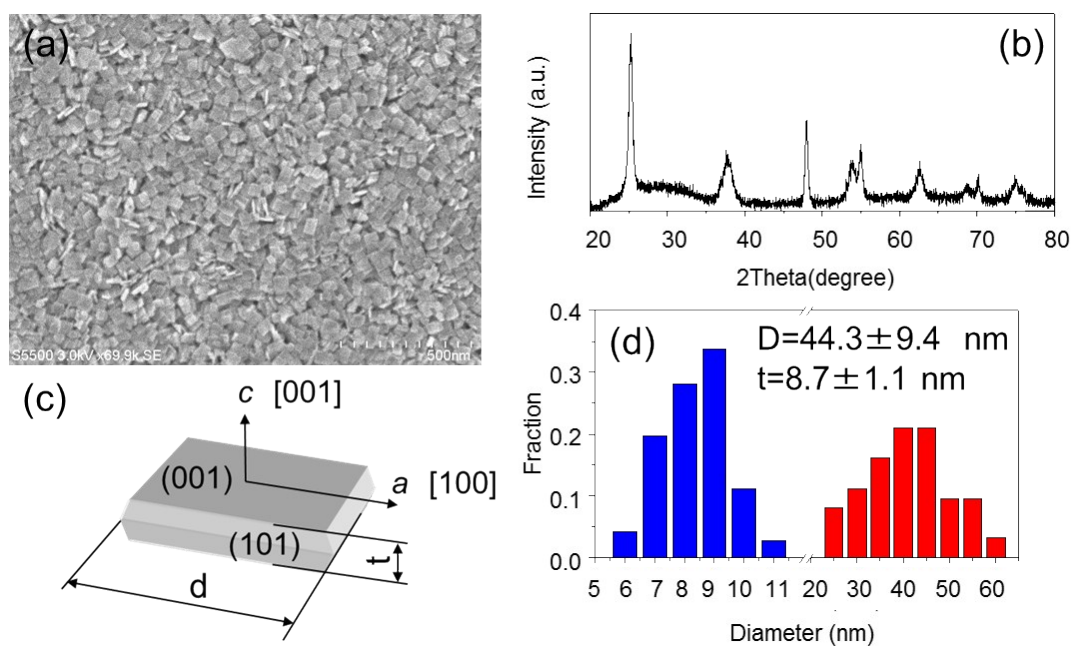


## Supporting Information

### **Self-Oriented TiO<sub>2</sub> Nanosheets in Films for Enhancement of Electron Transport in Nanoporous Semiconductor Network**

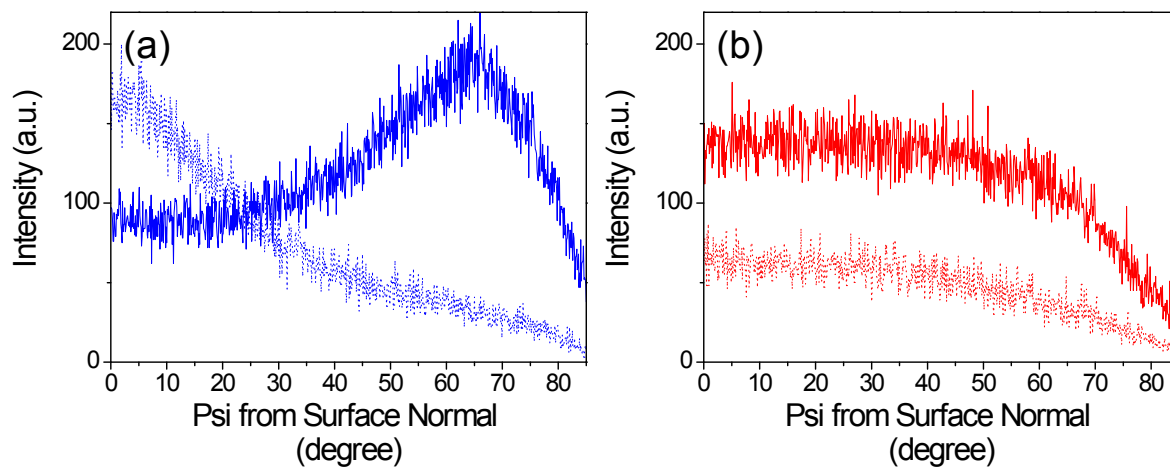
*Masato M. Maitani\**, *Chen Xu*, *Keitarou Hashimoto*, *Yurika Ueda*, *Eiichi Suzuki*, *Yuji Wada\**



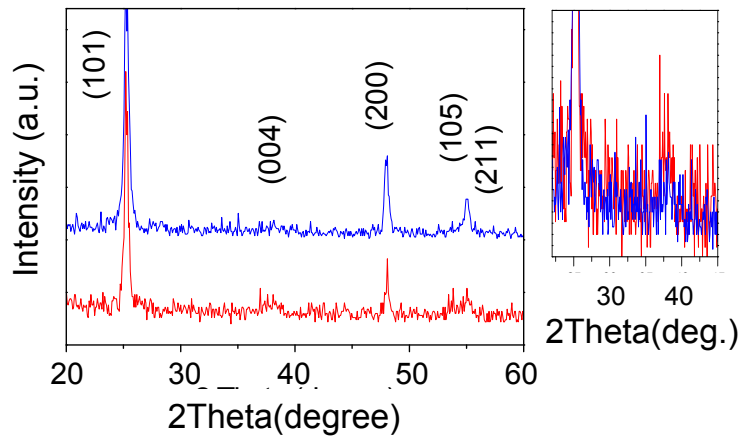
**Figure S1** (a) SEM images, (b) powder XRD, (c) schematic anatase nanosheet crystal, and (d) size distributions of as synthesized TiO<sub>2</sub> nanosheets.

pH	Tyr	Phe	Cys	Arg	Glu	Gly	His	Lys
1								
3.5								
4								
5								
7								

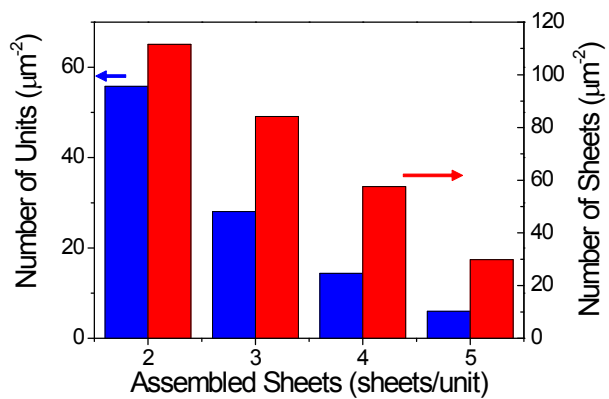
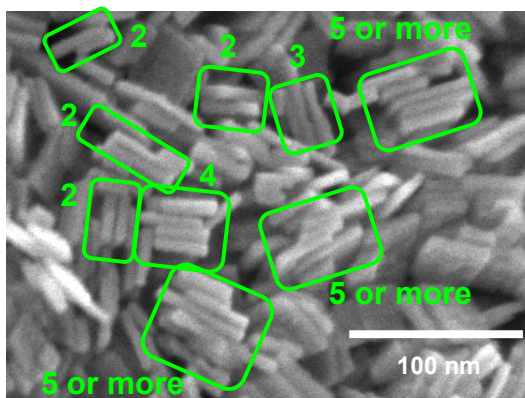
**Figure S2** Comprehensive results of SEM images in all assembly conditions.



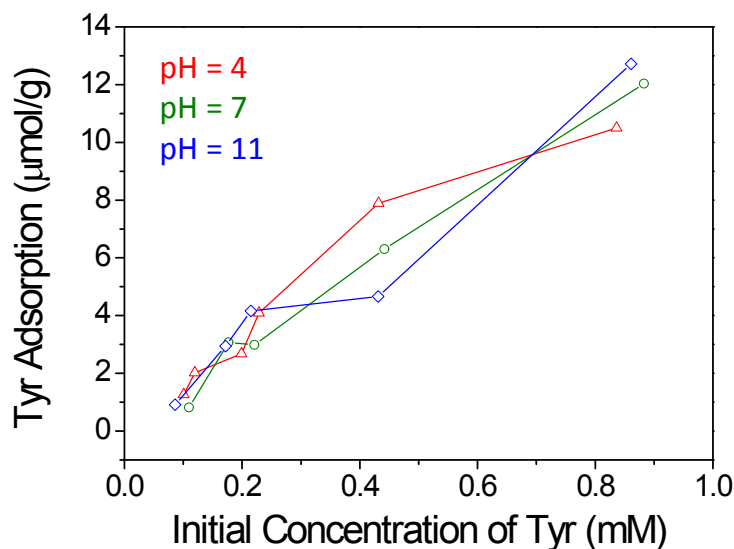
**Figure S3-1** Angle resolved XRD out-plane analysis in psi scans of (a) non-functionalized and (b) Tyr-functionalized  $\text{TiO}_2$  nanosheets on glass substrate with 2 theta of 25 degree (bold line) and 38 degree (dot line) attributed to anatase  $\text{TiO}_2$  (101) and (004) planes, respectively.



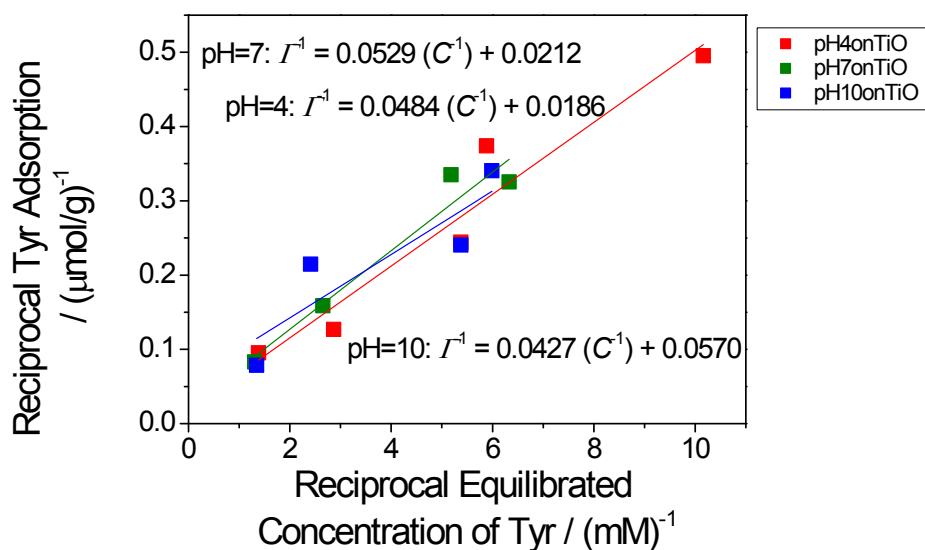
**Figure S3-2** X-ray diffraction in-plane analysis with non-functionalized (blue) and Tyr-functionalized (red)  $\text{TiO}_2$  indicating the (004) peak. The grazing angle of incident x-ray was 5 degree.



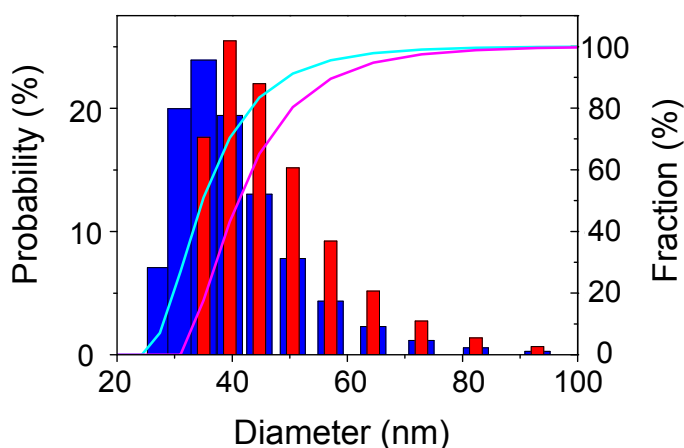
**Figure S4** Distribution analysis of nonparallel orientation with stacked nanosheets.



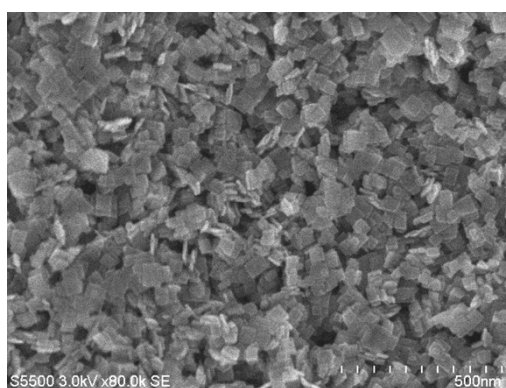
**FigureS5-1** Adsorption amount of Tyr on TiO<sub>2</sub> as a function of the concentration of Tyr in aqueous solution estimated by means of the comparison of the absorbance change of Tyr solution ( $\epsilon=1272 \text{ cm}^{-1} \text{ M}^{-1}$  at 274 nm) measured by UV-vis absorption spectroscopy before and after addition of TiO<sub>2</sub> (10g/L)



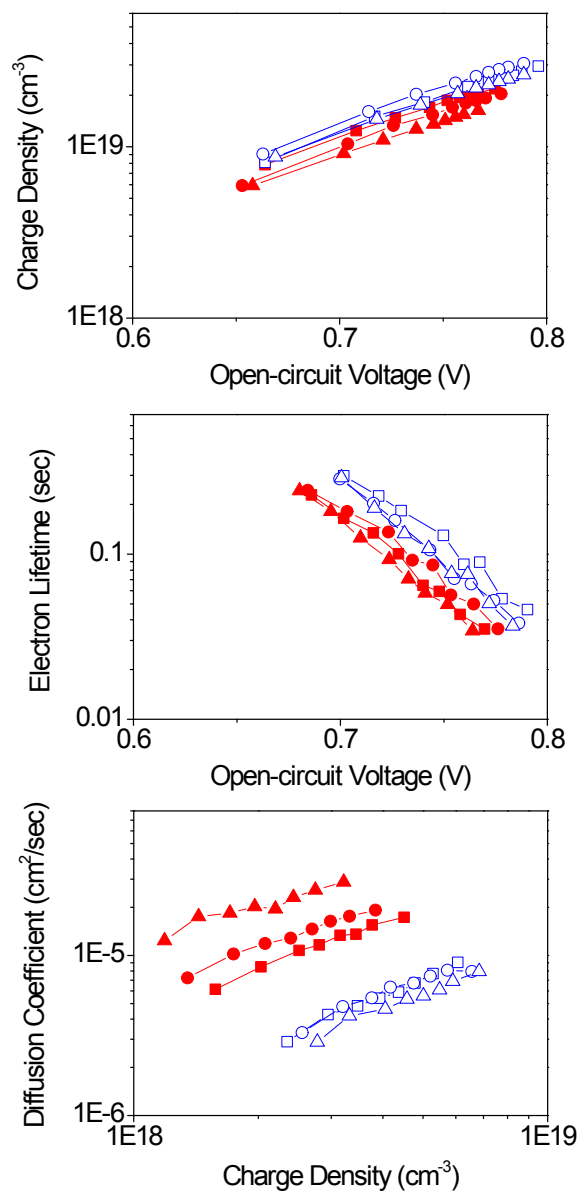
**FigureS5-2** Adsorption amount of Tyr on TiO<sub>2</sub> analysis based on Lineweaver-Burk equation,  $\frac{1}{\Gamma} = \frac{1}{\Gamma_{max}} + \frac{1}{\Gamma_{max} Kc}$ .



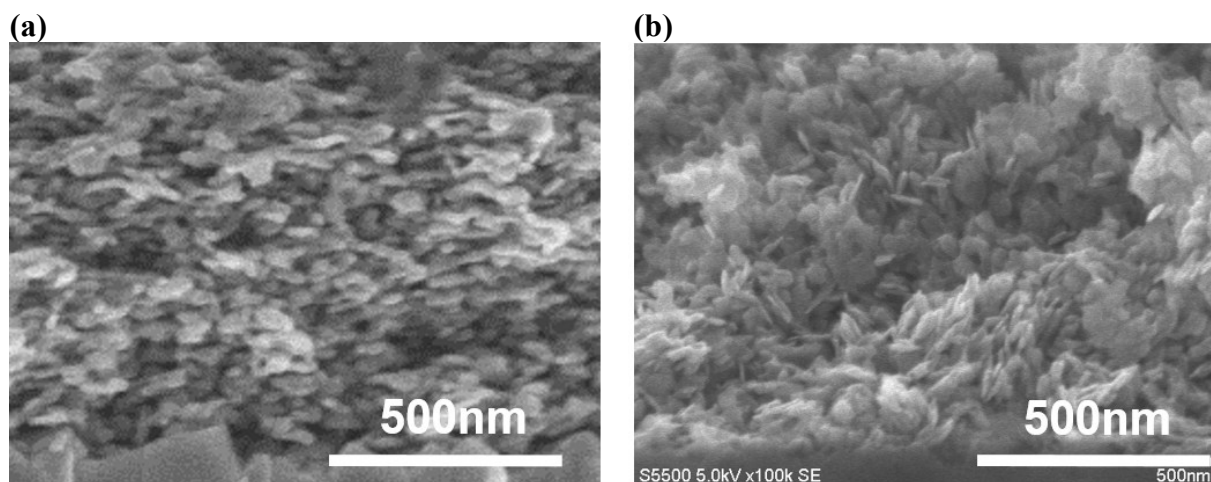
**Figure S6** Size distribution of  $\text{TiO}_2$  particles suspended in aqueous solution with (red) and without (blue) Tyr in HCl solution (0.01M) at pH4 controlled by an aqueous ammonium hydroxide (0.1M) addition measured by dynamic light scattering method.



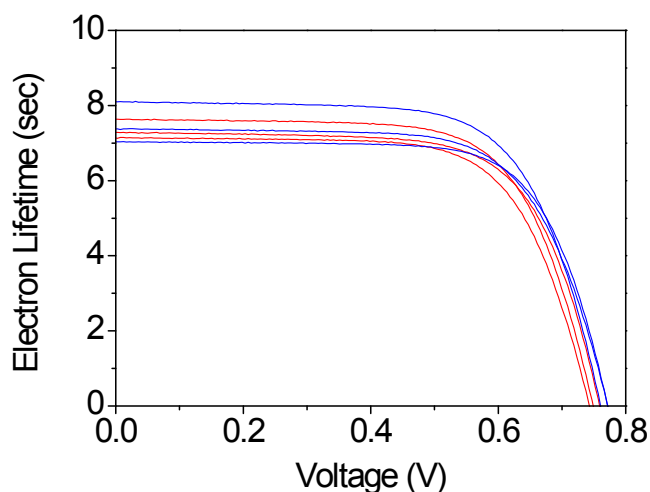
**Figure S7** The  $\text{TiO}_2$  film on glass prepared with Tyr-functionalized  $\text{TiO}_2$  at pH 4 (1mL of  $\text{TiO}_2$  suspension (3wt%) and 0.1mL of Tyr (0.5 equivalent molar))with addition of acetone (0.1mL) reducing the oreophobic property of water solvent as the control experiment revealing very little assembly indicating that the hydrophobic inter-particle interaction is one of key factor of self-assembly.



**Figure S8** The charge density as the function of open-circuit voltage (top), lifetime of electron as the function of open-circuit voltage (middle), and diffusion coefficient of electron as the function of charge density (bottom) in  $\text{TiO}_2$  in DSSC analyzed by means of charge extraction, transient short-circuit photocurrent, and transient open-circuit voltage, respectively, by modulating the incident.  $\text{TiO}_2$  porous films are composed of Tyr-functionalized (red), non-functionalized (blue)  $\text{TiO}_2$  nanosheets on FTO substrates. Multiple curves indicate the device-to-device deviations, while the representative results are exhibited in Figure 6.



**Figure S9** The cross-sectional SEM image of (a) non-functionalized and (b) Tyr-functionalized TiO<sub>2</sub> nanosheets in porous films possessing the thickness of more than a micrometer used for DSSC devices.



**Figure S10** The current-voltage curve of DSSC with TiO<sub>2</sub> porous films composed of Tyr-functionalized (red), non-functionalized (blue) TiO<sub>2</sub> nanosheets on FTO substrates. Multiple curves indicate the device-to-device deviations.

**Table S1** The cell performances of DSSC with TiO<sub>2</sub> porous films composed of Tyr-functionalized (Tyr-func.), non-functionalized (Non-func.) TiO<sub>2</sub> nanosheets on FTO substrates.

TiO <sub>2</sub>	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (mV)	FF	Efficiency (%)	<sup>a</sup> Dye Loading (μmol/cm <sup>3</sup> )	<sup>b</sup> Porosity (%)	<sup>c</sup> BET Surface Area (cm <sup>2</sup> /μm <sup>2</sup> ·cm <sup>2</sup> )
Tyr-func.	7.21±0.35	751±4.0	0.68±0.0	3.71±0.20	99.1	0.51	115
Non-func.	7.21±0.24	772±0.0	0.69±0.02	3.86±0.02	83.9	0.63	108

<sup>a</sup>Measured by UV-vis absorption spectra of solution containing tetrabutylammonium hydroxyde (0.1M) removing the dye-sensitizer from immersed TiO<sub>2</sub> films. <sup>b</sup>Calculated by weighing of TiO<sub>2</sub> films with measured volume with specific weight of pure anatase TiO<sub>2</sub> of 3.9g/cm<sup>3</sup>. <sup>c</sup>Brunauer–Emmett–Teller analysis with N<sub>2</sub> adsorption isotherm with scraped TiO<sub>2</sub> films from substrates.