Supporting Information (SI)

Effect of the LHCII Pigment-Protein Complex

Aggregation on Photovoltaic Properties of

Sensitized TiO₂ Solar Cells

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Figure S1. I-V curves of the solar cells sensitized at different concentrations of LHCII aggregates through physisorption on the anodes with a bare TiO₂ thin layer (100~300 nm) without APTES modification. Increasing the concentration of the LHCII aggregate solution by ~ 8 folds (shown with increased optical density) did not have much effect on the photocurrent of the solar cell, indicating that the physisorption of LHCII on bare TiO₂ was quite weak.



Figure S2. UV-Vis absorption of the chlorophylls pigment extracted from LHCII aggregates in the solution before (solid line) and after (dashed line) being injected into the solar cell for protein attachment. Pigment extraction and chlorophyll content calculation follows the method described in the experimental section of main text. Before injecting into the solar cell, the concentration of LHCII solution was 0.296 µg Chl/mL, which was reduced to 0.016 µg Chl/mL after incubating in the cell over 12 hrs. The lost LHCII was assumed to be adsorbed in the solar cell. The attachment efficiency (η_{attach}) can be calculated to be about 95% by

 $\eta_{attach} = 1 - C_{after} / C_{before})_{.}$



Figure S3. (A) I-V curve of a solar cell based on a bare sintered TiO_2 nanoparticle film (~10 μ m in thickness). (B) I-V curves of the solar cells built on bare APTES-FTO without the TiO_2 barrier layer, before and after sensitized with the small LHCII aggregates.



Figure S4. (A) I-V curves and (B) photocurrent response plots of bare and small LHCII aggregate sensitized TiO_2 solar cells with an ionic liquid electrolyte (Mosalyte ADE-250, Solaronix).



Figure S5. Raw data of photocurrent response curves of an APTES-TiO₂ solar cell before and after being sensitized with small-size LHCII aggregates under one-Sun illumination.

Normalization for all photocurrent response curves in Figure 7 in the main body of the manuscript is based on the equation below:

$$J_N = \frac{J_{LSSC} - J_{TiO_2}}{(J_{on_TiO_2})_{avg.}}$$

 J_N — Normalized current density of LSSC

 J_{LSSC} — Raw current density of LHCII-sensitized solar cell (LSSC) (red line in Fig. SI4)

 J_{TiO_2} — Raw current density of bare APTES-TiO₂ solar cell (black line in Fig. SI4)

 $(U_{on_TiO_2})_{avg.}$ Average of photocurrent density obtained from bare APTES-TiO₂ solar cell under illumination (blue dash circle regions shown in Fig. SI4).

Stability of Chlorophyll Sensitized Solar Cell



Figure S6. (A) The time dependence of the I-V curves of a Chls sensitized TiO_2 solar cell after cell assembling (molar ratio of Chl a : Chl b = 8:6). (B) The changes of *J*sc and *V*oc obtained from the I-V curves in (A). The value of *J*sc dropped particularly fast. (C) Photocurrent responses of Chl *a* sensitized solar cell under the illumination with the interference bandpass filter at a wavelength of 675±25 nm (covering the Qy region), measured during 5 days (120 hrs) after cell assembly.