Supporting Information

TiO_2−P3HT:PCBM Photoelectrochemical Tandem Cell for Solar-Driven Overall Water Splitting

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S1. Characterization of photoelectrodes

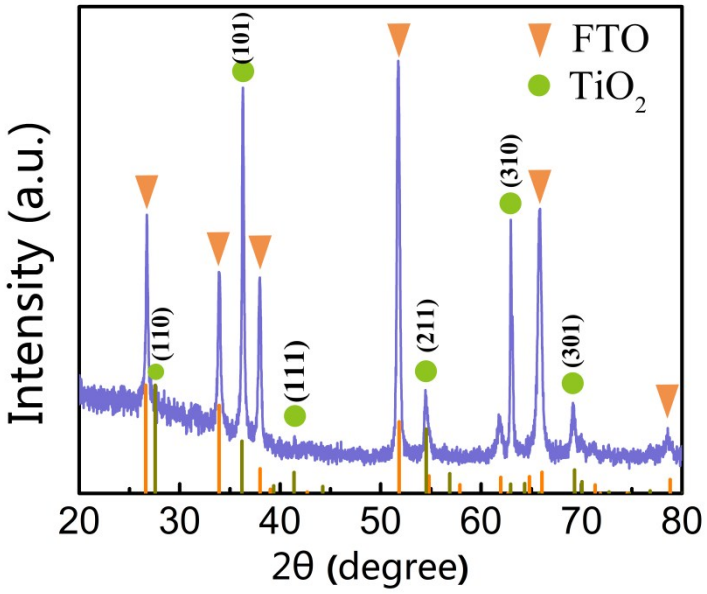

Fig. S1. X-ray diffraction pattern of TiO_2 NRs array.

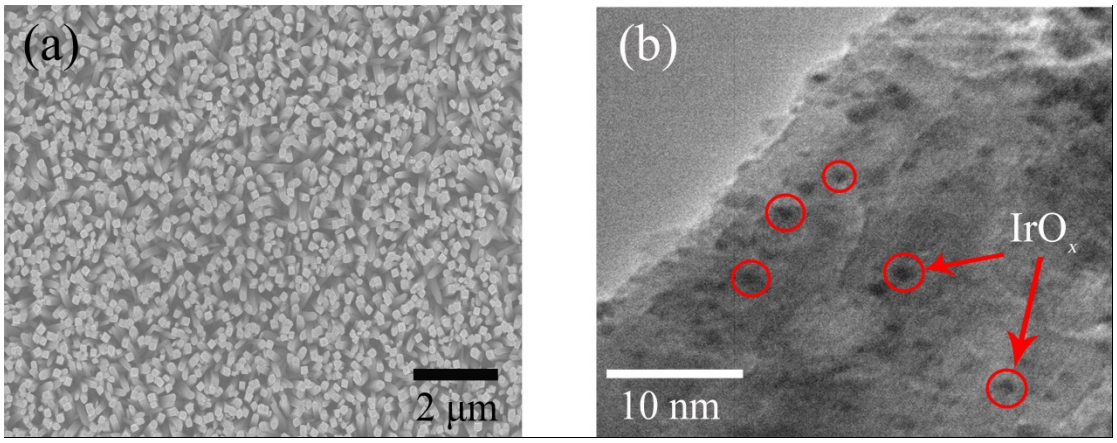

Fig. S2. (a) SEM image of pristine TiO_2 NRs array. (b) TEM image of TiO_2-IrO_x nanorod.

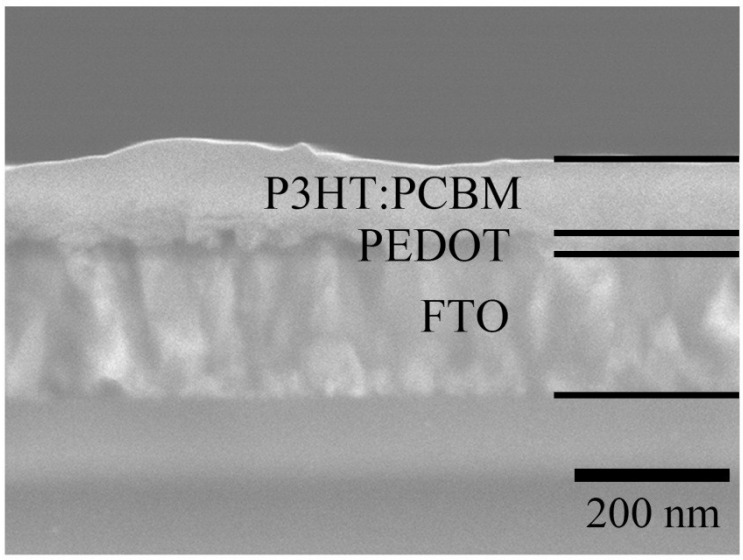

Fig. S3. Cross-sectional SEM image of P3HT:PCBM-Pt photocathode.

S2. Improvement of the PEC performance

J - *V* curves of PEDOT:PSS/P3HT:PCBM/TiO_2-Pt and CuI/P3HT:PCBM/TiO_2-Pt photocathodes were tested and shown in Fig. S4. The photocurrent density of PEDOT:PSS/P3HT:PCBM/TiO_2-Pt is -0.65 mA cm^{-2} at 0 V vs. RHE, and that of CuI/P3HT:PCBM/TiO_2-Pt is -5.0 mA cm^{-2} at 0 V vs. RHE which is a high value even approaching some metal oxide materials. However, as shown in Fig. S4a and Fig. S4b, the onset potential of both two photocathodes has not been improved, and the photocurrent densities in the potential range of +0.38 V ~ +1.0 V vs. RHE are still lower than that of the PEDOT:PSS/P3HT:PCBM-Pt photocathode.

As shown in Fig. S5a, the predicted maximum operating current density (J_{op}) is about 110 μA cm^{-2} for both the TiO_2-IrO_x–CuI/P3HT:PCBM/TiO_2-Pt and TiO_2-IrO_x–PEDOT:PSS/P3HT:PCBM/TiO_2-Pt PEC cells according to the intersections of the *J* - *V* curves of photoelectrodes.

The transient photocurrent response curves of the tandem PEC cells were measured in the two electrodes configuration. As shown in Fig. S5b, J is about 165 μA cm^{-2} for TiO_2-IrO_x–PEDOT:PSS/P3HT:PCBM-Pt cell, 88 μA cm^{-2} for TiO_2-IrO_x–PEDOT:PSS/P3HT:PCBM/TiO_2-Pt cell and 73 μA cm^{-2} for TiO_2-IrO_x–CuI/P3HT:PCBM//TiO_2-Pt, respectively. Despite the photocurrent densities of organic photocathodes have been improved a lot at 0 V vs. RHE by introducing CuI and TiO_2 into the photocathodes, the PEC performances of the tandem PEC cells are still not high. The reason is that the photocurrent densities of the tandem cells are depended on the intersections of the J - V curves of the photoelectrodes rather than the photocurrent densities of the photocathodes at 0 V vs. RHE. Therefore, not only the photocurrent, but also the onset potential of both two photoelectrodes are significant for the high efficient overall water splitting.

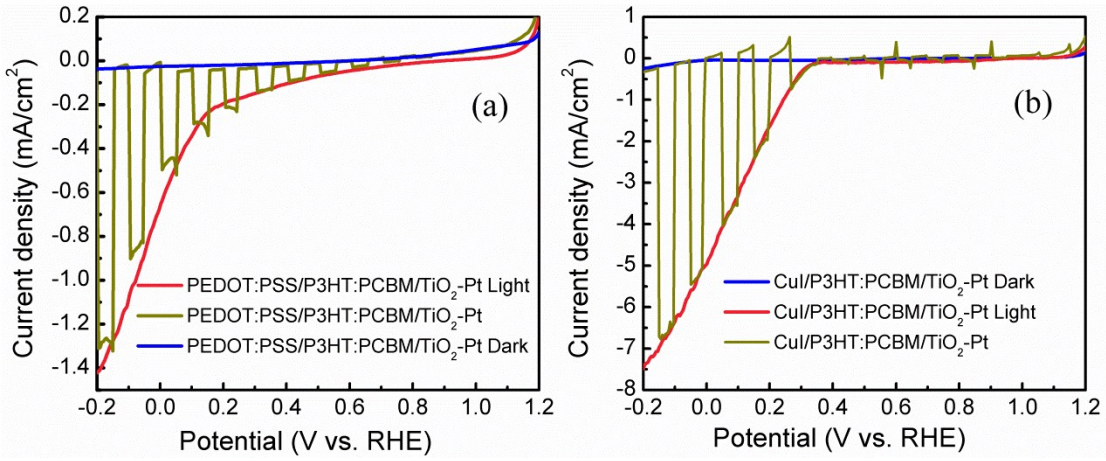

Fig. S4. (a) J - V curves of the PEDOT:PSS/P3HT:PCBM/TiO_2-Pt photocathode, (b) J - V curves of the CuI/P3HT:PCBM/TiO_2-Pt photocathode.

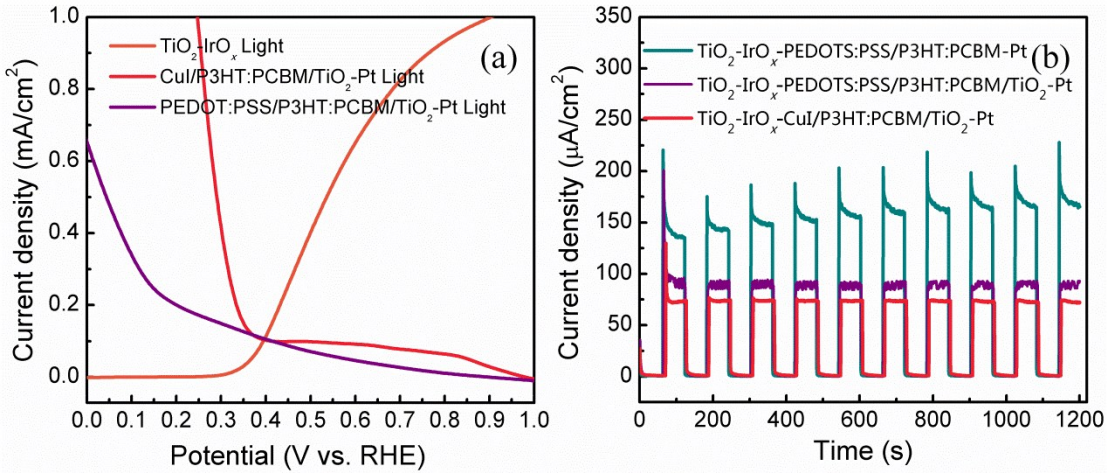

Fig. S5. *J* - *V* curves of TiO_2-IrO_x NRs photoanode, PEDOT:PSS/P3HT:PCBM/TiO_2-Pt photocathode, and CuI/P3HT:PCBM/TiO_2-Pt photocathode, respectively. (b) *J* - *t* curves of the externally short-circuited TiO_2-IrO_x–PEDOT:PSS/P3HT:PCBM-Pt, TiO_2-IrO_x–CuI/P3HT:PCBM/TiO_2-Pt and TiO_2-IrO_x–PEDOT:PSS/P3HT:PCBM/TiO_2-Pt PEC cell in electrolyte without sacrificial reagents and any other external energy supply except sunlight.

S3. Calculation of the faradic efficiency and solar-to-fuel conversion efficiency

To calculate the faradic efficiency (η_{faradic}) of the water splitting in the configuration of short-circuited electrodes, the following equation was applied:

$$\eta_{\text{faradic}} = \frac{2 \times n_{H_2}(\text{mol}) \times 96485(\text{C/mol})}{Q(\text{C})} \times 100\%, \qquad \text{(S1)}$$

in which Q is the total amount of charge passed through the external circuit during a certain time period as measuring the evolved H_2 gas.

The solar-to-fuel conversion efficiency of the water splitting (η) was calculated using the following equation:

$$\eta = \frac{1.23(\mathrm{V}) \times I(\mathrm{mA/cm^2})}{P(\mathrm{mW/cm^2})} \times 100\%, \qquad \text{(S2)}$$

in which I is the photocurrent density and P is the light intensity.