Electronic Supplementary Material (ESI) for Energy & Environmental Science.
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Supporting Information

Selectively Exposed Crystal Facet-Engineered TiO_2 Thin Film Photoanode for the Higher Performance of Photoelectrochemical Water Splitting Reaction

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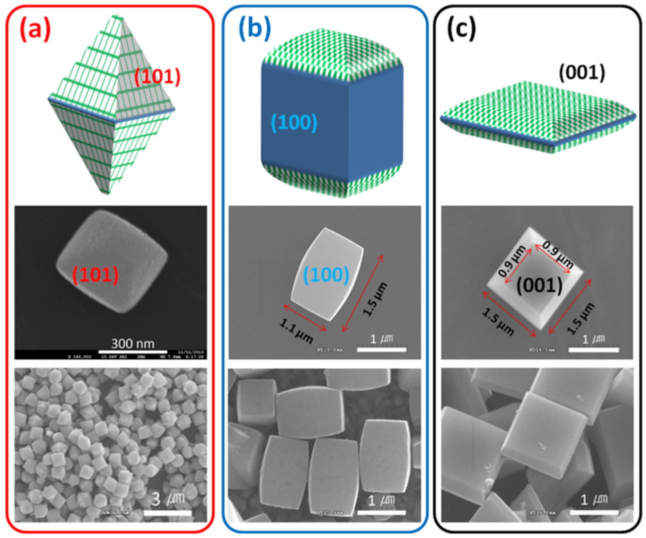

Figure S1. Scheme and typical SEM images of bi-pyramidal TO_{101} (a), cuboid TO_{100} (b) and plate TO_{001} (c) microcrystals.

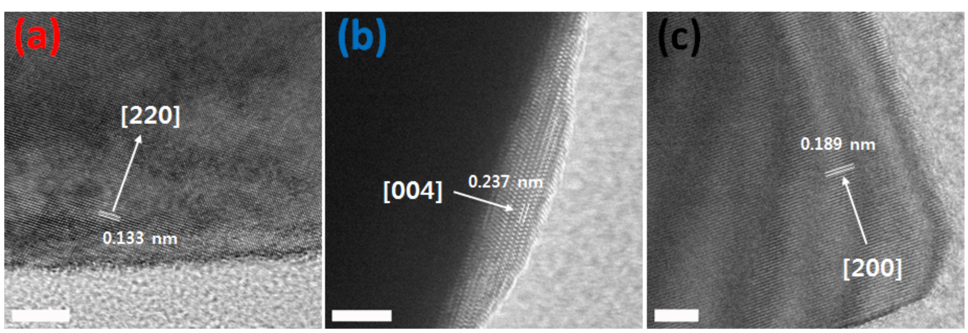

Figure S2. Typical HRTEM images of bi-pyramidal TO_{101} (a), cuboid TO_{100} (b) and plate TO_{001} (c) microcrystals. (Scale bar; 5 nm)

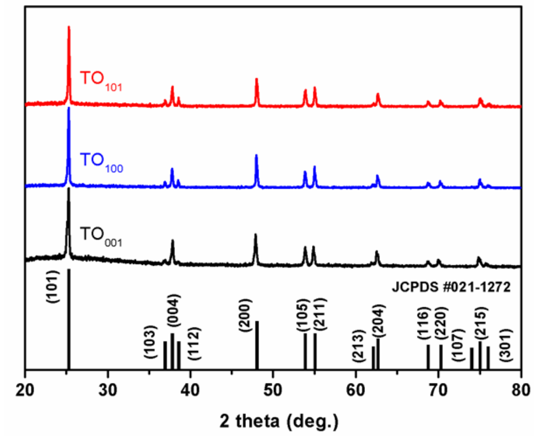

Figure S3. Typical XRD results of bi-pyramidal TO_{101} (red), cuboid TO_{100} (blue) and plate TO_{001} (black) microcrystals. AnataseTiO_2 PDF 021-1272 are used.

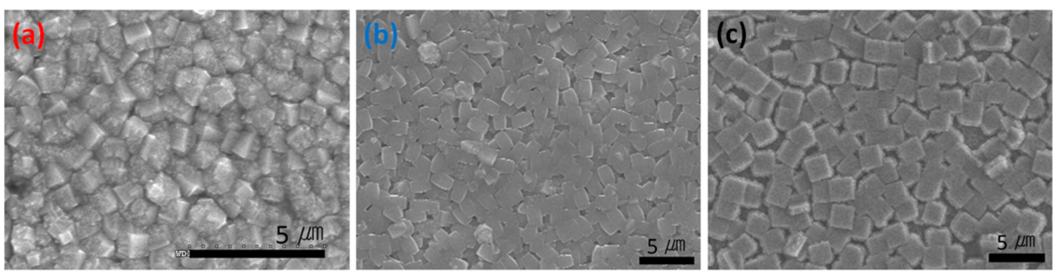

Figure S4. Typical top-viewed SEM images of sTO_{101} (a), sTO_{100} (b) and sTO_{001} (c).

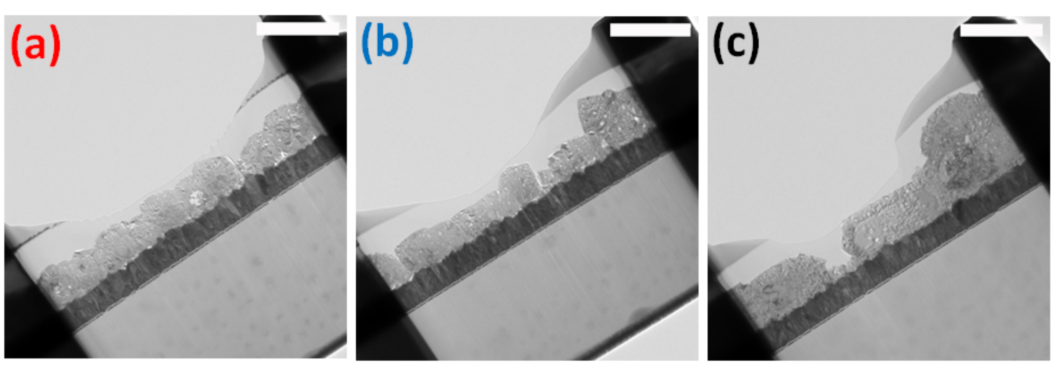

Figure S5. Typical TEM images with FIB of sTO_{101} (a), sTO_{100} (b) and sTO_{001} (c). (Scale bar; 1 μm)

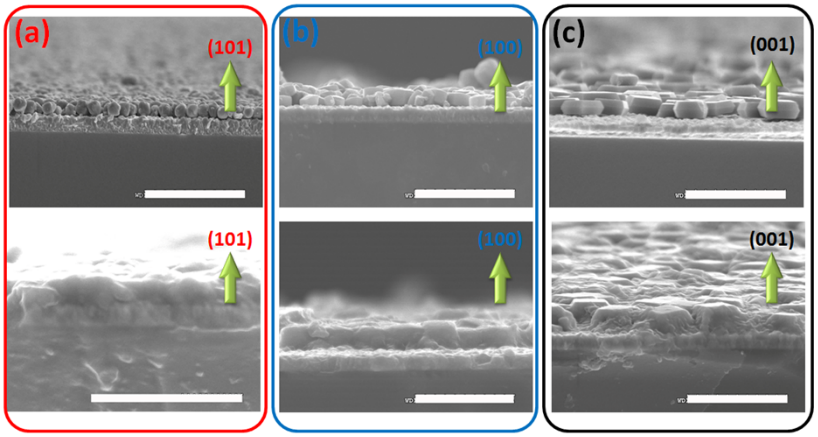

Figure S6. Typical cross-sectional SEM images (All scale bar; 5 µm) of mTO (upward) and sTO (down). (101)-faceted (a), (100)-faceted (b) and (001)-faceted (c) thin film.

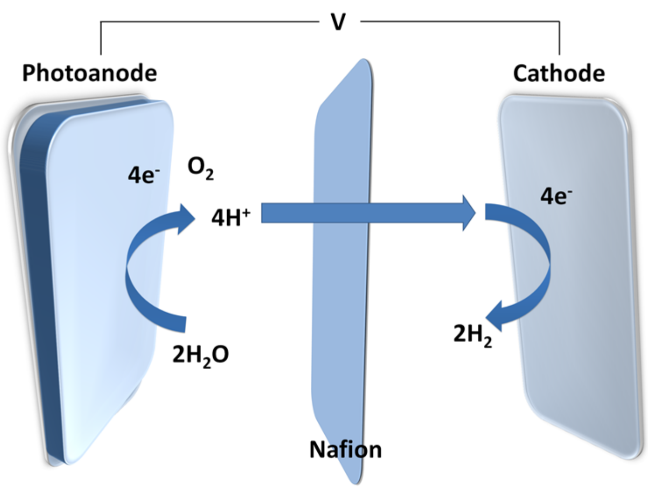

Figure S7. The schematic illustration of H_2 gas evolution by water splitting.

Using a Pt electrode and Ag/AgCl (2.0 M of KCl) reference electrode in an aqueous Na_2SO_4 solution (0.5 M, pH = 6.8) at room temperature, all of the PEC measurements were performed, and then, the applied bias was converted to the reversible hydrogen electrode (RHE) using the following Nernst equation;[1,2]

$$E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + E^{\mathrm{o}}_{\mathrm{Ag/AgCl}\ vs.\ \mathrm{NHE}} + 0.0591\ \mathrm{V\ x\ pH}$$

$$(E^{\mathrm{o}}_{\mathrm{Ag/AgCl}\ vs.\ \mathrm{NHE}} = 0.65\ \mathrm{V\ vs.\ NHE\ at\ 25\ ^{o}C})$$

where E_{RHE} is the potential *vs.* RHE, 0.0 V *vs.* RHE for water oxidation, E_{RHE} is the experimental potential measured *vs.* the Ag/AgCl reference electrode, and $E^{o}_{Ag/AgCl}$ *vs.* NHE is the standard potential of the Ag/AgCl *vs.* NHE (0.65 V at 25 °C).

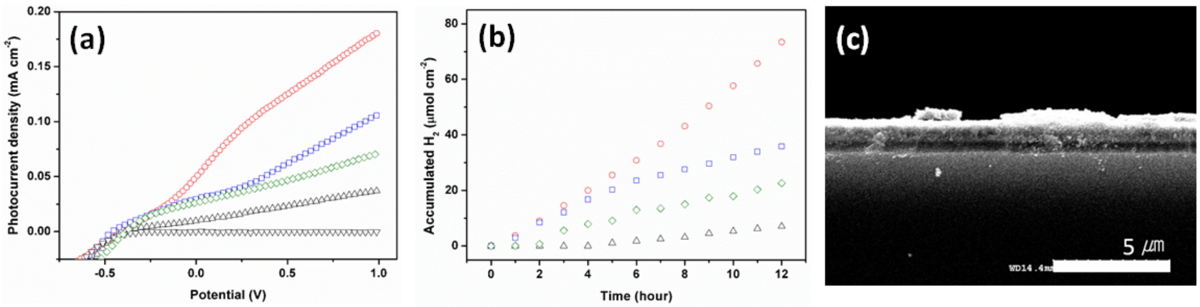

Figure S8. Comparison of I-V curve (a) and H_2 gas evolution (b) of sTO_{101} (red), sTO_{100} (blue), sTO_{001} (black) and typical TiO_2 electrode (green) under AM 1.5 G. Cross sectional SEM image of typical TiO_2 electrode (c).

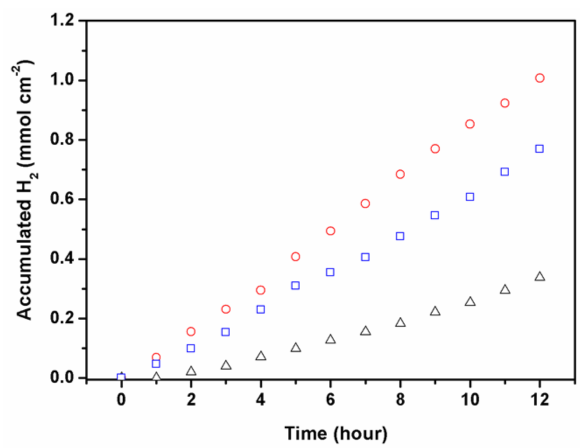

Figure S9. H_2 gas evolution rate of sTO_{101} (red), sTO_{100} (blue) and sTO_{001} (black) under UV irradiation.

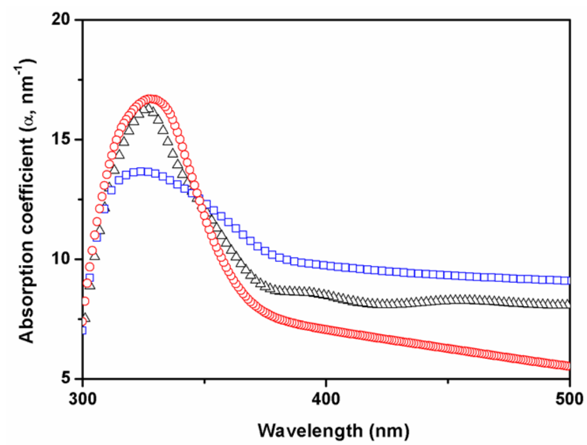

Figure S10. UV-vis optical absorption diffuse reflectance curves of sTO_{101} (red), sTO_{100} (blue) and sTO_{001} (black).

Absorption coefficient (α) with photon energy can be explained by using the following formula:[3]

$$\alpha(E) = \frac{-1}{d}\ln\left(T_{normalized}(E)\right) \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where α(E) is the absorption coefficient, d is the thickness of the film and T(E) is the optical transmittance of the film. After the measurement from optical transmittance of each film, the processed diffuse reflectance spectra of the secondary grown sTO films was calculated.

References

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2 T. W. Kim, K-S. Choi, Nanoporous $BiVO_4$ Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting, Science, 2014, 343, 990-994.

3 P. Sharma, I. Sharma, S. C. Katyal, Physical and Optical Properties of Binary Amorphous Selenium-Antimony Thin Films. J. Appl. Phys. 2009, 105, 053509.