

## Electronic Supporting Information

### TiO<sub>2</sub> photoanodes with exposed {0 1 0} facets grown by aerosol-assisted chemical vapor deposition of a titanium oxo/alkoxy cluster

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All data created during this research are openly available from the University of Bath data archive at <https://doi.org/10.15125/BATH-00644>

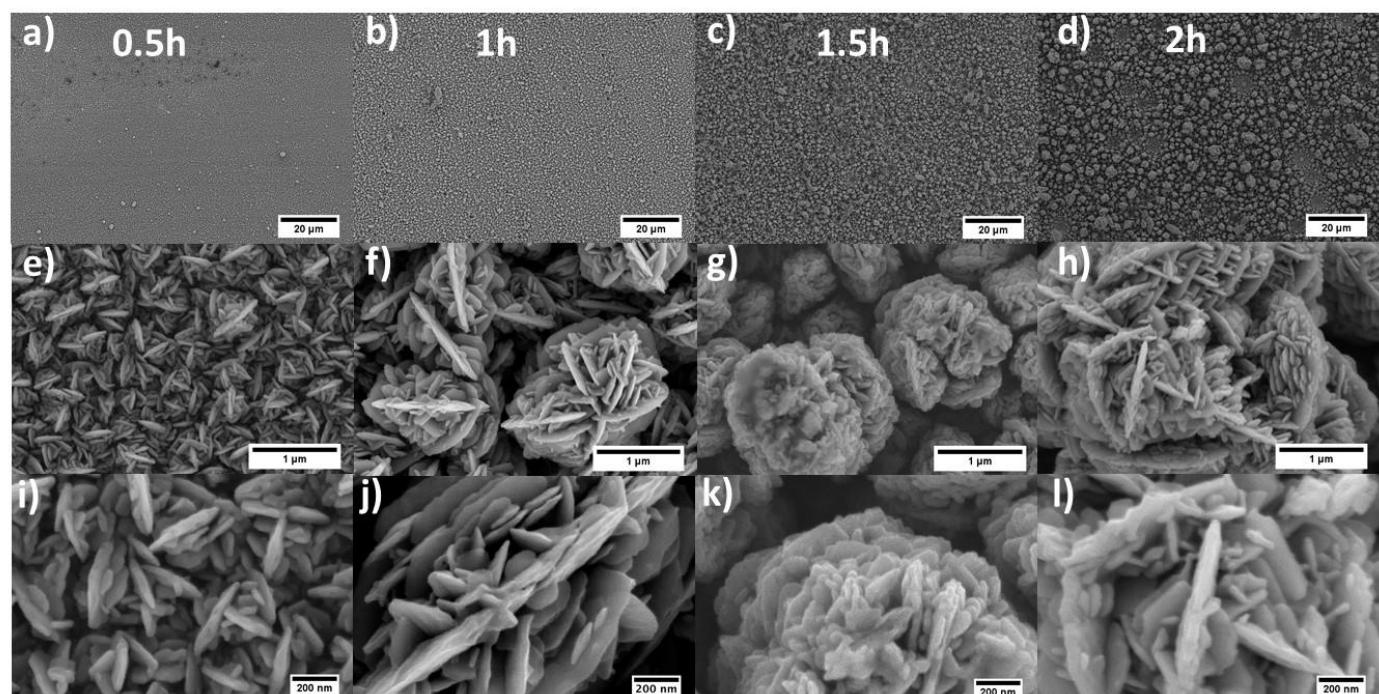


Fig. S1 SEM micrographs at different magnifications of TiO<sub>2</sub>-Rose-800 photoanodes deposited at different times (a, e, i) 0.5, (b, f, j) 1, (c, g, k) 1.5 and (d, h, l) 2h on top of FTO substrates.

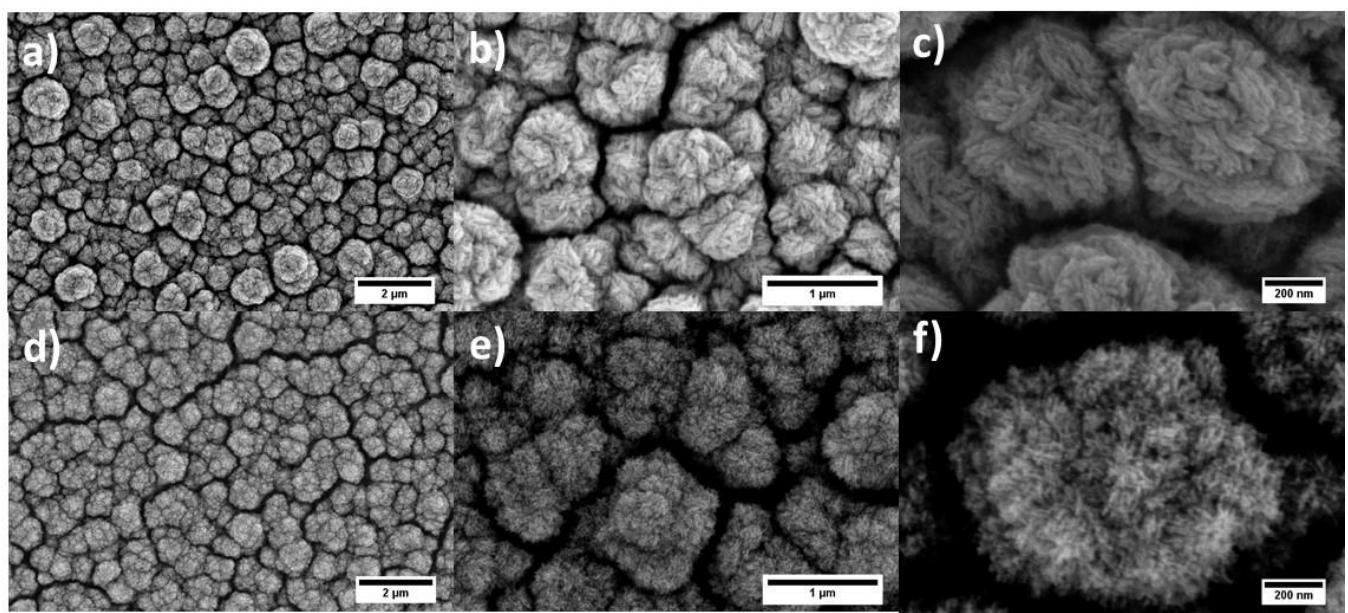


Fig. S2 SEM micrographs at different magnifications of (a-c)  $\text{TiO}_2$  deposited at 600 °C and (d-f) 700 °C for 1h on top of FTO-substrates.

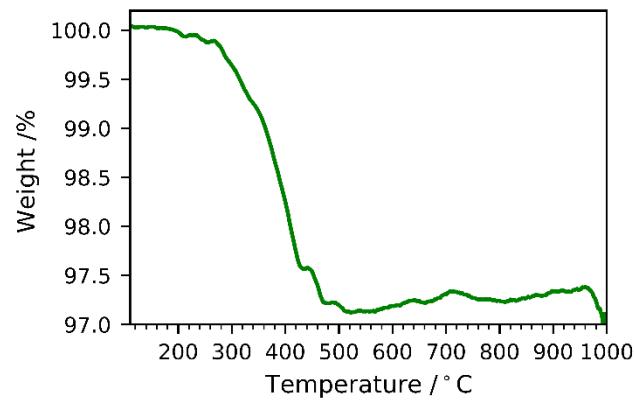


Fig. S3 Thermogravimetric analysis (TGA) in air of  $\text{TiO}_2$ -Rose-AD on FTO-ABS substrate.

Table S1 Atomic percentage (at%) composition of Ti, O and C of  $\text{TiO}_2$  photoanodes.

Sample	Ti (at%)	O (at%)	C (at%)
$\text{TiO}_2$ -Rose-800	21.9	59.9	18.2
$\text{TiO}_2$ -Rose-AD	12.4	31.2	55.7

Table S2 Ti 2p binding energies

Sample	Ti 2p <sub>1/2</sub> /eV	Ti 2p <sub>3/2</sub> /eV
TiO <sub>2</sub> -Rose-800	463.9	458.2
TiO <sub>2</sub> -Rose-AD	465.2	459.4

Table S3 O 1s binding energies of crystal lattice O-Ti<sup>4+</sup>

Sample	O <sup>2-</sup>
TiO <sub>2</sub> -Rose-800	529.4
TiO <sub>2</sub> -Rose-AD	530.7

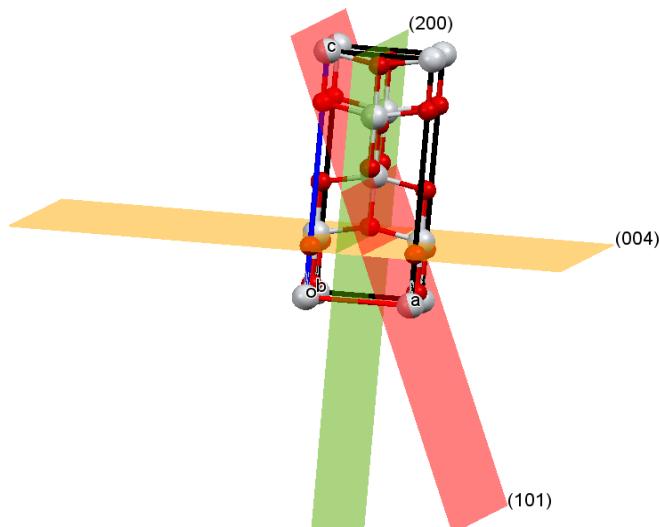


Fig. S4 Anatase  $\text{TiO}_2$  crystal structure showing different crystal planes: (0 0 4) in orange, (1 0 1) in red and (2 0 0) in green.

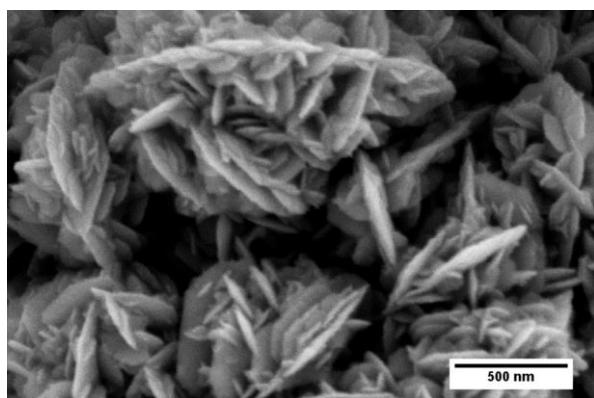


Fig. S5 SEM micrograph of  $\text{TiO}_2$ -Rose deposited on top of alumina at 500 °C.

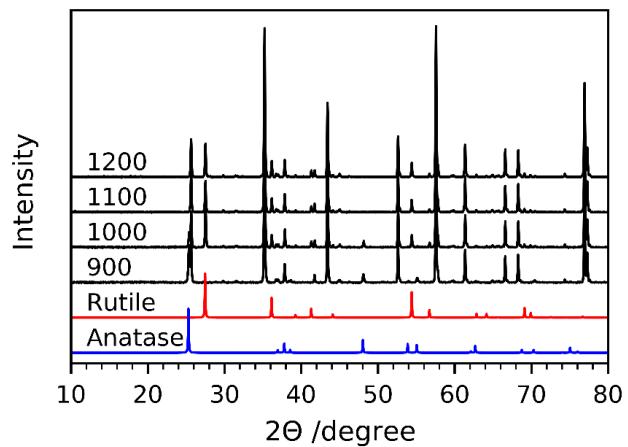


Fig. S6 XRD patterns of  $\text{TiO}_2$ -Rose on alumina substrates. Standard powder patterns of anatase (blue) and rutile (red)  $\text{TiO}_2$  are shown for comparison.

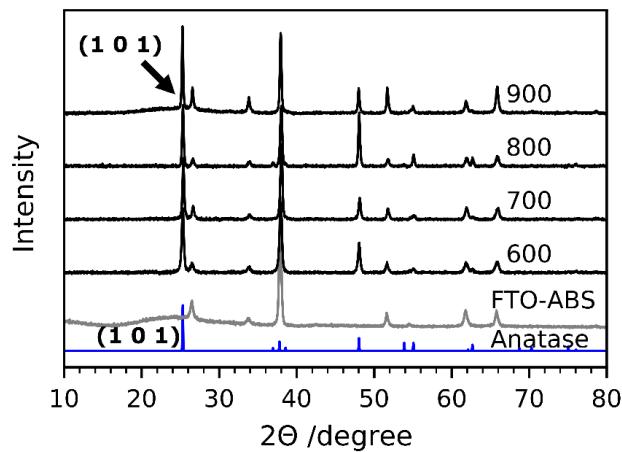


Fig. S7 XRD patterns of  $\text{TiO}_2$ -Rose films prepared using  $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$  and deposited on FTO-ABS substrate. Standard powder pattern of anatase (blue)  $\text{TiO}_2$  and FTO-ABS is also shown.

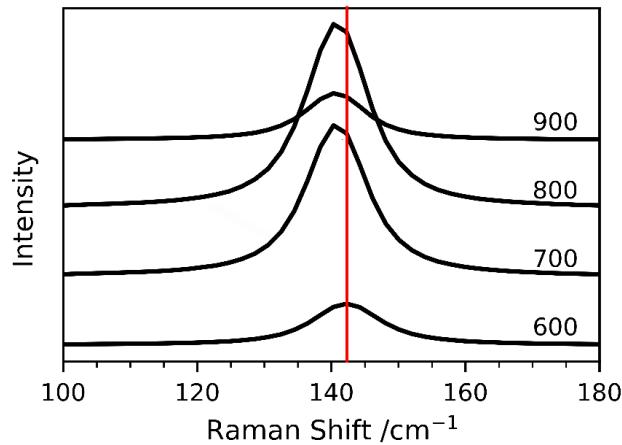


Fig. S8 Raman spectra of  $E_g$  Raman mode of anatase  $\text{TiO}_2$  ( $144 \text{ cm}^{-1}$ ) for  $\text{TiO}_2$ -Rose prepared using  $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$  precursor and annealed at 600, 700, 800 and 900 °C for 2h in air.

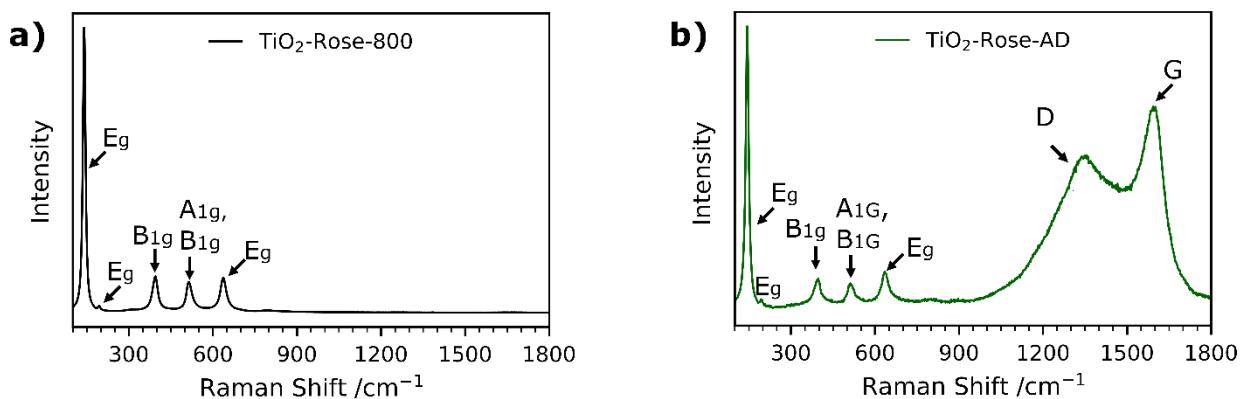


Fig. S9 Raman spectra of (a)  $\text{TiO}_2$ -Rose-800 and (b)  $\text{TiO}_2$ -Rose-AD photoanodes.

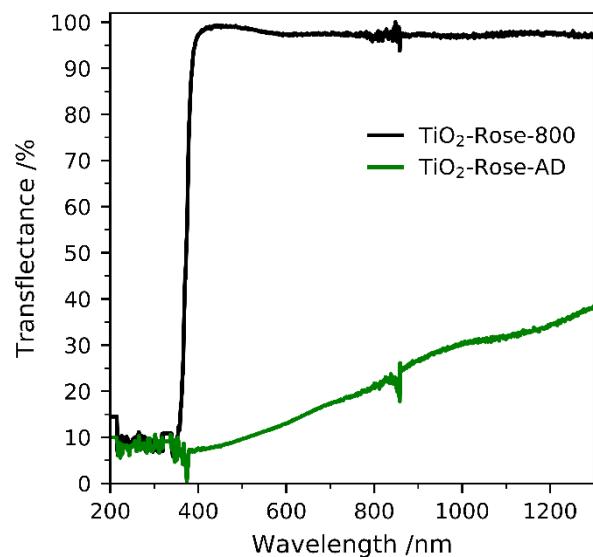


Fig. S10 UV-Vis spectra of  $\text{TiO}_2$ -Rose-800 and  $\text{TiO}_2$ -Rose-AD on quartz substrates.

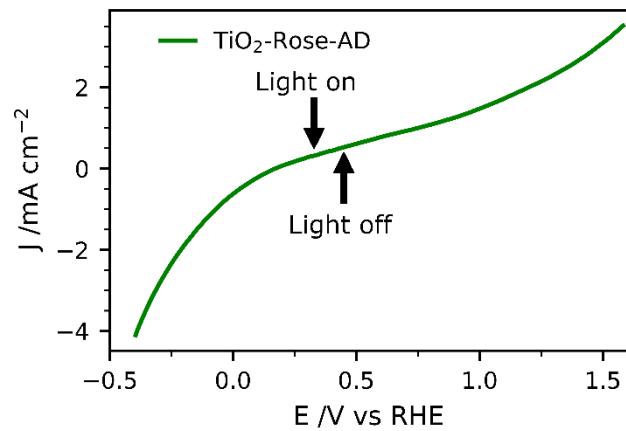


Fig. S11 Photocurrent potential curves of  $\text{TiO}_2$ -Rose-AD under 1 sun chopped illumination (AM 1.5G, 100 mW cm<sup>-2</sup>) in 1M KOH ( $\text{pH}=13.7$ ) solution.

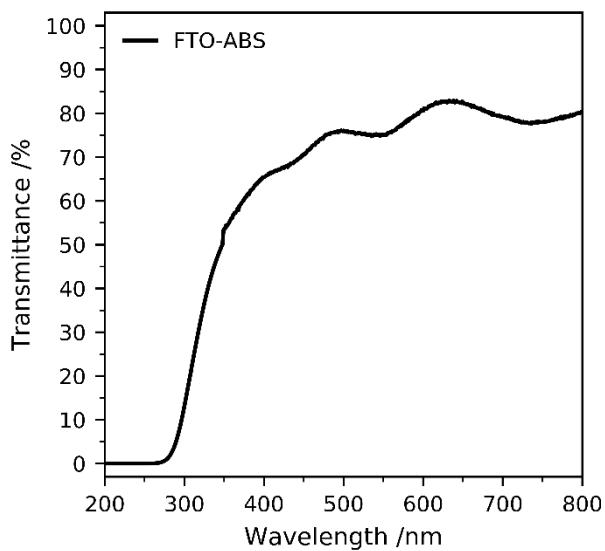


Fig. S12 UV- Vis spectrum of FTO-ABS substrate

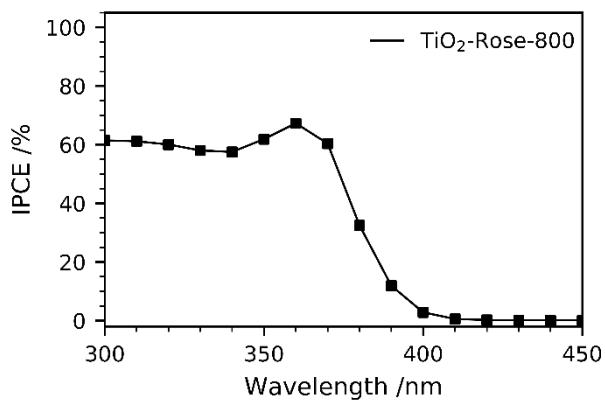


Fig. S13 Front-side IPCE spectra at  $1.23V_{RHE}$  of  $\text{TiO}_2$ -Rose-800.

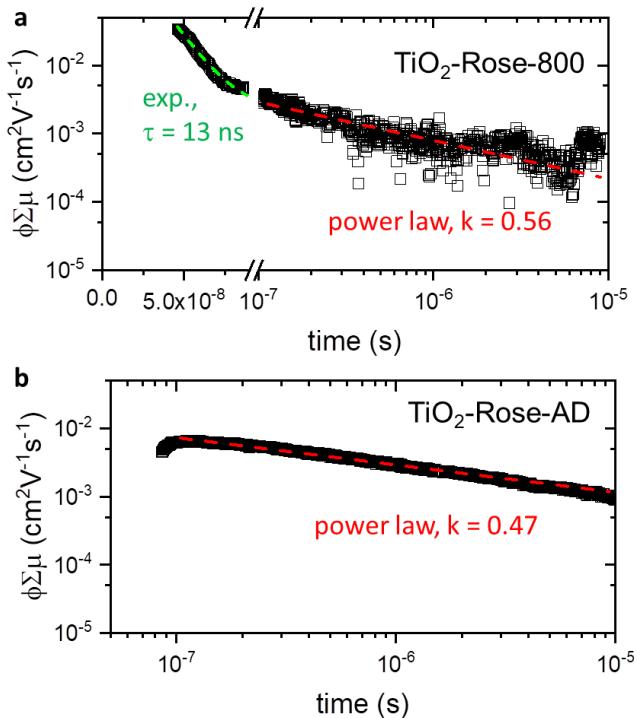


Fig. S14 Fitted curves of time resolved microwave conductance signals for (a)  $\text{TiO}_2\text{-Rose-800}$  and (b)  $\text{TiO}_2\text{-Rose-AD}$  using a 350 nm laser pulse with a photon flux of  $3.97 \times 10^{13}$  photons  $\text{cm}^2 \text{pulse}^{-1}$ .

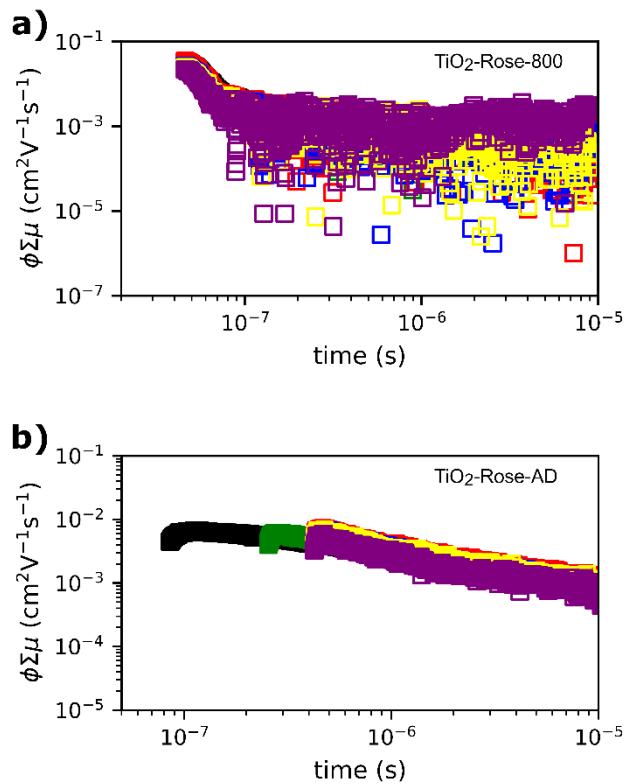


Fig. S15 Time resolved microwave conductance signals for (a)  $\text{TiO}_2\text{-Rose-800}$  and (b)  $\text{TiO}_2\text{-Rose-AD}$  using a 350 nm laser pulse with various photon flux intensities:  $3.97 \times 10^{13}$  (black),  $3.11 \times 10^{13}$  (green),  $2.0 \times 10^{13}$  (red),  $1.80 \times 10^{13}$  (blue),  $1.36 \times 10^{13}$  (yellow) and  $1.15 \times 10^{13}$  (purple) photons  $\text{cm}^2 \text{pulse}^{-1}$ .

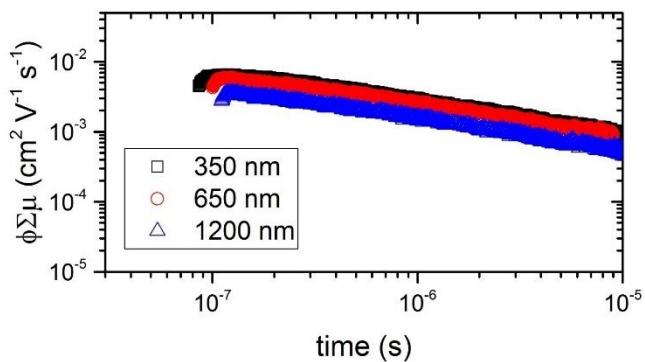


Fig. S16 Time resolved microwave conductance signals for  $\text{TiO}_2$ -Rose-AD using a 350, 650 and 1200 nm laser pulse with a photon flux of  $3.97 \times 10^{13}$ ,  $2.01 \times 10^{14}$  and  $1.22 \times 10^{14}$  photons  $\text{cm}^{-2}\text{pulse}^{-1}$ , respectively.

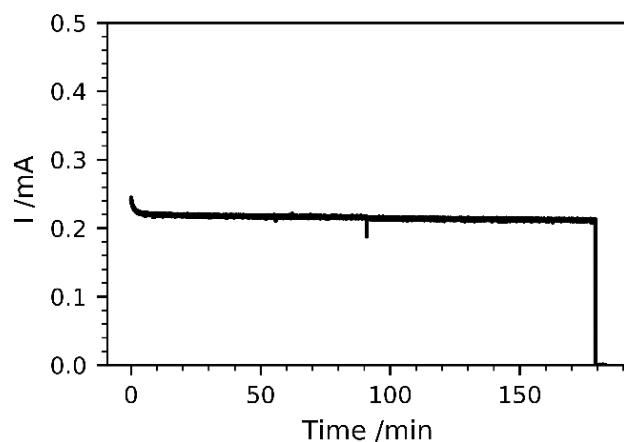


Fig. S17 Photocurrent-time curve of  $\text{TiO}_2$ -Rose-800 obtained during the  $\text{O}_2$  measurement experiment at  $1.23 \text{ V}_{\text{RHE}}$ . Simulated sunlight is switched off after 180 min.

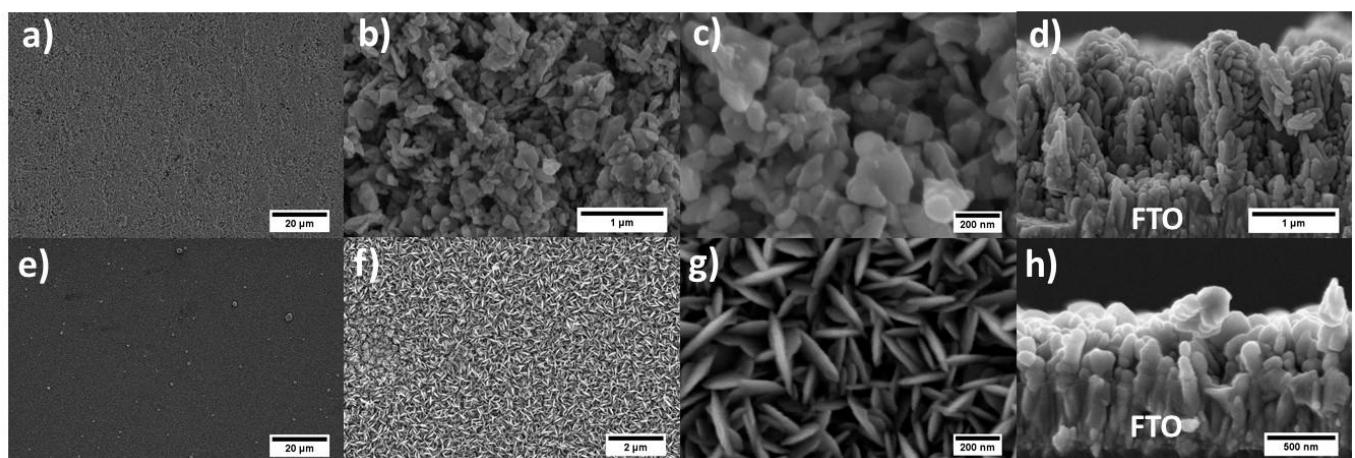


Fig. S18 SEM micrographs at different magnifications of (a-d)  $\text{TiO}_2$ -0.35M-800 photoanodes and (e-h)  $\text{TiO}_2$ -0.05M-800 photoanodes on top of FTO-substrates.

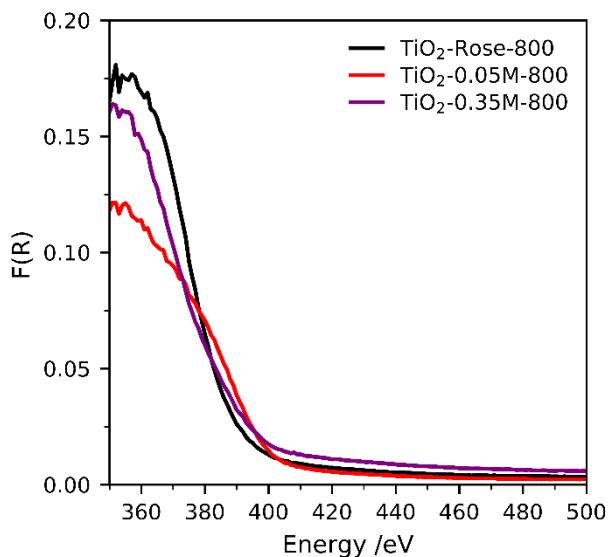


Fig. S19 Diffuse reflectance UV-Vis spectra of  $\text{TiO}_2$ -Rose-800,  $\text{TiO}_2$ -0.05M-800 and  $\text{TiO}_2$ -0.35M-800.

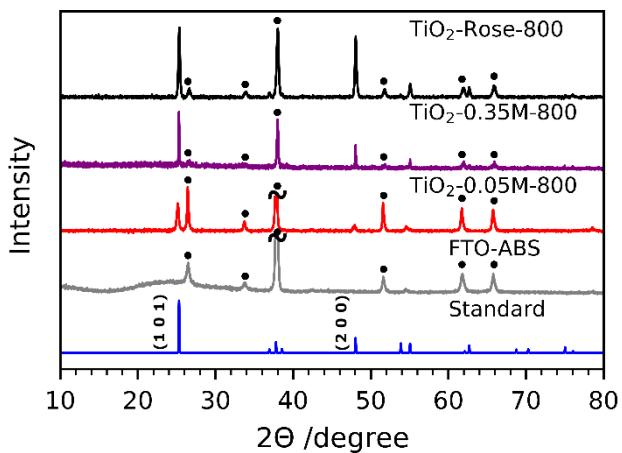


Fig. S20 XRD patterns of  $\text{TiO}_2$ -Rose-800,  $\text{TiO}_2$ -0.05M-800 and  $\text{TiO}_2$ -0.35M-800  $\text{TiO}_2$  films on FTO-ABS substrate. Standard powder patterns of anatase  $\text{TiO}_2$  (blue) and FTO-ABS (grey) are also shown for comparison.

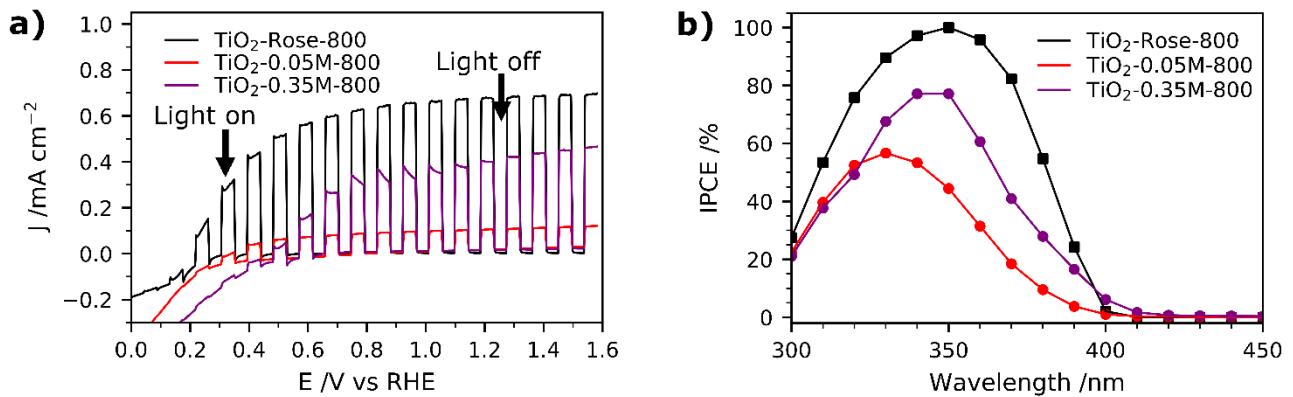


Fig. S21 (a) Photocurrent potential curves of  $\text{TiO}_2\text{-Rose-800}$ ,  $\text{TiO}_2\text{-0.05M-800}$  and  $\text{TiO}_2\text{-0.35M-800}$  under 1 sun chopped illumination (AM 1.5G,  $100 \text{ mW cm}^{-2}$ ). (b) IPCE spectra at  $1.23 V_{\text{RHE}}$  of  $\text{TiO}_2\text{-Rose-800}$ ,  $\text{TiO}_2\text{-0.05M-800}$  and  $\text{TiO}_2\text{-0.35M-800}$ . All measurements were performed in  $1\text{M KOH}$  ( $\text{pH}=13.7$ ).

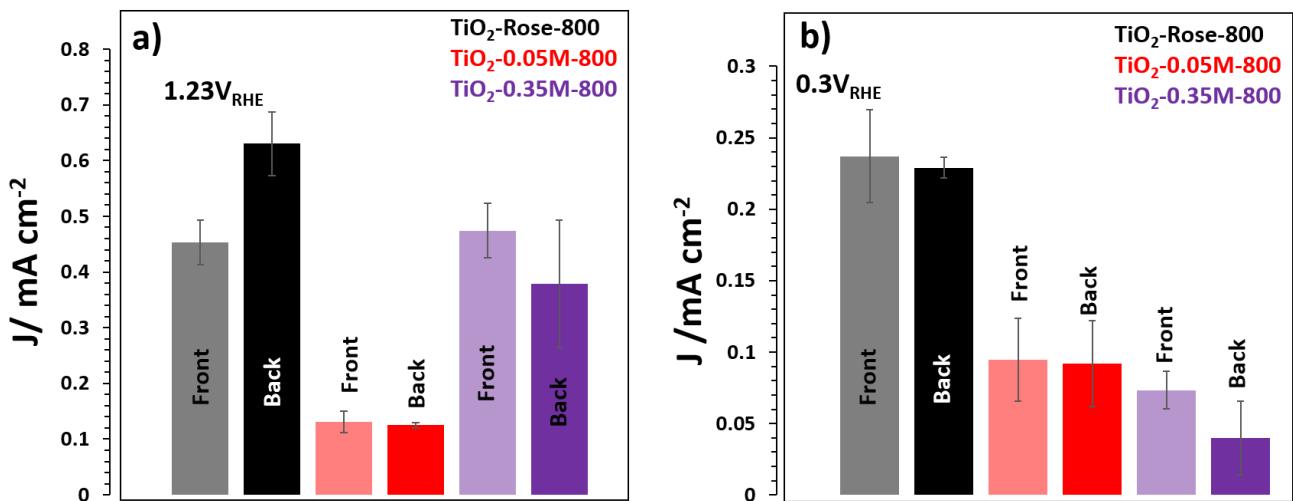


Fig. S22 Photocurrent obtained using front and backside illumination for  $\text{TiO}_2\text{-Rose-800}$ ,  $\text{TiO}_2\text{-0.05M-800}$  and  $\text{TiO}_2\text{-0.35M-800}$  at (a)  $1.23 V_{\text{RHE}}$  and (b)  $0.3 V_{\text{RHE}}$

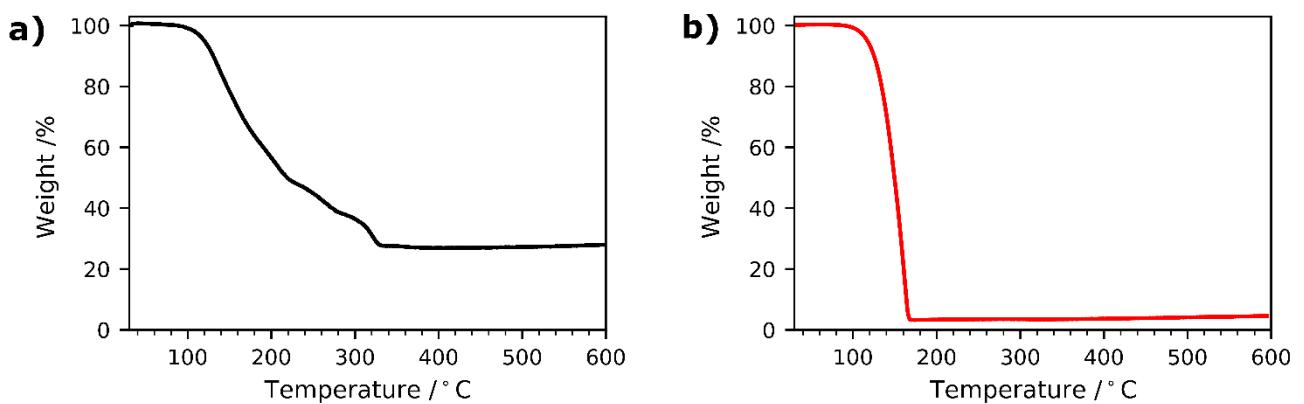


Fig. S23 (a) Thermogravimetric analysis (TGA) in Ar of  $\text{Ti}_2\text{O}_4(\text{OEt})_{20}$  and (b)  $\text{Ti}(\text{OEt})_4$