

Electronic Supplementary Information (ESI) for
Photoelectrochemical Determination of Intrinsic Kinetics of
Photoelectrocatalysis Processes at {001} Faceted Anatase TiO₂
Photoanode

Tao Sun,^a Yun Wang,^{a*} Mohammad Al-Mamun,^a Haimin Zhang,^a Porun Liu,^a and Huijun Zhao^{*a,b}

^a *Centre for Clean Environment and Energy, and Griffith School of Environment, Gold Coast Campus, Griffith university, QLD 4222, Australia.; Fax: +61 1-55528067; Tel: +61 1-55528261*

^b *Centre for Environmental and Energy Nanomaterials, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China*

E-mail: yun.wang@griffith.edu.au, h.zhao@griffith.edu.au

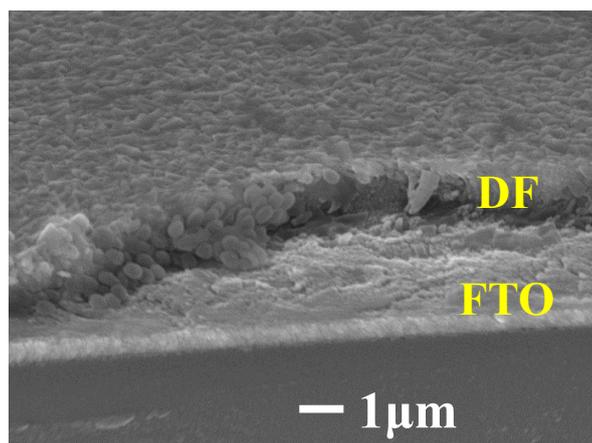


Fig. S1 The cross sectional FESEM image of the DF photoanode.

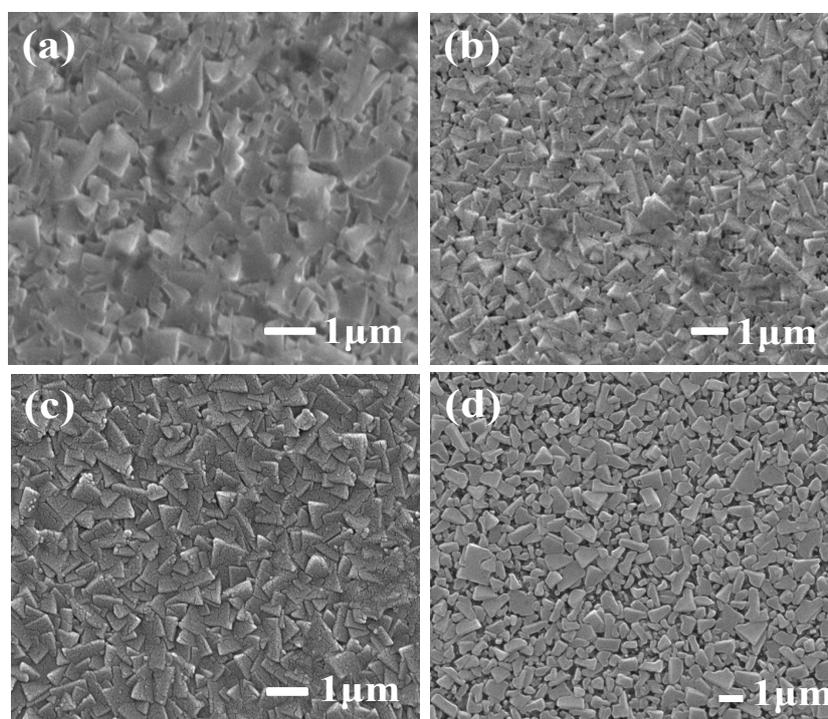


Fig. S2 SEM images of the DL photoanodes after hydrothermal treatment for (a) 2 hours; (b) 3 hours; (c) 4 hours; (d) 6 hours.

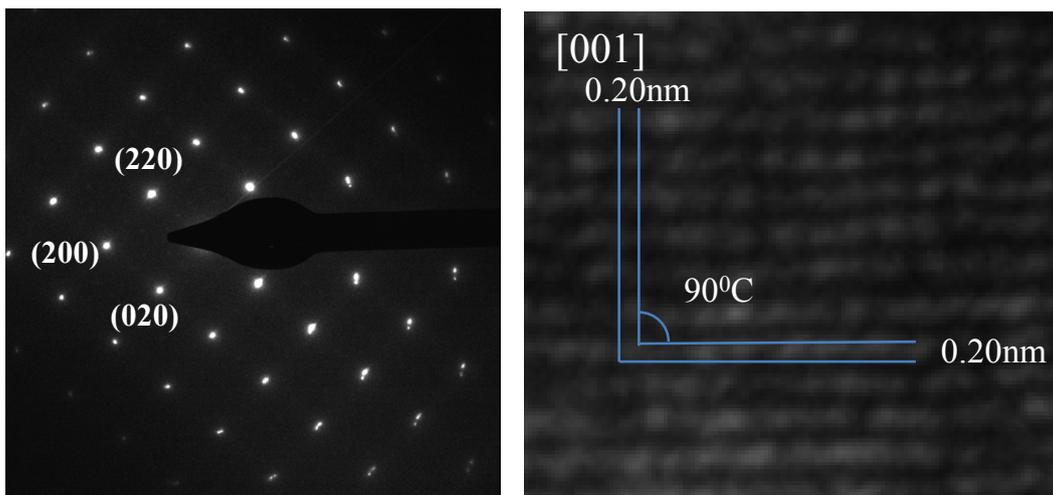


Fig. S3 SAED (right) and HRTEM (left) images of the A001 photoanode.

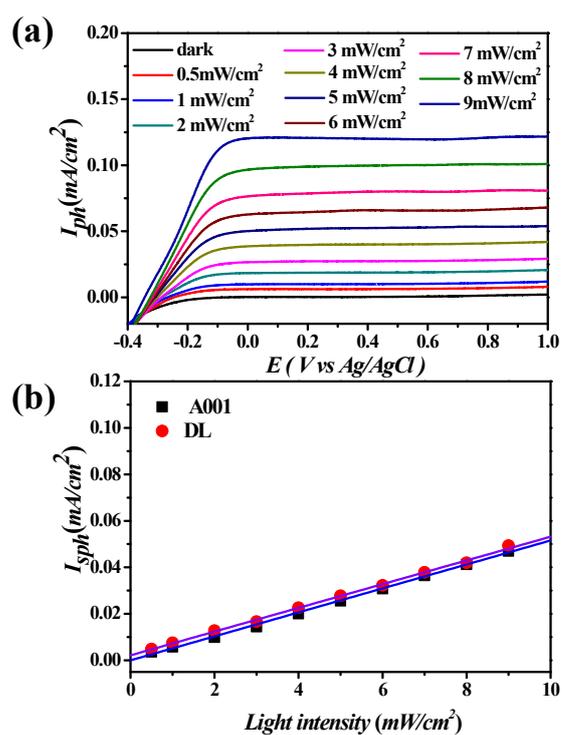


Fig. S4 (a) LSVs of the DF photoanode under different UV illumination intensities in 0.10M NaNO₃ solution at pH 4.0 with a scan rate of 10mV/s; and (b) Relationships of saturation photocurrent I_{sph} against different light intensities at the applied potential bias as +0.4V.

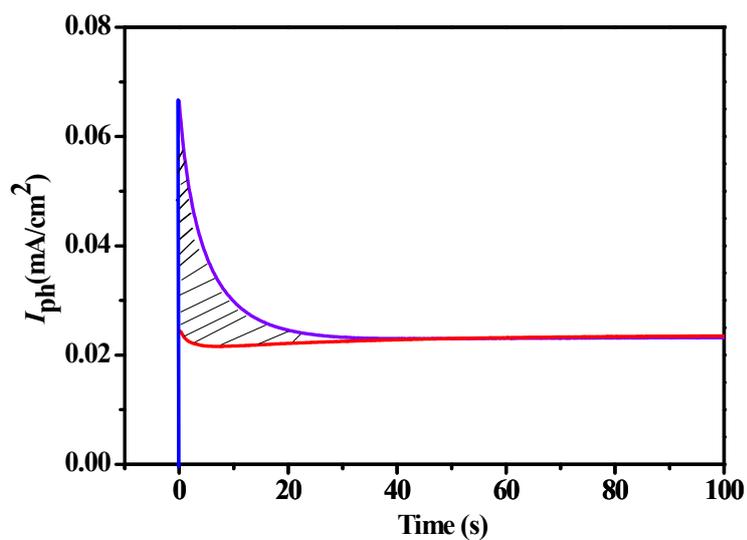


Fig. S5 The *ex-situ* transient photocurrent/time profile of the DL photoanode in 0.1 M NaNO₃ solution after the photoanode was pre-adsorbed in 0.1M NaNO₃ solution containing 0.1 mM oxalic acid at pH 4.0 for 10 min (—) or pre-adsorbed in 0.1M NaNO₃ solution without oxalic acid (—).

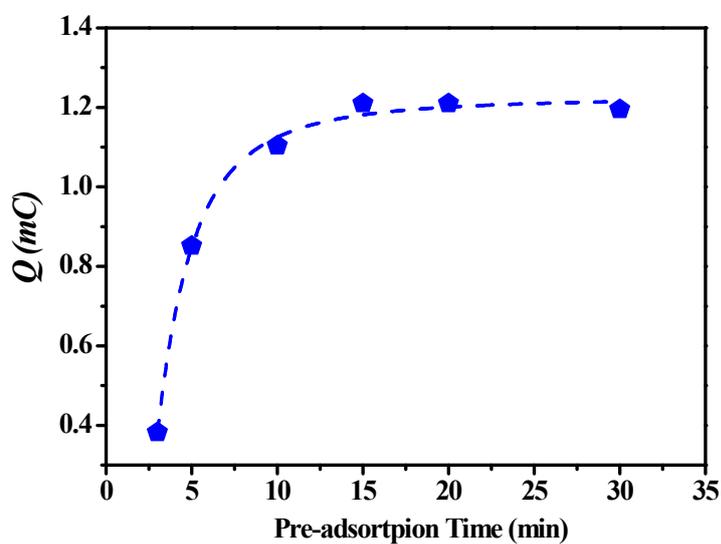


Fig. S6 Plot of the Q against the pre-adsorption time of the DL photoanode in 0.1M NaNO₃ solution containing 0.2 mM oxalic acid at pH 4.0.

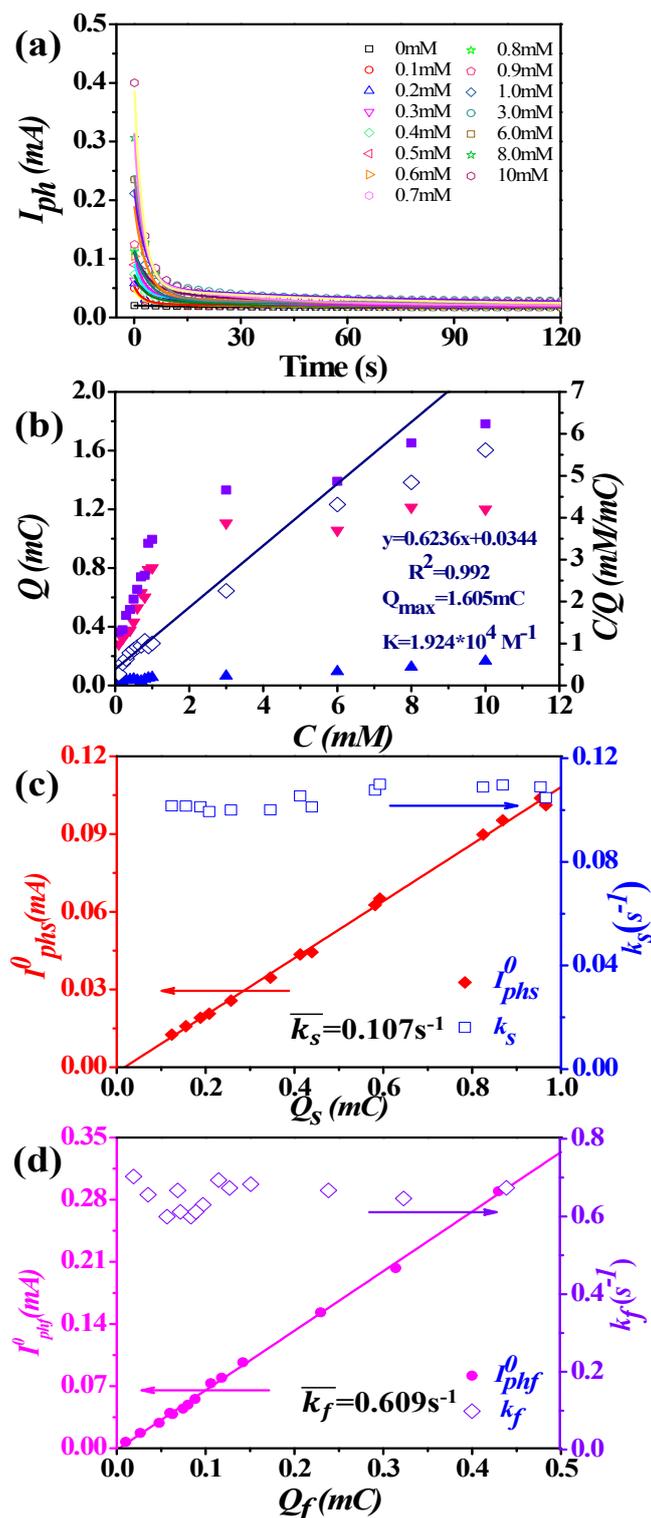


Fig. S7 (a) The photocurrent decay curves from photocatalytic degradation of adsorbed oxalic acid on the DF photoanode with different pre-adsorption concentrations at pH 4.0 and the curve-fitting data; (b) Plot of Q (\blacksquare), slow (\blacktriangledown) and fast kinetic components (\blacktriangle) against the concentration of oxalic acid, and fitting according to the Langmuir adsorption model (\diamond); (c) Plots of I_{phs}^0 and k_s versus the Q_s for the slow kinetics species: (\square) first – order constant (k_s), (\blacklozenge) initial reaction rate (I_{phs}^0); (d) Plot of I_{phf}^0 and k_f versus Q_f for the fast kinetics species (\diamond) first – order constant (k_f), (\bullet) initial reaction rate (I_{phf}^0).

Table S1 Fitting values of I_{phs}^0 , I_{phf}^0 , k_s , and k_f for the PEC degradation of adsorbed oxalic acid on the DL photoanode based on Eq. (2).

<i>C</i> (mM)	I_{phs}^0 (mA)	k_s (s⁻¹)	I_{phf}^0 (mA)	k_f (s⁻¹)
0.1	0.096	0.152	0.207	0.753
0.2	0.137	0.155	0.211	0.741
0.3	0.166	0.161	0.233	0.761
0.4	0.169	0.155	0.239	0.731
0.5	0.184	0.165	0.281	0.771
0.6	0.179	0.159	0.279	0.741
0.7	0.190	0.162	0.258	0.750
0.8	0.189	0.158	0.270	0.752
0.9	0.192	0.156	0.268	0.759
1.0	0.194	0.161	0.278	0.722
3.0	0.198	0.158	0.315	0.754
6.0	0.188	0.156	0.299	0.755
8.0	0.194	0.161	0.311	0.761
10.0	0.192	0.159	0.295	0.745

Table S2 Fitting values for Q_s , Q_f , and Q based on Eqs. (3) and (4).

<i>C</i> (mM)	Q_s (mC)	Q_f (mC)	Q (mC)
0.1	0.631	0.275	0.906
0.2	0.882	0.285	1.167
0.3	1.032	0.306	1.337
0.4	1.085	0.327	1.412
0.5	1.115	0.363	1.479
0.6	1.121	0.376	1.498
0.7	1.180	0.343	1.524
0.8	1.192	0.359	1.551
0.9	1.229	0.353	1.583
1.0	1.205	0.385	1.591
3.0	1.251	0.418	1.669
6.0	1.203	0.396	1.599
8.0	1.205	0.408	1.614
10.0	1.201	0.397	1.598

Eq. S(1)

$$\begin{aligned}I_{oxa} &= I_{ph} - I_{blank} \\Q &= \int_0^{\infty} I_{oxa} dt = \int_0^{\infty} (I_{ph} - I_{blank}) dt = \int_0^{\infty} (I_{phs}^0 e^{-k_s t} + I_{phf}^0 e^{-k_f t}) dt = Q_s + Q_f \\Q_s &= \int_0^{\infty} I_{phs}^0 e^{-k_s t} dt = I_{phs}^0 \int_0^{\infty} e^{-k_s t} dt = -\frac{I_{phs}^0}{k_s} (e^{-k_s \infty} - e^0) = \frac{I_{phs}^0}{k_s} (1 - e^{-k_s \infty}) = \frac{I_{phs}^0}{k_s} \\Q_f &= \int_0^{\infty} I_{phf}^0 e^{-k_f t} dt = I_{phf}^0 \int_0^{\infty} e^{-k_f t} dt = -\frac{I_{phf}^0}{k_f} (e^{-k_f \infty} - e^0) = \frac{I_{phf}^0}{k_f} (1 - e^{-k_f \infty}) = \frac{I_{phf}^0}{k_f}\end{aligned}$$

where I_{oxa} presents the photocurrent caused by oxidized of adsorbed oxalic acid, which is calculated by the overall photocurrent (I_{ph}) minus the photocurrent caused by the PEC oxidation of water (I_{blank}); Q presents the total transferred charge from the PEC oxidation of adsorbed oxalic acids, which consists the transferred charge from the slow (Q_s) and fast (Q_f) oxidation processes. And k_s and k_f are the rate constants for the fast and slow processes, respectively. I_{phs}^0 and I_{phf}^0 present the initial photocurrent generated from slow and fast PEC oxidations, respectively.