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Electronic Supplementary Information

Rapid formation of black titania photoanodes: pulsed laser induced oxygen release and enhanced solar water splitting efficiency

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Temperature simulation under pulsed laser irradiation

Temperature variations during laser irradiation can be described by the heat diffusion equation simplified to describe one-dimensional heat flow[1]

$$\rho C \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2} + \alpha I(z,t)$$

where T is the temperature function at time t and depth z, ρ is the mass density, C is the specific heat capacity, α is the optical absorption coefficient, κ is the thermal conductivity, and $I(z,t)$ is the laser power density. The laser power $I(z,t)$ is given by:

$$I(z,t) = I_0(t) \cdot (1-r) \cdot \exp(-\alpha z)$$

where r is the reflectance. The contribution from the incremental absorbance of the films caused by reflectance at the substrate surface was also included in the laser power distribution. $I_0(t)$ is described as a smooth pulse approximated by:

$$I_0(t) = I_0 \cdot \left(\frac{t}{\tau}\right)^{\beta} \cdot \exp\left(\beta\left(1-\frac{t}{\tau}\right)\right)$$

where I_0 is the incident pulse power density, τ is the pulse duration (KrF: 26 ns), and β determines the temporal pulse shape (KrF: 6.0). We carried out numerical simulations for the temperature variation for the excimer laser irradiation process using a difference approximation based on the above equations. The boundary conditions were T = 20 °C at t = 0 s (initial substrate temperature), T = 20 °C at the bottom of the substrate, and $\kappa \frac{\partial T}{\partial z} = 0$ at the interfaces (adiabatic conditions). The depth of interface was set as 250 nm (the film thickness). The physical constants used in the calculations are listed in Table 1.

Table 1 Physical properties used in numerical simulations.[1–4]

Material	α / cm^{-1}	r	κ / Wcm^{-1}K^{-1}	ρ / cm^3	C / Jg^{-1}K^{-1}
TiO_2	1,040,000	0.266	0.089	4.26	0.930
SnO_2	6,800,000	0.010	0.98	6.99	0.372

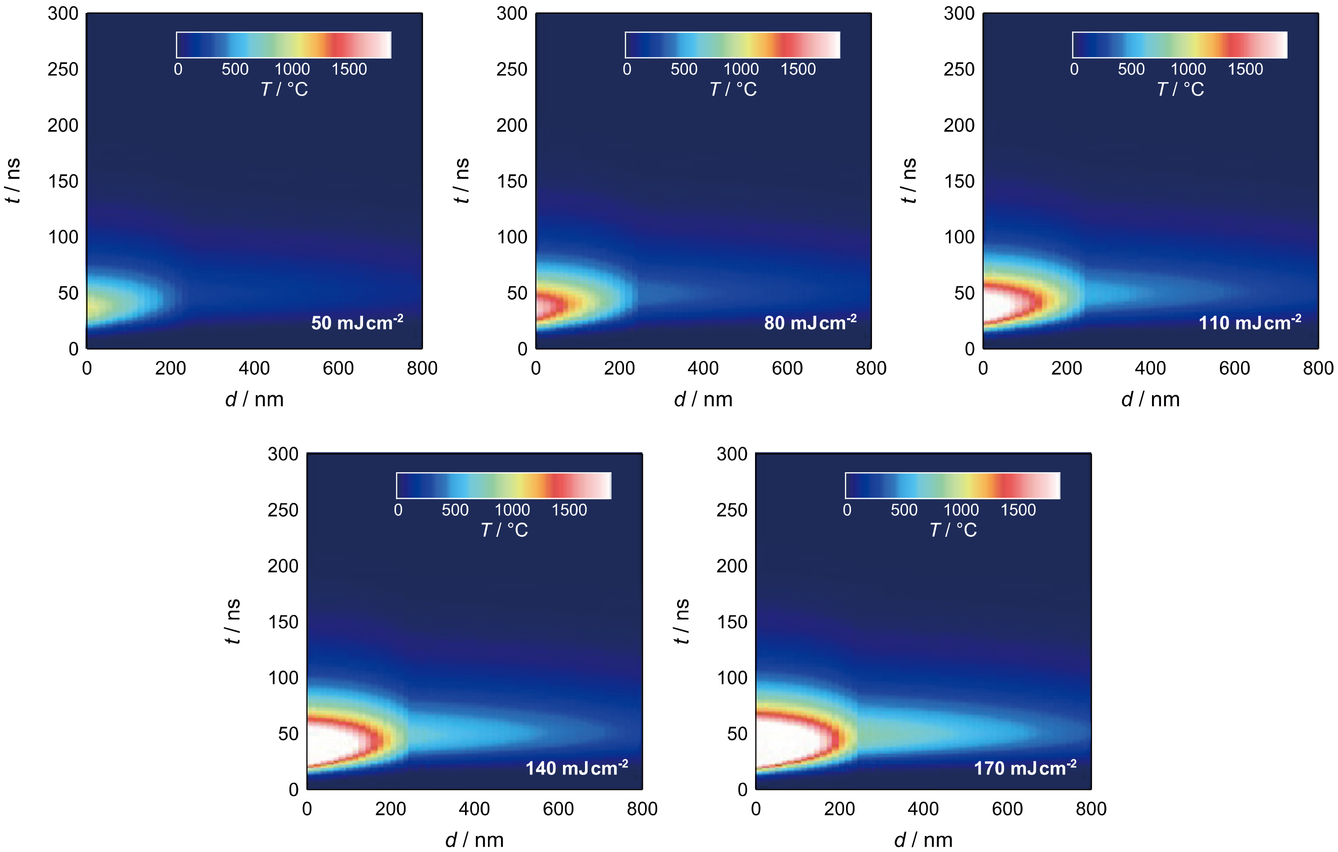

Figure S1: Numerical simulations of temperature map for depth (*d*) and time (*t*) of the TiO_2 thin films on the SnO_2 layers irradiated by KrF laser at 50, 80, 110, 140 and 170 mJ/cm^2. The white region exceeds the melting point of TiO_2 at 1843 °C

PEC property of TiO_{2-x} photoanodes prepared in air

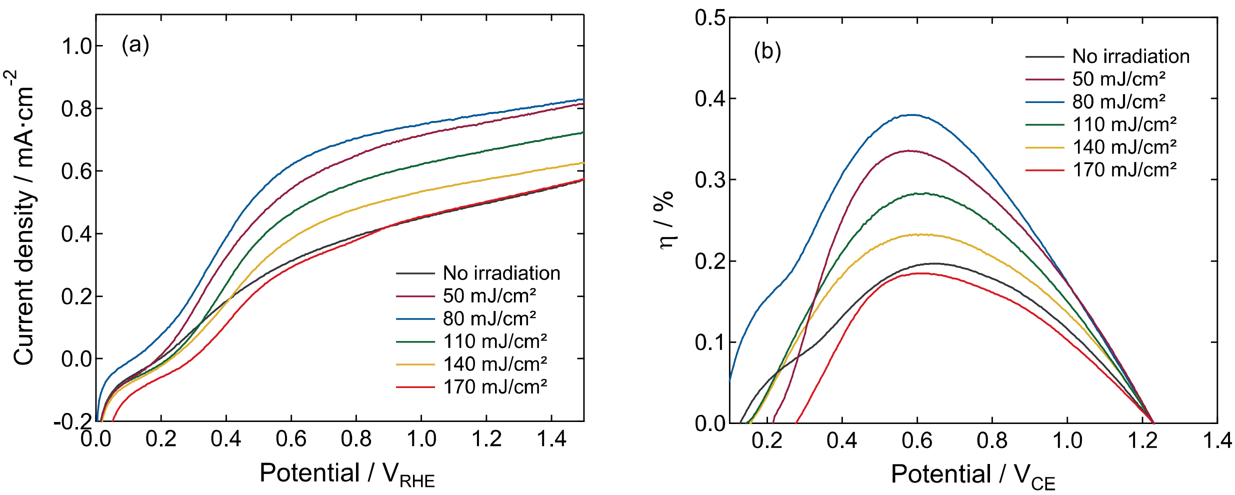

Figure S2: (a) *J-V* curves and (b) η of the pristine TiO_2 and laser irradiated TiO_{2-x} photoanodes under simulated solar light at 100 mW·cm^{-2} in 1 M KOH electrolyte (pH = 13.6). The laser irradiation was carried out in air. The dark current of all samples was less than 2 × 10^{-3} mA·cm^{-2}.

References

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