

Supplementary Information:

Facile Formation of Black Titania Films Using an Atmospheric-Pressure Plasma Jet

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Photocurrent Simulation Model

To qualitatively compare the transient photocurrents obtained from the reduced samples. An idealised model of porous photocatalytic films was solved using Mathematica software. The continuity expressions (Eqs. (1) and (2)) for electron and hole concentrations in a photocatalytic film were taken from de Araújo et al. ¹

$$\frac{\partial n_e}{\partial t} = aI_0 + D_e \frac{\partial^2 n_e}{\partial^2 x} - k_{rec} n_e n_h$$

$$\frac{\partial n_h}{\partial t} = aI_0 + D_h \frac{\partial^2 n_h}{\partial^2 x} - k_{rec} n_e n_h - k_c n_h$$

In these equations, the concentrations of holes and electrons ($n_h(x,t)$, $n_e(x,t)$) in a one dimensional photocatalyst is given by four terms;

- i. the creation term aI_0 where I_0 is the incident light intensity and a is the photoconversion efficiency,

- ii. the diffusion term $D_x \frac{\partial^2 n_x}{\partial^2 x}$ where D_x is the diffusion coefficient of x ,

- iii. the recombination term $k_{rec} n_e n_h$ where k_{rec} is the recombination rate of holes and electrons,

- iv. and the reaction term $k_c n_h$ where holes are lost as they react with the electrolyte solution with rate constant k_c .

In this model $x = 0$ was taken to be the conductive oxide / titania interface that acts as an ideal electron sink. The thickness of the film T_{film} was taken as 2.5 μm with the assumption of no electron transport across the film/electrolyte interface. This gave the boundary conditions $n_e(0, t) = 0$ and

similarly $\left. \frac{\partial n_h}{\partial t} \right|_{x=0} = 0$ and $\left. \frac{\partial n_e}{\partial t} \right|_{x=T_{film}} = 0$. In the time domain, the chopped illumination was represented as a square wave with period 120 seconds and duty cycle of 50%.

For comparing the effects of electron diffusion rates (De), the remaining coefficients were fixed at $I_0 = 2 \times 10^2$, $a = 10^5$, $D_h = 10^{-19} \text{m}^2 \text{s}^{-1}$, $k_{rec} = 10^{-6} \text{s}^{-1}$, $k_c = 0.2 \text{s}^{-1}$. These conditions represent a system where hole losses to electrochemical reactions are fast compared to recombination losses.

Under these assumptions, we have simulated cases where the electron diffusion coefficient varied from $D_e \cong D_h$ to $D_e \gg D_h$ (Figure 7 a).

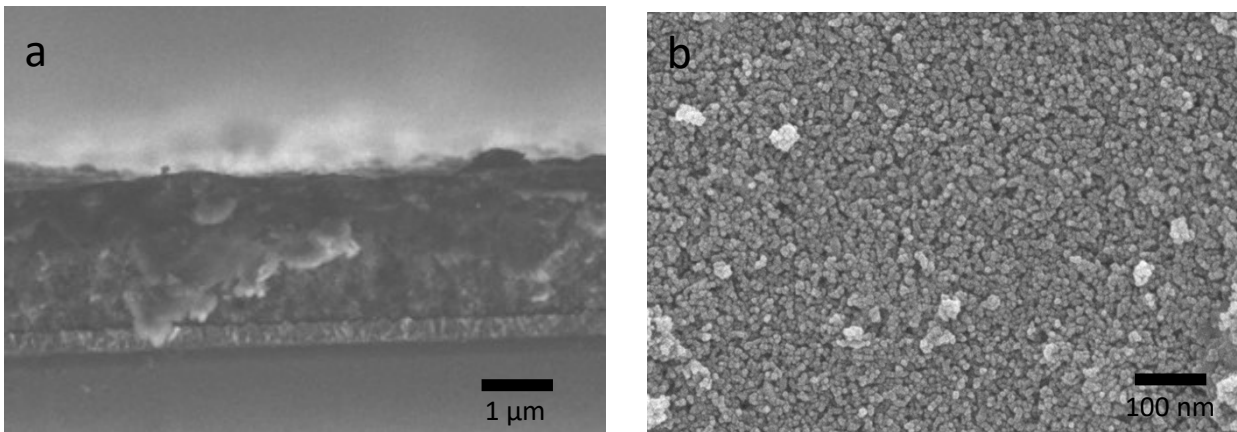


Figure S1: Cross-sectional SEM micrograph of the electrode showing the as deposited anatase, FTO and glass layers (a). SEM micrograph of the electrode surface showing the nano-porous morphology and nano-crystalline anatase particles (b).

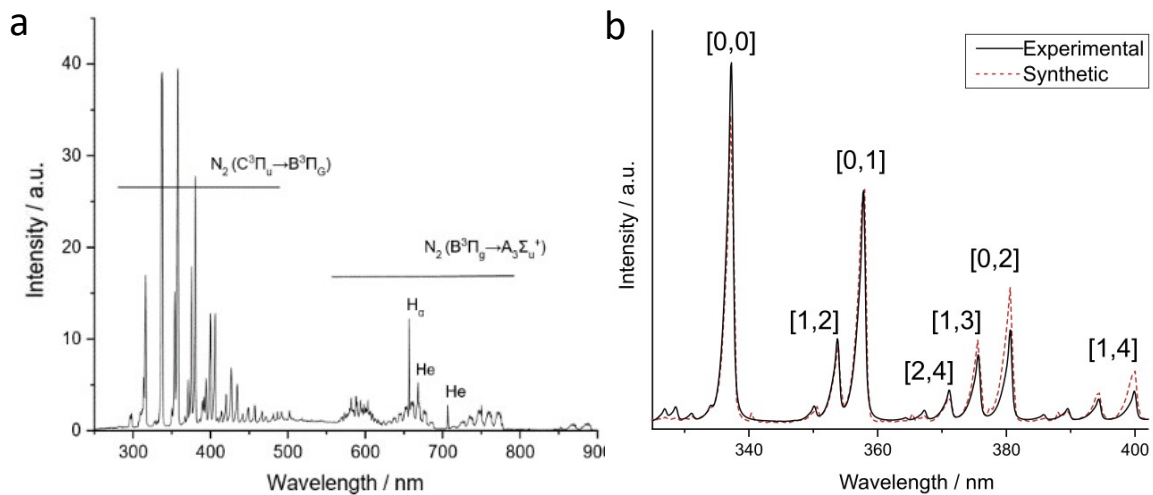


Figure S2: Optical emission spectrum of the plasma discharge highlighting the molecular nitrogen systems, hydrogen alpha and helium atomic emission lines. The most significant source optical emission is found to be ambient nitrogen that is entrained into the working gas at the jet orifice. (a) Synthetic spectrum fit to the N_2 second positive system at $T_{vib} = 5200 \pm 640$ K and $T_{rot} = 520 \pm 60$ K.

Tauc Analysis

The optical band gap is obtained from diffuse reflectance spectra, the raw reflectance spectra is initially transformed into absorbance spectra via application of the Kubelka-Munk function (1).

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \#(1)$$

Where R_∞ is the reflectance from an infinitely thick specimen. Tauc method is then applied to the transformed absorption spectra by setting the Kubelka-Munk transformed spectra $F(R_\infty)$ as the energy-dependent absorption coefficient α in expression (2).

$$(\alpha \cdot hv)^{1/\gamma} = B(hv - E_g) \#(2)$$

As TiO_2 is an indirect bandgap material, for analysis shared in the manuscript, a γ value of 2 is used in equation (2) to generate the Tauc plots. In a plot of hv vs $(F(R_\infty) \cdot hv)^{1/2}$, extrapolation to the abscissa of the linearly increasing region in the Tauc plot allows for estimation of the optical band gap.

In the case of materials that show significant absorbance in regions below the band gap energy, Tauc analysis is found to be prone to underestimating the actual band gap of materials. In order to have a better estimate, the sub-band gap absorption region is also extrapolated to higher incident energy values forming a second abscissa, the intersection point of these two lines are quoted as the estimated band gap energy. Further details, alongside the rationale for the analysis used are provided in the article below:

How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV-Vis Spectra P. Makuła, M. Pacia, and W. Macyk. *The Journal of Physical Chemistry Letters*, **2018**, 9 (23), 6814-6817

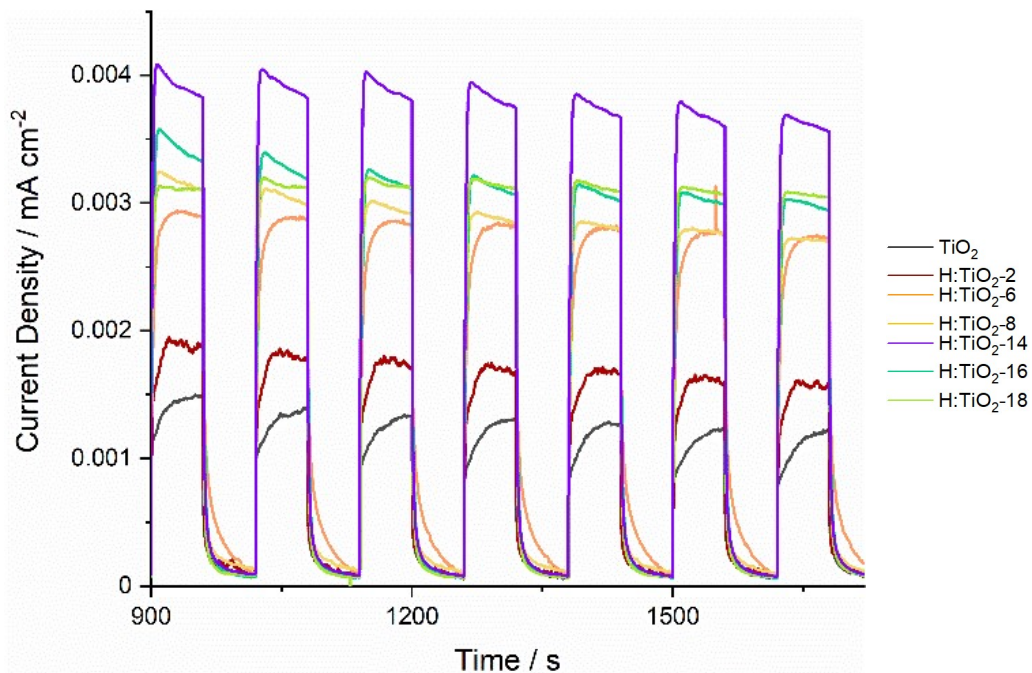


Figure S3: Photocurrent density from TiO_2 samples under chopped illumination at 420 nm.

