

Supporting Information

Radiative and non-radiative recombination pathways in mixed phase TiO₂ nanotubes for PEC water splitting

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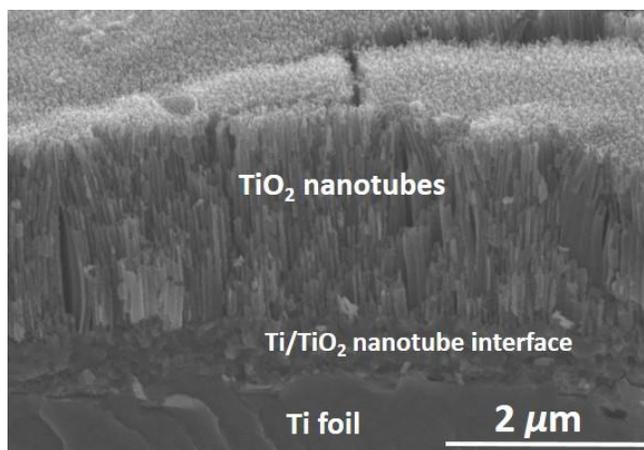


Figure S1. Cross-sectional image of TiO₂ nanotubes annealed 600 °C, which shows interface of Ti metal and TiO₂ nanotubes.

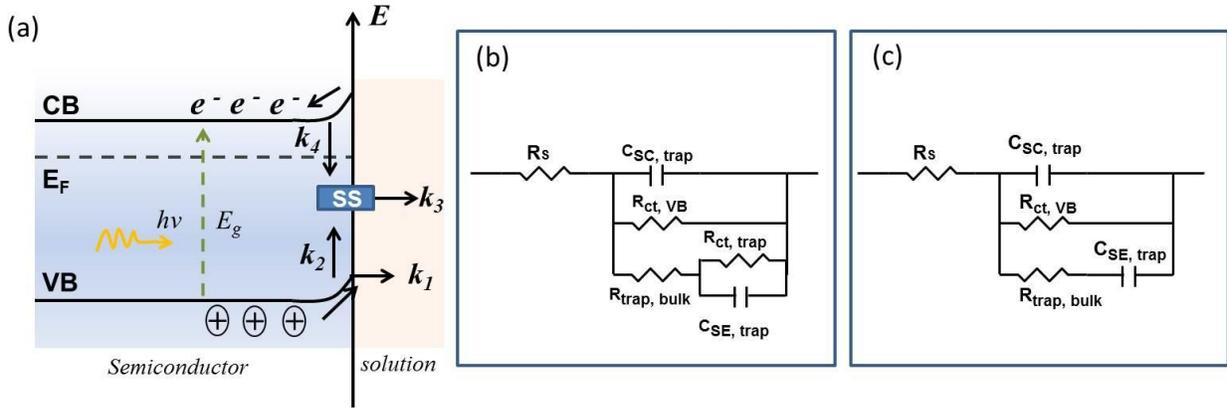


Figure S2. (a) Schematics of typical water oxidation kinetics involved in n-type semiconductor/solution interface during PEC water splitting. Here, k_1 represents the hole transfer rate from valence band to solution; k_2 is the rate of hole trapping in surface states; k_3 represents the hole transfer from surface states to solution; k_4 is the recombination rate of holes in surface states with electrons in conduction band. (b) Complete physical model, which describes water oxidation processes at semiconductor/solution interface (adopted from *ref.* [36]) where $R_{ct,trap}$ is analogous to hole transfer rate (k_3) from surface states to solution. (c) Simplified model used for photoelectrochemical impedance spectroscopy (PEIS) data fitting, in which surface trap charge transfer resistance is neglected ($R_{ct,trap}$). Since k_1 dominates the k_3 ($k_1 \gg k_3$) in semiconductors like TiO_2 , the hole transfer ability across the solution interface is represented by a single element $R_{ct,VB}$, as represented by k_1 in schematic (a).

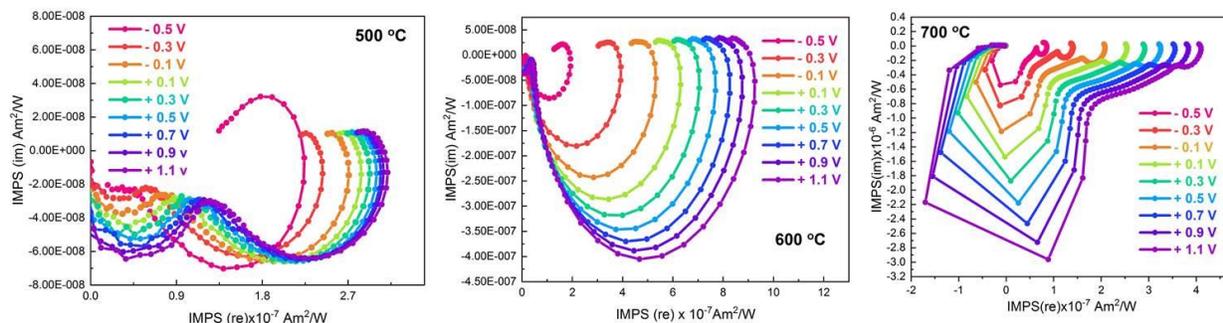


Figure S3. Intensity-modulated photocurrent spectroscopy (IMPS) spectra measured at different potentials (V) against Ag/AgCl for TiO₂ nanotubes annealed at different temperatures.

Few lines about IMPS and IMVS

IMPS and IMVS are electrochemical techniques similar to EIS (Electrochemical Impedance Spectroscopy). However, in IMPS/IMVS techniques rather than modulation of voltage or current (in case of EIS), the light intensity which falls on photoanode is modulated. In the process of experiments, fixed light intensity (I_0) is illuminated on the photoanode, along with this, a sinusoidal light wave will be superimposed to perturb the surface of photoanode. The angular frequency of the sinusoidal light wave is $2\pi f$. The output signal frequency is same but phase is shifted. During the measurement frequency dependent current/voltage will be measured, which is real part (re) as well and imaginary part (im) of photocurrent. By analyzing the recorded spectra, it is possible to extract charge transfer/transport parameters related to surface oxidation kinetics of the photoanode.

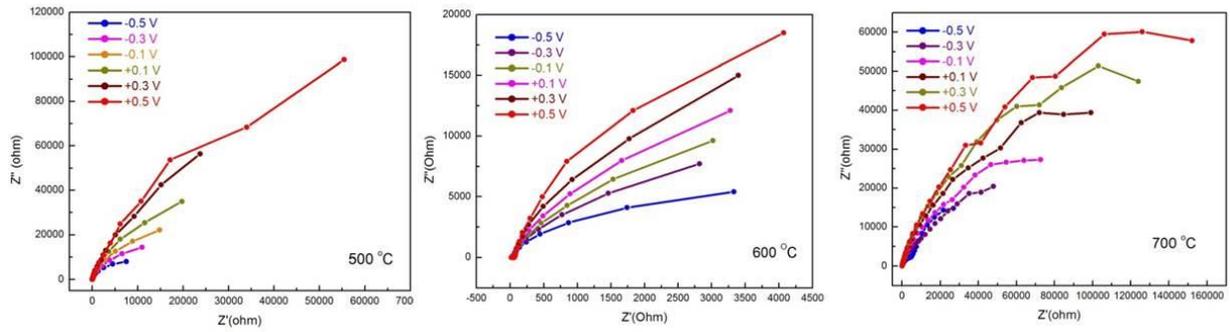


Figure S4. PEIS spectra measured at different potentials (V) against Ag/AgCl for TiO₂ nanotubes annealed at different temperatures.

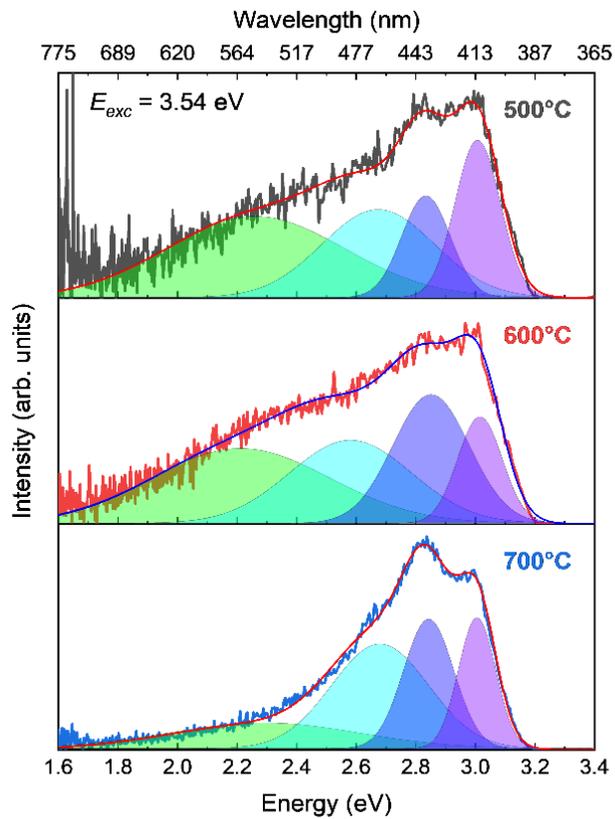


Figure S5. Multi-Gaussian fitting of PL spectra of TiO₂ nanotubes.

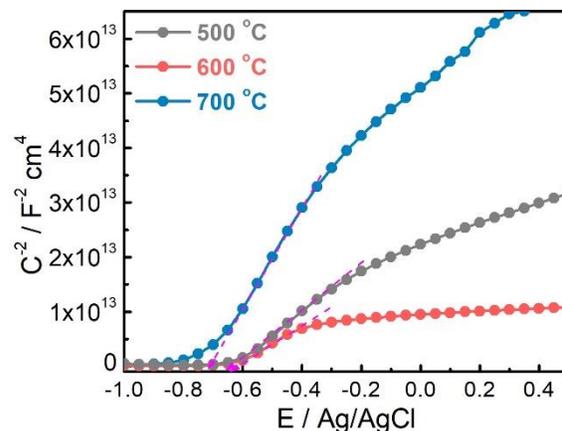


Figure S6. Mott-Schottky plots obtained from the bulk capacitance measurements in the dark.

Figure 8 represents the Mott-Schottky measurements conducted for the samples at a frequency 500 Hz in the dark with scan rate 100 mV/s. The intersection of tangents with potential axis gives the flatband potential of respective photoanode. The obtained E_{fb} is consistent with the photocurrent onset observed in I-V curves. The E_{fb} for the TNT 600 ($E_{fb} = -0.64 \pm 0.02 \text{ V vs. Ag/AgCl}$) shift towards positive side in comparison to the samples TNT700 ($E_{fb} = -0.72 \pm 0.03 \text{ V vs. Ag/AgCl}$), which indicates shift in Fermi level towards the conduction band thus improves the hole transfer efficiency and is consistent with the observed results from IMPS and EIS measurements. The charge carrier density corresponding to TNT600 ($N_d = 9.71 \pm 0.03 \times 10^{20} \text{ cm}^{-3}$), is higher compared to TNT500 ($N_d = 7.16 \pm 0.03 \times 10^{20} \text{ cm}^{-3}$) and TNT500 ($N_d = 3.45 \pm 0.02 \times 10^{20} \text{ cm}^{-3}$) also indicates the efficient charge transport/transfer rate across the photoanode/electrolyte interface