

Supplementary Information

Unveiling General Rules Governing Dimensional Evolution of Branched TiO₂ and Impacts on Photoelectrochemical Behaviors

Teera Butburee^{1,2*}, Yang Bai², and Lianzhou Wang^{2*}

¹National Nanotechnology Center, National Science and Technology Development Agency, 111 Thailand Science Park, Phahonyothin Rd., Khlong Nueng, Khlong Luang, Pathum Thani 12120, Thailand

²Nanomaterials Centre, School of Chemical Engineering and Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, St Lucia, QLD, 4072, Australia

*Corresponding Author, Email: teera.but@nanotec.or.th

Keywords: TiO₂, hierarchical nanostructures, dendritic nanostructures, branched nanostructures, PEC water splitting

S1: Various information regarding Figure 1

Table S1: summary of the conditions used for synthesizing the nanostructures in Figure 1

Samples	Dimension	Variables in the structure	Variable details	Crystal Phase	Synthesis Condition		
					PTO (g)	Water (mL)	DEG (mL)
e	1D	-diameter -crystal phase	diameter ~200 nm	Anatase	0.438	7.5	32.5
f			diameter ~500 nm	Anatase+rutile	0.438	10	30
g			diameter ~1200 nm	Anatase+rutile	0.438	12	28
h	2D	-position of branches -number of branches	Few branches begin to selectively grow on edges of the 2D main plate	Potassium Titanate	0.438	3	37
i			Fully grown branches on edges of the plate	Potassium Titanate	0.438	3.25	36.75
j			Branches are fully grown on the whole structure	Potassium Titanate	0.438	3.5	36.5
b	0D	-number and size of branches -crystal phase	Larger number of small branches	anatase	0.438	7.5	32.5
c			Less number of larger branches	Potassium Titanate+anatase	0.525	8	32
d			Less number of largest branches	Potassium Titanate+anatase	0.675	8.5	31.5

Hydrothermal treatment for these reaction was performed at 180 °C for 10 h.

S2: Examples of nanostructures obtained from PTO:water:DEG ratios that were out of appropriate ranges

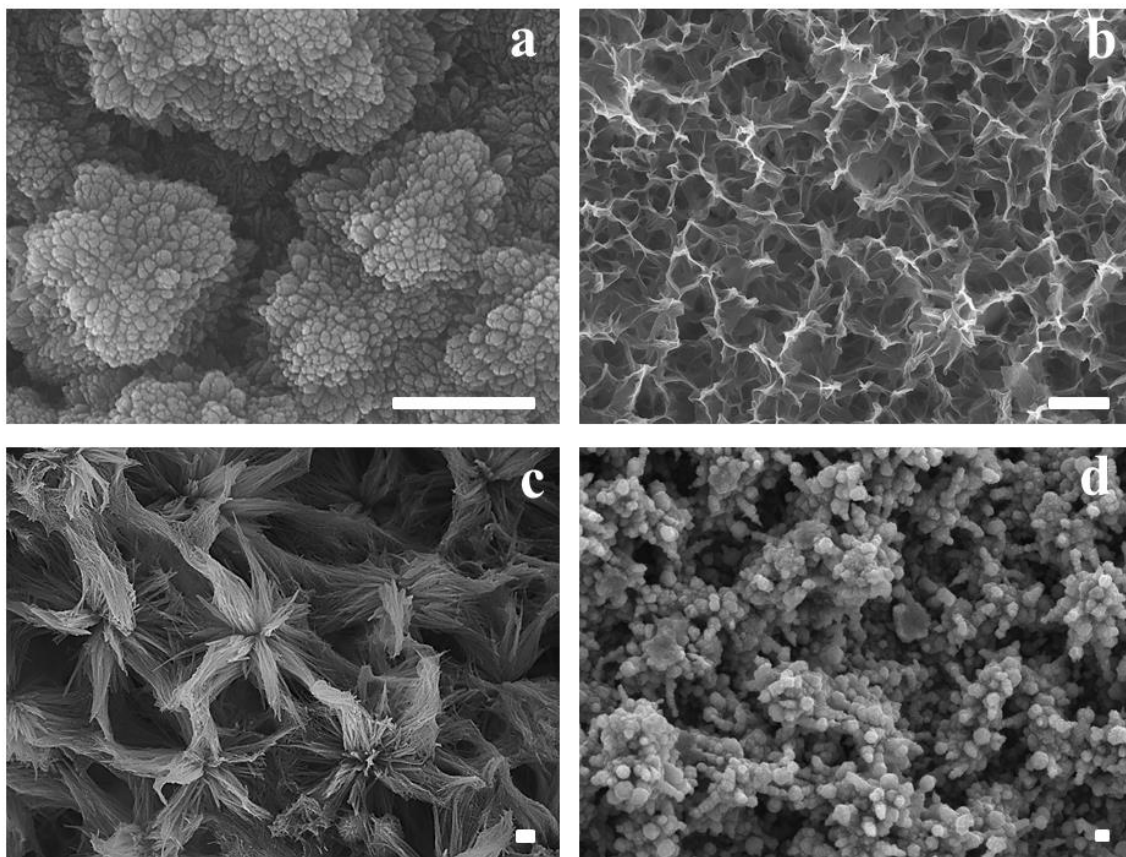


Figure S2 various irregular morphologies obtained when PTO:water:DEG were equal to: a) 0.55 g:30 mL:10 mL, b) 1.0 g: 20 mL:20 mL, c) 0.3g: 3 mL: 37, d) 0.44 g: 15 mL: 25 mL (scale bar = 1 μ m).

S3: Dissolved PTO precursor in different water:DEG ratios



a



b

Figure S3 a) the solution for synthesizing 2D (pH 5.1) and b) the solution for synthesizing 0D/1D (pH 4.8)

S4: FTIR of different dimensional solid films on FTO

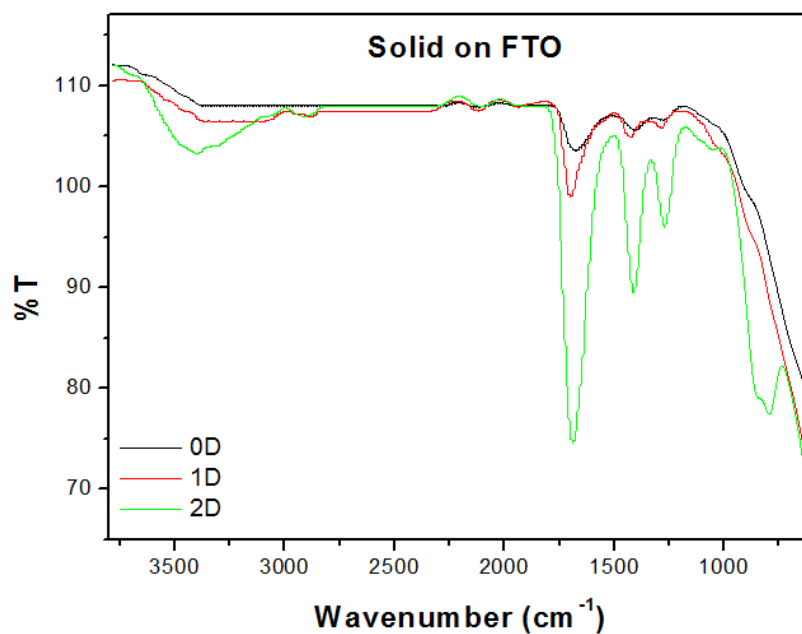


Figure S4 FTIR of 0D, 1D and 2D films. It is clear that the intensity of $\nu(\text{C}=\text{O})$ at $\sim 1700 \text{ cm}^{-1}$ of 2D is significantly higher than that of 1D and 0D. This evidence suggests that the low-dimension structure (0D) could be less bounded by oxalate group than that of the higher-dimension structures (1D and 2D)

S5: Time-dependent structural growth study

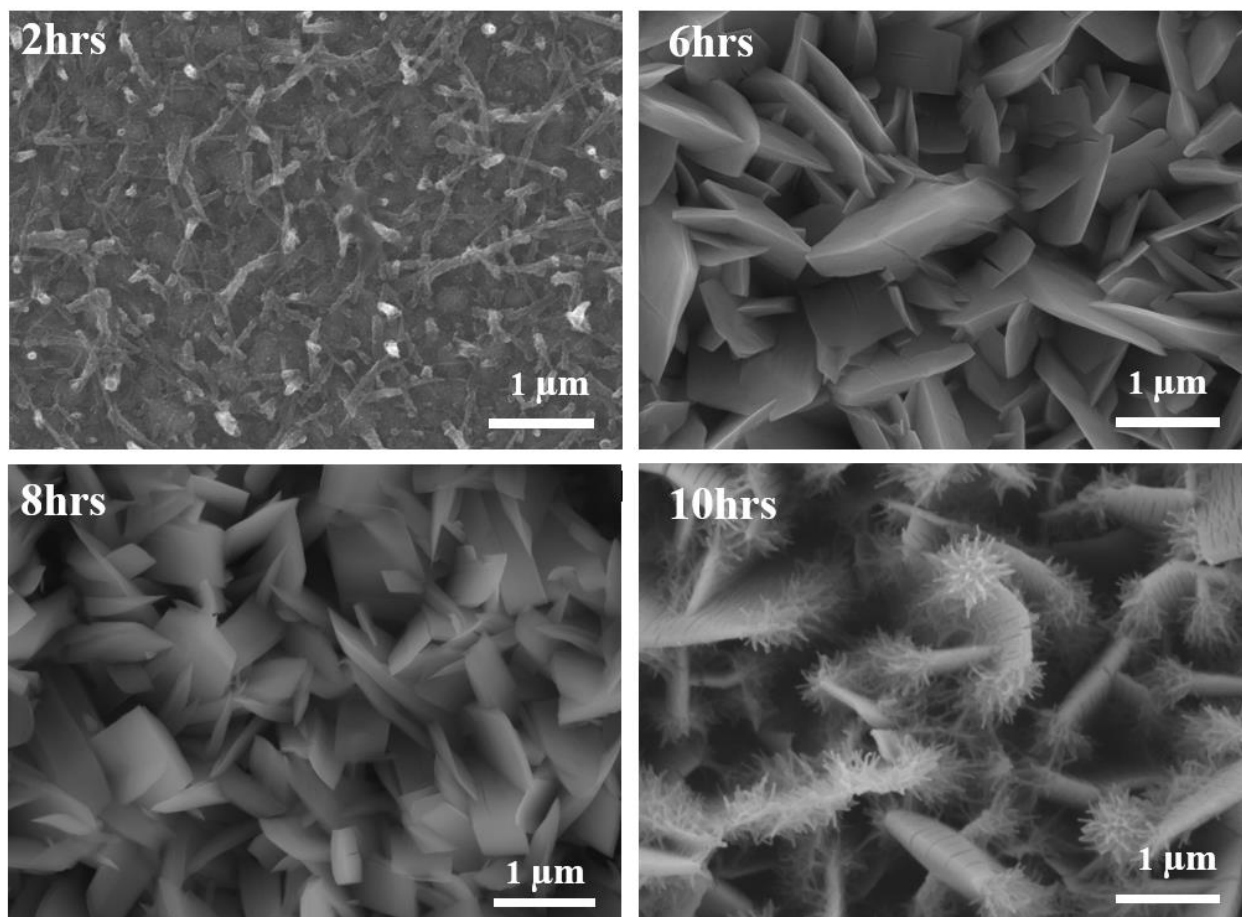


Figure S5 SEM analysis of the structural development of 2D branched nanostructures at various time. a) at 2, b) 6, c) 8, and d) 10 hours.

S6: FTIR analysis to monitor the time-dependent structural growth.

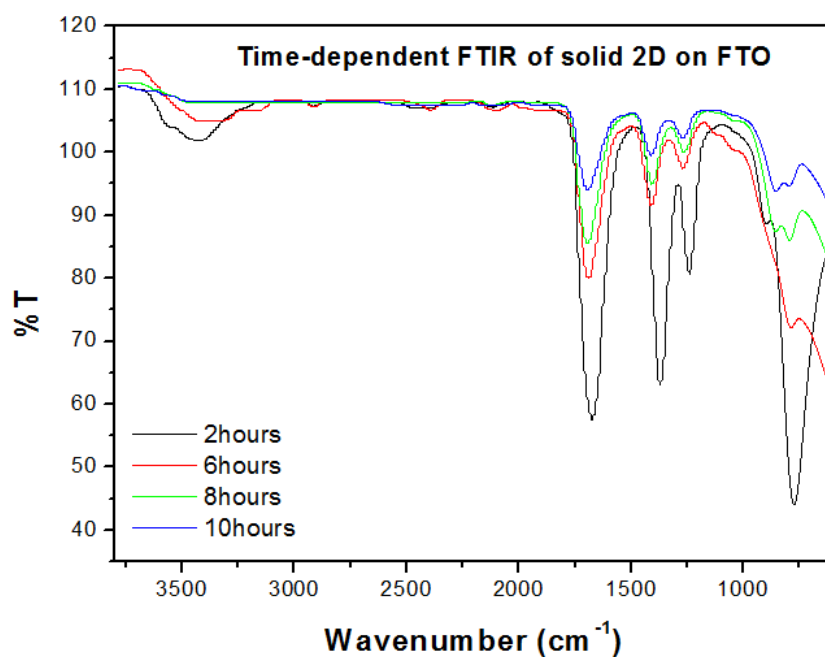


Figure S6 FTIR spectra of the 2D TiO₂ films on FTO at different reaction times. The results show that the amount of oxalate on the film is gradually decreased with increasing reaction time, as clearly seen from the decrease in the intensity of C=O peaks.

S7: HPLC analysis of the supernatants derived from different reaction times

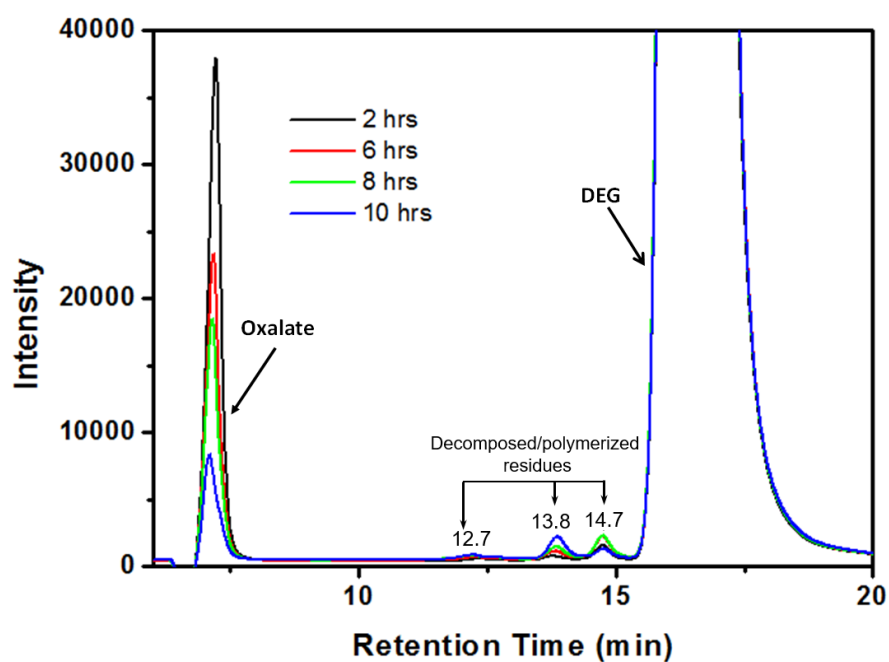


Figure S7 HPLC analysis of the supernatant based on the time dependent reactions. The results showed that the intensity of oxalate peaks was gradually decreased with increasing reaction time while the intensity of the decomposed products became higher. These results suggested that oxalate group could be decomposed/polymerized after the long reaction time.

S8: Control experiment: extra oxalate group added in the system

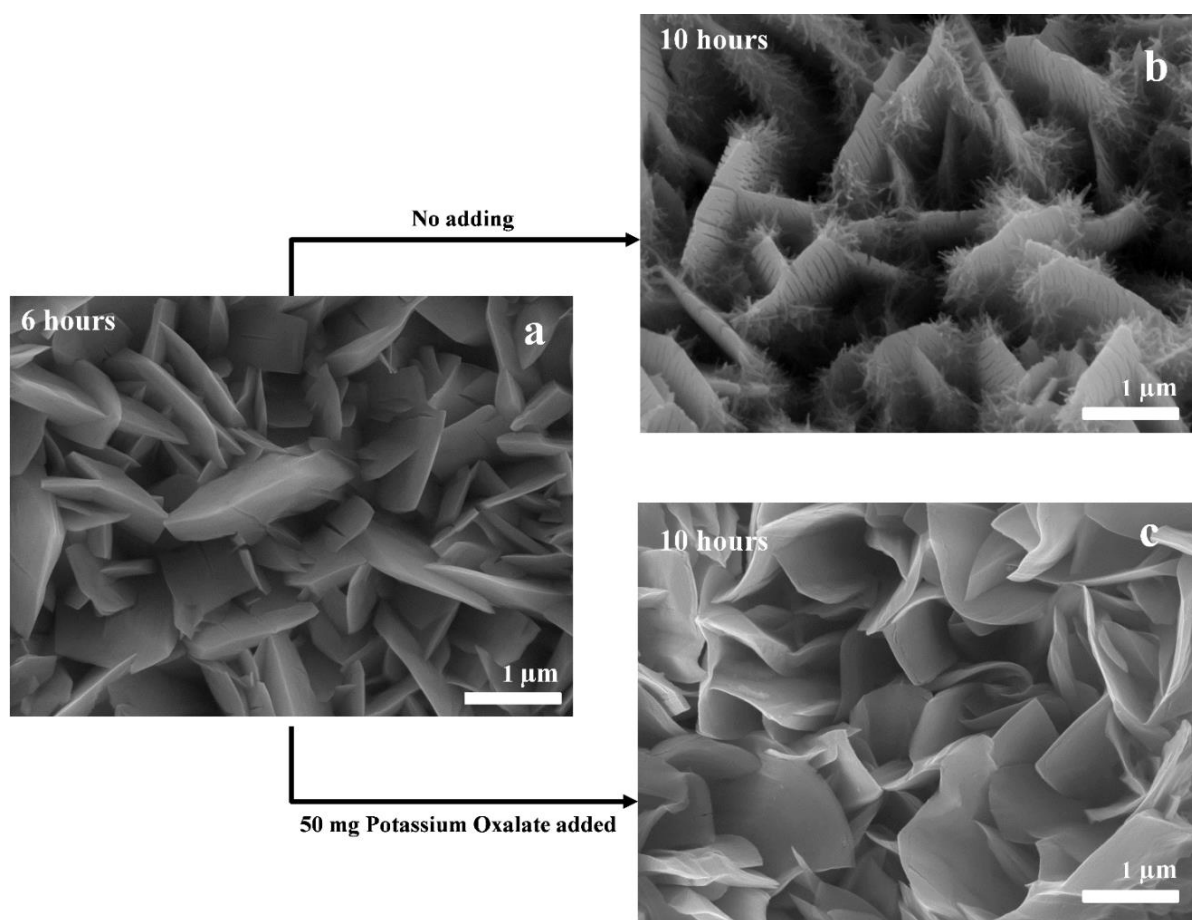


Figure S8 SEM images of 2D branched nanostructures in order to study effects of oxalate ligand. a) The structure obtained from the 6 hr reaction. b) The structure obtained after 10 hours without extra oxalate ligand added. Hair-like branches were formed. c) When extra oxalate ligand was added after 6 hours reaction, there was no branch observed even after 10 hours of the reaction.

S9: Microstructures of films when decreasing the amount of water (FTO side facing up)

Similar to the condition to synthesize the sample 1b (the ratio of PTO:water:DEG was 0.438g:7.5mL:32.5mL) if the amount of water was slightly decreased (PTO:water:DEG=0.438g:5mL:35mL) and the FTO side was up against the autoclave wall, the film became a mixture of 0D and 1D.

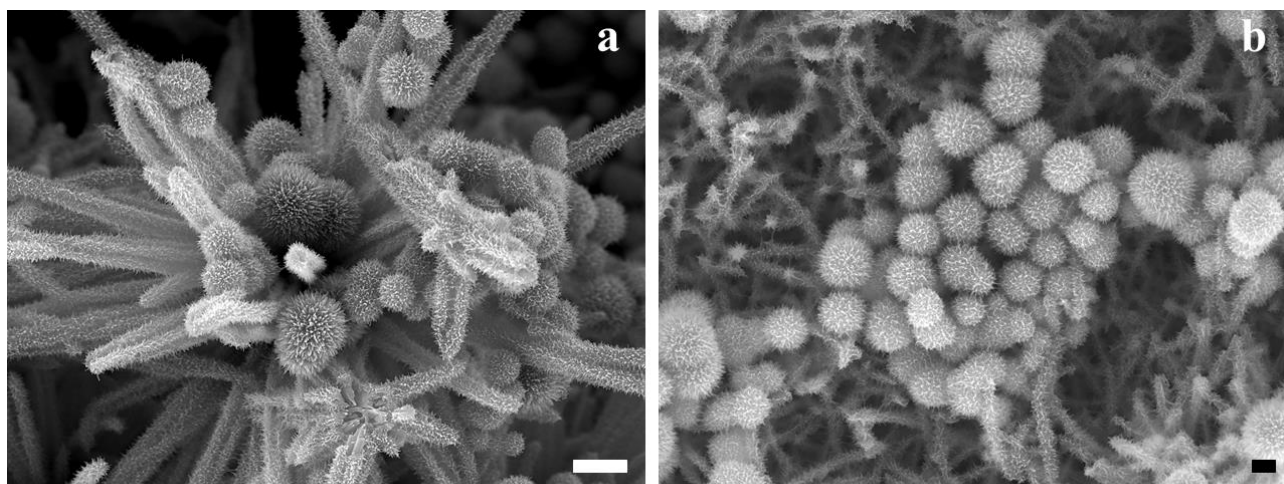


Figure S9 SEM images showing microstructures of film when the ratio of PTO:water:DEG was 0.438g:5mL:35mL. a) at high magnification and b) at low magnification. (scale bare=1 μ m).

This evidence suggests that lowering the amount of water could slow down the development of branches and the core structures have time to develop into a higher dimension of 1D. On the other hand, increasing water (as in the case of sample 1b) promotes the development of branches rather than the core structures. Therefore, the 0D-branched structures are formed quickly without the development of core structures. These 0D particles are deposited on FTO and obstruct the development of 1D. Only pure 0D can be observed as shown in Figure 1b and its cross-sectional image in Figure 5e.

S10: XRD of the best films of each dimensional nanostructure tested in this work.

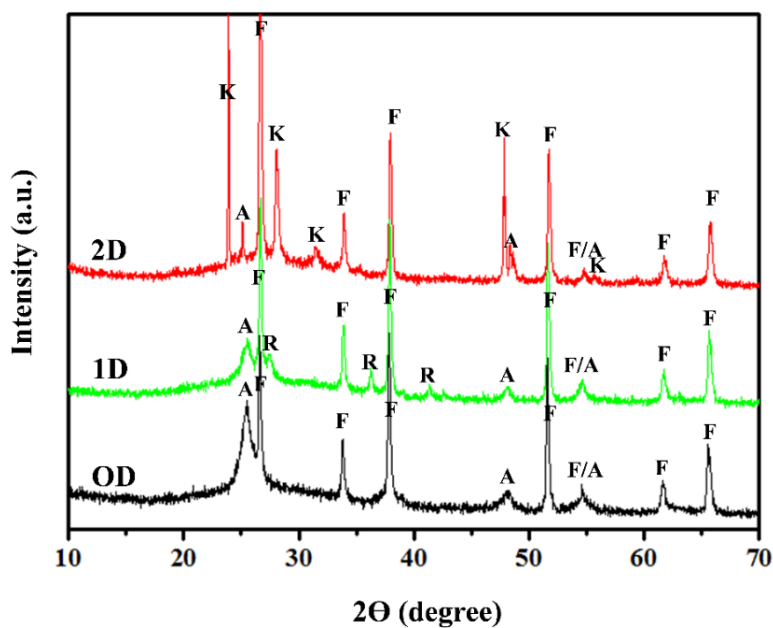


Figure S10 XRD patterns of the best dimensional films which were shown in the main text.

S11: KM function plot of dimensional films

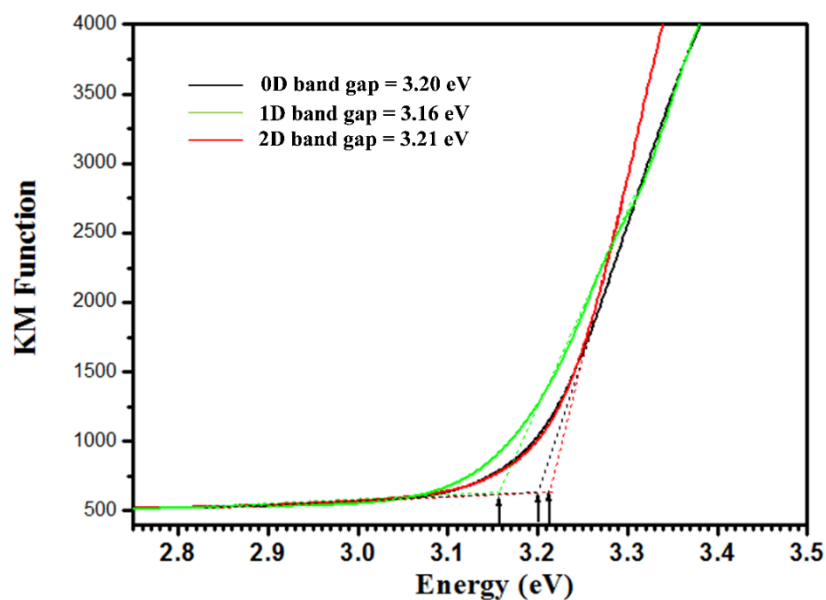


Figure S11 KM function plots evaluating the band gap of dimensional TiO₂ films. The band gaps of 0D, 1D and 2D films are 3.20, 3.16, and 3.21 eV, respectively.

S12: Analysis of gas products from PEC water splitting by a gas chromatography

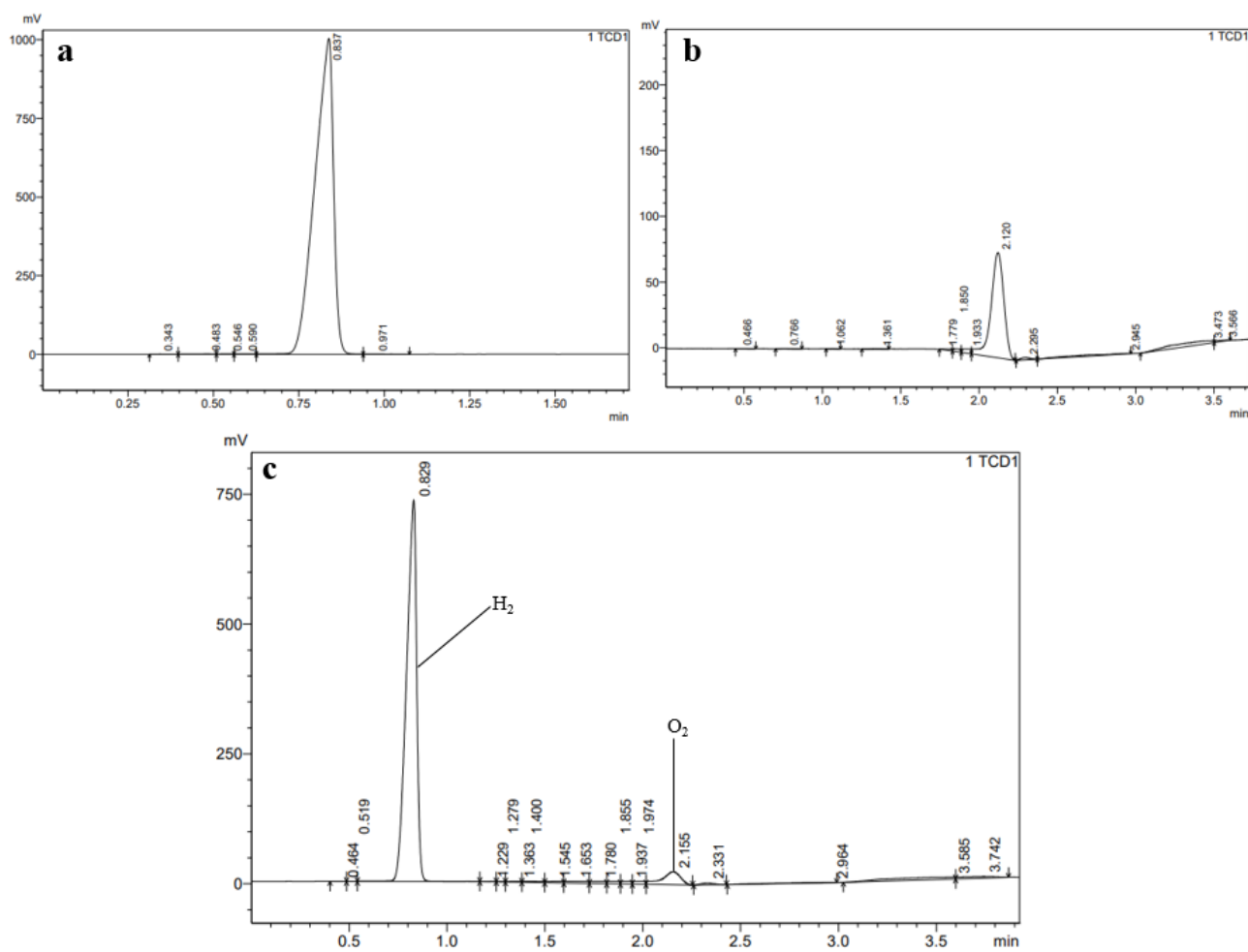


Figure S12 The GC chromatograms of the gas products. **a)** The standard hydrogen gas (H_2), **b)** the standard oxygen gas (O_2), and **c)** the example evolved gas products from PEC water splitting.

S13: Stability test

The stability tests were performed with the standard three-electrode configuration at the applied voltage of 1.23 V vs RHE using 1 M KOH as the electrolyte.

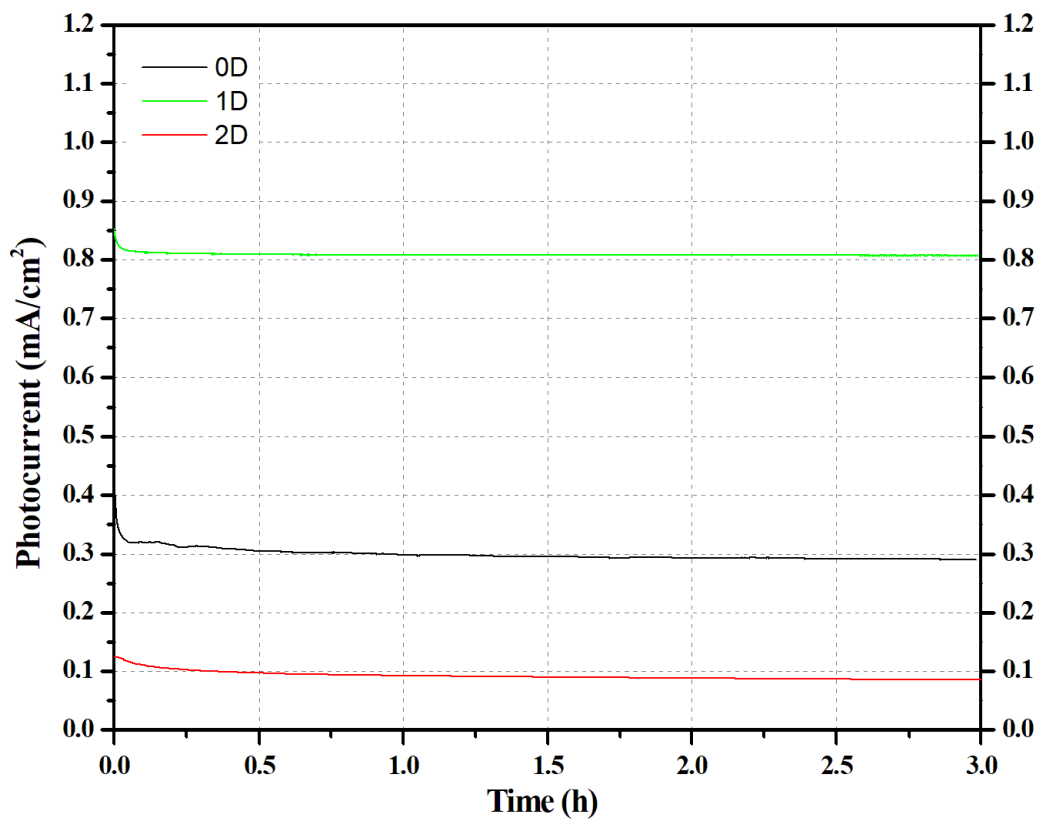


Figure S13 stability tests of various dimensional-BTN films.

S14: Open-circuit photovoltage decay (OCPVD) to determine the electron life time

The open-circuit voltage decay (OCPVD) is a well-established method to assess photogenerated electron life time of materials.¹ In a typical OCPVD test, the electrodes were left to reach the first equilibrium at the open circuit in the dark, followed by illumination until they reached the second equilibrium. After that, the light was turned off to monitor the voltage decay. As shown in Figure S14, after turning the light on, the photoelectrodes exhibited negative shifts due to the accumulation of electrons inside the nanochannels while the holes were scavenged by OH⁻ in the electrolyte.² When the photoelectrodes reached the steady state, the light was stopped; therefore, electrons recombined with holes again, causing the voltage decay. The higher recombination rate, the faster the time the electrodes reached the first equilibrium. In Figure S14, it is clear that the V_{oc} of 0D is decay back to $\sim -0.4V$ (first equilibrium) quicker than other samples, indicating the more rapid charge recombination. Comparing between the 1D sample with pure anatase and 1D with mixed anatase-rutile, it is clear that the mixed phase sample has a longer voltage decay time, indicating that the band-aligned 1D has much better charge separation and longer electron life time.

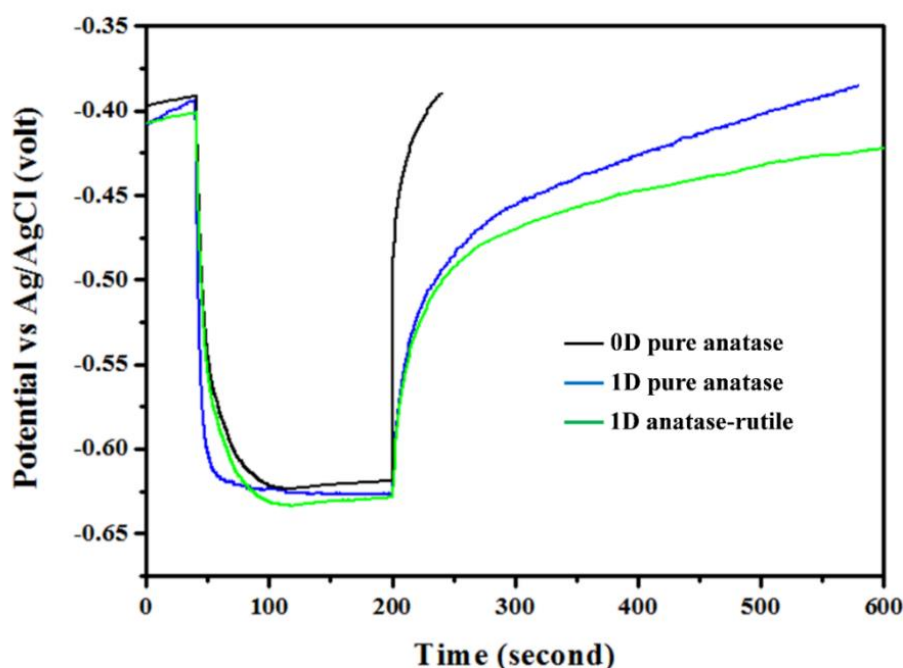


Figure S14 open-circuit photovoltage decay (OCPVD) determining effects of dimension band alignment towards electron life time.

S15: Nanoarchitectural characterization by time-dependent SEM and XRD analyses

Time-dependent SEM analysis found that the 1D-branched nanostructures with a mix phases of rutile+anatase are step-wise growth. The first step is the development of the trunk as the core, which happened during the first hour of synthesis, as shown in Figure S15.1a. After 2 hours, buds began to develop (Figure S15.1b) on the core structure, which is much quicker than in case of 2D that need quite long reaction time before branches begin to grow. As shown in Figure S15.1d, branches fully cover trunks within just 4 hours of synthesis.

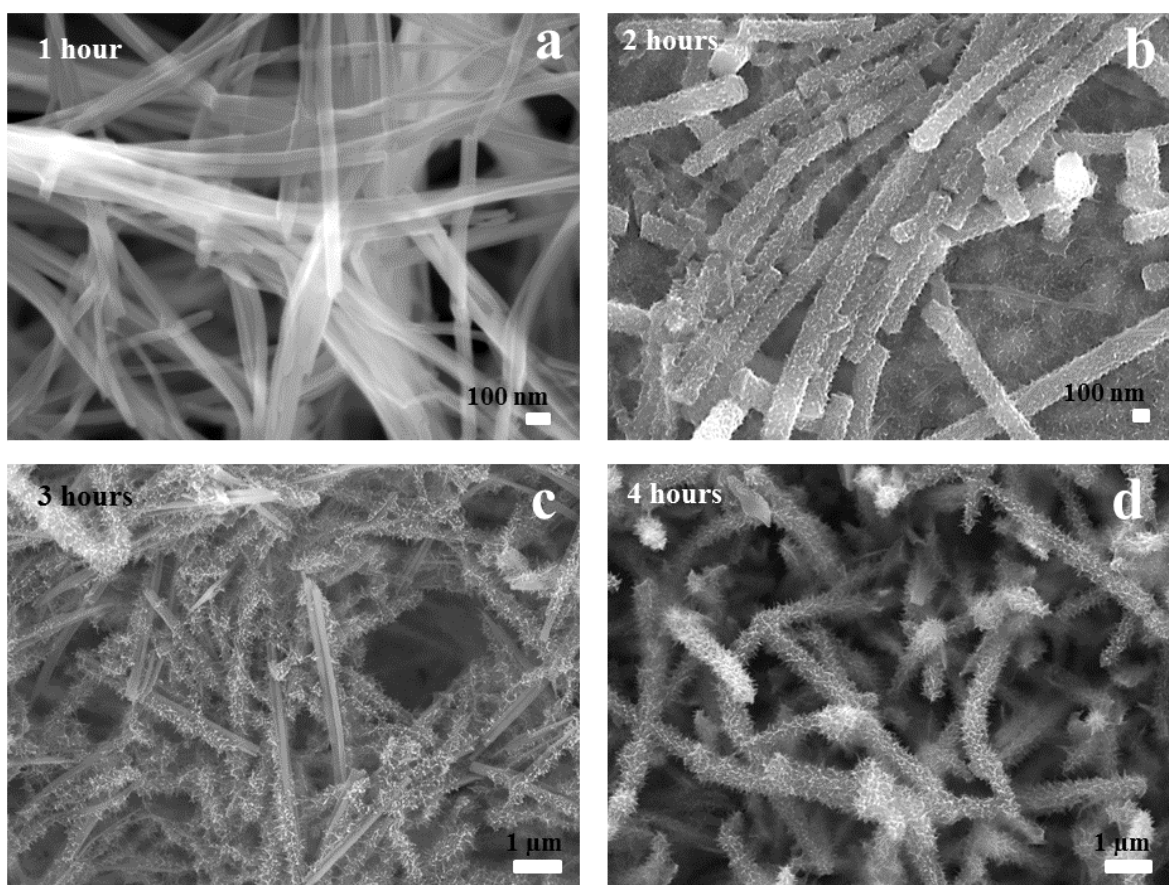


Figure S15.1 SEM images observing time-dependent structural development of 1D TiO₂ nanostructure from a) 1 hour, b) 2 hours, c) 3 hours, and d) 4 hours. It is clear that branches begin to grow much quicker than in the case of 2D as there are some branches observed after just 2 hours and fully cover the core structures after 4 hours.

The corresponding time-dependent XRD analysis reveals interesting phenomena. As seen in Figure S15.2a, in the first hour of synthesis, there appear only characteristic peaks of anatase. Then, after 4 hour of synthesis, rutile peaks are observed. The intensity of both anatase and rutile peaks tend to increase when the reaction time pass 8 hours. From these evidences, we propose that the crystal phase

of the trunks is anatase, while branches have both rutile and anatase growing simultaneously as shown in Figure S15.2b.

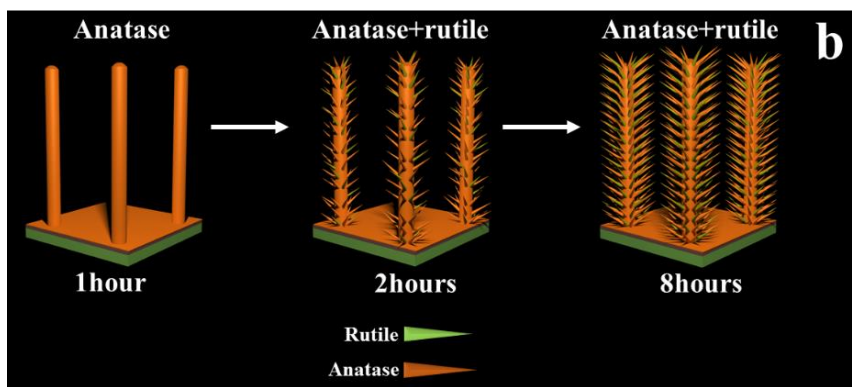
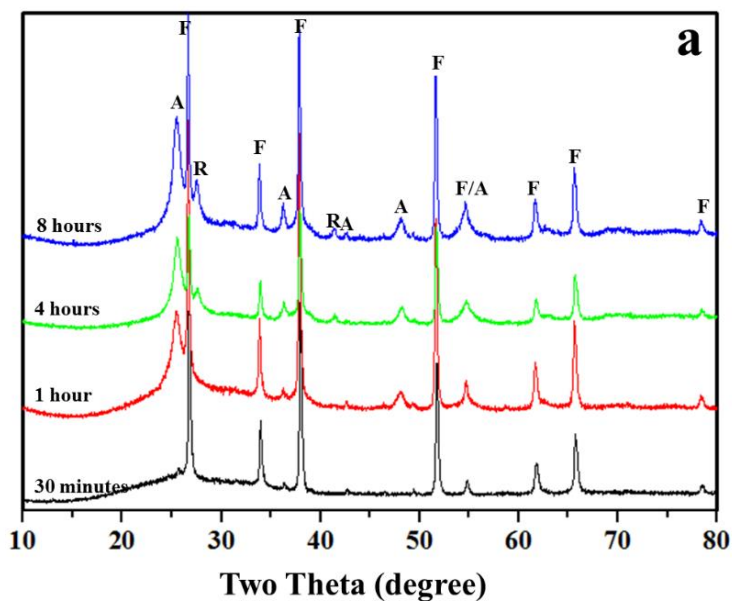


Figure S15.2 a) time-dependent XRD observation of band-aligned 1D film, and b) proposed growth processes.

S16: Long reaction time

Basically, the synthetic reactions in this work were completed within 10 h. We found that 10-hour reaction is sufficient to construct the dimensional nanostructures. For some recipes, the structures did not further grow after 10 hours. Moreover, longer reaction times than this could lead to a secondary layer with uncontrollable morphology in some recipes as shown in Figure S16a, or some impurity residues were found as shown in Figure S16b.

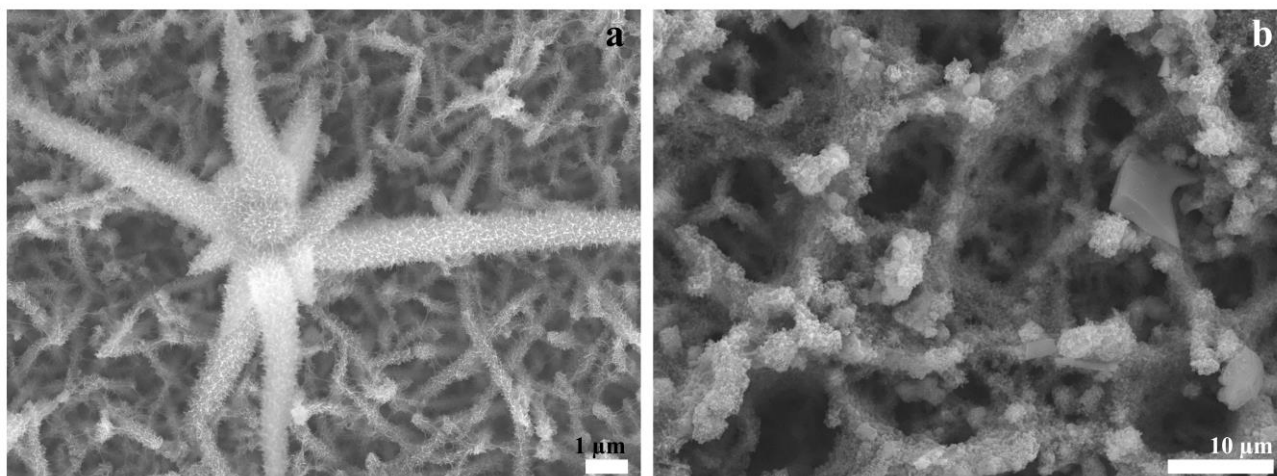


Figure S16 SEM images of the BNTs derived from the reaction time longer than 10 hours. **a)** An example structure derived from the recipes; PTO:water:GG of 0.438g:7.5mL:32.5mL with the reaction time of 16 h. **b)** An example structure derived from the recipes; PTO:water:GG of 0.438g:10mL:30mL with the reaction time of 24 h. All the samples were synthesized at the same fix temperature of 180 °C.

References

1. H. Cui, G. Zhu, Y. Xie, W. Zhao, C. Yang, T. Lin, H. Gu and F. Huang, *Journal of Materials Chemistry A*, 2015, **3**, 11830-11837.
2. B. H. Meekins and P. V. Kamat, *ACS Nano*, 2009, **3**, 3437-3446.