Electronic Supporting Information

Completely <001> Oriented Anatase TiO₂ Nanoarrays: Genetically Topotactic Growth and Orientation-Related Efficient Photocatalysis

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Scheme S1. Illustration of highly oriented $\{001\}$ -dominated anatase TiO₂ nanocrystals (left) and non-oriented arranged $\{001\}$ -dominated anatase TiO₂ nanocrystals (right) under UV irradiation.



Figure S1. Schematic illustration of HF-vapor oxidation.



Figure S2. STEM image of ANA12 corresponding to the area outlined by the yellow rectangle in Figure 2a.



Figure S3. Low-(left) and high-magnification (right) SEM images of samples synthesized at 140 °C for (a) 1.0 h, (b) 2.0 h, (c) 3.0 h, (d) 4.0 h, respectively.



Figure S4. XPS spectra of ANA4 and ANA2 samples. (a) Survey scans, (b) F_{1s} peaks, (c) Ti_{2p} peaks, and (d) O_{1s} peaks.

These spectra show the peak of F_{1s} as well as those of Ti, O, and C elements. The high-resolution XPS spectra of F_{1s} core electrons obtained from the precursor crystals reveal a symmetric peak centered at 684.7 eV, attributable to Ti–F species in oxofluorotitanate-typed compounds (Fig. S4b).¹⁻³ The atomic percentage of F species found from the precursor ANA2 was 22.7%, which is nearly three times of the content found from anatase TiO₂ nanoarrays (ANA4). The presence of F in the anatase TiO₂ nanoarrays (ANA4) can be attributed to surface-absorbed Ti-F species.⁴ These results further confirm that the obtained precursor is fluorine-containing crystals (TiOF₂).



Figure S5. XRD patterns of the as-synthesized samples at 140 °C for (a) 4.0 h, (b) 8.0 h, (c) 12 h, (d) 20 h, (e) 60 h, respectively. The bottom pattern with vertical bars is derived from the JCPDS card (No. 21-1272) of tetragonal anatase.



Figure S6. Low-(left) and high-magnification (right) SEM images of the samples grown at 140 °C for (a) 8.0 h, (b) 12 h, (c) 20 h, (d) 60 h, respectively.



Figure S7. (a) Raman spectra of the samples synthesized at 140 °C for 4.0-60 h. (b) is the enlarged spectra of (a) between 300 and 800 cm⁻¹.



Figure S8. (a) Photocatalytic degradation of AOII by ANA system, (b) UV–Vis spectral evolution of AOII with reaction time in ANA12 system.



Figure S9. SEM images of side view of (a) P25 and the as-synthesized samples grown at 140 $^{\circ}$ C for (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h, (f) 8 h, (g) 20 h, (h) 60 h, respectively.

The content of P25 on the P25 film (11.46 mg) is almost the same with the content of TiO₂ on ANA12 (11.20 mg). The thickness of P25 on the film is about 16 μ m, which is thicker than ANA12 (3.0 μ m), this can be attributed to the fluffy structure and low density of P25. The approximate value of the thickness of ANA1-60 were as follows: 0.7 μ m (ANA1), 1.0 μ m (ANA2), 1.4 μ m (ANA3), 2.0 μ m (ANA4), 2.5 μ m (ANA8), 3.0 μ m (ANA12), 7.0 μ m (ANA20), 24 μ m (ANA60).



Figure S10. The variation tendency of photocatalytic efficiency (PE), crystallographic preferred orientation (CPO) and the thickness of the as-synthesized samples .



Figure S11. UV–Vis diffuse reflectance spectra of ANA12 (red) and P25 (blue).



Figure S12. Corresponding photographs of ANA12 film surfaces before (a) and after (b) dripping water droplet.



Figure S13. A possible pathway for atrazine degradation under the photocatalysis of ANA12.



Figure S14. Photocatalytic degradation of atrazine by ANA12 in various cycling experiments.



Figure S15. The effect of tert-butyl alcohol (t-BuOH) (•OH scavengers) on the photodegradation of AOII dye by ANA12 system.



Figure S16. A possible pathway for AOII degradation under the photocatalysis of ANA12.



Figure S17. Photocatalytic degradation of AOII by ANA12 in repeated experiments: the test of stability and cycling.

References

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