

Supplementary Information

Phase Transition Behaviour and Mechanism of 2D TiO₂(B) Nanosheets through Water-mediated Removal of Surface Ligands

Shirui Xie,^a Lijing Fan,^a Yanxin Chen,^a Jiliang Cai,^a Fan Wu,^a Kecheng Cao^{*a} and Pengxin Liu^{*a}

Directory

| | |
|---|--------------------|
| Characterization of the TiO ₂ (B) nanosheets precursor..... | Fig. S1-3 |
| Characterization of calcined TiO ₂ (B)..... | Fig. S4-6 |
| Characterization of water phase-treated TiO ₂ (B)..... | Fig. S7-12 |
| Pretreated TiO ₂ (B) nanosheets with H ₂ O ₂ solution..... | Fig. S13-14 |

^a School of Physical Science and Technology, ShanghaiTech University, Shanghai, China.

Email: caokch@shanghaitech.edu.cn; liupx@shanghaitech.edu.cn

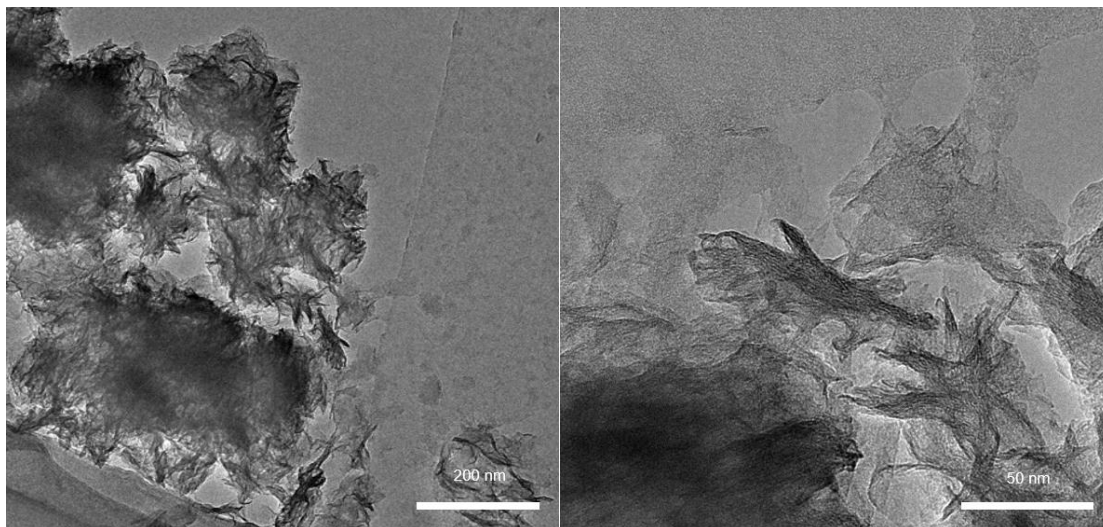


Fig. S1 Representative TEM images of the $\text{TiO}_2(\text{B})$ nanosheets precursor.

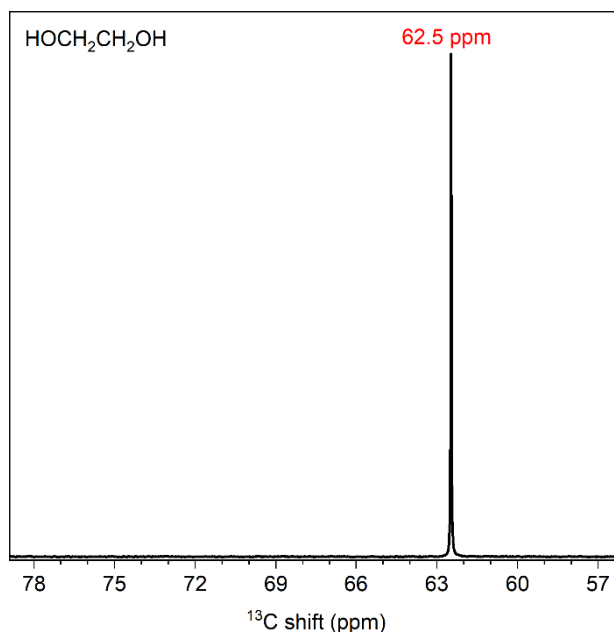


Fig. S2 ^{13}C ss-NMR of EG shows a singlet peak at 62.5 ppm, lower than the ^{13}C ss-NMR of $\text{TiO}_2(\text{B})$ nanosheets, which indicates a different chemical environment.

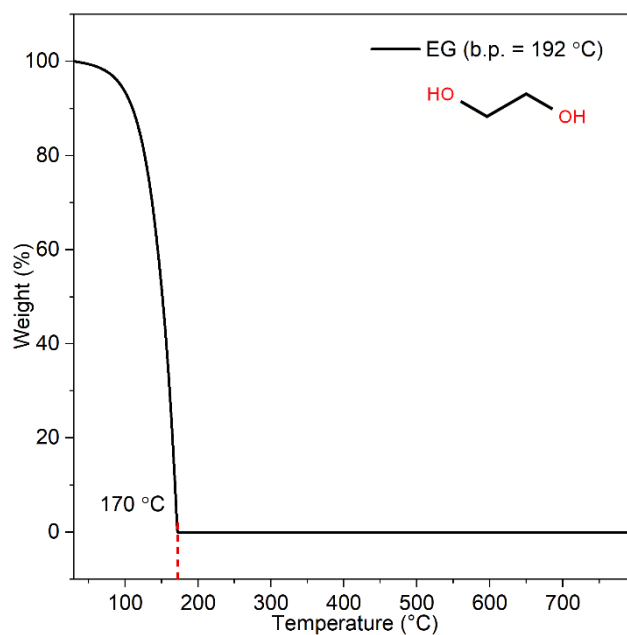


Fig. S3 TGA curve of free EG. In air flow, free EG completely evaporated at temperature lower than its boiling point.

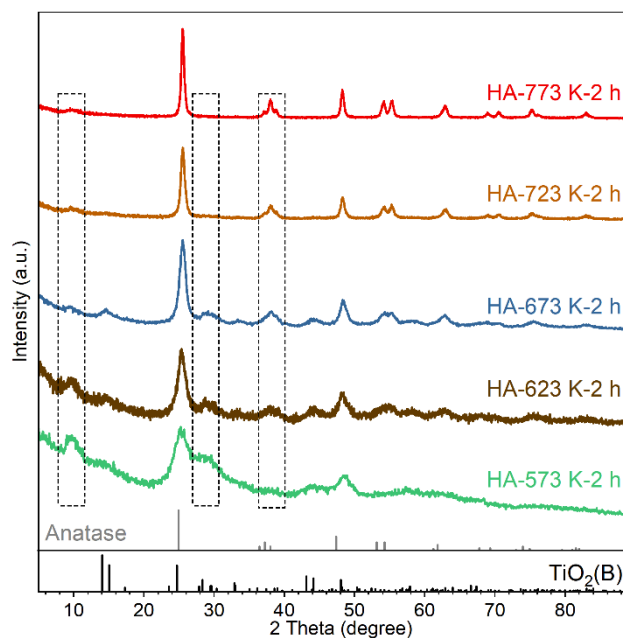


Fig. S4 XRD patterns of calcined TiO₂(B) nanosheets at different temperatures for 2 hours. The phase transition was completed at 773 K.

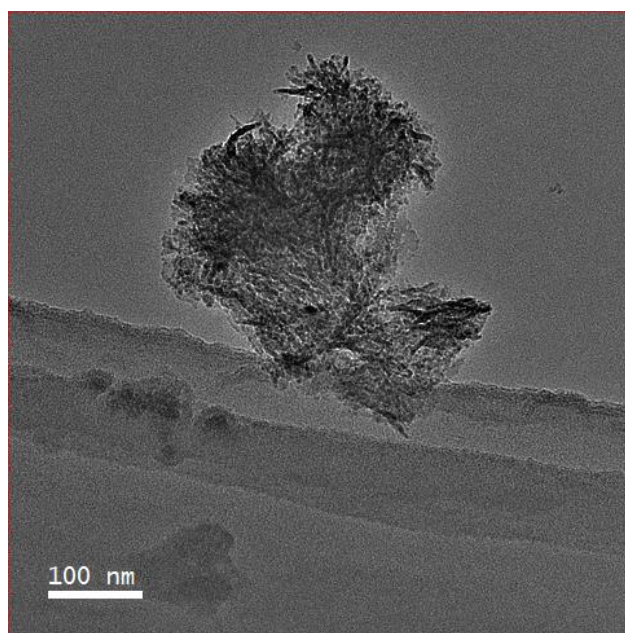


Fig. S5 Representative TEM image of HA-773 K-2 h.

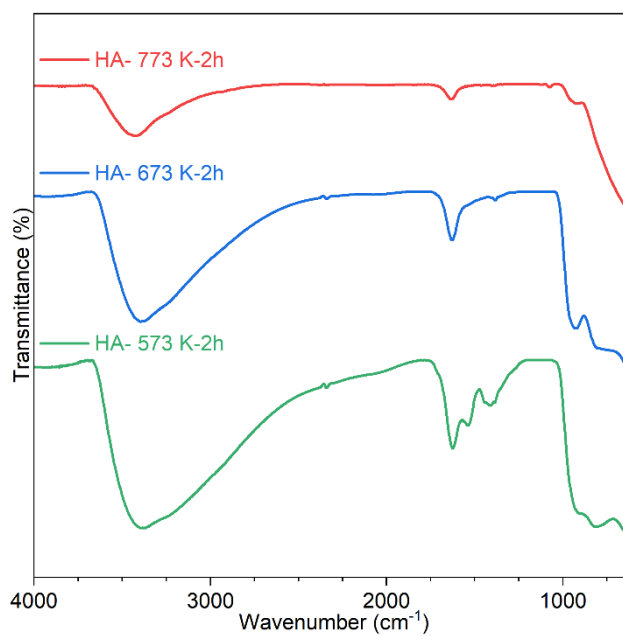


Fig. S6 FT-IR spectra of samples obtained after heat treatment in air at 573 K, 673 K, 776 K for 2 hours. As the temperature increased, the amount of EG ligand residue decreased, proved by the loss of intensities of peaks at 2932, 2872, 1080 cm^{-1} .

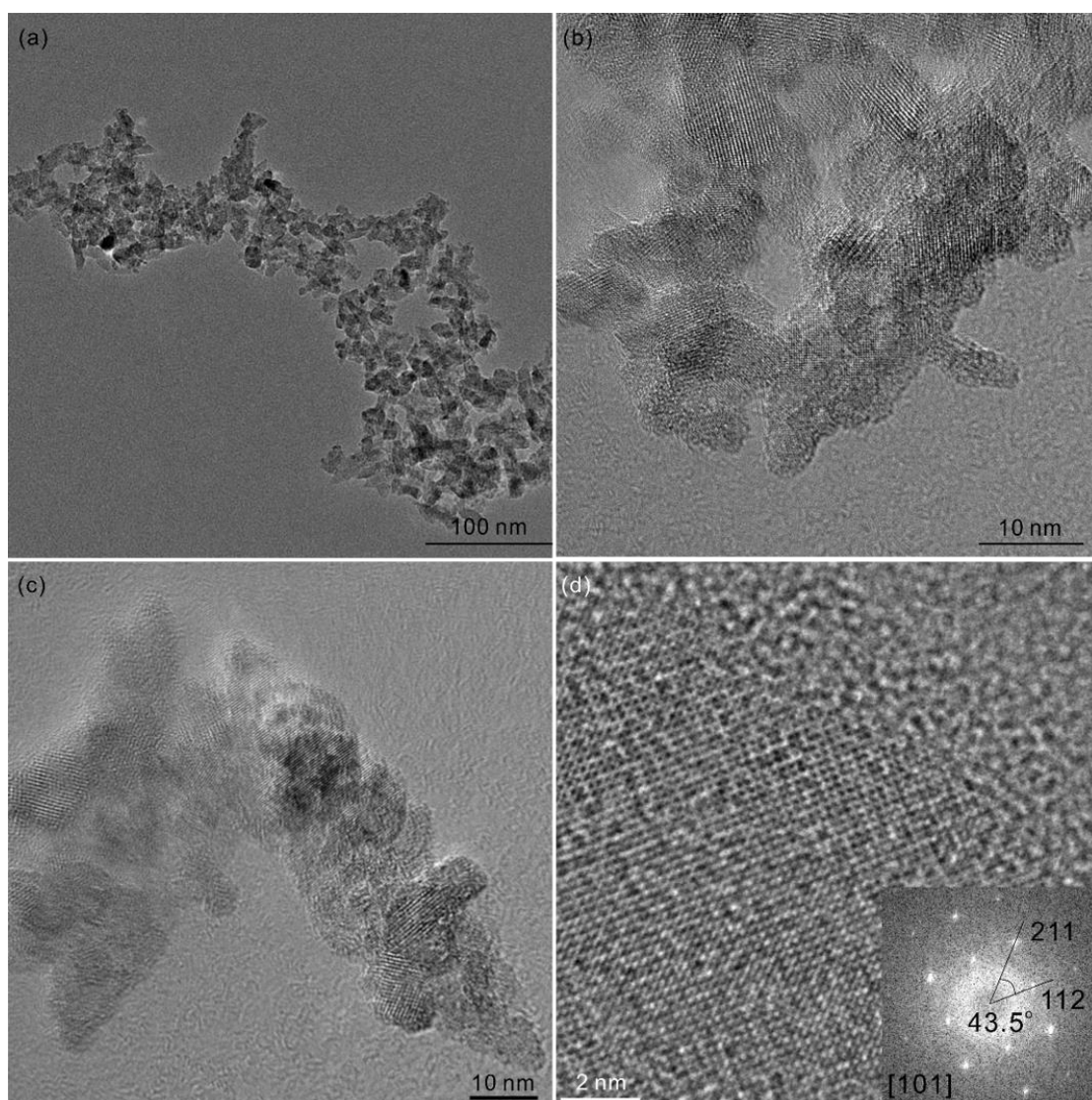


Fig. S7 (a) TEM image and (b, c, d) HRTEM images of HW-373 K-3 h, inset of (d) is the FFT result of the HRTEM image.

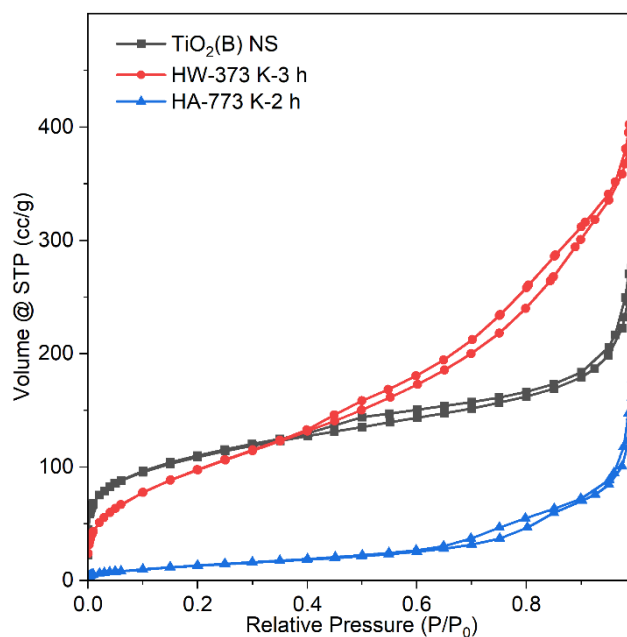


Fig. S8 BET curves of $\text{TiO}_2(\text{B})$ nanosheets, sample obtained after heating in water at 373K for 3 hours and sample obtained after heating in the air at 773K for 2 hours. Their specific surface area was 341.5 m^2/g , 214.9 m^2/g and 53.2 m^2/g , respectively.

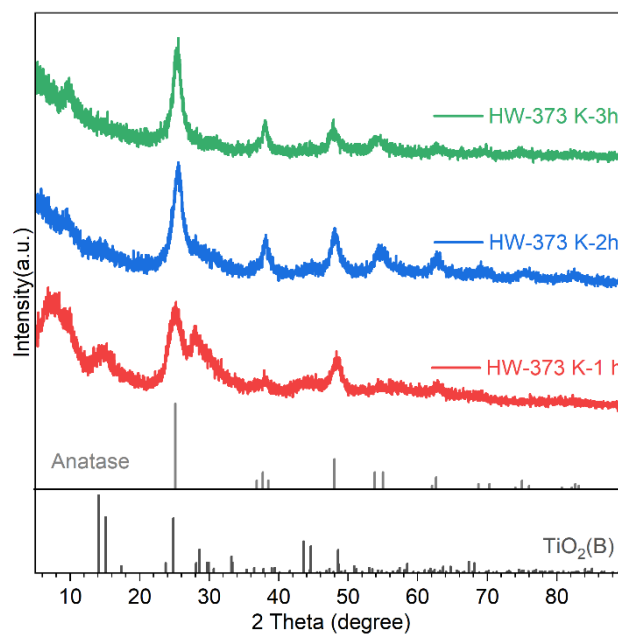


Fig. S9 XRD patterns of samples obtained after heating $\text{TiO}_2(\text{B})$ nanosheets in water at 373K for 1, 2, 3 hours, respectively. The decreased intensity of peaks at 28.6° and the increased intensity of peaks at 38.1° indicated the phase transition.

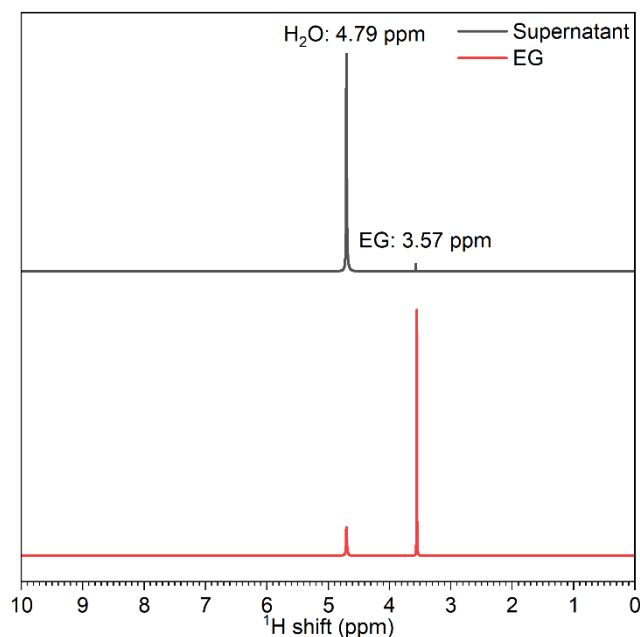


Fig. S10 NMR of supernatant after heating TiO₂(B) nanosheets in water, in comparison with the NMR of free EG, which proves that free EG is formed and released into the water phase from the material.

¹H NMR spectra were recorded on Bruker 500 MHz with 5 mm NMR tube and D₂O as solvent. ¹H chemical shifts were referenced to water at 4.79 ppm. Ethylene glycol was measured by 64 scans while supernatant was 128 scans.

Table S1 Quantification of surface ligands. *m* stands for the initial mass of materials for TGA, while *WL* stands for mass change in the 220 -450 °C range. *S* stands for surface area. ΔS stands for the differences of the initial surface area and the surface area of corresponding calcined samples at 450 °C.

| Sample | <i>m</i> /mg | <i>WL</i> /mg | <i>S</i> /m ² | ΔS /m ² | <i>n</i> _{-OH} /mmol | <i>n</i> _{EG} /mmol |
|--------------|--------------|---------------|--------------------------|----------------------------|-------------------------------|------------------------------|
| Precursor | 7.028 | 1.632 | 2.400 | 2.113 | 0.0374 | 0.0294 |
| HW-373 K-1 h | 6.588 | 0.884 | 1.989 | 1.686 | 0.062 | 0.0074 |
| HW-373 K-2 h | 10.026 | 0.909 | 2.449 | 1.964 | 0.0815 | 0.0040 |
| HW-373 K-3 h | 7.061 | 0.479 | 1.517 | 1.167 | 0.0532 | 0 |

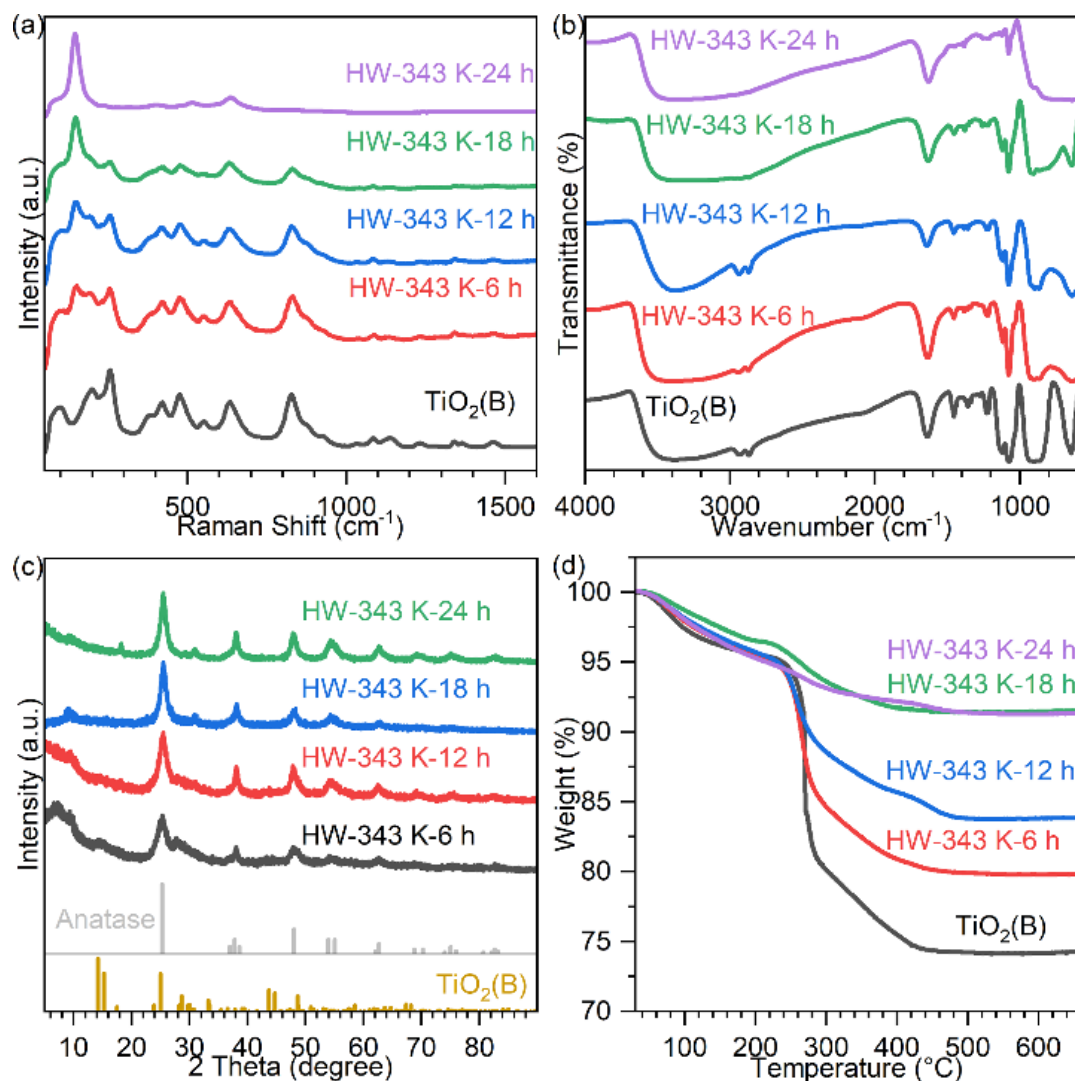


Fig. S11 (a) Raman, (b) FT-IR spectra, (c) XRD and (d) TGA results of time-tracking experiments by heating TiO₂(B) nanosheets in water at 343K for 6, 12, 18, 24 hours.

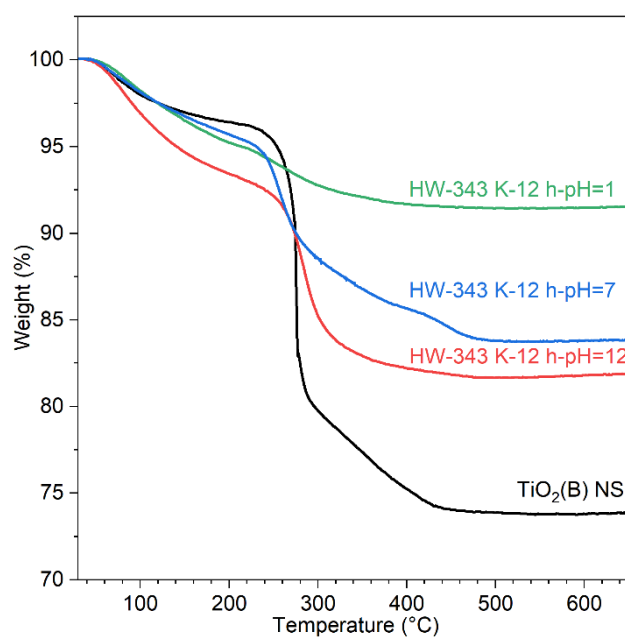


Fig. S12 TGA results of samples obtained after heating TiO₂(B) nanosheets in water at 343 K with pH = 1, 7, 12.

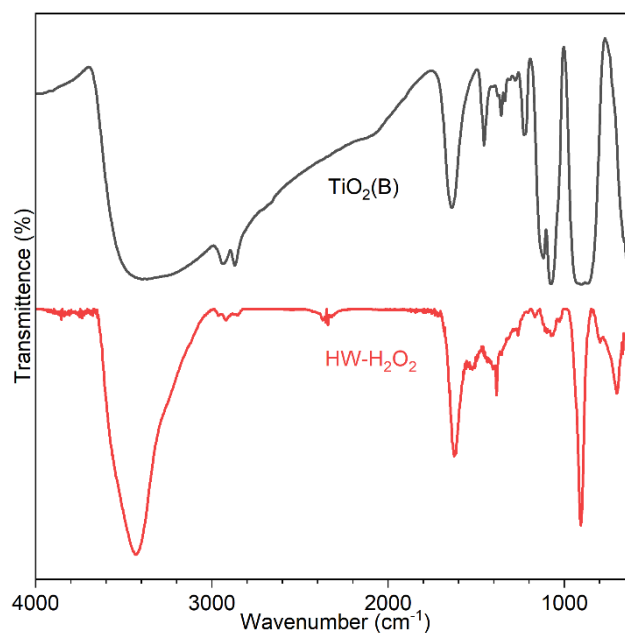


Fig. S13 FT-IR spectra of samples obtained after H₂O₂ treatment. The decreased peaks at 2932, 2872, 1080 cm⁻¹ proves that EG ligands are partly removed from the surface of the TiO₂(B) nanosheets.

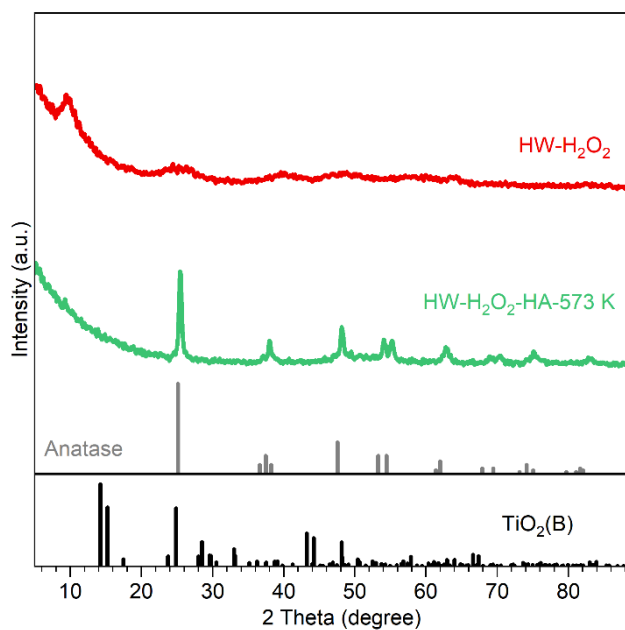


Fig. S14 XRD patterns of sample pretreated with H₂O₂ and the corresponding calcined sample. After treated with H₂O₂ for 12 hours, the TiO₂(B) nanosheets became amorphous and converted to well crystallized anatase after heated in the air at 573 K for 2 hours. Without H₂O₂ pretreatment, HA-573 K-2 h was not fully converted into anatase (see **Fig. S4**).