

Supporting Information for

Large-Scale Synthesis of Metastable TiO₂(B) Nanosheets with Atomic Thickness and Their Photocatalytic Properties

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Guolei Xiang, Tianyang Li, Jing Zhuang, Xun Wang*

Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

Contacting e-mail: wangxun@mail.tsinghua.edu.cn

¹⁰Experiment

Synthesis of Atomic Thickness Nanosheets of TiO₂(B) and Carbon Modification

All the reagents used in this work, including TiCl₃ aqueous solution (~15%), ethylene glycol and sodium iodide were of analytical grade from the Beijing Chemical Factory of China.

In a typical synthetic procedure, 1ml TiCl₃ aqueous solution and 1ml deionized water were mixed ¹⁵ with 30ml ethylene glycol in a 40ml Teflon-lined autoclave. After stirred for 10 seconds with a glass rod, the mixture was sealed and then kept at 150°C for 4 hours in an oven. The obtained products could be separated by centrifugation and were washed with water and ethanol for four times. Powder samples were dried at 60°C in an oven. To dope the samples with carbon, the as-obtained films were calcined at 250°C for 4 hours in a vacuum oven. And TiO₂(B) nanowires were prepared as reported ²⁰ previously¹⁶.

The synthesis process can also be performed in a flask and heated in an oil bath at 150°C for 4 hours.

Doping TiO₂(B) Nanosheets with Iodine

To dope TiO₂(B) nanosheets with iodine, the dried sample (0.3g) was mixed with sodium iodine aqueous solution (20 ml, 0.5mol/L) and stirred for 5 hours at room temperature. After the adsorptive ²⁵ equilibrium of I⁻ on the surface of the films, the materials were separated by centrifugation and further annealed at 100°C for 5 hours in an oven. The color gradually changed from white to dark yellow due to the migration of iodine to the channels of TiO₂(B).

Characterization

Crystal structures of the as-prepared samples were determined from X-ray diffraction (XRD) ³⁰ patterns, which were recorded on a Rigaku diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), operating at 40 kV and 200 mA and a scanning rate of 6° per minute. Morphologies of the products

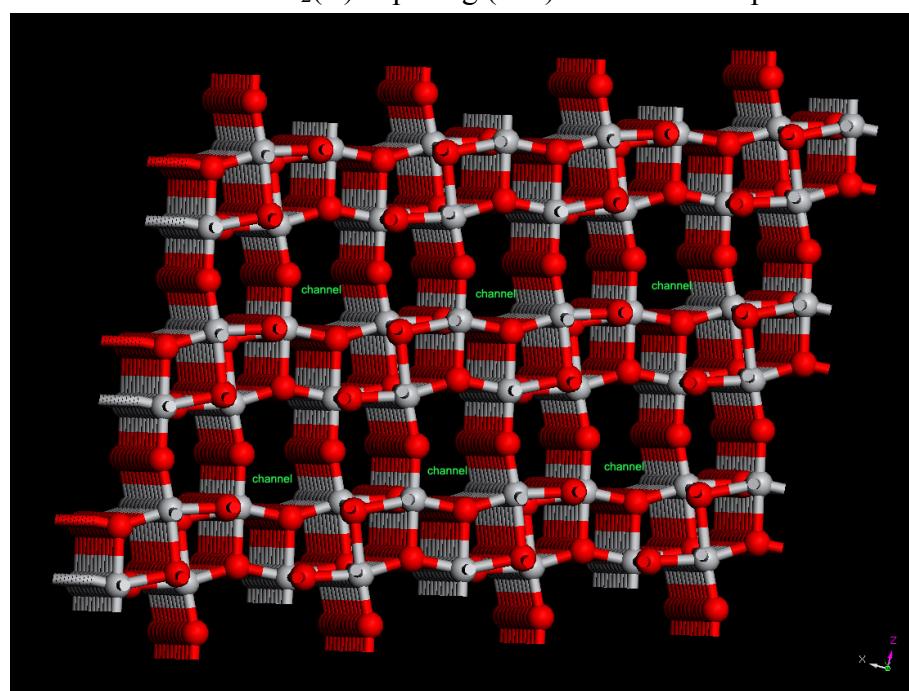
were investigated on a high-resolution transmission electron microscopy (HRTEM) of FEI Tecnai F20 with an accelerating voltage of 200 kV. Characterization of the thickness was conducted by Atomic force microscopy on SPA-300HV.

The nitrogen sorption isotherm was measured by volumetric method on an automatic adsorption instrument (Micromeritics, ASAP2010) at liquid nitrogen temperature (77 K). Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method from the data in a P/P_0 range between 0.05 and 0.2.

Photocatalytic Test

Photocatalytic degradation of Methyl Orange (MO) under ultraviolet and visible light was used to evaluate the reactivity of $\text{TiO}_2(\text{B})$ nanosheets and the modified products. Photocatalysts (0.05g, $\text{TiO}_2(\text{B})$ nanosheets, $\text{TiO}_2(\text{B}):C$, P25, $\text{TiO}_2(\text{B}):I$ and $\text{TiO}_2(\text{B})$ nanowires) were dispersed in 100ml deionized water by ultrasonication for 10 minutes and then mixed with MO (2ml, 1mmol/L) in a reactor. Before irradiation, the solutions were stirred in dark for 30 min to ensure the equilibrium of the working solution. Photocatalytic reactions of $\text{TiO}_2(\text{B})$ nanosheets, P25 and $\text{TiO}_2(\text{B})$ nanowires under UV light were irradiated by a 300W Xenon lamp. UV light was filtrated by a cut-off filter ($\lambda > 420\text{nm}$) to test the visible light reactivity of $\text{TiO}_2(\text{B}):C$ and $\text{TiO}_2(\text{B}):I$. The decreasing concentration of MO was reflected by monitoring the absorbency at 465nm. Before measuring the absorbency, the samples were centrifuged to remove the catalysts.

Figure S1. Ball and stick model of $\text{TiO}_2(\text{B})$ exposing (010) facet and the open channels as well as TEM images.



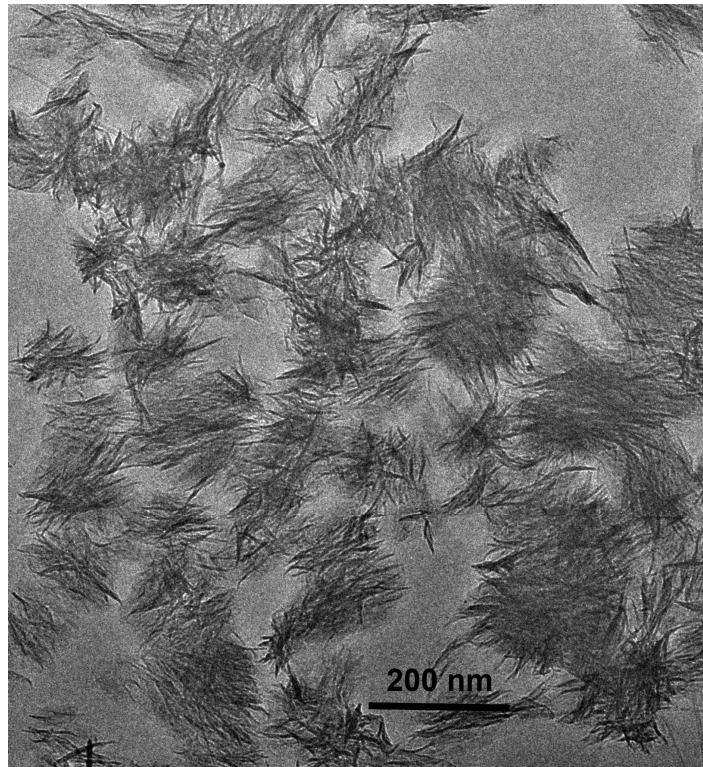
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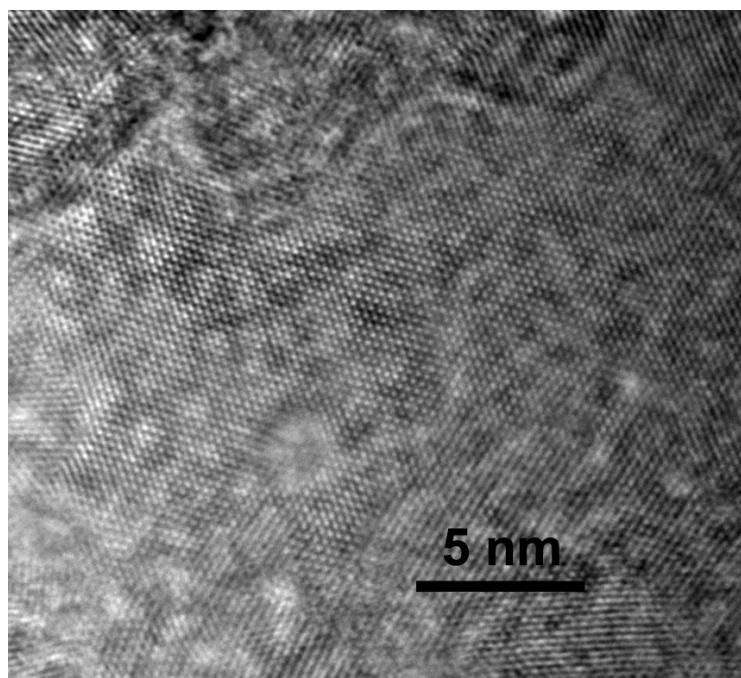


Figure S2. Results of $\text{TiO}_2(\text{B}):\text{C}$ calcined at 250°C for 4 hours and $\text{TiO}_2(\text{B}):\text{I}$ annealed at 100°C for 5 hours. (a) X-ray Photoelectron Spectroscopy (XPS) data of $\text{TiO}_2(\text{B}):\text{C}$. (b) XPS result of $\text{TiO}_2(\text{B}):\text{I}$. Photocatalytic degradation methyl orange $\text{TiO}_2(\text{B}):\text{C}$ (c) and $\text{TiO}_2(\text{B}):\text{I}$ (d) under visible light ($\lambda > 420\text{nm}$).

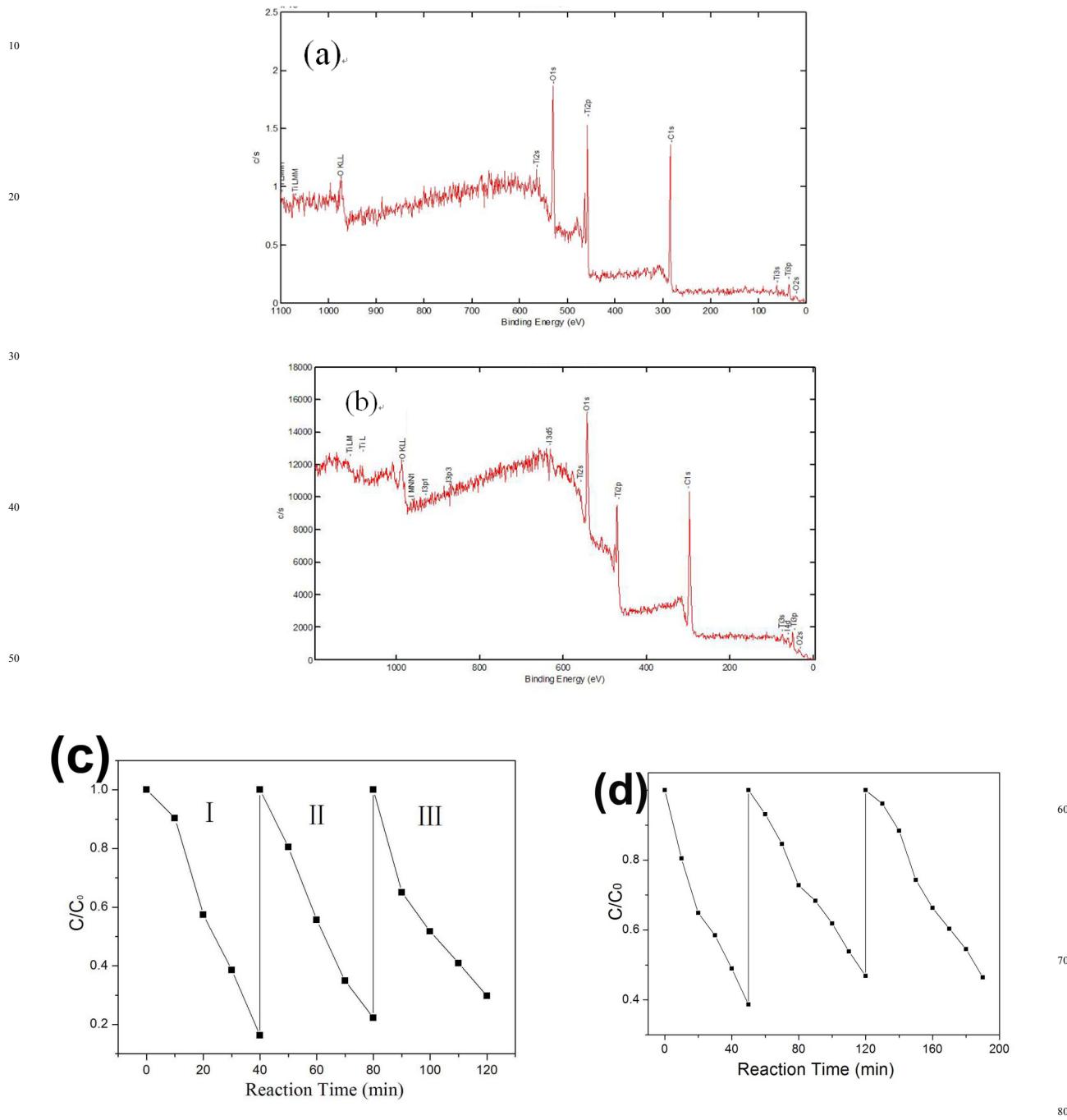
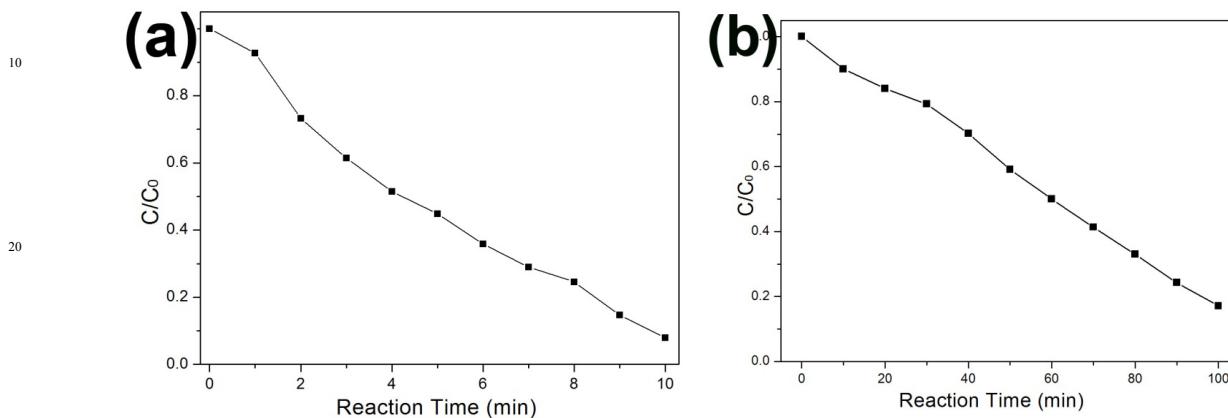
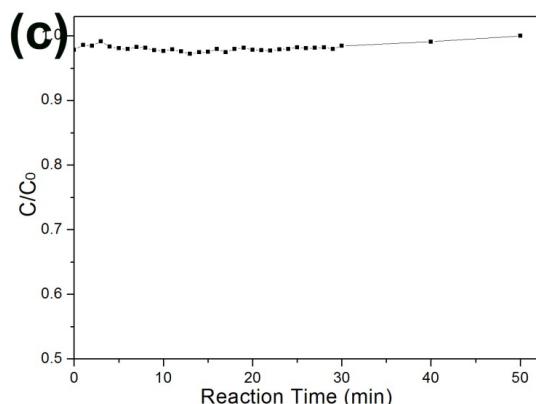


Figure S3. Photocatalytic degradation of MO under UV irradiation by (a) P25, (b) $\text{TiO}_2(\text{B})$ nanowires and (c) without any photocatalyst.



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Figure S3(b): Photocatalytic degradation of MO under UV irradiation by $\text{TiO}_2(\text{B})$ nanowires. The plot shows C/C_0 vs Reaction Time (min).



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Figure S3(c): Photocatalytic degradation of MO under UV irradiation without any photocatalyst. The plot shows C/C_0 vs Reaction Time (min).

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