Supporting Information

EXPERIMENTAL SECTION

Chemicals

Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer (Pluronic P123, PEO20–PPO70–PEO20, MW = 12000) was purchased from Sigma-Aldrich (USA). Titanium isoprppoxide (TTIP) was obtained from Aladdin Industrial Corporation (Shanghai, China). Concentrated hydrochloric acid, NaOH, and absolute alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. $NaBH_4$ was provided by Tokyo Chemical Industry Co. Ltd (TCI). All the chemicals were used as purchased without further treatment.

Synthesis of ultrathin TiO_2 nanosheets

In the synthesis of ultrathin TiO_2 nanosheets, 400 mg P123 was dissolved in 7.6 ml ethanol (EtOH) by an ultrasonic disperse method (solution A); and during vigorous stirring, 2 ml Titanium isopropoxide (TTIP) was added into 1.1 ml concentrated HCl solution (solution B) and stirred for 15 min. Then, solution A was added into solution B. After stirring for another 30 min, 5 ml mixed solution with 40 ml EG was transferred into a 90 ml autoclave and heated at 150 ^oC for 20 h. The products were washed and centrifuged with deionized water (DI water) and ethanol several times to remove the organic template. The white collections were dried at 60 ^oC for 24 h to obtain the raw-TiO_2 nanosheets. The raw-TiO_2 nanosheets were annealed at 400 ^oC for 1 h in the air. Then ultrathin TiO_2 nanosheets with a mixed phase of anatase and rutile were collected for the further use.

Fabrication of black TiO_2 nanosheets

0.2 g TiO_2 nanosheets and 0.2 g $NaBH_4$ were mixed and ground at room temperature for 15 min thoroughly. Then the mixture was transferred into a porcelain boat and was placed in a tubular furnace, heated from room temperature to 220-300 ^oC under an N_2 atmosphere at a heating rate of 10 ^oC/min. The heated temperature was kept at the designated temperature for 20 min. After naturally cooling down to room temperature, simply washed with deionized water and ethanol several times to remove unreacted $NaBH_4$ and dried at 60 ^oC, the colored TiO_2 nanosheets was obtained. A series of different colored TiO_2 nanosheets tuned from light blue to black can be prepared by controlling the reaction temperature.

Characterization

Transmission electronic microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) morphologies were recorded on a JEM-2100 (JEOL, Japan) to observe the nano-morphology of TiO_2 nanosheets. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Focus diffractometer (Bruker AXS, Germany) using Cu Kα radiation. FTIR were recorded on TENSOR 27 FTIR spectrometer using KBr disks to explore the chemical bands of TiO_2 nanosheets. UV-vis diffuse reflectance spectra (UV-vis DRS, Cary 500) were conducted on to test the light adsorption performance of samples. Raman spectra measurements were carried on Renishaw Microscope System RM2000 with a 50 mW Ar^+ laser at 514.5 nm. The photoluminescence (PL) spectroscopy excited with 320 nm laser light was collected to understand the generation and recombination of light-generated e^--h^+ pairs in photocatalysts. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALABMK spectrometer using electrostatic lens mode with a pass energy of 100 eV. All binding energies were calibrated by using the contaminant carbon (C1s =284.6 eV) as a reference.

Photocurrent measurements

In this study, the black TiO_2 nanosheets /FTO electrodes were employed as photoanodes, and prepared by drop-coating method. Typically, 10 mg powder was dispersed into 2 mL EtOH by ultrasonic dispersion. Then the suspension was dropped onto transparent conducting glass (fluorine doped SnO_2 layer, FTO, 2.5 × 2 cm, 20 Ω/square, Nippon sheet glass, Japan), and dried in air at 60 °C to eliminate ethanol. Then the photoanodes were pressed at 1000 kg cm^{-2} between stainless-steel plates in a hydraulic press using aluminium foil to prevent adhesion to form a film (2 × 2 cm). The Photocurrents in this study were tested using three electrode system and the black TiO_2 nanosheets/FTO electrode used as photoanodes, platinum electrode as counter electrode, and Ag/AgCl electrode as the reference electrode. 1.0 M NaOH purged with N_2 was used as the electrolyte. An AM 1.5 solar power system (66984 with an AM 1.5G filter, Newport, USA) was used as light irradiation source. An electrochemical workstation (CHI 660E, Chen Hua Instrument, China) was employed to measure the photocurrent intensity of the samples under illumination (100 mW cm^{-2}) and dark. The transient photocurrent curves were measured under an applied bias of 0.6 V.

Photocatalyticactivity tests

The H_2 evolution of TiO_2 nanosheets photocatalysts was conducted using LabSolar-3AG photocatalytic activity test system (Perfect light Co., Beijing, China). Generally, 50 mg TiO_2 nanosheets photocatalysts was suspended with 10 mL methanol in 100 mL deionized water, and 2 mL chloroplatinic acid (10^{-5} mol L^{-1}) was added into the suspension to load the Pt. A 300 W Xenon lamp was employed as the light source. The gas chromatograph (7900, Techcomp Co., Shanghai, China) was used to detect the concentration of H_2, and Ar was used as carrier gas. The photodegradation of methyl orange (MO) was evaluated by monitoring the suspension of methyl orange in an aqueous solution during the photocatalytic reaction. And an AM 1.5 solar power system (90 mW cm^{-2}) was employed as the light source. A glass vessel was used as the photoreactor. The TiO_2 nanosheets (50 mg) were suspended into methyl orange solution (50 mL, 25 mg/L). The solution was illuminated after stirring for 30 min in the dark to reach the adsorption equilibrium. And the concentration of aqueous methyl orange was determined using UV-vis adsorption spectra.

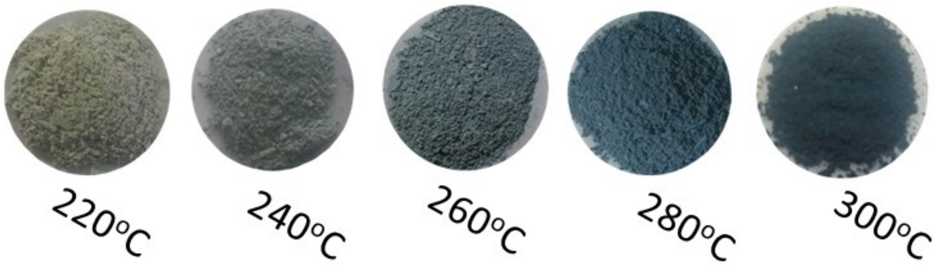

Fig. S1. The digital photos of the hydrogenated ultrathin TiO_2 nanosheets.

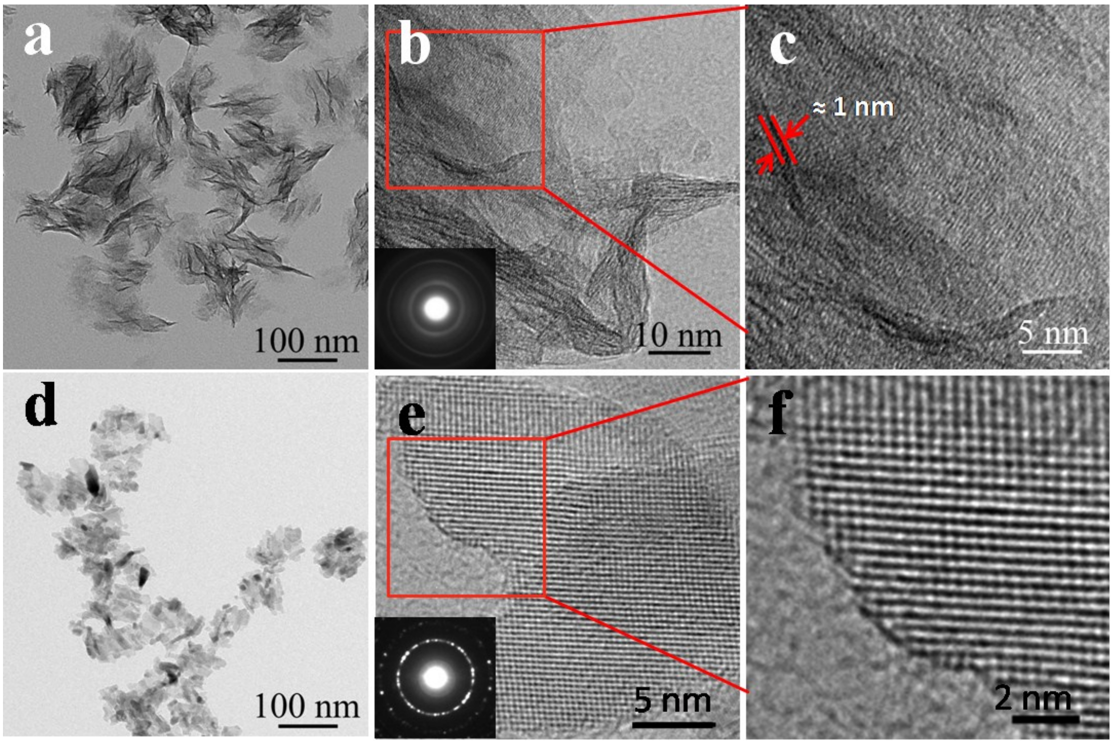

Fig. S2. TEM pictures of raw ultrathin TiO_2 nanosheets after hydrothermal reaction (a, b, c) and white TiO_2 nanosheets after being annealed (d, e, f).

The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were employed to characterize the microstructure of samples. Fig. S2a presents the morphology of raw TiO_2 nanosheets, which was prepared through the hydrothermal reaction. Raw TiO_2 nanosheets were determined that the thickness is less than 2 nm by observing the edge configuration (Figure S2c). The electron diffraction patterns showed in Fig. S2b indicate the polycrystalline and the low degree of crystallinity of raw TiO_2 nanosheets. Particularly, there is no clear crystal structure that can be observed in the magnifying picture (Fig. S2c), and it reveals the raw TiO_2 nanosheets need to be annealed to obtain the ideal crystal structure. Fig. S2d and e are the images of white TiO_2 nanosheets.

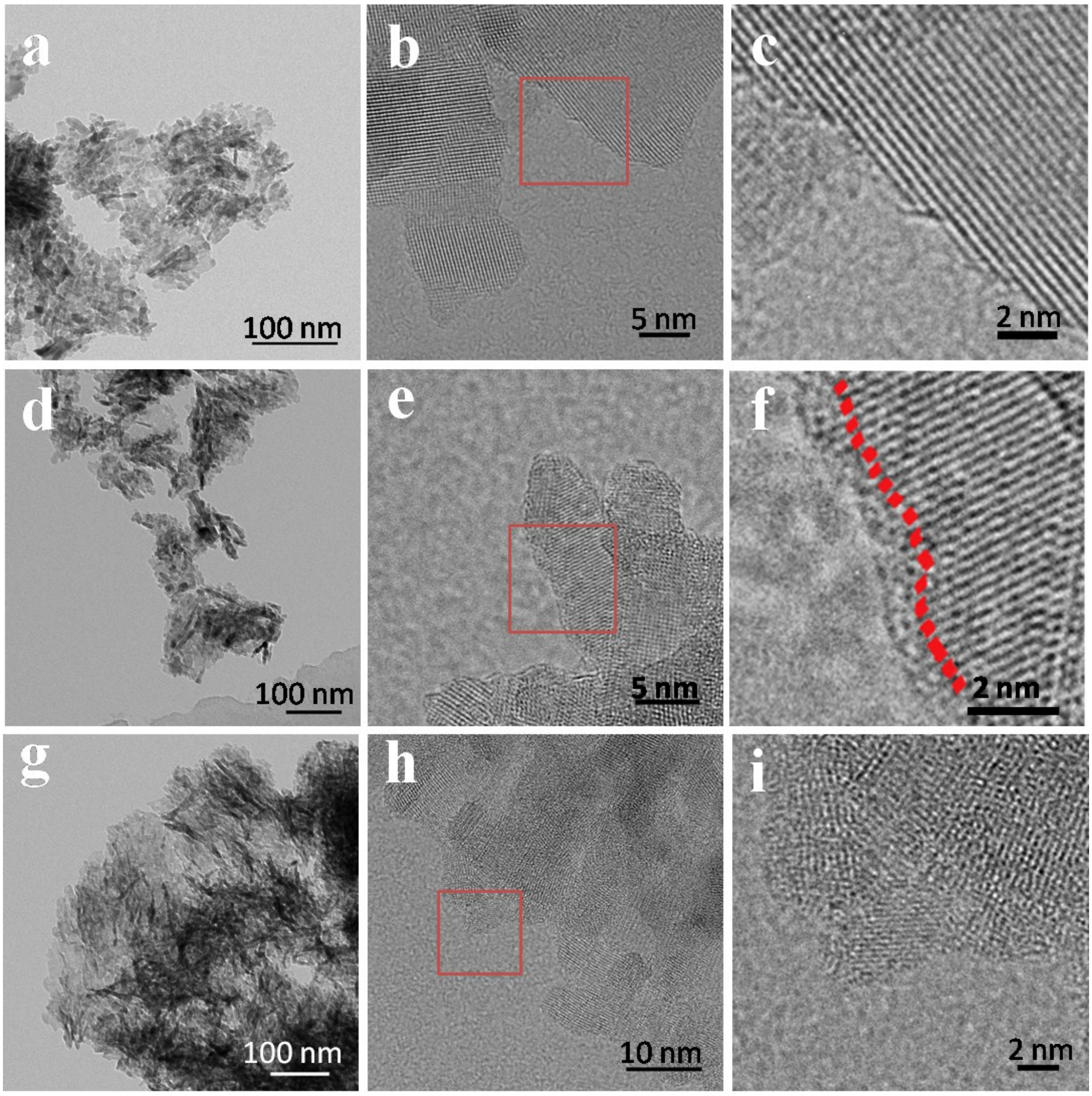

Fig. S3. Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) pictures of the samples hydrogenated at different temperatures (a-c: black-220 °C; d-f: black-260 °C; g-i: black-300 °C).

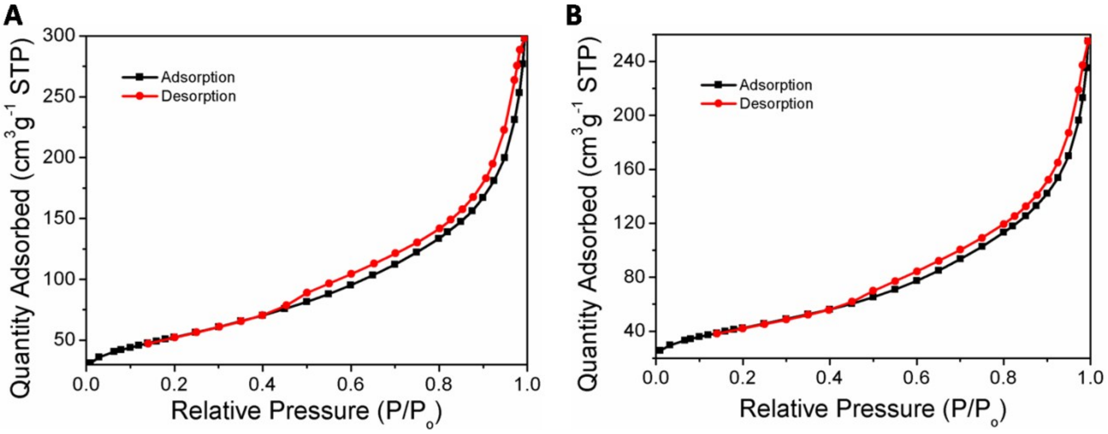

Fig. S4. Nitrogen adsorption–desorption isotherm obtained at 77 K for the white (A) and black (B) TiO_2 nanosheets (specific surface area: the white: 190.3 m^2 g^{-1}, the black: 179.6 m^2 g^{-1}).

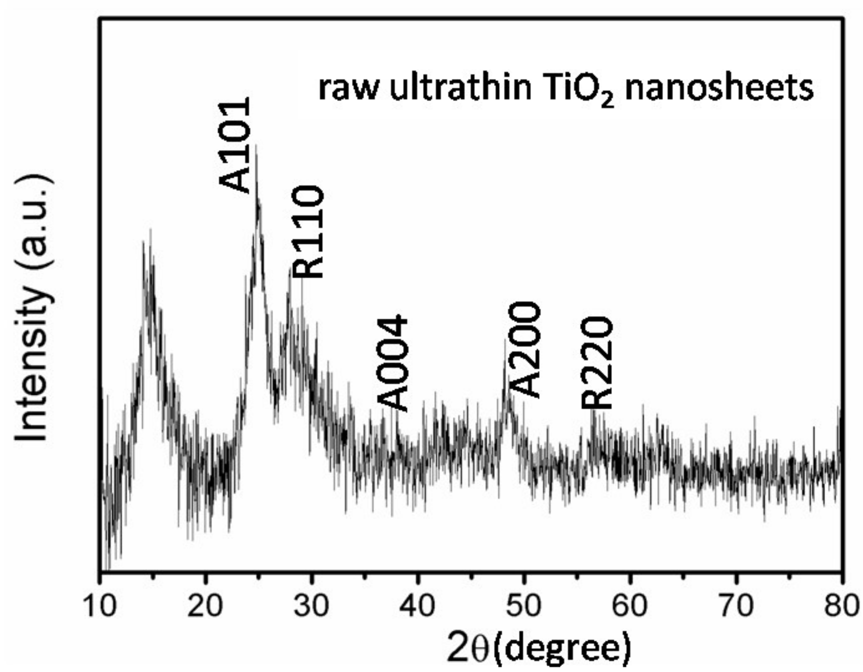

Fig. S5. The XRD pattern of raw ultrathin TiO_2 nanosheets after solvothermal treatment, which suggest the mixed phase of anatase and rutile and the low crystallization (A: anatase, R: rutile).

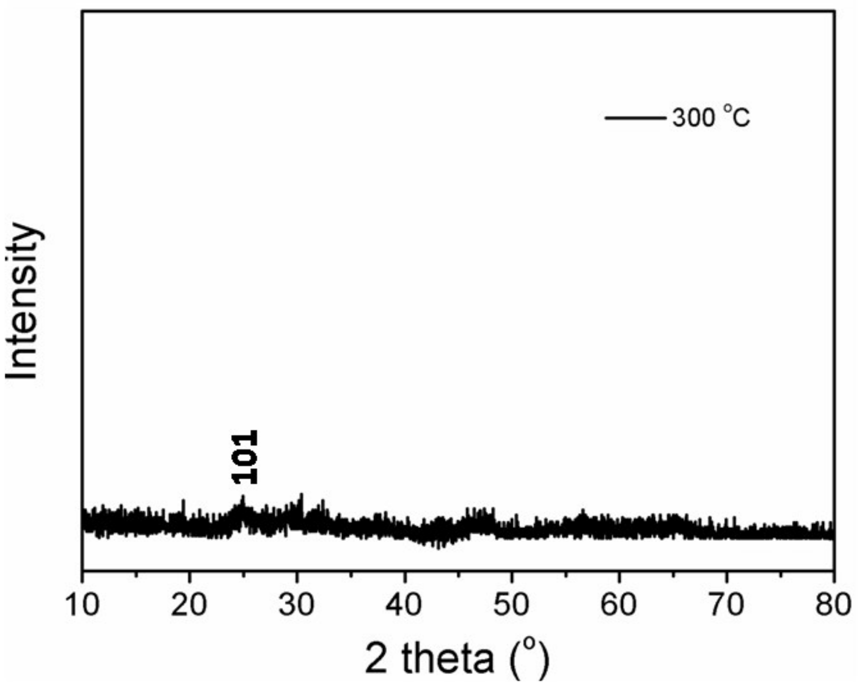

Fig. S6. The XRD pattern of black TiO_2 nanosheets (hydrogenated at 300^{o}C).

When the hydrogenation temperature was risen up to 300 ^{o}C, the XRD peaks vanished as shown in Fig. S6. It is mainly due to most of chemical bands of TiO_2 nanosheets are broken.

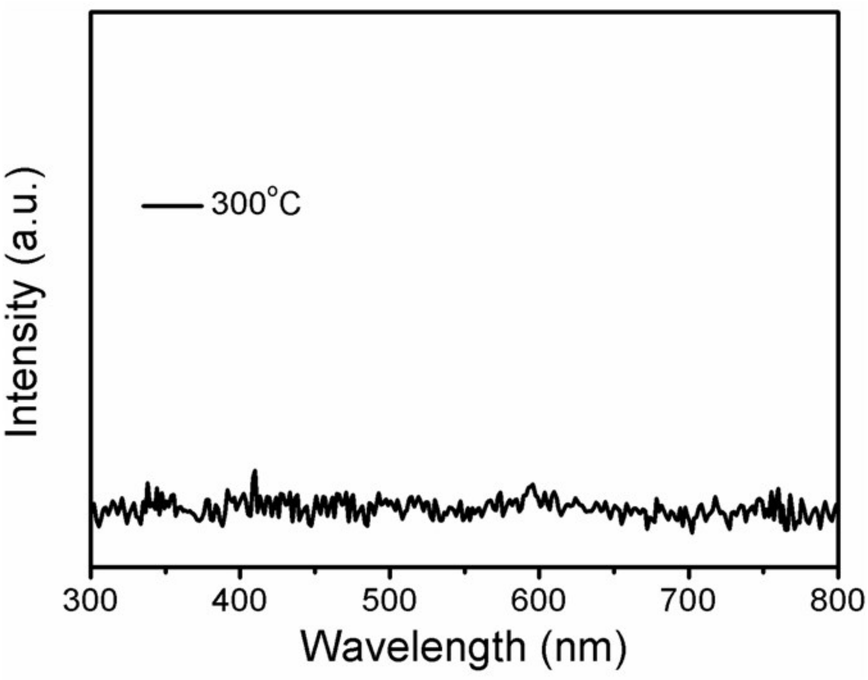

Fig. S7. Raman spectra of TiO_2 nanosheets (hydrogenated at 300°C).

When the hydrogenation temperature was risen up to 300 °C, the Raman peaks vanished as shown in Fig. S7. It is mainly due to most of chemical bands of TiO_2 nanosheets are broken.

Table 1. Core levels of Ti 2p for ultrathin white 2D TiO_2 nanosheets measured by XPS, and the binding energy differences between the standard reference and the measured values.

Chemical states		**Binding energy (eV)**		**References (eV) [1-4]**	**Binding energy difference (Ref - Measured) (eV)**
Ti 2p	White TiO_2 nanosheets		Anatase		
	Ti $2p_{1/2}$	463.9	Ti $2p_{1/2}$	465.3	1.4
	Ti $2p_{3/2}$	458.3	Ti $2p_{3/2}$	459.4	1.1
			Rutile		
			Ti $2p_{1/2}$	465.3	1.4
			Ti $2p_{3/2}$	459.3	1.0

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[3] B. Erdem, R. Hunsicker, G. Simmons, D. Sudol, V. Dimonie, M. El-Aasser, *Langmuir* **2001**, 17, 2664-2669.

[4] NIST X-ray Photoelectron Spectroscopy Database, http://srdata.nist.gov/xps/Default.aspx.