

Electronic Supplementary Information (ESI):

Room-temperature spontaneous crystallization of porous amorphous titania for high-surface-area anatase TiO₂ photocatalyst

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Experimental Section

Materials: Titanium(IV) n-butoxide was purchased from Tianjin Guangfu Fine Chemical Research Institute. Ethylene glycol was purchased from Beijing Chemical Works. Glycerol was purchased from Sinopharm Chemical Reagent Co. Ltd. Titania P25 with a BET surface area of about 50 m²/g was purchased from Beijing Entrepreneur Science & Trading Co. Ltd. All the above chemicals were used without further purification and deionized water was used in all experiments.

Preparation of porous amorphous TiO₂ (Am-TiO₂) via a light-driven approach: The Am-TiO₂ sample was prepared through a light-driven approach.^[S1] Typically, crystalline titanium glycolate (4.0 g), which was synthesized on a large scale according to the reported procedure,^[S2] was dispersed in water (400 mL) and then exposed to UV-light irradiation for 2 h. After the irradiation, the color of the solid sample turned from white (titanium glycolate) to intense blue because of the presence of Ti³⁺.^[S1] Finally, the blue solid product was separated from the mixture and dried in air, the O₂ molecules of which oxidize the Ti³⁺ to Ti⁴⁺ because the Ti³⁺ species are on the surface (internal and external) of the solid. The obtained product was the Am-TiO₂ sample described in this communication. The amorphous and porous feature of this precursor material was confirmed by X-ray diffraction and adsorption measurements. The BET surface area and pore size of this sample were about 540 m²/g and 1.8 nm, respectively. The UV-light source used in the experiment was a 125 W high-pressure mercury lamp.

Room-temperature transformation of Am-TiO₂ to An-TiO₂: Typically, the as-dried Am-TiO₂ sample (1 g) was put in a glass vial with a volume of 5 mL, and then the vial was covered with a lid. After stored for 80-90 days at room temperature (~ 25 °C), the Am-TiO₂ sample spontaneously transformed into An-TiO₂. During the whole transformation process, there were not solvents, additives and catalysts. It should be noted that once An-TiO₂ was formed, its structure was very stable because no further structural variation was observed.

General Characterization: The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 X-ray diffractometer using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) operated at 200 mA and 50 kV. The Raman spectra were obtained with a Renishaw Raman system model 1000 spectrometer with a 20 mW air-cooled argon ion laser (514.5 nm) as the exciting source (the laser power at the sample position was typically 400 μW with an average spot size of 1 μm in diameter). The transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images and the selected area electron diffraction (SAED) patterns were obtained on a Philips-FEI Tecnai G2S-Twin with a field emission gun operating at 200 kV. The nitrogen adsorption and desorption isotherms were measured by using a Micromeritics ASAP 2020M system. Prior to each measurement, the sample was evacuated at 300 K for 12 h to remove the adsorbed guest species such as water. The surface area data were calculated on the basis of the Brunauer–Emmett–Teller (BET) model. The thermal gravimetric analysis (TGA) curve was recorded on a NETZSCH STA 449C TG thermal analyzer from 25 to 800 °C at a heating rate of 10 °C min⁻¹ in N₂. The UV/Vis diffuse reflectance spectra were recorded on a Perkin-Elmer Lambda 20 UV/Vis spectrometer. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromatic X-ray source (Al KR $h\nu = 1486.6 \text{ eV}$). The energy scale of the spectrometer was calibrated using Au4f_{7/2}, Cu2p_{3/2}, and Ag3d_{5/2} peak positions.

The standard deviation for the binding energy (BE) values was 0.1 eV. The surface photovoltage spectroscopy (SPS) measurement was performed on home-made surface photovoltage equipment. The SPS measurement system consisted of a source of monochromatic light, a lock-in amplifier with a light chopper, a photovoltaic cell, and a computer. A 500 W xenon lamp and a grating monochromator were combined to provide the monochromatic light. A low chopping frequency of ~ 23 Hz was used. The photovoltaic cell was a sandwich-like structure consisting of ITO-sample-ITO.

Evaluation of photocatalytic activity: The photocatalytic activities of the TiO₂ samples were evaluated by photocatalytic H₂ evolution under UV-light irradiation. The photocatalytic reaction was performed in a quartz cell, which was connected with a closed gas circulation system and irradiated from an external light source. The UV-light source was a 125 W high-pressure Hg lamp. The main emission wavelength is 365 nm and the light intensity is about 20 mW/cm².

A photocatalyst (25 mg) was added into aqueous methanol solution (50 vol %, 50 mL) in the cell and the aqueous system was magnetically stirred during the whole photocatalytic testing. Before light irradiation, the system was evacuated to eliminate air and the temperature of the system during photocatalytic reaction was kept around 23 °C by a continuous flow of water. The evolved gases were detected *in situ* using an online gas chromatograph (Shimadzu, GC-2014C, TCD, Molecular sieve 5 Å, Argon gas), which was connected to the system and was equipped with a thermal conductivity detector.

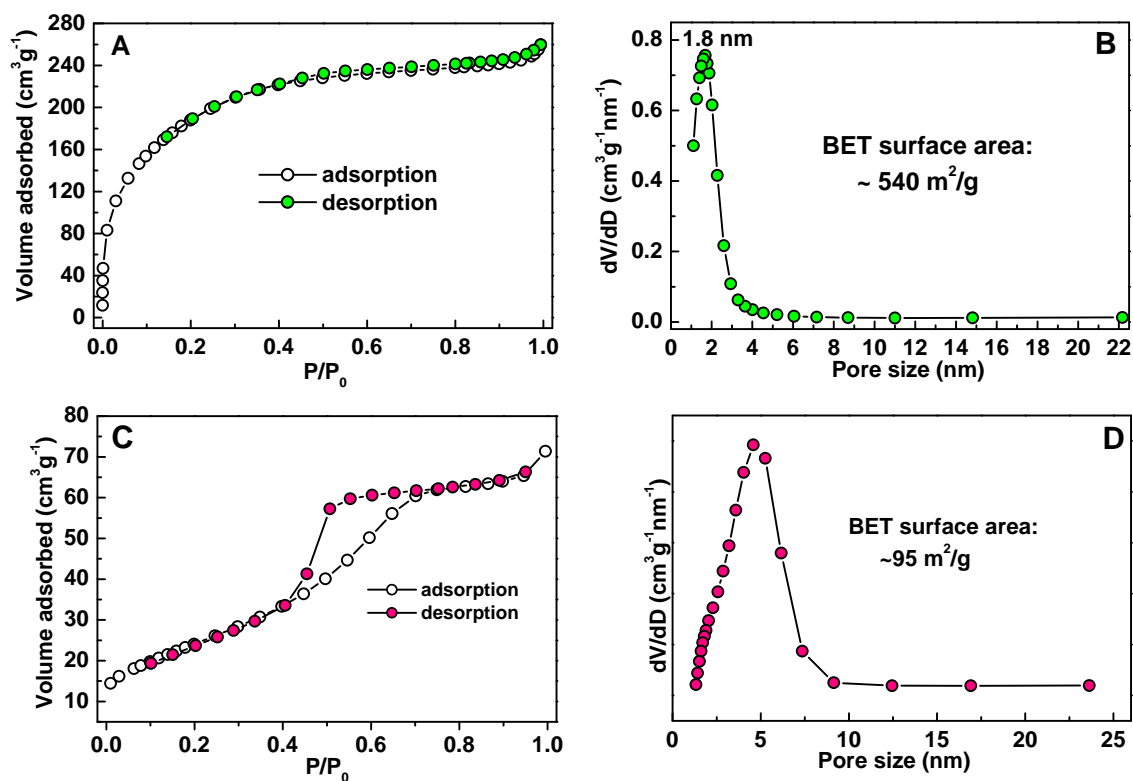


Fig. S1. (A) N₂ adsorption–desorption isotherms of Am-TiO₂ and (B) the corresponding pore size distribution derived from adsorption isotherm; (C) N₂ adsorption–desorption isotherms of TiO₂-400 and (D) the corresponding pore size distribution derived from adsorption isotherm.

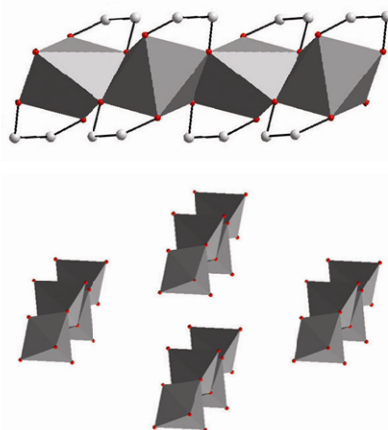


Fig. S2. (A) Polyhedral view of the 1D chain of titanium glycolate along the *c* axis; and (B) a periodic array assembled by the 1D chains in titanium glycolate. The O and C atoms are represented by red and white balls, respectively. The TiO₆ unit forms an octahedron (gray) with the O atoms at the vertices, and the TiO₆ octahedron connects to each other in an edge-shared manner.^[S3]

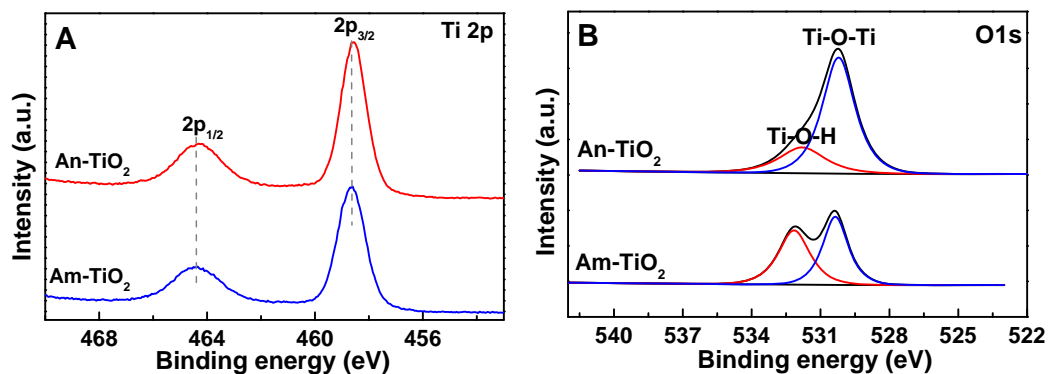


Fig. S3. High-resolution XPS spectra of (A) Ti2p and (B) O1s for Am-TiO₂ and An-TiO₂. The Ti2p XPS spectra for the two samples exhibit two similar peaks at 464.4 and 458.6 eV, which are assigned to the 2p_{1/2} and 2p_{3/2} core level of Ti⁴⁺, respectively.^[S4]

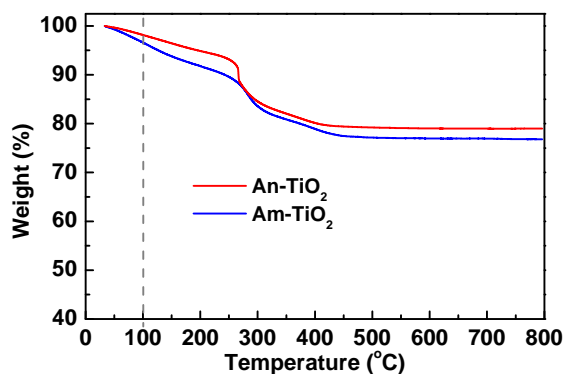


Fig. S4. TGA curves in N₂ for Am-TiO₂ and An-TiO₂. As shown in the figure, the weight loss for both Am-TiO₂ and An-TiO₂ occurs in a wide temperature range from room temperature to 800 °C. The weight loss at temperatures lower than 100 °C is because the removal of the physisorbed water, whereas the continuous weight loss above 100 °C is due to the removal of the energetically nonequivalent chemisorbed water molecules or hydroxide groups.^[S5]

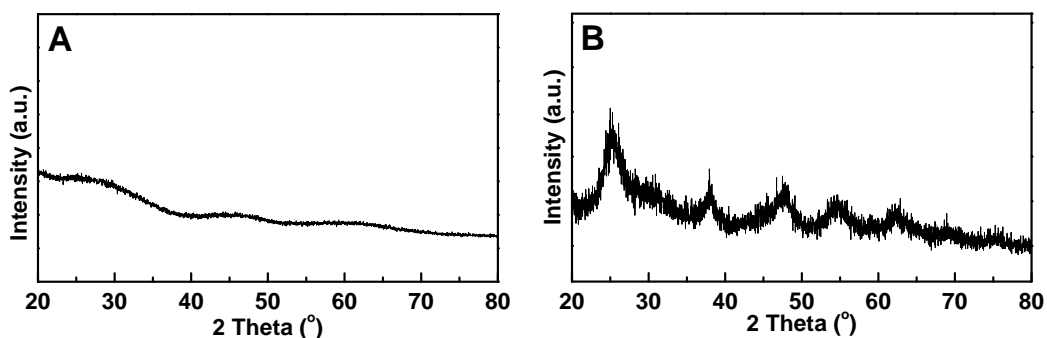


Fig. S5. XRD patterns of (A) ethanol-washed Am-TiO₂ kept in air for 6 months; (B) and Am-TiO₂ kept in water for 9 days.

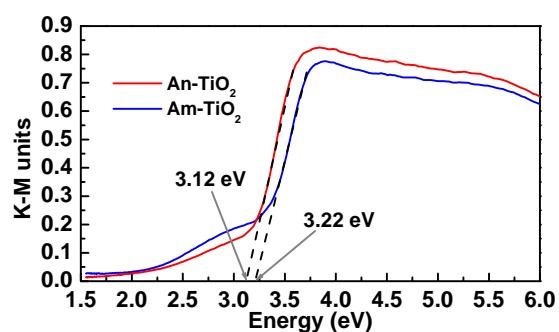


Fig. S6. UV/Vis diffuse reflectance spectra of Am-TiO₂ and An-TiO₂.

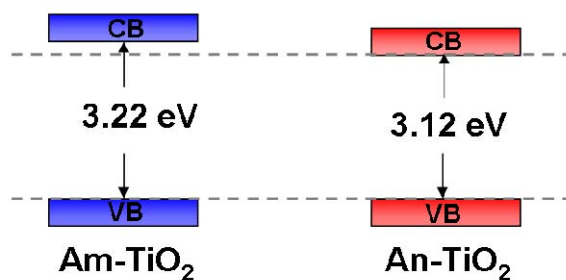


Fig. S7. Comparison of the band structure of Am-TiO₂ and An-TiO₂. CB and VB mean conduction band and valence band, respectively.

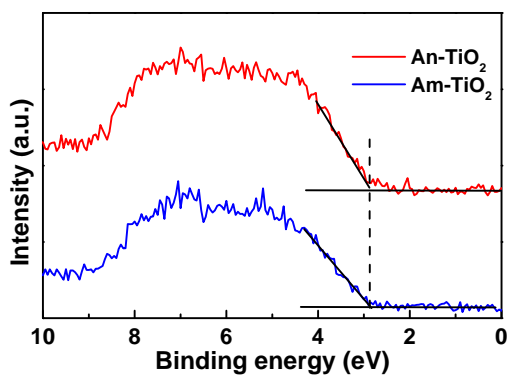


Fig. S8. Valence-band XPS spectra of Am-TiO₂ and An-TiO₂.

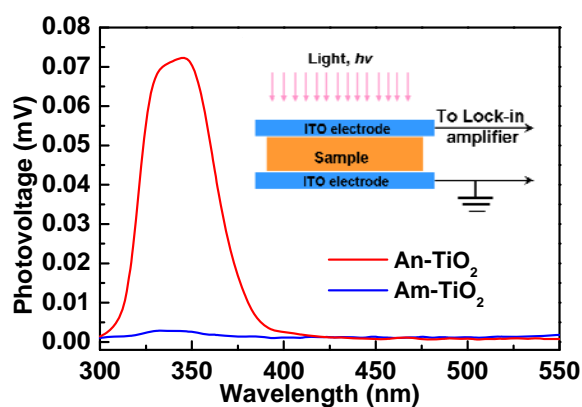


Fig. S9. Surface photovoltage (SPV) spectra of Am-TiO₂ (blue) and An-TiO₂ (red). Inset: Schematic setup of SPV measurement.

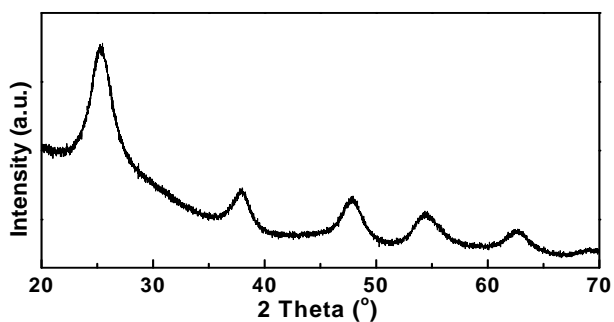


Fig. S10. XRD pattern of An-TiO₂ after 12 cycles of the catalytic H₂ evolution.

Table S1. Some recently-reported synthesis of porous anatase TiO₂ with large surface areas.

BET surface area (m ² ·g ⁻¹)	Crystallization temperature (°C)	References
580	400	Chem. Commun., 2003, 2078.
554	80	J. Am. Chem. Soc., 2003, 125, 14960.
400	Room temperature	This work
350 -400	450	J. Am. Chem. Soc., 2009, 131, 1802.
314	400	J. Phys. Chem. B 2004, 108, 2868.
305	400	Inorg. Chem., 2008, 47, 9870.
300	50	J. Am. Chem. Soc., 2010, 132, 12605.
290	60	J. Phys. Chem. C 2009, 113, 4031.
286	500	Mater. Sci. Semicond.Process., 2012, 15, 108.
284	500	J. Colloid Interface Sci., 2010, 341, 359.
250	140	J. Colloid Interface Sci., 2006, 302,530.
250	Room temperature	Mater. Chem. Phys., 2006, 97, 207.
245	400	J. Mater. Chem., 2012, 22, 22082.
245	100	Chem. Commun., 2008, 1184.
242	120	Crystal Growth & Design, 2009, 9, 1511.
227	140	J. Am. Chem. Soc., 2011, 133, 17652.
223	250	J. Mater. Chem., 2005, 15, 1263.
219	200	Powder Technol., 2009, 194, 149.
207	750	J. Mater. Chem., 2010, 20, 2206.
203	Room temperature	Nano Lett. 2011, 11, 3649.
201	350	Chem. Commun. 2000, 1755.
190	Room temperature	Chem. Mater., 2012, 24, 245.
167	550	J. Am. Chem. Soc., 2007, 129, 8406.
161	400	J. Phys. Chem. C, 2009, 113, 21258.
159	500	Adv. Funct. Mater. 2006, 16, 1067.
158	500	Chem. Mater., 2012, 24, 1268.
156	450	J. Phys. Chem. C, 2012, 116, 17440.
152	160	J. Hazard.Mate., 2010, 176,139.
155	180	Chem. Commun., 2012, 48, 6978.
135	380	Chem. Mater. 2003, 15, 3841.

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