

Electronic Supplementary File

Molten salt assisted synthesis of black titania hexagonal nanosheets with tunable phase composition and morphology

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Experimental details

Chemical

All chemicals were of analytical reagent grade and purchased from Sinopharm Chemical Reagent, and used without further purification.

Synthesis

In this work TiH_2 was chosen as a model molecule for the synthesis of black titania. Blue titania in the same molten salts system were synthesized with different raw materials, such as TiCl_3 , and titanium isopropoxide. In a typical process, Ti precursor, and metal chlorides salts ($\text{ZnCl}_2/\text{KCl} = 13/12$ by weight) in the weight ratio of reactants/solvent = 2:25 (solvent: ZnCl_2/KCl) were mixed and homogenized by grinding carefully. During the grinding process, ethanol was added to accelerate the homogenization. For each time, 1 mL ethanol was added until the mixture became a paste. The homogeneous mixture was filled into a ceramic crucible and then transferred to the muffle furnace. The furnace was ramped at $5\text{ }^\circ\text{C min}^{-1}$ to $400\text{ }^\circ\text{C}$ and kept at this temperature for 3 h. After naturally cooled to room temperature, the product was washed with a large amount of water to remove the salts and dried at $80\text{ }^\circ\text{C}$ overnight

Characterization

Powder X-ray diffraction (XRD) was performed by a Rigaku D/max-3B X-ray diffractometer with Cu $\text{K}\alpha$ line as the radiation source ($\lambda = 0.15406\text{ nm}$, 40 kV, 35 mA). Raman spectra were collected on a Thermal Dispersive Spectrometer using a laser with an excitation wavelength of 532 nm at laser power of 10 mW. The X-ray

photoelectron spectroscopy (XPS) analyses were carried out on a Escalab 250Xi XPS system with Al K α (1486.6 eV) source. EPR spectra were investigated using a Bruker EMX-8 spectrometer at 9.44 GHz at 300 K. The morphologies of the samples were observed on a JEOL-JEM 2100F transmission electron microscope (TEM) (100 kV) and a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) (5 kV). Diffuse reflectance spectra (DRS) and UV–visible absorption spectra were measured using a Hitachi U-4100 spectrometer with an integrating sphere accessory, using BaSO₄ as the reference material.

Photocatalysis testing

The photocatalytic activities of the as-prepared black TiO₂ samples were evaluated by the degradation of methylene orange (MO) in an aqueous solution under solar light irradiation with 400 W iodine gallium lamp. For each measurement, 100 mg of the as-prepared sample and 100 mL of MO aqueous solution (10 mg/L) were mixed under stirring. The suspension was held in the dark for 10 min to attain the adsorption-desorption equilibrium. Afterwards the mixture was subjected to irradiation, about 5mL of suspension was withdrawn and centrifuged in every 15min. The concentration of the residual MO was evaluated by monitoring the absorbance at 464 nm. The visible light experiment was conducted under the same condition with a 400 nm filter to cut off the UV light and allow only visible light (>400 nm) to pass through.

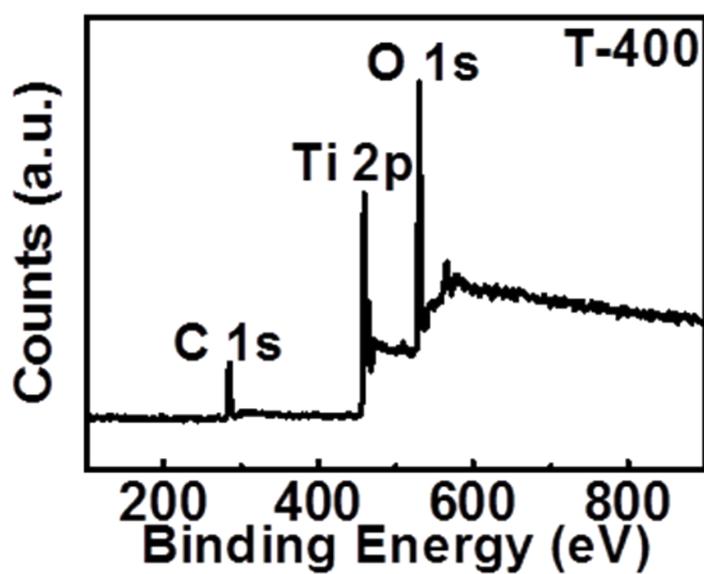


Fig. S1 XPS survey spectrum of T-400, indicating the effective remove of salt species (Zn^{2+} , K^+ , Cl^-) in T-400.

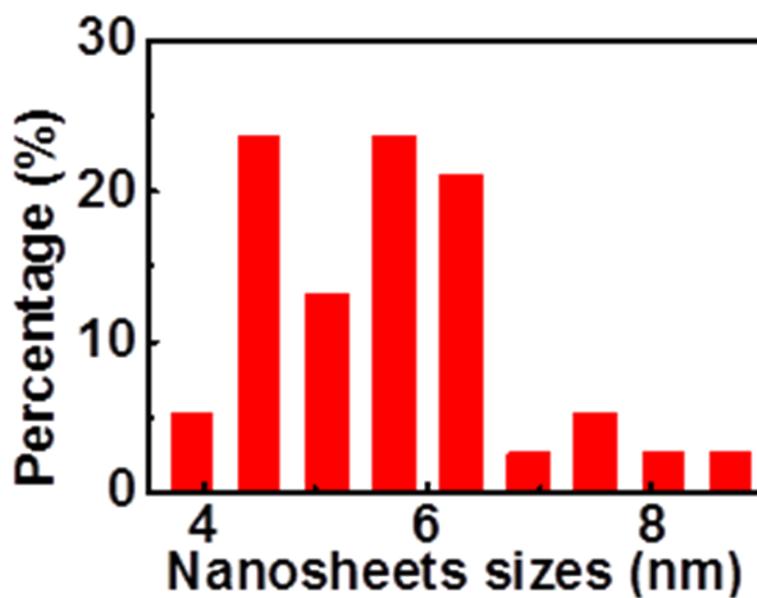


Fig. S2 The distribution of measured sizes of tiny nanosheets.

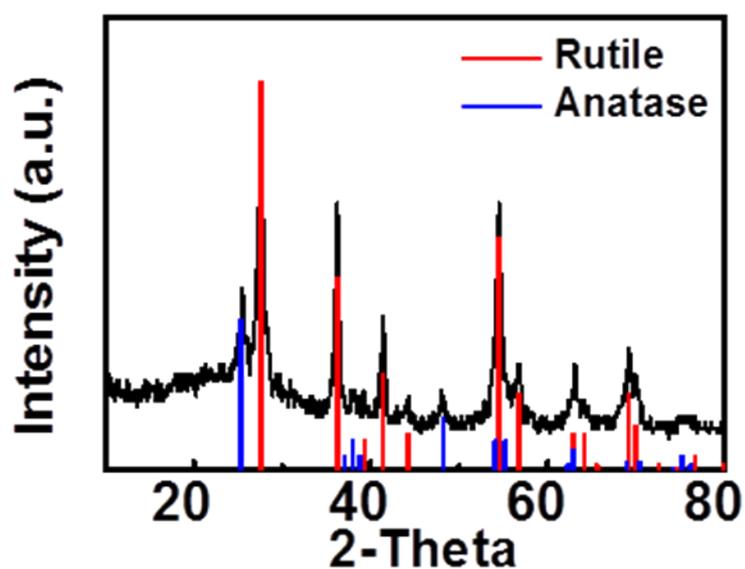


Fig. S3 The XRD spectra of the blue titania synthesized by using TiCl_3 as the Ti precursor at 400 °C.

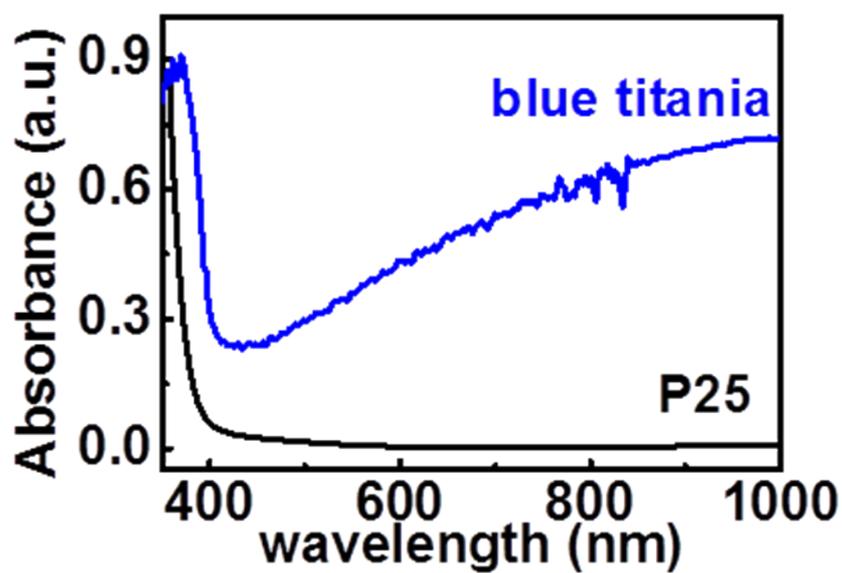


Fig. S4 UV-VIS-NIR diffuse reflectance of the blue titania synthesized by using TiCl_3 as the Ti precursor at 400 °C.

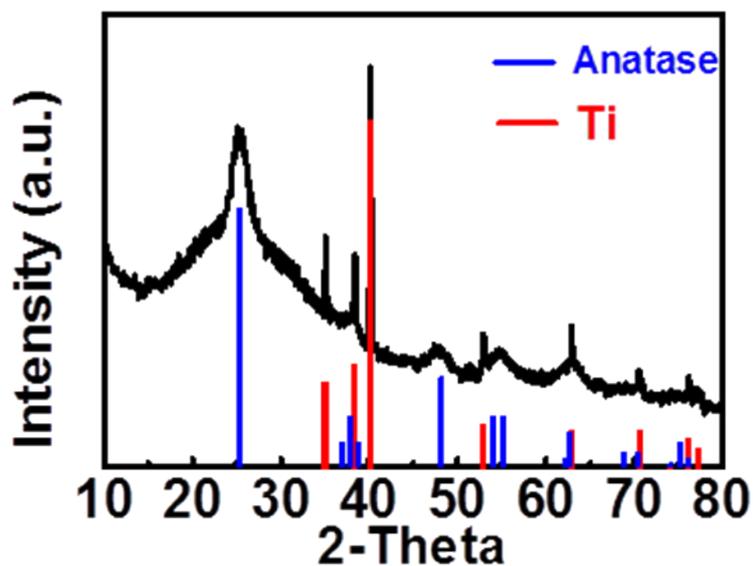


Fig. S5 The XRD spectra of the blue titania synthesized by using titanium isopropoxide as the Ti precursor at 400 °C.

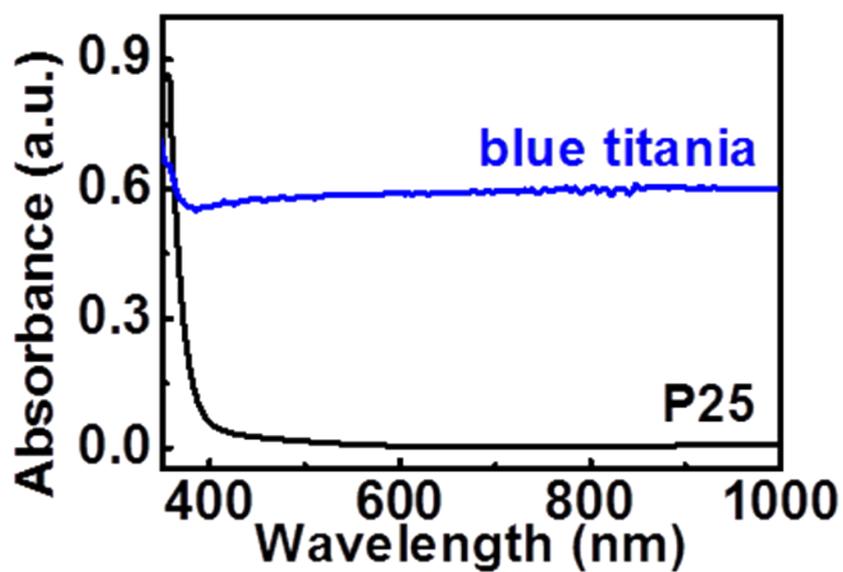


Fig. S6 UV-VIS-NIR diffuse reflectance of the blue titania synthesized by using titanium isopropoxide as the Ti precursor at 400 °C.