

Electronic Supplementary Information

Low-temperature fabrication of brown TiO₂ with enhanced photocatalytic activities under visible light

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1. Experimental

1.1 Fabrication of brown TiO₂

Brown TiO₂ was prepared by a one-step solution-based method under N₂ protection. Inside a glove box, the mineral oil-NaH mixture (Acros, 65 wt.% NaH) was rinsed with anhydrous hexane to obtain NaH powder. 5.0 ml of anhydrous dimethylformamide (Aldrich, DMF) was added to a quartzose round-bottom flask containing 100 mg of TiO₂ (Degussa, P-25) and 200 mg of NaH powder. The flask was then taken out of the glove box and connected to a Schlenk line. The suspension in the flask was stirred and heated at an elevated temperature (e.g., 150 °C) in N₂ for several hours (e.g., 4 hrs). To investigate the impact of UV irradiation on the reaction rate, some samples were prepared with a mercury lamp (maximum output wavelength at 365 nm) placed at a distance of 20 cm from the flask during the reaction. After reaction, the flask was cooled down to room temperature. The insoluble material was collected by centrifugation, and then sequentially washed with 2-propanol (International Laboratory USA, 99.7%), anhydrous acetone (Sigma-Aldrich, 99.99%) and absolute

ethanol (Sigma-Aldrich) each for three times and finally dried in a nitrogen stream. The representative samples and their fabrication parameters are shown in **Table S1**.

Table S1. Reaction parameters and resultant bandgaps for NaH-treated TiO₂ samples.

Sample index	Reaction temperature	Reaction time	UV illumination for reaction	Bandgap measured
P-25 (native)	—	—	—	3.04 eV
Sample A	150 °C	4 hrs	off	2.69 eV
Sample B	120 °C	4 hrs	on	2.32 eV
Sample C	150 °C	2 hrs	on	2.11 eV
Sample D	150 °C	4 hrs	on	1.82 eV

1.2 Characterizations

X-ray diffraction (XRD) measurements were performed using an X-ray diffractometer (Philips X'pert). Morphology studies were carried out using a transmission electron microscope (TEM) (Philips CM20, operating at 200 kV). Chemical compositional analysis was carried out using an energy dispersive X-ray spectrometer (EDS) equipped in the TEM. Surface chemical analysis was measured using an X-ray photoelectron spectrometer (XPS) (VG ESCALAB 220i-XL) equipped with a monochromatic Al K α (1486.6 eV) source. Optical properties were investigated using a diffuse reflectance UV-Vis absorption spectrophotometer (Perkin Elemer Lambda λ 750) equipped with an integrating sphere attachment. The spectra were recorded at room temperature from 200 to 800 nm. The BaSO₄ standard mirror was used as the reference. The electron spinning resonance (ESR) measurements were carried out at 8 K on a Bruker EMXplus EPR Spectrometer.

1.3 Photo-activity measurements

The photo-degradation abilities of the TiO₂ samples were tested as follows. Typically, 20 mg of the TiO₂ sample was added into a 20 ml aqueous solution of Phenol (20 mg/L). The mixture was stirred for 30 min in dark to allow the establishment of the absorption-desorption equilibrium between the Phenol and TiO₂. For the UV illumination source, a mercury lamp with the maximum output wavelength of 365 nm was used. For the visible light source, a 300 W tungsten lamp equipped with a UV cutoff ($\lambda > 420\text{nm}$) filter was used. The lamps were kept at a distance of 15 cm from the reaction vessel with the light intensity there measured to be 206 mW/cm². The diameters of reaction vessels were 4.0 cm. When the visible light source was used, a water filter was placed between the lamp and the reaction vessels for absorbing the heat and the infrared radiation over ~ 1100 nm. The temperature was maintained around 25 °C during the photocatalytic reaction. The Phenol concentration in the reaction solution (TiO₂ removed by centrifugation beforehand) was measured at ~ 270 nm by the UV-Vis spectrometer (Shimadzu UV-1700).

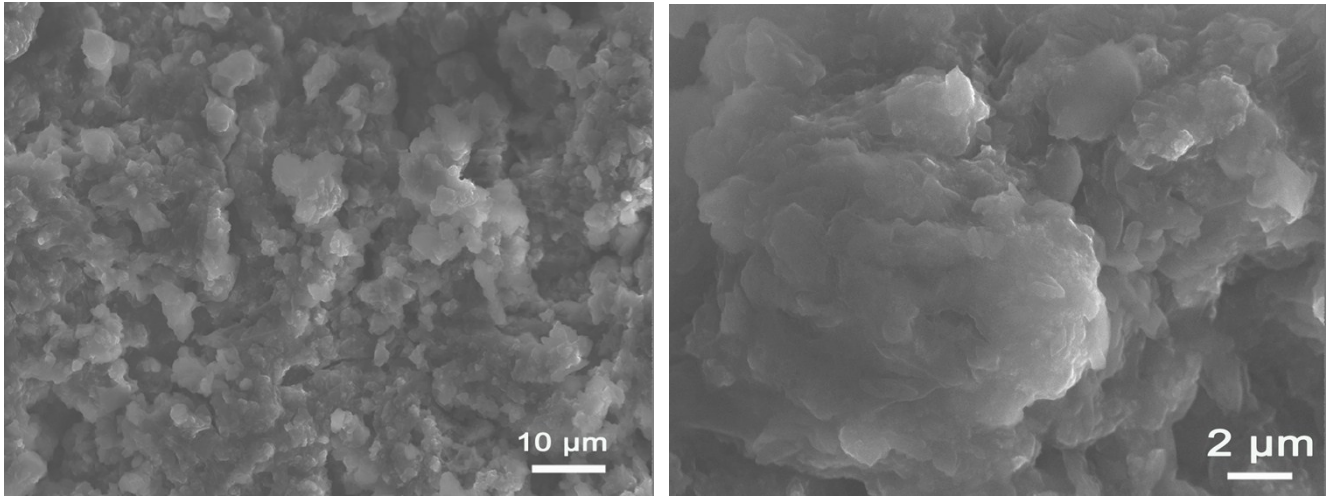


Figure S1. SEM images of the fabricated brown TiO₂ (Sample D) at different magnification.

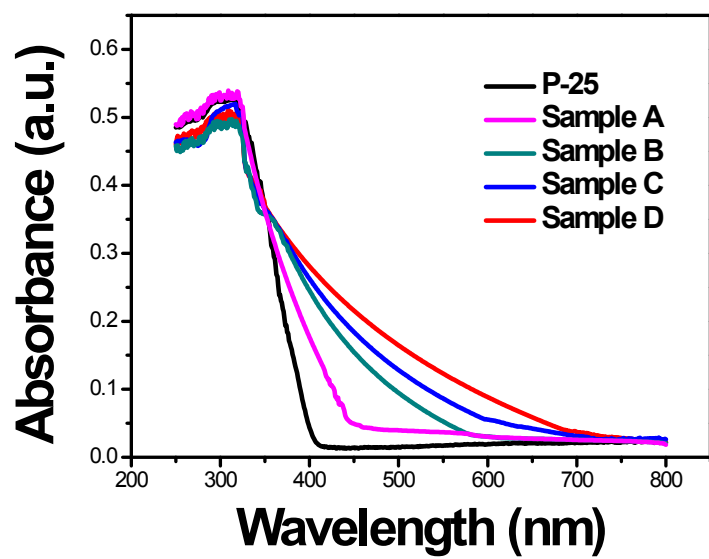


Figure S2. Absorption spectra of commercial TiO₂ (P-25) and Samples A-D.

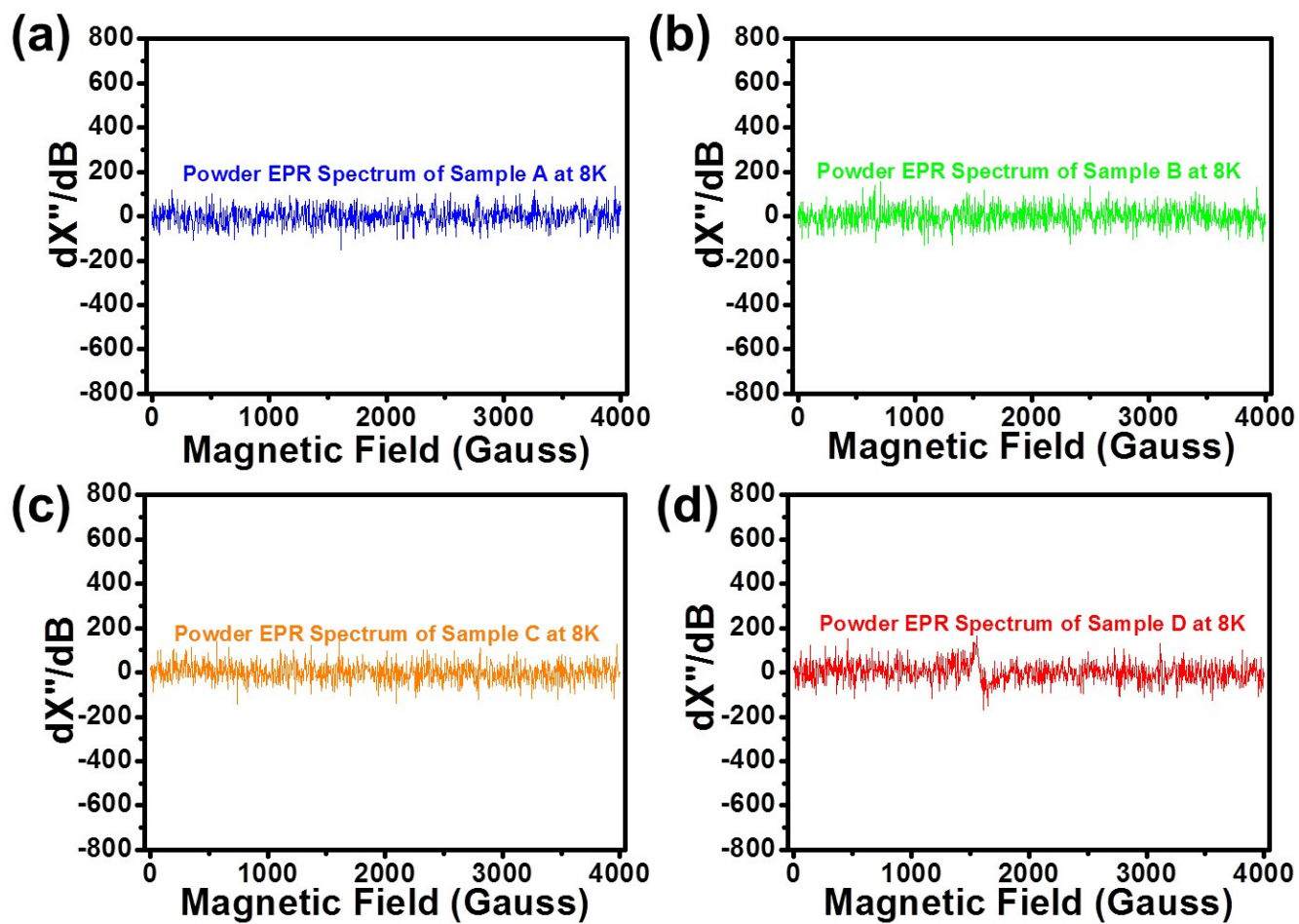


Figure S3. Powder EPR spectra of Samples A-D at 8 K.

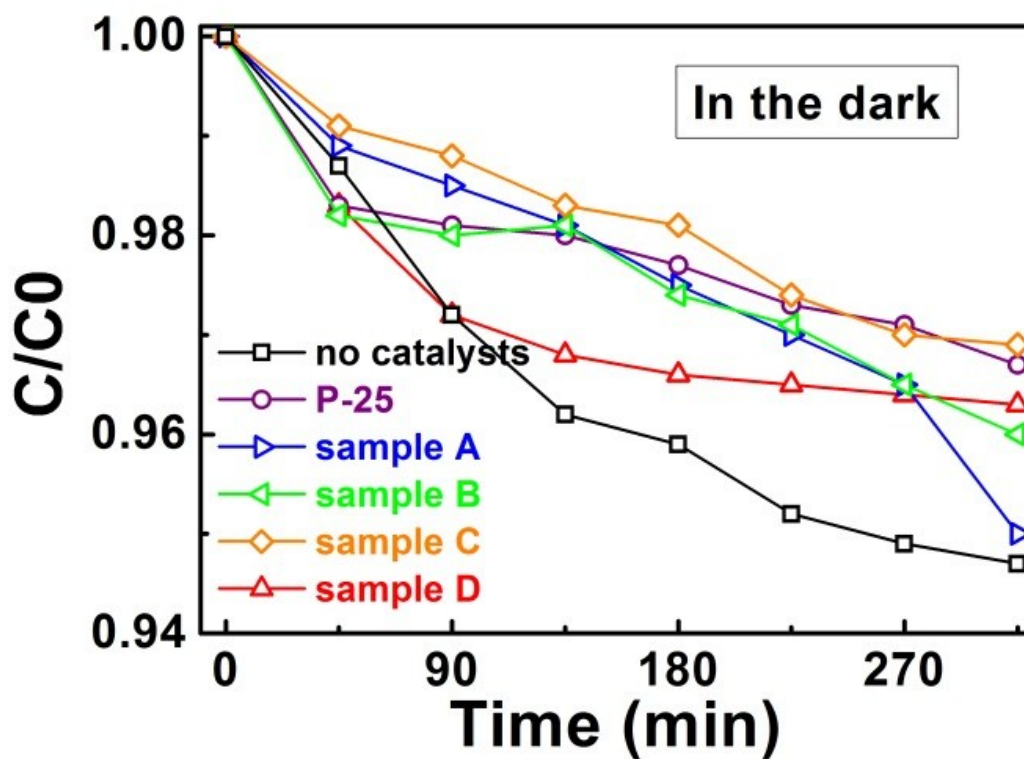


Figure S4. Photodegradation rates of phenol in dark for commercial TiO_2 (P-25) and Samples A-D.

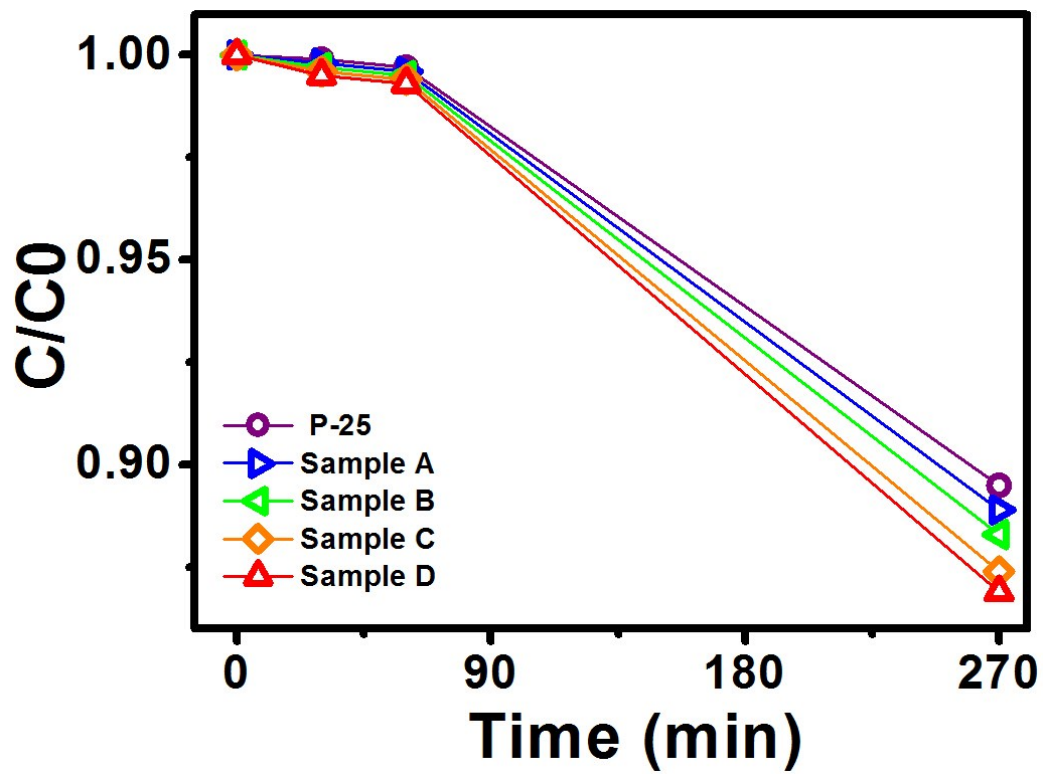


Figure S5. The second-time photodegradation rates of phenol under the visible light, measured with commercial TiO₂ (P-25) and Samples A-D.