

Supplementary material

Preparation of porous TiO₂ photocatalysts with different crystal phases and high catalytic activity by simple calcination of titanate nanofibers

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1. Materials

Sodium hydroxide, hydrochloric acid(36~38 %), analytical grade, were purchased from Shanghai Ling Feng Chemical Reagent Co. Ltd. Commercial anatase TiO₂(≥98 %), were obtained from Shanghai Choi Nano Science and Technology Co. Ltd. Absolute ethanol, were purchased from National Medicine Group Chemical Reagent Co. Ltd. All the reagent were used as received without any further purification, and ultrapure water was used for all experiments.

2. Preparation of catalysts

Preparation of titanate nanofiber: 1.0 g of NaOH was dissolved in a mixed solution containing 10 mL of deionized water and 55 mL of absolute ethanol, then 0.60 g of commercial anatase TiO₂ was added to the above solution and magnetically stirred for 1 h. Subsequently, the prepared suspension was transferred into an autoclave lined with Teflon and kept in the oven at 180 °C for 24 h. After cooling down to the room temperature, the precipitate was filtered and washed with deionized water repeatedly until the pH was about 8. The obtained product was sodium titanate nanofiber. Then the sodium titanate fibers were exchanged for 2-3 h in a 0.1 M aqueous solution of HCl and washed with deionized water until the water's pH was about 7. Finally the product was dried overnight in an infrared oven. The final product is titanate nanofiber (referred to as TN).

Preparation of TiO₂ photocatalysts with different phases: 0.20 g of titanate nanofibers were calcined in a muffle furnace under the temperature of 350 ~950 °C for 2 h to get the final products. The obtained samples were denoted as TN-W, where W corresponds to the calcination temperature. For example, TN-450 means the sample prepared by calcining titanate nanofibers at 450 °C for 2 h.

3. Photocatalytic experiments

Photocatalytic activity evaluation: The photocatalytic activity efficiencies for the prepared samples were tested by degradation of RhB in aqueous suspensions at room temperature using a homemade photocatalytic reactor equipped with a 300 W ultraviolet high pressure mercury lamp. The lamp was put in a double wall jacketed quartz cylinder. Cooling water circulated between two walls to cool down the lamp during the irradiation. Two fans were attached to the reactor to cool the lamp and the catalyst–pollutant suspensions respectively. The samples were kept at 20 cm from the lamp. 40 mg of the catalyst was added to 80 mL of 10 mg/L RhB solution(or 20 mg/L RhB solution) in a 100 mL quartz reaction tube. The reaction suspension was stirred in dark for 30 min to establish an adsorption–desorption equilibrium. After the lamp was turned on, about 4 mL of the sample was withdrawn at given intervals and then separated the photocatalyst by centrifugation. The liquid samples were analyzed by recording its absorbance at 554 nm by UV–Vis spectrometer (Shimadzu UV-2450).

4. Characterizations

X-ray diffraction (XRD) patterns of all samples were collected in the range 5–80° (2 θ), using a RigakuD/MAX 2550 diffract meter(Cu K radiation, λ = 1.5406 Å), operated at 40 kV and 100 mA. The surface morphology were characterized by transmission electron microscopy (TEM, JEM2000EX). The surface morphology were observed by a JEOL JSM-6360 LV scanning electron microscopy (SEM) operating at 15 KV. BET surface area measurements were carried out by N₂ adsorption at 77 K using an ASAP2020 instrument.

Table S1 The average crystalline size of different products

| | TN | TN-350 | TN-450 | TN-550 | TN-650 | TN-750 | TN-850 | TN-950 |
|----------------|----|--------|--------|--------|--------|--------|--------|--------|
| D _B | 0 | 8.9nm | < 5nm | 0 | 0 | 0 | 0 | 0 |
| D _A | 0 | 0 | 12.9nm | 17.3nm | 22.3nm | 31.6nm | 42.6nm | 0 |
| D _R | 0 | 0 | 0 | 0 | 0 | 0 | 46.0nm | 105nm |

Table S2 BET specific surface area, pore volume and size of different TiO₂ products

| Sample | BET Surface area (m ² /g) | Pore volume (cm ³ /g) | The average pore diameter (nm) |
|--------|--------------------------------------|----------------------------------|--------------------------------|
| TN-350 | 182.0 | 0.890 | 18.0 |
| TN-450 | 131.8 | 0.671 | 20.1 |
| TN-550 | 70.7 | 0.390 | 21.4 |
| TN-650 | 52.0 | 0.307 | 25.1 |
| TN-750 | 21.0 | 0.098 | 21.8 |
| TN-850 | 3.8 | 0.006 | 10.1 |
| TN-950 | 1.2 | 0.002 | 7.0 |

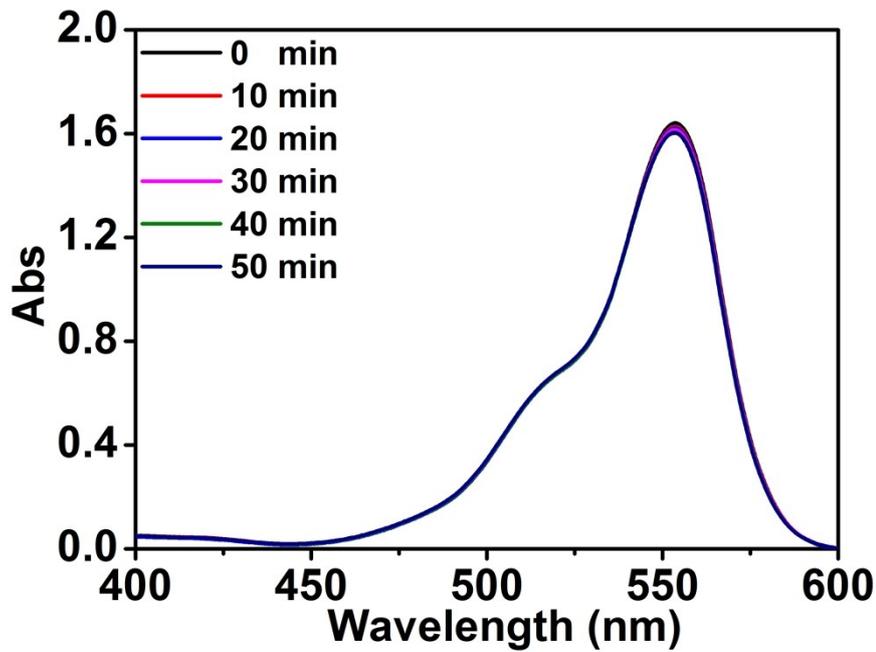


Fig S1 Photocatalytic degradation of 10 mg/L RhB without any photocatalysts

As we can see from the Fig S1, without any photocatalysts, under UV-light irradiating, the solution's absorbance almost not change. So the solution's self-degradation can be negligible.

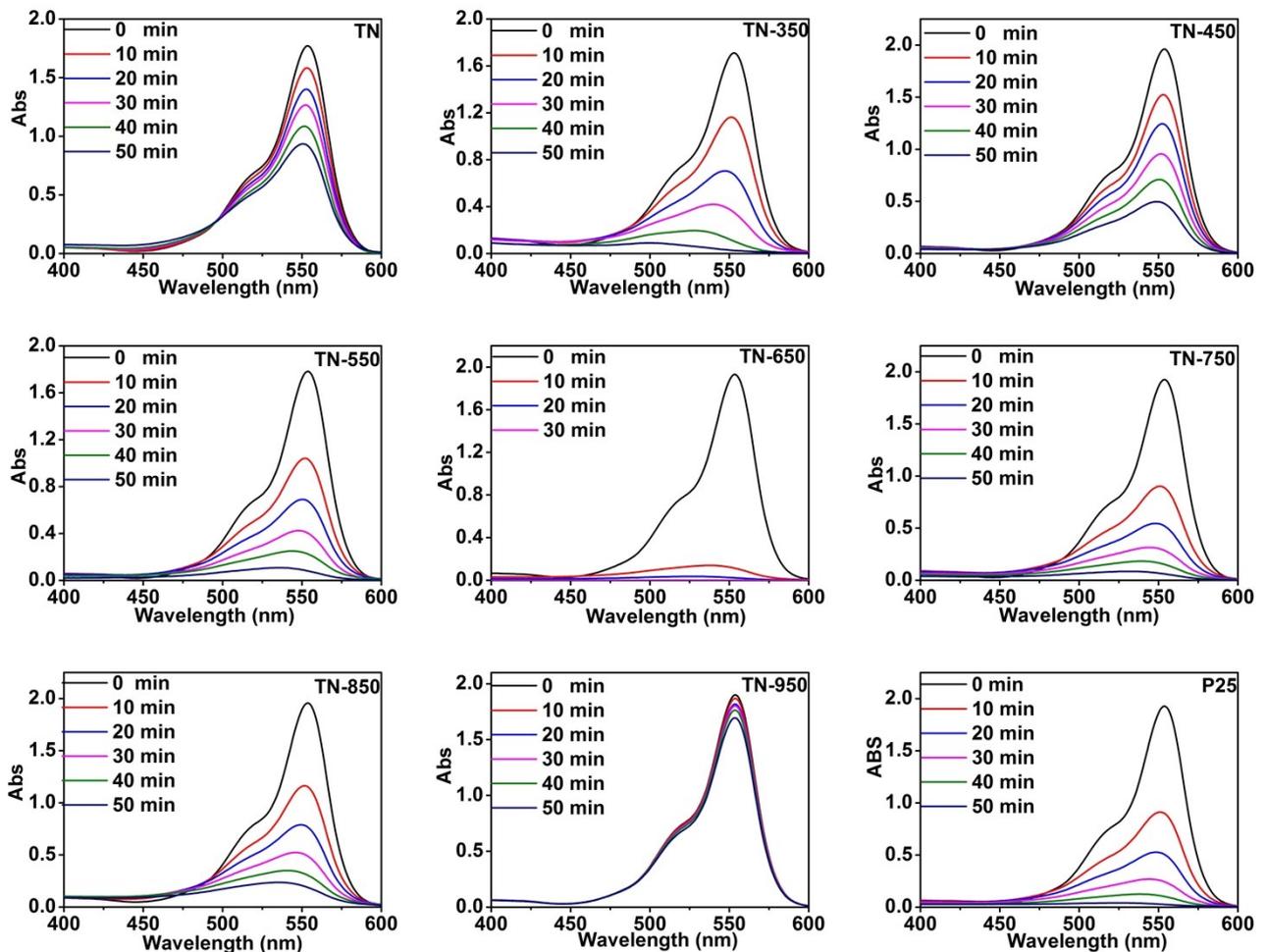


Fig S2 Photocatalytic degradation of 10 mg/L RhB with different simples

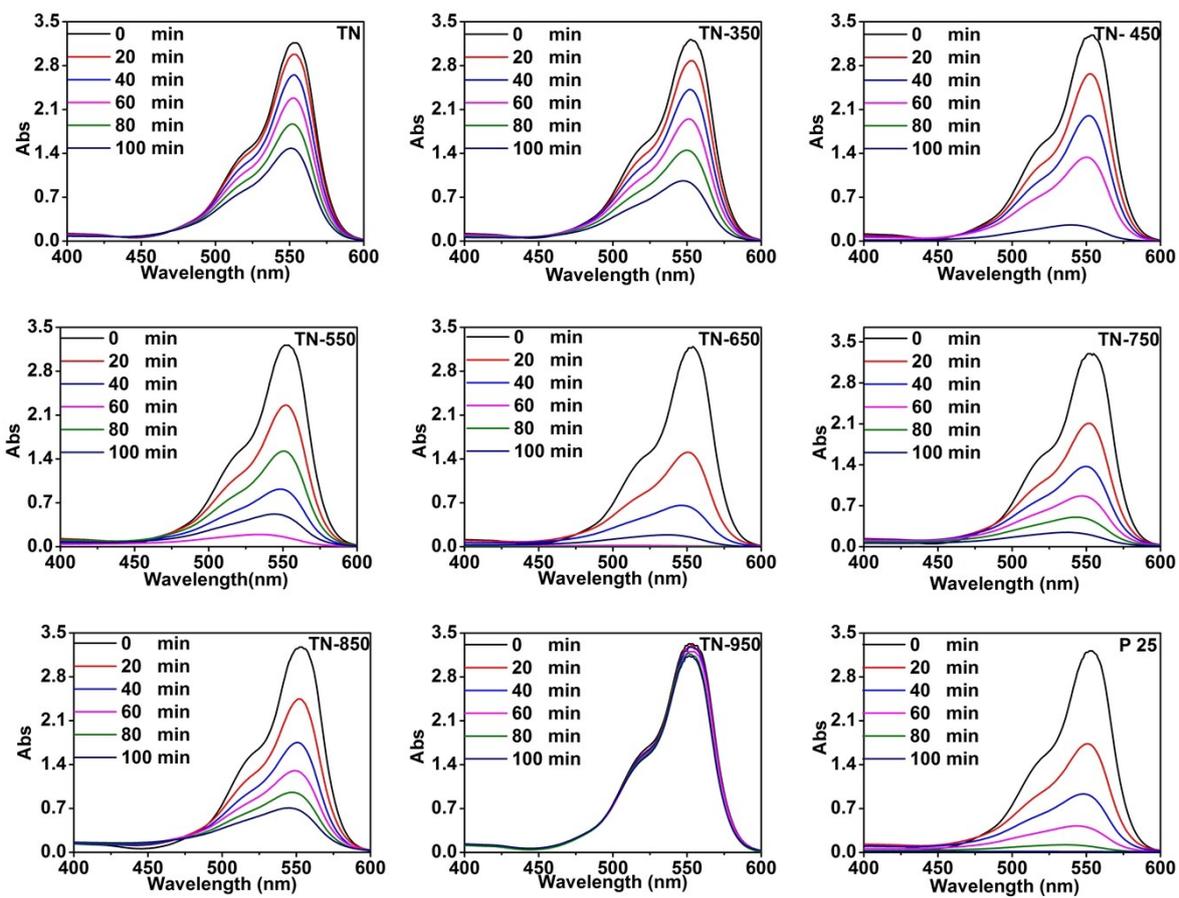


Fig S3 Photocatalytic degradation of 20 mg/L RhB with different simples