Electronic Supplementary Material for CrystEngComm

Supporting information

Controlled Growth of Monocrystalline Rutile Nanoshuttles in Anatase TiO_2 Particles under Mild Condition

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Experimental Section

Materials Preparation: In a typical synthesis, titanium tetra-n-butoxide (6.00 mL) was dissolved in 45.00 mL absolute ethanol, and then the solution was added drop-wise into 60.00 mL double-distilled deionized water under vigorous stirring. After complete addition, the suspension was kept on stirring at 70 °C for about 90 min to ensure the complete hydrolysis and the condensation of solution. Thus the amorphous TiO_2 was obtained and sampled for S5. Then the concentrate solution was divided into two equal parts for further use. (i) 80.00 mL 1.00 M HNO_3 was added and the mixture was continuously stirred at 70 °C for 8 h in airproof condition, which was labeled S7. (ii) 80.00 mL 1.00 M NaOH was added and the mixture was continuously stirred at 70 °C for 8 h in airproof condition. The sample was collected by centrifugation and double-distilled water was used to thoroughly wash the precipitation, which was labeled S6. Subsequently, 80.00 mL 1.00 M HNO_3 was added as a peptization reagent and the mixture was continuously stirred at 70 °C for 8 h in airproof condition, which was labeled S3. In this way, 0.05 M, 0.30 M, and 2.00

M HNO_3 were used as peptization reagents instead of 1.00 M HNO_3 and the as-prepared samples were labeled S1, S2 and S4, respectively. The all generated samples were collected for XRD analysis by sedimentation, centrifugation, washing and vacuum drying at 40 °C for 8 h. Thus, the various photocatalysts with different post-treatments were obtained and summarized in Table 1.

Characterization: Crystalline phases of the prepared powders from each major synthetic step were investigated by an X-ray diffraction method (XRD-6000 X-ray diffractometer (Shimadzu) with a Cu Kα radiation source and a fixed power source (40 kV and 40 mA)). The samples were scanned at a rate of 10° (2θ) / min over a range of 5-70°, which covers the main characteristic diffraction peaks of the titanate, anatase, and rutile. The dimension and morphology of the suspensions were examined using transmission electron microscopy (TEM, FEI Tecnai G2 T20 S-Twin) operating at an accelerating voltage of 200 kV. As further research, high-resolution transmission electron microscopy (HRTEM) and the corresponding fast Fourier transform (FFT) were introduced to analyze the microstructure of nanocrystallites.

Photocatalytic Reaction: The UV source was a high-pressure Hg lamp (100 W, Beijing Lighting Research Institute), and a cylindrical Pyrex vessel was positioned outside with a circulating water jacket (Pyrex) to cool the lamp. A 50 mL beaker was filled with 10.00 mL aqueous solution of methylene blue (MB) dye (30 μM) and HCl. The catalyst concentration was 1.00 g/L, and the starting pH value was about 2.5. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to the establishment of an adsorption/desorption equilibrium. The mixture was kept

under constant air-equilibrated conditions before and during the irradiation. At regular irradiation time intervals, the mixture was sampled (1.00 mL), centrifuged, and subsequently filtered through a millipore filter to separate the TiO_2 particles. The filtrates were analyzed by UV-vis spectra with a TU 1900 UV–vis spectrophotometer (Puxi Inc., Beijing, China) equipped with 1 cm quartz cells. The variations of the absorption band maximum (664 nm) were recorded and the change of dye concentration versus irradiation time $(C / C_0 \sim t)$ were thus obtained.

Figure Caption

Fig. S1 TEM image of the as-prepared sample S4. The serious aggregation of shuttle-like rutile nanorods is observed after peptization by high concentration of HNO_3 solution (2.00 M in our experiment).

Fig. S2 XRD patterns of the as-prepared samples S5-S7 and S3. The standard diffraction pattern of one type of protonated pentatitanate ($H_2Ti_5O_{11}•3H_2O$) is also reported. A-anatase; R-rutile; B-brookite; T-titanate.

Fig. S3 (a) TEM image of the as-prepared sample S7. Nearly no obvious 1D structure is formed in the absence of NaOH treatment. (b) TEM image of the as-prepared sample S6. The amorphous TiO_2 formed in the hydrolyzing process is transformed into lamellar titanate by appropriate NaOH treatment.

Figures

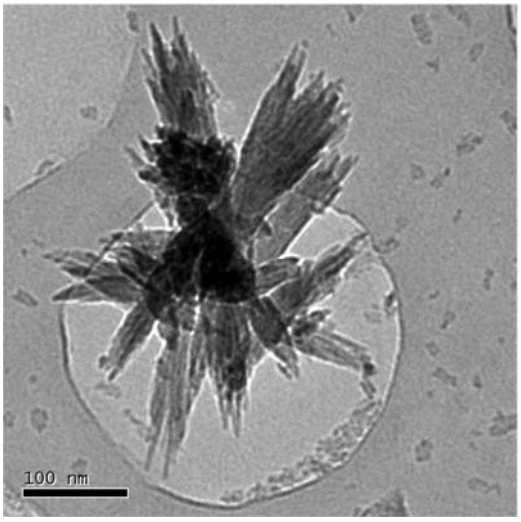

Fig. S1

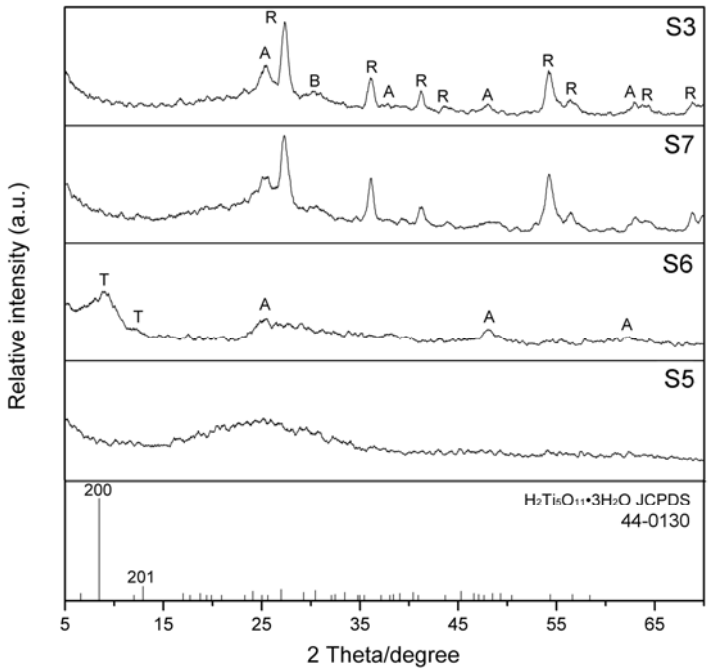

Fig. S2

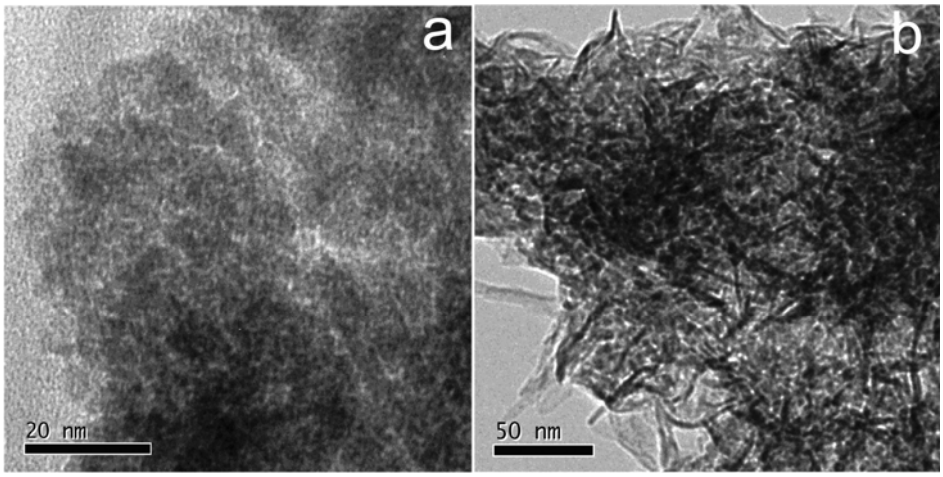

Fig. S3