Supporting information for

Single-crystalline rutile TiO_2 nano-flower hierarchical structures for the enhanced photocatalytic selective oxidation from amine to imine

Jing Bu,[a] Jun Fang,[b] Wan Ru Leow,[a] Kaihong Zheng,[a] Xiaodong Chen*[a]*

[a]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

[b]State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing 210009 (P.R. China)

*Corresponding Author. Prof. Dr. Xiaodong Chen E-mail: chenxd@ntu.edu.sg

Prof. Dr. Jun Fang E-mail: fangjun@njtech.edu.cn

Experimental

Synthesis of TiO_2 samples. All the chemicals used in this study were analytical grade and were applied directly without any further purification. In a typical synthesis, 1ml titanium tetrabutoxide and 1 ml $TiCl_4$ (1 M in toluene) were added into 10 ml toluene solution which was pre-acidified with 1 ml HCl (37%), then calculated amount of CTAB was added. The mixture was stirred and sealed in a Teflon autoclave and kept at 180 ^oC in the oven for 2 h for the solvent-thermal reaction. After the cooling down of the autoclave to room temperature, the obtained precipitation was centrifuged and washed with water and ethanol for 3 times, then the resulted powder was dried at 60 ^oC over night.

Characterization. X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000 X-Ray diffractometer (Cu-K_α source) with the scanning range from 20^o to 80^o. Raman spectrum was recorded on a Witec alpha300 SR Raman spectrometer using 488nm laser as the excited source. Diffuse reflectance UV-Vis spectra were acquired on a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA). Scanning Electron Microscopy (SEM) images were examined on JEOL JSM-7600F. Transmission Electron Microscopy (TEM) images were obtained on JEOL JEM-2010 with 200 kV accelerating voltage. BET and pore size distribution analysis were conducted on a Micromeritics ASAP2020 M^+C system.

Photocatalytic testing. In a typical run, 0.1 mmol benzylamine was dissolved into 5 mL acetonitrile as the solvent, followed by adding 25 mg rutile TiO_2 or P25 catalysts, 0.1 Mpa O_2 was used as the oxidant for the oxidation process. And the reaction was performed under visible light from a Xeon lamp equipped with 420 nm cut-off filter. And the conversion of benzylamine to N-benzylidenebenzylamine was determined by GC analysis using chlorobezene as the internal standard.

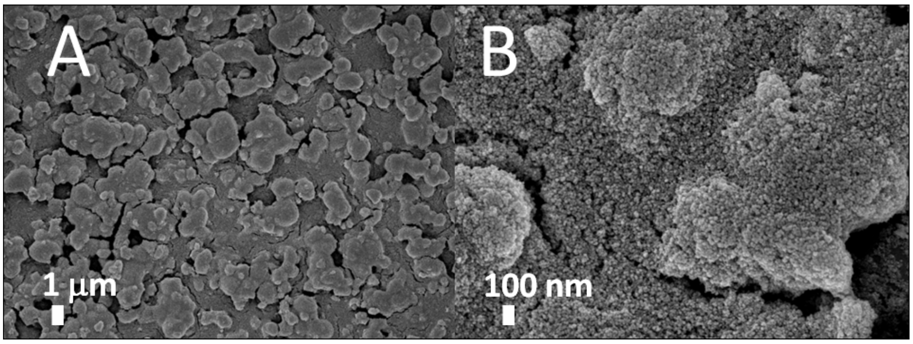

Fig. S1 SEM images of the solvent-thermal products using ethanol as the solvent to replace toluene while keeping the reaction condition identically.

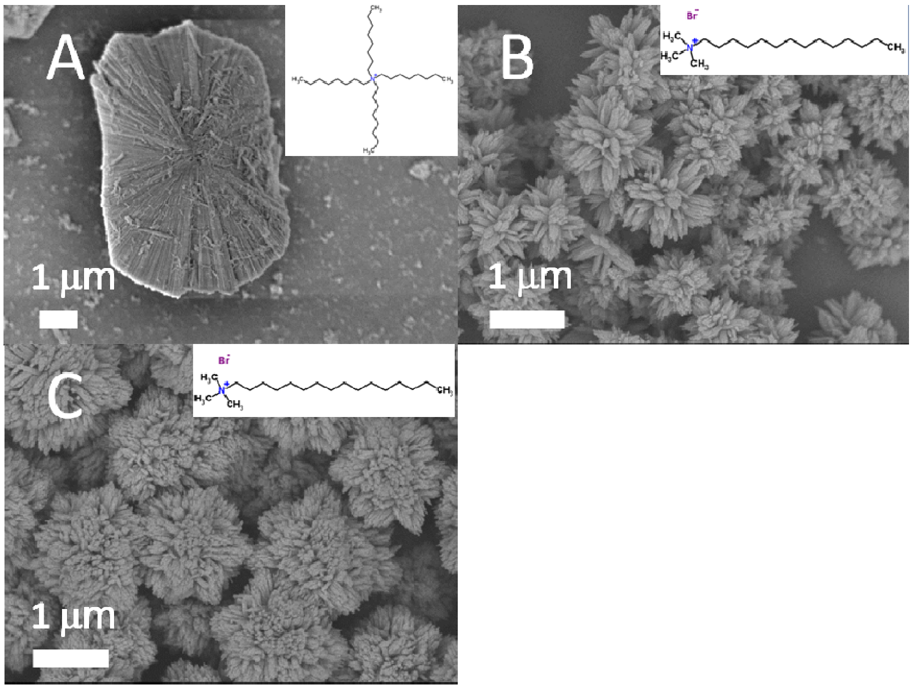

Fig. S2 SEM images of the solvent-thermal products using (A) Tetraoctylammonium Bromide (TOAB), (B) Tetradecyltrimethylammonium Bromide (TDAB) and (C) Cetyltrimethylammonium Bromide (CTAB) as the surfactants.

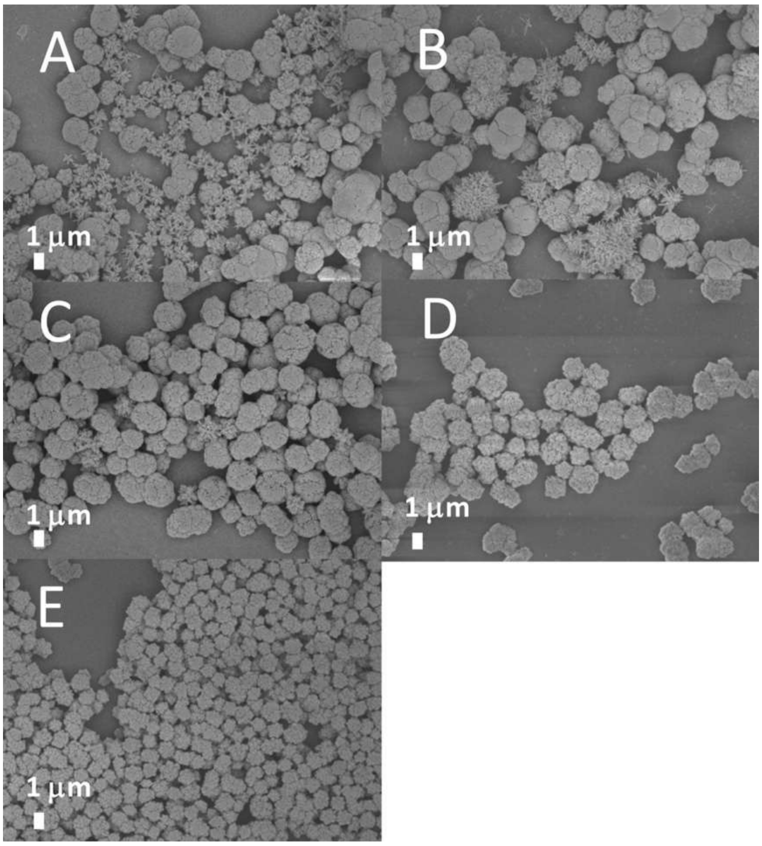

Fig. S3 SEM images of the TiO_2 samples using different molar ratio between CTAB and Ti precursor. (A) 0.2; (B) 0.4; (C) 0.6; (D) 0.8; (E) 1 (CTAB/Ti precursor)

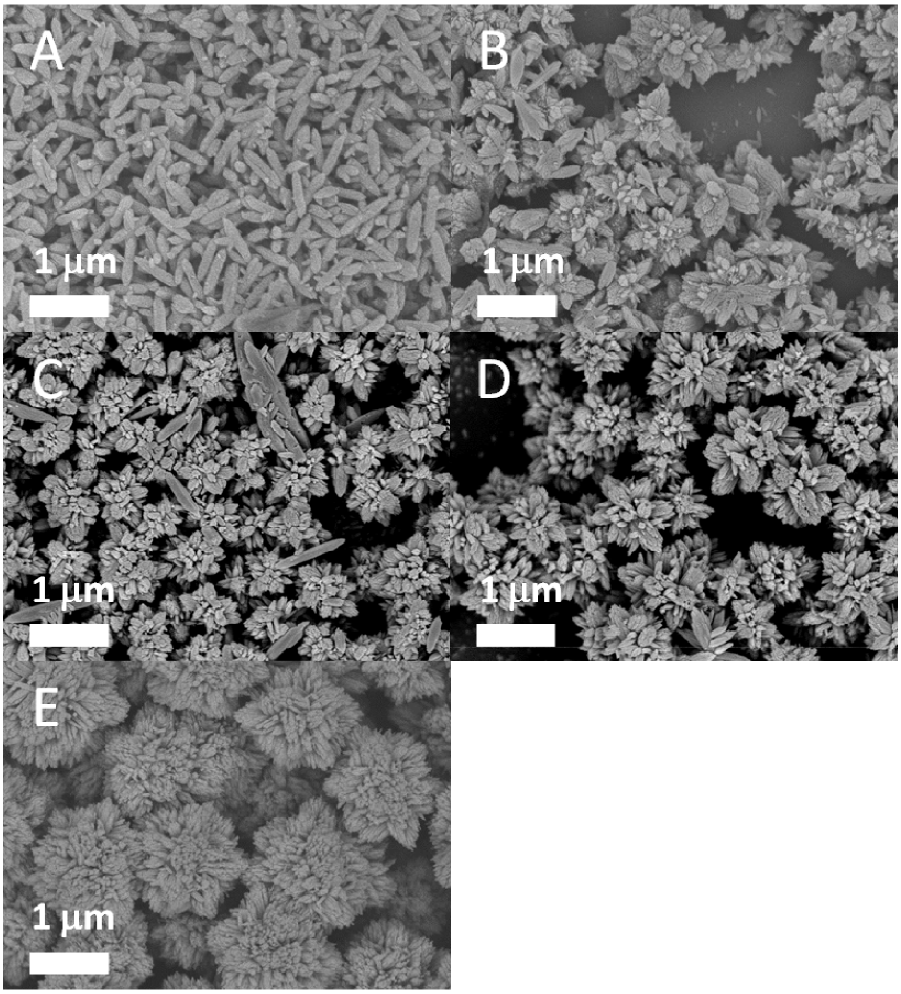

Fig. S4 SEM images of the TiO_2 samples prepared under different temperatures (A) 80 ^oC; (B) 100 ^oC; (C) 120 ^oC; (D) 160 ^oC; (E) 180 ^oC.

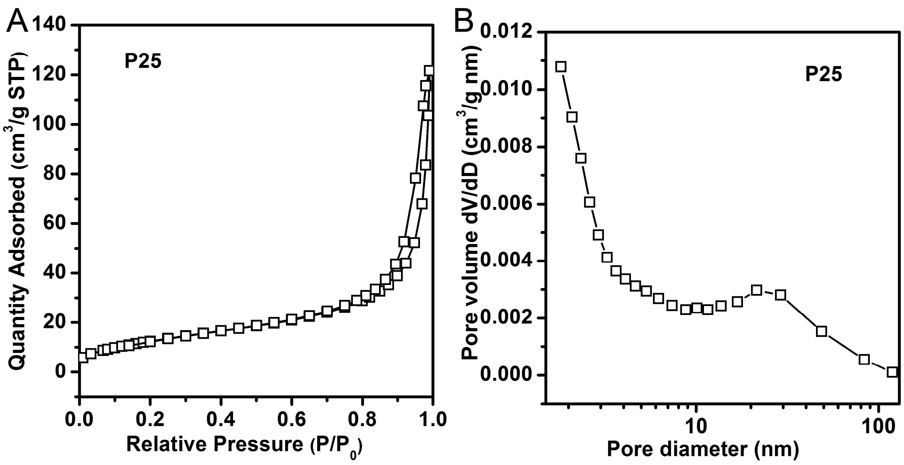

Fig. S5 (A) The N_2 adsorption-desorption isotherm of P25 TiO_2; (B) The pore size distributions of P25 TiO_2.

Table S1. Macroproperties of the rutile TiO_2 nano-flower structures and commercial P25.

Samples	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
TiO_2-nanoflower	43.9	0.098	7.73
P25	47.6	0.19	14.01