

Electronic Supplementary Information

Solvent-Free Synthesis of Titanosilicate Zeolites

Longfeng Zhu,^b Jian Zhang,^a Liang Wang,^{*a} Qinming Wu,^a Chaoqun Bian,^a Shuxiang Pan,^a Xiangju Meng,^a Feng-Shou Xiao^{*a}

^a Key Laboratory of Applied Chemistry of Zhejiang Province, Zhejiang University, Hangzhou 310028, China

^b School of Biology and Chemical Engineering, Jiaying University, Jiaying 314001, China

* Corresponding author. E-mail: liangwang@zju.edu.cn; fsxiao@zju.edu.cn

Experimental Section

Materials

All reagents were used without purification. Tetra-*n*-butyl titanate (TBOT), tetraethyl orthosilicate (TEOS), titanium sulfate, and isopropyl alcohol (IPA) were obtained from Shanghai Chemical Reagent Company. Fumed silica ($\text{SiO}_2 > 99$ wt.%) was supplied from Shenyang Chemical Reagent Co., Ltd. Tetrapropylammonium hydroxide (TPAOH, *ca.* 40 wt.%) and tetraethyl ammonium hydroxide (TEAOH, *ca.* 35 wt.%) were supplied by BASF Company. Ammonium fluoride (NH_4F), hydrogen fluoride (HF, *ca.* 40 wt.%), and hydrogen peroxide (H_2O_2 , *ca.* 30 wt.%) were obtained from the Aladdin Chemical Reagent Company. Hexane, 2-hexanol, 3-hexanol, 2-hexanone, 3-hexanone, and MeOH were also obtained from the Aladdin Chemical Reagent Company.

Synthesis

Solvent-free synthesis of S-TS-1 samples.

The S-TS-1 samples were synthesized from starting titanosilicate mixtures with molar ratios of $\text{SiO}_2/0.01\text{-}0.02\text{Ti}(\text{SO}_4)_2/0.1\text{-}0.15\text{TPAOH}/1.7\text{-}2.5\text{H}_2\text{O}$. As a typical run, 0.60 g of fumed silica was mixed with 0.508 g of TPAOH (40 wt.%). After grinding for 5 min, the solid mixture can be obtained, followed by addition of 0.024 g titanium sulfate and 0.015 g silicalite-1 seeds. After grinding for 10-20 min, the mixture was transformed to an autoclave, heating at 180 °C for 24-48 h. The product was collected by filtrating and washing with deionized water at room temperature and drying at 80 °C for 24 h. The products obtained were designated as S-TS-1- x , where x stands for $\text{SiO}_2/\text{TiO}_2$ ratios in the solid mixture.

Hydrothermal synthesis of C-TS-1 samples.

The C-TS-1 samples were hydrothermally synthesized from the starting titanosilicate gels with molar ratios of $\text{SiO}_2/0.01\text{-}0.02\text{TBOT}/0.3\text{TPAOH}/40\text{H}_2\text{O}/0.33\text{IPA}$. As a typical run for the synthesis of C-TS-1, (1) 0.154 g of TBOT was dissolved in 0.448 g of IPA, followed by the addition of 3.23 mL of TPAOH (40 wt.%) and 7.03 mL of water; (2) After stirring at room temperature for 1.5 h, 6 mL of water was added and stirred for another 15 min; (3) After adding 5 mL of TEOS into the gel and stirring for overnight, the gel was transferred into an autoclave to crystallize at 180 °C for 3 days. The product was collected by centrifuging and washing with deionized water at room temperature and drying at 80 °C for 24 h. The products obtained were designated as C-TS-1- x , where x stands for $\text{SiO}_2/\text{TiO}_2$ ratios in the gels.

Solvent-free synthesis of S-Ti-Beta sample.

The S-Ti-Beta samples were synthesized from the starting titanosilicate mixtures with molar ratios of $\text{SiO}_2/0.01\text{-}0.02\text{Ti}(\text{SO}_4)_2/0.15\text{-}0.20\text{TEAOH}/0.15\text{-}0.20\text{NH}_4\text{F}/2.3\text{-}3.0\text{H}_2\text{O}$. As a typical run, 0.60 g of fumed silica was mixed with 0.632 g of TEAOH (35 wt.%).

After grinding for 5 min, the solid mixture can be obtained, followed by addition of 0.024 g titanium sulfate, 0.055 g NH_4F , and 0.03 g all silica Beta seeds. After grinding for 10-20 min, the mixture was transformed to an autoclave, heating at 140 °C for 12-14 days. The product was collected by filtrating and washing with deionized water at room temperature and drying at 80 °C for 24 h. The products obtained were designated as S-Ti-Beta- x , where x stands for $\text{SiO}_2/\text{TiO}_2$ ratios in the solid mixture.

Hydrothermal synthesis of C-Ti-Beta sample.

The C-Ti-Beta samples were hydrothermally synthesized from the starting titanosilicate gels with molar ratios of $\text{SiO}_2/0.01\text{-}0.02\text{TBOT}/0.5\text{TEAOH}/0.5\text{HF}/3.0\text{-}6.0\text{H}_2\text{O}$. As a typical run, (1) 0.068 g of TBOT was dissolved in 2 g of H_2O_2 ; (2) 4.46 mL of TEOS and 4.2 mL of TEAOH (35 wt.%) were mixed, followed by the addition of titanium solution; (3) After stirring at room temperature for 12 h, 0.44 mL of HF was added. (4) At last, 0.06 g all silica Beta seeds were added. After the evaporation of the calculated amount of H_2O , the gel was transformed into a 30 mL autoclaves to crystallize at 140 °C for 10 days. The product was collected by filtrating and washing with deionized water at room temperature and drying at 80 °C for 24 h. The products obtained were designated as C-Ti-Beta- x , where x stands for $\text{SiO}_2/\text{TiO}_2$ ratios in the gels.

Characterization

X-ray powder diffraction (XRD) patterns were measured with a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using $\text{CuK}\alpha$ ($\lambda=1.5406 \text{ \AA}$) radiation. The N_2 sorption isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 2020M. UV-Vis spectra were measured on a PERKIN ELMER Lambda 20 spectrophotometer. The sample composition was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with a Perkin-Elmer 8000 OES. Scanning electron microscopy (SEM) experiments were performed

on Hitachi SU-1510 electron microscopes. Transmission electron microscopy (TEM) images were performed on a JEM-2100F electron microscopy (JEOL, Japan) with an acceleration voltage of 200 kV. ^{29}Si MAS NMR spectra were recorded on a Bruker AVANCEIII 500WB spectrometer.

Catalytic tests

The oxidation of hexane with H_2O_2 was performed in a 40 mL autoclave with a magnetic stirrer (900 rpm). Typically, organic substrate, solvent, and catalyst were mixed in the reactor. After increasing to the reaction temperature (the temperature was measured with a thermometer in an oil bath), H_2O_2 solution (30 wt.%) was introduced. After reaction, the products were analyzed by gas chromatography (GC-14C, Shimadzu, FID) with a flexible quartz capillary column (FFAP and OV-17).

Table S1. Si/Ti ratios and textural parameters of S-TS-1, C-TS-1, S-Ti-Beta, and C-Ti-Beta samples.

Sample	Si/Ti ^a	BET surface area (m ² /g)	Micropore area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)
S-TS-1-100	92	444	428	0.25	0.20
S-TS-1-50	47	460	418	0.30	0.20
C-TS-1-100	82	475	451	0.36	0.21
C-TS-1-50	43	450	427	0.32	0.20
S-Ti-Beta-100	146	477	461	0.24	0.22
C-Ti-Beta-100	141	509	489	0.26	0.23

^a Si/Ti ratios obtained from ICP-AES.

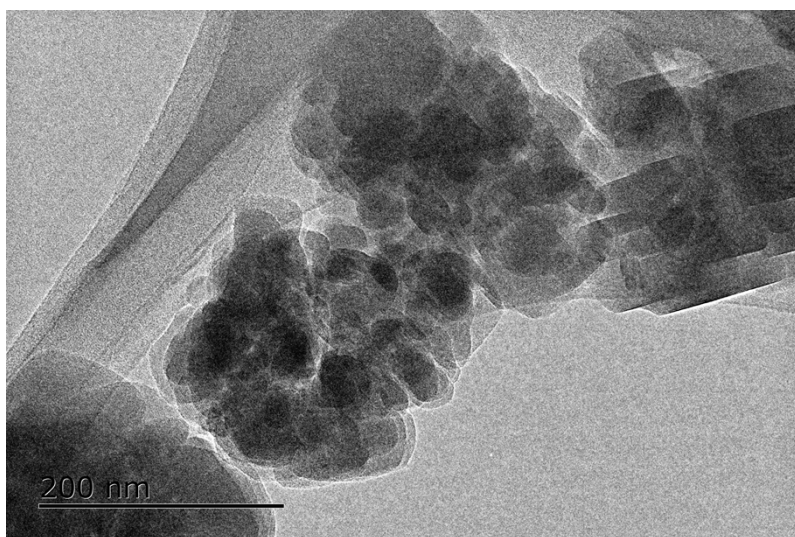
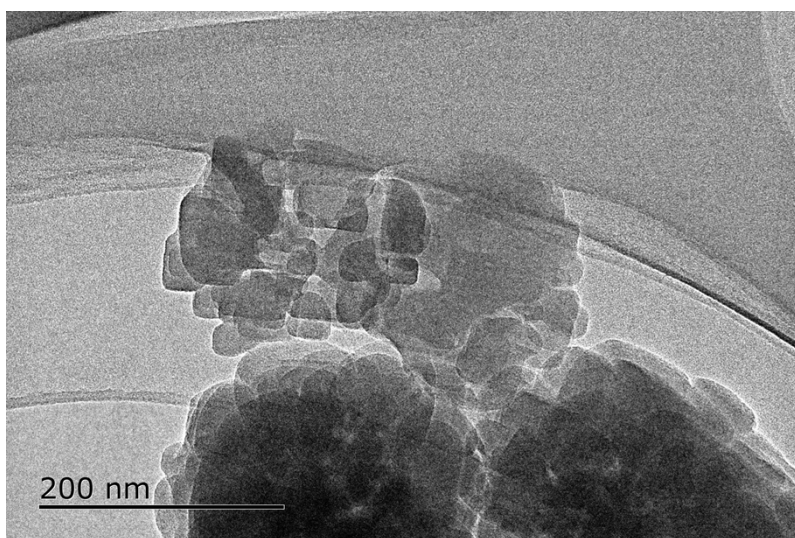
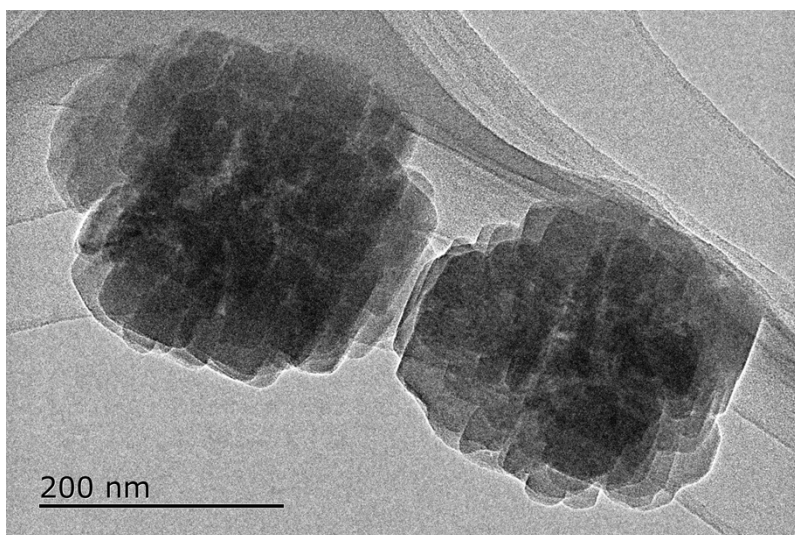


Figure S1. More high magnification TEM images of the solvent-free synthesis of TS-1. It is easy to observe that the zeolite particles are composed of smaller crystals.

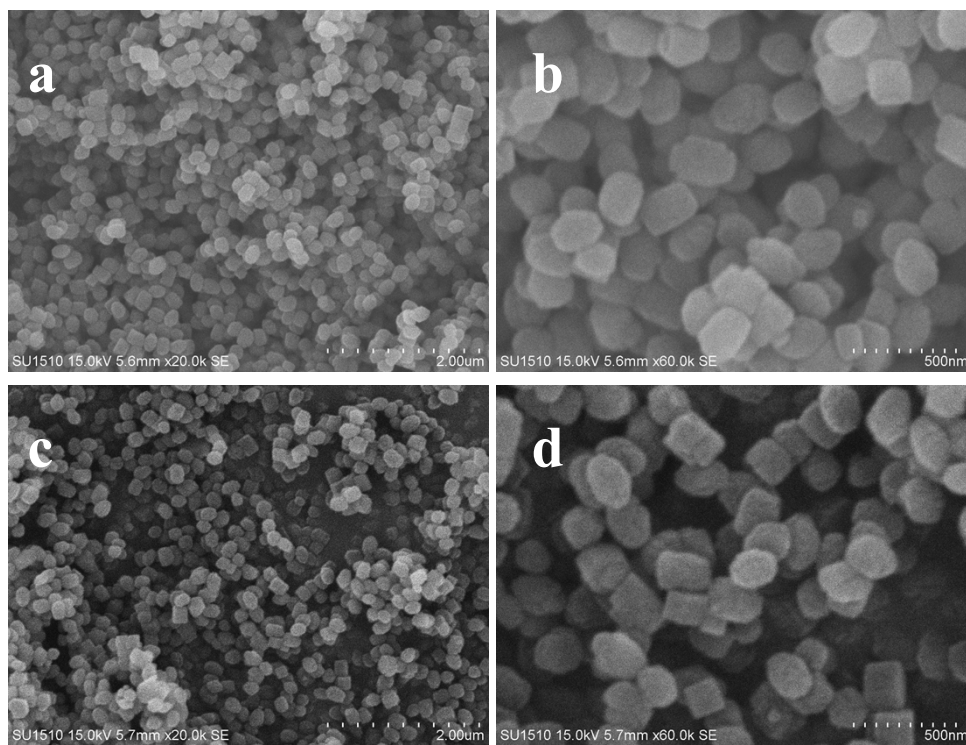
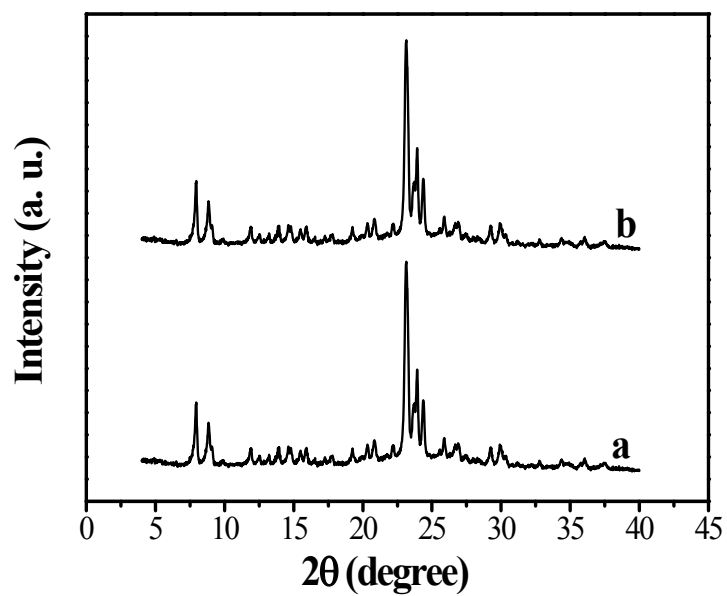


Figure S2. (Top) XRD patterns of (a) C-TS-1-100 and (b) C-TS-1-50; (Bottom) Low and high magnification SEM images of C-TS-1-100 (a, b) and C-TS-1-50 (c, d).

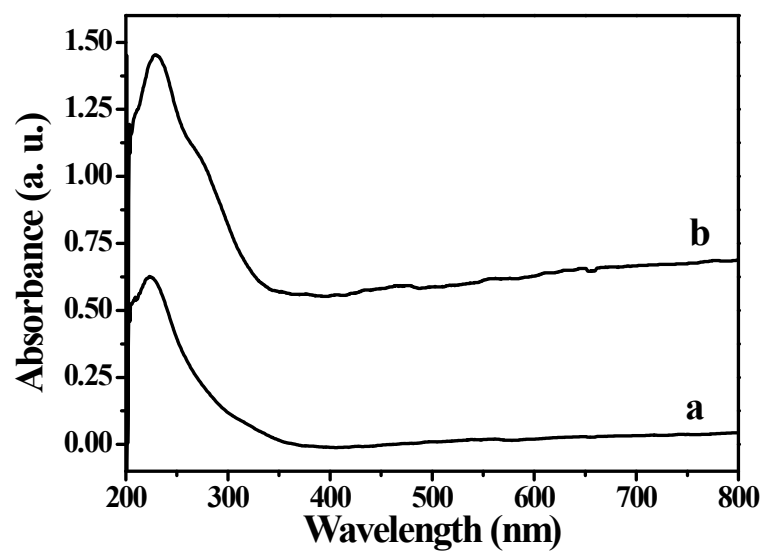


Figure S3. UV-visible spectra of (a) C-TS-1-100 and (b) C-TS-1-50.

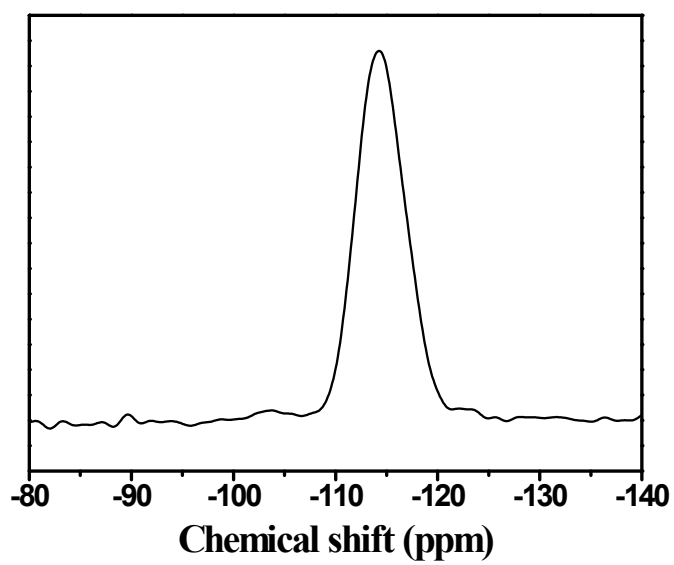


Figure S4. ^{29}Si MAS NMR spectrum of C-TS-1-100.

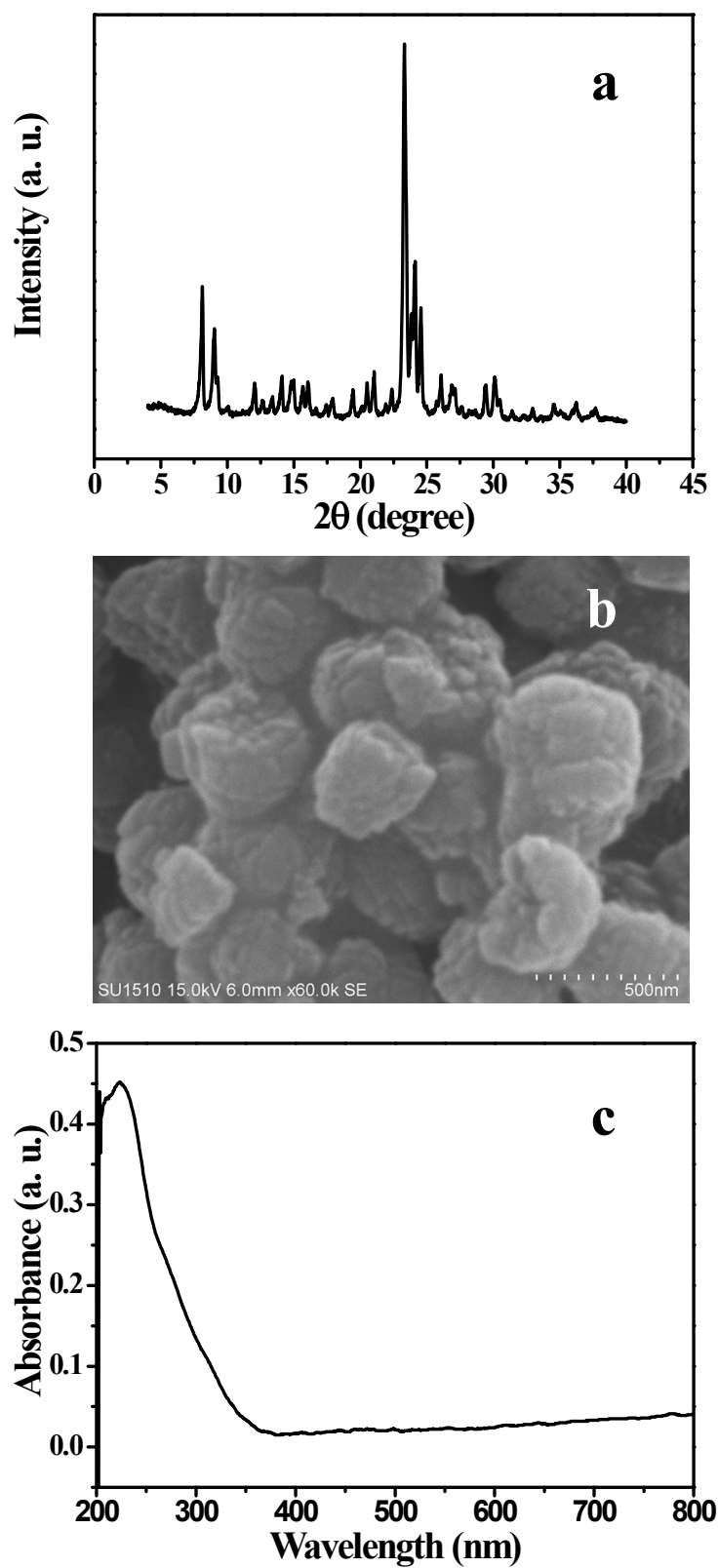


Figure S5. (a) XRD pattern, (b) SEM image, and (c) UV-visible spectrum of S-TS-1-50.

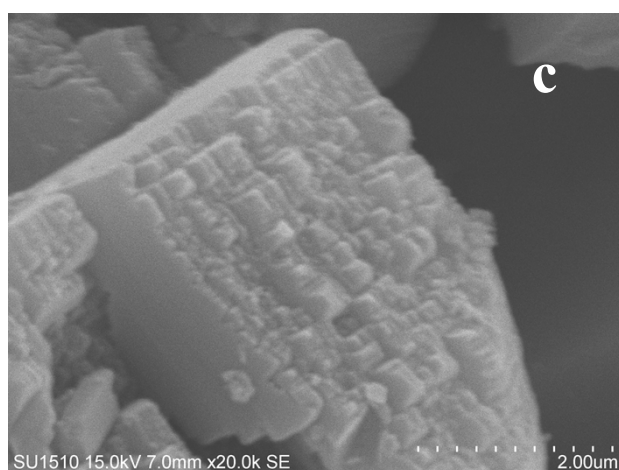
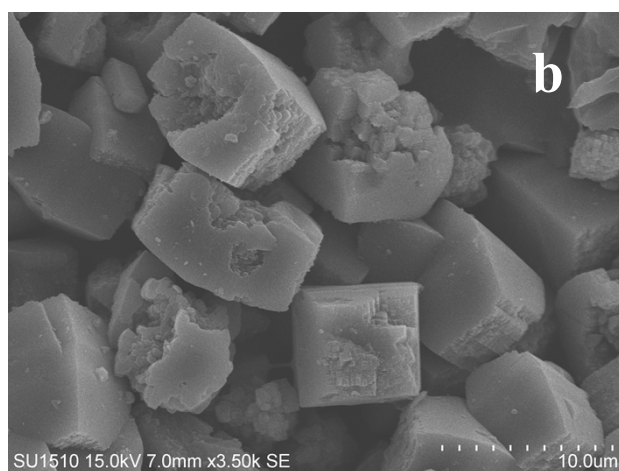
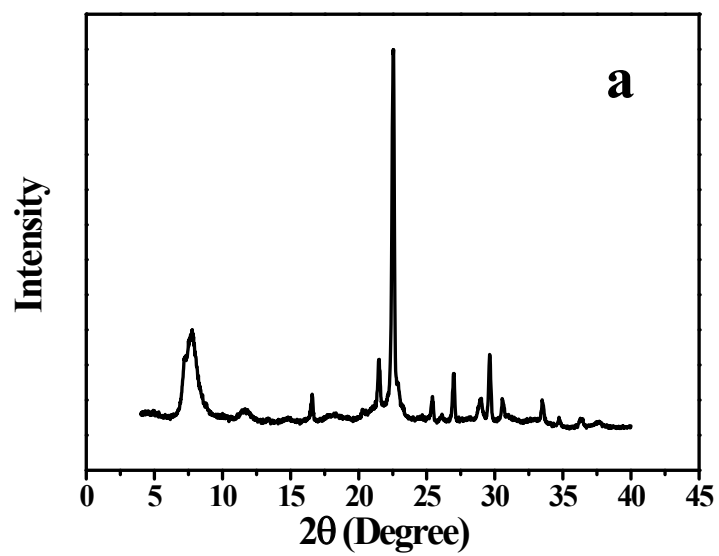


Figure S6. (a) XRD pattern, (b) low and (c) high magnification SEM images of S-Ti-Beta-100.

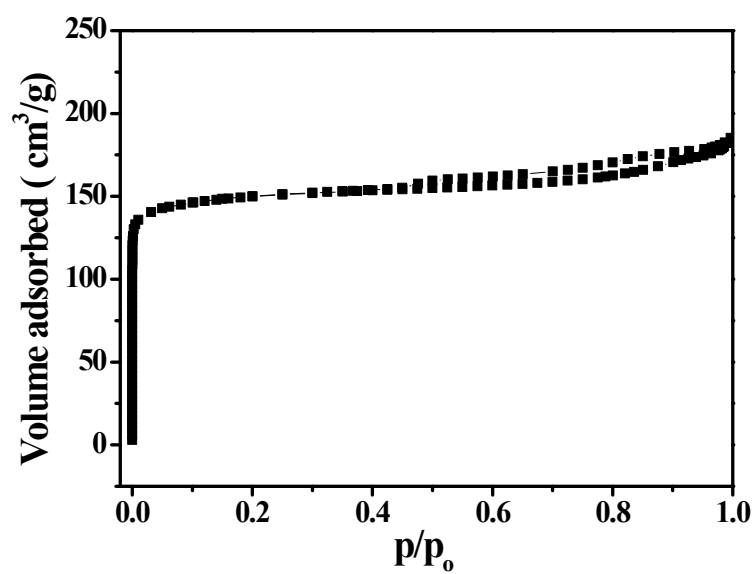


Figure S7. N₂ sorption isotherms of S-Ti-Beta-100.

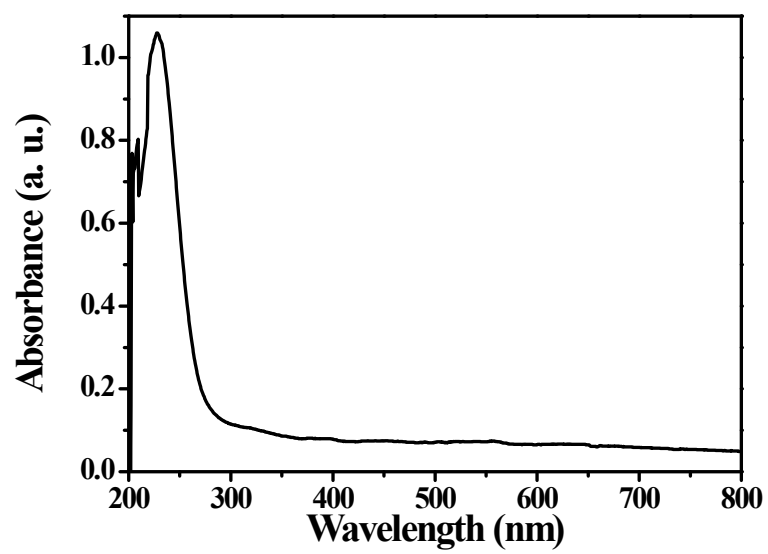


Figure S8. UV-visible spectrum of S-Ti-Beta-100.

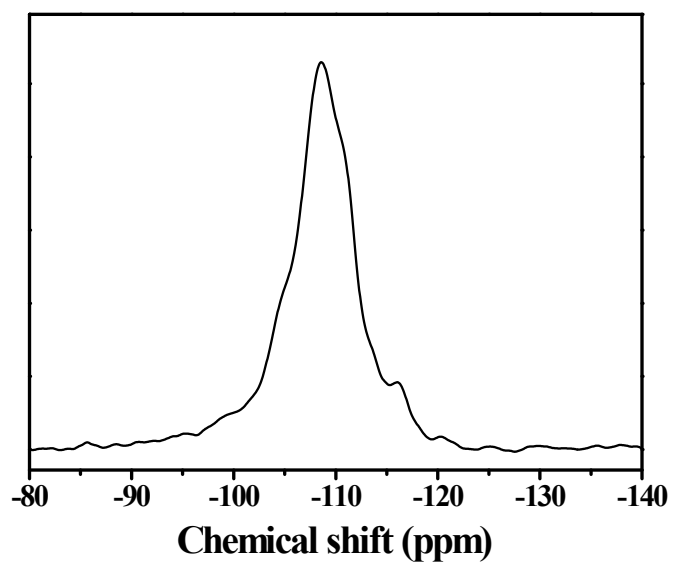


Figure S9. ^{29}Si MAS NMR spectrum of S-Ti-Beta-100.

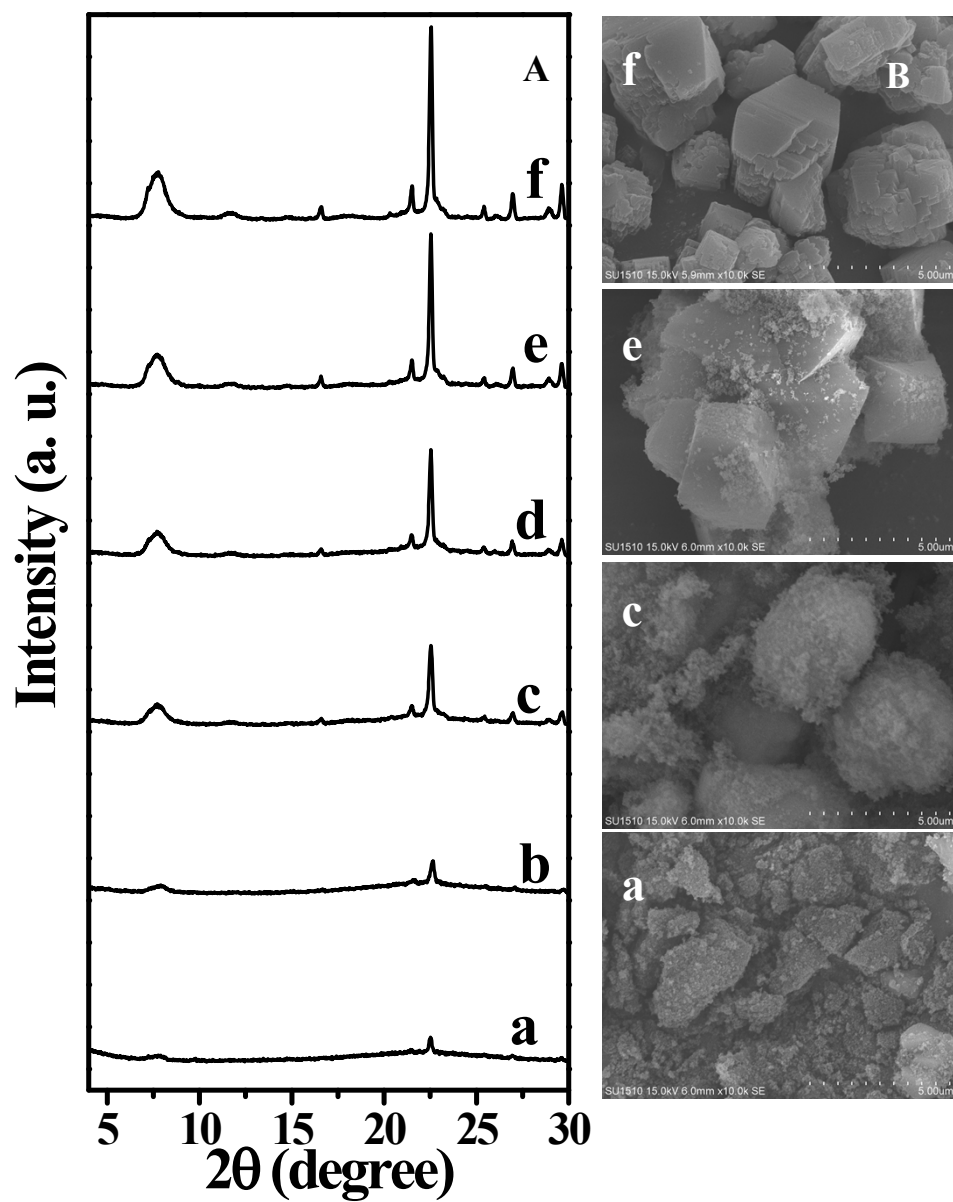


Figure S10. (A) XRD patterns, and (B) SEM images of S-Ti-Beta-100 samples crystallized at (a) 0, (b) 2, (c) 6, (d) 8, (e) 10, and (f) 12 days, respectively.