

## Supporting Information

### Designed Synthesis of TS-1 Crystals with Controllable *b*-Oriented Length

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**Synthesis of Materials.** All reagents were used without any further purification. Tetra-*n*-butyl titanate (TBOT), tetraethyl orthosilicate (TEOS) and isopropyl alcohol (IPA) were obtained from Shanghai Chemical Reagent Company (China).

Tetrapropylammonium hydroxide (TPAOH, ca. 12.6 %) was supplied by Changling Catalyst Company (China). Urea and xylene were supplied by Beijing Chemical Reagent Company (China). FC-4 was obtained from Shanghai Sinyca Corporation Limited (China). Cyclohexanone oxime was supplied by Alfa Aesar Reagent Company.

Sheet-like TS-1 crystals (TS-1-S) were hydrothermally synthesized from starting titanosilicate gels with molar ratios of  $\text{SiO}_2/0.02 \text{ TBOT}/0.3 \text{ TPAOH}/40 \text{ H}_2\text{O}/0.33 \text{ IPA}/0.074\text{-}0.368$  urea. Typically, (1) 0.154 g of TBOT was dissolved in 0.448 g of IPA, followed by addition of 10.26 mL of TPAOH (12.6 % wt.), 6 mL of water, and 5 mL of TEOS; (2) After stirring at room temperature for overnight, 0.5 g of urea was introduced into the gel; (3) After stirring for 4-5 h, the gel was transferred into an autoclave to crystallize at 180 °C for 24 h; (4) After filtrating at room temperature, drying at about 80 °C, calcining at 550 °C for 4 h, sheet-like TS-1 crystals (TS-1-S1) were obtained.

Chain-like TS-1 crystals (TS-1-C) were hydrothermally synthesized from starting titanosilicate gels with molar ratios of  $\text{SiO}_2/0.02 \text{ TBOT}/0.3 \text{ TPAOH}/40 \text{ H}_2\text{O}/0.33 \text{ IPA}/0.024\text{-}0.084$  fluoro carbon surfactant (FC-4). For comparison, normal TS-1 crystals were synthesized from a starting titanosilicate gel with a molar ratio of  $\text{SiO}_2/0.02 \text{ TBOT}/0.3 \text{ TPAOH}/40 \text{ H}_2\text{O}/0.33 \text{ IPA}$ .

**Characterization.** Scanning electron microscopy (SEM) experiments were performed on JEOL electron microscopes (FE-JSM 6700, Japan). Transmission electron microscopy (TEM) experiments were performed on a JEM 3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu K $\alpha$  radiation. UV-visible spectra were collected on PERKIN ELMER Lambda 20. The  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker Avance 500 spectrometer.

**Beckmann rearrangements.** Catalytic Beckmann rearrangements were carried out in a fixed-bed flow reactor. 0.2 g of catalyst was fixed with quartz wool in a stainless steel reactor. The reactor was placed inside a temperature-controllable vertical furnace. After flowing  $\text{N}_2$  at 350 °C for 2 h, 10 wt% of cyclohexanone oxime in toluene was fed into the reactor after vaporization by a pump with a rate of 2.0 mL/h. The reaction products were collected in an ice-water trap and analyzed using an Agilent 6890N GC.

**Adsorption experiments of xylene isomers.** Before the test, 0.2 g of the sample was evacuated at 180 °C for 2 h to remove the adsorbate. Adsorptive capacity of xylenes was measured by the difference in sample weight before and after the exposure to xylene vapor.

**DFT calculation method.** In this work, we used a computational package

called FIREBALL, which is based on density functional theory (DFT-LDA for this work) with a nonlocal pseudopotential scheme. The core of this method is a self-consistent version of the Harris-Foulkes functional with confined atomic-like orbitals used as a basis set for the determination of the occupied eigenvalues and eigenvectors of the one electron Hamiltonian. We recommend reader to Ref. [S1] for a detailed description of the method. Previous work on different systems demonstrated that FIREBALL package is capable to predict energetic structural properties of a variety of nanoscale systems. In this work, we chose a minimal basis set for Si ( $r_c = 4.9, 5.3$ ) and O ( $r_c = 3.3, 3.8$ ); the  $r_c$  values in parentheses are the cutoff of the wavefunctions (in atomic units,  $a_B$ ) for s and p, respectively.

The three MFI slabs are cut directly from the pure MFI (Si:O) zeolite crystal structure. As shown in Figure S1, the three orientations are based upon the original unit cell structure. In order to compare the total energy of three slabs that we cut from the MFI bulk structure, we keep the same amount of atoms in each slab fixed as 288 atoms. In Table S1, both the grand energy and cohesive energy (per atoms) are shown. The result demonstrates that the slab cut from the (010) direction shows the lowest energy, which indicates the higher stability in the direction growing during the entire zeolite synthesis procedure. Based on our computational result, we propose that MFI (010) surface is the more favorable orientation.

**Supporting References:**

S1. Lewis, J.P., et al., *Further developments in the local-orbital*

*density-functional-theory tight-binding method*, **Physical Review B**, 2001, **64**,

195103.

Table S1. The DFT calculated energy of three MFI slabs in (001), (010) and (101) orientations. Each slab has 288 atoms, and the energy unit is calculated in eV.

	001	010	101
Grand Energy	-325.62	-325.64	-325.59
(per atom)			
Average Energy	-7.65	-7.67	-7.62
(per atom)			

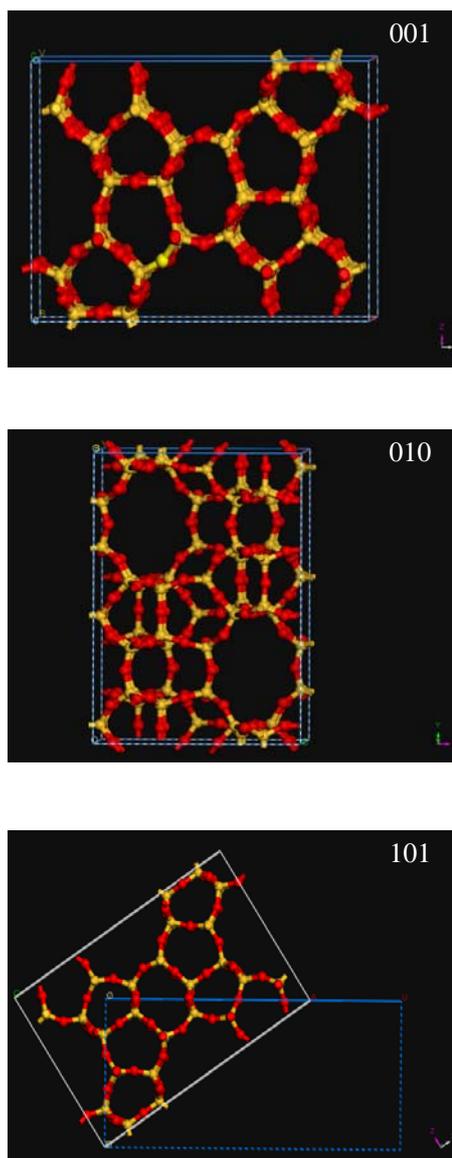


Figure S1. The three principal MFI frameworks in (001), (010) and (101) orientations.

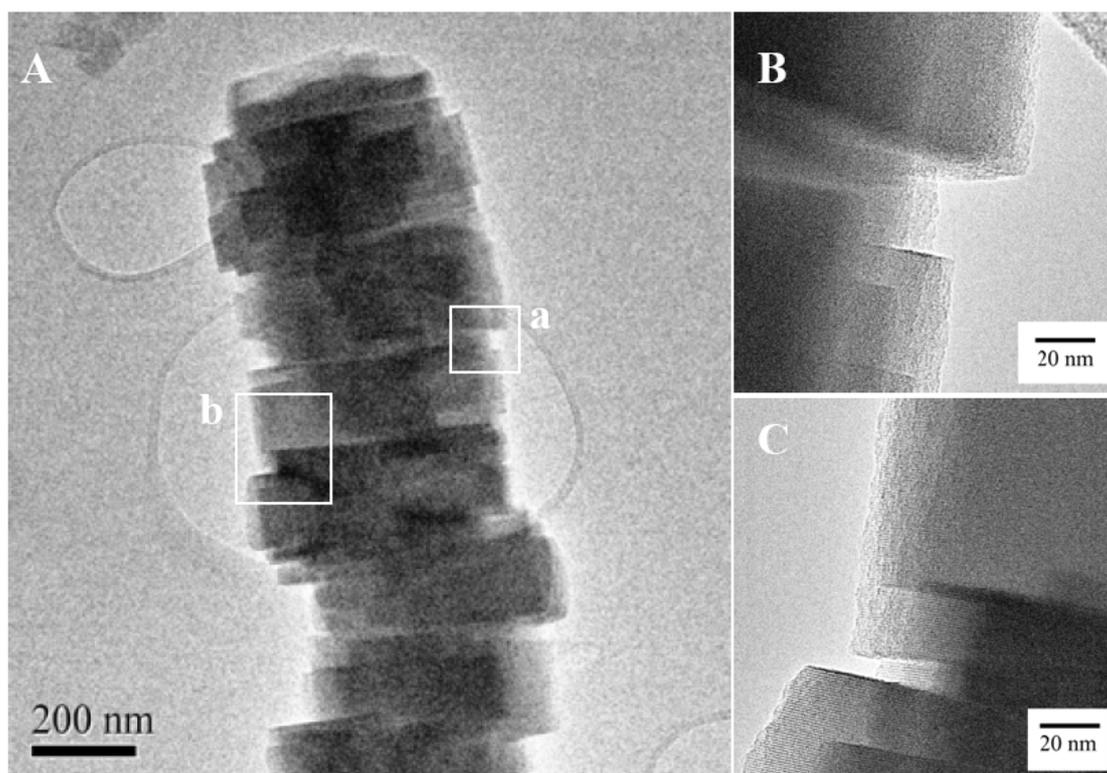


Figure S2. (A) TEM image of TS-1-C2. (B) and (C) are the enlargements for selected areas of (a) and (b) in (A). These images confirm that there are strong interactions between crystals.

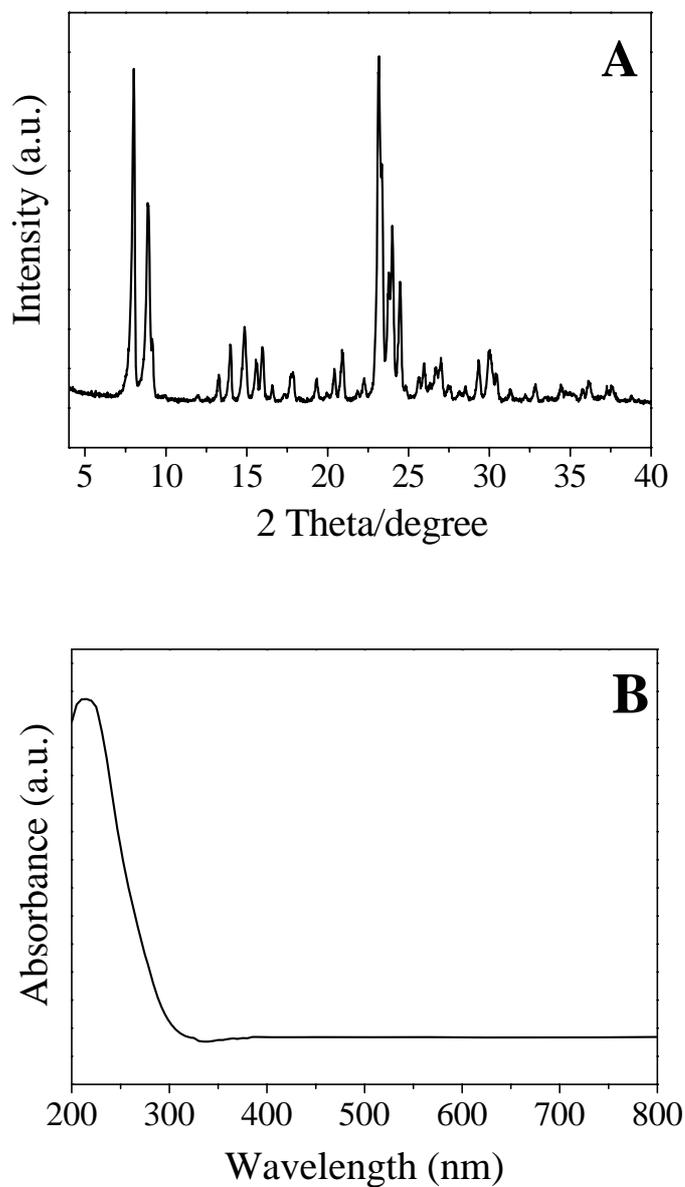


Figure S3. (A) XRD pattern and (B) UV-visible spectrum of TS-1-S1 synthesized at 180 °C from the starting gel with molar ratio of urea/SiO<sub>2</sub> at 0.368. These results indicate that TS-1-S1 with pure 4-coordinative Ti sites has good crystallinity.

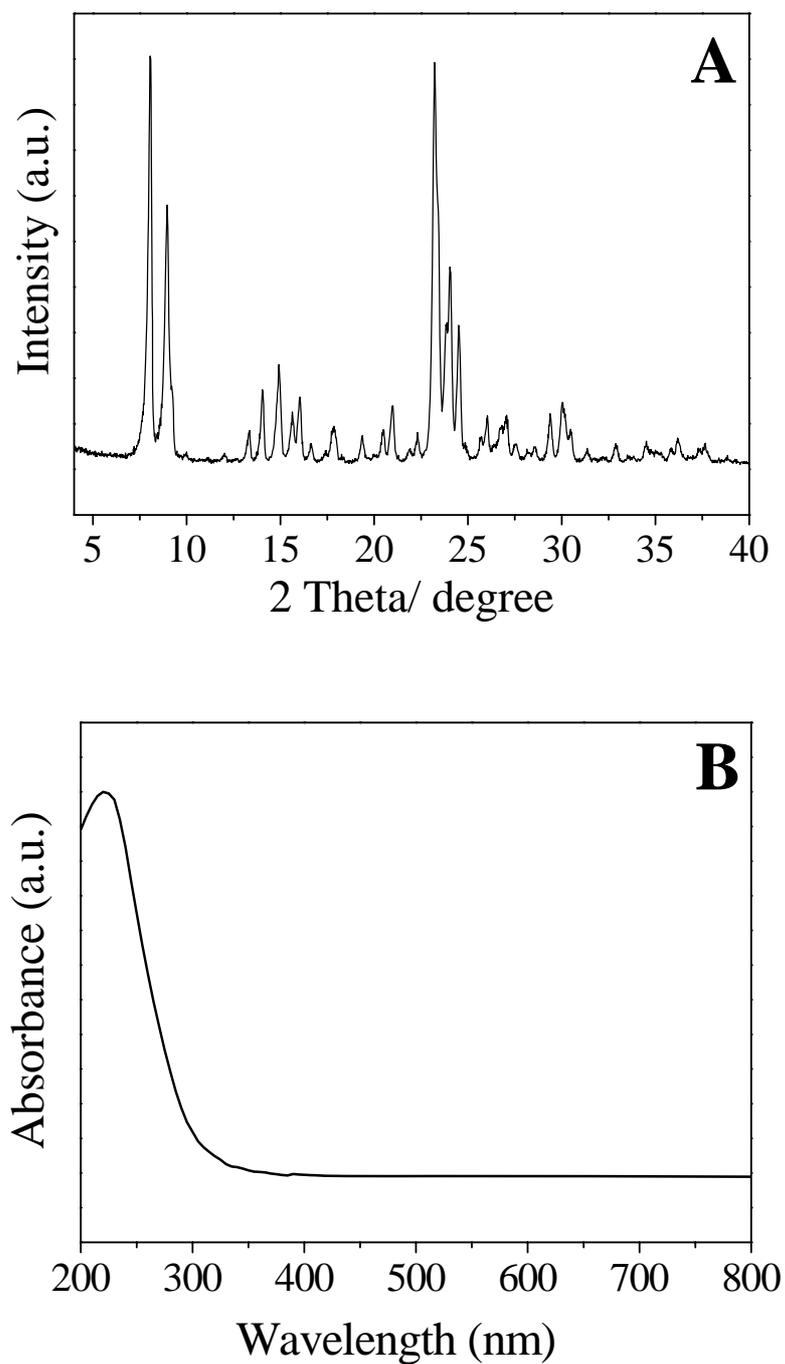


Figure S4. (A) XRD pattern and (B) UV-visible spectrum of TS-1-C2 synthesized at 180 °C from the starting gel with molar ratio of FC-4/SiO<sub>2</sub> at 0.084. These results indicate that TS-1-C2 with pure 4-coordinative Ti sites has good crystallinity.

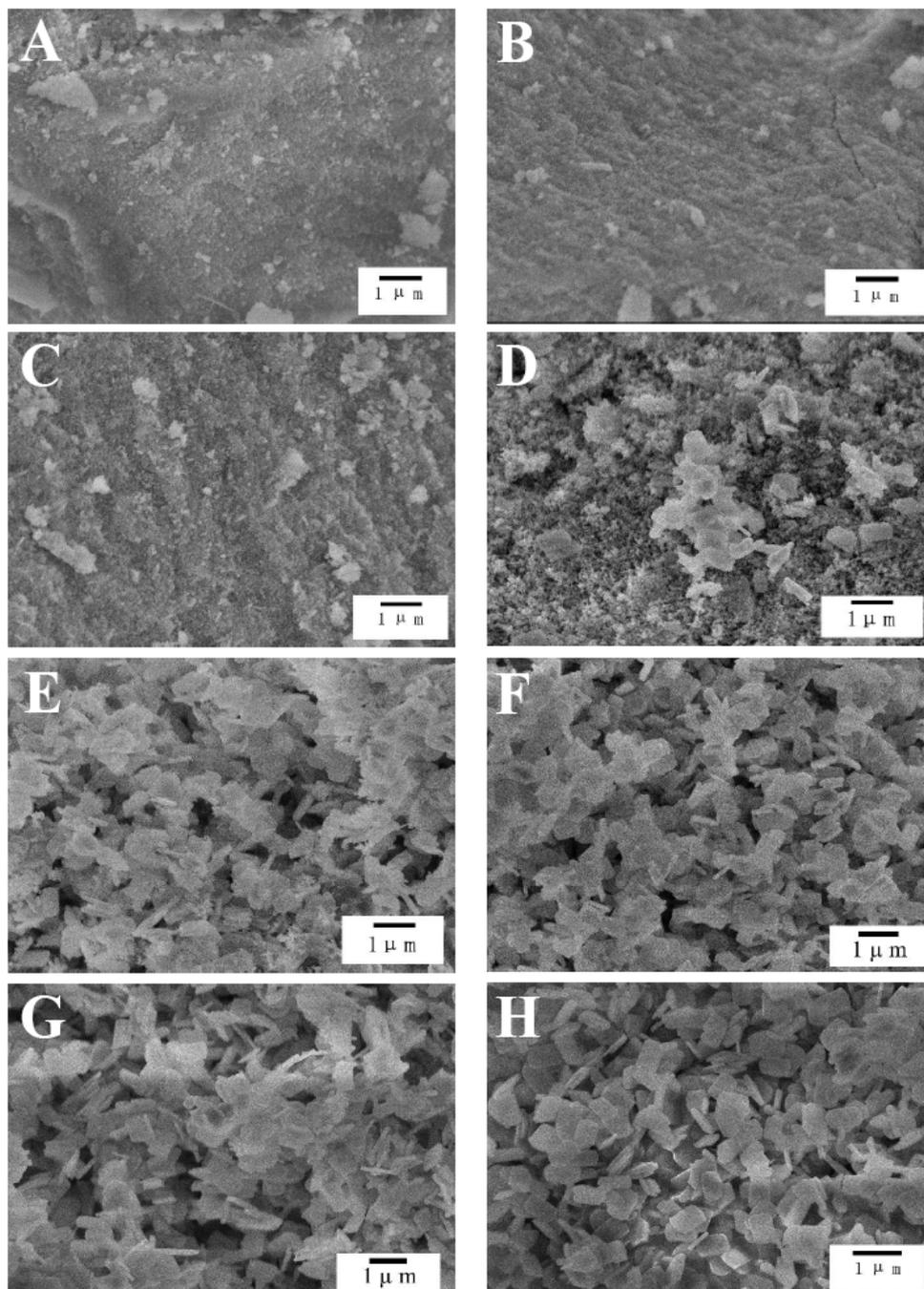


Figure S5. SEM images of TS-1-S1 crystallized at 180 °C for (A) 2.0, (B) 2.5, (C) 3.0, (D) 3.5, (E) 4.0, (F) 6.0, (G) 12.0, and (H) 24.0 h, respectively. These results suggest that the sheet-like crystals are mainly formed in the period of 3-4 h.

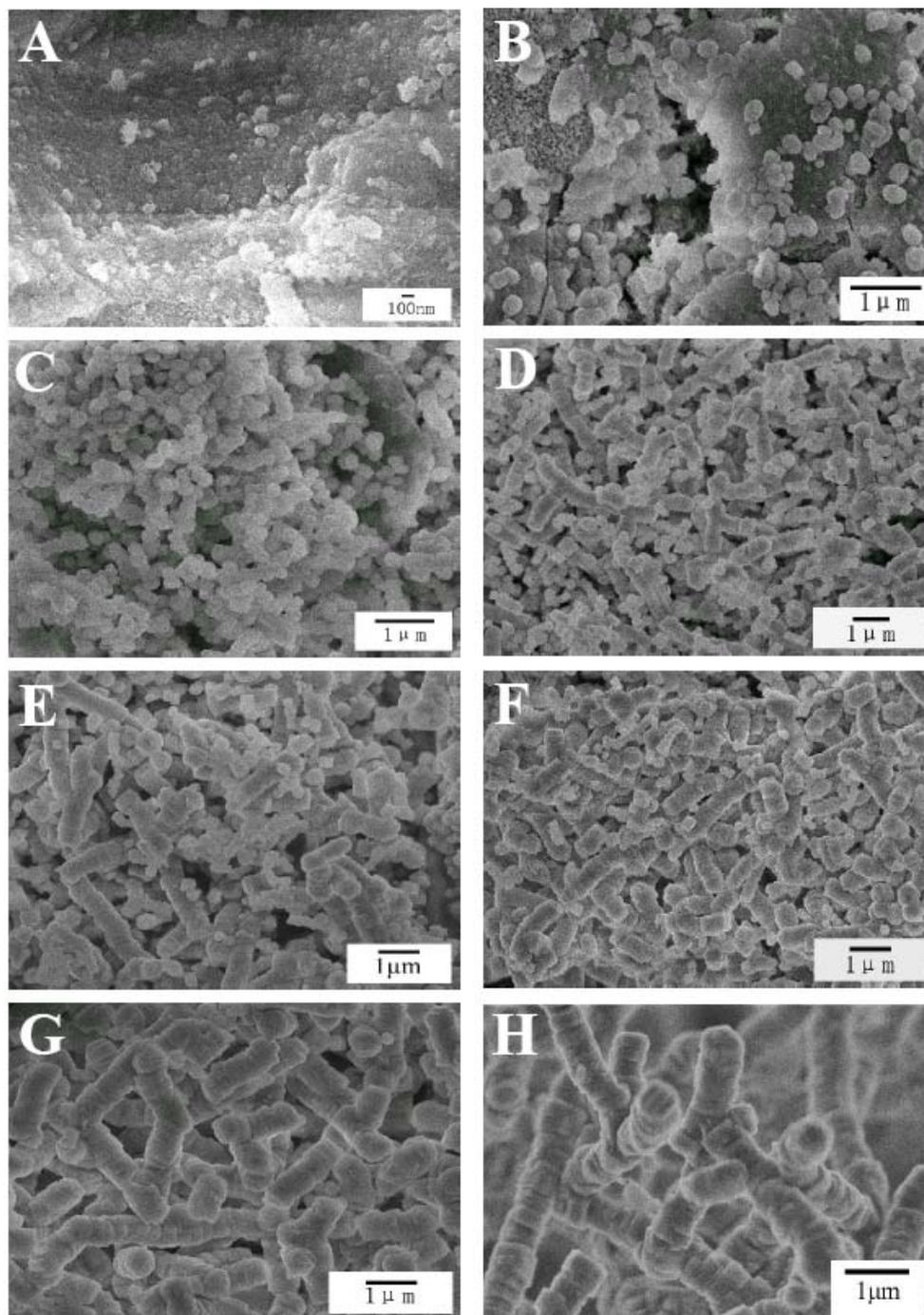


Figure S6. SEM images of TS-1-C2 synthesized at 180 °C for (A) 2.0, (B) 2.2, (C) 2.3, (D) 3.0, (E) 6.0, (F) 12.0, (G) 18.0, and (H) 24.0 h, respectively. These results indicate that chain-like crystals are mainly formed in the period of 2.3-3 h.

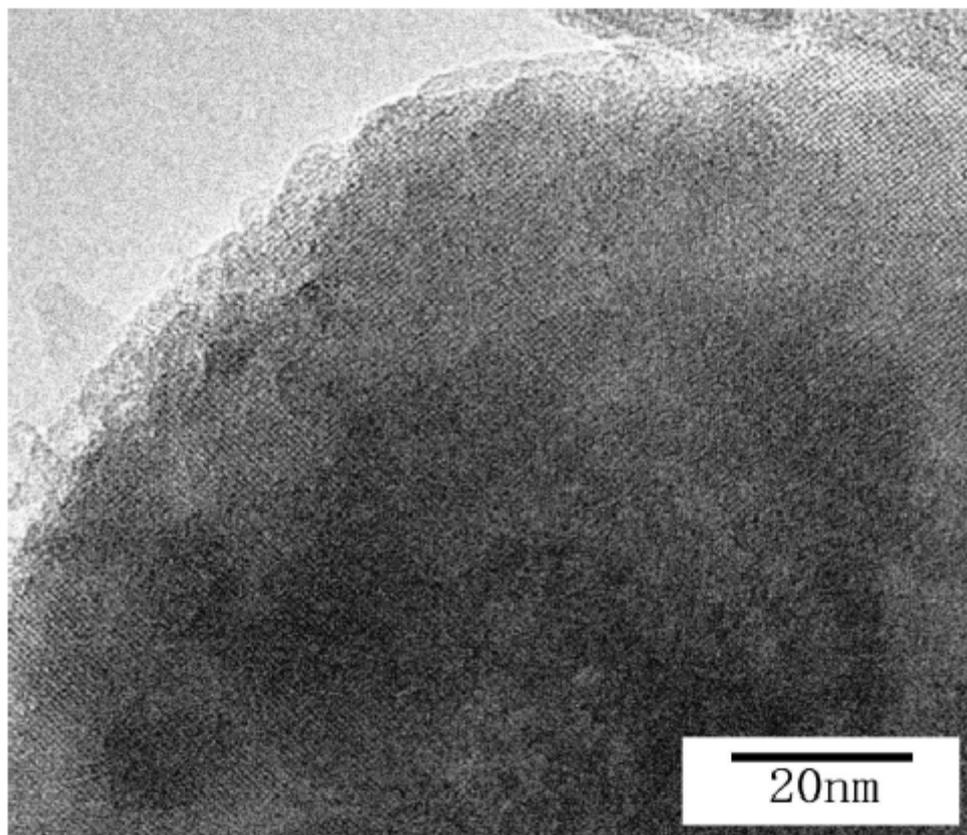


Figure S7. High-resolution TEM image of nanoparticles (100-350 nm) for the synthesis of TS-1-C2 product crystallized for 2.2 h at 180 °C. This image demonstrates that the nanoparticles for the synthesis of TS-1-C2 product crystallized for 2.2 h at 180 °C have become TS-1 zeolitic structure.

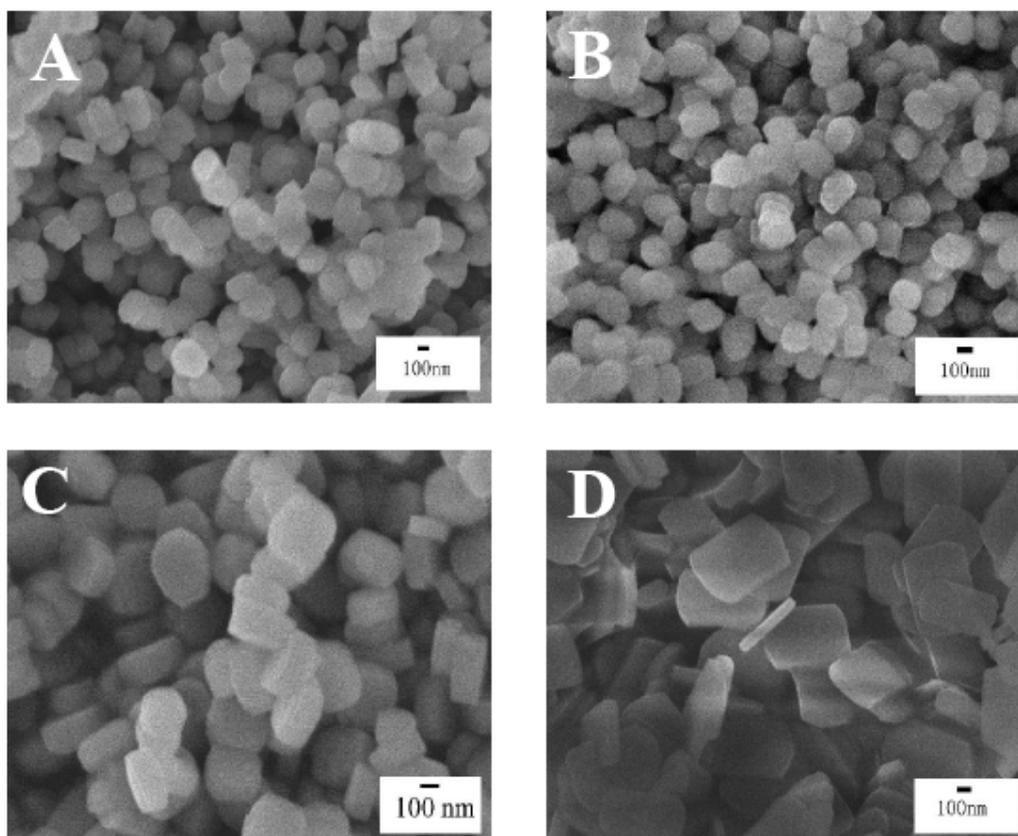


Figure S8. SEM images of TS-1-S synthesized at 180 °C for 24 h in the starting gels with molar ratios of urea with SiO<sub>2</sub> at (A) 0.074, (B) 0.147, (C) 0.221, and (D) 0.368, respectively. These results show that the length of TS-1 crystals along *b*-orientation could be adjusted by changing molar ratios of urea with silica.

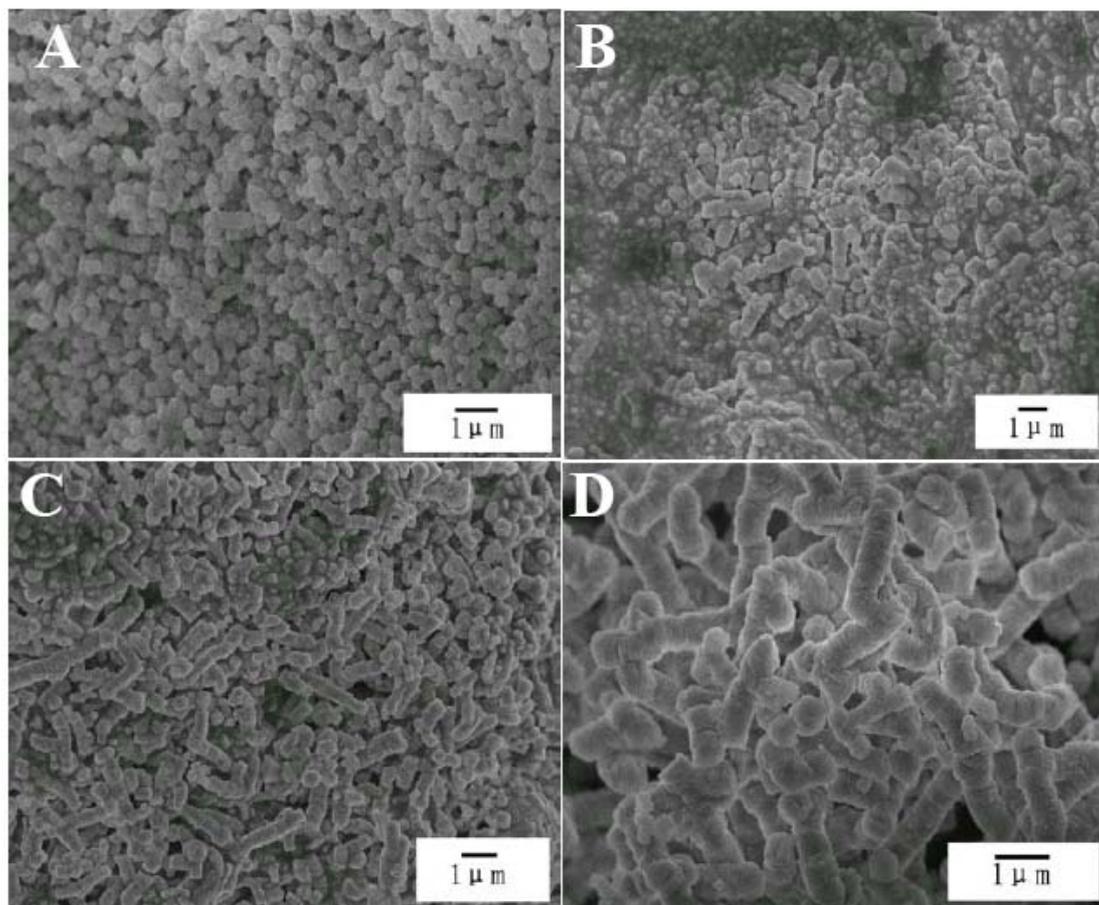


Figure S9. SEM images of TS-1-C synthesized at 180 °C for 24 h in the starting gels with molar ratios of FC-4 with silica at (A) 0.024, (B) 0.048, (C) 0.072, and (D) 0.084, respectively. These results show that the length of TS-1 crystals along *b*-orientation could be adjusted by changing molar ratios of FC-4 with silica.

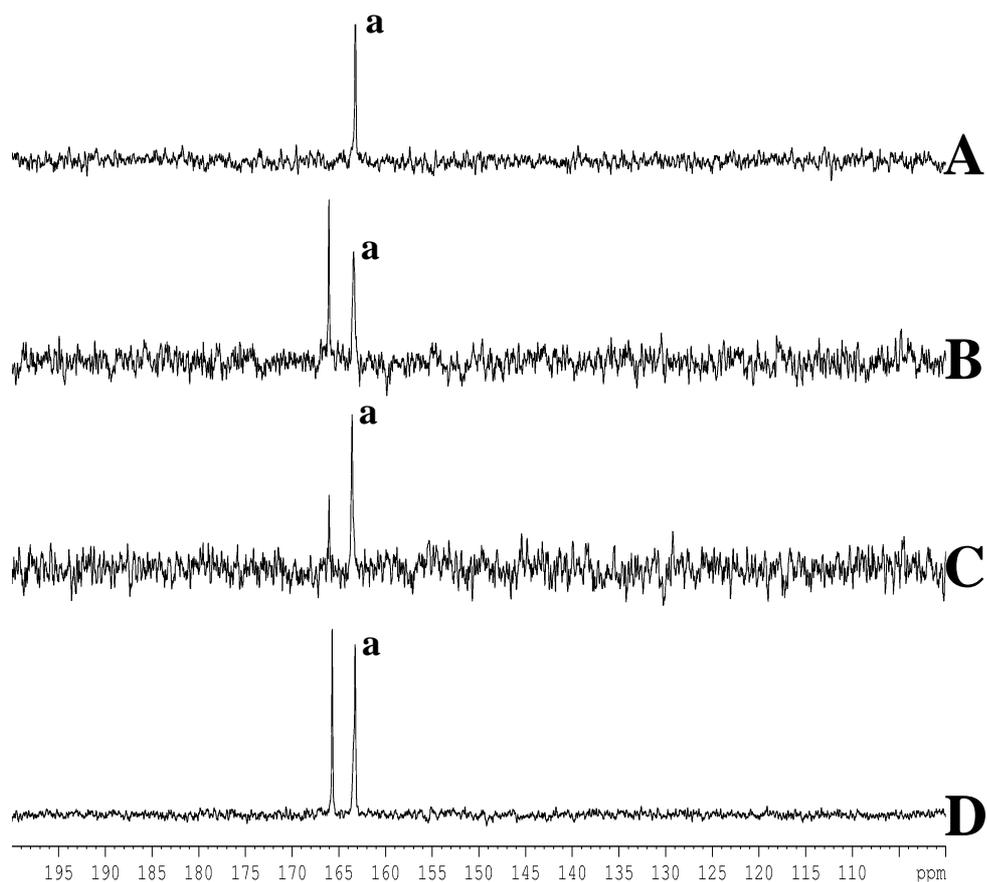
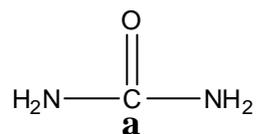


Figure S10.  $^{13}\text{C}$  NMR spectra of urea treated at 180 °C for (A) 0, (B) 3.0, (C) 4.0, and (D) 5.0 h, respectively. These results suggest that partial molecules of urea still exist during the crystallization time of 3-5 h.



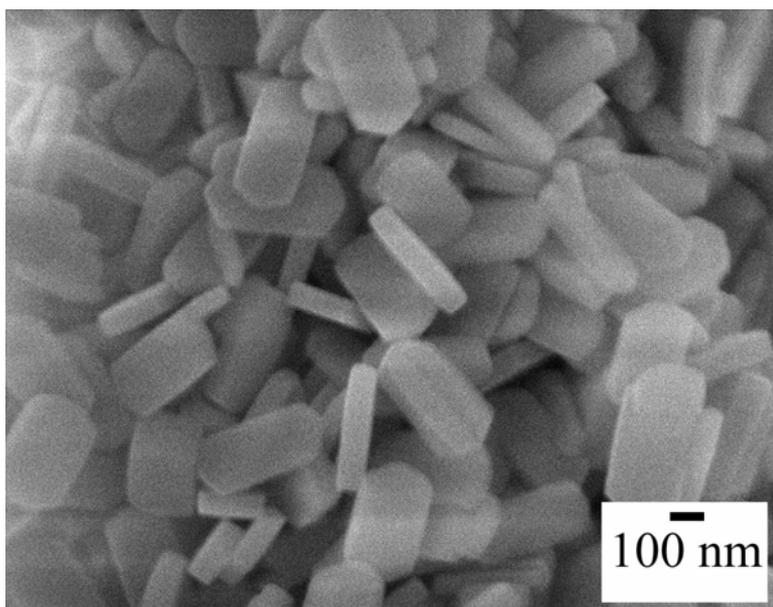
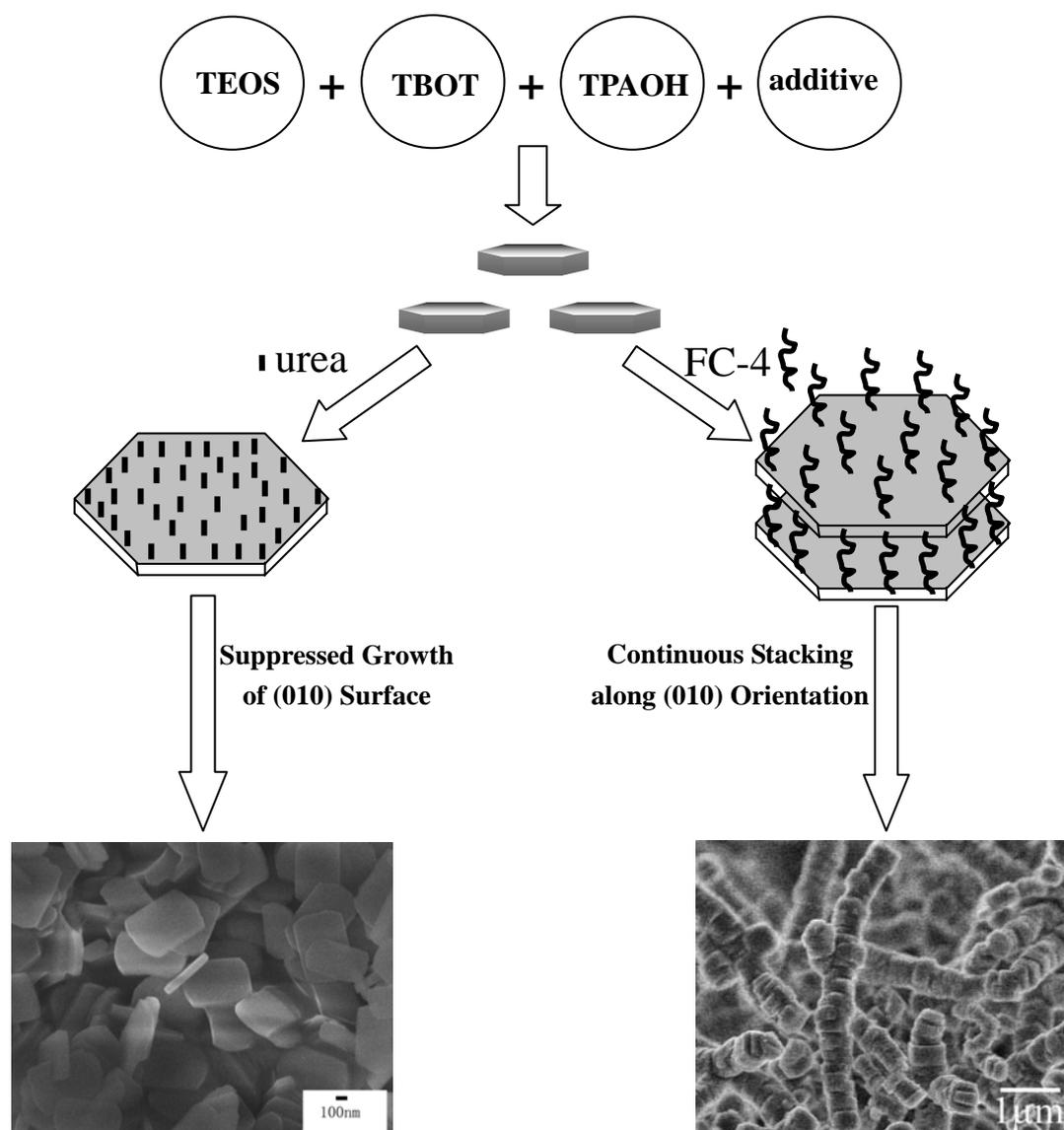


Figure S12. SEM image of sheet-like crystals of S-I synthesized at 180 °C from the gel with molar ratio of urea with silica at 0.368. This image shows that the sample has good crystallinity and the crystalline morphology is sheet-like.



Scheme S1. Proposed mechanism on the formation of TS-1-S crystals or TS-1-C crystals in the presence of urea or FC-4. After preferential adsorption of urea on (010) surface, the crystal growth along (010) orientation could be suppressed, giving TS-1-S crystals. On the contrary, FC-4 surfactants could be adsorbed on the two nearby TS-1 crystals. As a result, FC-4 is served as a linker for the two nearby TS-1 crystals. After continuous linking TS-1 crystals, TS-1-C crystals are formed finally.