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# MFI zeolite nanosheets with post-synthetic Ti grafting for catalytic epoxidation of bulky olefins using $H_2O_2$

Jaeheon Kim,[ab] Joonsoo Chun,[ab] and Ryong Ryoo*[ab]

[a.] Department of Chemistry, KAIST, Daejeon 305-701, Korea

[b.] Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon 305-701, Korea

## Synthesis of MFI zeolite nanosheets

For the synthesis of MFI zeolite nanosheets, hydrothermal synthesis was performed at 150 °C using a bromide form of a diammonium surfactant as a zeolite structure-directing agent (SDA), $[C_{18}H_{37}\text{-}N^+(CH_3)_2\text{-}(CH_2)_6\text{-}N^+(CH_3)_2\text{-}C_6H_7][Br^-]_2$. In a typical synthesis of a zeolite nanosheet, 0.84 g of surfactant was clearly dissolved in 12 ml of a 0.14 M NaOH aqueous solution. To this solution, 1 g of fumed silica as a silica source was added at once, shaken strongly by hand for 10 minutes, and subsequently aged at 60 °C with magnetic stirring overnight. The resulting gel had the following molar ratio: 100 $SiO_2$/ 7.5 surfactant/ 5 $Na_2O$/ 4000 $H_2O$. The gel was transferred to a Teflon-lined stainless steel autoclave and heated to 150 °C while tumbling. After 4 d, the precipitated white powder was collected by filtration and dried at 100 °C. The dried sample was calcined at 550 °C to remove the organics.

## Preparation of TS-1, D-TiNS, D-TiM41 and G-TiM41

TS-1 and D-TiNS were prepared by following a procedure in the literature.[1] D-TiM41 was prepared using cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich), also by following a procedure in the literature.[2] For the preparation of G-TiM41, pure silica MCM-41 was synthesized using CTAB via a previously established method.[2] Ti was then grafted onto MCM-41 by the same method for the Ti grafting of G-TiNS.

## Preparation of Ti-containing MFI zeolite nanosheets by the B-to-Ti method

For the preparation of Ti-containing MFI zeolite nanosheets by the B-to-Ti method, a MFI zeolite borosilicate nanosheet was synthesized by following a synthesis procedure similar to one in the literature,[3] except for the use of a boron source (boric acid) instead of an aluminium source (aluminium sulfate) and the absence of bulk crystal seeding process. $[C_{18}H_{37}\text{-}N^+(CH_3)_2\text{-}(CH_2)_6\text{-}N^+(CH_3)_2\text{-}C_6H_7][Br^-]_2$ was used as an SDA in this synthesis. The final gel composition in a molar ratio was 100 $SiO_2$/ 3.3 $B(OH)_3$/ 7.5 SDA/ 30 $Na_2O$/ 18 $H_2SO_4$/ 5000 $H_2O$. The synthesis gel was reacted in an autoclave at 150 °C for 46 h while tumbling. After the reaction, the resulting zeolite powder was collected by filtration/drying and calcined at 550 °C. The calcined zeolite was treated by an excess amount of a 2 M HCl aqueous solution. The HCl-treated zeolite was filtered and sufficiently washed with water. After drying, Ti was loaded into the resultant zeolite by wet-impregnation methods using titanium (IV) butoxide (TBOT) 1-butanol solution. The molar ratio was 100 $SiO_2$/ 1 TBOT/ 300 1-butanol. The TBOT-impregnated zeolite sample was calcined at 550 °C to remove organics. The resultant zeolite was denoted as ‘S-TiNS’.

## Catalytic measurement

The reaction was carried out in a Pyrex batch reactor which was equipped with a reflux condenser. In a typical catalytic reaction, 35 mg of the catalyst and 12 mmol of olefins were added to 10 ml of acetonitrile (Junsei, 99 %). After agitation of the resulting mixture at 60 °C for 10 min under magnetic stirring, the reaction was started by adding 3.3 mmol of $H_2O_2$ (35 wt% in water, Sigma-Aldrich) to the reaction mixture. The reaction was conducted for 2 h at 60 °C. The reaction solution was collected and filtered to remove the catalysts. The filtered solution was analyzed by gas chromatography equipped with a HP-5 capillary column (J&W Scientific; 30-m-long, 0.32-mm-i.d., and 0.25 μm thick) and a flame ionization detector. The conversion of olefin was calculated on the basis of the amount of oxidant. The hydrogen peroxide efficiency was determined by an iodometric method. After the catalytic reaction, the catalyst was filtered and sufficiently washed with ethanol and acetone. The recovered catalyst was dried at 100 °C and calcined at 550 °C for 3 h under air for recyclability tests.

## References

1. K. Na, C. Jo, J. Kim, W.-S. Ahn, and R. Ryoo, *ACS Catal.*, 2011, **1**, 901.
2. K.A. Koyano, and T. Tatsumi, *Microporous Mater.*, 1997, **10**, 259.
3. J.-C. Kim, S. Lee, K. Cho, K. Na, C. Lee, and R. Ryoo, *ACS Catal.*, 2014, **4**, 3919.

## Fourier-transform infrared measurement for MFI zeolite nanosheet

The Fourier transform infrared (FT-IR) absorption spectrum was taken from the zeolite nanosheet before Ti grafting (Fig. S1) to detect any internal framework defects that may insert Ti isomorphously into the internal framework. However, no significant signal for nest silanol groups (3400 cm$^{-1}$) corresponding to internal framework defects could be detected in the FT-IR spectrum of the parent nanosheet. This result indicated that the tetrahedral Ti-sites in G-TiNS would mostly be grafted onto the silanol groups existing on the external surface of the nanosheet. In addition, the FT-IR spectrum was also taken from the zeolite nanosheet after Ti grafting (Fig. S1). The FT-IR spectrum showed a decrease of the peak for isolated silanols (3750 cm$^{-1}$) compared to the peak before grafting. This indicated that the silanols on the external surface were utilized during the Ti grafting step.

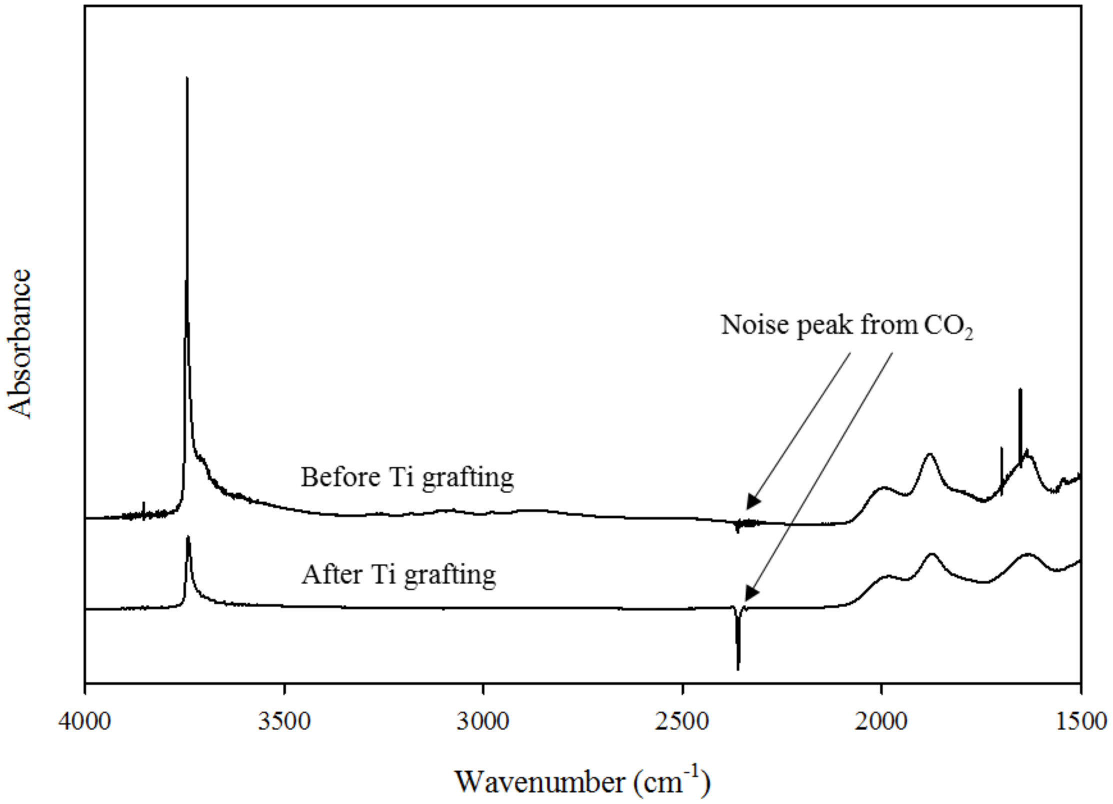

**Fig. S1** FT-IR spectra of a MFI zeolite nanosheet before and after Ti grafting

## Post-treatment with a silylating agent or $NH_4F$

A post-treatment with hexamethyldisilazane (*i.e.*, HMDZ, a silylating agent) for Ti/NS or a $NH_4F$ treatment for the MFI zeolite nanosheet before grafting could increase the epoxide selectivity of the resulting catalysts for the epoxidation of 1-hexene using $H_2O_2$. In a typical treatment with a silylating agent, 0.2 g of G-TiNS was initially degassed for 3 h under a vacuum at 300 °C. Then, under an inert condition, the degassed G-TiNS was poured into a 3 ml toluene solution containing 0.8 mmol of HMDZ. The slurry was heated to 100 °C and aged for 5 h under magnetic stirring. After cooling to room temperature, the slurry was filtered and washed with anhydrous toluene and acetone. The silylated G-TiNS was dried under a vacuum at 30 °C. In a typical treatment with $NH_4F$, as-synthesized MFI zeolite nanosheets were added to a $NH_4F$ aqueous solution. The mixture had a molar ratio of 100 $SiO_2$/ 25 $NH_4F$/ 6000 $H_2O$. It was heated to 100 °C and aged under magnetic stirring for 12 h. After cooling to room temperature, the $NH_4F$-treated zeolite was collected by filtration, dried, and calcined at 550 °C. The calcined zeolite was similarly grafted with Ti in the present work. The detailed catalytic results are shown below.

**Table S1** Catalytic results for the epoxidation of 1-hexene using $H_2O_2$ (reaction condition: 35 mg of catalyst, 12 mmol of 1-hexene, 3.3 mmol of $H_2O_2$, 10 mL of acetonitrile, 60 °C 2 h)

| Catalyst | Conversion of max (%) | Selectivity to epoxide (%) |
|---|---|---|
| Silylated G-TiNS | 3.3 | 82 |
| $NH_4F$-treated NS with Ti grafting | 3.5 | 85 |

## Characterizations

X-ray powder diffraction (XRD) patterns were measured with a Rigaku Multiflex diffractometer equipped with Cu Kα radiation (30 kV, 40 mA). $N_2$ adsorption-desorption isotherms were measured with a Micromeritics TriStar II volumetric sorption analyzer at the temperature of liquid nitrogen. Prior to the adsorption analysis, all samples were degassed under a vacuum for 6 h at 300 °C. The surface areas were analyzed by the BET equation from the adsorption branch in the range of $0.05 < P/P_0 < 0.20$. The external surface areas were calculated by the *t*-plot method. The pore size distributions were analyzed from the adsorption isotherm using the Barrett-Joyner-Halenda (BJH) algorithm. Scanning electron micrograph (SEM) images were taken with FEI Verios 230 instrument operating at 1.0 kV in the beam deceleration mode. Transmission electron microscope (TEM) images were taken with a Tecnai G2 F30 at an operating voltage of 300 kV. The diffuse reflectance ultra-violet (DR-UV) spectra of titanosilicate samples were measured with a Jasco UV-vis spectrometer (V570) in DR mode. Prior to the IR measurements, the MFI zeolite nanosheet sample was shaped into a pellet form. The pellets were then degassed for 3 h at 300 °C in an in-situ IR cell. After cooling to room temperature, the IR spectrum was measured with an FT-IR spectrometer (Bruker Vector 33).

**Table S2** Textural properties of MFI zeolite nanosheets before and after Ti grafting

| Sample | BET surface area ($m^2 g^{-1}$) | Total pore volume ($ml g^{-1}$) |
|---|---|---|
| Before Ti grafting | 612 | 0.72 |
| After Ti grafting | 609 | 0.71 |

**Table S3** Psychochemical properties of the MFI zeolite titanosilicate nanosheet as prepared by the B-to-Ti substitution method

| | |
|---|---|
| BET surface area ($m^2 g^{-1}$) | 653 |
| Total pore volume ($cm^3 g^{-1}$) | 0.62 |
| Si/Ti (analyzed by ICP) | 103 |

**Table S4** Catalytic results for the epoxidation of 1-hexene and cyclooctene using $H_2O_2$ with the MFI zeolite titanosilicate nanosheet catalyst prepared by the B-to-Ti substitution method (reaction condition: 35 mg of catalyst, 12 mmol of 1-hexene, 3.3 mmol of $H_2O_2$, 10 mL of acetonitrile, 60 °C 2 h)

| Substrate | Conversion of max (%) | Selectivity to epoxide (%) |
|---|---|---|
| 1-hexene | 3.3 | 74 |
| cyclooctene | 9.6 | 94 |

**Table S5** Recyclability tests of G-TiNS and G-TiM41 for the epoxidation of cyclooctene (reaction condition: 35 mg of catalyst, 12 mmol of 1-hexene, 3.3 mmol of $H_2O_2$, 10 mL of acetonitrile, 60 °C 2 h)

| Run | G-TiNS | | G-TiM41 | |
|---|---|---|---|---|
| | Conversion of max (%) | Epoxide selectivity (%) | Conversion of max (%) | Epoxide selectivity (%) |
| 1 | 10.5 | 95 | 4.3 | 79 |
| 2 | 9.4 | 95 | 2.1 | 75 |
| 3 | 8.4 | 94 | 0.8 | 75 |

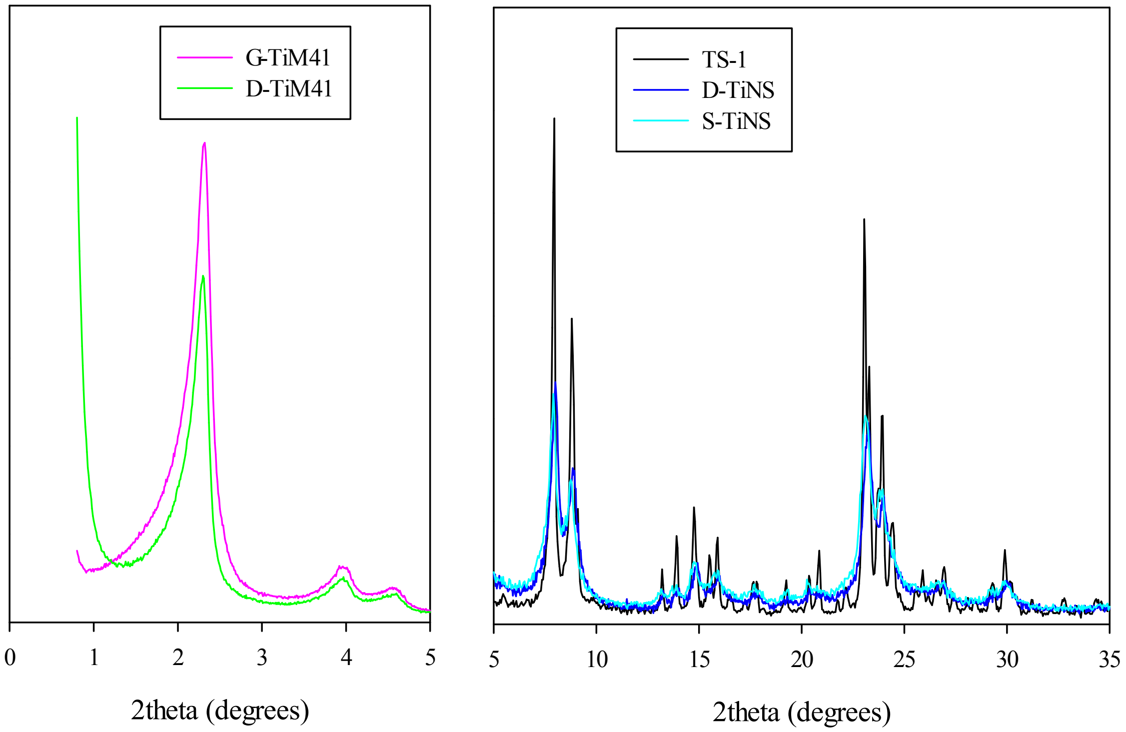

**Fig. S2** (a) low-angle XRD patterns of D-TiM41 and G-TiM41 (b) high-angle XRD patterns of TS-1, D-TiNS and S-TiNS

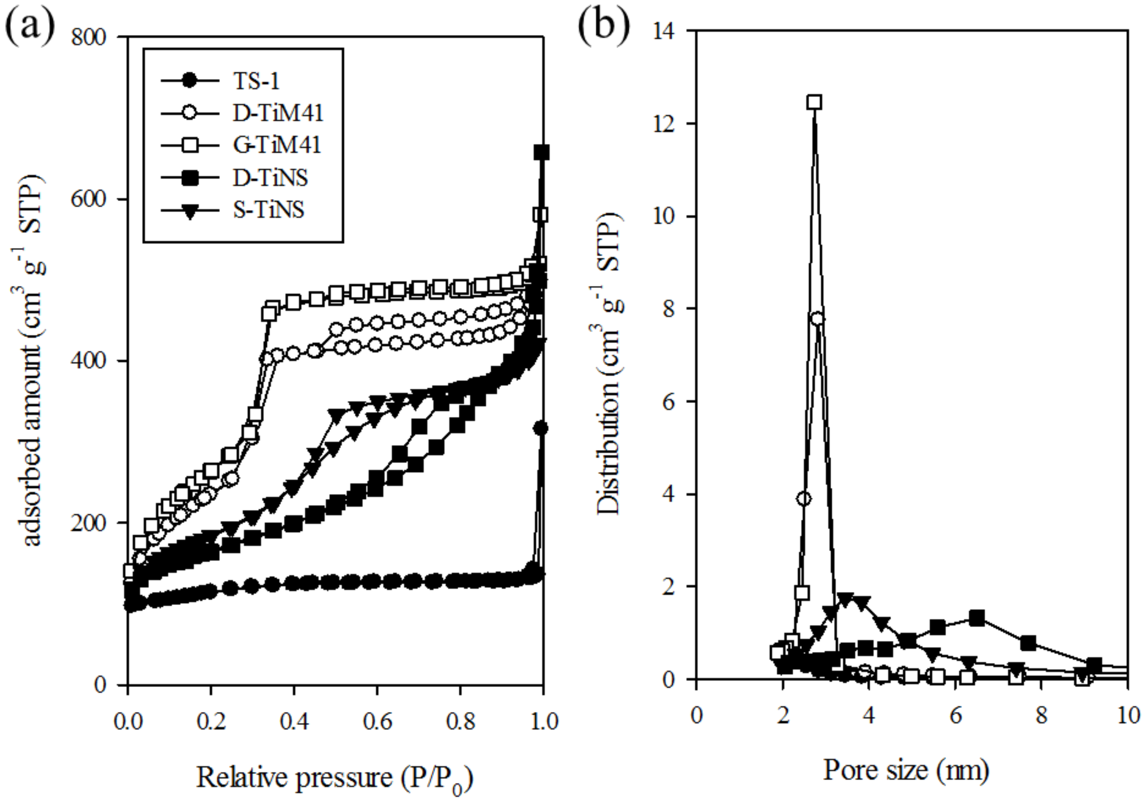

**Fig. S3** (a) $N_2$ sorption isotherms and (b) pore size distributions of TS-1, D-TiM41, G-TiM41, D-TiNS, and S-TiNS

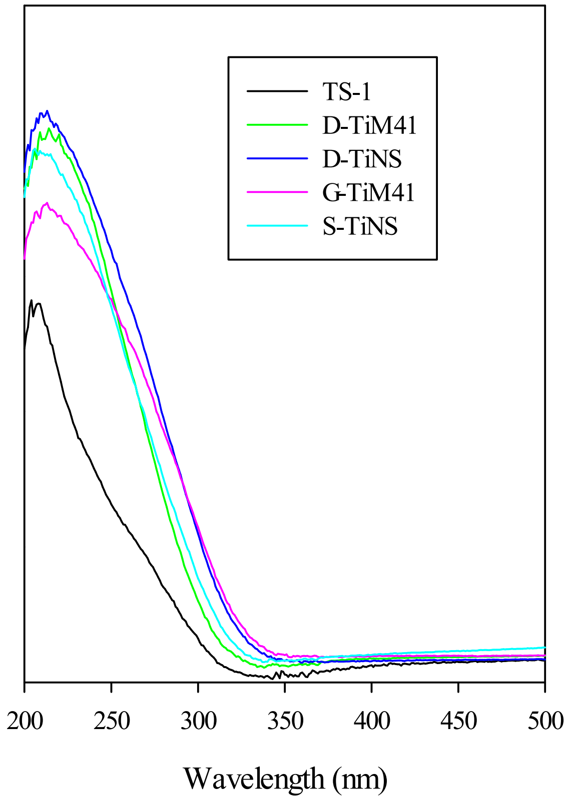

**Fig. S4** DR-UV spectra of TS-1, D-TiNS, D-TiM41, G-TiM41, and S-TiNS

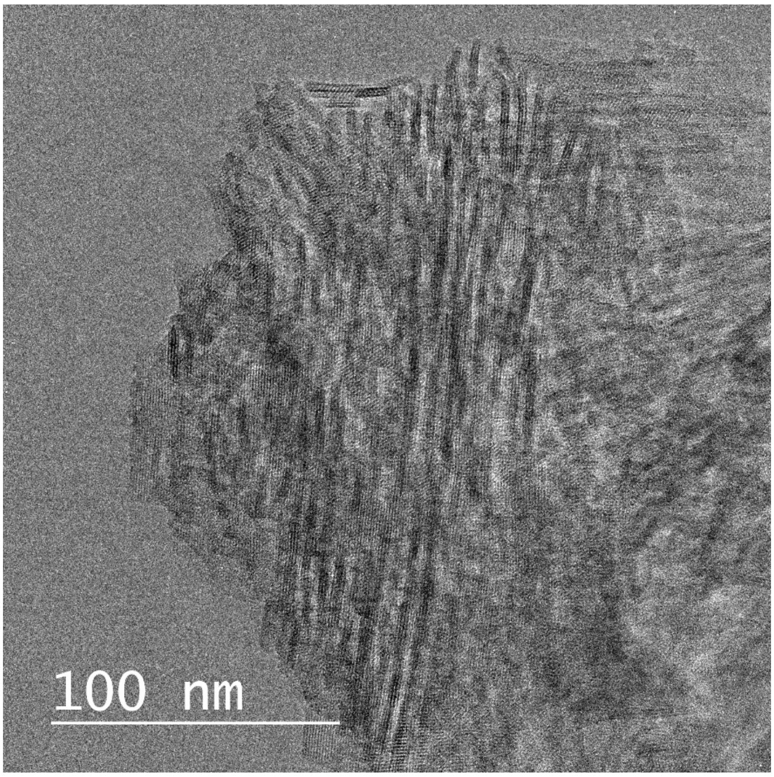

**Fig. S5** TEM image of a MFI zeolite nanosheet before Ti grafting

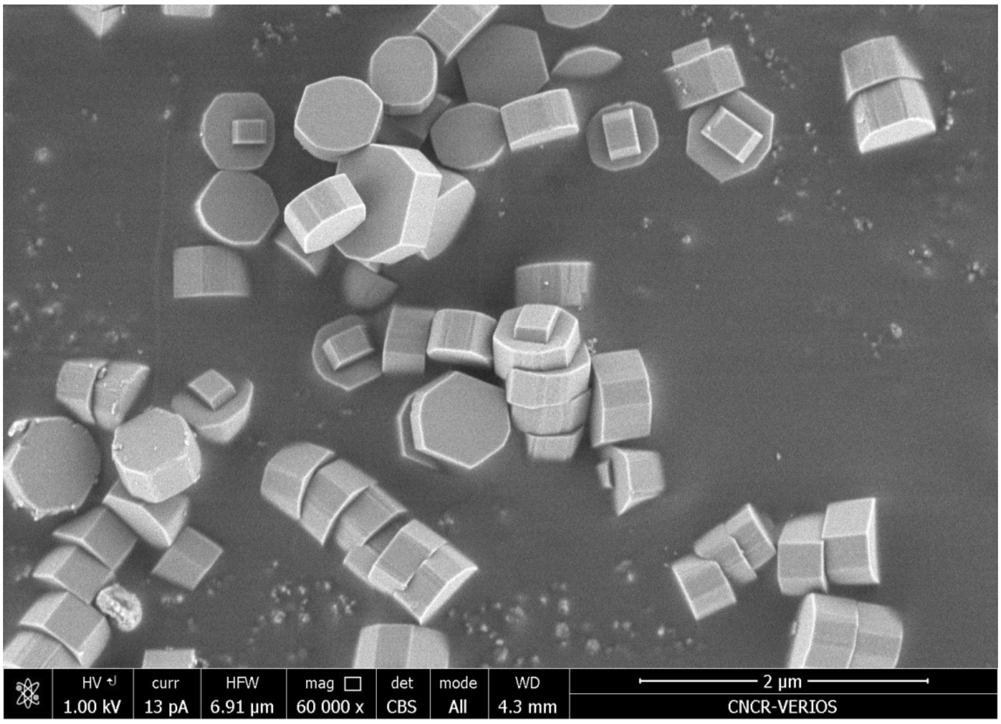

**Fig. S6** SEM image of TS-1