## **Supporting Information**

## MFI Titanosilicate Nanosheets with Single-Unit-Cell Thickness as an Oxidation Catalyst Using Peroxides

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**Figure S1.** Low-angle powder XRD patterns (A) of as-synthesized TS-1 products, and Ar adsorption isotherms (B) and corresponding micropore size distribution derived by non-local density-functional theory (B, inset) of calcined TS-1 products.



**Figure S2.** DR-UV spectra of (A) bulk TS-1, (B) nanosheet TS-1 and (C) Ti-MCM-41 before (down) and after (up) fluoride treatment.



**Figure S3.** Powder XRD patterns of (A) bulk TS-1, (B) nanosheet TS-1 and (C) Ti-MCM-41 before (down) and after (up) fluoride treatment.



**Figure S4.**  $N_2$  adsorption isotherms and pore size distributions (inset) of (A) bulk TS-1, (B) nanosheet TS-1 and (C) Ti-MCM-41 before and after fluoride treatment. The closed circles correspond to the titanosilicates before fluoride treatment, while the open circles denote those after fluoride treatment.



**Figure S5.** IR spectra of (A) bulk TS-1, (B) nanosheet TS-1 and (C) Ti-MCM-41 before (down) and after (up) fluoride treatment.

| Catalyst  | Oxidant  | Olefin epoxidation |       |                  |        |             |     |     |             |      |     |     |      |
|-----------|----------|--------------------|-------|------------------|--------|-------------|-----|-----|-------------|------|-----|-----|------|
|           |          | 1-Hexene           |       |                  |        | Cyclohexene |     |     | Cyclooctene |      |     |     |      |
|           |          | $\mathbf{C}^{a}$   | $S^b$ | $\mathbf{E}^{c}$ | $OC^d$ | С           | S   | E   | OC          | С    | S   | E   | OC   |
|           |          | (%)                | (%)   | (%)              | (%)    | (%)         | (%) | (%) | (%)         | (%)  | (%) | (%) | (%)  |
| Bulk TS-1 | $H_2O_2$ | 19.7               | 99    | 97               | 20.3   | 1.2         | 99  | 86  | 1.4         | 0.6  | 99  | 84  | 0.7  |
|           | TBHP     | 2.2                | 99    | 98               | 2.2    | 1.1         | 99  | 97  | 1.1         | 0.5  | 99  | 96  | 0.5  |
| Ti-MCM-41 | $H_2O_2$ | 1.5                | 71    | 72               | 2.1    | 9.8         | 14  | 74  | 13.2        | 6.6  | 74  | 71  | 9.3  |
|           | TBHP     | 2.8                | 85    | 88               | 3.2    | 15.5        | 35  | 86  | 18.0        | 11.4 | 81  | 87  | 13.1 |
| Nanosheet | $H_2O_2$ | 13.9               | 95    | 89               | 15.6   | 10.5        | 43  | 84  | 12.5        | 9.4  | 91  | 83  | 11.3 |
| TS-1      | TBHP     | 4.5                | 99    | 94               | 4.8    | 28.7        | 74  | 95  | 30.2        | 17.5 | 94  | 93  | 18.8 |
| Nanosheet | $H_2O_2$ | 12.8               | 95    | 81               | 15.8   | 25.0        | 69  | 87  | 28.7        | 15.3 | 95  | 86  | 17.8 |
| F-TS-1    | TBHP     | 5.3                | 99    | 93               | 5.7    | 33.7        | 91  | 94  | 35.9        | 23.6 | 95  | 92  | 25.7 |

Table S1. Catalytic activities of titanosilicate catalysts for olefin epoxidations for 2 h at 60°C.

<sup>*a*</sup>Conversion of olefin relative to the maximum possible (%); <sup>*b*</sup>Epoxide selectivity (%); <sup>*c*</sup>Oxidant efficiency = (amount used for olefin oxidation)/(amount used for olefin oxidation + amount decomposed) x 100 (%); <sup>*d*</sup>Oxidant conversion (%)

**Table S2.** Catalytic reaction results of silylated nanosheet TS-1 for epoxidation of 1-hexene using  $H_2O_2$ .

| Sample                   | Conversion<br>(%) | Epoxide selectivity<br>(%) | Oxidant efficiency<br>(%) |
|--------------------------|-------------------|----------------------------|---------------------------|
| Nanosheet TS-1           | 13.9              | 95                         | 89                        |
| Silylated nanosheet TS-1 | 8.9               | 96                         | 93                        |

Table S3. The effect of fluoride treatment on textural properties of titanosilicates.

| Sample           | Si/Ti<br>(ICP) | BET surface area<br>(m <sup>2</sup> g <sup>-1</sup> ) | Total pore volume<br>(cm <sup>3</sup> g <sup>-1</sup> ) | Average mesopore<br>diameter (nm) |  |
|------------------|----------------|---|---|-----------------------------------|--|
| Bulk TS-1        | 55             | 393   | 0.20  | -                                 |  |
| Bulk F-TS-1      | 56             | 395   | 0.21  | -                                 |  |
| Nanosheet TS-1   | 57             | 580   | 0.61  | 6.3                               |  |
| Nanosheet F-TS-1 | 54             | 558   | 0.62  | 7.5                               |  |
| Ti-MCM-41        | 61             | 861   | 0.73  | 3.1                               |  |
| F-Ti-MCM-41      | 45             | 556   | 0.52  | 3.9                               |  |