

Supplementary information

Stabilisation of molecular TiO₄ species on the pore surface of mesoporous silica for photocatalytic H₂ evolution

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Experimental section

Chemicals

Hexadecyltrimethylammonium bromide (C₁₆TMABr) was purchased from FUJIFILM Wako Pure Chemical Corp. Tetramethylammonium hydroxide aqueous solution (25 wt%) and titanium tetraisopropoxide were purchased from Tokyo Chemical Industry Co. Fumed silica (Cab-O-Sil M5) was purchased from Inoxia Ltd.

Synthesis of Ti-MCM-41

Ti-containing mesoporous silica (Ti-MCM-41), used as a reference photocatalyst, was hydrothermally synthesized according to the literature.^{S1} The incorporated Ti-oxo species existed as isolated tetrahedral coordination in the framework of MCM-41. Deionised water (25 mL) was mixed with C₁₆TMABr (3.4 g) and the mixture was magnetically stirred overnight until the solution was homogenised. Tetramethylammonium hydroxide aqueous solution (2.2 g), fumed silica (1.4 g), and titanium tetraisopropoxide (120 µL) were then added into the solution and stirred at room temperature for 1.5 h. The mixture was transferred to the teflon-lined autoclave (50 mL) and hydrothermally treated at 135 °C for 14 h. After cooling to room temperature, the solid was collected by centrifugation at 4000 rpm for 6 min and washed five times with deionised water. The obtained sample was dried at 60 °C overnight and then calcined in air at 550 °C for 6 h.

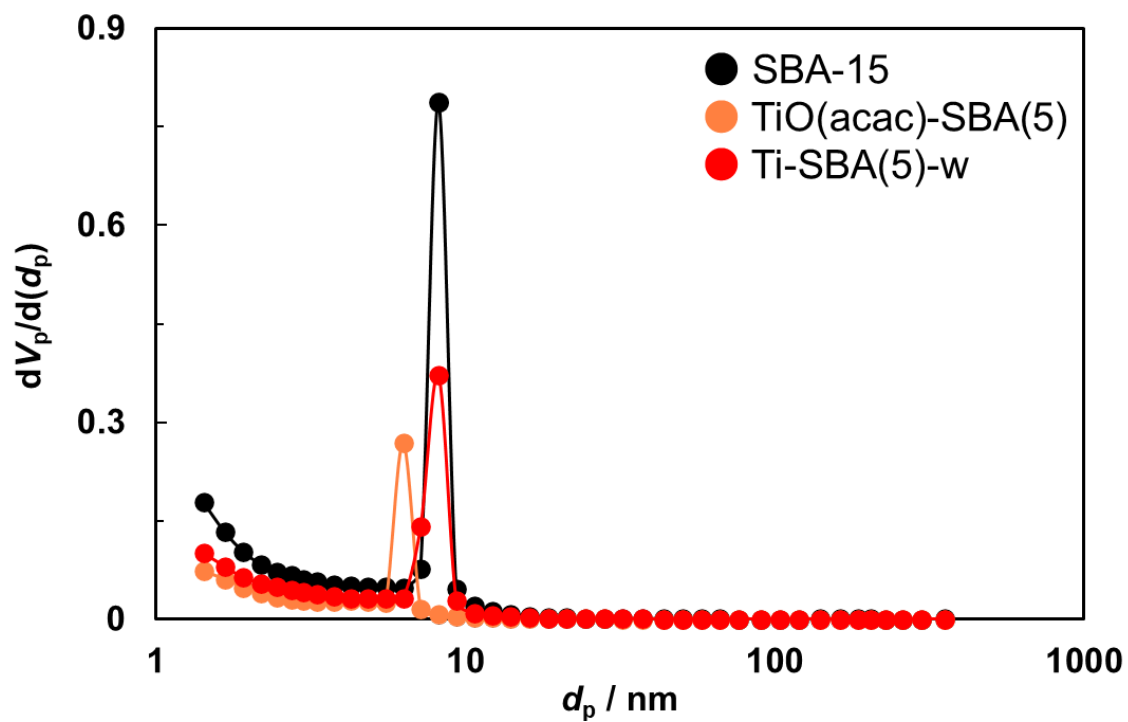


Fig. S1 BJH pore size distributions of SBA-15, TiO(acac)-SBA(5) and Ti-SBA(5)-w.

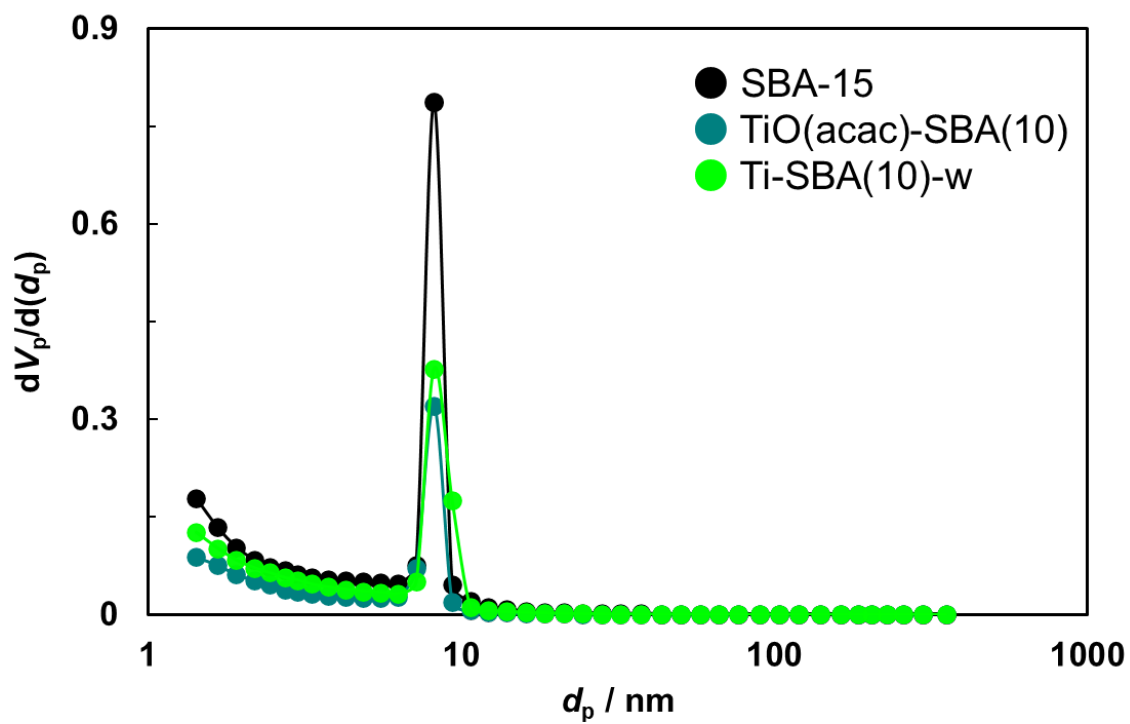


Fig. S2 BJH pore size distributions of SBA-15, TiO(acac)-SBA(10) and Ti-SBA(10)-w.

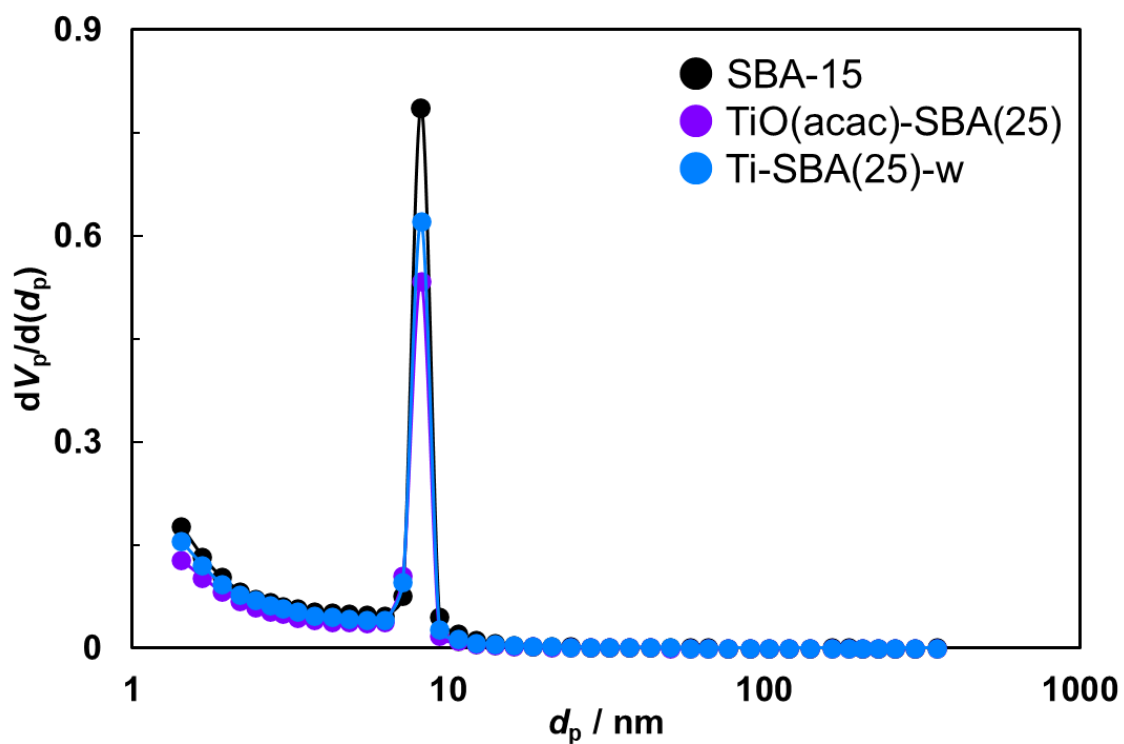


Fig. S3 BJH pore size distributions of SBA-15, TiO(acac)-SBA(25) and Ti-SBA(25)-w.

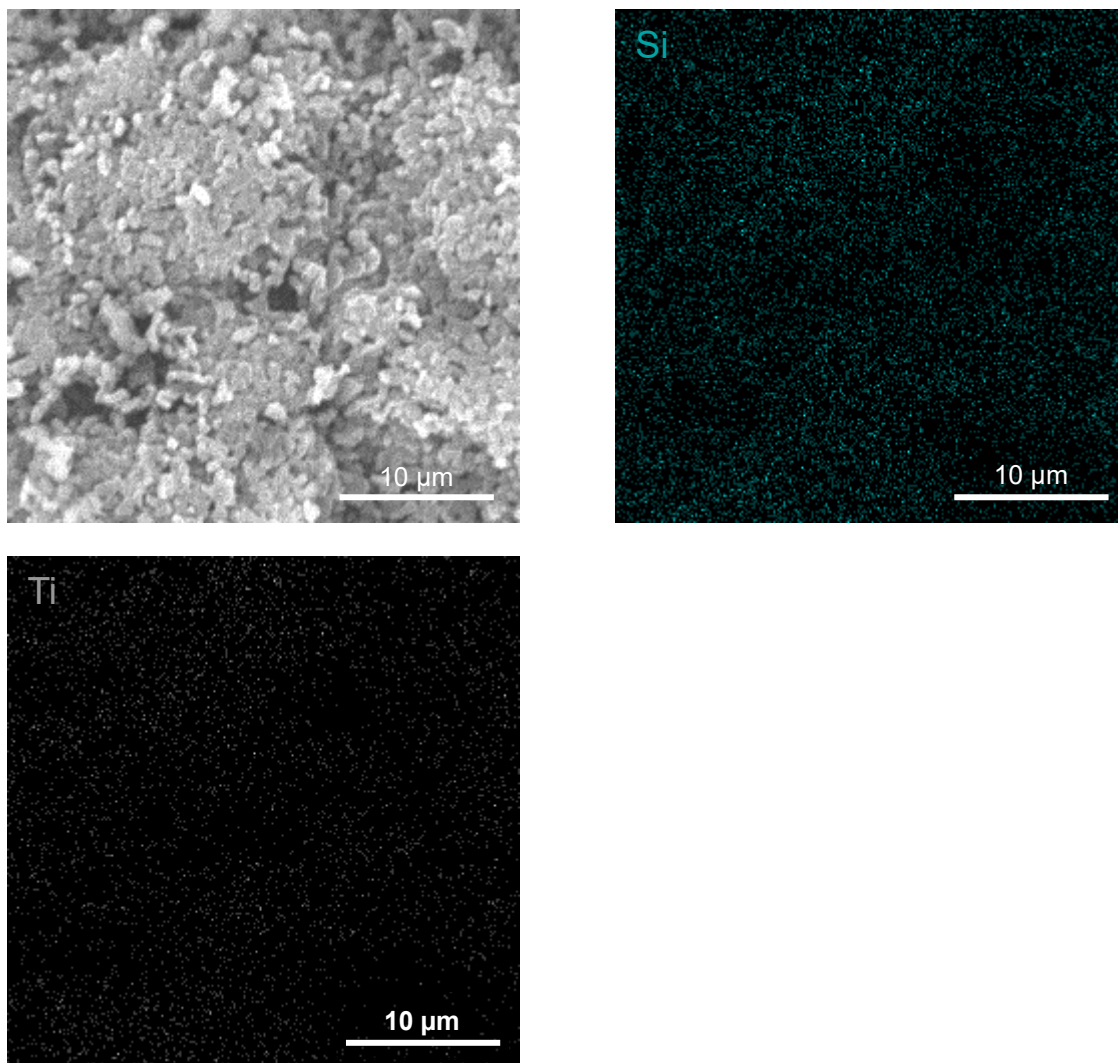


Fig. S4 SEM images and EDX elemental map of TiO(acac)-SBA(25).

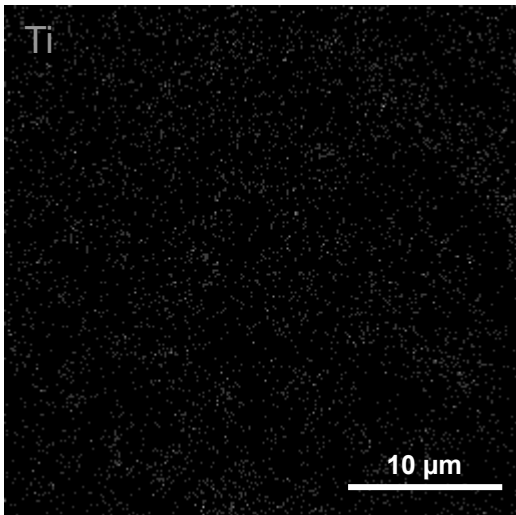
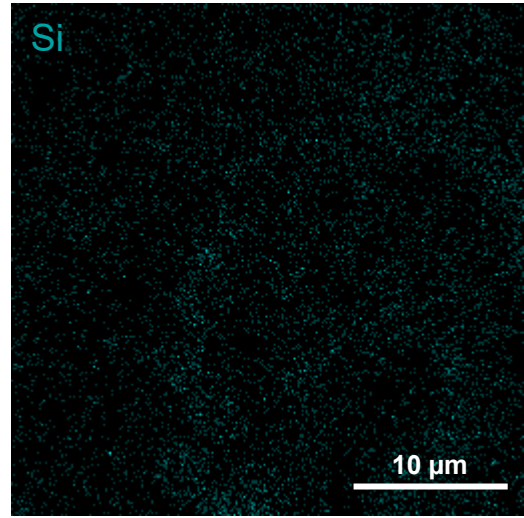
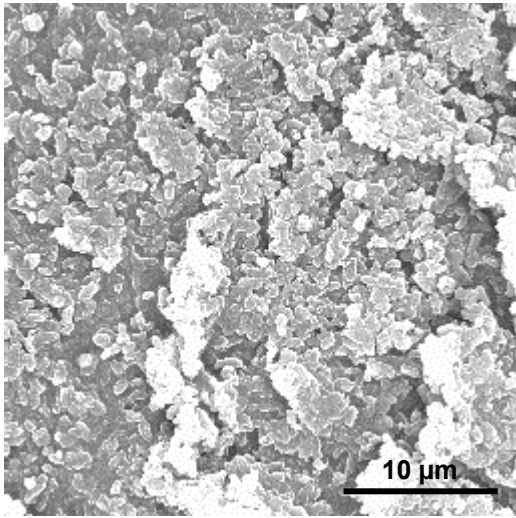


Fig. S5 SEM images and EDX elemental map of Ti-SBA(25)-w.

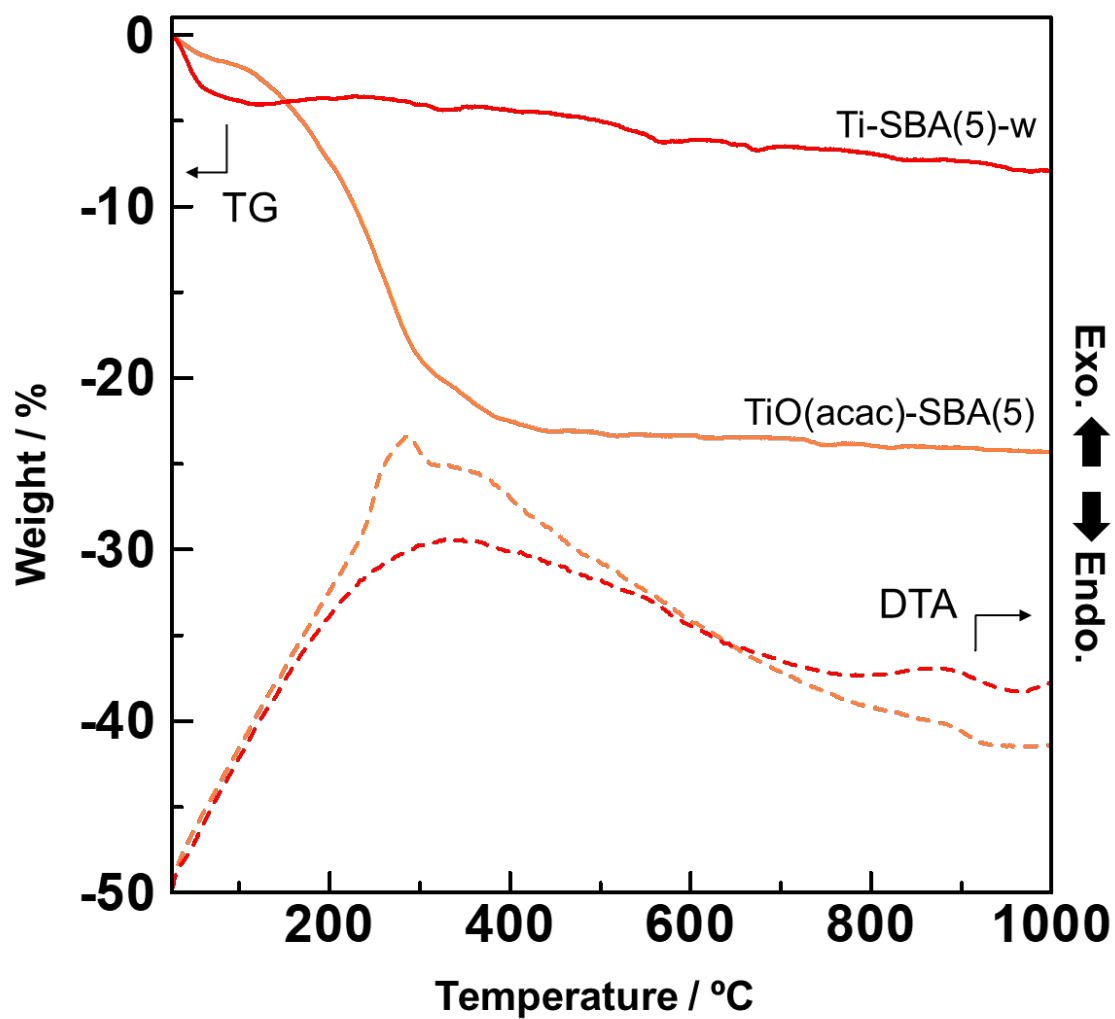


Fig. S6 TG-DTA curves of TiO(acac)-SBA(5) and Ti-SBA(5)-w.

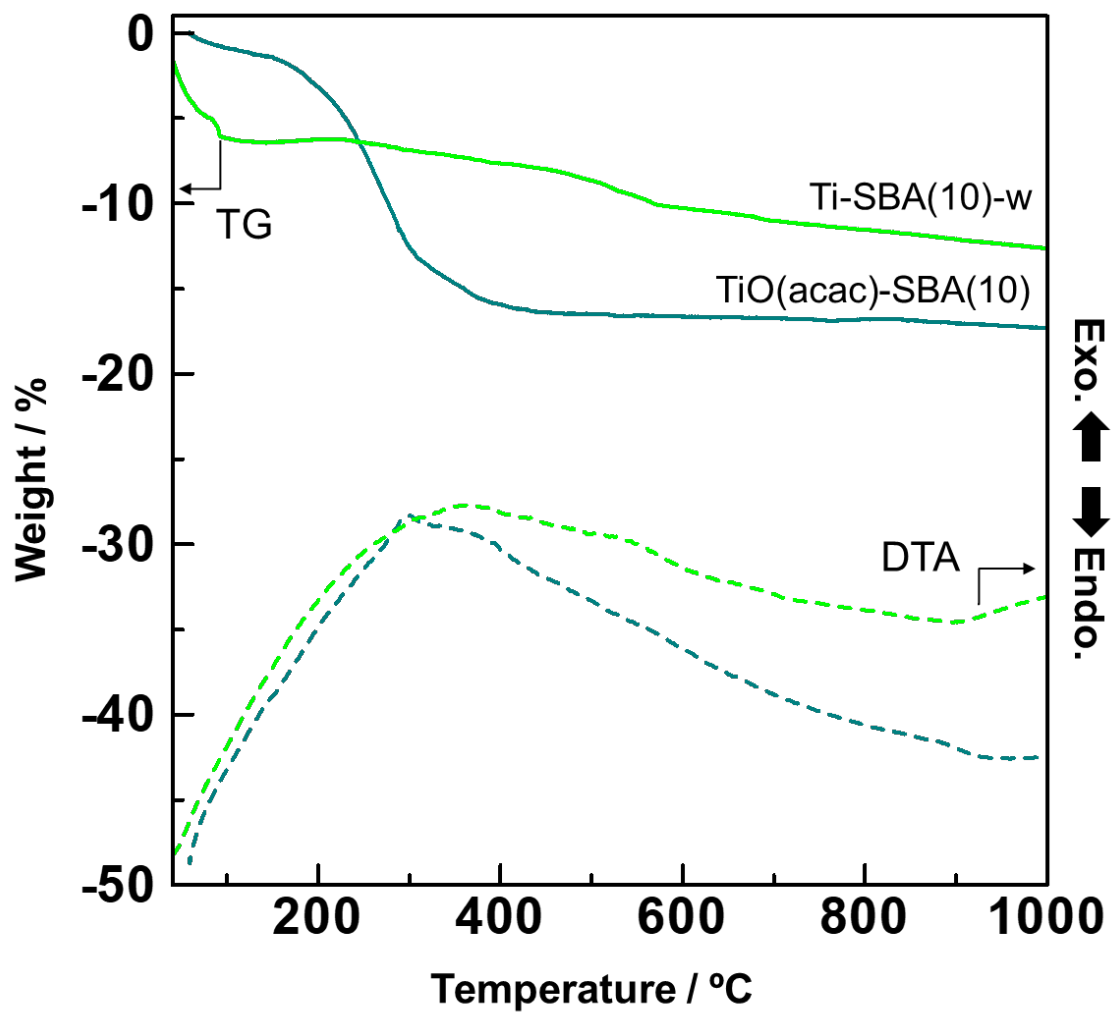


Fig. S7 TG-DTA curves of TiO(acac)-SBA(10) and Ti-SBA(10)-w.

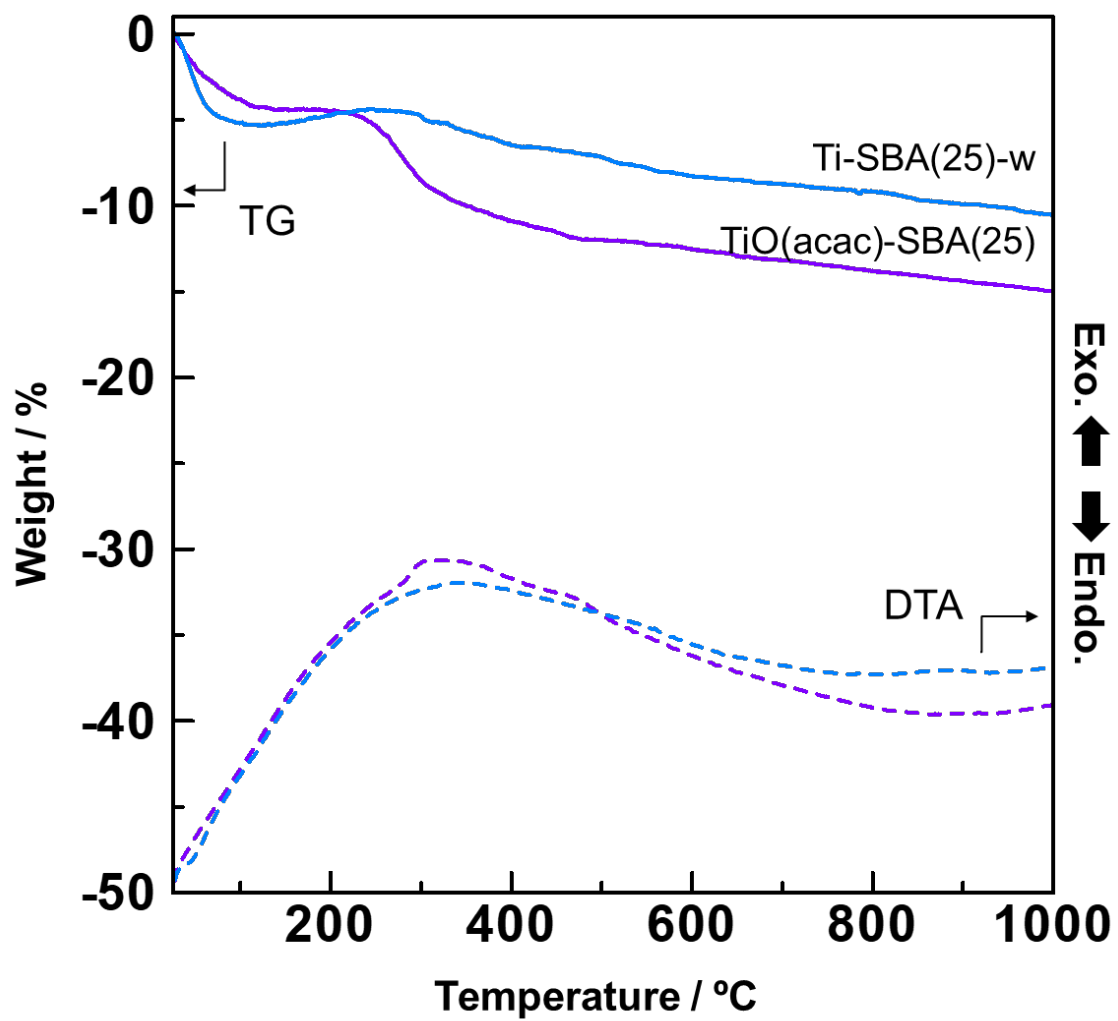


Fig. S8 TG-DTA curves of TiO(acac)-SBA(25) and Ti-SBA(25)-w.

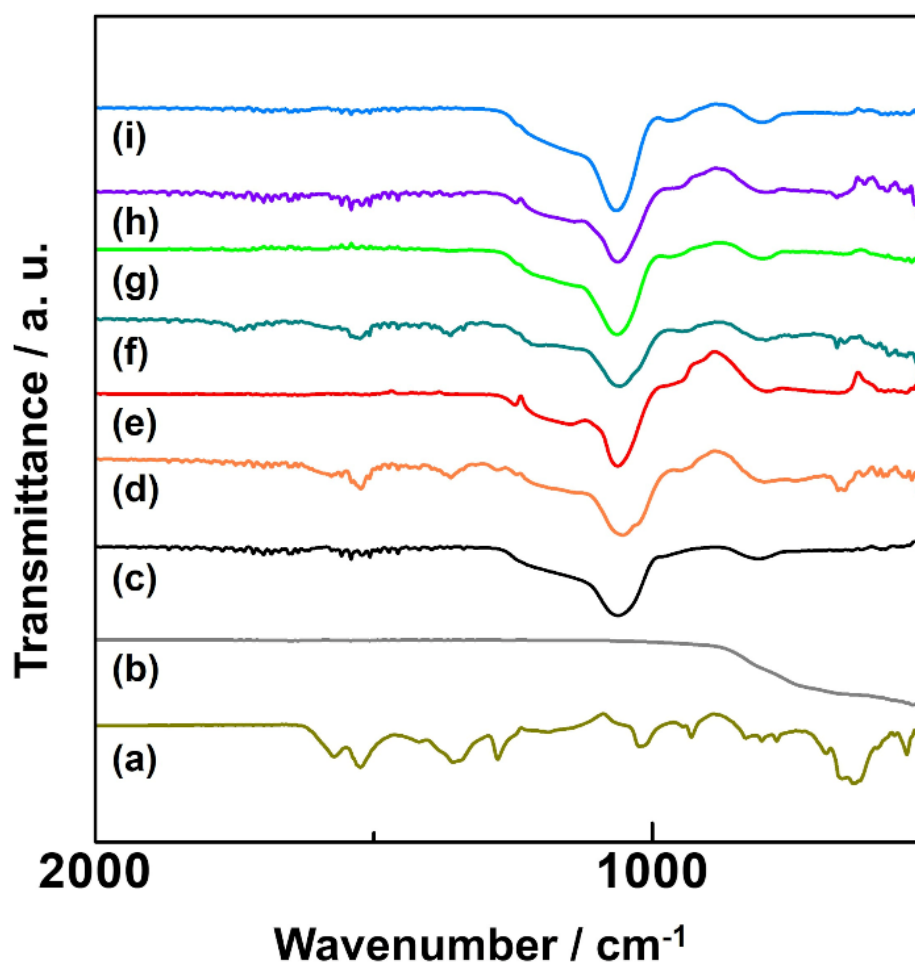


Fig. S9 FT-IR spectra of (a) TiO(acac)₂, (b) P25, (c) SBA-15, (d) TiO(acac)-SBA(5), (e) Ti-SBA(5)-w, (f) TiO(acac)-SBA(10), (g) Ti-SBA(10)-w, (h) TiO(acac)-SBA(25) and (i) Ti-SBA(25)-w.

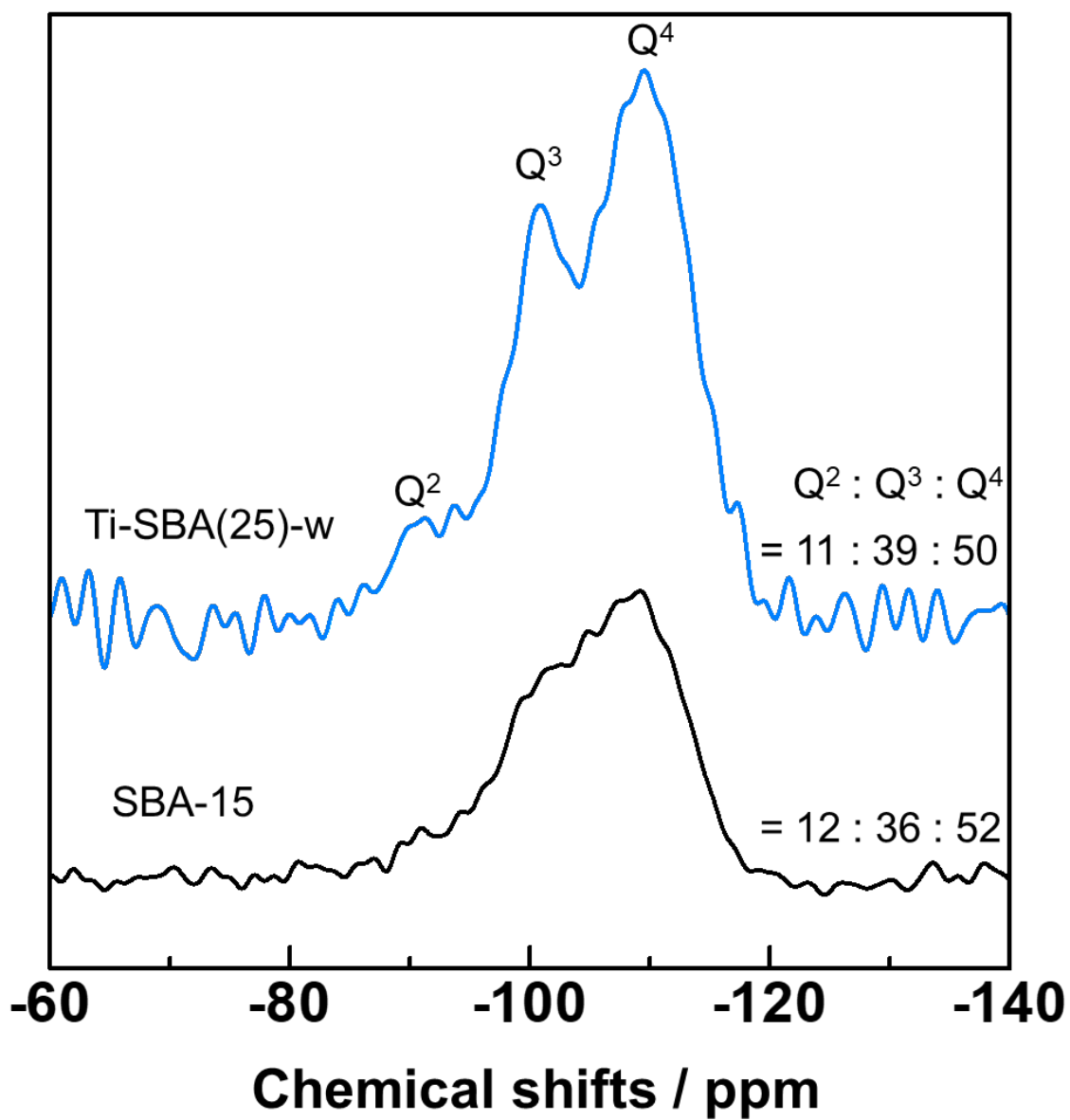


Fig. S10 Solid-state ^{29}Si MAS NMR spectra of SBA-15 and Ti-SBA(25)-w. The integral Q^2 , Q^3 and Q^4 signal ratios are shown on the right.

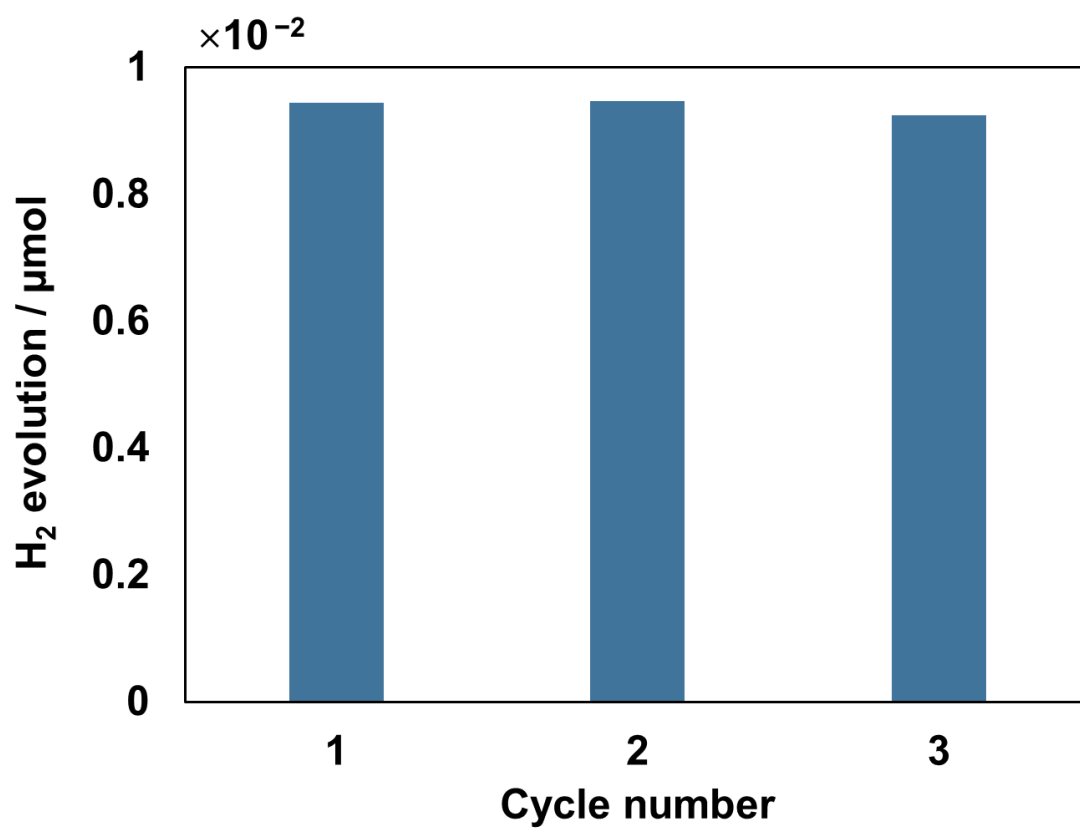


Fig. S11 Cycling performance of Ti-SBA(25)-w for photocatalytic H₂ evolution from aqueous methanol solution.

Table S1 H₂ evolution from aqueous methanol solution using different photocatalysts

Sample	Si/Ti^a ratio	TiO₂ amount / wt%	H₂ evolution (2 h) / μmol	TOF^b / h⁻¹
Ti-SBA(5)-w	45	2.9	0.014	0.0013
Ti-SBA(10)-w	64	2.0	0.0098	0.00038
Ti-SBA(25)-w	120	1.1	0.012	0.0028
SBA-15	–	–	n. d.	–
Ti-MCM-41	120	1.1	0.0054	0.0013
P25	–	100	0.0039	0.000010

^a Calculated from SEM-EDX. ^b Turnover frequency (TOF, h⁻¹) was calculated from the following formula: TOF = [H₂ evolution rate (mol h⁻¹)]/[amount of immobilised Ti atoms on the sample (mol)].

Supporting References

S1. T. Blasco, A. Corma, M. T. Navarro and J. P. Pariente, *J. Catal.*, 1995, **156**, 65–74.