

Electronic Supporting Information (ESI)

Two-dimensional transition metal dichalcogenides as metal source of metal-organic frameworks

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SI-1 Experimental Section

Characterization.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku SmartLab diffractometer with Cu K_a radiation ($\lambda = 0.15418$ nm). Morphologies of solid samples were characterized with a field-emission scanning electron microscope (NOVA NanoSEM 450). Ar adsorption/desorption isotherms were recorded at 87 K on a Quantachrom Autosorb-iQ instrument. Prior to measurement, samples were outgassed at 130 °C overnight. Diffuse reflectance UV-Vis spectroscopy (DR/UV-Vis) experiments were conducted with a JASCO 550 spectrophotometer. FT-IR spectra were recorded using an EQUINOX55 Fourier transform infrared spectrometer (Bruker, Germany) by means of KBr pellet technique. A Tecnai G2 Spirit (FEI Co.) operated at 120kV was used for general microstructure inspection. High resolution transmission electron microscopy (HRTEM) characterization of the microstructure was carried out on a JEM-2100 (JEOL Co.) operated at 200kV. To prepare samples for TEM analysis, dispersion of samples were coated on carbon-coated copper grid (200 mesh, Zhongjingkeyi Co.) and dried in air. Nonmetallic elemental analysis was carried out with a Vario EL III Elemental Analyzer. Metallic elemental analysis was conducted by Inductively Coupled Plasma (ICP) over a Perkin Elmer OPTIMA 2000DV apparatus.

Synthesis of NH₂-MIL-125(Ti): 2.24 g of NH₂-BDC (99%, Alfa Aesar) and 0.056 g TiS₂ (99.9%, Sigma-Aldrich) were dissolved in a solution containing 27 ml DMF (99.8%, Shanghai Chemical Reagent Inc.) and 3 ml dry MeOH (99.5%, Shanghai Chemical Reagent Inc.) with stirring. The mixture was then transferred to a 50 ml Teflon-lined autoclave and solvothermally treated at 160 °C under static condition for 96 h. After cooling down, the solid product was centrifuged, washed with DMF and methanol and finally dried in an oven at 60 °C overnight.

Synthesis of NH₂-MIL-125(Ti) under reflux: 2.24 g of NH₂-BDC (99%, Alfa Aesar) and 0.056 g TiS₂ (99.9%, Sigma-Aldrich) were dissolved in a solution containing 27 ml DMF (99.8%, Shanghai Chemical Reagent Inc.) and 3 ml dry MeOH (99.5%, Shanghai Chemical Reagent Inc.) with stirring. The mixture was then transferred to a 250 ml round bottom flask fitted with a reflux condenser and solvothermally treated at 160 °C for 48 h with stirring. After cooling down, the solid product was centrifuged, washed with DMF and methanol and finally dried in an oven at 60 °C overnight.

Synthesis of MIL-167: A precursor solution composed of 1.585 g of H₄DOBDC (98%, Macklin) and 0.028 g of TiS₂ dispersed in 4.4 ml of DMF and methanol mixture (v:v=1:1) was heated at 180 °C for 24 h in a 25 ml Teflon-lined autoclave. Obtained product was then washed with copious of acetonitrile. Finally, the product was centrifuged and repeatedly washed with DEF before drying under vacuum.

Photocatalytic Rhodamine B degradation: 20 mg of the NH₂-MIL-125(Ti) was dispersed in 50 ml aqueous solution of RhB (95%, Sigma-Aldrich) (concentration: 100 mg L⁻¹). The suspension was then stirred for 1 h in the dark to allow equilibrium adsorption of dye molecules. Consequently the dispersion was irradiated under a 500 W Xe arc lamp with a 420 nm cut off filter as the light source. 0.22 μ l aliquots of dispersion irradiated at different times were taken out and analyzed with UV-Vis light spectrometry to determine the concentration of RhB molecules as a function of irradiation time.

SI-2 Elemental analysis

Table S1 Element analysis of NH₂-MIL-125(Ti) (24:1-160-96h) crystals. .

Element	Content (%)
Ti	19.2 ^a
C	35.4 ^b
N	8.1 ^b
H	4.3 ^b

^aMetal element content of sample was measured by ICP ^bC, N, H element content were measured by Vario EL III Elemental Analyzer

SI-3 Further information obtained from Ar adsorption/desorption isotherm of NH₂-MIL-125(Ti)

Table S2 Sorption data of NH₂-MIL-125(Ti) (24:1-160-96h) crystals.

	S_{BET} (m ² g ⁻¹) ^a	V_{micro} (cm ³ g ⁻¹) ^b	V_{total} (cm ³ g ⁻¹) ^c	$V_{\text{micro}}/V_{\text{total}}$
24:1-160-96h	911.8	0.34	0.47	0.72

^aSurface area calculated with BET model. ^bPore size distribution and total pore volume were calculated with NLDFT model. ^cMicropore volume was calculated with SF model.

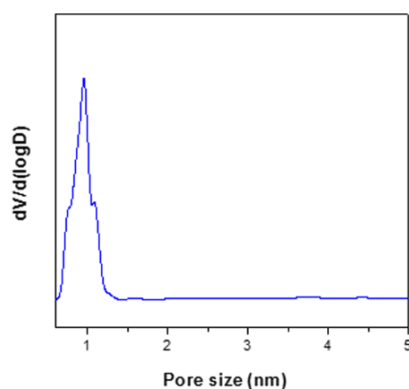


Fig. S1 Pore size distribution of NH₂-MIL-125 (24:1-160-96h). The pore size distribution was determined by non-local density functional theory (NLDFT).

Table S3 Sorption data of NH₂-MIL-125(Ti) (24:1-160-48h under reflux) crystals.

	S_{BET} (m ² g ⁻¹) ^a	V_{micro} (cm ³ g ⁻¹) ^b	V_{total} (cm ³ g ⁻¹) ^c	$V_{\text{micro}}/V_{\text{total}}$
24:1-160-48h	1082.6	0.40	0.47	0.85

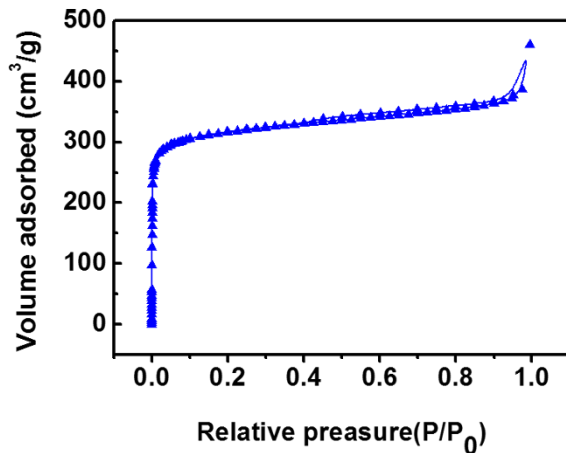


Fig. S2 Ar adsorption/desorption isotherm of NH₂-MIL-125(Ti) synthesized under reflux.

SI-4 Diffusion reflectance analysis

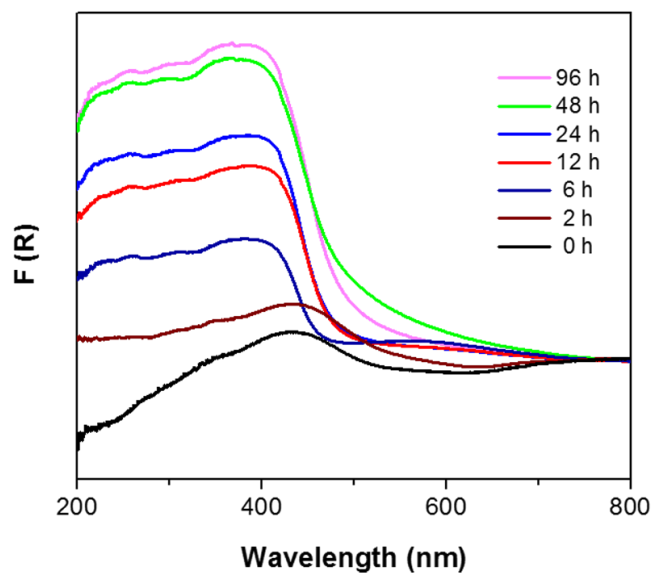


Fig. S3 Diffusion reflectance spectra of solid products obtained at 160 °C for different reaction times.

SI-5 FT-IR spectra of prepared NH₂-MIL-125(Ti) powders

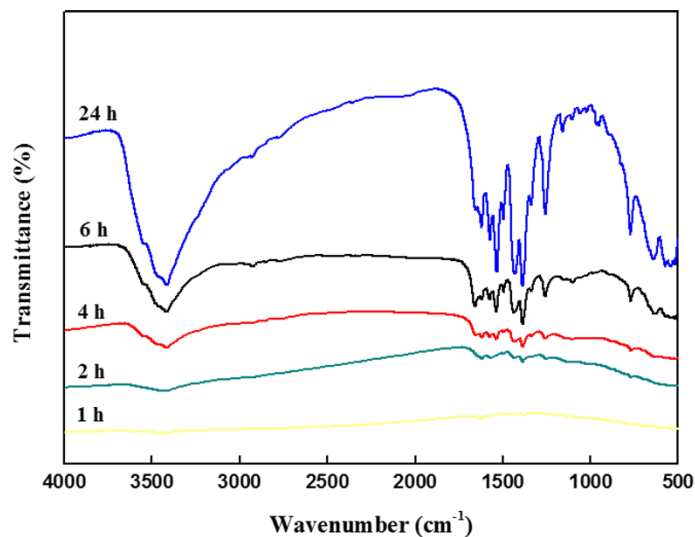


Fig. S4 FT-IR spectra of NH₂-MIL-125(Ti) crystals synthesized with NH₂-BDC/TiS₂ molar ratio of 24 at 160 °C for different times.

The FT-IR spectra of prepared sample showed characteristic vibration peaks of NH₂-MIL-125(Ti). To be specific, vibration bands located around 1600 and 1500 cm⁻¹ could be assigned to carbonyl asymmetric stretching vibrations, whereas vibration bands located at about 1440 and 1400 cm⁻¹ could be assigned to carbonyl symmetric stretching vibrations and vibration bands located at 1250 cm⁻¹ belonged to the C-H symmetric stretching vibrations of benzene ring.

SI-6 Investigation of the influence of synthetic temperature and duration on final morphology of NH₂-MIL-125(Ti)

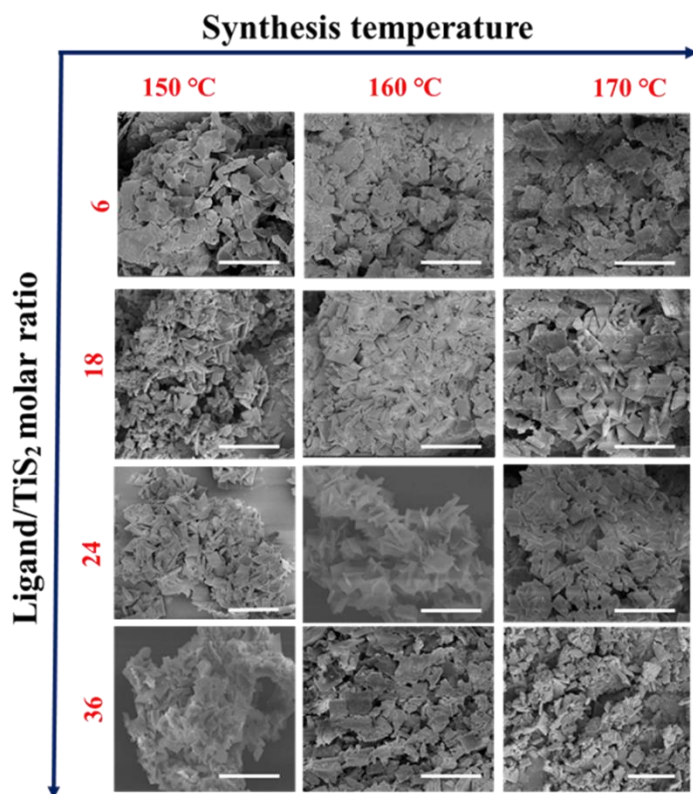


Fig. S5 SEM images of NH₂-MIL-125(Ti) obtained with varied synthesis temperature and ligand/TiS₂ molar ratio (Indicated in the graph). The scale bar corresponded to 4 μ m.

SI-7 Crystal structures and information of bond length

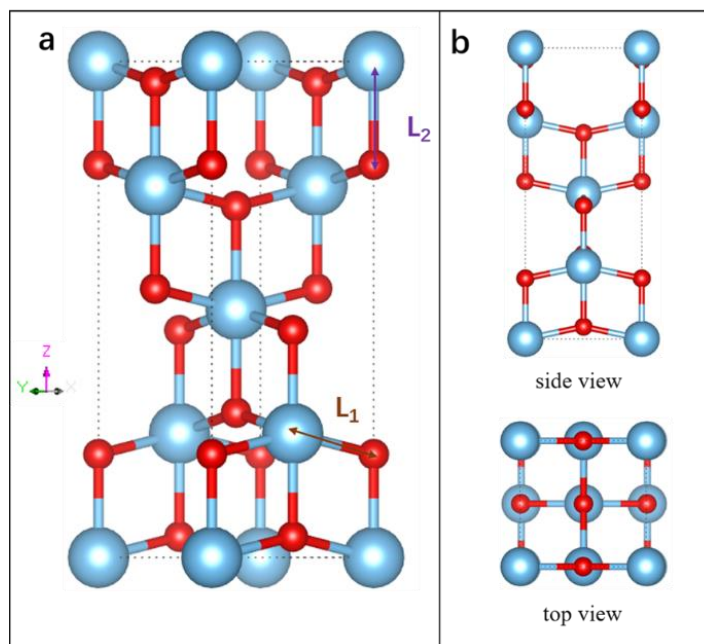


Fig. S6 a) Crystal structure of TiO₂-anatase; b) TiO₂-anatase (side and top view).

Table S4 Ti-O bond length of TiO₂-anatase.

Bond	Length (Å)
O -- Ti (L ₁)	1.93
O -- Ti (L ₂)	1.97

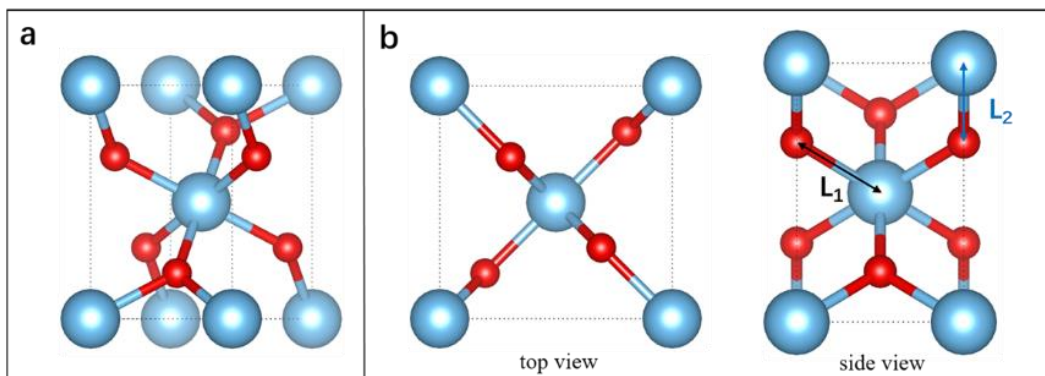


Fig. S7 a) Crystal structure of TiO₂-rutile; b) TiO₂-rutile (side and top view).

Table S5 Ti-O bond length of TiO₂-rutile.

Bond	Length (Å)
O -- Ti (L ₁)	1.95
O -- Ti (L ₂)	1.98

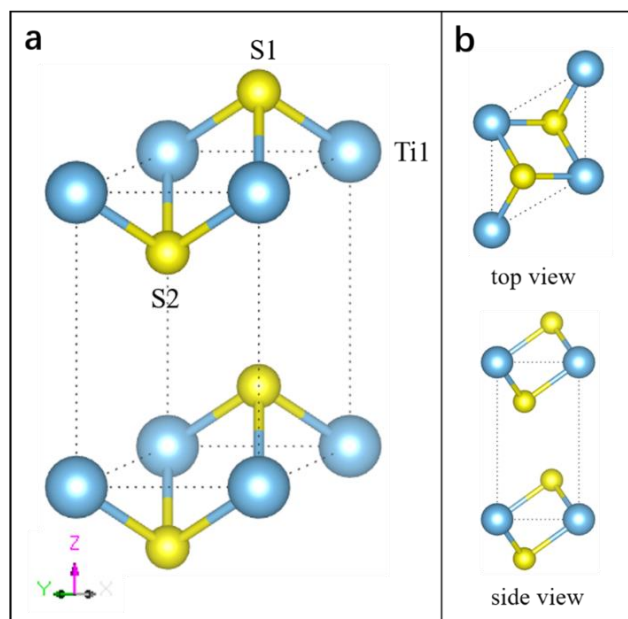


Fig. S8 a) Crystal structure of TiS₂; b) TiS₂ (side and top view).

Table S6 Ti-S bond length of TiS₂.

Bond	Length (Å)
S 2 -- Ti 1	2.43
S 1 -- Ti 1	2.43

SI-8 Calculation methods of formation energies

All calculations were implemented in Vienna *ab Initio* Simulation Package (VASP) within the density functional theory (DFT). In order to characterize the stability of TiO₂ with TiS₂, we defined their formation energy as follows:

$$E_{\text{formation}} = (xE_{\text{Ti}} + yE_{\text{M}} - E_{\text{Ti}_x\text{M}_y}) / (x + y) \quad (1)$$

where E_{Ti} , E_{M} , and $E_{\text{Ti}_x\text{M}_y}$ are energies of elemental titanium, O₂ molecule or elemental sulfur and bulk TiO₂ or bulk TiS₂ calculated from VASP, respectively.

Table S7 The formation energies of TiO₂ and TiS₂.

	formation energy (eV)
TiO ₂ _rutile	2.92
TiO ₂ _anatase	2.94
TiS ₂ _layered	1.24

SI-9 SEM and XRD characterization of prepared MIL-167 powders

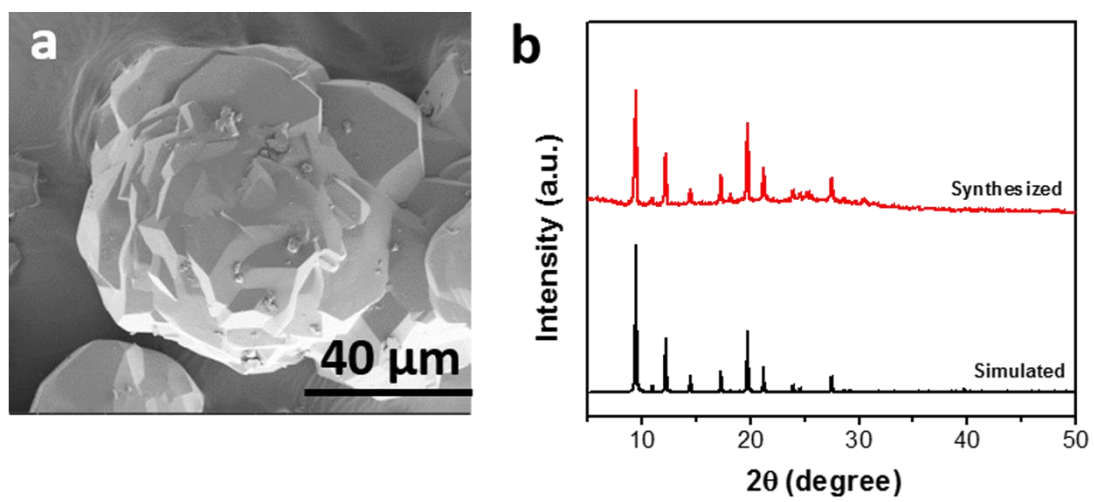


Fig. S9 SEM image a) and XRD pattern b) of MIL-167 derived from TiS_2 precursors.