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# Two-dimensional transition metal dichalcogenides as metal sources of metal-organic frameworks\*

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By taking advantage of the layered structure and decent M–X bond strength of transition metal dichalcogenides (TMDCs), herein versatile Ti-MOFs were successfully prepared with layered titanium disulfide (TiS<sub>2</sub>) as the titanium source. In addition, the phase evolution mechanism, CO<sub>2</sub> adsorption capacity and photocatalytic degradation performance of the prepared Ti-MOFs were investigated in detail.

Transition metal dichalcogenides (TMDCs) are a class of layered compounds with the formula  $MX_2$ , where M represents a transition metal from group IV, V or VI and X stands for a chalcogen.  $MX_2$  exhibit a "sandwich" structure with two chalcogen atomic layers separated by a transition metal atomic layer.<sup>1</sup> The weak van der Waals interlayer interaction facilitates intercalation of foreign atoms or molecules into interlayer galleries.<sup>2</sup> Recent decades witnessed tremendous attention being paid to TMDCs as a consequence of their unique direct bandgap, atomic-scale thickness, strong spin–orbit coupling, optoelectronic properties, favourable electronic properties originating from the layered structure and the presence of d-electrons of

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<sup>c</sup> EMS Energy Institute, Departments of Energy and Mineral Engineering and of Chemical Engineering, The Pennsylvania State University, University Park, PA, 16802, USA transition metals.<sup>3</sup> Nevertheless,  $MX_2$  are rarely used as metal precursors for the synthesis of inorganic compounds. Owing to the decent M-X bond strength as well as the existence of interlayer galleries,  $MX_2$  are vulnerable to nucleophilic attack and therefore may serve as monodispersed metal ion sources under hydrothermal/solvothermal conditions. Moreover, since  $MX_2$  are extremely air and moisture stable, it is not necessary to strictly control the storage and experimental conditions.

Synthesis of Ti-based metal-organic frameworks (Ti-MOFs) may be a representative example demonstrating the capacity of MX<sub>2</sub> as competent metal sources. Ti-MOFs are particularly attractive due to their unique redox activity and photocatalytic properties.<sup>4</sup> Nevertheless, one challenging issue facing the facile synthesis of Ti-MOFs resides in the high reactivity of the commonly used titanium precursors. Liquid titanium isopropoxide (TPOT) and titanium chloride have been widely employed in the synthesis of Ti-MOFs.<sup>5</sup> They are vulnerable to fast hydrolysis as well as evaporation even upon transient exposure to moisture. The only exception is the employment of a solid organometallic Ti precursor, dicyclopentadienyl titanium(IV) dichloride ([Cp<sub>2</sub>Ti<sup>IV</sup>Cl<sub>2</sub>]), as the titanium source of titanium(IV) trans-1,4-cyclohexanedicarboxylate (COK-69).6 It was noted that undesired cyclopentadienyl and chloride anions as side products may interfere with the synthesis of Ti-MOFs. Therefore, it may be a better choice in case the adverse effect of the side products could be simultaneously minimized.

Herein we explored the potential of layered  $\text{TiS}_2$  as the metal precursor for the formation of Ti-MOFs. Taking  $\text{Ti}_8\text{O}_8(\text{OH})_4(\text{bdc-NH}_2)_6$  (NH<sub>2</sub>-MIL-125(Ti)),<sup>7</sup> the most widely studied Ti-MOFs, as an example, herein we first demonstrated that the layered structure of solid TiS<sub>2</sub> precursors not only significantly facilitated the nucleophilic attack of 2-amino-benzene-1,4-dicarboxylate (NH<sub>2</sub>-BDC) ligands under solvothermal conditions therefore promoting the facile synthesis of NH<sub>2</sub>-MIL-125(Ti), but also eliminated the introduction of potentially undesired side products (like TiO<sub>2</sub>).

 $NH_2$ -MIL-125 products were prepared *via* a facile solvothermal method as described in the Experimental section (SI-1, ESI<sup>†</sup>).

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental details, further information obtained from the Ar adsorption/desorption isotherm of NH<sub>2</sub>-MIL-125(Ti), calculation methods of formation energies, detailed investigation of the influence of synthetic temperature and duration on microstructures of NH<sub>2</sub>-MIL-125(Ti) and FI-IR spectra of NH<sub>2</sub>-MIL-125(Ti) powders (in PDF format). See DOI: 10.1039/c8cc01258j

In brief,  $TiS_2$  powders were first dispersed in a mixed DMFmethanol solution of  $NH_2$ -BDC under stirring. Consequently the suspension was transferred to a Teflon-lined autoclave. After solvothermal treatment under controlled conditions, yellow precipitates were obtained and then repeatedly washed with anhydrous methanol and DMF before further characterization. The whole reaction, which represented a brand new strategy for the facile synthesis of  $NH_2$ -MIL-125(Ti), could be expressed as in eqn (1):

$$\mathrm{TiS}_{2} + \mathrm{H}_{2}(\mathrm{bdc}\operatorname{-NH}_{2}) \rightarrow \mathrm{Ti}_{8}\mathrm{O}_{8}(\mathrm{OH})_{4}(\mathrm{bdc}\operatorname{-NH}_{2})_{6} \downarrow + \mathrm{H}_{2}\mathrm{S} \uparrow$$
(1)

Accompanied by the formation of desired product  $NH_2$ -MIL-125(Ti), the side product, gaseous  $H_2S$ , was spontaneously phase segregated from the reaction medium so that any interference from the side products was minimized. Moreover, the simultaneous removal of gaseous  $H_2S$  from the reaction medium favored the forward shift of equilibrium by Le Châtelier's principle.<sup>8</sup>

Commercially available layered TiS<sub>2</sub> precursors were used without further pretreatment. After solvothermal treatment with NH<sub>2</sub>-BDC under controlled conditions (at 160 °C for 96 h), the layered TiS<sub>2</sub> precursors were fully converted to the NH<sub>2</sub>-MIL-125 phase as revealed by the XRD pattern (Fig. 1a)<sup>7</sup> and elemental analysis (SI-2, ESI†). SEM results further indicated that the prepared NH<sub>2</sub>-MIL-125(Ti) powders were highly uniform (~1.6  $\mu$ m) and exhibited a well-developed truncated bipyramid shape (Fig. 1b).

The surface area and porosity of the prepared NH<sub>2</sub>-MIL-125(Ti) were determined by measuring the Ar adsorption/desorption isotherms at 87 K (Fig. 1c). The results revealed that the as-prepared NH<sub>2</sub>-MIL-125(Ti) exhibited a type I isotherm according to the BDDT classification, a BET surface area of 911.8 m<sup>2</sup> g<sup>-1</sup> and a micropore volume of 0.34 cm<sup>3</sup> g<sup>-1</sup> (SI-3, ESI†). The lower BET surface area may be attributed to lower crystallinity caused by



Fig. 1 (a) Powder XRD pattern of  $NH_2$ -MIL-125 obtained at 160 °C for 96 h; (b) SEM image of  $NH_2$ -MIL-125; (c) Ar adsorption/desorption isotherm of  $NH_2$ -MIL-125(Ti) and (d) CO<sub>2</sub> adsorption isotherm of  $NH_2$ -MIL-125 at 25 °C.

the accumulation of  $H_2S$  in the reaction which could be alleviated in an open system (SI-3, ESI<sup>†</sup>). In addition, substantial intergrowth between NH<sub>2</sub>-MIL-125 crystals as evidenced from the SEM image (Fig. 1b) may be responsible for the lower BET surface area either.

Considering the existence of substantial free amine functional groups in the framework, herein the  $CO_2$  adsorption behavior of the prepared  $NH_2$ -MIL-125(Ti) was further investigated. Fig. 1d showed a maximum  $CO_2$  adsorption capacity of 2.4 mmol  $g^{-1}$  at 1 atm and 298 K, which was comparable with those of other  $NH_2$ -MIL-125(Ti) powders reported in the literature.<sup>9</sup>

To fully elucidate the growth mechanism of NH<sub>2</sub>-MIL-125(Ti) crystals, a microstructural evolution process of layered TiS<sub>2</sub> precursors was further investigated. It was observed that UV-vis peaks of the solid products changed with gradual prolongation of the synthesis time (SI-4, ESI<sup>+</sup>), which could be attributed to the unceasing consumption of the layered TiS<sub>2</sub> precursors and the formation of NH2-MIL-125(Ti) products. Simultaneously, a gradual change in color occurred (from dark black characteristic of the layered TiS<sub>2</sub> precursors to bright yellow characteristic of NH2-MIL-125(Ti)). Moreover, the XRD patterns indicated that the (001) reflections (corresponding to the interlayer spacing) derived from the layered TiS<sub>2</sub> precursors attenuated significantly and broadened with gradual prolongation of the synthesis time, indicating disordered stacking and reduced crystallinity of TiS<sub>2</sub> nanosheets along the *c*-axis upon solvothermal treatment.<sup>10</sup> In comparison with the layered TiS<sub>2</sub> precursors (Fig. 3a), the high-resolution TEM image of products obtained after solvothermal treatment for 0.5 h (Fig. 3b) showed substantial amorphous regions, which was indicative of the partially disordered crystal structure. After a lapse of 2 h, NH<sub>2</sub>-MIL-125(Ti) crystals began to form as reflected by the XRD pattern (Fig. 2b, 2 h) and FT-IR spectra (SI-5, ESI<sup>+</sup>). The corresponding SEM image further demonstrated that substantial NH<sub>2</sub>-MIL-125(Ti) nucleus had been generated and aggregated on the surface of the layered TiS2 precursors (Fig. 4b). Further prolonging the synthesis time to 4 h resulted in the formation of the NH<sub>2</sub>-MIL-125(Ti) phase with not only larger grain size but also the appearance of



Fig. 2 Photographs of (a)  $TiS_2$  and samples obtained at 160 °C for different synthesis times and (b and c) crystallization evolution of NH<sub>2</sub>-MIL-125 by XRD for different times.

truncated octahedral morphology (Fig. 4c). When the synthesis time was further extended to 24 h, it was observed that most TiS<sub>2</sub> microplates had been converted to uniform, truncated octahedron-shaped NH<sub>2</sub>-MIL-125(Ti) microcrystals (Fig. 4d). Based on the abovementioned results, the proposed formation mechanism of NH<sub>2</sub>-MIL-125(Ti) was illustrated in Fig. 4e. Herein we deduced that with gradual release of free titanium species from the layered TiS<sub>2</sub> precursors under nucleophilic attack by NH<sub>2</sub>-BDC ligands, the NH<sub>2</sub>-MIL-125(Ti) crystals preferentially nucleated on the surface of the layered TiS<sub>2</sub> precursors since the concentration of nutrients located at the solution-TiS<sub>2</sub> interface was the highest due to concentration polarization. Consequently, the formed NH<sub>2</sub>-MIL-125(Ti) nuclei gradually grew larger, began to merge with each other and ultimately converted to well-developed NH2-MIL-125(Ti) crystals (following the Ostwald ripening mechanism) by unceasing consumption of the layered TiS<sub>2</sub> precursors. It was worth noticing that with the prolongation of synthesis time, the (001) diffraction peaks of the layered TiS<sub>2</sub> precursors gradually shifted to a lower angle (Fig. 2c), therefore demonstrating slight expansion of the unit cell induced by solvothermal treatment.<sup>11</sup>

It should be emphasized that an obvious advantage of using the layered TiS<sub>2</sub> precursors lay in that the NH<sub>2</sub>-MIL-125(Ti) crystals could be obtained from TiS<sub>2</sub> under a wide range of synthesis conditions (the synthesis temperature ranging from 150 to 170 °C and the NH<sub>2</sub>-BDC/TiS<sub>2</sub> molar ratio ranging from 6 to 36). Another interesting phenomenon found in the experiment was that under different reaction conditions all NH<sub>2</sub>-MIL-125(Ti) crystals possessed identical morphology (truncated bipyramids, shown in SI-6, ESI†), which was remarkably different from previous studies<sup>12</sup> and therefore was a clear indication of a thermodynamic equilibrium process.

Considering the photosensitivity of Ti-MOFs, the visible-light diffusion reflectance behavior of the prepared NH<sub>2</sub>-MIL-125(Ti) was further investigated. From the UV-vis spectra of NH<sub>2</sub>-MIL-125(Ti) (Fig. 5a) it was observed that the sample exhibited remarkable visible-light absorption. Two absorption bands at 325 nm and 415 nm could be attributed to  $ATA^{2-}Ti^{4+} \rightarrow ATA^{-}Ti^{3+}$  transition within TiO<sub>5</sub>(OH) inorganic clusters.<sup>9a</sup> The UV-vis spectra of NH<sub>2</sub>-MIL-125(Ti) showed an absorption edge of ~520 nm, which was identical to that of truncated bipyramid-shaped NH<sub>2</sub>-MIL-125(Ti) as reported in previous studies.<sup>12</sup> Simultaneously,



Fig. 3 High-resolution TEM images of (a) raw TiS\_2 crystals and (b) the sample after solvothermal treatment at 160  $^\circ C$  for 0.5 h.



Fig. 4 SEM images of (a) TiS<sub>2</sub> precursor, and NH<sub>2</sub>-MIL-125 prepared at 160 °C for (b) 2 h, (c) 4 h and (d) 24 h. Scale bars correspond to 4  $\mu$ m. (e) Schematic illustration of solvothermal conversion of layered TiS<sub>2</sub> precursors to NH<sub>2</sub>-MIL-125.



Fig. 5 (a) Diffusion reflectance spectra of NH $_2$ -MIL-125 and (b) photocatalytic degradation of RhB by NH $_2$ -MIL-125.

the bandgap was calculated to be 2.38 eV, therefore indicating a low energy threshold for the promotion of valence electrons to higher orbits and inspiring us to investigate the potential photocatalytic activity of NH<sub>2</sub>-MIL-125(Ti) upon exposure to visible-light irradiation. As a model reaction, herein the degradation of rhodamine B (RhB) was conducted to evaluate the photocatalytic activity of the prepared NH<sub>2</sub>-MIL-125(Ti).<sup>13</sup> As shown in Fig. 5b, the removal efficiency of RhB in the dark was only 25% (following a preferential adsorption mechanism), while the total removal efficiency of RhB was significantly increased to 80% upon exposure to visible light irradiation (following the photocatalytic degradation mechanism), which was considerably superior to other NH<sub>2</sub>-MIL-125(Ti) as reported in the literature.<sup>14</sup>

Besides  $TiS_2$ ,  $TiO_2$  was also employed as the titanium source and it was anticipated that the  $TiO_2$  phase could be converted to NH<sub>2</sub>-MIL-125 upon solvothermal treatment with NH<sub>2</sub>-BDC ligands. Nevertheless, our results showed that TiO<sub>2</sub> in the form of both rutile and anatase phases could not be converted to the NH<sub>2</sub>-MIL-125(Ti) phase at all, although precursor solution compositions, solvothermal treatment conditions and crystal sizes of TiO<sub>2</sub> had been significantly optimized. The difficulty in converting TiO2 into NH2-MIL-125 could be attributed to the ultra-high Ti-O bond strength (the Ti-O bond has a shorter length compared with the Ti-S bond; detailed information can be found in SI-7, ESI<sup>+</sup>) as well as the nonlayered structure, which may effectively prevent the nucleophilic attack by NH<sub>2</sub>-BDC ligands. Simultaneously, formation energies of TiO<sub>2</sub> and TiS<sub>2</sub> were calculated by using the density functional theory (shown in SI-8, ESI<sup> $\dagger$ </sup>). The results revealed that TiO<sub>2</sub> (anatase or rutile) had a pretty higher stability compared with TiS<sub>2</sub>. To the best of our knowledge, no other solid inorganic titanium sources had been reported to be competent for NH<sub>2</sub>-MIL-125(Ti) synthesis.

Our approach was by no means confined to  $NH_2$ -MIL-125(Ti) synthesis. For instance, MIL-167<sup>15</sup> crystals with well-developed morphology could also be obtained with the layered TiS<sub>2</sub> precursors as the solid titanium source. Both SEM and XRD results (shown in SI-9, ESI†) were in good agreement with previous reports.

In conclusion, by taking advantage of the layered structure and decent M-X bond strength of MX<sub>2</sub>, for the first time we have obtained high quality MOF materials with MX<sub>2</sub> as metal sources. Taking NH<sub>2</sub>-MIL-125(Ti) as an example, in contrast to traditional liquid titanium precursors like TPOT and TiCl<sub>4</sub>, the layered TiS<sub>2</sub> precursors possessed several advantages like easy handling, resistant to air and moisture, free from interference by undesired side products and driving the reaction equilibrium forward. Moreover, NH<sub>2</sub>-MIL-125(Ti) prepared from the layered TiS<sub>2</sub> precursors exhibited considerable BET surface area, CO<sub>2</sub> adsorption capacity as well as excellent Rhodamine photodegradation performance. At present, versatile TMDCs (e.g. of Zr<sup>IV</sup>, Hf<sup>IV</sup>, V<sup>IV</sup>, Mo<sup>IV</sup>, and Ta<sup>V</sup>) with diverse morphologies<sup>1b,16</sup> are fully developed showing potentially widespread application prospects in the facile synthesis of MOFs with unique frameworks, diverse microstructures and enhanced performance. Moreover, by accurate control of the conversion ratio of the layered MX<sub>2</sub> precursors, it is highly promising to prepare MOF-TMDC composites with controlled architectures and MOF/TMDC ratios. Relying on the coupling effects between MOFs and TMDCs, it is highly likely that they hold great promise in fields of adsorption, photocatalysis, energy storage and conversion.

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### Conflicts of interest

There are no conflicts to declare.

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