

Supporting Information

Amorphous 2D MoS₃ Nanosheets with Porous Structures for Scavenging Toxic Metal Ions from Synthetic Acid Mine Drainage

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1. Experimental

1.1 Chemicals and Reagents

Ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$) and dimethylformamide (DMF) were purchased from Sigma Aldrich. Absolute ethanol, concentrated HCl solution (32.5 wt%), nitric acid, sodium hydroxide, metal nitrate salts were analytical grade obtained from local chemical companies.

1.2 Preparation of amorphous 2D MoS_3 nanosheets

0.1 mol/L $(\text{NH}_4)_2\text{MoS}_4$ were solution (1000 mL) was prepared by dissolving $(\text{NH}_4)_2\text{MoS}_4$ solids in a conical flask under N_2 protection. The $(\text{NH}_4)_2\text{MoS}_4$ solution was magnetically stirred, when 5 M HCl solution was added slowly until the solution pH reached 1.0. During the reaction, amorphous MoS_3 were formed as dark precipitate and there was H_2S gas generated as well. Then, the resulting dark precipitate was filtered, and washed with DI water until solution pH became 6.0-7.0. Absolute ethanol and carbon disulfide were used to wash the precipitate sequentially.

Amorphous 2D MoS_3 nanosheets were prepared by liquid exfoliation. Typically, 0.1 g of amorphous MoS_3 was mixed with 100 mL of DMF under ultrasonic radiation with the power of 40 kHz and 200W for 5 h. Then, the suspended mixture was centrifuged at 1000 rpm for 10 min to remove the bulk MoS_3 . The obtained amorphous 2D MoS_3 nanosheets were dried in a freeze dryer at -65°C overnight.

1.3 Sample Characterization

The shape and morphology of amorphous 2D MoS_3 nanosheets was tested by FE-SEM (MLA650F) and TEM (JEOL-2100). Energy Dispersive Spectroscopy (EDS) Analysis were performed by Oxford 50mm² X-Max SDD x-ray detector. Powder XRD equipment (Bruker D8) was used to characterize the crystallinity of amorphous 2D MoS_3 nanosheets at a scan rate of $2^\circ\text{C}/\text{min}$. XPS spectra of samples before and after metal uptake were obtained by Thermo XPS spectrometer. Brunauer-Emmett-Teller (BET) surface area and pore volume were measured at 77 K by nitrogen sorption using a Micromeritics ASAP 3000 instrument. The pore size distribution was calculated using the BJH method. Raman spectra of samples before and after metal adsorption process were collected by raman microscope

(Renishaw). Inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer) was used to test metal concentration in solution. Ex-situ AFM observations were made by tapping mode using a Veeco Multimode (IVa) Scanning Probe Microscope.

1.4 Adsorption Tests

The effects of solution pH, metal concentration and residence time on metal uptakes by amorphous 2D MoS₃ nanosheets were systematically studied under magnetic stirring at 298 K. The solution pH was controlled by concentrated nitric acid and sodium hydroxide solution. After adsorption, the solid residue were filtered by microfiltration PVDF membrane with 0.2 μm pores. The metal concentration in the filtrate were analyzed by ICP-OES.

The uptake capacities of metal ions by amorphous 2D MoS₃ nanosheets was obtained, based on the equation:

$$Q_e = \frac{(C_o - C_f)V}{m} \quad (S-1)$$

where C_o and C_f are the initial and final concentrations of metal ions (mg/L). V (L) is the metal solution volume. Q_e (mg/g) is adsorption capacity of metal ions. m (g) denote the mass of the sorbent.

Adsorption distribution constant (K_d) is an important parameter for understanding the mobility and distribution of metal ions between aqueous solution and sorbent materials. The equation of K_d is as follows:

$$K_d = \frac{C_o - C_f}{C_f} \times \frac{V}{m} \quad (S-2)$$

where K_d (mL/g) is the adsorption distribution constant; C_o and C_f (mg/L) are initial and final metal concentration in solution, respectively; V (mL) is the metal solution volume; m (g) is the mass of sorbent material used in adsorption process.

The mechanisms of kinetic adsorption were investigated by the pseudo-second-order model.

Pseudo-second-order adsorption equation (S-3):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{e,cal}^2} + \frac{t}{Q_{e,cal}} \quad (S-3)$$

where Q_e (mg/g) and Q_t (mg/g) are the metal uptake at equilibrium and any time t (min), respectively; $Q_{e,cal}$ (mg/g) is the calculated metal uptake; t is the shaken time (min); k_2 (g/mg/min) are the equilibrium rate constant of the second-order sorption respectively.

The Langmuir method in Eq(S-4) were used to model the adsorption isotherm:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{k_L \cdot Q_{max}} \quad (S-4)$$

where C_e (mg/L) is the equilibrium concentration, Q_e (mg/g) is the amount of metal ions adsorbed at equilibrium, Q_{max} (mg/g) is the maximum amount of adsorbed metals. k_L (L/mg) the constant corresponding to the adsorption energy.

1.5 Recycling Tests

Recycling performance of amorphous 2D MoS₃ nanosheets was investigated by 4 consecutive adsorption-stripping cycles. The adsorption conditions in each cycle are as follow: pH=2, synthetic acid mine drainage solution (400 mg/L Al, 900 mg/L Fe, 300 mg/L Mg, 100 mg/L Ca, 105 mg/L Cu, 125 mg/L Cd, 50 mg/L Hg and ~5200 mg/L SO₄²⁻), T = 298 K, and time =40 min. For stripping, the spent amorphous 2D MoS₃ nanosheets loaded with heavy metals were treated by a mixture solution of 1M thiourea and 1M HCl for 1 hour to strip the adsorbed metal ions, then washed with DI water for the next adsorption cycle.

2. Results

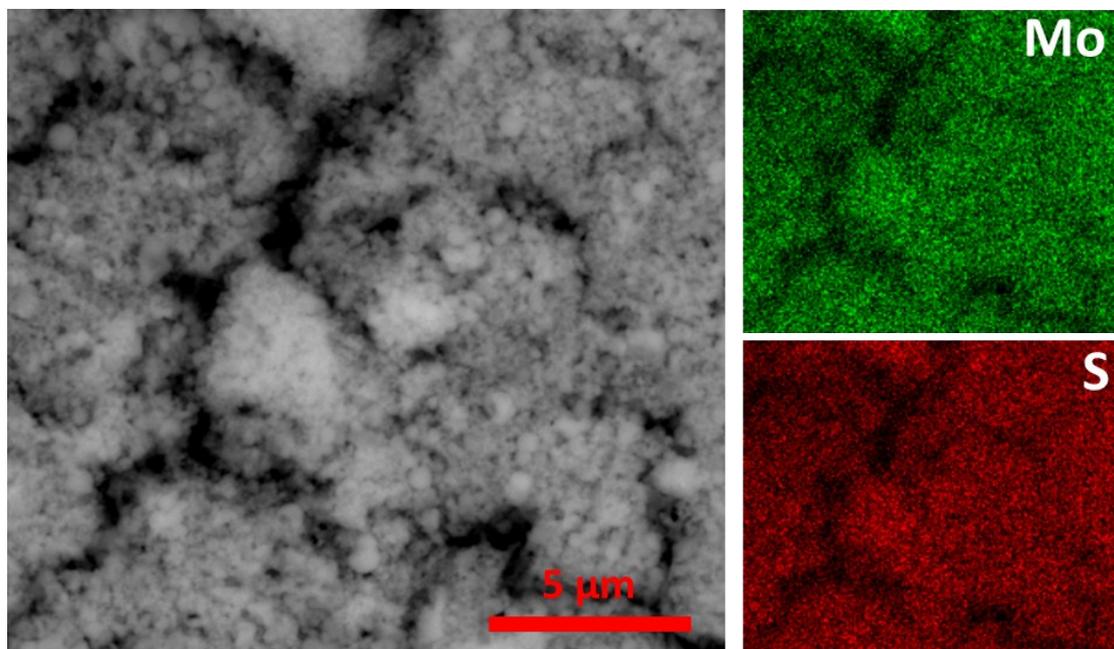


Figure S1. SEM and EDS mapping images of the prepared bulk α -MoS₃ materials before exfoliation.

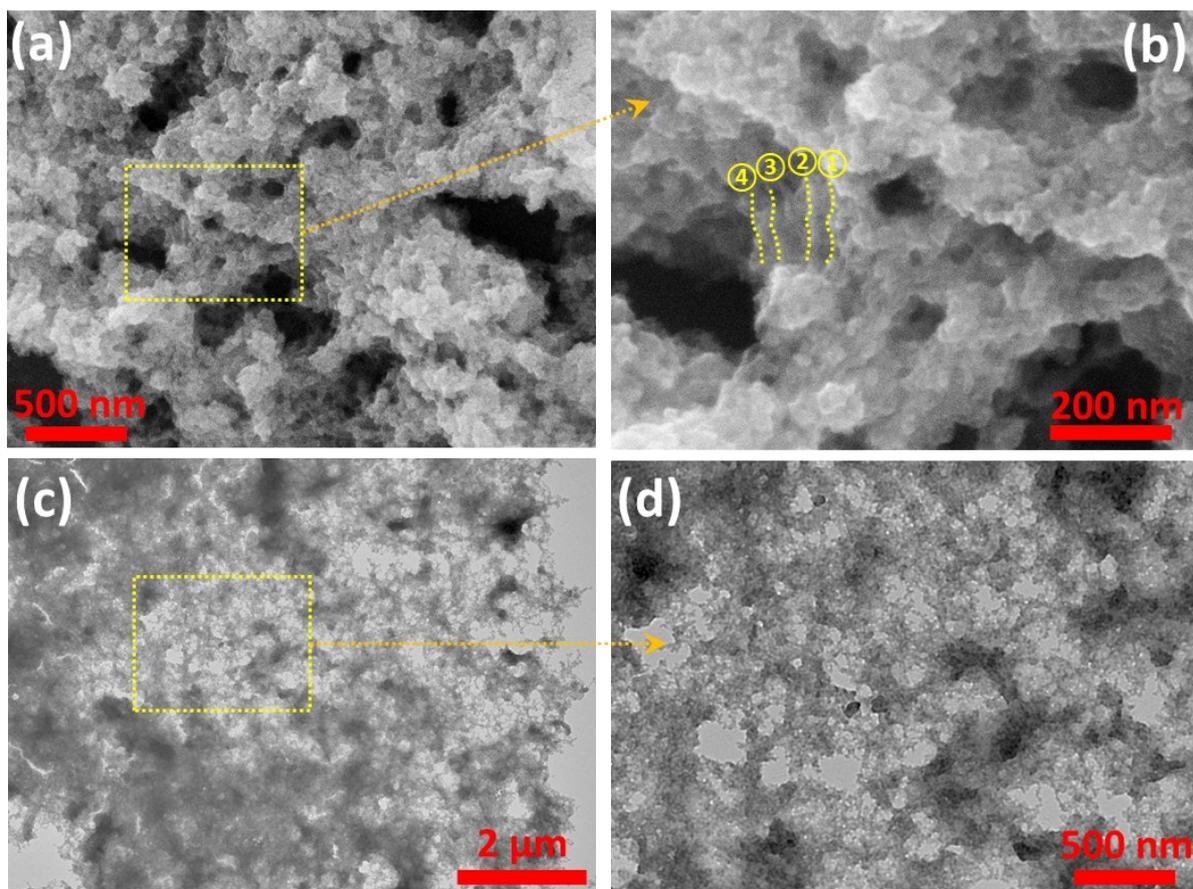


Figure S2. (a) FE-SEM images of prepared α -MoS₃ materials before exfoliation; (b) The enlarged image of the rectangle area in (a). Yellow dotted lines (①②③④) in (b) suggest the α -MoS₃ materials exhibits layer-by-layer stacks. (c, d) TEM images of physical aggregate of exfoliated 2D α -MoS₃ nanosheets.

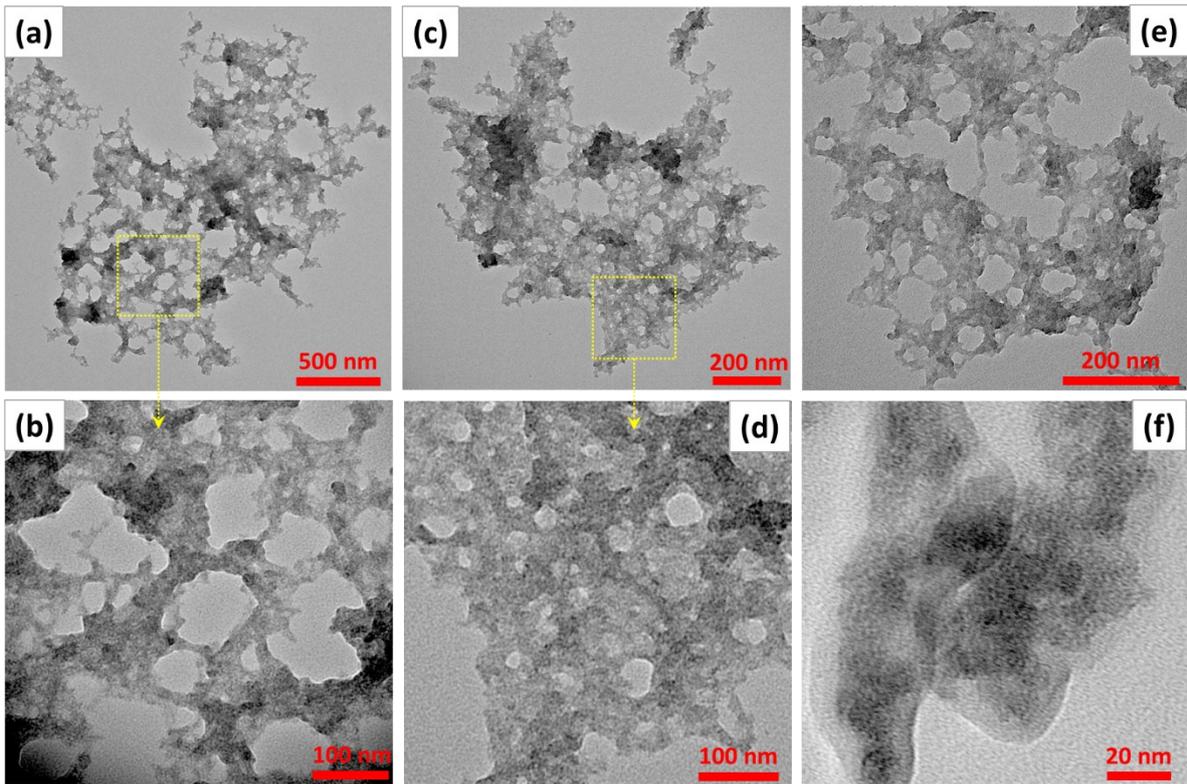


Figure S3. Extra TEM images of exfoliated 2D α -MoS₃ nanosheets with the porous structures. Enlarged images (b) and (d) are originally from the yellow rectangles in (a) and (c), respectively. High-resolution image (f) is the amorphous structure of 2D α -MoS₃ nanosheets.

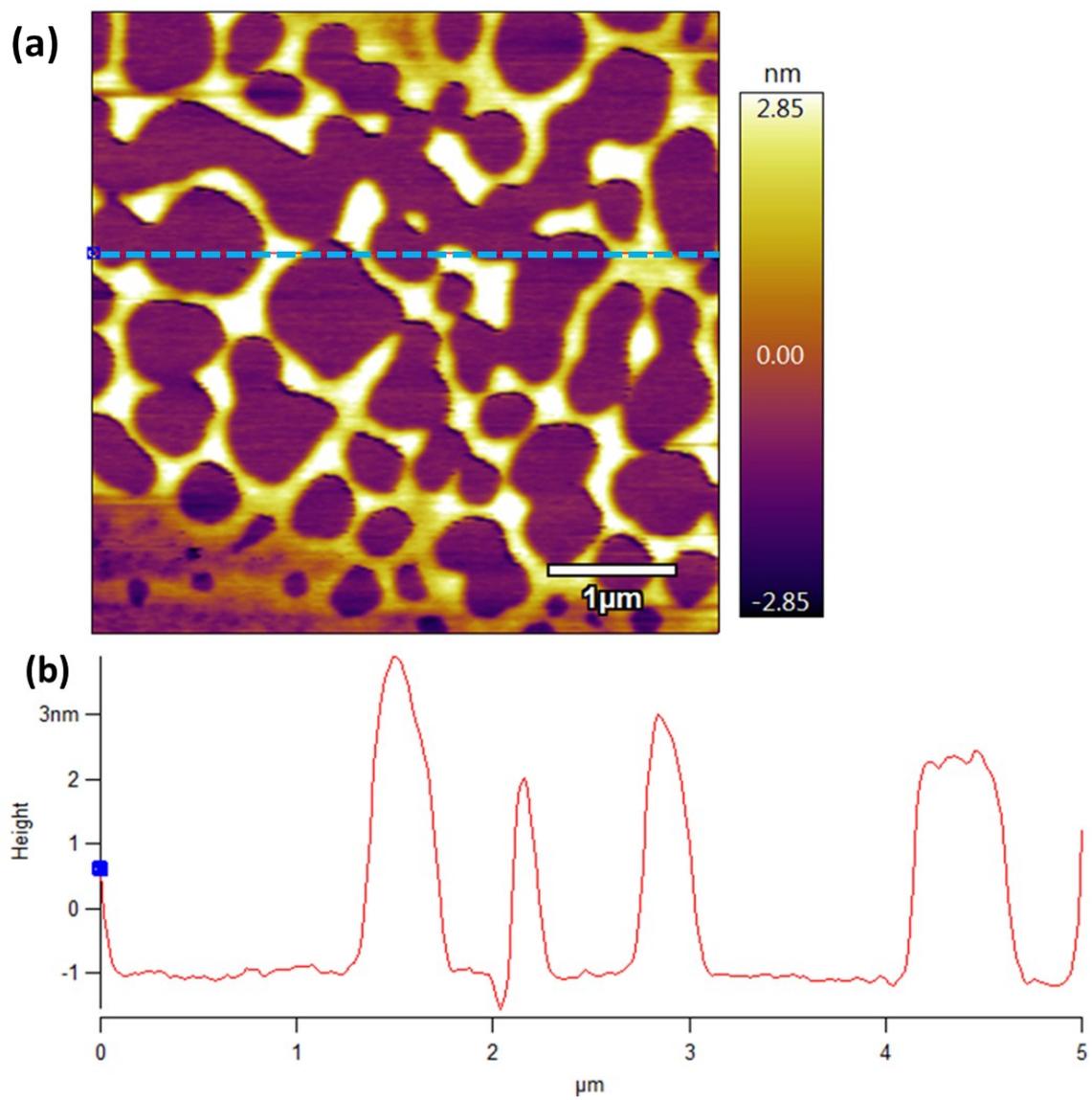


Figure S4. (a) AFM height image of exfoliated 2D α - MoS_3 nanosheets with the porous structures; (b) Height profiles along the blue dotted lines in image (a).

Table S1. Rate constants for the pseudo-second-order models of Cu(II), Cd(II) and Hg(II) ions on amorphous 2D MoS₃ nanosheets (include m/V = 0.25 mg/mL, T = 298 K).

Metal concentration and Solution pH	Metal ions	Pseudo-second-order		
		$Q_{e,cal}$ mg/g	k_2 (g/mg/min)	R ²
C ₀ =50 mg/L pH=2	Cu(II)	53.48	0.001387	0.9939
	Cd (II)	80	0.001284	0.9952
	Hg (II)	200	0.011364	1.000
C ₀ =50 mg/L pH=6	Cu(II)	200	0.006188	1.000
	Pb (II)	200	0.011628	1.000
	Hg (II)	200	0.1000	1.000

Table S2. Constants for the Langmuir isotherms of Cu(II), Cd(II) and Hg(II) ions on amorphous 2D MoS₃ nanosheets (include m/V = 0.25 mg/mL, T = 298 K).

Metal ions and Solution pH	Langmuir Isotherm		
	Q _{max} (mg/g)	k _L (L/mg)	R ²
Cu(II) pH=2	81.6994	0.04509	0.9985
Cd(II) pH=2	118.7648	0.05803	0.9978
Hg(II) pH=2	990.1000	0.1187	0.9970
Cu(II) pH=6	236.9668	1.0933	0.9999
Cd(II) pH=6	383.1418	0.2155	0.9958
Hg(II) pH=6	1851.8500	0.1151	0.9964

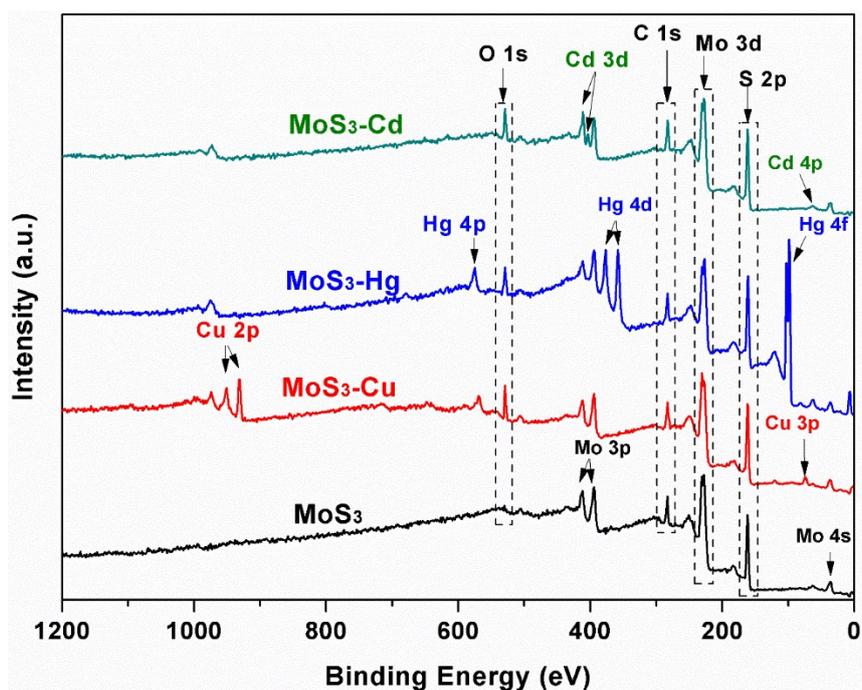


Figure S5. XPS survey scan spectra of 2D amorphous MoS_3 nanosheets and metal-loaded MoS_3 nanosheets.

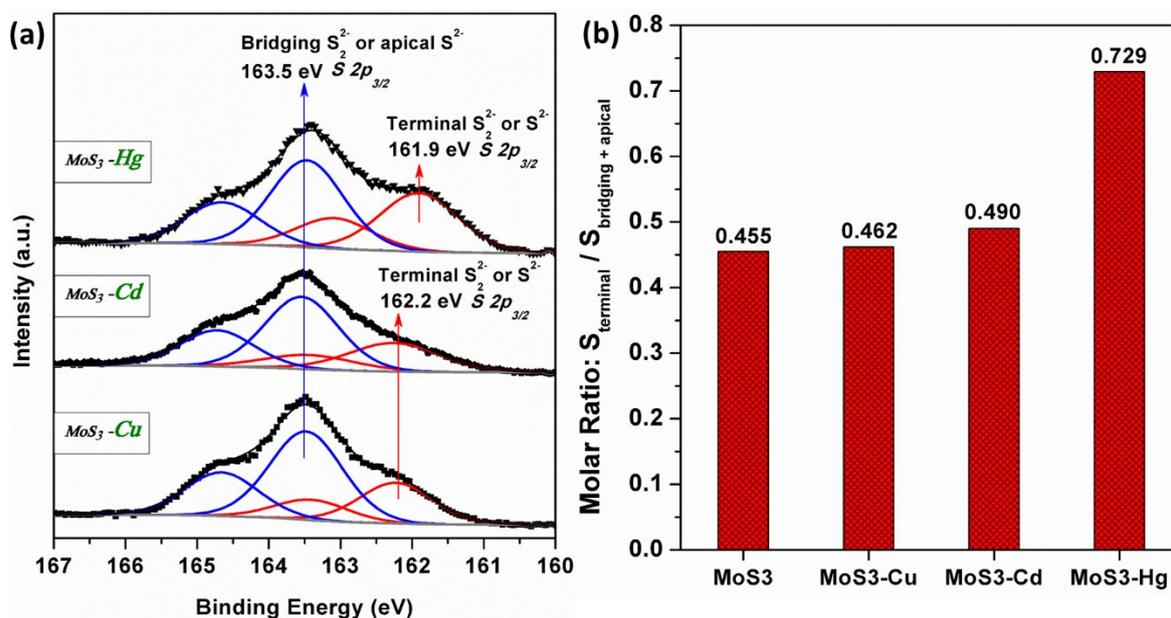


Figure S6. (a) High resolution XPS spectra of S 2p for metal-loaded MoS_3 nanosheets. (b) The molar ratio of $\text{Sulphur}_{\text{terminal}} / \text{Sulphur}_{\text{bridging + apical}}$ for both 2D $\alpha\text{-MoS}_3$ nanosheets and metal-loaded MoS_3 nanosheets, based on the area ratio between terminal sulphur and bridging + apical sulphur in Figure 2(d) and Figure S3(a).

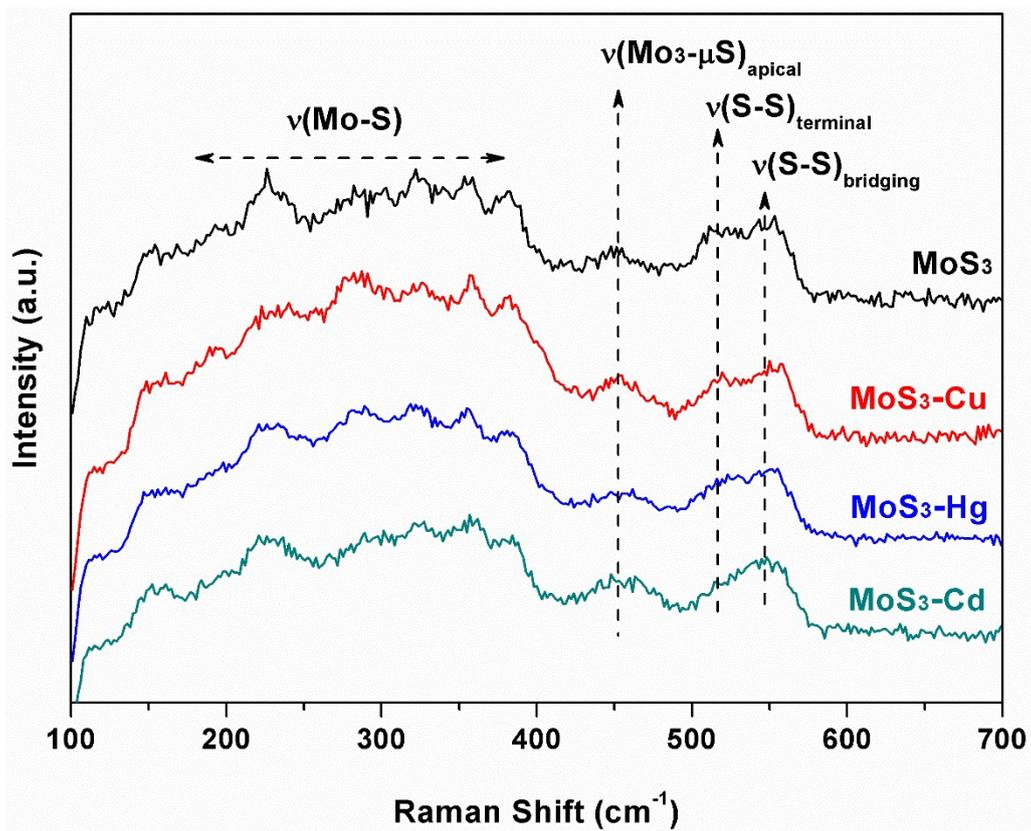


Figure S7. Raman spectra of 2D amorphous MoS₃ nanosheets and metal-loaded MoS₃ nanosheets.

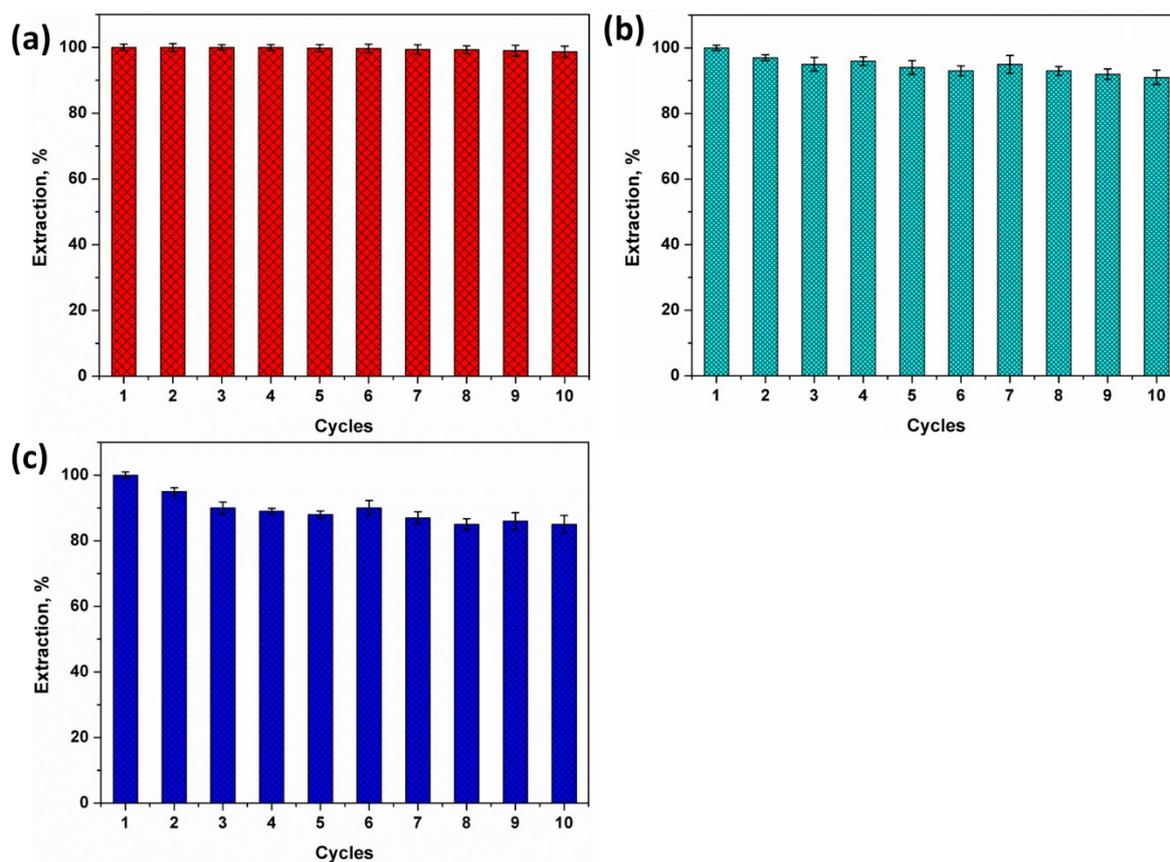


Figure S8. The adsorption and reusability of 2D α -MoS₃ nanosheets for removing Cu(II), Cd(II) and Hg(II) ions from synthetic acid mine drainage (AMD). (a) Hg(II) removal in 10 consecutive cycles; (b) Cd(II) removal in 10 consecutive cycles; (c) Cu(II) removal in 10 consecutive cycles. The composition of AMD solution includes 400 mg/L Al, 900 mg/L Fe, 300 mg/L Mg, 100 mg/L Ca, 105 mg/L Cu, 125 mg/L Cd, 50 mg/L Hg and ~ 5200 mg/L SO₄²⁻ at pH=2. Experimental conditions: m/V = 0.8 mg/mL, temp=25°C and time=40 min.

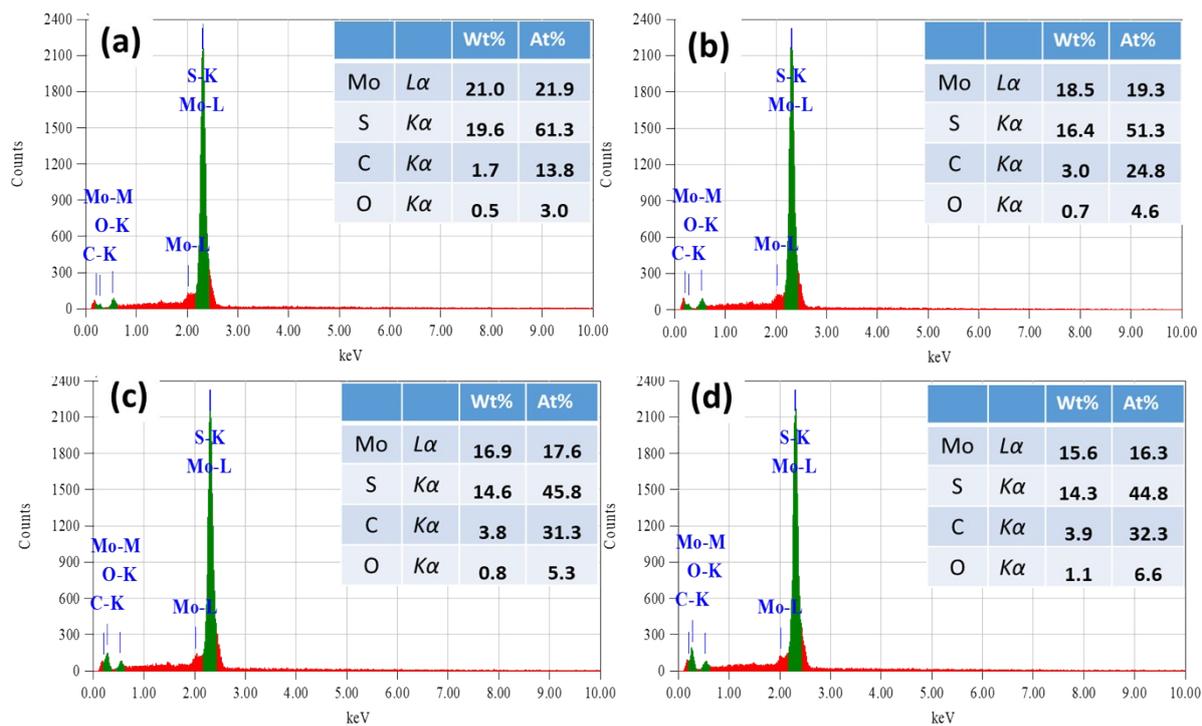


Figure S9. EDS analysis of the chemical stability of 2D amorphous MoS₃ nanosheets under different pHs. (a) newly prepared 2D α -MoS₃ nanosheets; (b) 2D α -MoS₃ nanosheets soaked in pH=2 solution for 2 days; (c) 2D α -MoS₃ nanosheets soaked in pH=4 solution for 2 days; (d) 2D α -MoS₃ nanosheets soaked in pH=6 solution for 2 days. Temperature for all the tests is 25 °C.