

Supporting Information

Unique Lead Adsorption Behavior of Activated Hydroxyl Group in Two-Dimensional Titanium Carbide

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1. Materials and methods

1.1. Preparation

The Ti_3AlC_2 powders were made by mixing elemental titanium (Alfa Aesar, Ward Hill, USA, 99 wt.% purity, particle size $< 40\ \mu\text{m}$), aluminum (Alfa Aesar, Ward Hill, USA, 99 wt.% purity, particle size $< 40\ \mu\text{m}$) and graphite (Alfa Aesar, Ward Hill, USA, 99 wt.% purity, particle size $< 48\ \mu\text{m}$) powders in a 3:1.5:2 molar ratio. The powders were ball-milled for 48 h and cold pressed into cylindrical discs (15 mm diameter and 10 mm height) under pressure of 1 GPa. The discs were placed in a tube furnace under flowing argon, Ar, and heated to 1730 K for 1 h at a heating rate of 20 K/min. After cooling to room temperature, the discs were then milled for 2 h to obtain powders for further study (400 mesh).

The MAX powder was immersed in 40 % HF (Fisher Scientific, Fair Lawn, NJ) at 313 K for 10 h to exfoliate Al layers. Then the filtered MXene solution was alkaline activation treatment by 5 % NaOH solution for 2h. The variation of morphology was observed by scanning electron microscopy (SEM). The elemental compositions were detected by energy dispersive spectroscopy (EDX). Nine random spots have been performed to calculate the elemental composition.

After alkaline activation treatment, the deionized water was used to wash Al-MXene sample to remove the residue impurities until the solution have a pH of 6.8-7.2. Finally, the supernatant was filtered and vacuum desiccated at 343 K for 24 h until reaching a constant weight.

All chemicals are of analytical grade from Tianjin Reagent Station (Tianjin, China), Pb(II) solution (1000 mg/L) was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ solid into the doubly deionized water; the reference adsorbent 001x7, the commercial polystyrene cation exchange resin with 7%

crosslinking degree and 4.2 meq/g total exchanger capacities, was purchased from Zhengguang Resin Co. Ltd. (Zhejiang Province, China). Prior to use, 001x7 was subjected to a flushing sequence with 1% HCl, 1% NaOH and the deionized water, while the alk-MXene powders were directly used.

1.2. Batch lead sorption experiments

Batch sorption tests for Pb(II) uptake evaluation were carried out by traditional bottle-point methods. The detailed experimental methods were developed as follows:

The effects of solution pH on Pb(II) uptake

Here, 0.025 g of the resulting material alk-MXene powders were introduced into 150 ml plastic bottles with 50 mL solution containing 50 mg/L Pb(II) ions. To adjust the various solution pH's (1.0-7.0) 1% NaOH and 1% HNO₃ were used. The bottles were then transferred into an incubator shaker at the desired temperature for above 10 h to ensure sorption equilibrium. Finally the resulting solutions were filtered through 0.45 micrometers membranes and the equilibrium solution pH and corresponding Pb(II) contents were determined.

Competition experiments

To start the tests, 0.025g alk-MXene powders were added into 50 mL solution containing 50mg/L Pb(II) ions and the common Ca(II)/Mg(II) cations were also introduced into the above bottles for competition consideration. The commercial ion-exchange resin 001x7 was used for comparison. The plastic bottles were then transferred into a SHZ-85 model incubator shaker with thermostat and shaken under 200 rpm for 20 h, and the equilibrium Pb(II) contents were assayed.

Kinetic tests

Sorption kinetic tests were performed in 1500 mL solution bottles by sampling 1mL-solution at various time intervals. The initials solution volume is 1000 mL and containing 50 mg/L Pb(II)

and 0.2 g alk-MXene. An automatic fraction collector (SBA-100 Huxi) was employed to collect the samples at various times.

Adsorption isotherms

The temperatures effects on adsorption were also performed by adding 0.025 g adsorbent into 50 mL solution containing Pb(II)=10, 20, 50, 100, 150, 200, 250, 300 mg/L respectively. The above solutions were subjected to shaking under 200 rpm for 20 h to ensure sorption equilibrium. The SHZ-85 model incubator shaker was also used to control the temperature (293 K/303K/325K). The equilibrium solutions were then filtered and the residual Pb(II) content was determined. From these tests, the exact balance of the sorption capacities and equilibrium Pb(II) concentrations can be obtained

Simulated drinking water treatments

In this set of experiments, 1 g alk-MXene powders were added into a large bottle containing 1000 mL (of a solution containing Pb(II)=500 μ g/L Ca(II) = 40 mg/L, Mg(II) = 80 mg/L, Na(I) = 100 mg/L).

A peristaltic pump (Lange-580, China) was used to ensure a constant flow rate of feeding solution and an automatic fraction collector was used for collecting the effluent samples. A mechanical stirrer was also employed to ensure a homogeneous reaction. Prior to sampling the effluents, 30 min static settling was necessary to avoid the possible sorbent leakage. Note that the alk-MXene powders exhibit excellent sedimentation properties for Pb(II) sequestration and 5 minutes were enough to achieve the solid-liquid separation (Fig. S7), finally, we can get the desired the effluent by intermittent sedimentation-sampling history and determine the collected effluent concentrations as well as its corresponding treated volumes.

Sorption-regeneration tests

To evaluate the regeneration properties of the resulting alk-MXene, 0.1g sorbent powders were introduced into a 100mL solution containing $\text{Pb(II)}=100\text{mg/L}$, $\text{Ca(II)}=200\text{mg/L}$, $\text{Mg(II)}=\text{Na(I)}=100\text{mg/L}$, then the above bottle was transferred into a SHZ-85 model incubator shaker with thermostat and shaken under 200 rpm for 20 h, and the equilibrium Pb(II) contents were assayed and the amounts of adsorbed Pb(II) were also calculated.

Next, A high-velocity centrifuge used for obtaining the solid-liquid separation and the Pb(II) -loaded alk-MXene was subjected to regeneration by introducing the binary 0.1% HNO_3 +5% $\text{Ca(NO}_3)_2$ solution as regenerant. Similar to the adsorption process, the obtained flasks were also transferred into a SHZ-85 model incubator shaker under 200 rpm for 5 h. finally, we can obtained the amounts of stripping Pb(II) and calculate regeneration efficiency.

1.3 Analysis and characterization

X-ray diffraction (XRD) patterns were obtained with a powder diffractometer (Siemens D500, Germany) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a step scan of $0.02^\circ/\text{s}$ per step. Si powder was added to some samples as an internal standard to calibrate the diffraction angles and the instrumental peak broadening.

A field emission scanning electron microscope, SEM (Zeiss Supra 50VP, Germany), was used to obtain high magnification images of the treated samples and conduct elemental analysis via energy-dispersive X-ray (EDX) spectroscopy. After sonication, the 2D sheets were investigated by transmission electron microscopy, TEM (JEOL JEM-2100, Japan), with an accelerating voltage of 200 kV. The TEM samples were prepared by suspending the powders in isopropyl alcohol and placing a drop of the latter on a lacey carbon coated 200 mesh Cu grid.

The concentrations of the Pb(II) ions were determined by a Shimadzu AA-6800 atomic

absorption spectrometer equipped with a graphite furnace atomizer and a deuterium background correction.

XPS analysis of given samples was performed with a spectrometer (ESCALAB-2, Great Britain) equipped with a Mg K α X-ray source (1253.6 eV photons) and FT-IR spectrometer (Nexus870, USA) of alk-MXene loaded with Pb(II) ions was examined with a pellet of powered potassium bromide and sorbent in 400-4000 cm⁻¹.

1.4. Computational details

All calculations are performed based on the density functional theory (DFT), which was implemented in the Vienna ab initio Simulation Package (VASP) code ^{s1}. The exchange-correlation functional is using the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) ^{s2}, and the ion-electron interaction is described with the projector augmented wave (PAW) method ^{s3}. The cutoff energy of plane-wave basis is set at 520 eV. The conjugated gradient method is adopted during geometry optimization, and the criterion of energy convergence is 10⁻⁶ eV/cell. The Brillouin zone is represented by Monkhorst-Pack special *k*-points mesh ^{s4} of 6 \times 6 \times 1, 4 \times 4 \times 1, 3 \times 3 \times 1 for 2 \times 2, 3 \times 3, 4 \times 4 supercell, respectively. The smearing width of the partial occupancies, which are determined using the Methfessel-Paxton smearing scheme ^{s5}, is 0.1 eV. A large vacuum space of 20 Å is used for avoid any interaction between an MXene sheet. The electronic structure computations of a 3 \times 3 supercell including pristine and Pb occupation MXene sheets are calculated using 12 \times 12 \times 1 *k* points.

Table S1 The average chemical compositions of the samples under different states.

Sample	Elements (at.%)					
	Ti	Al	C	O	F	Na
The MAX pristine	61.12	16.58	22.30	-	-	-
MXene (40% HF, 4h)	47.11	0.12	29.1	9.56	14.11	-
Alk-MXene (40% HF, 4h+5%NaOH, 2h)	46.52	0.11	24.1	22.14	3.85	3.28

Table S2 Comparison of Pb(II) cation adsorption capacities of various adsorbents

Sorbent	Sorption Capacity (Q_{\max} mg/g)	Equilibrium time	Kinetic model (k)	Sorption performance
Porous NiFe₂O₄ adsorbent ^[S6]	~48.98	60 min	Pseudo-first -order (k=0.229)	The Q_{\max} was obtained at pH=5.0, 308K.
Titanium phosphate encapsulated ion exchange ^[S7]	~331	190 min	Pseudo-second -order (k=0.038)	Large sorption capacity (331mg/g) by encapsulated TiP and the effluents in column tests reach below 10 µg/L with treated capacity 1100 kg water/kg sorbent.
Chemically modified corncobs ^[S8]	~43.4	60 min	Pseudo-first -order (k=0.072)	The Q_{\max} was 43.4mg/g with 0.2 g dose addition and initial Pb(II)= 0.1-2.0 mmol/L
Manganese oxide coated zeolite ^[S9]	~74.52	180 min	NA	Optimal pH=4-6 and Q_{\max} was tested at 318 K with initial Pb(II) =700 mg/g.
Graphene oxide ^[S10]	~328	180 min	NA	Large sorption capacity was achieved of 328 mg/g with initial Pb(II) =5-300 mg/L, 0.125 g/L sorbent, pH 6.8, at 298 K.
Multiwalled carbon nanotubes/polyacrylamide composites ^[S11]	~29.71	4 hours	NA	The evaluated effluent is about 1 mg/L with initial Pb(II)=10 mg/L; the Q_{\max} =29.7 with 0.4g/L dose, 293 K and pH = 5.0.
Eggshell membrane modified with ammonium thioglycolate ^[S12]	~32.47	4 hours	Pseudo-second -order (k=0.059)	The treated capacities were about 750 BV in column tests with initial Pb(II) =8.10 mg/L
Takovite-alumino silicate composite ^[S13]	~47.2	20 min	Pseudo-first -order (k=0.086)	The fast kinetic behavior was observed and 20 min is enough to approach the sorption equilibrium with initial Pb(II) 8 µmol mL ⁻¹
Titanium dioxide/carbon nanotube composites ^[S14]	~137	60 min	Pseudo-second -order (k=0.26)	The Q_{\max} was assayed about 137 mg/g at pH=6.0, 298 K
Attapulgit clay@Carbon ^[S15]	~263.8	30 h	NA	Large sorption capacities were increased by carbon addition

				with 1.6 fold ATP capacity (105.2 mg/g); while the poor sorption kinetics (30 hours)
Activated carbon enteromorpha prolifera by zinc chloride activation^[S16]	~147	60 min	Pseudo-first -order (k=0.051)	The Q _{max} was obtained with the values of 147 mg/g at pH= 5.0, 298 K and initial Pb(II) = 10-60 mg/L.
Cross-linked poly(acrylic acid) hydrogel^[S17]	~117.9	14 hours	NA	Moderate sorption capacity at pH=6.0, 298K with a slow sorption kinetic performance
Natural diatomite^[S18]	~25.91	110 min	Pseudo-first -order (k=0.026)	The Q _{max} was obtained with about 25.9 mg/g by varying initial Pb(II) content 10-500 mg/L at 298 K, 2 g/L sorbent
Zeolite-kaolin-bentonite^[S19]	~117.9	4 hours	Pseudo-second -order (k=0.018)	NA
Tourmaline^[S20]	~108	14 hours	NA	The maximum mass of Pb(II) adsorbed (Q _m), was 108 mg/g on tourmaline of 0.5-50 µm at an initial pH=5.0,
Layered 2D-alk-MXene	~140.1	2 min	NA	High selectivity with Pb(II) effluent about 2 µg/L for 4500 kg water/kg sorbent, Short equilibrium time of 2 min in the present study

Table S3 Calculated formation energies.

Reaction equations	Pb coverage (Θ)	E_{form}
$\text{Ti}_3\text{C}_2(\text{OH})_2 + \text{Pb}(\text{NO}_3)_2 \rightarrow \text{Ti}_3\text{C}_2(\text{O}_2\text{H}_{2-2m}\text{Pb}_m) + \text{HNO}_3$	1/4	0.334
	1/9	-0.376
	1/16	-0.841
$\text{Ti}_3\text{C}_2(\text{OH}_n\text{Na}_{1-n})_2 + \text{Pb}(\text{NO}_3)_2 \rightarrow \text{Ti}_3\text{C}_2(\text{O}_2\text{H}_n\text{Na}_{2-2m-n}\text{Pb}_m) + \text{NaNO}_3$	1/4	-0.653
	1/9	-1.440
	1/16	-1.463
$\text{Ti}_3\text{C}_2(\text{OH})_2 + \text{Ca}(\text{NO}_3)_2 \rightarrow \text{Ti}_3\text{C}_2(\text{O}_2\text{H}_{2-2m}\text{Ca}_m) + \text{HNO}_3$	1/4	2.124
	1/9	1.470
	1/16	-0.101
$\text{Ti}_3\text{C}_2(\text{OH})_2 + \text{Mg}(\text{NO}_3)_2 \rightarrow \text{Ti}_3\text{C}_2(\text{O}_2\text{H}_{2-2m}\text{Mg}_m) + \text{HNO}_3$	1/4	1.023
	1/9	0.478
	1/16	-0.206

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Fig. S1

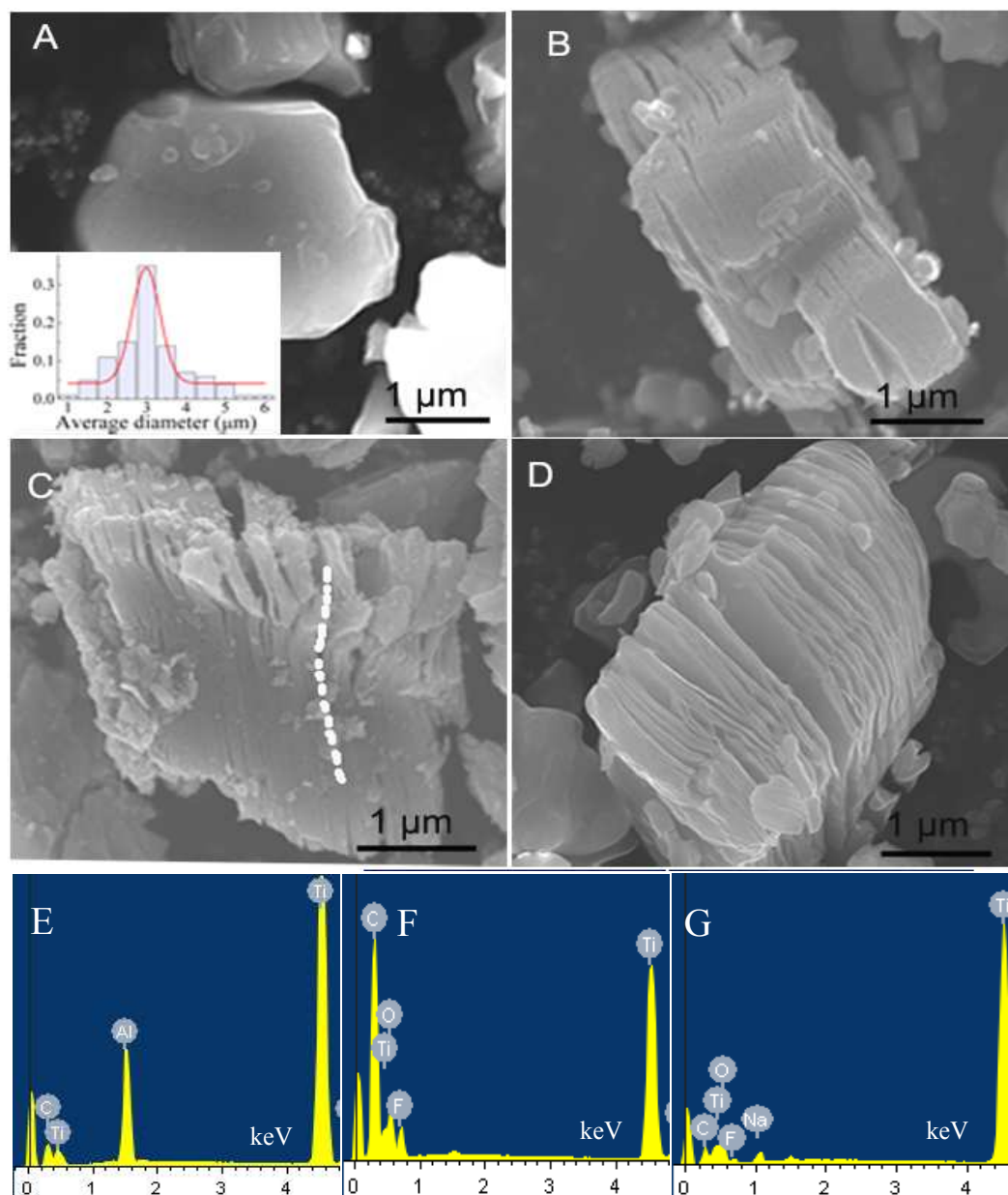


Fig. S1. The SEM graphs of MAX samples after exfoliating in 40%HF for different times and then alkalizing in 5% NaOH solution. (A) The pristine one. The inset is the histogram of average diameter. (B) 30 min. (C) 4 h. (D) Immersed in NaOH for 2h. (E) Elemental compositions of the pristine one. (F) Elemental compositions of the sample immersed in HF solution for 4h. (G) Elemental compositions of the simple immersed in NaOH for 2h.

Fig. S2

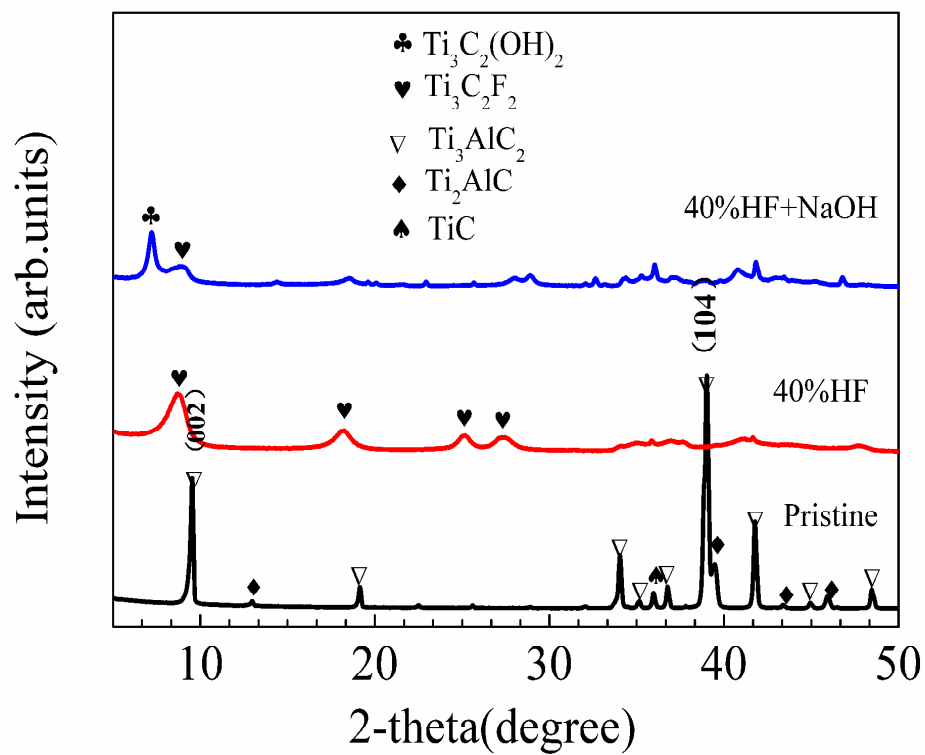


Fig. S2. XRD patterns of Ti_3AlC_2 samples under different states.

Fig. S3

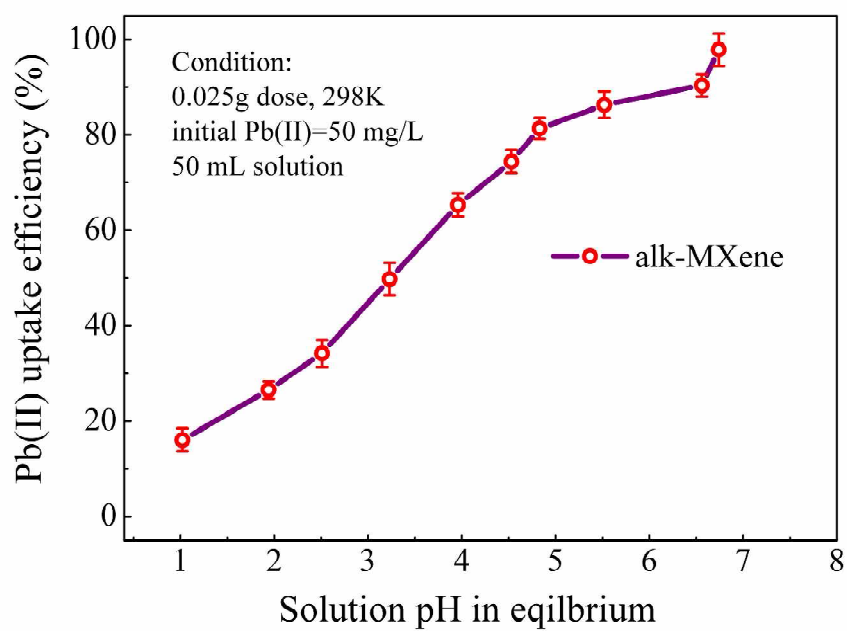


Fig. S3 Effect of solution pH on the uptake of lead ions onto alk-MXene powders

Fig. S4

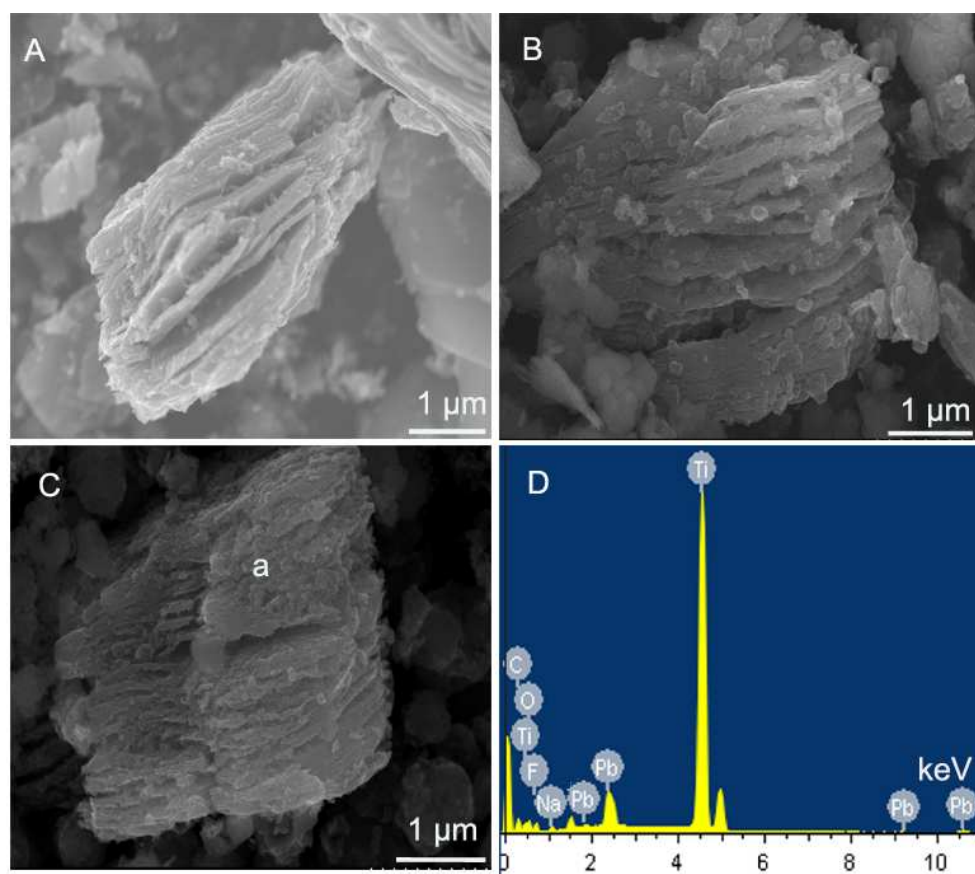


Fig. S4. SEM observations of alk-MXene sample during adsorption process. (A) 1 min. (B) (A) 2 min. (C) 15 min. (D) elemental compositions of a dot in (C).

Fig. S5

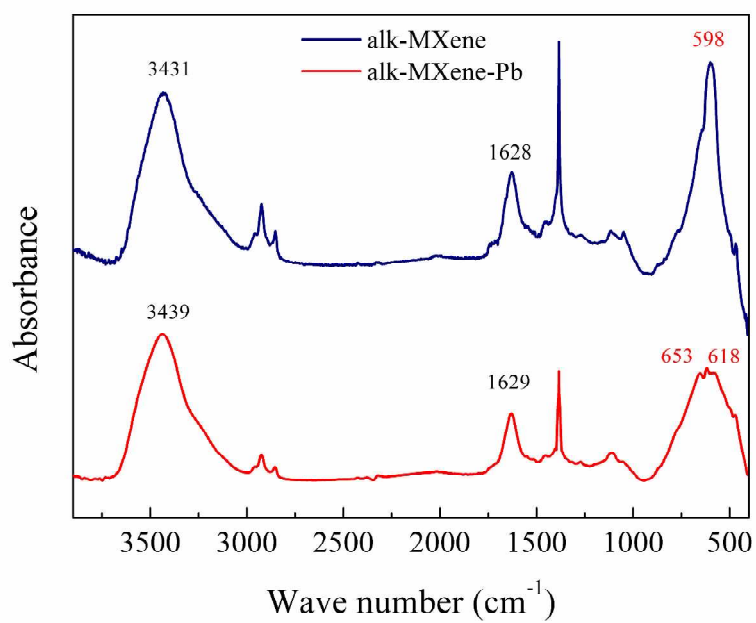


Fig. S5. FT-IR spectra of alk-MXene samples before and after adsorption of lead ions.

Fig. S6

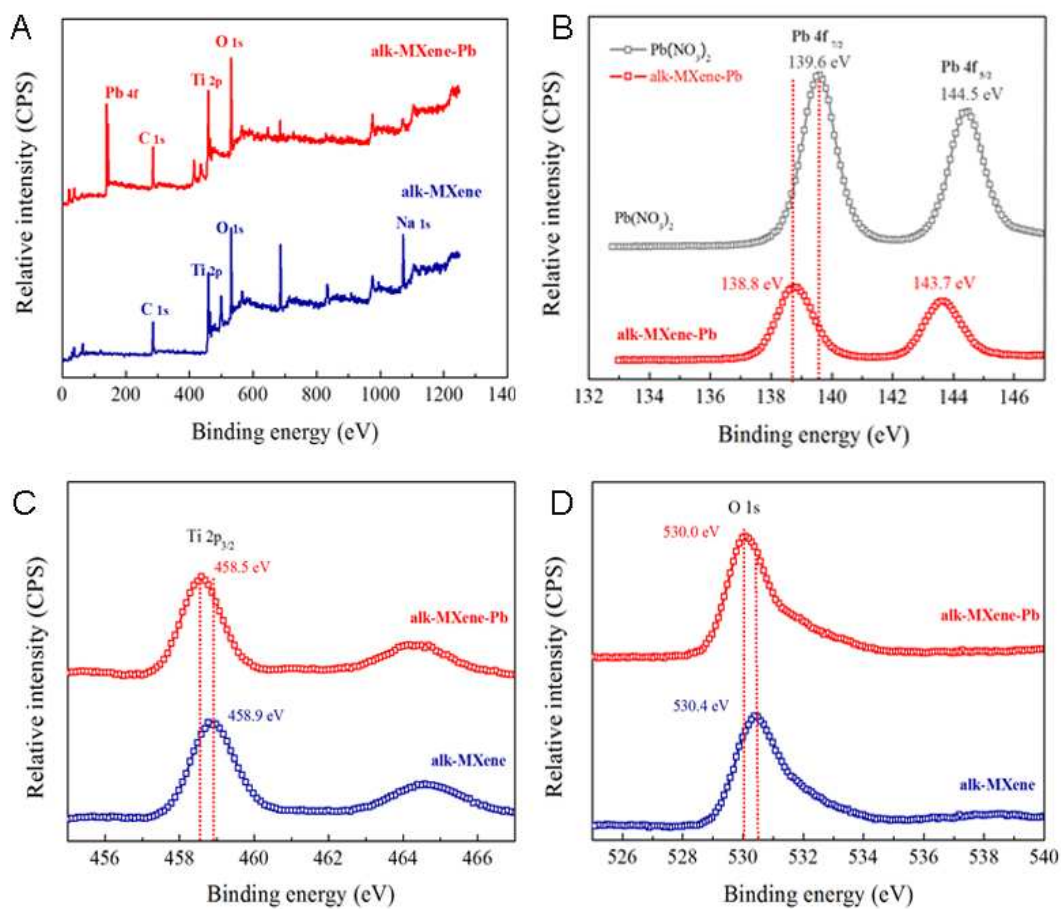


Fig. S6 (A) XPS spectra of alk-MXene samples before and after adsorption of lead ions. (B) the Pb 4f spectra comparison of $\text{Pb}(\text{NO}_3)_2$ and that onto alk-MXene samples. (C-D) the Ti 2p and O 1s binding energy shifting before and after lead uptake.

Fig. S7

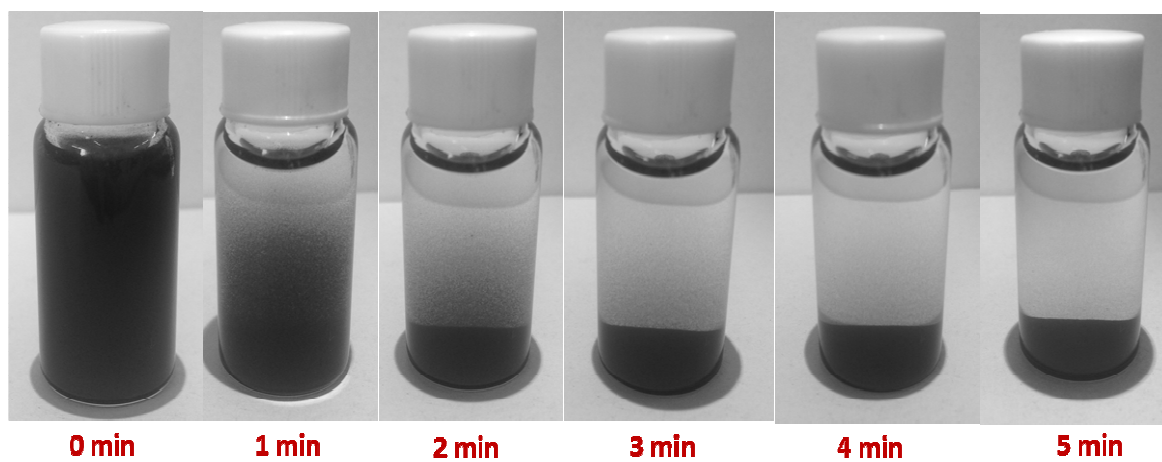


Fig. S7. Static settling properties in various time intervals of alk-MXene with the process of lead uptake.

Fig. S8

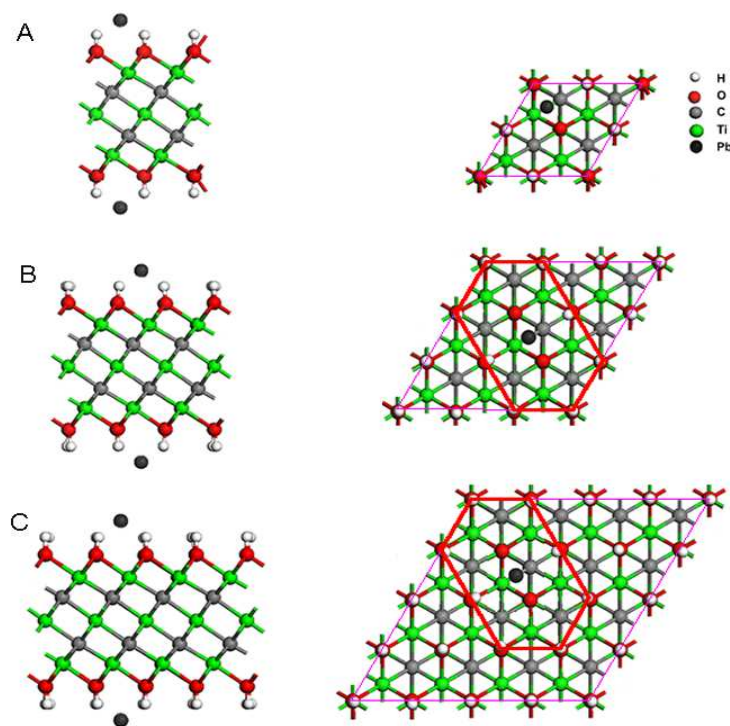


Fig. S8. Top (left) and side (right) sketch map of $\text{Ti}_3\text{C}_2(\text{O}_2\text{H}_{2-2m}\text{Pb}_m)$ after Pb atom replaces two H atoms. (A) 1/4 ML; (B) 1/9 ML; (C) 1/16 ML.

Fig. S9

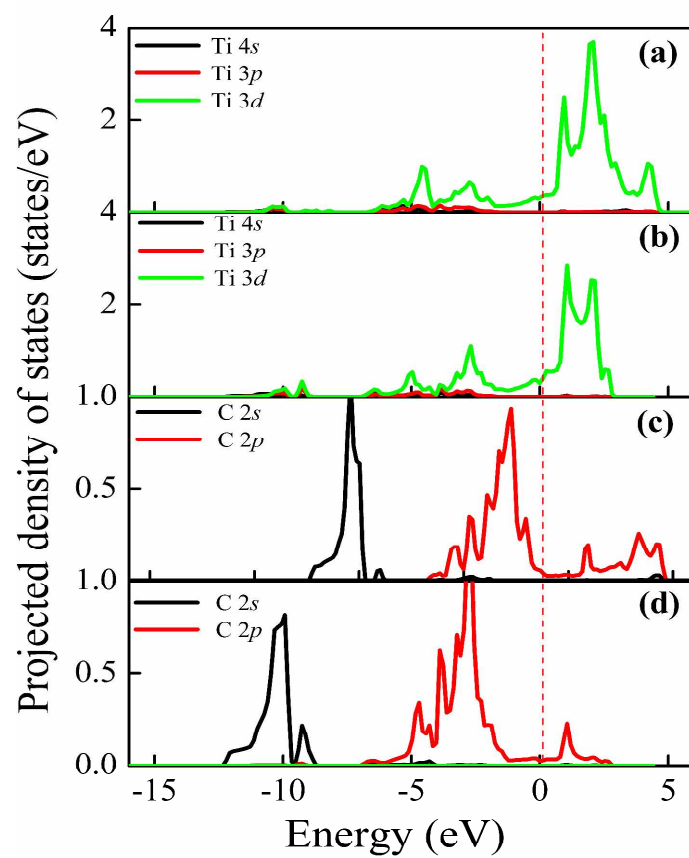


Fig. S9 Projected density of states. (a) Ti atom of $\text{Ti}_3\text{C}_2(\text{O}_2\text{H}_{2-2m}\text{Pb}_m)$; (b) Ti atom of pristine $\text{Ti}_3\text{C}_2(\text{OH})_2$; (c) C atom of $\text{Ti}_3\text{C}_2(\text{O}_2\text{H}_{2-2m}\text{Pb}_m)$; (d) C atom of pristine $\text{Ti}_3\text{C}_2(\text{OH})_2$.

Fig. S10

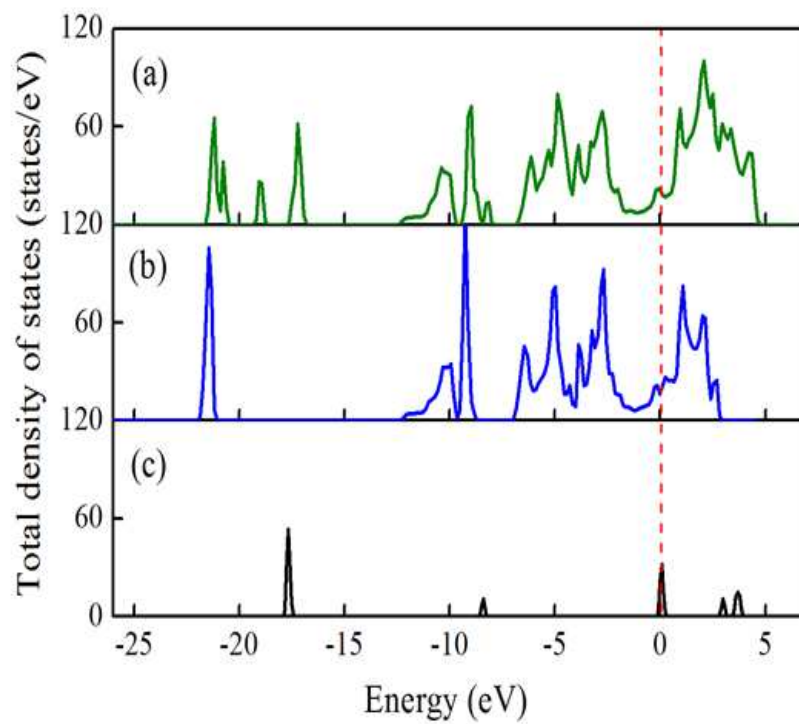


Fig. S10. Total density of states. (a) $\text{Ti}_3\text{C}_2(\text{O}_2\text{H}_{2-2m}\text{Pb}_m)$ for 1/9 ML; (b) pristine $\text{Ti}_3\text{C}_2(\text{OH})_2$ for 1/9 ML; (c) free Pb atom.