

## RESEARCH ARTICLE

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Cite this: *Inorg. Chem. Front.*, 2023, 10, 6566Fabrication of ultrathin two-dimensional MOF nanosheets with cage-like cavities showing excellent adsorption for lead(II)<sup>†</sup>Hongwei Sun,<sup>a</sup> Ke-Zhong Wang,<sup>a</sup> Meng-Ru Yao,<sup>a</sup> Cai-Xia Yu,<sup>\*a</sup> Yue-Hai Song,<sup>a</sup> Jing Ding,<sup>a</sup> Yan-Li Zhou,<sup>id</sup><sup>a</sup> Dong Liu<sup>id</sup><sup>\*b</sup> and Lei-Lei Liu<sup>id</sup><sup>\*a</sup>

In this work, we present a top-down method for the preparation of 2D MOF nanosheets with cavity structures. The pro-ligand 25,26,27,28-tetrakis[(carboxyl)methoxy]calix[4]arene was elaborately selected, and a layered MOF with cavity structures was constructed. The large molecular skeleton and cup-shaped feature of the calix[4]arene caused large layer separations and weak interlayer interactions among the 2D layers, which enabled the layered MOF to be readily delaminated into ultrathin 2D MOF nanosheets. Owing to the cup-shaped feature of the calix[4]arene, there are permanent cage-like cavities loaded on the as-prepared MOF nanosheets. By decorating oxygen-containing functional groups (carboxyl and ether groups) in the cage-like cavities, the resultant **Cu-MOF** nanosheets showed excellent adsorption performance for Pb<sup>2+</sup>. The intimate contact and sufficient interactions on the exposed surface areas of **Cu-MOF** nanosheet resulted in ultrahigh adsorption selectivity and anti-interference ability for Pb<sup>2+</sup>, together with an outstanding Pb<sup>2+</sup> uptake capacity of 738.65 mg g<sup>-1</sup>, which were obviously better than those of its 3D precursor. The possible adsorption mechanism was systematically investigated by the investigations of zeta potential, FT-IR, XPS, and DFT calculations. This study opens the door to achieving ultrathin MOF nanosheets with cavity structures, which would well expand the applications of MOF nanosheets.

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## Introduction

Lead (Pb), one of the most pervasive and dangerous industrial pollutants, can accumulate over time in the human body and cause serious damage to the brain, liver, kidneys, reproductive system, and immune system.<sup>1</sup> The efficient and selective removal of Pb<sup>2+</sup> from aqueous solutions, especially with outstanding anti-interference capability, remains a great challenge.<sup>2–4</sup> Owing to the adjustable composition, ordered pore structure, and large specific surface area of metal-organic frameworks (MOFs), the new type of crystalline porous materials have been increasingly applied in the field of adsorption.<sup>5–8</sup> By ligand pre-design or MOF post-functional-

ization, different functional groups can be purposely introduced into the pores or cavities of the frameworks,<sup>9</sup> creating more active sites for the capture of target pollutants.<sup>10–13</sup> In this process, functional groups worked as catchers for pollutants, and the pores/cavities acted as containers for stabilizing the adsorbed pollutants to avoid desorption.<sup>14–16</sup> MOF materials have achieved excellent performance in pollutant removal, especially in the improvement of the selectivity by modifying the adsorption sites,<sup>17–20</sup> while the difficulty and limited accessibility to the active sites buried in the framework of bulky MOFs made a significant discount on their adsorption performances, including adsorption selectivity and uptake capacities.<sup>21</sup>

The abovementioned drawbacks may be solved by two-dimensional (2D) MOF nanosheets, highly open structures with sufficiently exposed surfaces and accessible active sites.<sup>22–26</sup> The 2D MOF nanosheets hold the structural characteristics of both bulky MOFs and 2D materials, such as versatile compositions and functions, exposed surface area, innumerable accessible surface-active sites, and nanoscale thickness, which were facile for the interaction with substrate molecules, affording improved performance in catalysis, sensing, separation, *etc.*<sup>27–32</sup> The significance of the synthesis of 2D MOF nanosheets was greatly highlighted by these attractive

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properties and applications.<sup>33–35</sup> However, few studies on pollutant capture by 2D MOF nanosheets have been reported thus far.<sup>36</sup> The loss of pore structures for the exfoliated 2D MOF nanosheets may be the key factor. The incorporation of pores or cavity structures into the open structure of 2D MOF nanosheets can be an efficient strategy to expand their applications in adsorption, which was expected to acquire highly selective and efficient adsorption performance.<sup>22</sup>

To obtain the 2D MOF nanosheets with pores or cavity structures, a ligand containing cavity structures is highly desirable, and the as-constructed 2D MOF nanosheets could not only be modified with predesigned functional groups but also hold cavity structures that are conducive to adsorption. Thus, the ligand design is of great significance for the synthesis of functionalized 2D MOF nanosheets. Calix[*n*]arenes (*n* = 4, 6, and 8) are a class of well-known macrocycles with a special cup-shaped cavity structure,<sup>37</sup> which have been used as building blocks for the construction of porous MOFs.<sup>38–40</sup> In view of the large molecular skeleton and cup-shaped feature of the calix[*n*]arene, the as-synthesized bulk MOFs tend to form layered structures with large layer separations and weak inter-layer interactions, which would be facile for its exfoliation.<sup>41</sup> Owing to the cup-shaped feature of the calix[4]arene, there are permanent cage-like cavities loaded on the as-exfoliated MOF nanosheets. Moreover, the structural characteristics of the convenient modification for both the lower and upper rims of the calix[*n*]arene could endow the 2D MOF nanosheets with specific adsorption sites.<sup>42</sup>

Inspired by the unique structure with predesigned adsorption sites and cavities for the calix[*n*]arene-based MOF nanosheets, a calix[4]arene macrocycle was considered to be incorporated into the backbones of MOF nanosheets. Besides, the borderline acid of Pb<sup>2+</sup> was likely to bind to the oxygen-containing functional groups, according to the hard–soft acid–base (HSAB) theory.<sup>43</sup> Thus, the pro-ligand 25,26,27,28-tetrakis [(carboxyl)methoxy]calix[4]arene (H<sub>4</sub>L; Scheme S1†) locked in

the cone conformation was elaborately selected for the construction of 2D MOF nanosheets. In the design, there are four carboxyl groups decorated on the lower rims of H<sub>4</sub>L, some of which can coordinate with metal ions for MOF construction, and the left ones can serve as catchers for Pb<sup>2+</sup>; there is no functional group decorated on the upper rims of H<sub>4</sub>L, which would be facile for the formation of the layered structure (Scheme 1). Herein, a layered MOF, {[Cu<sub>1.5</sub>(HL)(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O}<sub>*n*</sub> (Cu-MOF), was synthesized by the solvothermal reaction of CuCl<sub>2</sub>·2H<sub>2</sub>O with the pro-ligand H<sub>4</sub>L, which can be readily delaminated into 2D MOF nanosheets *via* a simple ultrasound method (Scheme 1). The extensively accessible and uncoordinated oxygen-containing functional groups (carboxyl and ether groups) in the cage-like cavities acted as adsorption sites, and the cavities loaded on MOF nanosheets served as pollutant containers. The intimate contact and sufficient interactions with Pb<sup>2+</sup> on the exposed surface areas of MOF nanosheets not only achieved highly efficient capture, greatly enhancing Pb<sup>2+</sup> uptake capacity (738.65 mg g<sup>−1</sup>), but also resulted in ultra-high adsorption selectivity and anti-interference ability.

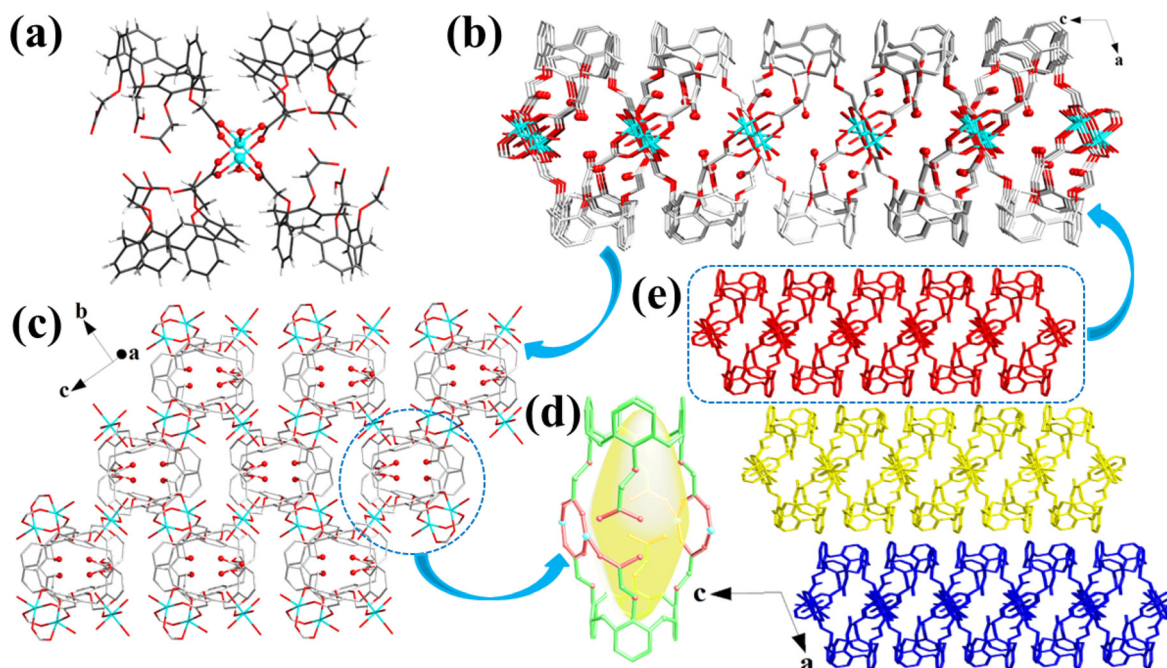
## Results and discussion

### Characterization of Cu-MOFs

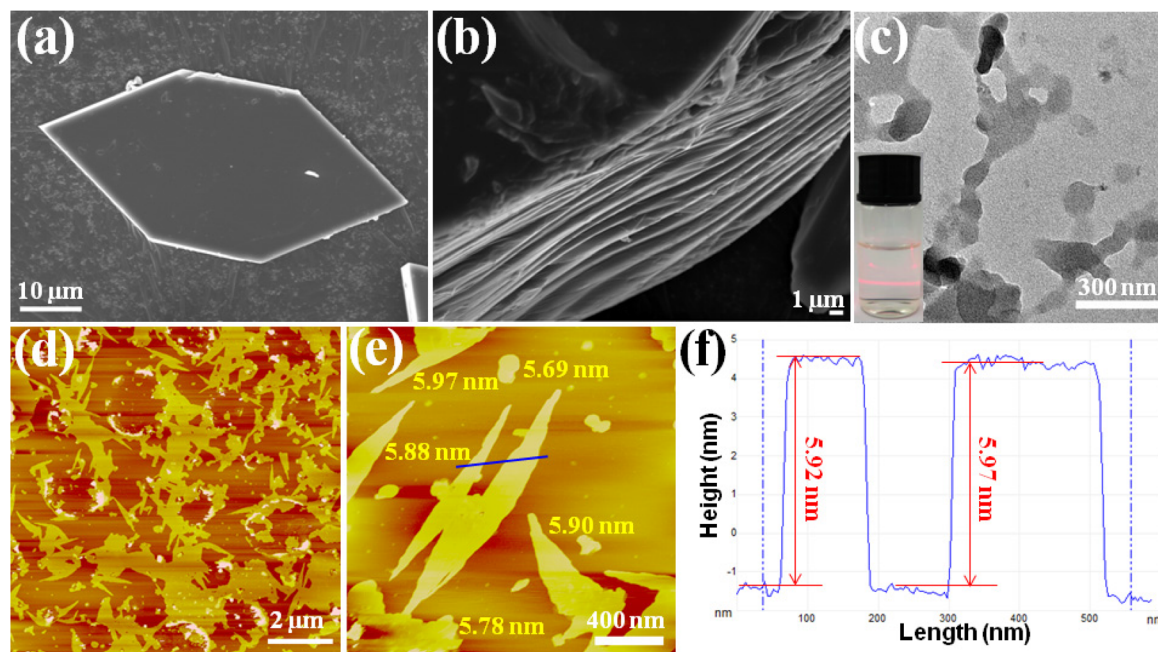
Cu-MOFs crystallized in a monoclinic space group *C2/c*. Two Cu(H<sub>2</sub>O) subunits are linked by four carboxylate groups, affording a [Cu<sub>2</sub>(HL)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] secondary building unit (Fig. 1a). These secondary building units are interconnected by their equivalent ones to construct a 2D structure (Fig. 1b). Notably, the unique cup-shaped feature and large molecular skeleton of the calix[4]arene enabled the as-constructed 2D layers to be loosely packed, yielding a 3D motif with a layered stacking structure (Fig. 1e), which was confirmed by scanning electron microscopy (SEM; Fig. 2b). Moreover, the view of the 3D structure presented a large layer spacing between the layers in Cu-



**Scheme 1** Schematic illustration of the construction of 2D MOF nanosheets with cavity structures for pollutant removal.



**Fig. 1** (a) View of the  $[\text{Cu}_2(\text{HL})_4(\text{H}_2\text{O})_2]$  secondary building unit in Cu-MOFs. Color codes: cyan, Cu; red, O; gray, C; light gray, H. (b and c) View of the 2D structures in Cu-MOFs. (d) Cage-like cavity in Cu-MOFs. (e) 3D motif in Cu-MOFs.



**Fig. 2** (a) SEM image of the hexagonal Cu-MOF. (b) SEM image of the cross-section of the Cu-MOF. (c) TEM image of Cu-MOF nanosheets; inset: photograph of the Tyndall effect of Cu-MOF nanosheet suspension. (d and e) AFM images of Cu-MOF nanosheets. (f) Height profile, color-coded blue, is measured along the corresponding track shown in (e).

MOFs (Fig. 1e), indicating a weak interlayer interaction in the layers. The large layer spacing would be facile for the insertion of solvent molecules into the interlayers and further destroy the interlayer interactions in bulk MOFs, causing the exfoliation more convenient. Interestingly, the cage-like cavities were

formed in the 2D layers of Cu-MOFs (Fig. 1d), which were decorated with uncoordinated carboxyl ( $-\text{COOH}$ ) and ether ( $-\text{O}-$ ) groups in them; these uncoordinated oxygen-containing groups can be utilized for  $\text{Pb}^{2+}$  capture and the cavities acted as containers to accommodate the adsorbed  $\text{Pb}^{2+}$ . Based on



these observations, the calix[4]arene is an ideal building block for the construction of 2D MOF nanosheets with cage-like cavities, which not only facilitate MOF exfoliation and pollutant capture but also prevent the adsorbate from desorption. The water stability of **Cu-MOFs** was verified by powder X-ray diffraction (PXRD) measurements, and the PXRD patterns kept almost the same as those of the experimental sample (Fig. S1†) after soaking in a range of solutions (pH 3.0–11.0) for 24 h.

### Exfoliation of Cu-MOF nanosheets

Top-down exfoliation is regarded as an efficient method to prepare MOF nanosheets, by using an external force to disintegrate the interlayer interaction of layered MOFs. The unique layered structure provides convenience for **Cu-MOFs** to achieve ultrathin nanosheets, and a simple and convenient ultrasound-induced liquid phase exfoliation method was selected. The hexagonal **Cu-MOF** (Fig. 2a) was dispersed in a MeOH/isopropanol (4 : 1, V/V) solution, under continuous sonication in an ice-water bath for 6 h. After that, the content of  $\text{Cu}^{2+}$  in the solution was analyzed, and no  $\text{Cu}^{2+}$  was detected. The result indicated that there was no **Cu-MOF** degradation in the exfoliation. The obtained milky colloidal suspension with significant Tyndall effects (inset in Fig. 2c) is indicative of the achievement of the ultrathin nanosheets. The detailed morphology of the nanosheets was examined by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The TEM image (Fig. 2c), which displayed a flaky sheet-like morphology, further confirmed the achievement of the ultrathin MOF nanosheets. The AFM images displayed in Fig. 2d–2e show flat layers with lateral dimensions in the micrometer range, and they were measured to be  $5.8 \pm 0.1$  nm in height (Fig. 2f). The single layer thickness of the 2D MOF nanosheets was calculated to be 1.88 nm based on single-crystal X-ray structure determination, implying that there are approximately 3 layers in total for the obtained 2D MOF nanosheets.

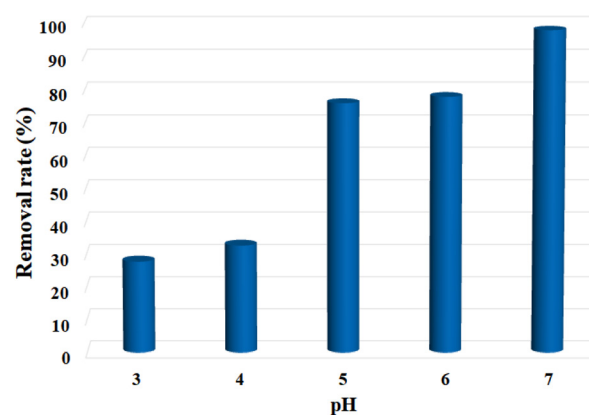
After exfoliation, the structural integrity of the 2D MOF nanosheets remained as anticipated, which was confirmed by a series of measurements. As shown in Fig. S2,† the PXRD patterns of the derived 2D nanosheets matched those of the bulk MOF, and the exfoliation into the extremely thin nanosheets is the reason for the decrease in the strength of these distinctive peaks.<sup>44,45</sup> Fourier transform infrared (FT-IR) spectra (Fig. S3†) and thermogravimetric analysis (TGA) curves (Fig. S4†) provided additional evidence for the structural integrity of the nanosheets. The peaks in the FT-IR spectrum of the MOF nanosheets were in good agreement with those of the bulk **Cu-MOF** samples (Fig. S3†), and no obvious difference was observed in the TGA curves between the two samples (Fig. S4†). The synthesized 2D MOF nanosheet not only retained the structural integrity but also held high water stability. After soaking in an aqueous solution (pH 2.0–7.0) for 12 h, it could keep the same patterns as those of the original sample (Fig. S5†). The aforementioned findings demonstrated that the few-layer MOF nanosheets were successfully synthesized with high structural integrity and water stability *via* a straightforward ultrasonic approach. In addition, the unique

backbone of the calix[4]arene can be responsible for the facile exfoliation and high structural integrity of the MOF nanosheets.

### Pb<sup>2+</sup> adsorption studies

In view of the unique structure and fair water stability of the **Cu-MOF** nanosheets, the  $\text{Pb}^{2+}$  adsorption performance was studied. First, the effect of solution pH was investigated, since the pH value strongly affects the adsorption performance of heavy metal ions. As shown in Fig. 3, the  $\text{Pb}^{2+}$  removal rate was low at pH 3.0, and it presented a drastic increase with the increase in pH, reaching the highest signal at pH 7.0. When the pH exceeds 7.0,  $\text{Pb}^{2+}$  hydroxide precipitation may occur. As a result, the optimal pH of 7.0 was chosen for the subsequent sorption experiments. Second, the effect of adsorbent dosage on  $\text{Pb}^{2+}$  adsorption was investigated, which is essential to attain high removal efficiency. The  $\text{Pb}^{2+}$  removal ratios were assessed by adding the adsorbents at different dosages (40, 60, 100, 140, 180, and 220 mg L<sup>-1</sup>) into a certain  $\text{Pb}^{2+}$  solution (10 ppm). As shown in Fig. S6,† the  $\text{Pb}^{2+}$  removal rate increased with the growing adsorbent dosage, and it went up to 98.11% at 100 mg L<sup>-1</sup>. The further increase in adsorbent dosages to 140, 180, and 220 mg L<sup>-1</sup> resulted in almost equal removal rates to that of 100 mg L<sup>-1</sup>. In consideration of the removal performances and adsorption cost, the adsorbent dosage of 100 mg L<sup>-1</sup> (5 mg/50 mL) was selected for the following investigations.

The maximum uptake capacity, a crucial factor in determining an adsorbent's effectiveness and applicability in a wastewater disposal system, was evaluated by the investigation of adsorption isotherms. The value of  $q_e$  (equilibrium adsorption capacity), as presented in Fig. 4, increased with the increase in  $\text{Pb}^{2+}$  concentrations until it eventually reached its maximum value of 738.65 mg g<sup>-1</sup>. Fig. S7† displays the plots for the relevant data fitted by the Langmuir and Freundlich models. According to the correlation coefficients shown in Table S1,† the Langmuir model ( $R^2 = 0.999$ ) better fits the data, demonstrating that  $\text{Pb}^{2+}$  adsorption on MOF nanosheets was primar-



**Fig. 3** pH effect on the removal efficiency of  $\text{Pb}^{2+}$  by MOF nanosheets.  $C_0 = 10$  ppm,  $m_{\text{adsorbent}} = 5$  mg,  $V = 50$  mL, pH = 3.0–7.0.



Fig. 4  $Pb^{2+}$  adsorption isotherm for MOF nanosheets.

ily a monolayer adsorption behavior. The maximum uptake capacity was determined to be  $746.26 \text{ mg g}^{-1}$ . The estimated  $Pb^{2+}$  uptake capacity matched the experimental data well ( $738.65 \text{ mg g}^{-1}$ ), which was higher than that of the majority of  $Pb^{2+}$  adsorbents (Fig. 5 and Table S2†).

An adsorbent's reusability and stability are essential for the sustainable use of resources. To examine the repeatability of MOF nanosheets, the  $Pb^{2+}$ -loaded samples were submerged in  $0.1 \text{ mmol L}^{-1} \text{ HNO}_3$  for desorption. The cycle performance shown in Fig. S8† demonstrates that MOF nanosheets hold a good regeneration ability. The  $Pb^{2+}$  removal rate decreased slightly with the increase in cycle number, and it could hold a removal rate of more than 84% even after five cycles. The minor reduction in  $Pb^{2+}$  adsorption capacity may be caused by the combined factors including insufficient desorption, trace amounts of the adsorbent loss and sample degradation. Moreover, the PXRD patterns of the regenerated MOF

nanosheets matched those of the 2D MOF nanosheets (Fig. S9†), which are completely different from those of the calix[4]arene pro-ligand, confirming the stability of the 2D adsorbents. The stability was further supported by the FT-IR analysis, in which no obvious spectral change was observed after adsorbent regeneration (Fig. 8). These results revealed that the 2D MOF nanosheet retained its framework structure after the adsorption–desorption cycles.

For an adsorbent, poor selectivity would not only result in the binding of advantageous light elements, lowering their levels in the water, but also foul adsorbents, limiting their capacities to remove target pollutants. Thus, high selectivity is crucial for the practical use of an adsorbent, and it is of great necessity to explore the selective adsorption performance of Cu-MOF nanosheets. The adsorbents were added into aqueous solutions with different single metal ions (10 ppm) of  $Pb^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Sr^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ , and  $Ba^{2+}$ , respectively. After reaching adsorption equilibrium, the removal efficiency for each ion was assessed. The result shown in Fig. 6

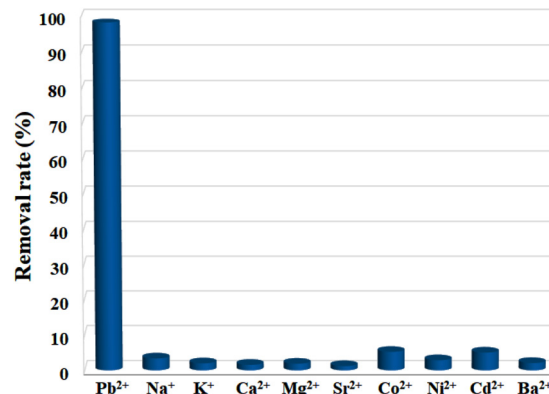


Fig. 6 Selective adsorption of MOF nanosheets for different metal ions.

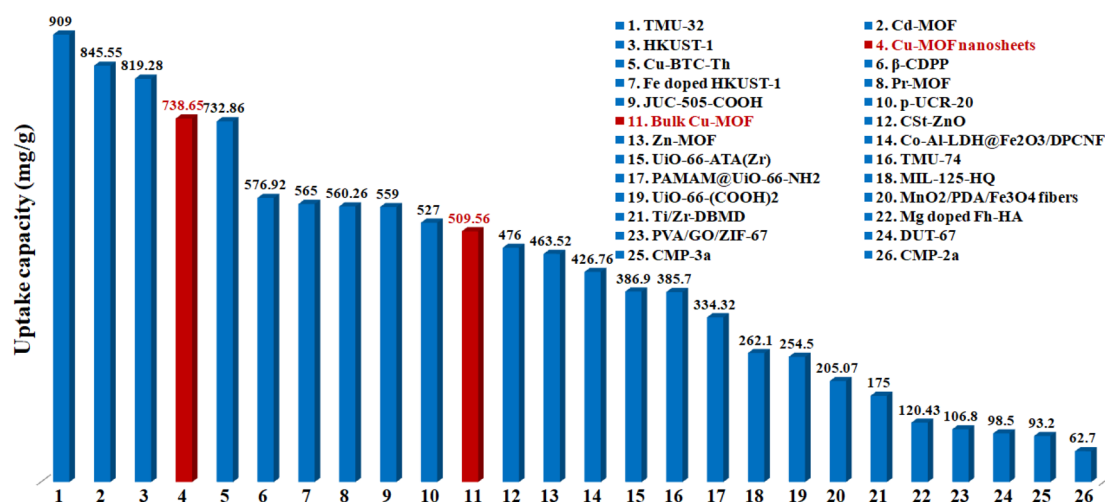


Fig. 5 Comparison of the maximum  $Pb^{2+}$  adsorption capacity for MOF nanosheets (no. 4) and bulk Cu-MOFs (no. 11) with various adsorbents (Table S2†).

demonstrates that  $\text{Pb}^{2+}$  has a substantially higher removal efficiency than that of other ions under the same condition. The removal efficiency for  $\text{Pb}^{2+}$  was 98.11%, while for other metal ions, the removal efficiencies were less than 5.08%. Thus, **Cu-MOF** nanosheets hold high selectivity for  $\text{Pb}^{2+}$ .

Coexisting ions are ubiquitous in aquatic systems, which might pose an effect on  $\text{Pb}^{2+}$  removal. It is highly desirable to assess the anti-interference performance of MOF nanosheets. The 2D nanosheets were added into a mixed solution containing  $\text{Pb}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ba}^{2+}$ , with a concentration of 10 ppm for each ion. After reaching adsorption equilibrium, 97.47% of  $\text{Pb}^{2+}$  was removed from the mixture (Table 1). The distribution coefficient  $K_d$  ( $\text{mL g}^{-1}$ ) was calculated to assess the MOF nanosheets' affinities for  $\text{Pb}^{2+}$  in the presence of mixed ions,<sup>46</sup> and the  $K_d$  value was calculated to be  $3.84 \times 10^5 \text{ mL g}^{-1}$  (Table 1). By comparison with the  $K_d$  value for  $\text{Pb}^{2+}$  in a solution (10 ppm) without any competing ions ( $5.20 \times 10^5 \text{ mL g}^{-1}$ ), an ultra-high anti-interference ability toward interfering ions was obtained for **Cu-MOF** nanosheets. In daily life, the concentrations of some coexisting ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  in drinking water were significantly higher than that of  $\text{Pb}^{2+}$ , thus it is imperative to explore  $\text{Pb}^{2+}$  adsorption behavior in the presence of other excess metal ions. The metal ions including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ba}^{2+}$  at a concentration of 50 ppm were separately added into the certain  $\text{Pb}^{2+}$  solution (10 ppm). After achieving adsorption balance, the  $\text{Pb}^{2+}$  removal performances were evaluated, respectively. As shown in Fig. 7, with high concentrations of different competing ions, the removal efficiencies for  $\text{Pb}^{2+}$  were no less than 88.17%. Encouraged by the good anti-interference performance of MOF nanosheets, the  $\text{Pb}^{2+}$  (10 ppm) removal performance was further evaluated in the presence of highly concentrated mixed ions. As presented in Table 1, even in the presence of 50 ppm (five times) of mixed competing ions, the removal ratio for  $\text{Pb}^{2+}$  can reach up to 86.71%, together with an excellent  $K_d$  value.

The above-mentioned results of selectivity and anti-interference experiments indicated the strong affinity of **Cu-MOF** nanosheets toward  $\text{Pb}^{2+}$  and ultrahigh anti-interference ability toward interfering ions, which can be ascribed to the following reasons. On the one hand, the numerous carboxyl and ether groups decorated on MOF nanosheets have the characteristics of a borderline base, making it easy to interact with the borderline acids of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$ , and soft acid of  $\text{Cd}^{2+}$  but challenging with the hard acids of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,

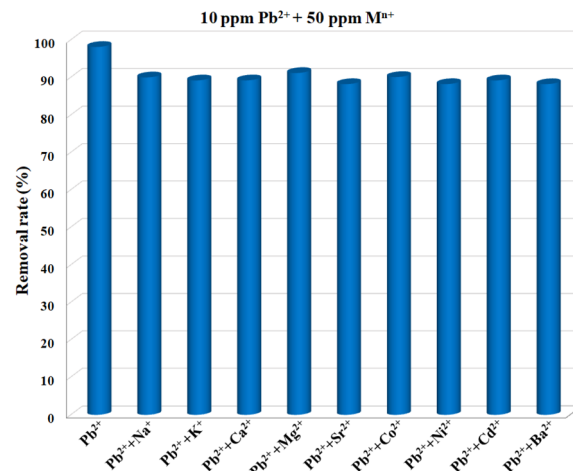


Fig. 7 Effect of the coexistent ions (50 ppm) on  $\text{Pb}^{2+}$  (10 ppm) removal by MOF nanosheets.

and  $\text{Ba}^{2+}$ .<sup>43</sup> The obtained low removal performance for  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  shown in Fig. 6 could be attributed to their much higher hydration energies ( $1915 \text{ kJ mol}^{-1}$  for  $\text{Co}^{2+}$ ,  $1980 \text{ kJ mol}^{-1}$  for  $\text{Ni}^{2+}$ , and  $1755 \text{ kJ mol}^{-1}$  for  $\text{Cd}^{2+}$ ) as compared to the obviously lower hydration energy for  $\text{Pb}^{2+}$  ( $1425 \text{ kJ mol}^{-1}$ ).<sup>47</sup> On the other hand, the larger ionic radius of  $\text{Pb}^{2+}$  ( $0.119 \text{ nm}$  for  $\text{Pb}^{2+}$ ,  $0.069 \text{ nm}$  for  $\text{Ni}^{2+}$ ,  $0.075 \text{ nm}$  for  $\text{Co}^{2+}$ , and  $0.095 \text{ nm}$  for  $\text{Cd}^{2+}$ ) could be allowed for more convenient interaction with the functional groups on the adsorbents.<sup>48</sup> Moreover, the close contact and sufficient interactions on the exposed surface area would well enhance the adsorption selectivity of the **Cu-MOF** nanosheets, affording ultrahigh selectivity.

### Mechanism studies

To further understand the selective adsorption behavior of **Cu-MOF** nanosheets, the possible adsorption mechanism was investigated by a combination of techniques including zeta potential, FT-IR spectroscopy, and X-ray photoelectron spectroscopy (XPS). After  $\text{Pb}^{2+}$  adsorption, the zeta potential of the nanosheets changed from  $-31.88 \text{ mV}$  to  $-4.95 \text{ mV}$  (Fig. S10†), which is direct evidence for electrostatic adsorption. To further corroborate the electrostatic interaction in  $\text{Pb}^{2+}$  adsorption, the zeta potential of MOF nanosheets was examined at various pH levels. As shown in Fig. S11a,† the potential of MOF nanosheets rapidly declined as the solution pH increased. The result is understandable since the adsorption sites were protonated and covered with  $\text{H}^+$  at lower pH, affording higher potentials; when the solution pH increased, the deprotonation of the adsorbents led to a lower potential for the MOF nanosheets. Nevertheless, the removal rate of  $\text{Pb}^{2+}$  followed an opposite trend, increasing dramatically as the solution pH rose (Fig. S11b†). Thus, the lower potential is beneficial for positively charged  $\text{Pb}^{2+}$  adsorption. The above-mentioned results indicated that the electrostatic interaction played a crucial role in  $\text{Pb}^{2+}$  adsorption. While at  $\text{pH} = 3.0$ , the MOF nanosheets

Table 1 Selective adsorption parameters of MOF nanosheets toward  $\text{Pb}^{2+}$

Metal ions	$C_0$ (ppm)	$\text{Pb}^{2+}$ removal rate (%)	$K_d$ ( $\text{mL g}^{-1}$ )
$\text{Pb}^{2+}/\text{M}^{n+}$	10/0	98.11	$5.20 \times 10^5$
$\text{Pb}^{2+}/\text{M}^{n+}$	10/10	97.47	$3.84 \times 10^5$
$\text{Pb}^{2+}/\text{M}^{n+}$	10/50	86.71	$6.52 \times 10^4$

$\text{M}^{n+}$  represent the mixed competition ions of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ba}^{2+}$

exhibited a removal rate of 27.94% for  $\text{Pb}^{2+}$  (Fig. S11b†), which revealed the presence of other interactions in  $\text{Pb}^{2+}$  adsorption.

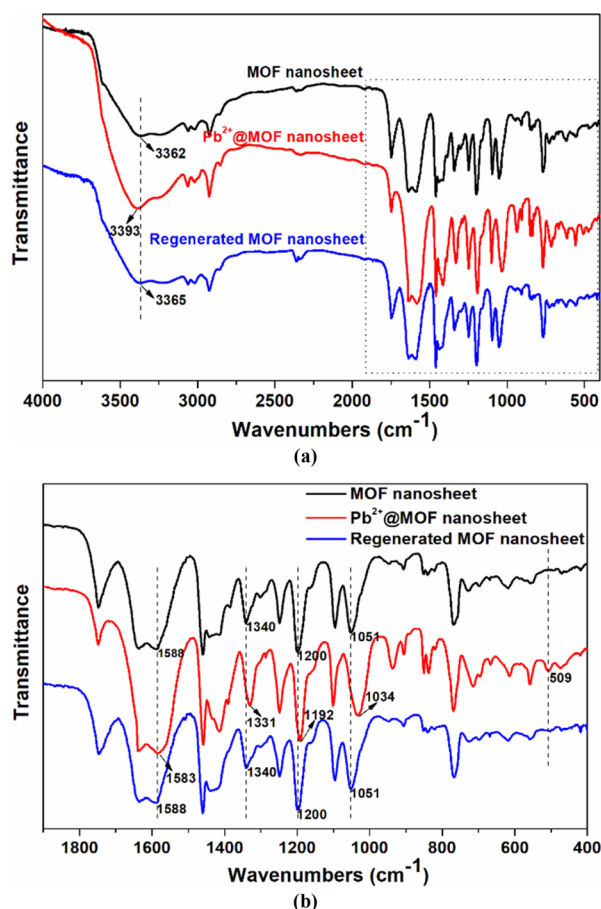
Then, a new question arose: what force, besides electrostatic attraction, is responsible for  $\text{Pb}^{2+}$  adsorption? For the answer, measurements of FT-IR and XPS spectra were conducted. In Fig. 8b, a new peak appeared at  $509\text{ cm}^{-1}$  after  $\text{Pb}^{2+}$  adsorption, assigned to the stretching vibration of the Pb–O bond, which vanished after  $\text{Pb}^{2+}$  desorption, providing direct evidence for the coordination interactions between  $\text{Pb}^{2+}$  and O atoms. The peak shifts of the asymmetric and symmetric vibration of the aromatic ethers ( $=\text{C}-\text{O}-\text{C}-$ ), from  $1200$  and  $1051\text{ cm}^{-1}$  to  $1192$  and  $1034\text{ cm}^{-1}$  after  $\text{Pb}^{2+}$  adsorption, proved the interactions between  $\text{Pb}^{2+}$  and ether groups. Moreover, the peaks at  $3362$ ,  $1588$ , and  $1340\text{ cm}^{-1}$  are attributed to the carboxyl ( $-\text{COOH}$ ) vibration in MOF nanosheets, which shifted to  $3393$ ,  $1583$ , and  $1331\text{ cm}^{-1}$  after  $\text{Pb}^{2+}$  adsorption, demonstrating the coordination between carboxyl groups and  $\text{Pb}^{2+}$ .

The interactions between MOF nanosheets and  $\text{Pb}^{2+}$  were further investigated by XPS studies. The new peaks of Pb 4f, Pb 4d, and Pb 4p that emerged following  $\text{Pb}^{2+}$  adsorption provided more evidence for  $\text{Pb}^{2+}$  adsorption onto MOF

nanosheets (Fig. S12a†). The high-resolution XPS of Pb 4f gave detailed information on Pb species. As shown in Fig. S12b,† two peaks centered at  $143.3\text{ eV}$  and  $138.4\text{ eV}$  were attributed to Pb  $4f_{5/2}$  and Pb  $4f_{7/2}$ , which showed a remarkable shift of  $1.0\text{ eV}$  to a lower binding energy, by comparison with  $\text{Pb}^{2+}$  binding energies of purified  $\text{Pb}(\text{NO}_3)_2$  located at  $144.5\text{ eV}$  (Pb  $4f_{5/2}$ ) and  $139.6\text{ eV}$  (Pb  $4f_{7/2}$ ).<sup>49</sup> The notable peak shift demonstrated a strong affinity between  $\text{Pb}^{2+}$  and MOF nanosheets.<sup>50</sup> The energy separation of  $4.9\text{ eV}$  between the peaks of Pb  $4f_{5/2}$  ( $143.5\text{ eV}$ ) and Pb  $4f_{7/2}$  ( $138.6\text{ eV}$ ) further supported the notion that coordination interaction, not merely the electrostatic contact, accounted for  $\text{Pb}^{2+}$  adsorption.<sup>51,52</sup> These findings are coincident with zeta potential studies and FT-IR analysis, and the strong electrostatic attractions and coordination interactions between  $\text{Pb}^{2+}$  and the carboxyl/ether groups are the key factors affecting  $\text{Pb}^{2+}$  adsorption.

The density functional theory (DFT) calculation was further introduced for the investigation of the adsorption mechanism between the adsorbent and  $\text{Pb}^{2+}$  at the molecular level. Due to the time-consuming nature of the DFT calculation, the structural unit of the cage-like cavity in **Cu-MOF** was selected as a representative theoretical model for calculation. Five models were constructed, in which  $\text{Pb}^{2+}$  was encapsulated in the cage-like cavities. The optimized coordinated geometries for the cage-like building unit, possible interactions, Gibbs free energy ( $\Delta G$ ), and interaction distances (Pb–O) are shown in Fig. 9. In model a,  $\text{Pb}^{2+}$  was interacted with four O atoms from four ether groups and one O atom from a deprotonated carboxyl group (Fig. 9a). Model b shows that  $\text{Pb}^{2+}$  was chelated by four O atoms from ether groups (Fig. 9b). The  $\Delta G$  value of Model b ( $-145.48\text{ kcal mol}^{-1}$ ) is more positive than that of model a ( $-149.23\text{ kcal mol}^{-1}$ ), indicating that the interactions of  $\text{Pb}^{2+}$  with both carboxylate and ether groups in model a are more thermodynamically favorable. For other models (Fig. 9c–e),  $\text{Pb}^{2+}$  was chelated with one carboxylate group in Model c and two carboxylate groups in Model d, and bridged by two carboxylate groups in Model e, respectively. The  $\Delta G$  values ( $-113.36\text{ kcal mol}^{-1}$  for Model c,  $-94.97\text{ kcal mol}^{-1}$  for Model d, and  $-74.94\text{ kcal mol}^{-1}$  for Model e) of these models are much positive than those of model a. These results illustrate that the combined action between carboxylate and ether groups with  $\text{Pb}^{2+}$  is more effective than the interactions of the independent ether or carboxylate group with  $\text{Pb}^{2+}$ , which is consistent with the FT-IR analysis. As a result, the carboxylate and ether groups in the cage-like cavity worked together to capture  $\text{Pb}^{2+}$ . In addition, the average distance of the Pb–O bond in model a ( $2.27\text{ \AA}$ , Fig. 9) is obviously shorter than that in other models ( $2.69\text{ \AA}$  for Model b,  $2.70\text{ \AA}$  for Model c,  $2.63\text{ \AA}$  for Model d and  $2.77\text{ \AA}$  for Model e), which further illustrates that the cooperative interaction of the carboxylate and ether groups has a stronger affinity for  $\text{Pb}^{2+}$ , leading to more efficient extraction of  $\text{Pb}^{2+}$ .

An essential factor in describing the adsorption behavior is the adsorption binding energy. Adsorption happens spontaneously indicated by a negative adsorption binding energy; otherwise, adsorption requires external energy.<sup>53</sup> The smaller



**Fig. 8** Comparison of the FT-IR spectra at  $400\text{--}4000\text{ cm}^{-1}$  (a) and  $400\text{--}1900\text{ cm}^{-1}$  (b) for MOF nanosheets,  $\text{Pb}^{2+}$ @MOF nanosheets, and regenerated MOF nanosheets.





Fig. 9 (a–e) Optimized cage-like cavity in Cu-MOFs through DFT simulation and identification of the possible types of interactions with  $\text{Pb}^{2+}$  during the adsorption process. Color codes: cyan, Cu; brown, Pb; red, O; gray, C; light gray, H.

the value of the adsorption binding energy, the stronger the adsorption binding affinity.<sup>54</sup> The adsorption binding energies for  $\text{Pb}^{2+}$  and various metal ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ba}^{2+}$ , were calculated with the aid of DFT calculations, to clarify the selective adsorption of Cu-MOF nanosheets. The resulting adsorption binding energies, interaction distances and the optimized equilibrium adsorption configurations are shown in Fig. 10. The adsorption binding energy for  $\text{Pb}^{2+}$  was negative, which revealed that  $\text{Pb}^{2+}$  adsorption on Cu-MOF nanosheets was a spontaneous behavior. The negative adsorption binding energy ( $-7.16$  eV) of  $\text{Pb}^{2+}$  is significantly lower than that of other metal ions (Fig. 10), indicating that the cage-like cavity has an obviously higher affinity for  $\text{Pb}^{2+}$ , which is in good agreement with the result of ultra-high  $K_d$  values of  $\text{Pb}^{2+}$  shown in Table 1. Moreover, the obviously shorter interaction distance for the Pb–O bond shown in Fig. 10 further verifies the strong affinity for  $\text{Pb}^{2+}$ .

The above-mentioned results on the experimental and theoretical investigations demonstrated an ultrahigh adsorption selectivity of Cu-MOF nanosheets toward  $\text{Pb}^{2+}$ . As a comparison, the selective adsorption performance of 3D Cu-MOF was investigated. High selectivity can also be achieved for  $\text{Pb}^{2+}$  (Fig. S13†), while it is inferior to that of the MOF nanosheets. For the anti-interference ability of 3D Cu-MOFs, it is obviously lower than that of 2D Cu-MOF nanosheets (Fig. S14 and Table S3†). To better understand the lower selectivity and anti-interference ability for 3D Cu-MOFs, the measurements of zeta potential, FT-IR spectroscopy, and XPS were performed to

investigate the possible adsorption mechanism. Similar results were obtained, which were presented in Fig. S15–S17 in the ESI,† followed by relevant analysis on the adsorption mechanism of 3D Cu-MOFs, revealing a similar adsorption mechanism to that of the 2D MOF nanosheets. Thus, 3D Cu-MOFs with the same framework structure, but different dimensions, as that of its 2D counterpart presented similar adsorption mechanisms but lower adsorption selectivity and anti-interference ability. This result is understandable. For these MOF adsorbents, the strong electrostatic attractions and coordination interactions are the key factors affecting  $\text{Pb}^{2+}$  adsorption. Specifically, before close contact with pollutant molecules, the adsorption driving force is electrostatic attraction, which showed low selectivity; while in close contact with pollutant molecules, the main interaction is the coordination interaction, that is, the adsorption binding energies dominated the adsorption process, which showed high selectivity. For the 2D MOF nanosheets, the exposed surface area provided the adsorption sites with more chance for close contact and sufficient interaction with pollutant molecules, which made the adsorption binding energies greatly contribute to the adsorption process, substantially enhancing the adsorption selectivity of the 2D MOF nanosheets. For the 3D MOF adsorbents, it is difficult for the buried adsorption sites in the frameworks to contact pollutant molecules closely, thus the adsorption driving force, electrostatic attraction, dominated the adsorption for most of the time. As a result, the insufficiently close contact results in lower adsorption selectivity for 3D Cu-MOF.





Fig. 10 DFT calculation models for metal ions of  $\text{Pb}^{2+}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ba}^{2+}$ .

The adsorption isotherms were further investigated to estimate the maximum adsorption capacity of 3D **Cu-MOFs**. As expected, the limited access to the buried adsorption sites in the framework resulted in a lower  $\text{Pb}^{2+}$  adsorption capacity of  $509.56 \text{ mg g}^{-1}$  for 3D **Cu-MOF** (Fig. S18–S19†). These results revealed that well-improved  $\text{Pb}^{2+}$  adsorption performance can be achieved by MOF exfoliation. In contrast to 3D porous adsorbents, the 2D **Cu-MOF** nanosheets not only inherit the structural characteristics of MOFs, such as periodic structures with predesigned adsorption sites, but also overcome the drawbacks of 3D porous materials, such as restricted access to the active sites, which made the adsorption sites fully utilized, affording well-enhanced adsorption performance. Different from the conventional MOF nanosheets, **Cu-MOF** nanosheets were decorated with cavity structures that were beneficial for adsorption, there were predesigned adsorption sites (uncoordinated carboxyl and ether groups) decorated in the cavity structures. The exposed surface area of **Cu-MOF** nanosheets endowed the sites with accessibility for close contact and sufficient interactions with target pollutants, which greatly enhanced the adsorption selectivity and uptake capacity.

## Conclusions

In conclusion, an ultrathin 2D MOF nanosheet with cage-like cavities has been built based on the calix[4]arene for the first time. The as-prepared ultrathin nanosheets, with a thickness of  $5.8 \pm 0.1 \text{ nm}$ , showed extremely selective adsorption performance toward  $\text{Pb}^{2+}$ , even with the existence of highly concentrated competing ions. The adsorption capacity of  $\text{Pb}^{2+}$  can

reach up to  $738.65 \text{ mg g}^{-1}$ , exceeding that of most adsorbents. The adsorption performances of 2D **Cu-MOF** nanosheets, including adsorption selectivity, anti-interference ability, and uptake capacity, are obviously better than those of 3D **Cu-MOFs**, which can be ascribed to the unique structure of the exposed surface area with cavity structures. The calix[4]arene, an ideal building block for the construction of 2D materials with cage-like cavities, not only facilitates the exfoliation of the 3D precursor but also provides the cavity structures and adsorption sites that are beneficial for adsorption. The intimate contact and sufficient interactions between the active sites in the cavities on the exposed surface areas with pollutant molecules could achieve highly efficient capture and ultra-high adsorption selectivity. Our work may provide a perspective for broadening the scope of functionalities on 2D materials in the future, and create many high-performance adsorbents.

## Data availability

All experimental data is available in the ESI.†

## Author contributions

L.-L. Liu and D. Liu conceived and directed the project. C.-X. Yu wrote the manuscript and analyzed the data. H. Sun and K.-Z. Wang performed the experiments and analyzed preliminary results. All the authors discussed the results and gave approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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