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Superselective Removal of Lead from Water by Two-Dimensional MoS<sub>2</sub> Nanosheets and Layer-Stacked Membranes

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1 **Super-selective Removal of Lead from Water by Two-Dimensional**  
2 **MoS<sub>2</sub> Nanosheets and Layer-stacked Membranes**

3  
4 *Research article*

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7  
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## 23 Abstract

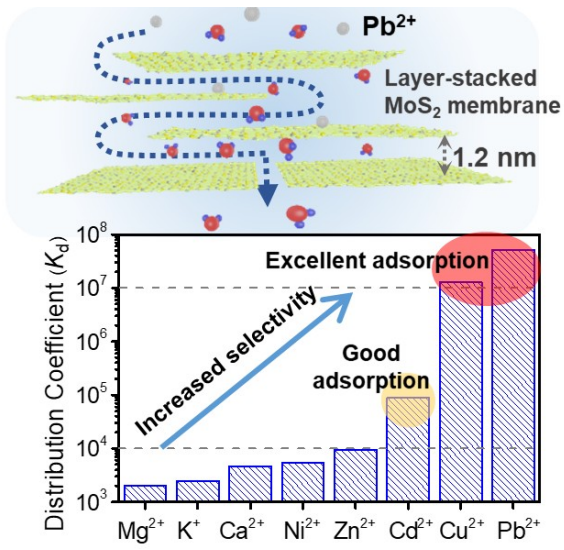
24 Point-of-use (POU) devices with satisfactory lead ( $\text{Pb}^{2+}$ ) removal performance are urgently  
25 needed in response to recent outbreaks of lead contamination in drinking water. This study  
26 experimentally demonstrated the excellent lead removal capability of two-dimensional (2D)  
27  $\text{MoS}_2$  nanosheets in aqueous form and as part of a layer-stacked membrane. Among all materials  
28 ever reported in the literature,  $\text{MoS}_2$  nanosheets exhibit the highest adsorption capacity (740  
29 mg/g), and the strongest selectivity/affinity towards  $\text{Pb}^{2+}$  with a distribution coefficient  $K_d$  that is  
30 orders of magnitude higher than that of other lead adsorption materials ( $5.2 \times 10^7$  mL/g). Density  
31 functional theory (DFT) simulation was performed to complement experimental measurements  
32 and to help understand the adsorption mechanisms. The results confirmed that the cation  
33 selectivity of  $\text{MoS}_2$  follows the order  $\text{Pb}^{2+} > \text{Cu}^{2+} \gg \text{Cd}^{2+} > \text{Zn}^{2+}, \text{Ni}^{2+} > \text{Mg}^{2+}, \text{K}^+, \text{Ca}^{2+}$ . The  
34 membrane formed with layer-stacked  $\text{MoS}_2$  nanosheets exhibited a high water flux (145 L/  
35  $\text{m}^2/\text{h}/\text{bar}$ ), while effectively decreasing  $\text{Pb}^{2+}$  concentration in drinking water from a few mg/L to  
36 less than 10  $\mu\text{g}/\text{L}$ . The removal capacity of the  $\text{MoS}_2$  membrane is a few orders of magnitude  
37 higher than that of other literature-reported membrane filters. Therefore, the layer-stacked  $\text{MoS}_2$   
38 membrane has great potential for POU removal of lead from drinking water.

39

40 KEYWORDS: layer-stacked  $\text{MoS}_2$  membrane; point-of-use device; lead contamination; drinking  
41 water; super-selective adsorption; high adsorption capacity

42

43 **Table of Contents (TOC)**



44

## 45 INTRODUCTION

46 Toxic heavy metal contamination of freshwater and drinking water has become a critical  
47 challenge for human society. Particularly, lead ( $\text{Pb}^{2+}$ ) has been recognized as one of the most toxic  
48 metals worldwide and there have been cases of lead contamination of tap water in various cities  
49 (e.g., Washington, DC; Flint, MI; and Newark, NJ) in the United States. A major source of lead in  
50 drinking water is the lead-containing plumbing in water distribution systems like pipes, solders,  
51 and fittings. As aged lead-containing pipelines are still used, lead concentrations can be on the  
52 order of tens of milligrams per liter in the aftermath of man-made mismanagement or natural  
53 disasters.<sup>1,2</sup> This is several orders of magnitude higher than the U.S. EPA lead action level (15  $\mu\text{g}/$   
54 L) and the WHO guideline value (10  $\mu\text{g}/\text{L}$ ).<sup>3,4</sup> Long-term exposure to lead, even at extremely low  
55 concentrations, increases the blood lead level due to its bio-accumulative nature, causing severe  
56 adverse health effects in the nervous system and brain, particularly in infants and children.<sup>5</sup>

57 To remove lead from drinking water, especially for daily-use in rural areas or for  
58 responding to emergency lead contamination incidents, portable point-of-use (POU) adsorption  
59 technologies are essential because of their flexibility, ease of operation, and cost effectiveness.  
60 Some promising adsorbents targeting heavy metal remediation have been recently identified,  
61 including metal–organic frameworks (MOFs),<sup>6, 7</sup> graphene-based materials,<sup>8</sup> covalent organic  
62 frameworks,<sup>9, 10</sup> layered nanomaterials<sup>11-14</sup>, and natural materials like biochar<sup>15</sup>. However, sorption  
63 materials that have ultrahigh affinity and selectivity to lead are still lacking. High selectivity is  
64 extremely important because one challenge hindering effective removal of lead from drinking  
65 water is the presence of interfering species. In addition, the adsorption materials used in POU  
66 applications should possess attributes such as high porosity, adsorption-site accessibility, and

67 homogeneous binding sites to achieve fast kinetics and high capacity.

68 Two-dimensional (2D) molybdenum disulfide ( $\text{MoS}_2$ ), one of the most widely researched  
69 transition metal dichalcogenides (TMDs), is an ideal adsorbent material for heavy metal  
70 remediation because of its large surface area, and is abundant active sulfur sites that have a high  
71 affinity to heavy metals.<sup>16, 17</sup> Although  $\text{MoS}_2$  is a naturally occurring mineral, the direct use of  
72 bulk  $\text{MoS}_2$  in heavy metal remediation is impossible because the interlayer spacing (0.63 nm) is  
73 so small that targeted heavy metal ions are unable to access the interior sulfur atoms. Synthetic  
74 2D  $\text{MoS}_2$  nanomaterials (*e.g.*, flower-like aggregates) have been explored as adsorbents for toxic  
75 transition metal ( $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ) remediation, showing moderate-to-high adsorption  
76 capacities<sup>18-25</sup>. However, little investigation has been done to quantify the affinity and selectivity  
77 of  $\text{MoS}_2$ -based adsorbents.<sup>26</sup> The surface area of  $\text{MoS}_2$  available for adsorption is also  
78 compromised due to the aggregation of  $\text{MoS}_2$  nanosheets during hydrothermal synthesis. In  
79 contrast, the exfoliated  $\text{MoS}_2$  monolayers possess the highest theoretical surface area. However,  
80 limited work has been done investigating its application as an adsorbent in a POU device for lead  
81 ion removal.

82 To address the above research needs, we systematically studied the adsorption of  $\text{Pb}^{2+}$  by  
83  $\text{MoS}_2$  monolayers and the effects of interfering ions and compared its selectivity and capacity to  
84 that of other heavy metal ions. Batch tests and DFT simulations were used to unveil the  
85 selectivity and adsorption mechanisms of  $\text{MoS}_2$  towards various ions. The layer-stacked  $\text{MoS}_2$   
86 structure with confined and ordered nanochannels was employed as a POU filter, and its  
87 performance and mechanism for removing Pb in continuous filtration was investigated to reveal  
88 the potential in practical applications.

89

## 90 MATERIALS AND METHODS

91 **MoS<sub>2</sub> monolayer and membrane preparation.** To prepare chemically exfoliated monolayer  
92 MoS<sub>2</sub> nanosheets,<sup>27</sup> 5 ml of 1.6 M n-butyllithium in hexane solution was added to ~500 mg of  
93 bulk MoS<sub>2</sub> powder (~ 2 μm, Sigma-Aldrich), and the mixture was kept at room temperature  
94 for 2 d in a nitrogen-filled glovebox with mild stirring. The resulting lithium-intercalated product  
95 was rinsed with hexane to remove organic reactants and by-products. The purified intercalated  
96 product was immediately exfoliated by reaction with DI water in an ultrasonic bath for 1 h. MoS<sub>2</sub>  
97 nanosheets well-dispersed in solution were obtained after dialysis of the dispersion against DI  
98 water to remove inorganic byproduct LiOH. The total MoS<sub>2</sub> concentration was determined  
99 through digestion in 0.2 M HNO<sub>3</sub> and 0.5 M H<sub>2</sub>O<sub>2</sub> solution, followed by measurement of the  
100 soluble Mo species concentration in ICP-OES (Agilent 720, Agilent Technologies, Santa Clara,  
101 CA). Dispersions of chemically exfoliated MoS<sub>2</sub> samples were stored in 4 °C for further use. To  
102 prepare layer-stacked MoS<sub>2</sub> membranes, a dispersion containing 4 mg MoS<sub>2</sub> was filtered through  
103 a polyethersulfone (PES) ultrafiltration membrane with a nominal pore size of 30 nm (Sterlitech,  
104 Kent, WA), generating an MoS<sub>2</sub> membrane with a thickness of ~ 600 nm.

105 **Metal ion adsorption by suspended MoS<sub>2</sub> nanosheets.** Metal cation adsorption by MoS<sub>2</sub>  
106 nanosheets was studied in batch experiments. The metal cations tested include Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>,  
107 Ni<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup> in their nitrate salt forms. After mixing MoS<sub>2</sub> nanosheets (100 mg/  
108 L) with individual cations (~ 5 mg/L) in 10 mL buffer solutions (MES, 10 mM, pH 6) for 1 d,  
109 cation-adsorbed nanosheets were removed through 0.22 μm PES syringe filters (VWR), and the  
110 cation concentrations in the filtrate solutions were determined using ICP-OES or ICP-MS  
111 (Agilent 7700 Series) for low concentration ( ≤ 10 μg/L). The removal is calculated as  $R = 100 \times$

112  $(C_0 - C_f)/C_0$  %, where  $C_0$  and  $C_f$  are the initial and final cation concentrations (mg/L),  
113 respectively. The distribution coefficient is calculated as  $K_d = (V[(C_0 - C_f)/C_f])/m$ , where  $V$  is the  
114 solution volume (mL), and  $m$  is the adsorbent mass (g).

115 To characterize the competitive adsorption of metal cations, batch experiments were  
116 carried out with a mixed solution containing ~5 mg/L of each cation ( $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  
117  $Zn^{2+}$ ,  $Cu^{2+}$  and  $Pb^{2+}$ ) and 100 mg/L  $MoS_2$  nanosheets. A solution mimicking tap water  
118 composition was prepared by spiking DI water with NaCl (280 mg/L),  $CaCl_2$  (150 mg/L) and  
119  $MgSO_4$  (75 mg/L). Batch tests were also used to understand the  $Pb^{2+}$  removal capacity, kinetics,  
120 and selectivity.

121 In order to test the regeneration capability of  $MoS_2$ , we used a strong chelating agent  
122 EDTA, which has a Pb-EDTA<sup>2-</sup> formation constant of approximately  $10^{18}$  to recover Pb from  
123  $MoS_2$ . In each repeated test, 50 mg/L  $Pb^{2+}$  and 100 mg/L  $MoS_2$  was added to 40 mL of pH 6  
124 buffer solution, and the sample was then mixed for 2 h before the solid Pb- $MoS_2$  was collected by  
125 vacuum-filtration onto a PES membrane. To recover the  $MoS_2$ , 40 mL of 5 mM EDTA solution  
126 was added to the collected Pb- $MoS_2$  to allow the release of Pb from  $MoS_2$  for 2 h, then the  
127 regenerated  $MoS_2$  was recollected by vacuum filtration for use in the next cycle.

128 **Pb removal by layer-stacked  $MoS_2$  membranes.** The filtration experiments were performed  
129 using a dead-end stirred cell filtration system (Model 8050, EMD Millipore) with a total internal  
130 volume of 50 mL and an active surface area of 13 cm<sup>2</sup>. The solution in the chamber was  
131 continuously mixed with a suspended magnetic stirrer at 200 rpm. The chamber was filled with  
132 aqueous solution containing  $Pb^{2+}$  at various concentrations (0.25, 1, 3 mg/L), which was  
133 continuously supplied from a stock solution in a plastic container. The filtration experiments



134 were started by applying ~ 10 psi pressure to the chamber by means of compressed N<sub>2</sub>. Ten-mL  
135 samples of the filtrate were periodically collected and analyzed by ICP-MS.

136 **Density functional theory (DFT) simulations.** All simulation results were calculated using DFT  
137 software VASP.<sup>28</sup> The exchange-correlation functional was described using generalized gradient  
138 approximation (GGA) with Perdew-Burke-Ernzerhof (PBE),<sup>29</sup> and the ion-electron interaction  
139 was treated with the projector augmented wave (PAW) method.<sup>30</sup> The cutoff energy was 520 eV  
140 and the energy convergence criterion was 10<sup>-5</sup> eV/cell. The conjugate gradient method was  
141 adopted for the geometry optimization. The Brillouin zone was represented by a  
142 Monkhorst–Pack special k-point mesh<sup>31</sup> of different sizes depending on the MoS<sub>2</sub> size. For all  
143 calculations, the van der Waals (vdW) interaction was included using a dispersion correction term  
144 from the DFT-D3 method.<sup>32</sup> A large vacuum space of 30 Å was used to avoid any interaction of  
145 the MoS<sub>2</sub> sheets with their images. The electron localization function (ELF) calculation was also  
146 performed for detailed data analysis.<sup>33</sup> ELF is derived from the calculation of Pauli repulsion with  
147 values normalized between 0 and 1.<sup>34</sup> Notably, the Hubbard U correction was not added here  
148 since little changes were found for the electronic structure of MoS<sub>2</sub> in previous studies.<sup>35-38</sup>

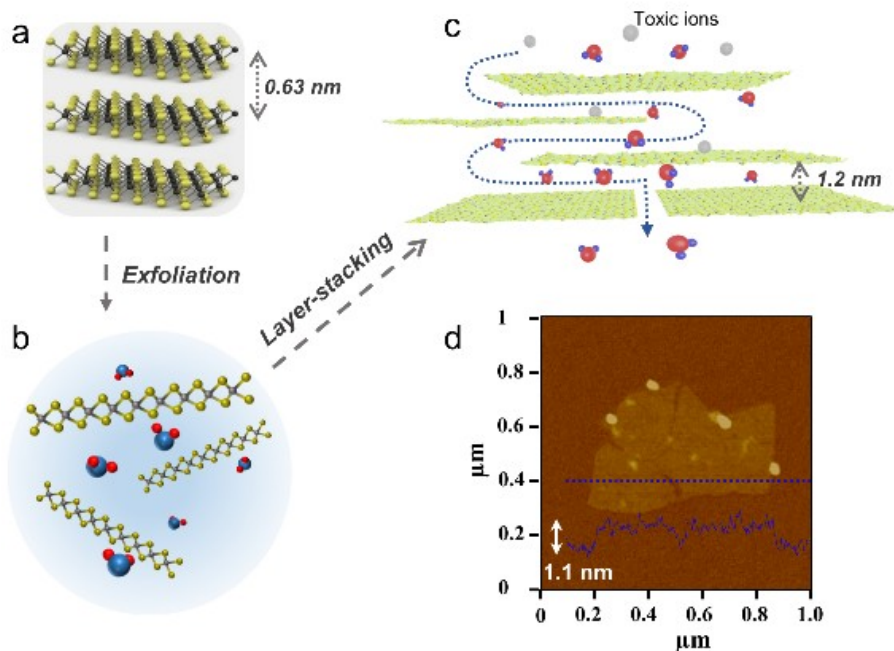
149 **Material and membrane characterization.** MoS<sub>2</sub> nanosheets were characterized through  
150 transmission electron microscopy (TEM), atomic force microscopy (AFM), and X-ray  
151 photoelectron spectroscopy (XPS). TEM images were obtained with a JEM-2100F. The AFM  
152 images were obtained in air using a Bruker Dimension Icon in tapping mode. The XPS  
153 measurement was conducted with a K-Alpha XPS spectrometer (Thermo Scientific Ltd, East  
154 Grinstead, UK). The zeta potential measurement was performed on a Zetasizer Nano-ZSP  
155 analyzer (Malvern, Westborough, MA). Cross-sectional images of a layer-stacked MoS<sub>2</sub> were

156 recorded by a field emission SEM (Zeiss Gemini Ultra-55, Jena, Germany).

157

## 158 **RESULTS AND DISCUSSION**

159 **Synthesis of MoS<sub>2</sub> nanosheets and layer-stacked membranes.** We prepared MoS<sub>2</sub> monolayer  
160 nanosheets from MoS<sub>2</sub> bulk material through chemical exfoliation,<sup>27, 39</sup> engineered them into  
161 layer-stacked membranes, and tested the Pb removal by both configurations of MoS<sub>2</sub> (Figure 1a-  
162 c). The as-prepared MoS<sub>2</sub> nanosheets were highly dispersible in water because of their uniformly  
163 distributed negative charge on the surface (*e.g.*, each MoS<sub>2</sub> unit cell is believed to carry -0.25  
164 eV),<sup>40</sup> as confirmed by a zeta potential of -40 to -50 mV in a wide pH range (Figure S1a).  
165 According to the TEM (Figure S1b) and AFM (Figure 1d) images, a majority of the exfoliated  
166 MoS<sub>2</sub> nanosheets had a lateral dimension of 100 to 500 nm and a monolayer thickness of ~1.1  
167 nm. The phase composition of MoS<sub>2</sub> nanosheets characterized by XPS (Figure S1c-d) consisted  
168 of 40% 2H-MoS<sub>2</sub> and 60% 1T-MoS<sub>2</sub>, which is consistent with the results of exfoliation-induced  
169 phase transformation reported previously.<sup>39</sup> Layer-stacked MoS<sub>2</sub> membranes were fabricated by  
170 filtration leading to a stable interlayer spacing of ~ 1.2 nm, which was naturally formed and  
171 stabilized by a balance between attractive van der Waals and repulsive hydration forces according  
172 to our previous study.<sup>41</sup> In this stacked configuration, MoS<sub>2</sub> membranes maintain an ultrahigh  
173 surface area, exposing all sulfur atoms on each nanosheet as accessible metal-binding sites, and  
174 thus potentially enabling a POU device with continuous water flow as well as high metal  
175 adsorption capacity.



176

177 **Figure 1.** Schematic illustration of exfoliating bulk MoS<sub>2</sub> materials (a) to create an aqueous suspension of  
 178 MoS<sub>2</sub> monolayer nanosheets (b) and reassembling the nanosheets into a layer-stacked MoS<sub>2</sub> membrane (c)  
 179 for adsorptive filtration targeting the removal of toxic ions. (d) The AFM image of a monolayer MoS<sub>2</sub>  
 180 nanosheet with a depth profile revealing a thickness of ~ 1.1 nm.

181

182 **Selectivity of MoS<sub>2</sub> nanosheets towards different cations.** To determine the selectivity of

183 MoS<sub>2</sub> towards different cations, we first evaluated the adsorption of several toxic transition metal

184 cations (Ni<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup>) and some common background cations (Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>)

185 by MoS<sub>2</sub> monolayers in batch experiments (see details in Table S1 and S2). Figure 2a (blue

186 hatched bars) shows the calculated removal of various cations in individual ion tests. MoS<sub>2</sub>

187 nanosheets demonstrated nearly complete removal of Pb<sup>2+</sup> and Cu<sup>2+</sup> by effectively decreasing their

188 concentrations from 5 mg/L, to 4 and 1 μg/L respectively. In comparison, the removal efficiency

189 was relatively high (~ 90%) for Cd<sup>2+</sup>, moderate (30 to 50%) for Zn<sup>2+</sup>, Ni<sup>2+</sup> and Ca<sup>2+</sup>, and very low

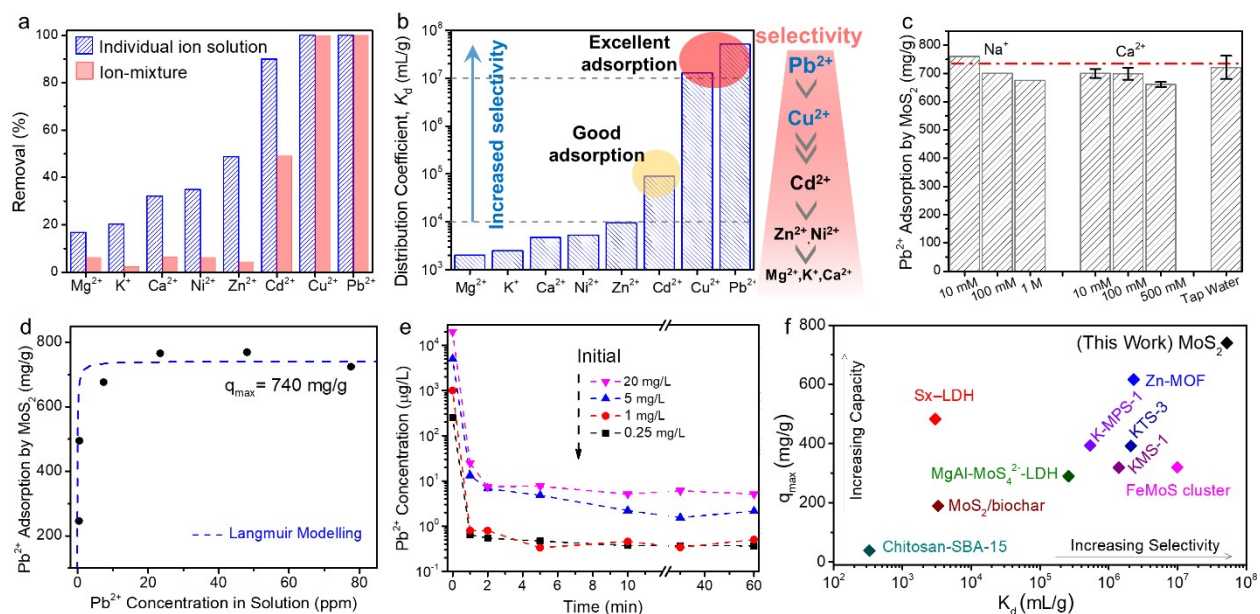
190 (< 20%) for Mg<sup>2+</sup> and K<sup>+</sup>. In addition, the high affinity of MoS<sub>2</sub> nanosheets towards Pb<sup>2+</sup> can be

191 demonstrated by a low threshold concentration (0.1 mM) that induces visible aggregation of

192 MoS<sub>2</sub> nanosheets within half an hour. While for poorly adsorbed ions (e.g., Mg<sup>2+</sup>), a higher  
 193 threshold concentration for aggregation (0.5 mM) was observed (Figure S2).<sup>42</sup>

194 To directly compare the affinity of MoS<sub>2</sub> nanosheets towards different cations in a  
 195 competitive environment, we also conducted the adsorption experiments in an ion mixture  
 196 containing all eight cations of the same concentration (~ 5 mg/L). As shown in Figure 2a (red  
 197 unhatched bars), MoS<sub>2</sub> nanosheets maintained excellent removal of Pb<sup>2+</sup> and Cu<sup>2+</sup> by decreasing  
 198 their concentrations from ~ 5 mg/L to a few micrograms per liter, which was in good agreement  
 199 with those observed in individual ion tests. However, the removal of each of the other cation  
 200 species was much lower than that when tested individually, indicating that the preferred  
 201 adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> significantly decreased the available sorption sites for other ions.

202



203

204 **Figure 2.** Characterization of the selectivity and capacity of Pb<sup>2+</sup> adsorption by suspended MoS<sub>2</sub>  
 205 nanosheets. (a) Removal of various cations by MoS<sub>2</sub> nanosheets in individual ion solutions and in a  
 206 mixture containing all ions of equal concentration (5 mg/L). (b) Distribution coefficients K<sub>d</sub> of various  
 207 cation species. (c) Pb<sup>2+</sup> removal by MoS<sub>2</sub> in the presence of Na<sup>+</sup>, Ca<sup>2+</sup> or tap water impurities. The dashed  
 208 line represents the maximum removal capacity observed in the pure water baseline experiment. (d)  
 209 Isotherm of Pb<sup>2+</sup> adsorption by MoS<sub>2</sub> fitted by Langmuir model (dash line). (e) Kinetics of Pb<sup>2+</sup> adsorption

210 at various initial  $\text{Pb}^{2+}$  concentrations. (f) Comparison of the adsorption capacity ( $q_{max}$ ) and distribution  
211 coefficient ( $K_d$ ) of  $\text{MoS}_2$  nanosheets with those of other benchmark materials reported in the literature.<sup>6, 11,</sup>  
212 <sup>43-55</sup>  
213

214 The affinity of  $\text{MoS}_2$  nanosheets to various cations can be compared by calculating their  
215 distribution coefficients  $K_d$  (Figure 2b). According to the individual cation test results, the  $K_d$   
216 values of  $\text{MoS}_2$  nanosheets for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  are both  $>10^7$  mL/g, which are 2 to 4 orders of  
217 magnitude higher than those for other metal cations, revealing the excellent adsorptive selectivity  
218 of  $\text{MoS}_2$  nanosheets towards  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ . To further reveal the relative affinity of  $\text{MoS}_2$   
219 nanosheets to  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , we conducted competitive tests where the initial concentrations of  
220  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  remained constant at  $\sim 5$  mg/L, but the initial concentrations of  $\text{MoS}_2$  nanosheets  
221 were reduced from 100 mg/L to 30, 15, and 5 mg/L, respectively. As shown in Figure S3 and  
222 Table S3, at lower concentrations (30 and 15 mg/L) of  $\text{MoS}_2$  nanosheets,  $\text{Pb}^{2+}$  removal was still  
223 close to 100%, while the removal of  $\text{Cu}^{2+}$  decreased from 100% to 91.2% and 36.1% respectively.  
224 These results indicate that when  $\text{MoS}_2$  was limited in quantity, its adsorption sites highly  
225 preferred  $\text{Pb}^{2+}$  over  $\text{Cu}^{2+}$ . Only when the concentration of  $\text{MoS}_2$  further decreased to 5 mg/L was  
226 there a slight decline in  $\text{Pb}^{2+}$  removal, whereas  $\text{Cu}^{2+}$  removal was very low (6.1%).

227 Overall, the  $\text{MoS}_2$  monolayer displayed an adsorption affinity in the order  $\text{Pb}^{2+} > \text{Cu}^{2+} \gg$   
228  $\text{Cd}^{2+} > \text{Zn}^{2+}$ ,  $\text{Ni}^{2+} > \text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  (Figure 2b). This is consistent with the hard-soft principle in  
229 Lewis acid-base theory, i.e., the sulfur sites on  $\text{MoS}_2$  offer strong soft-soft interactions towards  
230 soft acids (metal ions such as  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$ ). The high affinity/selectivity towards  $\text{Pb}^{2+}$  over  
231 hard acid species ( $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) reveals the great promise of using  $\text{MoS}_2$  nanosheets in the  
232 development of household POU devices for the removal of lead from drinking water. In addition,  
233 we tested the interference of  $\text{Pb}^{2+}$  adsorption by high concentrations of common cations (e.g.,  $\text{Na}^+$

234 and  $\text{Ca}^{2+}$ ) that are ubiquitous in drinking water. We found that the presence of a high  
235 concentration of these background ions (up to 1 M  $\text{NaNO}_3$ , 1 M  $\text{Ca}(\text{NO}_3)_2$ , or concentrations  
236 characteristic of a tap water mimic, with detailed composition data in the Supporting  
237 Information) did not affect  $\text{Pb}^{2+}$  removal by  $\text{MoS}_2$  (Figure 2c).

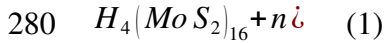
238 The  $\text{Pb}^{2+}$  adsorption capacity and kinetics were further studied to elucidate the removal  
239 mechanism. The adsorption of  $\text{Pb}^{2+}$  onto  $\text{MoS}_2$  monolayers was examined by varying the initial  
240  $\text{Pb}^{2+}$  concentration in the range of 25 to 150 mg/L. As shown in Figure 2d, the adsorption  
241 isotherm data can be better fitted by the Langmuir model than the Freundlich model (Figure S4),  
242 indicating the adsorption of a monolayer  $\text{Pb}^{2+}$  onto the  $\text{MoS}_2$  nanosheet surface. According to the  
243 model,  $\text{MoS}_2$  nanosheets have a maximum adsorption capacity of 740 mg/g toward  $\text{Pb}^{2+}$  (Figure  
244 2d and Figure S5). The  $\text{Pb}^{2+}$  removal also depends on pH conditions (Figure S6). Higher removal  
245 capacity is found at neutral pH ( $\sim 740$  mg/g) than at acidic conditions (e.g.,  $\sim 350$  mg/g at pH 3).  
246 The decrease in  $\text{Pb}^{2+}$  adsorption at lower pH indicates that the  $\text{Pb}^{2+}$  captured by  $\text{MoS}_2$  may be  
247 attributed to the ion exchange with protons on the nanosheets ( $\text{H}_{0.25}\text{MoS}_2$ ),<sup>40</sup> the deprotonation of  
248 which is inhibited by low pH. Similar  $\text{Pb}^{2+}$  adsorption mechanisms and pH effects have been  
249 observed with other functional materials.<sup>43, 55</sup> In this study, pH 6 was adopted to investigate the  
250 fundamental interactions between  $\text{MoS}_2$  and  $\text{Pb}^{2+}$  in order to avoid the interference of possible  
251 hydroxide precipitate at alkaline conditions. Fast removal kinetics (2-3 logs  $\text{Pb}^{2+}$  removal within 2  
252 min, as shown in Figure 2e) was observed regardless of initial  $\text{Pb}^{2+}$  concentration in solution  
253 (0.25 to 20 mg/L). The regeneration of  $\text{MoS}_2$  can be achieved by using strong chelating agents  
254 with a formation constant higher than  $10^{11.4}$  (Figure S7). In our study, EDTA with a formation  
255 constant of  $10^{18}$  was chosen for regeneration. The regeneration of  $\text{MoS}_2$  could maintain a 85-95%  
256 lead removal in 2 to 5 repeated regeneration cycles (Figure S8). The slight reduction in removal

257 efficiency during regeneration was likely caused by the aggregation or partial oxidation of MoS<sub>2</sub>  
258 nanosheets.

259 Overall, the MoS<sub>2</sub> nanosheets studied in this work have superior lead adsorption  
260 capabilities compared with other materials reported so far. As shown in Figure 2f, our exfoliated  
261 MoS<sub>2</sub> nanosheets demonstrate a high Pb<sup>2+</sup> adsorption capacity (740 mg/g) and an extremely high  
262 affinity  $K_d$  ( $5.2 \pm 1.9 \times 10^7$  mL/g), outperforming previously reported materials including MOFs,  
263 layered metal sulfides, and sulfur-functionalized nanomaterials.<sup>6, 11, 43-49</sup> Note that adsorbents with  
264  $K_d$  values in the order of magnitude of  $10^4$  are considered to have outstanding selectivity.<sup>56</sup>  
265 Examples include sulfur-based sorbents such as S<sub>x</sub>- and MoS<sub>4</sub><sup>2-</sup>-intercalated LDH ( $10^3$  to  $2.6 \times 10^5$   
266 mL/g),<sup>11, 46</sup> layered metal sulfides ( $5.4 \times 10^5$  to  $2.1 \times 10^6$  mL/g),<sup>43, 47, 49</sup> MoS<sub>2</sub> hydrogel ( $1.32 \times 10^4$  mL/  
267 g),<sup>50</sup> and others ( $10^3$ - $10^5$  mL/g).<sup>53-55</sup> More details can be found in Table S4. The MoS<sub>2</sub> nanosheets  
268 indeed exhibit the highest  $K_d$  ( $10^7$  mL/g) among all materials to the best of our knowledge,  
269 demonstrating their excellent selectivity toward Pb<sup>2+</sup>.

270 **Investigation of adsorption mechanism.** To further elucidate the adsorption mechanisms, we  
271 used DFT simulation based on first-principle calculations to study the interactions between metal  
272 ions and 2H-MoS<sub>2</sub>. 2H-MoS<sub>2</sub> was chosen for modelling because of its thermodynamic stability  
273 and common presence in nature. As MoS<sub>2</sub> nanosheets are partially reduced during the  
274 intercalation/exfoliation process, they are negatively charged and have a formula of H<sub>0.25</sub>MoS<sub>2</sub> or  
275 MoS<sub>2</sub><sup>-0.25</sup>.<sup>40</sup> According to this formula, we built a 4×4 MoS<sub>2</sub> supercell with 4 hydrogen atoms  
276 evenly distributed on the surface (H<sub>4</sub>(MoS<sub>2</sub>)<sub>16</sub>, Figure S14). Since all reactions take place in  
277 aqueous solution, the ions are present in the hydrated form, and the number of water molecules in  
278 the hydration shell is determined based on literature data.<sup>57</sup> Therefore, the adsorption of a divalent

279 metal ion ( $M^{2+}$ ) onto  $MoS_2$  can be described in equation 1.

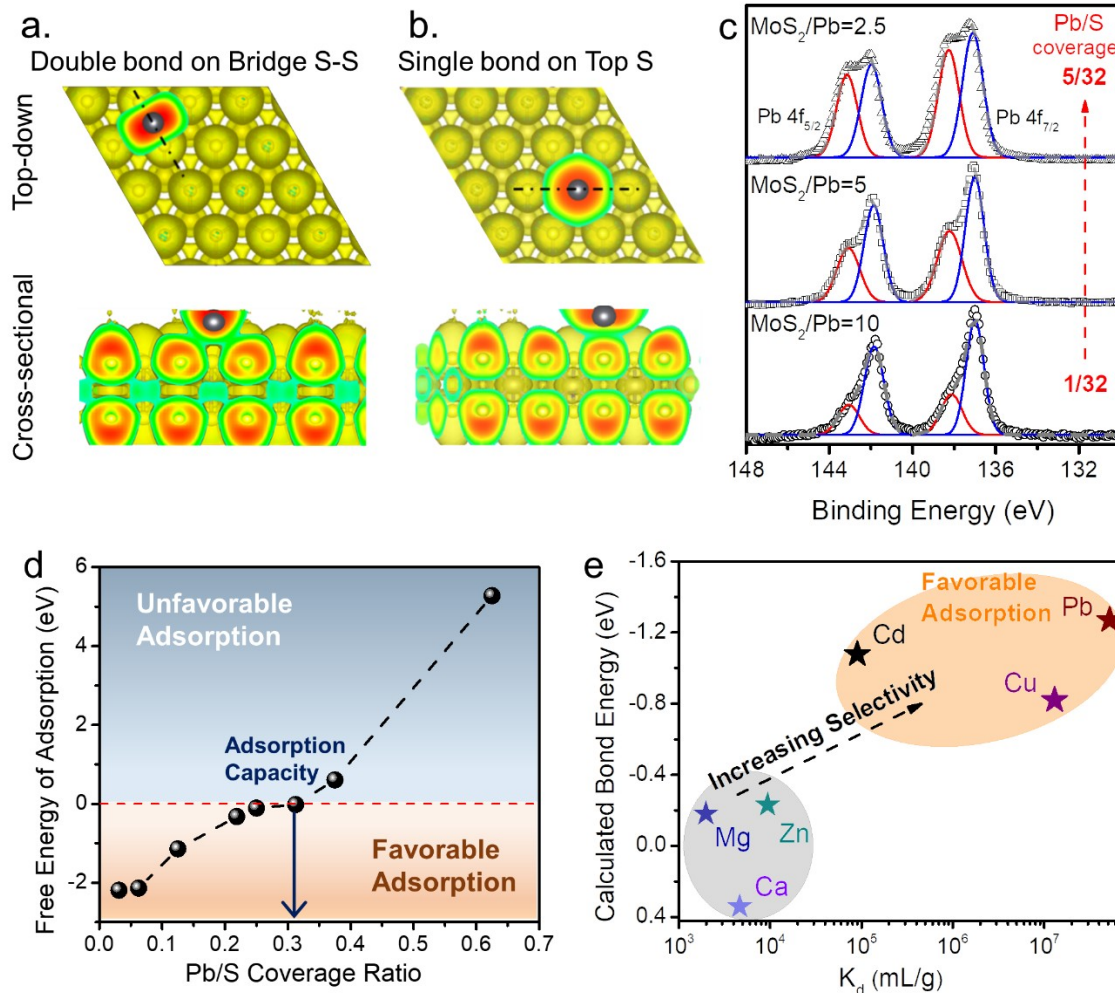


281 where  $n$  varies in the range of 1 to 24 depending on the Pb/S coverage ratio ranging from 1/32 to  
282 3/4. Accordingly, the corresponding free energy of adsorption ( $\Delta G_{f,ads}$ ) is calculated by the  
283 following equation:

284  $\Delta G_{f,ads} = E_{[M_n(MoS_2)_{16}]^{2n-4}} + 4E_{(H_2O)_2} + (n-2)E_{(H_2O)_4} - E_{H_4(MoS_2)_{16}} - nE_{(H_2O)_4} - nE_{M^{2+}}$  (2)

285 where  $E$  represents the internal energy of the corresponding compound, which can be obtained  
286 from the first-principle DFT calculations. A detailed illustration of the adsorption reaction and  
287 the methodology used to calculate the free energy is discussed in the Supporting Information. A  
288 negative free energy  $\Delta G_{f,ads}$  indicates that the adsorption is energetically favorable, and vice versa.  
289





290

291 **Figure 3.** Mechanistic investigation of lead adsorption by DFT simulation and XPS spectra. The top-  
 292 down and cross-sectional views of the electron localization function (ELF, with detailed explanation in  
 293 Supporting Information) for the Pb-MoS<sub>2</sub> double bond formed on a bridge S-S site (a) and a single bond  
 294 formed on a top-S site (b). (c) XPS spectra of Pb peaks with the Pb/S coverage ratio increasing from 1/32  
 295 to 5/32, which correspond to the MoS<sub>2</sub>-Pb mass ratio ranging from 10 to 2.5 (see SI for calculation  
 296 process). The peaks at higher (red) and lower (blue) binding energies are most likely attributed to single  
 297 bonds on the top-S and double bonds on the bridge S-S sites, respectively. (d) The free energy of Pb<sup>2+</sup>  
 298 adsorption on MoS<sub>2</sub> surface as a function of Pb/S coverage ratio. (e) The maximum bond energy for the  
 299 binding between cations and MoS<sub>2</sub>.

300 The binding mechanisms between Pb<sup>2+</sup> and MoS<sub>2</sub> nanosheets are affected by the Pb/S  
 301 coverage ratio. The most stable (energetically favorable) binding site on MoS<sub>2</sub> is the Bridge S-S  
 302 site (Figure 3a), where a Pb<sup>2+</sup> binds to two neighboring S-atoms with an equal bond length of ~  
 303 2.7 Å. However, when the Pb/S coverage ratio increases, the dominating binding site shifts to the

304 Top-S site, where a  $\text{Pb}^{2+}$  binds to only one S atom with a bond length of  $\sim 2.5 \text{ \AA}$  (Figure 3b). The  
305  $\text{Pb-MoS}_2$  double bond formed at the Bridge S-S position (binding energy of  $-1.3 \text{ eV}$ ) is stronger  
306 than the single bond at the Top-S position (binding energy of  $-1.0 \text{ eV}$ ). A more detailed  
307 description of the binding mechanism, formation energy, bond length, geometry, and effects of  
308 Pb-S coverage can be found in Tables S5 and S6, Figures S19 to S22. The simulation results are  
309 correlated with the deconvolution of Pb 4f peaks in the XPS spectra at different Pb/S coverage  
310 ratios. As shown in Figure 3c, when the Pb/S coverage ratio increases from 1/32 to 5/32 (i.e., the  
311  $\text{MoS}_2/\text{Pb}$  mass ratio decreases from 10 to 2.5), the component peak at higher binding energy (red  
312 line) increases in strength, corresponding to more single bonds on Top-S sites, while the  
313 component peak at lower binding energy (blue line) becomes weaker, corresponding to less  
314 double bonds on the Bridge-S-S sites. The XPS results are consistent with the simulation results.

315 The overall free energy ( $\Delta G_{\text{f,ads}}$ ) for Pb adsorption onto  $\text{MoS}_2$  is strongly affected by the  
316 Pb/S coverage (Figure 3d). The free energy of adsorption increases with increasing Pb/S coverage  
317 ratio, indicating that the adsorption of Pb becomes weaker when more Pb is adsorbed onto  $\text{MoS}_2$   
318 surfaces. The free energy becomes positive when Pb/S coverage is over 0.31, demonstrating that  
319 the adsorption of more Pb beyond the 31% coverage is energetically unfavorable. The 31%  
320 coverage amounts to an adsorption capacity of 802 mg/g, which is very close to our experimental  
321 results (740 mg/g).

322 To understand the stronger selectivity towards  $\text{Pb}^{2+}$  than towards other cations, the binding  
323 energy for other cations were also calculated using the DFT model. The favorable binding  
324 mechanism for each metal species is shown in Table S7. It was found that for almost all divalent  
325 cations except  $\text{Ca}^{2+}$ , the most stable (energetically favorable) binding mechanism is the double

326 bond formed at Bridge S-S sites. The binding of  $\text{Ca}^{2+}$  is unique because the bonds on all binding  
327 sites exhibit a positive formation energy, indicating unfavorable adsorption. The formation energy  
328 of the most favorable binding of each cation on the  $\text{MoS}_2$  nanosheet is correlated with the  
329 experimentally measured  $K_d$  values in Figure 3e. In general, a negative formation energy of  
330 around -1 eV (for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ ) corresponds to a high  $K_d$  value (above  $10^5$  mL/g),  
331 demonstrating good consistency between simulation and experimental results. Among all metal  
332 ions analyzed, the formation energy of Pb- $\text{MoS}_2$  has the most negative value (-1.3 eV), indicating  
333 stronger bonding and more facile interactions of  $\text{Pb}^{2+}$  than those of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  with  $\text{MoS}_2$   
334 nanosheets, consistent with its highest  $K_d$  value measured experimentally. The formation energy  
335 of  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  is much less negative or becomes positive ( $> -0.4$  eV), consistent with  
336 their low  $K_d$  values (below  $10^4$  mL/g) measured experimentally. *It's worth noting that the*  
337 *interactions between  $\text{MoS}_2$  and representative ions were simulated exclusively with 2H- $\text{MoS}_2$ , and*  
338 *the potential effects of various  $\text{MoS}_2$  phases on the adsorption efficiency should be investigated*  
339 *via experimental tests and theoretical simulations in the future studies.*

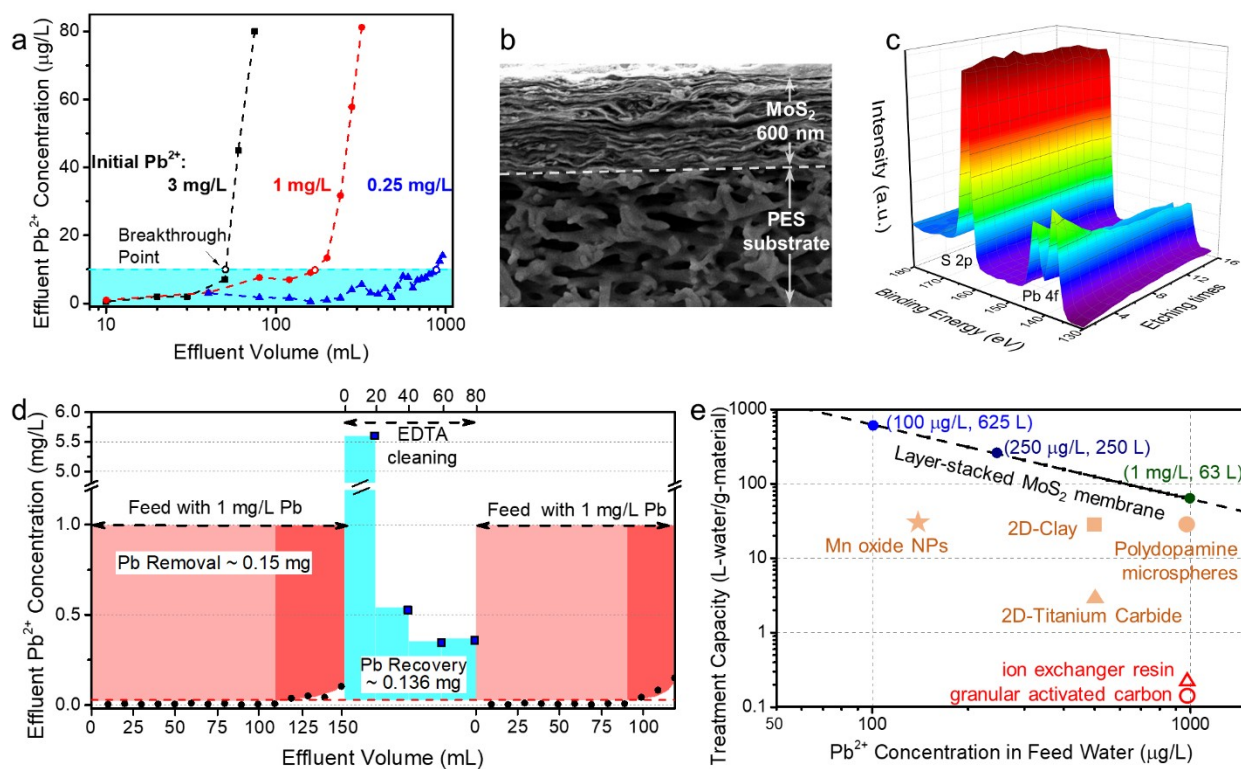
340 Besides adsorption, metal ion removals can be potentially caused by redox reactions and/  
341 or precipitation formation with  $\text{MoS}_2$  nanosheets or soluble molybdate species. To explore if  
342 these mechanisms are present in removing  $\text{Pb}^{2+}$  and other metal ions tested here, we carried out  
343 extensive XPS characterization of the metal-adsorbed  $\text{MoS}_2$  samples (Pb-, Cu-, Cd-, Ni-, Zn-  
344  $\text{MoS}_2$ ). As shown in Figure S9a, compared to the pristine  $\text{MoS}_2$ , all metal-adsorbed  $\text{MoS}_2$   
345 samples exhibit similar Mo and S peak positions and intensities. Meanwhile, the absence of  
346 oxidized S at 168 eV and constant 1T/2H ratios indicate no direct redox reaction occurring  
347 between  $\text{MoS}_2$  and metal species tested here (Figure S9b and S9c). This is consistent with the  
348 previous findings that  $\text{MoS}_2$  can not reduce  $\text{Pb}^{2+}$  or  $\text{Cu}^{2+}$ , although redox reaction contributes

349 greatly to the removal of  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  that leads to oxidized S and reduced 1T/2H ratios.<sup>26</sup> We  
350 observed weak peaks of molybdate, which often co-exists in the  $\text{MoS}_2$  suspension due to slow  
351 oxidative dissolution of  $\text{MoS}_2$  by ambient oxygen. Based on the XPS characterization (Figure  
352 S9b), even if we assume all the molybdate contributes to Pb removal by forming precipitates, the  
353 precipitation accounts for less than ~10 % of the total Pb removal (see Supporting Information  
354 for calculation).

355

356 **Layer-stacked  $\text{MoS}_2$  as POU filter.** Excellent capacity and selectivity are the pre-requisites for  
357  $\text{MoS}_2$  monolayers as potential building blocks for a POU filter. With these aspects demonstrated  
358 above, we further used  $\text{MoS}_2$  monolayers to synthesize a layer-stacked  $\text{MoS}_2$  membrane, and  
359 explored its potential for POU removal of lead from drinking water. The  $\text{MoS}_2$  membranes were  
360 tested in filtration experiments with feed water containing various concentrations of  $\text{Pb}^{2+}$ . The  
361 membrane maintained a constant water flux ( $145 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) due to stable 2D nanochannels  
362 formed between stacked  $\text{MoS}_2$  nanosheets with an interlayer distance of 1.2 nm (Figure S10). The  
363 interlayer spacing is large enough to allow  $\text{Pb}^{2+}$  to enter the 2D nanochannels in the  $\text{MoS}_2$   
364 membrane and adsorb it onto the channel walls. As a result,  $\text{Pb}^{2+}$  concentration is efficiently  
365 lowered from 0.25-3 mg/L in the feed water, to less than 10  $\mu\text{g/L}$  in the effluent, which is the  
366 WHO guideline value. Since the  $\text{MoS}_2$  membrane mainly removes  $\text{Pb}^{2+}$  by adsorption, there  
367 would be a breakthrough point when the effluent concentration rises above 10  $\mu\text{g/L}$ . The total  
368 effluent volume at the breakthrough point defines the treatment capacity of the adsorptive  
369 membrane. As shown in Figure 4a, when the  $\text{Pb}^{2+}$  concentration in feed water was 0.25, 1, and 3  
370 mg/L, the treatment capacity of the  $\text{MoS}_2$  membrane was 800, 180, and 70 mL, respectively. It is

371 estimated that the residence time of  $\text{Pb}^{2+}$  in the  $\text{MoS}_2$  membrane is merely 0.02 s (see calculation  
 372 in Figure S10), so the breakthrough is most likely controlled by a dynamic process instead of  
 373 reaching an equilibrium condition for adsorption. Therefore, the treatment capacity of  $\text{MoS}_2$   
 374 membranes can be further improved by increasing the residence time, e.g., by synthesizing a  
 375 thicker membrane (Figure S12).



376  
 377 **Figure 4.** Layer-stacked  $\text{MoS}_2$  membrane as a POU filter. (a) The performance of  $\text{MoS}_2$  membranes in  
 378 filtering a feed water containing 0.25 to 3 mg/L  $\text{Pb}^{2+}$ . The treatment capacity is defined as the total  
 379 effluent volume at the breakthrough point, which was reached when the effluent  $\text{Pb}^{2+}$  concentration  
 380 reached 10  $\mu\text{g/L}$ . The cross-sectional SEM (b) and XPS depth profile (c) of the  $\text{MoS}_2$  membrane after  
 381 filtering  $\text{Pb}^{2+}$  water (see Figure S11 for detailed peak intensity evolution). (d) The regeneration of  $\text{MoS}_2$   
 382 membrane using EDTA cleaning. (e) Treatment capacities (L-water/g-material) of  $\text{MoS}_2$  membranes and  
 383 other adsorptive membranes reported in the literature. Membranes fabricated by commercial materials are  
 384 represented by red hollow symbols, and those by lab-synthetic materials are represented by amber filled  
 385 symbols.

386 SEM and XPS were used to characterize a used  $\text{MoS}_2$  membrane after being tested with  
 387 1 mg/L  $\text{Pb}^{2+}$  feed solution and reaching the breakthrough point in filtration. The  $\text{MoS}_2$  membrane

388 maintains a stacked structure as shown in the cross-sectional SEM image (Figure 4b). The  
389 distribution of adsorbed lead in the MoS<sub>2</sub> membrane can be observed in the depth profile of the S  
390 2p and Pb 4f peaks obtained by etching 300 nm (15 times × 20 nm etching depth) into the MoS<sub>2</sub>  
391 membrane during XPS characterization (Figure 4c). The Pb/S atomic ratio is high (12 %) on the  
392 membrane surface, and gradually decreases to around 5 % at 100 nm depth and below. The  
393 higher Pb content on the membrane top surface could be partially attributed to the diffusion of  
394 Pb<sup>2+</sup> ions from water during drying. The relatively constant Pb/S ratio in the membrane interior  
395 confirms that adsorption instead of membrane exclusion is the dominant Pb<sup>2+</sup> removal  
396 mechanism.

397         The regeneration ability of the MoS<sub>2</sub> membrane was evaluated by using EDTA cleaning  
398 to remove the adsorbed Pb<sup>2+</sup> ions from the membrane after a filtration experiment. As shown in  
399 Figure 4d, the MoS<sub>2</sub> membrane adsorbed 0.15 mg Pb<sup>2+</sup> from the first filtration cycle, and the  
400 EDTA cleaning by flushing with 80 mL EDTA solution recovered approximately 0.136 mg Pb<sup>2+</sup>  
401 from the membrane, leading to a recovery of more than 90 %. It is worth noting that the  
402 concentration of recovered Pb<sup>2+</sup> in the first 20 mL EDTA solution was as high as 5.5 mg/L,  
403 demonstrating the effectiveness in regenerating MoS<sub>2</sub> membranes. A second filtration cycle was  
404 performed after EDTA cleaning, and the regenerated MoS<sub>2</sub> membrane could reduce Pb<sup>2+</sup>  
405 concentration to less than 10 µg/L with a treatment capacity of 90 mL, equivalent to nearly 90%  
406 of the original treatment capacity of a fresh MoS<sub>2</sub> membrane.

407         The treatment capacity of a POU filter is calculated by considering a conservative 65.6  
408 mg/g lead removal capacity of the MoS<sub>2</sub> membrane (based on the tests shown in Figure S12). As  
409 shown in Figure 4e, the POU device demonstrates a treatment capacity of 63 to 625 L-water/g-  
410 MoS<sub>2</sub> depending on the initial Pb<sup>2+</sup> concentration in tap water. For instance, when Pb<sup>2+</sup>

411 concentration in the water is 100 and 250  $\mu\text{g/L}$ , a POU device containing 1 g of  $\text{MoS}_2$  membrane  
412 could effectively treat 625 and 170 L water, respectively. The treatment capacity of  $\text{MoS}_2$   
413 membrane is several orders of magnitude higher than that of adsorptive membranes made of  
414 commercial or lab-synthetic materials reported in the literature<sup>12, 58, 59</sup>. The superb performance  
415 can be attributed to the high adsorption capacity and selectivity of  $\text{MoS}_2$  nanosheets as well as  
416 the fully accessible sulfur sites in the 1.2-nm 2D nanochannels enabled by the layer-stacking  
417 structure.

418 The leaching of  $\text{MoS}_2$  nanosheets and soluble Mo species from  $\text{MoS}_2$  membranes is also  
419 characterized in the filtration experiments. During the Pb adsorption and EDTA cleaning process,  
420 we observed a low concentration of leached Mo species ( $< 0.1 \text{ mg/L}$ ) in the filtrate (Figure S13).  
421 This is due to the slow oxidation of chemically exfoliated  $\text{MoS}_2$  to soluble molybdate ions as was  
422 reported previously.<sup>60</sup> To the best of our knowledge, molybdate ions have not been reported to  
423 generate environmental toxicity or negative human health impacts at such low concentrations.  
424 The leaching problem can also be potentially addressed by using more stable  $\text{MoS}_2$  prepared by  
425 ultrasonication, which significantly slows down Mo leaching (Figure S13). Loose nanosheets  
426 were not observed throughout all filtration tests, nor during a batch test where external pressure  
427 was removed, a condition that can accelerate nanosheet release if applicable (Figure S14). This  
428 structural stability is consistent with our previous finding that the strong vdW forces between  
429  $\text{MoS}_2$  nanosheets could potentially prevent the layer-stacked  $\text{MoS}_2$  nanosheets from releasing in  
430 water.<sup>41</sup>

431 **Environmental Implications.** Our findings suggest that emerging 2D  $\text{MoS}_2$  nanosheets can find  
432 important applications like lead removal from drinking water.  $\text{MoS}_2$ 's superb lead adsorption

433 capabilities are evidenced by its adsorption capacity (740 mg/g) and its extremely high  
434 distribution coefficient  $K_d$  ( $5.2 \times 10^7$  mL/g), both of which are among the highest for materials that  
435 have ever been reported to the best of our knowledge. Additionally, once assembled into a layer-  
436 stacked membrane, the unique 1.2-nm 2D nanochannels formed between MoS<sub>2</sub> nanosheets make  
437 all the surface sulfur sites fully accessible for lead adsorption, while allowing water to permeate  
438 through the membrane at a fast speed. The layer-stacked MoS<sub>2</sub> membrane could effectively  
439 remove Pb<sup>2+</sup> in drinking water from a few mg/L to less than 10 µg/L, with a treatment capacity a  
440 few orders of magnitude higher than that of membrane filters fabricated with commercial or other  
441 nanomaterials. An additional advantage of the MoS<sub>2</sub> membrane is that the nanochannels also  
442 enable the rejection of lead-containing particulates, a common form of lead contamination in tap  
443 water due to the corrosion of drinking water distribution pipes.<sup>61</sup> MoS<sub>2</sub> has also been reported to  
444 have excellent antimicrobial/antifouling properties,<sup>62, 63</sup> another important feature for multi-  
445 functional membrane applications. With exfoliation and synthesis methodology maturing, the  
446 cost and complexity of MoS<sub>2</sub> nanosheet production is expected to continuously decrease.  
447 Therefore, we believe that MoS<sub>2</sub> membrane-based technology holds great promise as a POU  
448 device installed in households, schools, or public utilities to remediate lead contamination and  
449 safeguard drinking water quality for the public.

450

451

452 **Associated Content**

453 **Supporting Information**



454 The Supporting Information is available free of charge on the ACS Publications website. This  
455 document includes additional characterization of MoS<sub>2</sub> nanosheets and membranes,  
456 supplementary adsorption results, DFT modeling process and results.

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467

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