Interaction of Pb\(^{2+}\) ions in water with two-dimensional molybdenum disulfide

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Abstract

The removal of heavy metal contaminants from water is important for public health, and recently many two-dimensional (2D) materials with high specific surface areas are being studied as promising new active components in water purification. In particular, 2D MoS\(_2\) nanosheets have been used for the removal of various heavy metals, but usually in either in complex geometries and composites, or in the chemically exfoliated metallic 1T-MoS\(_2\) phase. However, the interaction of heavy metals dissolved in water with unmodified semiconducting 2H-MoS\(_2\) is not well studied. In this paper, we report a detailed fundamental investigation of how Pb\(^{2+}\) ions interact with 2H-MoS\(_2\). We observe small solid clusters that form on the MoS\(_2\) surfaces after exposing them to Pb(NO\(_3\))\(_2\) aqueous solutions as shown by atomic force microscopy and transmission electron microscopy, and for liquid phase exfoliated MoS\(_2\) we observe the nanosheets precipitating out of dispersion along with insoluble solid granules. We use a combination of x-ray photoelectron spectroscopy and x-ray diffraction to identify these solid clusters and granules as primarily PbSO\(_4\) with some PbMoO\(_4\). We put forth an interaction mechanism that involves MoS\(_2\) defects acting as initiation sites for the partial dissolution in aqueous oxygenated conditions which produces MoO\(_4^{2-}\) and SO\(_4^{2-}\) ions to form the solids with Pb\(^{2+}\). These results are an important contribution to our fundamental understanding of how MoS\(_2\) interacts with metal ions and will influence further efforts to exploit MoS\(_2\) for water remediation applications.

1. Introduction

Heavy metal contamination in water is a serious health hazard, and there is a need to develop new methods to remove contaminants such as As, Cd, Cr, Cu, Ni, Pb, Hg, etc [1, 2]. In particular, Pb is a very dangerous contaminant in water because it causes serious health effects even at very low concentrations [2, 3]. Recently, nanomaterials [4] including various inorganic and organic [5] structures have been used for the removal of heavy metals from water. Two-dimensional (2D) materials and especially molybdenum disulfide (MoS\(_2\)) in various forms have increasingly been studied for the removal of heavy metals [6–11] due to their high specific surface areas. However, many of these efforts have involved rather complex geometries and chemical modifications of MoS\(_2\), such as forming a 3D interconnected macroporous framework of MoS\(_2\) [12], MoS\(_2\) coated biochar [6], MoS\(_2\)/reduced graphene oxide composite [13–15], composites with quantum dots [16], carbon nanotubes [17], and Fe\(_3\)O\(_4\) nanoparticles [18–20]. Meanwhile, some recent papers have presented some possible mechanisms of the interaction between MoS\(_2\) chemically exfoliated with n-butyllithium, which forms the metallic 1T-MoS\(_2\) phase and metal ions. These works include a reductive adsorption pathway for Ag\(^{+}\) ions to
form Ag metal by Wang et al[11], and a reactive pathway between Pb$^{2+}$ and Pb$^{4+}$ ions to form PbMoO$_4$ by Mondal et al[21]. In the past couple of years, there have been various methods applied to modified MoS$_2$ to remove Pb from water including phase engineering[22], defect engineering[23], control of interlaying spacing[24, 25], and vertical alignment of nanosheets[26].

However, these works do not elucidate the fundamental details of the interaction unmodified MoS$_2$ alone with Pb ions. Thus, there is still a need to clearly determine the fundamental nature of the interaction between unmodified semiconducting 2H-MoS$_2$, which is a more stable form of MoS$_2$ that can be achieved under much milder conditions, and Pb$^{2+}$ ions. Here in this paper we present a detailed study of the interaction between Pb$^{2+}$ ions in water with unmodified semiconducting 2H-MoS$_2$. We show that small clusters appear on the MoS$_2$ surface after exposure to Pb(NO$_3$)$_2$ solution using atomic force microscopy (AFM), which result in clear Pb peaks in x-ray photoelectron spectroscopy (XPS) along with peaks indicating other compounds combining Pb, O, Mo, and S. We also show that a dispersion of bulk liquid phase exfoliated MoS$_2$ nanosheets quickly turns murky upon exposure to the Pb(NO$_3$)$_2$ solution, and along with x-ray diffraction (XRD) suggest the possible formation of insoluble PbSO$_4$ and PbMoO$_4$, which can contribute to the removal of Pb from water by precipitation. The resulting compounds are visible as solid precipitates. The XRD results also indicate intercalation of some species between the MoS$_2$ layers. The clusters are also visible in transmission electron microscopy (TEM). The Raman and photoluminescence (PL) spectra of MoS$_2$ before and after Pb interaction show only minor changes, suggesting the MoS$_2$ remains largely the same, although there are indications of slight n-doping. Overall, we have found evidence that the interaction between Pb$^{2+}$ ions and MoS$_2$ is a combination of reaction to form new compounds, complexation or adsorption, and intercalation. The underlying mechanism is due to the oxidation and dissolution of MoS$_2$ at defect sites to produce MoO$_5^{2-}$ and SO$_4^{2-}$ ions. These results will be important to all researchers working in the area of 2D materials for environmental remediation because they indicate that there may be multiple mechanisms of interaction between the contaminants and sorbents based on 2D materials.

2. Methods

2.1. Chemicals and materials
Pb(NO$_3$)$_2$: Sigma-Aldrich, ACS reagent $\geq$ 99.0% 2-propanol: VWR Chemicals BDH, ACS $\geq$ 99.5%
Acetone: VWR Chemicals BDH, ACS $\geq$ 99.5%
Sodium dodecylbenzenesulfonate (SDBS): Sigma-Aldrich, technical grade
MoS$_2$: Sigma-Aldrich, powder

2.2. Mechanical exfoliation
Atomically thin MoS$_2$ samples were obtained by mechanical exfoliation from a bulk crystal of MoS$_2$ (SPI Supplies) by using scotch tape, and deposited onto a Si substrate coated with a 300 nm SiO$_2$ layer. The substrate was initially cleaned in sequential baths of acetone and 2-propanol, and blown dry with ultrahigh purity nitrogen before MoS$_2$ exfoliation. Single layer and multilayer MoS$_2$ flakes were identified by optical microscopy and Raman spectroscopy.

2.3. Chemical vapor deposition (CVD) of MoS$_2$
The CVD growth of MoS$_2$ was conducted following similar procedures from the literature[27, 28]. The SiO$_2$/Si growth substrate was sonicated in sequential baths of acetone and 2-propanol for 5 min each, followed by oxygen plasma cleaning (Harrick Plasma, PDC-32G) at high RF power (18 W). The growth was conducted in a horizontal tube furnace (ThermoFisher Lindberg) with 1 inch diameter quartz tube. The precursors were 100 mg of S powder (Alfa Aesar, precipitated, 99.5%) placed at the upstream end of the heating zone, and 15 mg of MoO$_3$ (Sigma-Aldrich, ACS reagent, $\geq$99.5%) placed in a boat bent from Mo foil at the center of the heating zone. The polished surface of the SiO$_2$/Si growth substrate was placed face down across the Mo boat. The furnace was heated at 650 °C for 30 min in vacuum with 300 sccm flow of ultrahigh purity Ar, followed by opening the furnace lid and cooling by an external fan.

2.4. Liquid phase exfoliation (LPE)
LPE was used to produce MoS$_2$ dispersions following similar procedures from the literature[29]. A 6 g mass of bulk powder MoS$_2$ (Sigma-Aldrich) was mixed in 110 ml of 1% wt/vol sodium dodecylbenzenesulfonate (SDBS) aqueous solution and subjected to tip sonication (Branson Digital Sonifier 450D) with a 3 mm tip for 2 h at 50% amplitude. The resulting mixture was then centrifuged for 30 min at 3200 RCF and the supernatant containing the dispersed nanosheets was extracted and used for further experiments.
2.5. Interaction with Pb ion solution
Mechanically exfoliated MoS₂ nanosheets on SiO₂/Si wafers were immersed in 0.1 mM aqueous solutions of Pb(NO₃)₂ in micropure water (18 MΩ) (equivalent to 20.7 ppm of Pb). After rinsing thoroughly with micropure water, they were blown dry with ultrahigh purity nitrogen. Liquid phase exfoliated dispersions of MoS₂ nanosheets were exposed to Pb by mixing 50 ml of the dispersions with 100 ml of a 10 mM solution of Pb(NO₃)₂ aqueous solution (equivalent to 2072 ppm of Pb) and stirring on a magnetic stir-plate overnight. The lower concentration was used for AFM imaging of mechanically exfoliated nanosheets so that the clusters would be further apart and easier to image, while the higher concentration was used for other samples subjected to XPS and XRD to achieve higher signals.

2.6. Thermal treatment
The sample of mechanically exfoliated MoS₂ on SiO₂/Si with clusters after Pb(NO₃)₂ exposure was heated in a tube furnace under vacuum pressure with 200 sccm ultrahigh purity Ar gas flow at 300 °C for 2 h.

2.7. Atomic force microscopy (AFM)
AFM images were taken using a Multimode V system (Bruker Inc.) in ScanAsyst mode with ScanAsyst-Air tips (tip diameter: 2 nm). The images were processed in Gwyddion [30]. To help identify the same locations on samples, we made marks on the Si substrate using a diamond scribe pen. We then used the optical microscope on the AFM system to search for distinctive-looking larger MoS₂ flakes that were deposited during mechanical exfoliation near the target flakes.

2.8. Raman and photoluminescence (PL) spectroscopy
Raman spectroscopy, photoluminescence spectroscopy, and optical microscopy were conducted on a WITec alpha300R system confocal Raman microscope system. Raman and PL spectra were obtained with a 532 nm excitation laser and 100 × objective lens with ~1 μm laser spot size. The laser power was kept to 0.3 mW to minimize damage to the MoS₂ samples. Raman and PL maps were acquired by taking single Raman and PL spectra in a 10 μm × 10 μm spatial map with 400 × 400 pixels. The acquisition time per pixel was 1 s.

2.9. X-ray photoelectron spectroscopy (XPS)
Elemental analysis by XPS was conducted using continuous polycrystalline MoS₂ films that were prepared by CVD growth as described above to accommodate the x-ray spot size (>0.1 mm). The MoS₂ film was dipped in a 10 mM solution of Pb(NO₃)₂ solution for 30 min, followed by thorough rinsing before characterization with XPS. An as-synthesized MoS₂ sample was also characterized similarly. The spectra were analyzed using CasaXPS. The XPS system was a Vacuum Generators 220i-XL system and we used monochromated Al Kα radiation.

2.10. Transmission electron microscopy (TEM)
To prepare samples for TEM imaging, as-dispersed MoS₂ and dispersions after exposure to Pb(NO₃)₂ were dropped onto 400 mesh Cu lacey carbon grids (01824 from Ted Pella). Imaging was performed using a Philips CM 12 TEM operating at 80 kV.

2.11. X-ray diffraction (XRD)
Mixtures of Pb-treated and untreated MoS₂ dispersions were centrifuged to pellet out the nanosheets, the supernatants were removed, and the pellets were lyophilized for approximately two days to obtain powder samples for powder x-ray diffraction (PXRD) measurements. To dry the samples more thoroughly, they were left under vacuum in a desiccator for one day. To perform the PXRD measurements, bulk, untreated, and treated exfoliated powders were first placed as small mounds in the center of a quartz substrate. Isopropanol was then sprayed on both sides of the powder and was allowed to soak into the powders. The quartz substrate was then gently tilted and tapped on its sides to spread the powders onto the substrate as films. The PXRD patterns of the films were taken using a Siemens D5000 Powder x-Ray Diffractometer operating at a scan rate of 3° min⁻¹ with copper K-α radiation.

3. Results
The interaction of 2D MoS₂ with Pb²⁺ ions was studied by introducing pristine MoS₂ samples from mechanical exfoliation, CVD, and LPE to Pb(NO₃)₂ aqueous solutions. Each of these sample preparations allowed for different aspects of the resulting changes in morphology, chemical composition and bonding, and structure to be characterized as described below.
3.1. Morphology of Pb$^{2+}$ interactions with MoS$_2$

The interaction of Pb$^{2+}$ on mechanically exfoliated MoS$_2$ monolayers from aqueous solution was investigated by AFM. The pristine as-exfoliated MoS$_2$ surface is shown in the AFM image of figure 1(a). This sample includes monolayer, bilayer and trilayer regions of MoS$_2$. After being immersed in a lead nitrate (Pb(NO$_3$)$_2$) solution at 0.1 mM concentration and then rinsed with micropure water and blown dry with ultrahigh purity nitrogen gas, AFM imaging reveals small nanometer–tall protrusions or nanoparticles clearly visible on the MoS$_2$ surface, and not on the surrounding SiO$_2$ substrate as shown in figures 1(b)–(c). The composition and structure of the nanoparticles are not known from AFM imaging alone, so further chemical and structural characterization were conducted (see section below). We have previously used AFM imaging of chemically functionalized MoS$_2$ to study reaction mechanisms and kinetics, and use spatial indicators to find the same locations on the samples before and after interactions (see Methods for more details) [31–33].

3.2. Chemical and elemental analysis

XPS was conducted after the MoS$_2$ was dipped in the Pb(NO$_3$)$_2$ solution for 30 min to determine the composition and chemical bonding and to try to chemically identify the clusters that were observed by AFM. MoS$_2$ films grown by CVD (see Methods for more details) were used in these experiments rather than mechanically exfoliated MoS$_2$ to accommodate the larger x-ray spot size. The resulting 2–4 nm thick film of multilayer MoS$_2$ grown on SiO$_2$/Si is shown in figure S1, which is available online at stacks.iop.org/JPMA/3/024007/mmedia along with its XPS spectrum in figure S2. The XPS spectrum of MoS$_2$ after interaction with Pb(NO$_3$)$_2$ aqueous solution is shown in figure 2. Similar to the spectrum of the as-grown MoS$_2$ in figure S2, there are Mo–related peaks (the Mo$^{4+}$ 3d$_{3/2}$ and Mo$^{4+}$ 3d$_{5/2}$ peaks in figure 2(a)) [34, 35], and S-related peaks (the S 2p$_{3/2}$ and S 2p$_{1/2}$ peaks in figure 2(b)) [34, 36, 37]. In addition, Mo$^{6+}$ was also detected in MoS$_2$ before and after interaction with Pb, likely due to a small remainder of the MoO$_3$ growth precursor [38–40]. In figure 2(b), the S 2p$_{3/2}$ peak likely comes from MoS$_2$ [34], whereas the S 2p$_{1/2}$ peak may partially come from the S powder precursor [37]. In figure 2(c), there are no N peaks emerging at ~407 eV for nitrates [41], suggesting that the NO$_3$ ions were not bonded to the MoS$_2$ surface and were likely rinsed away.

Prominent Pb 4f peaks appear in figure 2(c) after immersion in the Pb(NO$_3$)$_2$ solution indicating the presence of Pb on MoS$_2$ surfaces. We have identified peaks that likely correspond to Pb–S bonding [22], PbMoO$_4$ [42, 43], and PbSO$_4$ [44]. These results suggest that there is chemisorption of the Pb onto the MoS$_2$ surface by forming a Pb–S bond, as well as a reductive reaction between Pb and MoS$_2$, which is reported to form MoO$_2$$^2$ and SO$_4$$^{2-}$ [11, 45], to form the new PbMoO$_4$ and PbSO$_4$ compounds.

3.3. Raman and photoluminescence spectroscopy

Raman and photoluminescence (PL) spectroscopy were conducted by acquiring spectra in spatial maps on mechanically exfoliated MoS$_2$ samples before and after the interaction with Pb$^{2+}$. The maps, rather than single spectra, allow any spatial inhomogeneities to be captured [31, 46]. An optical microscope image of the MoS$_2$ flakes is shown in figure 3(a); the rectangle marks the area in which the Raman and PL maps were acquired. Representative Raman spectra before and after interaction with Pb$^{2+}$ are shown in figure 3(a). The main peaks are the A$_{1g}$ mode, which is an out-of-plane vibration mode, and the E$_{2g}$ mode, which is an in-plane vibration mode [47]. These peaks are largely unchanged after Pb interaction, indicating that the crystal structure of the MoS$_2$ has not been significantly altered or disrupted. We do not observe any LA(M) peak (see supporting information, figure S3) that would otherwise accompany an increase in defects [48]. However, the height ratio of

**Figure 1.** Morphology of MoS$_2$ after Pb interaction. (a) AFM image of pristine as-exfoliated MoS$_2$. (b) AFM image in the same region as (a) after dipping in Pb(NO$_3$)$_2$ aqueous solution. The large yellow arrows in (a) and (b) indicate the same spot on the sample. Small protrusions appear on MoS$_2$ but not on SiO$_2$ substrate. The small green arrow indicates an example of a location where the edge has more clusters. (c) Enlarged AFM image in the region marked by the dashed square in (b).
the A\textsubscript{1g} to E\textsubscript{1g} Raman peaks decreased after the interaction with Pb\textsuperscript{2+}, which can be more readily seen in the Raman maps in figures 3(b)–(c). This change is consistent with some increasing n-doping because the A\textsubscript{1g} vibration is more sensitive to electron-phonon coupling [49]. The PL spectra before and after interaction with

Figure 2. Chemical analysis of Pb interaction with MoS\textsubscript{2}. X-ray photoelectron spectroscopy (XPS) spectra of CVD-grown MoS\textsubscript{2} after immersion in aqueous solutions of Pb(NO\textsubscript{3})\textsubscript{2} at 10 mM concentration for 30 min. (a) Mo 3d peaks. (b) S 2p peaks. (c) Pb 4f peaks. (d) O 1s peaks. (e) Mo 3p and N 1s peaks. Mo\textsuperscript{6+} 3d in (a) and O 1s in (d) indicate the existence of unreacted MoO\textsubscript{3} which can be detected from CVD-grown MoS\textsubscript{2}. Pb 4f in (c) demonstrates the bonding between Pb and S, while PbSO\textsubscript{4} and PbMoO\textsubscript{4} are also produced during the reaction. There are no N peaks in (e) indicating that all nitrates were rinsed away.

Figure 3. Raman and photoluminescence spectroscopy as-exfoliated MoS\textsubscript{2} and after Pb interaction. (a) Representative Raman spectra of as-exfoliated MoS\textsubscript{2} and after Pb interaction. Inset: optical microscopy image of as-exfoliated MoS\textsubscript{2} flake. The dashed rectangle represents the area of mapping in panels (b), (c), (e), (f). (b) Map of the height ratio of the A\textsubscript{1g} and E\textsubscript{1g} Raman peaks for as-exfoliated MoS\textsubscript{2} and (c) of the same area after Pb interaction. (d) Representative PL spectra of as-exfoliated MoS\textsubscript{2} and after Pb interaction. (e) Map of the height ratio of the A\textsuperscript{−} trion and B exciton peaks from PL spectra for the as-exfoliated MoS\textsubscript{2}, and (f) of the same area after Pb interaction.
Pb\(^{2+}\) are shown in figure 3(d), and are also largely unchanged, showing that the MoS\(_2\) is still semiconducting and has PL emission. However, the height ratio of the A\(^-\)trion to the B exciton peaks is increased, which is also consistent with some increasing n-doping\[^{50}\]. The corresponding PL maps are shown in figures 3(e), (f). The n-doping may be due to remaining NO\(_3\)^- ions that are not incorporated into solids upon the MoS\(_2\) interaction with Pb(NO\(_3\))^2; further details of the proposed mechanism of reaction is described below in the discussion section. In general, however, we note that these changes are all relatively small and the changes to the Raman and PL spectra are not substantial.

### 3.4. Structural analysis of bulk LPE samples

A bulk liquid phase exfoliated dispersion of MoS\(_2\) nanosheets was prepared in order to perform further structural characterization using methods that are not suitable for mechanically exfoliated flakes or CVD-grown films. The dispersion was prepared using probe sonication and centrifugation (see Methods section). After mixing with a 10 mM aqueous solution of Pb(NO\(_3\))^2, the dispersion was stirred overnight. We observed an obvious change in the color and transparency of the mixture, with a murkier and lighter appearance after the interaction as shown in the photograph in figure 4(a), suggesting some significant physical change. After waiting for some time (~1 h), the nanosheets start to precipitate out as shown in figure 4(b), and there are even visible white solid granules that form, as shown in the inset of figure 4(b), suggesting that the MoS\(_2\) flakes are no longer stably dispersed and that a new solid phase has formed.

The dispersions of 2D MoS\(_2\) nanosheets before and after interaction with Pb was dropped onto lacey carbon grids and characterized using TEM as shown in figures 4(bc) and (d). Before the interaction, the dispersion contains thin and flat nanosheets of MoS\(_2\) with clean surfaces as shown in figure 4(c). However, after the Pb interaction, the nanosheet shown in figure 4(d) is less flat and has nanoparticles on the surface, particularly around the edges, suggesting the formation of a new solid. From the earlier XPS results, we believe that the deposits only contain Pb, Mo, S, and O, since all the nitrates were rinsed away by the ultrapure water.
To further analyze the compositions of the resulting materials after MoS$_2$ was exposed to the Pb(NO$_3$)$_2$ solution, samples of both the as-dispersed MoS$_2$ and after it interacted with the Pb$^{2+}$ ions were prepared using a freeze-drying process (see Methods for more details) and characterized by XRD as shown in figure 5. Any solid precipitates that were formed after Pb$^{2+}$ exposure were also collected in the dried powder. The XRD pattern of as-dispersed MoS$_2$ is shown in the blue curve (figure 5(a)), and has several distinct peaks that closely match those of the reference bulk MoS$_2$ material. They indicate the crystal structure of MoS$_2$ is largely intact when compared to the reference spectrum [51], but with the peaks broadened because the nanosheets are smaller in lateral
dimensions and have less overall stacking order than the bulk material. We note that we are using a higher concentration of Pb(NO$_3$)$_2$ solution here so that the changes are more obvious in XRD, and a lower concentration with the AFM measurements so that the clusters are sufficiently sparse for clear imaging.

The XRD pattern of the MoS$_2$ dispersion after mixing with Pb(NO$_3$)$_2$ is shown in the red curve in figure 5(c). It was smoothed using a Savitzky-Golay finite impulse response smoothing filter of polynomial order 5 to reduce the noise and show the peaks more clearly (black curve) [52]. First, there is a sharp, distinct peak at about 12.3°. We attribute this peak to the (002) peak of the MoS$_2$ material. However, it occurs at a lower angle than the (002) peak in the initial dispersion of about 14.2°, meaning that there is a larger interlayer spacing [53, 54], which is likely due to intercalation or incorporation of some small species between the MoS$_2$ layers. These diffraction angles correspond to interlayer spacings of 6.2 Å for the initial MoS$_2$ material (very similar to the accepted 6.5 Å spacing along the c-axis for MoS$_2$ [55]), and 7.2 Å for the material after Pb exposure.

Second, there are some broad peaks centered at about 20°, 27°, and 42°. The broadness of these peaks is likely due to contributions from multiple compounds and from very small particles. Because the earlier XPS results indicated the presence of only Pb, Mo, O, and S, we have identified possible contributions from PbMoO$_4$ [21, 56] and PbSO$_4$ [57], whose reference XRD patterns are shown in figure 5. The Pb-containing compounds are consistent with the XPS results described earlier. There are multiple overlapping peaks in these regions that may contribute to the overall broadened peaks, so it is difficult to isolate the individual contributions, and we believe that they may co-exist in the small clusters that form on the MoS$_2$ nanosheet surfaces.

We have also conducted XRD measurements of the white precipitates that form upon exposure of the MoS$_2$ dispersion to Pb(NO$_3$)$_2$ (shown in the photograph figure 4(b)). The XRD spectrum of these solids are shown in figure 4(b), and features several sharp peaks that are very close to those of PbSO$_4$, and may also have some contributions from PbMoO$_4$. We note that the peak positions are a bit shifted, suggesting possible strain effects in the particles which may have arisen due to how they formed in conjunction with the MoS$_2$ nanosheets. XPS measurements of the white precipitates (supporting information, figure S4) show contributions from O, N, C, Mo, S, and Pb, also consistent with PbSO$_4$ and PbMoO$_4$ although we were not able to definitely quantify the relative amounts. In combination, we believe that these results suggest the white precipitate is primarily PbSO$_4$.

4. Discussion

4.1. Mechanisms of interactions between Pb$^{2+}$ and MoS$_2$

The results described above indicate that multiple parallel pathways may be occurring when Pb$^{2+}$ ions dissolved in water interact with the 2D MoS$_2$ nanosheets, resulting in the formation of different solid phases, primarily PbMoO$_4$ and PbSO$_4$ based on XRD and XPS, as well as intercalation between the MoS$_2$ layers. In this section, we will discuss the likely overall mechanisms of these interactions.

There are two key properties of MoS$_2$ that contribute to the interaction of Pb$^{2+}$ ions with MoS$_2$. First, point defects in the basal plane of MoS$_2$ have a higher electron density of states [31], and thus higher reactivity. Second, MoS$_2$ has been shown to gradually dissolve in water in the presence of oxygen as described this reaction pathway [45]:

$$\text{MoS}_2 + \frac{3}{2} \text{O}_2 + 3\text{H}_2\text{O} \rightarrow \text{MoO}_2^{2-} + 2\text{SO}_4^{2-} + 6\text{H}^+.$$  (1)

Thus, there are MoO$_2^{2-}$ and SO$_4^{2-}$ ions generated that can react with the Pb$^{2+}$ ions to form PbMoO$_4$ and PbSO$_4$, respectively. We speculate that the increased reactivity at point defects and edges increases the rate of formation of MoO$_2^{2-}$ and SO$_4^{2-}$ ions, and also that the small clusters or particles observed in AFM and TEM imaging are preferentially located at defects and are composed of PbMoO$_4$ and PbSO$_4$. The XPS peaks corresponding to PbSO$_4$ are stronger than those for PbMoO$_4$, suggesting there is more of that material being formed, consistent with the relative amounts of the MoO$_2^{2-}$ and SO$_4^{2-}$ ions being generated in equation (1). The XRD for the white precipitates also strongly suggests PbSO$_4$.

We note that the dissolution rate for the semiconducting 2H-MoS$_2$ that we are using is much slower than that of the metallic chemically exfoliated 1T-MoS$_2$ (about eight times slower [45]), so we still have predominantly intact 2H-MoS$_2$ throughout our experiments. We also note that we measured the pH of the MoS$_2$ liquid exfoliated dispersion to be ~2.77 when first formed, and ~2.45 after interaction with Pb; the acidity is due to the H$^+$ formation in equation (1). Since PbSO$_4$ and PbMoO$_4$ both have very low solubilities, at these pH levels without the appropriate counterions we expect both compounds to be fairly insoluble, in agreement with our observation of solid precipitates.

There is also a difference in observed behavior between the mechanically exfoliated and liquid phase exfoliated MoS$_2$. The mechanically exfoliated nanosheets are relatively pristine, with high crystallinity and a low concentration of initial defects. Thus, we are able to observe clear clusters upon interaction with the Pb(NO$_3$)$_2$ solution in AFM and TEM, although their overall concentration on the surface is low enough that we do not see
any Raman peaks related to PbMoO$_4$ and PbSO$_4$ (see figure S3). We used a lower concentration of Pb(NO$_3$)$_2$ of 0.1 mM to make the clusters were clearly discerned in AFM images. In contrast, the LPE method uses tip sonication which produces much smaller nanosheets with more defects and less ordered stacking. Thus, it likely has more initiation sites for the dissolution reaction to occur and for Pb$^{2+}$ to react and form clusters of PbMoO$_4$ and PbSO$_4$. We used a higher concentration of Pb(NO$_3$)$_2$ of 10 mM so that the differences in the XRD signals would be clearer. These factors combined so that we see distinct macroscopic granules of insoluble material precipitate out of solution. The appearance of the MoS$_2$ flake after Pb$^{2+}$ interaction in the TEM image in figure 4(d) shows some roughness across the plane, possibly due to locations where the dissolution process has taken place according to equation (1). Since the flakes are smaller, it is also easier for species to intercalate between the layers of the liquid phase exfoliated MoS$_2$ than the mechanically exfoliated material.

Some further points regarding the Pb$^{2+}$ interaction with MoS$_2$ will be noted here. It may be possible to form Pb–S complexes, either at initial defect sites with increased density of states, or at the basal plane where the lone pair on the S atom acts as a Lewis base while the empty 6p orbital on the Pb$^{2+}$ ion acts as a Lewis acid [58–60]. Thus, there may be some Pb atoms adsorbed on the MoS$_2$ surface, which is also consistent with the Pb–S bonds found in our XPS results. We also note that Raman and PL spectra indicating electron doping once the PbMoO$_4$ and PbSO$_4$ have formed on the MoS$_2$ surface, perhaps due to an overall electron donating effect of the oxygen atoms. The clusters visible in AFM imaging would easily be misidentified as Pb metal or Pb(0) without the experiments conducted here.

The formation of clusters that we attribute to PbMoO$_4$ and PbSO$_4$ is significant because it shows that the Pb is not merely being adsorbed onto the MoS$_2$ surface, but it is being incorporated into new compounds. This behavior differs from the interaction of Ag$^+$ ions with chemically exfoliated 1T-MoS$_2$, where there is a reduction to Ag(0) [11]. Based on our XPS results, we do not observe any Pb(0). The reaction here is more similar to the interaction of chemically exfoliated 1T-MoS$_2$ with higher concentrations of Pb$^{2+}$ and Pb$^{4+}$, which led to the formation of PbMoO$_4$ [21]. These results are all consistent with the water and oxygen induced dissolution of MoS$_2$ that has previously been reported, with the 1T phase degrading much more quickly than the 2H phase [45].

4.2. Implications for water remediation

The results we have shown here suggest that when MoS$_2$ is used as a sorbent for removing Pb$^{2+}$ ions from water, there are multiple pathways by which the ions can leave: reaction to form new compounds, complexation or adsorption, and intercalation. The most direct route to removing Pb$^{2+}$ would likely be to form large volumes of either liquid phase exfoliated or chemically exfoliated dispersions of MoS$_2$, which then would allow the Pb to be incorporated into PbMoO$_4$ and PbSO$_4$, which will then precipitate out of solution and can be easily physically removed or filtered. In this mode of removal, there is no benefit to forming more complex geometries or composites of MoS$_2$ with other materials, which would only add processing steps without improving removal.

Waste water with higher concentrations of Pb may benefit from using 1T-MoS$_2$ due to its higher dissolution rate to produce more MoO$_4^{2-}$ and SO$_4^{2-}$ ions. However, the use of the toxic and hazardous n-butyllithium to generate the chemically exfoliated 1T-MoS$_2$ may not be desirable for sensitive applications such as treating drinking water. Water with lower concentrations of Pb may be more suited to the 2H-MoS$_2$ as we have used here as it dissolves more slowly in water, and thus will not produce an excess concentration of MoO$_4^{2-}$, since the recommended health advisory level for Mo in water is only 40 ppb [61], while the amount of Mo released by dissolution of 1T-MoS$_2$ can reach several mM [45], which is equivalent to hundreds of ppm. Although the MoS$_2$ cannot be reused if it is being transformed into Pb-containing compounds, the bulk powder MoS$_2$ source material is fairly inexpensive, with a similar order of magnitude specific cost as activated carbon, which makes it potentially more economical than more energy-intensive removal methods like distillation or reverse osmosis. Further studies will be needed to determine the optimal parameters for practical application of MoS$_2$ in the removal of Pb, but our results show that it is a promising potential material.

5. Conclusions

In conclusion, we have studied the interaction of Pb$^{2+}$ ions in aqueous solution with unmodified 2H-MoS$_2$ nanosheets and found the reactive formation of clusters of PbMoO$_4$ and PbSO$_4$, as well as adsorption and intercalation. The clusters are clearly visible in AFM and TEM imaging, and they are identified as PbMoO$_4$ and PbSO$_4$ by XPS and XRD. When liquid phase exfoliated 2H-MoS$_2$ is used, there is enough of the solids formed for them to precipitate out of solution as visible granules. The mechanism of this interaction is related to the point defects on the MoS$_2$ basal plane and at the edges, and the dissolution in water in the presence of oxygen that is initiated at these defects. These results are important for a fundamental understanding of how Pb$^{2+}$ ions in water interact with MoS$_2$ in future water remediation applications.
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