amorphous molybdenum selenide nanosheet as an efficient trap for the permanent sequestration of vapor-phase elemental mercury

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1. introduction

mercury (hg), which is widely present in industrial flue gas and hg-laden consumables, poses tremendous environmental risks due to its high transportability, long-distance persistence, and hypertoxicity.[1] according to the newly released global mercury assessment, the annual emission of anthropogenic hg to the immediate environment increased to 2500 tons in 2015 compared to 2000 tons in 2008.[2] among the various forms of hg emitted, centralized control of elemental mercury (hg⁰) faces the greatest challenge due to its volatility and insolubility, which leads to limitations of traditional air-pollution control techniques for efficient degradation.[3] for example, hg emitted from industrial boilers/smelters generally includes hg⁰, oxidized mercury (hg²⁺) and particulate-bound mercury (hgₚ).[4] hg²⁺ and hgₚ can be efficiently captured by wet acid and particulate control facilities, while hg⁰ persists in flue gas and acts as the main hg form emitted to air.[5] thus, controlling hg⁰ emissions is the key challenge for relieving the increasing mercury pollution worldwide.[2b] the techniques used for hg⁰ pollution remediation generally rely on sorbents with surface functional groups (including halogens, oxygen/oxides, sulfur/sulfide, etc.) that can accommodate hg⁰.[6] the activity, abundance, accessibility, and species of the functional groups coinfluence the hg⁰ uptake capacity and rate. moreover, the environmental stability of the final product is also an essential parameter to evaluate the feasibility of techniques. for a decent sorbent, it is important to take advantage of all of these requirements. for example, mineral sulfides (ms) were recently found to be potentially hg⁰ immobilization because they were capable of fully converting hg⁰ into metabolically inactive and environmentally stable mercury sulfide (hgₙ).[6] after adjusting the activity and accessibility of the sulfide species, molybdenum disulfide (mos₂) sheets exhibited an obvious enhanced hg⁰ capture performance compared to bulky zinc monosulfide (zns). mos₂ sheets exhibited an obvious enhanced hg⁰ capture performance compared to bulky zinc monosulfide (zns). mos₂ sheets exhibited an obvious enhanced hg⁰ capture performance compared to bulky zinc monosulfide (zns). mos₂ sheets exhibited an obvious enhanced hg⁰ capture performance compared to bulky zinc monosulfide (zns). mos₂ sheets exhibited an obvious enhanced hg⁰ capture performance compared to bulky zinc monosulfide (zns). mos₂ sheets exhibited an obvious enhanced hg⁰ capture performance compared to bulky zinc monosulfide (zns). mos₂ sheets exhibited an obvious enhanced hg⁰ capture performance compared to bulky zinc monosulfide (zns). mos₂ sheets exhibited an obvious enhanced hg⁰ capture performance compared to bulky zinc monosulfide (zns).
disulfide ligand (S$_2^-$) that exhibited a higher affinity toward Hg$^0$ than the monosulfide (S$^2^-$) in MoS$_2$.[8]

Previous studies have strongly indicated that the rational design of an Hg$^0$ remediator by combining different physical and chemical properties of the sorbent may derive an ideal material for permanent Hg$^0$ sequestration. However, sorbents that include abundant functional groups exhibiting easy accessibility and high activity to simultaneously achieve a high capacity and rapid rate have rarely been realized. Even after the MSs were nanosized to achieve adequate exposure of the abundant sulfides (≥50% molar ratio), the Hg$^0$ uptake capacity over the best MSs only reached less than 5% of its corresponding theoretical value, assuming that one mole of sulfide combines with one mole of Hg$^0$.[4] This insufficiency suggests that sulfide itself has limited affinity toward Hg$^0$, and it is imperative to develop new functional groups to break through this barrier.

When searching for alternatives to the previously reported groups to significantly enhance the Hg$^0$ uptake performance, it was observed that the binding affinity constant between Hg and selenium is 10$^6$ times higher than the binding affinity constant between Hg and sulfur, but the solubility of mercury selenide (HgSe) is 10$^3$-fold lower.[9] Selenide is the optimal natural ligand to combine with Hg to neutralize its neurotoxicity.[10] These factors indicate not only that selenide-based sorbents may exhibit a significantly improved adsorption performance compared to their sulfide counterparts but also that the obtained adsorbate (HgSe) will exhibit excellent environmental stability. To realize adequate selenide exposure, a nanosheet structure is preferential. Therefore, nanosheet-structured molybdenum diselenide (MoSe$_2$) is a promising candidate. However, MoSe$_2$ has at least three drawbacks, i.e., the synthetic inconvenience of requiring high temperature, relatively narrow layer spaces to exert its structural advantages to allow Hg$^0$ in, and the lack of a diselenide ligand (Se$_2^2^-$) that is likely to exhibit higher affinity to Hg$^0$ than monoselenide (Se$^2^-$).[11] Coincidentally, amorphous molybdenum selenides (MoSe$_a$, a>2) generally contain rich Se$_2^2^-$ ligands.[12] Moreover, unlike MoS$_x$, which is generally in an irregular phase,[13] MoSe$_a$ can be spontaneously solidified into a nanosheet at a relatively low temperature as it is the precursor for MoSe$_2$ and shares a similar morphology with MoSe$_2$. [14] Based on this similarity, the increased surface area of MoSe$_a$ compared to the surface area of MoSe$_2$[15] indicates that more active ligands would be exposed in MoSe$_a$. Therefore, it is reasonable to speculate that MoSe$_a$ would be a potential sorbent for Hg$^0$ sequestration from industrial and domestic sources.

In this work, a rationally engineered amorphous MoSe$_a$ was demonstrated to be an efficient trap for permanent vapor-phase Hg$^0$ sequestration due to its morphologic and structural properties. The as-derived adsorption performance reached more than 1000 mg g$^{-1}$, the highest recorded value compared to previously developed sorbents tested in fixed-bed reactors. This work not only presents a potential alternative to traditional selections as a Hg$^0$ remediator with minimum environmental effects but also provides guidance for the future design of effective Hg$^0$ sorbents from a new perspective.

2. Results and Discussion

2.1. Structural and Morphologic Analyses

Figure 1a presents the X-ray diffraction (XRD) pattern of MoSe$_a$ as synthesized. Only two weak and broad peaks were observed at 25–40° and 50–55°, which matches with the characteristic XRD peaks of amorphous MoSe$_a$ reported in previous studies.[14,15] No well-defined XRD peak was recorded for MoSe$_a$ indicating its amorphism. The amorphous phase was further proven by high-resolution transmission electronic microscopy (HRTEM) images showing that no characteristic lattice fringe was observed for MoSe$_a$, while TEM images clarified

Figure 1. a–d) XRD, TEM (inserted with HRTEM), Mo 3d and Se 3d patterns of amorphous MoSe$_a$; e–h) the corresponding counterparts of well-crystallized MoSe$_2$. 
that MoSe$_a$ existed in nanosheets (as shown in Figure 1b). This structure is in line with our proposal that MoSe$_a$, as the precursor for MoSe$_3$, shares similar structural properties with its crystallized phase. Moreover, to determine the valences of the molybdenum and selenide species in MoSe$_a$ and better predict its adsorption behavior and capacity, the X-ray photoelectron spectroscopy (XPS) patterns of Mo 3d and Se 3d were recorded and are presented in Figure 1c,d, respectively. As shown, the Mo 3d envelope shows a doublet, with the Mo 3d 5/2 and 3d 3/2 peaks centering at 228.0 and 231.1 eV, respectively, which suggests that all molybdenum exists in Mo$^{4+}$ in MoSe$_a$, with negligible amounts of other valence states detected.$^{[16]}$ For selenide, the Se 3d doublet of MoSe$_a$ at 53.1 and 54.0 eV is designated as the Se 3d 5/2 and 3d 3/2 characteristic peaks of monoselenide (Se$^-$), while the Se 3d peaks at 54.2 and 55.0 eV are due to the presence of diselenide (Se$_2^-$).$^{[2]}$ The XPS results demonstrate the copresence of Se$^-$ and Se$_2^-$ in amorphous MoSe$_a$ and that their molar ratio was nearly 1:1, giving a total charge of the Se species in MoSe$_a$ of negative four (Se$_4^-$), which matches with the total charge of the molybdenum species (Mo$^{4+}$). The presence of Se$_2^-$ was expected to exhibit superior affinity toward Hg$^0$ over Se$_2^-$, similar to S$_2^-$ that is superior to S$^2^-$. In addition, the molar ratio of molybdenum and selenide in MoSe$_a$ was calculated based on the XPS results to be 1:3, which is helpful to derive its theoretical Hg$^0$ adsorption capacity. Thus, amorphous MoSe$_a$ is denoted as MoSe$_a$ in the following context.

For comparison, the characteristic counterparts of well-crystallized MoSe$_3$ are shown in Figure 1e–h. The characteristic peaks in the XRD results perfectly index to the (002), (100), (103), (105), and (110) crystal planes of MoSe$_3$ (JCPDS29-0914), which indicates that crystalline MoSe$_3$ was successfully derived from amorphous MoSe$_a$ (as shown in Figure 1a–d).$^{[17]}$ The TEM image shows that as prepared MoSe$_3$ exhibited an almost identical nanosheet structure with its precursor, while the HRTEM results indicate that the nanosheet was formed by the stacking of 3–4 layers in the <001> direction because the fringe of the side-viewed nanosheet matches the lattice parameter between its (002) planes (0.68 nm) (as shown in Figure 1f).$^{[18]}$ This assignment is reasonable based on the classic BFDH model, which relates the growth rate of specific crystal planes to their lattice fringes in an inverse proportion to self-assemble into specific morphologies.$^{[19]}$ In Figure 1g, it is shown that as in MoSe$_a$, the molybdenum species in MoSe$_3$ also presents as Mo$^{4+}$, which is neutralized by 100% Se$^2^-$ anions instead of a 1:1 mixture of Se$_2^-$ and Se$^2^-$ (as shown in Figure 1h).

The Brunauer–Emmett–Teller (BET) surface areas of MoSe$_1$ and MoSe$_2$ were 107.5 and 34.6 m$^2$ g$^{-1}$, respectively. Based on TEM images, MoSe$_3$ and MoSe$_2$ share almost identical morphologies with each other, strongly hinting that the formation of MoSe$_2$ from MoSe$_3$ may be achieved via an in situ crystallization process with the loss of 1/3 of selenide anions.$^{[20]}$ Generally, an interlayer space larger than 0.6 nm is indispensable for nitrogen (van der Waals diameter of ~0.3 nm) to permeate and form stable bimolecular layers to measure the areas of both the top and bottom surfaces.$^{[21]}$ When the interlayer space is less than 0.3 nm, no N$_2$ can penetrate; however, when the interlayer space is between 0.3 and 0.6 nm, only a monolayer of adsorbed N$_2$ can be formed. For MoSe$_2$, the interlayer space between the MoSe$_2$–MoSe$_2$ layers is only 0.36 nm (shown in Figure S1, Supporting Information). By contrast, the increased BET surface area of amorphous MoSe$_1$ is probably attributed to its widened interlayer spaces (>0.6 nm), as the morphologies of the sorbents before and after annealing were negligibly changed. According to a previous study, an interlayer space of ~0.3 nm was not adequate for Hg$^0$ to form stable compounds, while an increased space of >0.6 nm was able to perform Hg$^0$ chemisorption.$^{[11b]}$ Although the understanding of MoSe$_1$ at the molecular level is still limited to date, its appropriate interlayer spaces may improve the accessibility of functional groups; hence, increasing its Hg$^0$ sequestration performance.

### 2.2. Hg$^0$ Uptake Capacity

As shown in Figure 2a, amorphous MoSe$_1$ exhibited a twofold higher maximum Hg$^0$ adsorption capacity ($Q_m$, 1670 mg g$^{-1}$) than that of well-crystallized MoSe$_3$ (740 mg g$^{-1}$), although their theoretical values ($Q_T$) were not significantly different (as calculated by assuming that one mole of selenide can combine with one mole of Hg$^0$). The $Q_m$ of MoSe$_1$ is equal to 93% of its corresponding $Q_T$, while MoSe$_2$ only performs at a 46% ratio, further supporting our above assumptions that amorphous MoSe$_1$ has a lattice space suitable for Hg$^0$ permeation (as shown in Figure 2b), because $Q_m$ can only have such a close value to $Q_T$ in MoSe$_1$, if the selenides located in the interlayer spaces are adequately exploited.$^{[11b]}$ On the contrary, the $Q_m$ of MoSe$_2$ is inferior to the $Q_m$ of MoSe$_1$, probably because the narrow interlayer spaces in MoSe$_2$ did not allow Hg$^0$ to permeate and form a stable configuration.

To further prove this point, a density functional theory (DFT) calculation was conducted for Hg$^0$ adsorption over the MoSe$_2$ surface and interlayer interval, for which all the stable configurations are shown in Figure S2 in the Supporting Information. The hollow sites were responsible for Hg$^0$ immobilization over the MoSe$_1$ (002) surface with a binding energy of ~56.9 kJ mol$^{-1}$ (listed in Table S1 in the Supporting Information), while Hg$^0$ adsorption over the MoSe$_2$ (100) surface had a binding energy of ~125.8 kJ mol$^{-1}$. This difference indicates that the (100) edges are preferential for Hg$^0$ adsorption over MoSe$_1$, which is generally in line with the results of a previous study.$^{[22]}$ The Mulliken charge transfer from the adsorbent to adsorbed mercury further evidenced the superiority of the (100) edges (0.044 e) over the (002) surfaces (0.008 e) for anchoring mercury. However, no reasonable configuration can be derived (as shown in Figure 2c) after calculating the Hg$^0$ capture between the interlayer spaces of MoSe$_2$, which indicates that the active sites located in the space intervals are inaccessible to Hg$^0$. This inaccessibility primarily caused the $Q_m$ of MoSe$_2$ to be significantly inferior to its corresponding $Q_T$. On the contrary, although the molecular structure of MoSe$_1$ remains unknown, the $Q_m$ of MoSe$_1$ accounts for nearly 100% of its $Q_T$, indicating the interlayer spaces of amorphous MoSe$_1$ are available for Hg$^0$ immobilization (as shown in Figure 2d). This assumption is generally in line with our assumptions regarding the interlayer spaces derived from the BET surface area results.
2.3. Hg$^0$ Uptake Rate

As shown in Figure 3a, MoSe$_3$ exhibited an normalized outlet Hg$^0$ concentration (to the inlet Hg$^0$) concentration of less than 0.15, regardless of temperature, during the 6 h experiments. Only 1 mg of sorbent was used with a gas hourly space velocity (GHSV) of 7200 000 h$^{-1}$, which is thousands of times higher than under real-world conditions. These results indicate the superior fast kinetics of Hg$^0$ adsorption over MoSe$_3$. The optimal reaction temperature of 50$^\circ$C was probably because a relatively high temperature provided the reaction with more activation energy. However, further increasing the temperature would lead to the possible decomposition of the adsorbate, i.e., HgSe, and adversely influence Hg$^0$ sequestration. The same trend was observed for Hg$^0$ adsorption over MoSe$_2$. However, the normalized outlet Hg$^0$ concentration reached as high as 0.39, 0.28, 0.48 and 0.62 at 25, 50, 75, and 100$^\circ$C. These values are suppressed by the performance by MoSe$_3$. The optimal temperature of 50$^\circ$C was selected to derive the breakthrough curves to further investigate the Hg$^0$ adsorption rate over the as-synthesized sorbents.

As shown in Figure 3c,d, $Q_e$ at 50$^\circ$C of MoSe$_3$ and MoSe$_2$ reached more than 1000 and 200 mg g$^{-1}$, respectively, under a 1.5 mg m$^{-3}$ of Hg$^0$ feed. For MoSe$_2$, nearly 80 h was needed for the adsorption rate to equal the desorption rate (equilibrium state), which was 5.5 times longer than the time required for MoSe$_3$. From the slope of the breakthrough curves (marked as dashed lines in Figure 3c,d), it is clear that the initial Hg$^0$ adsorption rate of MoSe$_3$ is obviously faster than the initial Hg$^0$ adsorption rate of MoSe$_2$, primarily due to the adsorption sites in amorphous MoSe$_3$ exhibiting higher affinity toward Hg$^0$ than the adsorption sites in MoSe$_2$ as the abundances of the sites are both adequate at the initial stage in an open space where the Hg$^0$ concentration is not high enough. The specific initial Hg$^0$ capture rate of MoSe$_3$ was determined by simulations using different kinetic models (as shown in Figure 4a–d). As shown, the pseudo-first-order, pseudo-second-order, Elovich, and Intraparticle diffusion models derived correlation coefficients ($R^2$) of 0.9980, 0.9672, 0.8846, and 0.9779, respectively. Except for the pseudo-first-order kinetic model, the simulations by the other three models induced relatively high deviations from the experimental data. The Hg$^0$ adsorption rate ($R_a$) as calculated by pseudo-first-order kinetics was 240 µg g$^{-1}$ min$^{-1}$.

To provide evidence that Se$_2^{2-}$ accounts for the increased Hg$^0$ uptake rate of MoSe$_3$ compared to MoSe$_2$, Hg-TPD was conducted to determine the adsorbate species on MoSe$_3$ and MoSe$_2$ (as shown in Figure 5a). As shown, the characteristic desorption/decomposition peaks for Hg-laden MoSe$_3$ and MoSe$_2$ centered at $\approx$260$^\circ$C, both of which were due to the existence of HgSe with no other mercury-related species detected. The Hg 4f 7/2 and 5/2 doublets located at 99.5 and 103.2 eV were indicative of spent MoSe$_3$, which matched the binding energy of the Hg–Se bond, further proving that the mercury in MoSe$_3$ exists as HgSe (as shown in Figure 5b).

Figure 2. a) Adsorption capacity comparison between MoSe$_3$ and MoSe$_2$; b) proposed nanosheet structure of MoSe$_3$ and MoSe$_2$; c) DFT study of Hg$^0$ adsorption over MoSe$_2$; and d) assumed scenario for Hg$^0$ adsorption over MoSe$_3$.
as shown in Figure 5c, Se\(^{2-}\) significantly decreased in spent MoSe\(_3\) with the increase of Se\(^{2-}\) species, suggesting that the Hg\(^0\) removal over MoSe\(_3\) can be expressed by the following reaction at the initial stage:

\[
\text{Hg}^0 + \text{Se}^{2-} \rightarrow \text{HgSe} + \text{Se}^{2-} \quad (1)
\]

On the contrary, for MoSe\(_2\), due to absence of Se\(^{2-}\) ligands (as shown in Figure 5d), Se\(^{2-}\) provides the only possible active sites for Hg\(^0\) accommodation to form HgSe\(_2\):

\[
2\text{Hg}^0 + \text{MoSe}_2 \rightarrow 2\text{HgSe} + \text{Mo}^0 \quad (2)
\]

Thus, it is reasonable to attribute the greatly increased Hg\(^0\) adsorption rate of MoSe\(_3\) to the existence of Se\(^{2-}\) chelating sites with high affinity to Hg\(^0\).

### 2.4. Comparison with Previously Reported Sorbents

The \(Q_e\) and \(R_a\) of MoSe\(_3\) were compared with those of previously reported Hg\(^0\) sorbents tested under similar conditions, and the full results are listed in Table S2 in the Supporting Information. Moreover, **Figure 6** shows some typical sorbents at their optimal temperatures to provide a clearer comparison, where a rate equal to zero indicates that the adsorption rate was not reported. As shown in Table S2 in the Supporting Information and Figure 6, the rationally designed MoSe\(_3\) outperformed all the previously reported sorbents for Hg\(^0\) sequestration and had a relatively decent performance. Specifically, the adsorption capacity of MoSe\(_3\) was at least 500, 10, and 5 times greater than the adsorption capacities of carbon-, sulfide-, and selenium-based materials, respectively, while its adsorption rate was at least one order of magnitude higher. Compared to a copper selenide (CuSe)-based sorbent, the adsorption capacity of MoSe\(_3\) was shown to be threefold greater, and its adsorption rate was improved by twofold. Even at 75 and 100 °C that are not the optimal operation temperature for MoSe\(_3\), MoSe\(_3\) still exhibited the highest adsorption capacities compared to the capacities of previously reported sorbents at their optimal temperatures (as shown in Table S2 and Figure S3, Supporting Information). These improvements are mainly attributed to the rational design because: 1) the affinity between selenide/selenium and Hg\(^0\) is superior to the affinity between sulfide/sulfur and Hg\(^0\) and 2) the abundance of diselenide and its corresponding accessibility are significantly enhanced in MoSe\(_3\) compared to other selenide/selenium-based sorbents. The excellent performance of MoSe\(_3\) for Hg\(^0\) sequestration indicates its great potential to be widely applied under real-world conditions.
2.5. Implications for Real-World Applications

To quantitatively determine the potential of MoSe3 for Hg0 adsorption, three typical flue gas atmospheres were chosen to simulate the real-world conditions, i.e., N2 plus O2, simulated flue gas (SFG) from coal combustion flue gas and SFG from smelting flue gas. As shown in Figure 7a, the presence of oxygen (O2) had a negligible influence on Hg0 capture over MoSe3, which indicates that MoSe3 exhibits excellent resistance to oxidation at relatively low temperatures (50 °C). Its decent resistance toward oxidation also indicates that MoSe3 may be a promising trap for Hg0 decontamination from domestic sources.

As shown in Figure 7b, the Hg0 removal performance was slightly inhibited by coal combustion flue gas, possibly because: 1) the presence of water vapor (H2O) competed with Hg0 for active sites[27] and/or 2) the addition of nitrogen monoxide (NO) plus O2 oxidized the active selenide sites into inert selinite species.[28] An injection strategy is generally adopted for Hg0 capture from coal combustion flue gas. In an injection scenario, the sorbent is injected before the air pollution control devices with a residence time of less than 30 min.[28] Thus, a 30 min timespan is the most critical parameter to evaluate the suitability of sorbents to be applied to treat coal combustion flue gas. Considering this prerequisite, MoSe3 is still a potential sorbent for Hg0 capture from coal combustion flue gas because the Hg0 removal performance over MoSe3 was negligibly influenced by simulated SFG within 30 min with an extremely high GHSV of 7200 000 h\(^{-1}\).

For simulated smelting flue gas, a high concentration of SO2 also had a negligible detrimental effect on Hg0 sequestration (as shown in Figure 7c). This property distinguished the MoSe3 sorbent from the traditional Boliden–Norzink process adopting mercurous chloride (HgCl2) as the adsorption liquor to transform vapor-phase Hg0 into Hg2Cl2 solid, the performance of which is significantly inhibited by the presence of abundant SO2. This inhibitive effect is primarily attributed to SO2 being able to reduce HgCl2 and introduce redundant Hg0 into the flue gas.[29] Moreover, the adsorbent and adsorbate in the Boliden–Norzink process are both hypertoxic[30] and are preferentially replaced by harmless selenide compounds. Thus, it is proper to conclude that MoSe3 is also an ideal alternative to HgCl2 for Hg0 remediation in smelting flue gas.

More importantly, the as-formed HgSe over the MoSe3 surface is ultrastable when environmentally exposed, which is manifested by its extremely low leachability (as shown in Table S3 in the Supporting Information and Figure 7d). The leaching ratio of HgSe is even lower than the leaching ratio of its sulfide counterpart (HgS), which is renowned as the most stable form of naturally enriched mercury ore.[24] The mercury concentration in leachate of 0.36 µg L\(^{-1}\) is far below the safe limit (200 µg L\(^{-1}\)) mandated by the United States Environmental Protection Agency (EPA) for classifying a material as hazardous waste.[31] Moreover, the extremely low leaching of mercury from the MoSe3 surface even meets the upper mercury content limit in drinking water (2.0 µg L\(^{-1}\)) as imposed by the EPA,[32] suggesting that Hg-laden HgSe can be directly dumped and
landfilled with a minimum reemission risk. Vapor-phase Hg\(^0\) can be permanently sequestered from a hypertoxic and volatile form into the most inert and stable form (HgSe) on MoSe\(_3\).

### 3. Conclusions

To realize a simultaneous high capacity and rapid rate of Hg\(^0\) capture from various sources, the amorphous MoSe\(_3\) nanosheet synthesized by a one-step hydrothermal method was used for the first time for permanent Hg\(^0\) sequestration. Compared to the well-crystallized MoSe\(_2\) nanosheet, MoSe\(_3\) performed better primarily because of its abundant and accessible Se\(^{2-}\) ligands, which exhibited excellent affinity toward Hg\(^0\). The adsorption capacity reached more than 1000 mg g\(^{-1}\), which is the highest recorded value compared to previously reported sorbents tested in a fixed-bed reactor. The uptake rate reached high as 240 \(\mu\)g g\(^{-1}\) min\(^{-1}\) and was enhanced compared to traditional Hg\(^0\) traps by orders of magnitude. Moreover, the MoSe\(_3\) nanosheet showed excellent resistance to complicated gas atmospheres from various industrial/domestic sources, and the as-formed adsorbate HgSe exhibited extremely low leachability when environmentally exposed. This work not only proposes an ideal sorbent for Hg\(^0\) decontamination from variable industrial and domestic sources but also provides guidance for the future design of efficient sorbents with a new mindset of morphologic and structural optimization.

### 4. Experimental Section

**Sorbent Preparation:** MoSe\(_3\) was prepared using a one-step hydrothermal method. In a typical procedure, 2 mmol of sodium molybdate (Na\(_2\)MoO\(_4\), Sinopharm) was dissolved in deionized water. In a separate beaker, 6 mmol of selenium powder (Se, Aladdin) was added to 15 mL of a hydrazine hydrate solution (N\(_2\)H\(_4\)·H\(_2\)O, 80%, Sinopharm) and stirred for at least one day. Then, the Na\(_2\)MoO\(_4\) solution was poured into the beaker containing selenium and hydrazine hydrate. The mixture was then heated to 180°C for 12 hours, followed by cooling to室温. The precipitate was filtered, washed with ethanol, and dried in vacuum. The as-prepared MoSe\(_3\) nanosheet was then further purified by repeated washing with deionized water and ethanol.

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**Figure 5.** a) Hg-TPD patterns of MoSe\(_3\) and MoSe\(_2\); b,c) Hg 4f and Se 3d patterns of spent MoSe\(_3\); and d) diagrammatic illustration of the selenide species difference between MoSe\(_3\) and MoSe\(_2\).

**Figure 6.** Equilibrium adsorption capacity and adsorption rate comparison between MoSe\(_3\) and previously reported sorbents for Hg\(^0\) sequestration.
into the Se-N2H4·H2O mixture, which was transferred into a Teflon-lined autoclave and heated in an oven at 180 °C for 12 h. The as-obtained black solid was separated by filtration, washed with deionized water and ethanol several times, and dried at 70 °C under vacuum for one night to produce amorphous MoSe3. For comparison, well-crystallized MoSe2 was synthesized by annealing MoSe3 at 450 °C under pure argon (Ar) for 10 h.

**Sorbent Characterization:** The crystallinity of the sorbents was measured by X-ray diffraction (XRD, D8 Bruker AXS, Germany) with two theta from 10° to 80° in Cuα (λ = 0.154 nm) radiation. A transmission electron microscope (JEOL 2100F, Japan) was used to determine the morphologies of the as-prepared sorbents. The fresh and spent sorbents were characterized by their X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi) spectra with a C 1s binding energy value of 284.8 eV as the reference. Spent MoSe3 was obtained by pretreating fresh MoSe3 under 1.5 mg m−3 Hg0 for 120 h. The Brunauer–Emmett–Teller surface area of the sorbents was determined by the N2 adsorption and desorption method with a BET analyzer (ASAP 2020, Micromeritics, USA). Before BET testing, the prepared sorbents were purged in pure N2 for 4 h to obtain a clean surface.

**Determination of the Hg0 Adsorption Capacity and Rate:** The maximum Hg0 adsorption capacities of MoSe3 and MoSe2 were determined by a nested tube reactor (as shown in Figure S4, Supporting Information). The Hg0 source was placed in the bottom of the inner reactor without a lid, while the sorbent was settled on the top of the inner reactor and separated by a filter paper that was capable of permeating Hg0 but inert for Hg0 adsorption. Before the tests began, the sorbents without and with filter paper, which were denoted as $W_{\text{sorbent}}$ and $W_{\text{in}}$, respectively, were both weighed. Then, the Hg0 source in the sealed tube reactor was heated by an oil bath at 140 °C and held for 1 d. The Hg0 concentration reached a nearly infinite value in the sealed nested reactor and attacked every possible adsorption site on MoSe3 or MoSe2. Then, the filter paper with sorbents was taken out, and its weight ($W_{\text{out}}$) was determined again. The maximum Hg0 uptake capacity ($Q_m$, mg g−1) of the sorbents was calculated by Equation (3)

$$Q_m = \frac{W_{\text{out}} - W_{\text{in}}}{W_{\text{sorbent}}}$$  \hspace{1cm} (3)

As the Hg0 uptake rate must be derived by fitting breakthrough curves and requires in situ Hg0 concentration detection, a fixed-bed reactor was used to test Hg0 capture (as shown in Figure S5, Supporting Information) under pure N2. Under this condition, the temperature affected the Hg0 adsorption behavior since the temperature significantly affected the site activity (adsorption rate) and desorption behavior (desorption rate).[24] When the adsorption rate equaled the desorption rate, the sorbent was penetrated and reached an equilibrium adsorption capacity ($Q_e$) with $Q_e < Q_m$. Thus, investigating the impact of temperature was the first step to properly define the corresponding adsorption rate. In the fixed-bed reaction system, the total flow rate was precisely controlled by mass flow controllers (MFCs) to be 300 mL min−1. A Dynacal Hg0 permeation device (VICI Metronics) was used to produce a constant feed of Hg0 vapor. A fixed-bed reactor made of Pyrex with an inner diameter of 1 cm was placed into a tubular furnace equipped with a temperature adjustment system to control the reaction temperature. The concentration of Hg0 was detected with a mercury analyzer (VM3000, Mercury Instrument, Inc.) and continuously recorded by a connected computer. Before each test, the Hg0 carried by different carrier gases bypassed the reactor and was used to detect the inlet Hg0 concentration ($C_{\text{in}}$). Until the fluctuation of $C_{\text{in}}$ was less than 10 µg m−3 within 30 min, Hg0 could pass through the sorbent. The as-recorded Hg0 concentration was denoted as the outlet Hg0.
concentration \( C_{out} \). Hence, the real-time Hg\(^0\) adsorption capacity \( Q_t \) (mg g\(^{-1}\)) was calculated by Equation (2)

\[
Q_t = \frac{1}{m} \int_{t_1}^{t_2} (C_{in} - C_{out}) \times f \times dt
\]

(4)

where \( f \) (m\(^3\) min\(^{-1}\)) is the gas flow rate, \( m \) (g) is the mass of the sorbent, and \( t \) (min) is the adsorption process duration time. To obtain the equilibrium Hg\(^0\) capture capacity \( Q_{eq} \) in this case, \( t_1 \) and \( t_2 \) were denoted as zero and the time \( C_{eq} = C_{out} \) (equilibrium time), respectively. Despite a relatively high \( C_{eq} \), slightly enhances the \( Q_{eq} \), appropriate \( C_{eq} \) is also required for sorbents with different \( Q_m \) to limit the total experimental time and avoid the fluctuations of \( C_{in} \). Based on the preliminary experiments, a \( C_{eq} \) of 1.5 mg m\(^{-3}\) was used to significantly decrease the experimental errors resulted from dramatic fluctuations in a lengthy test.

Then, the Hg\(^0\) adsorption rate of MoSe\(_3\) was obtained by simulation with different kinetic models, i.e., a pseudo-first-order model, pseudo-second-order model, Elovich model, and Intra-particle diffusion model. The optimal model with the highest coefficient factor \( R^2 \) was chosen to describe the kinetic behavior of Hg\(^0\) adsorption on the MoSe\(_3\) surface.

1) Pseudo-first-order model

The pseudo-first-order kinetic model was based on the mass balance. The Hg adsorption rate was proportional to the difference between the equilibrium capacity and the adsorbed amount at any time, as described as follows

\[
\frac{dQ_t}{dt} = k_1 (Q_{eq} - Q_t)
\]

(5)

Equation (3) could be modified to the following equation based on the initial conditions of \( t = 0, Q_t = 0 \)

\[
Q_t = Q_{eq} (1 - e^{-k_1 t})
\]

(6)

where the pseudo-first-order kinetic constant \( k_1 \) (min\(^{-1}\)) can be determined by fitting the adsorption breakthrough curve.

2) Pseudo-second-order model

The pseudo-second-order model considers that the surface diffusivity is inversely proportional to the square of the concentration variation on the sorbent surface, which could be described by Equation (5)

\[
\frac{dQ_t}{dt} = k_2 (Q_{eq} - Q_t)^2
\]

(7)

Equation (5) could be modified to the following equation based on the initial conditions of \( t = 0, Q_t = 0 \)

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_{eq}^2} + \frac{1}{Q_{eq} t}
\]

(8)

where the pseudo-second-order kinetic constant \( k_2 \) (mg g\(^{-1}\) min\(^{-1}\)) can be determined by fitting the adsorption breakthrough curve.

3) Elovich model

The Elovich model assumes that sorption takes place in two phases: 1) a fast initial reaction associated with the movement of the sorbate to external sites and 2) a slower diffusion in and out of the micropores over the sorbent. This model can be described by the following equation

\[
\frac{dQ_t}{dt} = \alpha e^{-\beta Q_t}
\]

(9)

where \( \alpha \) (mg g\(^{-1}\) min\(^{-1}\)) represents the initial rate and \( \beta \) (min\(^{-1}\)) is related to the extent of surface coverage and the activation energy for chemisorption. This equation can be modified into

\[
Q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t
\]

(10)

4) Intra-particle diffusion model

The intraparticle diffusion model assumes that the intraparticle diffusivity is constant and that the diffusion direction is radial. The model can be interpreted by the following equation

\[
Q_t = k_d t^{0.5} + C
\]

(11)

where \( k_d \) (mg g\(^{-1}\) min\(^{-1/2}\)) represents the intraparticle diffusion rate constant and \( C \) (mg g\(^{-1}\)) is proportional to the boundary layer.

First Principle Calculation: Please refer to the Supporting Information, First Principle Calculation section.

Mercury Temperature Programmed Desorption/Decomposition (Hg-TPD): To identify the mercury species adsorbed on the surface of the sorbent, mercury temperature-programmed desorption (Hg-TPD) tests were conducted. Before the Hg-TPD tests, MoSe\(_3\) and MoSe\(_2\) were pretreated with 1.5 mg m\(^{-3}\) Hg\(^0\) balanced in N\(_2\) at 50 °C for 30 min to assure that enough mercury was accumulated on the surface of the sorbent. Then, the Hg\(^0\) feed was cut off, and the Hg-laden sorbents were purged by pure N\(_2\) at 50 °C until the outlet Hg\(^0\) concentration stably equaled zero. The Hg-TPD tests were conducted from 50 to 450 °C with a heating rate of 10 °C min\(^{-1}\).

Hg\(^0\) Adsorption Activity Test under Simulated Real-World Conditions: For Hg\(^0\) removal under real-world conditions, Hg\(^0\) generally exists in an open instead of a closed space, and the Hg\(^0\) adsorption capacity cannot reach its maximum value. Thus, the fixed-bed reactor was selected to simulate the real-world conditions in which the Hg\(^0\) feed continuously flows through the sorbents. Three typical gas atmospheres, i.e., N\(_2\) plus 5% oxygen (O\(_2\)), coal combustion flue gas, and nonferrous smelting flue gas, were adopted. The coal combustion flue gas contained 5% O\(_2\), plus 5% oxygen (O\(_2\)), 300 ppm nitrogen monoxide (NO), 300 ppm sulfur dioxide (SO\(_2\)), 12% carbon dioxide (CO\(_2\)), and 8% water vapor (H\(_2\)O) carried by N\(_2\), and the smelting flue gas comprised 5% O\(_2\), plus 1.5% SO\(_2\). The different flue gas components were supplied by compressed gas cylinders containing N\(_2\), O\(_2\), SO\(_2\), CO\(_2\), and NO. Water vapor (H\(_2\)O) was introduced into the reactor by a separate flow of N\(_2\). The total flow rate was precisely controlled by MFCs. Sorbent dosages of 1 mg were adopted in all experiments, which is much lower than a real-world situation to avoid the possible influence of flue gas components being concealed by excessive sorbent used.

Mercury Leaching Test: Please refer to the Supporting Information, Mercury Leaching Test section.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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