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Morphology-controlled synthesis and sulfur modification of 3D hierarchical layered double hydroxides for gaseous elemental mercury removal

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GRAPHICAL ABSTRACT

ABSTRACT

Porous structure and effective active site are beneficial for gaseous elemental mercury (Hg\textsubscript{0}) capture. Two kinds of hierarchical porous layered double hydroxides (LDHs) were synthesized through an in-situ growth method. Sulfur was used for the modification of these LDHs to enhance Hg\textsubscript{0} removal performance. Two as-prepared NiAl-S\textsubscript{4}@SiO\textsubscript{2} microspheres displayed three-dimensional morphologies, accordingly exhibited as core-shell and urchin-like morphologies. XRD, BET, FTIR, TEM and SEM were employed to investigate the structure effect on Hg\textsubscript{0} uptake. The results indicated that after S-modification, the Hg\textsubscript{0} removal efficiencies as well as SO\textsubscript{2} resistance were enhanced. The Hg\textsubscript{0} removal performances follow the order of: NiAl-S\textsubscript{4}@SiO\textsubscript{2}-urchin > NiAl-S\textsubscript{4}@SiO\textsubscript{2}-core at 100 °C. The mechanism for Hg\textsubscript{0} removal was discussed based on the results of TPD, EDX and XPS. The porous structure of NiAl-S\textsubscript{4}@SiO\textsubscript{2} composite was beneficial for gas transformation and intercalated [S\textsubscript{4}]\textsuperscript{2-} ions were favorable for mercury uptake. The polysulfide combined with adsorbed mercury and formed HgS. Such materials exhibit promising potential for mercury uptake from S-Hg mixed flue gas.

1. Introduction

In recent years, mercury emission has aroused global attention due to its high volatility, long persistence and bioaccumulation effect in the environment [1,2]. Once assimilated by water microorganisms, mercury will increase its toxicity through the formation of dimethylmercury [3]. Some combustion sources are regarded as the primary anthropogenic mercury emission contributors such as coal-fired power plants and non-ferrous smelting plants [4]. Mercury primarily exists as elemental mercury (Hg\textsuperscript{0}), oxidized mercury (Hg\textsuperscript{2+}), and particle-bound mercury (Hg\textsuperscript{0}) in...
various kinds of flue gases. Generally, \( \text{Hg}^{2+} \) can be removed by wet flue gas desulfurization (WFGD), and \( \text{Hg}^0 \) can be easily captured by electrostatic precipitator (ESP) or fabric filter (FF) devices [5–7]. However, \( \text{Hg}^0 \) is difficult to be removed due to its high volatility and low solubility in water. To efficiently remove \( \text{Hg}^0 \), a series of methods have been investigated, such as adsorption, catalytic oxidation and wet absorption processes [8]. The adsorption method is widely used in the smelting industry, while the presence of \( \text{SO}_2 \) can reduce \( \text{Hg}^{2+} \) in solution to gaseous \( \text{Hg}^0 \), resulting in mercury secondary contamination. The efficiency of catalytic oxidation can usually be as high as 90%. However, such removal efficiency is subjected to various conditions (gas flow rate, ammonia concentration and chlorine concentration). Compared with these methods, adsorption technology is considered as the most promising one due to its low cost, easy operation and high efficiency. In the past, injection of powered activated carbon is used to control vapor-phase \( \text{Hg}^0 \) [9,10]. However, the high adsorbent loss and operation cost limited its wide application to some kinds of flue gas with high concentration of \( \text{Hg}^0 \). Some low-cost transition metal oxides were indicated as economic and effective alternative sorbents [11,12]. However, these materials can be easily deactivated by \( \text{SO}_2 \) due to the formation of sulfates which occupies the activated sites [13]. Therefore, novel adsorbents with \( \text{SO}_2 \) resistance and high \( \text{Hg}^0 \) adsorption capacity should be developed.

Recently, researchers found that some minerals, such as pyrite (\( \text{FeS}_2 \)), pyrrhotite (\( \text{FeS} \)), and nano-ZnS, are good candidates for \( \text{Hg}^0 \) uptake due to the strong affinity of sulfur toward mercury [14–16]. Sulfur-impregnated active carbon was investigated for mercury adsorption, and the mercury removal efficiency was enhanced compared with that of virgin carbon [17–19]. Our previous studies also indicated that sulfur clusters impregnation can enhance the \( \text{Hg}^0 \) adsorption of CoFe-LDH [18]. Researcher also successfully synthesized a highly porous K-Pt-Sx chalcogels to remove \( \text{Hg}^0 \) uptake due to the strong affinity of sulfur toward mercury [20]. Furthermore, most of the sulfide materials have low reaction rate and low atom utilization ratio. Moreover, the previous research did not put more attention on \( \text{SO}_2 \) resistant characteristics.

Layered double hydroxides (LDHs), a family of inorganic layered materials, have attracted tremendous interest and been extensively applied in drug delivery, catalysis, and environmental remediation [21]. In general, LDH compounds represent with a formula of \([\text{M}^2\text{II}]_y\cdot\text{M}^3\text{III}_z\)\((\text{OH})_{2y}\)\((\text{A}_n\text{A}^m)^{y-}\cdot y\text{H}_2\text{O}\). The interlayer spacing was occupied by anions and water molecules [22]. The virgin LDH materials have a low atomic utilization and relatively small specific surface area due to their stacking structure. However, the layered board made of metal cations and rich ionic surface —OH group, which can interact with other nanomaterials or polymeric molecules, generated three-dimensional (3D) nanocomposites with special morphologies [23,24]. The core-shell structure is often synthesized for various applications and believed to be beneficial for heterogeneous reactions. In a core-shell structure, the LDHs can act as either shell component or core materials. When LDH acted as the core, the shell@LDH composites can be regarded as the surface modification of LDH nanoparticles to improve LDHs' functionality. When the LDH grows outside, the LDH@core composites showed some unique physicochemical properties, such as large surface area, uniform dispersity and layered structure [25–28]. In general, these porous solid skeletons made 3D LDH materials filled with unidirectional or multidirectional media, which have some tiny interconnected or partly interconnected pores. Such porous structures can facilitate the transfer of gas in the material. Meanwhile, abundant active —OH groups existed on LDH's surface. This kind of combination can also be deemed to combine the advantages of the functional materials and LDH. Especially the core of silica, which has abundant surface active —OH group, can interact effectively with LDH nanoparticles to form functional nanocomposites, and can also prevent magnetic nanoparticles from aggregation in wide pH ranges and improve their chemical stability [29–33]. Considering all the excellent properties, the 3D hierarchical porous LDH@core materials have a promising application for eliminating gaseous pollutants [34]. LDH materials can provide reaction sites for the intercalated polysulfide tunability. To the best of our knowledge, some LDH hybrids with polysulfides have been reported for the capture of mercury vapor, but the morphology-controlled synthesis and sulfur modification of 3D hierarchical LDH was a paucity of research [35].

Herein, we designed NiAl-LDH nanoparticles and impregnated them by polysulfides of \([\text{S}_4]\)\(2^-\) for adsorption purpose. The synthesis of such materials used nontoxic chemicals or environmentally benign solvents, which accorded with the green chemistry principles [36]. The ultrasound-assisted co-precipitation method has been applied to synthesize NiAl@SiO\(_2\) in order to fabricate the homogenous LDH nanostructure on the surface of SiO\(_2\) core. The LDH galleries provide protective space for the inserted \([\text{S}_4]\)\(2^-\) groups. The polysulfides of \([\text{S}_4]\)\(2^-\) contains a series of S—S bonds, each of which can react with \( \text{Hg}^0 \) to form \( \text{S—Hg—S} \) linkages. We also investigate the introduction of \([\text{S}_4]\)\(2^-\) into the NiAl-LDH interlayer structure and its \( \text{Hg}^0 \) capture ability. The \( \text{Hg}^0 \) removal mechanism of the LDHs modified with \( S \) is also investigated in this study.

2. Experimental section

2.1. Materials preparation

**Materials:** Tetraethyl orthosilicate (\( \text{Si} \)(\( \text{OC}_2\text{H}_5\))\(_2\)), ethanol absolute, nitric acid (\( \text{HNO}_3 \)), sodium sulfide nonahydrate (\( \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \)), nickel nitrate hexahydrate (\( \text{Ni(NO}_3\))\(_2\) \( \cdot 6\text{H}_2\text{O} \)) and sulfur were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ammonium hydroxide solution, aluminum isopropoxide (\( \text{Al(OPr)}\(_3\)) and urea were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China).

**Synthesis of SiO\(_2\) spheres:** The modified stober method was used to prepare monodispersed SiO\(_2\) [37]. Generally, 9.15 mL of Tetraethyl orthosilicate (TEOS) was first quickly dissolved in a mixture solution of 50 mL ethanol, 30 mL deionized water and 10 mL ammonia (25–28 wt%). The white suspension was then stirred at a speed 800 rpm for 18 h and the obtained product was washed and filtrated with ethanol thoroughly several times followed by drying in an oven at 60 °C.

**Synthesis of AlOOH primer sol:** Al(\( \text{OPr}\))\(_3\) was employed in fabricating the AlOOH primer sol. Typically, Al(\( \text{OPr}\))\(_3\) (23 g) was first dissolved in deionized water (200 mL) by stirring at 85 °C for 1 h to form a clear solution, and followed by addition of \( \text{HNO}_3 \) (1 M) to keep the pH value at the range of 3–4. The solution was then stirred at 85 °C for 2 h and dried in a rotary. The obtained product (about 6 g) was milled and dissolved in deionized water under ultrasonic treatment for 1 h. The white solution was subsequently transferred into a three-mouth flask, then deionized water (120 mL) and \( \text{HNO}_3 \) (19 mL, 1 M) were added and refluxed gently with stirring for 6 h. Lastly, the AlOOH primer sol was obtained after slow cooling to room temperature. The precipitated material was washed and filtrated with ethanol, and dried under vacuum for 6 h [38].

**Synthesis of NiAl@SiO\(_2\) composites:** The hybrids were prepared through an in situ growth technique. Firstly, as-prepared SiO\(_2\) (1.65 g) was dissolved in deionized water under ultrasonic treatment for 1.5 h, the prepared AlOOH (0.72 g) was then dispersed in the solution with vigorous agitation (500 rpm), followed by withdrawing via centrifugation, and then washed thoroughly with ethanol. The resulting material was dried in air for 2 h. The hybrid (0.15 g) was transferred into a 200 mL Teflon-lined stainless steel autoclave containing \( \text{Ni(NO}_3\))\(_3\) \( (0.01 \text{ mol}) \) and various.
concentration of urea (0.0225 g and 0.288 g), then heated at 100 °C for 48 h, followed by cooling to ambient temperature. The obtained product was then washed and filtrated with ethanol thoroughly several times to remove unreacted nitrates. Finally, vacuum drying at 60 °C for 6 h to collect the solid product [38].

Synthesis of NiAl-S₄@SiO₂ composites: The hybrids were prepared through a routine anion-exchange reaction. Na₂S (0.5 mmol) and sulfur (1.5 mmol) were first dissolved in 100 mL deionized water and then heated at 100 °C. After vigorous stirring about 1 h, different morphologies of NiAl@SiO₂ (0.08 g) were slowly added in the solution. Finally, the resulting NiAl-S₄@SiO₂ composites were separated by centrifugation, rinsed with deionized water and vacuum dried at 60 °C.

2.2. Materials characterization

FT-IR spectroscopy was used to characterize the as-prepared materials’ surface properties. X-ray photoelectron spectroscopy (XPS) results were recorded with an Ultra DLD (Shimadzu-Kratos) spectrometer with Al Kα as the excitation source, and the C 1s line at 284.6 eV was used as a reference for the binding energy calibration. X-ray diffraction (XRD) patterns were performed to analyze the material’s structure, which was tested by using a Shimadzu XRD-6100 diffractometer with Cu-Kα radiation. The data were recorded at a scan rate of 10 deg·min⁻¹ in the 2θ range from 10 to 70°. Raman scattering spectra were performed on a SENTERRA R200. The 633 nm line of Ar⁺ laser was used for the excitation. The microstructures, such as the crystallization, morphology, dispersity and particle size of the materials were characterized by field emission scanning electron microscopy (SEM, JSM-7001F) and transmission electron microscopy (TEM, JEM-2100). The BET (Brunauer-Emmett-Teller) surface areas of the samples were determined using N₂ adsorption at 77 K using a quartz tube (Quantachrome 2200e).

2.3. Hg⁰ removal experiments

The Hg⁰ adsorption activity of the as-prepared samples was tested in a lab-scale fixed-bed quartz reactor. As shown in Fig. S1, the experimental device is made of a mercury permeation quartz tube, a fixed-bed reactor, a cold vapor atomic adsorption spectrometer (CVASS) and an online data acquisition system. Generally, O₂, SO₂, and mercury vapor were carried out by pure N₂, and the total gas flow rate was 500 mL/min. 20 mg of each adsorbent was placed in the quartz tube with a diameter of 0.5 cm. The simulated gas passed through the samples and Hg⁰ concentration was detected by CVASS. The concentration of Hg⁰ was calibrated by Lumex RA 915+. To ensure the accuracy of the experiments, the simulated gas bypassed the reactor and the inlet gas was detected, meanwhile, the inlet concentration of Hg⁰ was stringently controlled at 1.2 mg/m³. SO₂ (500 ppm, 1000 ppm and 2000 ppm) was chosen when investigating the resistance effect of SO₂. The Hg⁰ removal efficiency was calculated according to Eq. (1):

$$\eta = \frac{H_{\text{in}} - H_{\text{out}}}{H_{\text{in}}}$$  \hspace{1cm} (1)

where η represents the removal efficiency, the Hₘ₀ is the inlet concentration of Hg⁰, and Hₘ₀ is the outlet concentration of Hg⁰; the reaction time of each test was 100 min.

Furthermore, mercury temperature programmed desorption (Hg-TPD) method was built to evaluate the desorption performance of as-prepared materials. Before each test, the sorbents were firstly adsorbed for 30 min at 100 °C with 4% O₂ balanced with N₂ (total flow rate is 500 mL/min). Then, the materials were regenerated by heating from 100 to 500 °C in a pure N₂ carrier gas. The heating rate was set at 5 °C/min. The mercury signal was recorded by CVASS online system.

3. Results & discussion

3.1. Characterization of as-prepared composites

3.1.1. Surface analysis of as-prepared samples

As shown in Fig. 1, the FT-IR spectrum was employed to analyze the functional groups of the as-prepared materials. For the spectrum of SiO₂, the broad high-intensity bands can be distinguished in the TEOS films: one at 1050 cm⁻¹, assigned to the asymmetric stretching bonds of Si–O–Si in [SiO₄] tetrahedron associated with the motion of oxygen in Si–O–Si antisymmetrical stretch. Another peak centered at 944 cm⁻¹, which was assigned to the Si–OH stretching mode [39]. The bands at 796 cm⁻¹ was assigned to the Si–O–Si symmetric stretch. For the spectrum of NiAl-LDH, an obvious peak appearing at 1340 cm⁻¹ corresponded to the NO₃⁻ of the NO₃⁻-LDH. Obviously, the peaks at 1340 cm⁻¹ for different morphologies of NiAl-S₄@SiO₂ and NiAl-S₄@SiO₂ were not clear. Especially for the NiAl-S₄@SiO₂, there was no peak detected, suggesting that NO₃⁻ ions of NiAl-NO₃⁻LDH were successfully exchanged by [S₄]²⁻. Moreover, the successful ion-exchange and entrance of [S₄]²⁻ in the intercalation were further demonstrated by Laser Raman spectra in Fig. 2(a). It could be seen that the Raman shift of S₈ were centered at 156.70 cm⁻¹, 220.61 cm⁻¹ and 475.25 cm⁻¹. After the intercalation of anions into the NiAl@SiO₂ and NiAl-LDH, the main S–S bands remained the same, but the intensity and position changed for certain bands. Meanwhile, the peaks of different morphologies of NiAl-S₄@SiO₂ were nearly consistent with the reported values for MgAl-S₄ [35]. It was indicated that all synthesized NiAl-S₄@SiO₂ materials had S–S bonds and some interactions between the inserted [S₄]²⁻ guests and the NiAl@SiO₂ layer.

3.1.2. Structure analysis of as-prepared samples

To further explore the microstructure of the as-prepared materials, the XRD patterns of SiO₂, NiAl-LDH, NiAl@SiO₂ and NiAl-S₄@SiO₂ microspheres with different interior architectures were shown in Fig. 3. For SiO₂, the peaks centered at 24.14°, 37.83°, 45.21° and 63.20°, with some interactions between the inserted [S₄]²⁻ guests and the NiAl@SiO₂ layer.

**Fig. 1.** FT-IR analysis of as-prepared materials.
were assigned to the NiAl-LDH structure. After SiO2 coating with AlOOH layer and in situ growth of LDH microspheres, the XRD patterns of two morphologies of NiAl@SiO2 exhibited a series of reflections. It was noted that the reflection intensity of amorphous SiO2 gradually increased from curve NiAl@SiO2-urchin to NiAl@SiO2-core. Meanwhile, the reflection intensity of NiAl-LDH gradually decreased, which indicated that the gradual disappearance of the core accompanied by the decrease of alkaline concentration in the growth process of LDH shell. For different morphologies of NiAl-S4@SiO2, the new emerging peaks centered at 23.02°, 25.8°, 26.72°, 27.86° and 28.66°, corresponding to the \(d_{\text{basal}}\) values (0.28–0.35 nm), were assigned to sulfur structure (JCPDS NO. 42-1278). The reflection intensity of SiO2 and NiAl-LDH decreased simultaneously, comparing to NiAl@SiO2. The \(d_{\text{basal}}\) values of 0.76 nm corresponds to the interlayer spacing of NO3-LDH. The two NiAl-S4@SiO2 intercalates showed same \(d_{\text{basal}}\) value (0.8 nm), but smaller than that of NiAl@SiO2. This indicated that the [S4]\(^{2-}\) ions existed in the interlayer space. Considering the thickness of the LDH layer and the \(d_{\text{basal}}\) of the two NiAl-S4@SiO2, the height of gallery (0.32 nm = 0.8–0.48) corresponded to the [S4]\(^{2-}\) anions in the interlayer [40]. Meanwhile, such intercalation changed the position of intensity of reflection to some extent. However, the peaks at \(d = 0.14\) nm (the planes of the LDH layers) were not changed, which indicated that the stability of the LDH layers remained unchanged through the ion-exchange process. This result was also supported by the SEM images.

SEM and TEM images of as-prepared materials were shown in Fig. 4. Fig. 4(a)–(d) displays typical TEM images of as-synthesized well-dispersed flowerlike microspheres, which were composed of numerous nanoflakes intercrossing with each other. Obviously, the limited growth space allowed the LDH nuclei vertically to pack on the core surface as a near-spherical morphology. Fig. 4(a) revealed the core-shell structure; the shell of NiAl-LDH was closely connected to SiO2. Fig. 4(b) exhibited the morphology of urchin spherical structure; the LDH nuclei vigorously packed on the core surface and the size of SiO2 was significantly smaller than that in Fig. 4(a). It implied that part of SiO2 was etched away. Such result was consistent with the data of EDX. With the addition of sulfur to NiAl@SiO2, the basic NiAl@SiO2’s structure was not changed, but the [S4]\(^{2-}\) ions embed into the layered structure. The hierarchical structure was further illustrated from the SEM images in Fig. 4(e)–(h). It can be seen that the SiO2 particles arranged closely and spread out uniformly. When NiAl-LDH coated on the SiO2, the morphology didn’t change except an extra layer of lamellar structure appeared on the SiO2 surface.

In addition, the BET surface area, pore volume and pore size of as-prepared samples were detected. As the data listed in Table 1 and Table S1, the surface area of virgin NiAl-LDH and SiO2 were 31 and 13 m\(^2\)/g, respectively. While the BET surface of NiAl@SiO2-core (49 m\(^2\)/g) was much larger than that of SiO2. This implied that the synthesized highly dispersed NiAl-LDH materials were deposited on the surface of SiO2 and formed a core-shell structure in which the rich porous of NiAl-LDH encapsulated SiO2 particles. The BET surface area of NiAl@SiO2-urchin (88 m\(^2\)/g) was noticeably higher than that of NiAl@SiO2-core. After sulfur was added to the NiAl@SiO2, the pore volume of NiAl@SiO2 decreased and the surface area declined enormously.

In generally, the original pore structure will be blocked with the addition of polysulfide into the interlayer of NiAl-LDH. The different morphologies of the NiAl@SiO2 made sulfur disperse on the
layer surface and interlayer to different degrees. The variation of the morphology had great influence on surface areas and pore volume, which may result in the differences in the Hg⁰ adsorption capacity.

3.2. Hg⁰ removal performance over NiAl@SiO₂ and NiAl-S₄@SiO₂ composite

3.2.1. Hg⁰ removal performance over as-prepared samples

The Hg⁰ removal performances of different as-prepared samples were evaluated in a fixed-bed reactor. As shown in Fig. 5, the Hg⁰ removal efficiencies of the as-prepared samples were evaluated under 4% O₂ with a total flow rate of 500 mL/min. Obviously, Hg⁰ removal efficiency increased when sulfur added. Pure SiO₂ had the lowest removal efficiency because no adsorption sites existed on its surface. NiAl-LDH performed poorly in Hg⁰ adsorption, with a removal efficiency of less than 10% after 100 min reaction. When sulfur coated on the NiAl-LDH, the removal efficiency was 30% higher than that of virgin NiAl-LDH in 100 min reaction. While the Hg⁰ removal efficiencies of NiAl@SiO₂ of two different morphologies were nearly the same. The removal efficiencies were approximately 15% higher than that of virgin SiO₂. However, it was obvious that NiAl-S₄@SiO₂-core and NiAl-S₄@SiO₂-urchin had the highest removal efficiency under such reaction conditions, and the removal efficiency was over 90% in 100 min adsorption. After 300 min reaction, the Hg⁰ removal efficiency can also keep at 62%. The reaction activities follow the order of NiAl-S₄@SiO₂-urchin > NiAl-S₄@SiO₂-core > NiAl-S₄ > NiAl@SiO₂-urchin > NiAl@SiO₂-core > NiAl-LDH > SiO₂.

3.2.2. Effect of gas compositions on Hg⁰ removal

Furthermore, the effects of different gas composition on the activities of two NiAl-S₄@SiO₂ materials were tested and the results were shown in Fig. 6. For NiAl-S₄@SiO₂-urchin, when the simulated gas had 4% O₂, the calculated Hg⁰ removal efficiency was 85.05%. To further investigate the effect of O₂ on Hg⁰ removal, 8% O₂ was added in the simulated gas, and the Hg⁰ removal efficiency decreased to 80.42%. The NiAl-S₄@SiO₂-core showed the same tendency, the Hg⁰ removal efficiency decreased from 70.47% to 68.12% when O₂ increased from 4% to 8%. However, the two materials showed almost the same adsorption capacity under 4% O₂ and pure N₂. Obviously, the excessive O₂ resulted in inactivation of mercury adsorption. The effect of SO₂ was also investigated. In the presence of 1000 ppm SO₂ + 4% O₂, SO₂ had no significant influences on mercury removal, and the two NiAl-S₄@SiO₂ materials decreased about 5% and 2% respectively, compared with the condition of 4% O₂. Under the condition of 2000 ppm SO₂ + 4% O₂, the removal efficiencies of NiAl-S₄@SiO₂-core decreased to 36%, and the NiAl-S₄@SiO₂-urchin decreased to 68.5%, respectively.
3.3. Hg\textsuperscript{0} removal mechanism over NiAl@SiO\textsubscript{2} and NiAl-S\textsubscript{4}@SiO\textsubscript{2} composite

The XPS spectra of O 1s, Hg 4f and S 2p for the NiAl-S\textsubscript{4}@SiO\textsubscript{2}-urchin were given in Fig. 7. As the spectrum of O 1s shown in Fig. 7 (a), O 1s peaks were separated into three peaks in NiAl-NO\textsubscript{3}-LDH. Concerning the virgin and spent NiAl-S\textsubscript{4}@SiO\textsubscript{2}-urchin, the BE values range of 532.5–532.8 eV, 531.6–531.9 eV and 530.6–531 were accordingly assigned to hydroxyls of O\textsubscript{a}, NO\textsubscript{3} of O\textsubscript{b} and surface adsorbed oxygen from defect-site of O\textsubscript{c}, respectively. While after reaction under Hg\textsuperscript{0} atmosphere, all the peaks migrated left for about 0.3 eV, which indicated that there is oxygen vacancy involved in NiAl-NO\textsubscript{3}-LDH [41].

As shown in Fig. 7(b), the S 2p spectra peaks were separated into two peaks, among which the BE value range of 168.4–168.8 and 163.1–164 eV were accordingly assigned to SO\textsubscript{4}\textsuperscript{2-} and polysulfide, respectively. Compared with the NiAl-S\textsubscript{4}@SiO\textsubscript{2}-urchin under Hg\textsuperscript{0} atmosphere, the S 2p peak around 164 eV was almost absent. It implied that the S groups mainly existed as S\textsubscript{2} in HgS. The rise of the peak at 168.4–168.8 eV were attributed to the generated SO\textsubscript{4}\textsuperscript{2-} [42].

Fig. 7(c) showed that three peaks that belong to Hg 4f were detected. After reaction under Hg\textsuperscript{0} atmosphere, the BE value at 102.63 eV was assigned to Si, and the peaks centered at 104.63 and 100.43 eV were the characteristic peak of Hg 4f 5/2 and Hg 4f 7/2, respectively. For the NiAl-S\textsubscript{4}@SiO\textsubscript{2}-urchin under S–Hg mixed gas condition, there was no obvious change in its spectra. It could speculate that the polysulfides were combined with mercury to form HgS [35].

As shown in Raman patterns in Fig. 2(b), the S–S bonds disappeared in all LDH-S\textsubscript{4} samples after Hg adsorption. For the control sample of S\textsubscript{8}, the S–S bond stretching peaks remained nearly unchanged. Such spectra further indicated that the S–S bonds of the polysulfides in the interlayer space of the LDH structure were the driving force for the Hg capture through the formation of HgS.

Fig. 6. Effect of gas compositions on Hg\textsuperscript{0} removal efficiencies over different morphologies of NiAl-S\textsubscript{4}@SiO\textsubscript{2} materials. Mass of catalyst: 20 mg; time: 300 min; temperature: 100°C; total flow rate: 500 mL/min, concentration of mercury: 1.2 mg/m\textsuperscript{3}; gas components: 4% O\textsubscript{2}.

Fig. 7. XPS analysis for NiAl-S\textsubscript{4}@SiO\textsubscript{2}-urchin under and S–Hg adsorption and Hg adsorption: (a) O 1s; (b) S 2p; (c) Hg 4f.
Moreover, to further investigate the stability of $S\text-Hg$, Hg-TPD experiments were employed. The Hg-TPD curves were collected under the heating rate of 5 °C/min. After 80 min reaction, pure N2 was inlet at the temperature increasing from 100 to 500 °C. As shown in Fig. 8, the mercury desorption temperature was almost consistent around 200 °C. For the NiAl@SiO2 of different morphologies in Fig. S2, the mercury signal was not obvious due to the lower Hg$^0$ removal efficiency experiments.

Obviously, the intercalated $[S_4]^{2-}$ in NiAl@SiO2 layer had a high potential affinity for mercury driven by the strong tendency to react with $S-S$ bonds forming $S-S\text-Hg-S$ species and ultimately HgS. The mercury desorption temperature was almost consistent around 200 °C. For the NiAl@SiO2 of different morphologies in Fig. S2, the mercury signal was not obvious due to the lower Hg$^0$ adsorption capacity. This result accorded with the Hg$^0$ removal efficiency experiments.

Especially the NiAl-S4@SiO2-urchin showed unique physicochemical properties and remarkable influence on Hg$^0$ removal.

The theoretical adsorption mechanism can be deduced according to the formula of NiAl-S4@SiO2. Generally, the polysulfide of $[S_4]^{2-}$ consists $S^-\text-S$ and $S^2-$, in which $S^2-$ plays a main ingredient in the process of absorption mercury. However, the remnant $S^-\text-S$ has no affinity to mercury, and it is easily oxidized to form $SO_4^{2-}$ or $SO_3^{2-}$ in the basic LDH environment. Based on the above observations and the complexation chemistry of polysulfides, the mechanism of mercury capture can be described by Scheme 1 and Eqs. (2)–(4):

$$3\text{Hg}^0 + [S_4]^{2-} \rightarrow 3\text{HgS} + S^2-$$  \hspace{1cm} (2)

$$3\text{HgS} + S^2-\text-LDH \rightarrow 3\text{HgS} + SO_4^{2-}$$  \hspace{1cm} (3)

The total reaction of NiAl-S4@SiO2 with Hg$^0$ is:

$$3\text{Hg}^0 + S_4 \rightarrow 3\text{HgS} + SO_2$$  \hspace{1cm} (4)

Obviously, based on the XPS, Raman and Hg-TPD results, gaseous Hg$^0$ was adsorbed in the interlayer of NiAl-S4@SiO2 composite. Pure NiAl@SiO2 which has a porous structure can benefit gaseous Hg$^0$ adsorption. Such adsorption is mainly via a chemisorption mechanism and the interlayered $[S_4]^{2-}$ ions react with Hg$^0$ to form the stable HgS. Therefore, regeneration of the adsorbent is difficult to implement. However, mercury can be released from HgS through thermal decomposition method. It provides a method for mercury enrichment through spent NiAl-S4@SiO2 composite. Meanwhile, the unique structure and physicochemical properties of NiAl-S4@SiO2-urchin make it accommodate more polysulfides, which have a better resistance to the position of SO2.

### Table 2
EDX analysis of as-prepared samples.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Adsorption capacity (mg/g)</th>
<th>Si/O ratio</th>
<th>S ratio</th>
<th>Hg/S ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl-S4@SiO2-urchin</td>
<td>7.70</td>
<td>8.21</td>
<td>0.19</td>
<td>0.95</td>
</tr>
<tr>
<td>NiAl-S4@SiO2-core</td>
<td>6.25</td>
<td>6.95</td>
<td>0.42</td>
<td>0.72</td>
</tr>
<tr>
<td>NiAl-S4</td>
<td>1.92</td>
<td>2.14</td>
<td>0</td>
<td>0.28</td>
</tr>
<tr>
<td>$S_4$</td>
<td>1.20</td>
<td>1.21</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>NiAl-LDH</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 3
Mercury vapor adsorption capacity of various absorbents in this work and references.

<table>
<thead>
<tr>
<th>Materials</th>
<th>T (°C)</th>
<th>Surface area (m²/g)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl-S4@SiO2-core</td>
<td>100</td>
<td>14</td>
<td>6.25</td>
<td>This work</td>
</tr>
<tr>
<td>NiAl-S4@SiO2-urchin</td>
<td>100</td>
<td>28</td>
<td>7.70</td>
<td>This work</td>
</tr>
<tr>
<td>[MoS4]$^{2-}$/CoFe-LDH</td>
<td>100</td>
<td>112.08</td>
<td>1.39</td>
<td>[18]</td>
</tr>
<tr>
<td>WPL-HNO3</td>
<td>203</td>
<td>931</td>
<td>0.7</td>
<td>[19]</td>
</tr>
<tr>
<td>Mn-Fe spinel</td>
<td>100</td>
<td>128</td>
<td>0.75</td>
<td>[12]</td>
</tr>
<tr>
<td>SJFeS</td>
<td>80</td>
<td></td>
<td>&gt;2.73</td>
<td>[16]</td>
</tr>
</tbody>
</table>
Scheme 1. Ion exchange and reaction scheme of NiAl-S₄@SiO₂ and the binding modes of [S₄]²⁻ at different concentration regimes and proposed arrangements of interlayer species in LDH gallery.

4. Conclusions

In summary, NiAl-S₄@SiO₂ of two morphologies was successfully synthesized via an in-situ growth method. The SiO₂ and LDH host layer provide a stable environmental space for the interlayer polysulfide guests. The S–S bonds of the polysulfides are the driving force for Hg⁰ capture through the formation of HgS. The remaining S²⁻ ions are easily oxidized to SO₄²⁻, which further form SO₄-LDH. Such materials have a high Hg⁰ adsorption capacity with low BET surface areas. Meanwhile, the NiAl-S₄@SiO₂–urchin composite exhibits better performance in Hg⁰ capture and a higher SO₂ resistance capacity than the others due to the unique physico-chemical properties. Therefore, such incorporation of [S₄]²⁻ groups into LDH@SiO₂ materials might be highly attractive for Hg vapor capture and potential application in realistic natural gas conditions.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2018.10.062.

References
