Membrane-based gas separation exhibits many advantages over other conventional techniques; however, the construction of membranes with simultaneous high selectivity and permeability remains a major challenge. Herein, (LDH/FAS)$_n$-PDMS hybrid membranes, containing two-dimensional sub-nanometre channels were fabricated via self-assembly of unilamellar layered double hydroxide (LDH) nanosheets and formamidine sulfonic acid (FAS), followed by spray-coating with a poly(dimethylsiloxane) (PDMS) layer. A CO$_2$ transmission rate for (LDH/FAS)$_{25}$-PDMS of 7748 GPU together with CO$_2$ selectivity factors (SF) for SF (CO$_2$/H$_2$), SF(CO$_2$/N$_2$) and SF(CO$_2$/CH$_4$) mixtures as high as 43, 86 and 62 respectively are observed. The CO$_2$ permselectivity outperforms most reported systems and is higher than the Robeson or Freeman upper bound limits. These (LDH/FAS)$_n$-PDMS membranes are both thermally and mechanically robust maintaining their highly selective CO$_2$ separation performance during long-term operational testing. We believe this highly-efficient CO$_2$ separation performance is based on the synergy of enhanced solubility, diffusivity and chemical affinity for CO$_2$ in the sub-nanometre channels.
The separation of CO$_2$ is a crucial process for the purification of natural gas/syngas, flue gas recycling from thermal cracking and greenhouse gas mitigation. Membrane-based CO$_2$ separation possesses a number of advantages, such as high-efficiency, simple process/equipment and low energy consumption. Recently, two-dimensional (2D) nanosheet-based membranes have provoked wide attention for gas, liquid and ion separation. Molecules located in these membranes transport through slit-like pores between stacked nanosheets or via micropores in the nanosheets. The size of the channels and physicochemical properties of the building blocks play key roles in determining permeability and selectivity of these membranes. Porous 2D metal-organic framework (MOF) and zeolite-based membranes sieve gas molecules through their uniform micropores, while non-porous graphene oxide (GO), MXene and layered transition-metal dichalcogenide nanosheets are normally fabricated as layered-stacking membranes to achieve gas separation. Although excellent selectivity may be realised by such 2D membranes, they generally suffer from low permeability resulting from limited layered spacing and pore size. Most of these 2D nanosheet-based membranes can only successfully achieve the separation of one or two of the three important binary gas mixtures; CO$_2$/H$_2$, CO$_2$/N$_2$ and CO$_2$/CH$_4$. In addition, the high cost and poor reproducibility of these membranes hinder their practical application. Therefore, there is still an urgent unmet need to develop high-performance membranes with simultaneously CO$_2$ high selectivity and permeability using cost-effective methods.

Exfoliated layered double hydroxide (LDH) nanosheets are regarded as ideal building blocks for ultraslim membranes. Previously reported LDH membranes mainly used the interlayer CO$_2$–anion as the CO$_2$ carrier; it is not an efficient CO$_2$ transport carrier, and so leads to moderate CO$_2$ separation performance. Reassembly of LDH host nanosheets with suitable guest molecules to construct superlattice membranes is an approach to precisely adjust the gallery height from nanometre to sub-nanometre scale. In a key feature of LDH nanosheets is their CO$_2$-philic nature due to their inherent basicity to bind acidic CO$_2$. These physicochemical attributes allow us to facilitate CO$_2$ transport in LDH-based superlattice membranes. Another effective strategy to improve the permeability of CO$_2$ is the hybridisation with reactive carriers, such as amine and amide functional groups into the membranes by virtue of their reversible reactivity towards CO$_2$. However, the introduction of a large number of carrier pathways normally increases the disorder of the membranes, resulting in tortuous diffusion issues with resultant decreased transport rate for CO$_2$. One solution to this issue is the confinement of a CO$_2$ transport medium between lamellar-stacked LDH nanosheets to construct a highly oriented membrane with regular gas transport channels, to generate high-flux and highly selective gas permeability. However, such membranes have neither been proposed theoretically nor demonstrated experimentally.

Inspired by these concepts, we have fabricated 2D membranes with an ordered superlattice structure via alternating layer-by-layer (LBL) assembly of MgAl-LDH nanosheets and formamide sulfonic acid (FAS), followed by coating a thin layer of poly(dimethylsiloxane) (PDMS) (Fig. 1 and Supplementary Fig. 1). Size-dependent gas diffusion was enhanced by tuning the parallel-stacked 2D channels with a suitable interlayer spacing. Chemical-selectivity was realised through the basic sites on the surface of CO$_2$-philic LDH laminates and CO$_2$ binding via amide groups in the FAS layer. As a result, the synergistic effects among these functional elements induce an enhanced CO$_2$ separation performance, which surpasses the 2008 Robeson upper bound limits and most of the previous reports.

Results and discussion

Microstructure and morphology of MgAl-LDH nanosheets. Monolayer LDH nanosheets were obtained by exfoliating a bulk sample in formamide. Highly crystalline, MgAl(CO$_3$)$_2$-LDH platelets were first prepared by a urea-assisted hydrothermal method. X-ray diffraction (XRD) pattern of the MgAl(CO$_3$)$_2$-LDH (blue line in Fig. 2a) can be indexed as a prototypical layered structure exhibiting a harmonic series (0 0 l) of Bragg peaks at 2θ = 12.1°, 24.2°, 35.3°, 38.6°, 47.5° corresponding to the (003), (006), (012), (015), (018) Bragg reflections, respectively, in addition to Bragg peaks at 2θ = 61.4° and 62.8° that index as the (110) and (113) reflections of the CO$_3$–intercalated hydrotalcite phase. The interlayer CO$_2$–was exchanged for NO$_3$– by acid treatment under an N$_2$ atmosphere for ease of subsequent exfoliation. Compared with MgAl(NO$_3$)$_2$-LDH, the XRD pattern of MgAl(NO$_3$)$_2$-LDH (red line in Fig. 2a) shows a shift in the (003) Bragg reflection from 2θ = 12.1° to 10.1°, indicating interlayer expansion and successful replacement of CO$_3$– by NO$_3$–. Top-view (along c-axis) scanning electron microscopy (SEM) image (Fig. 2b) reveals a hexagonal structure and primary platelet diameters in the range 1–3 μm, consistent with the average particle size of ~1.2 μm obtained by the dynamic light scattering (DLS) analysis (Supplementary Fig. 2). After delamination in formamide, the characteristic Bragg peaks associated with bulk LDH disappear (Supplementary Fig. 3), indicating a complete exfoliation of LDH platelets. The thick MgAl(NO$_3$)$_2$-LDH platelets were exfoliated into single-layer nanosheets with a thickness of ~0.8 nm, which gives an aspect ratio (platelet diameter/platelet thickness) of these nanosheets of ca. 450 (Fig. 2c). Additionally, high-resolution transmission electron microscopy (HRTEM) image (Supplementary Fig. 4) indicates the ultrathin nature and uniform thickness of the delaminated LDH nanosheets.

Preparation of the (LDH/FAS)$_n$-PDMS membranes. These ultra-high aspect ratio LDH nanosheets and FAS were alternatingly deposited to fabricate (LDH/FAS)$_n$ membranes by a LBL assembly method. The thickness of the membrane was controlled by changing the bilayer number n. After drying at room temperature (~25°C) for 1 h, hydrated (LDH/FAS)$_n$ membranes were obtained due to the moisture-absorbing ability of the LDH nanosheets. A thin layer of PDMS was then deposited on the surface of (LDH/FAS)$_n$ to produce a locked-in heterostructure with consistent moisture content. The assembly process of the (LDH/FAS)$_n$ membranes was monitored by UV–Vis absorption spectroscopy. Figure 2d shows two absorption bands at 224 and 272 nm attributed to FAS, whose intensities increase almost linearly with the bilayer number (inset of Fig. 2d), indicating a successful step-by-step and controllable growth process. Fourier-transform infrared (FTIR) spectrum (Supplementary Fig. 5) of the as-prepared (LDH/FAS)$_n$ membranes exhibit strong absorption bands at 1640 and 3352 cm$^{-1}$, which are characteristic absorptions of C–N (thiol) and C–N (sulphydryl) functional groups from FAS, respectively. X-ray photoelectron spectroscopy (XPS) (Supplementary Figs. 6 and 7 and Table 1) indicates the formation of a strong electrostatic interaction between the anionic FAS and positively charged LDH nanosheets, we believe this strong interaction plays an important role in ensuring the stability of the membrane structure, which will be discussed later.

Top-view scanning electron microscopy (SEM) image (Fig. 3a) of the (LDH/FAS)$_{25}$ membrane reveals a densely covered surface without any visible defects or wrinkles. The optical image (Fig. 3a, inset) suggests good membrane homogeneity and flexibility. Side-view SEM image (Fig. 3b) shows a uniform membrane thickness of ~50 nm for (LDH/FAS)$_{60}$ with an interlocked lamellar structure. The cross-sectional HRTEM image (Fig. 3b, inset) reveals a high...
nanosheet preferred orientation, highly ordered sub-nanometre channels as result of periodic stacking of LDH nanosheets and FAS.

The powder XRD of the membrane (Fig. 3c) contains a Bragg reflection at $2\theta = 10.76^\circ$, which we attribute to a periodic repeat length of 0.82 nm from the assembled multilayer. The appearance of this broad Bragg diffraction feature demonstrates significant long-range order arising from parallel alignment of the LDH nanosheets on the substrate. The overall thickness of the structure may be obtained by multiplying the interlayer spacing and the number of bilayers, which is in good agreement with the result observed by cross-sectional SEM image. By subtracting the thickness of 0.48 nm for one single-layer LDH nanosheets, the distance between the adjacent LDH nanosheets is estimated to be 0.34 nm, as shown in Fig. 3d. In view of the kinetic diameter of CO$_2$ (0.33 nm), this gallery height is advantageous for the separation of CO$_2$ and other gases with kinetic diameters larger than this interlayer separation.

After coating with PDMS, the wettability of the hybrid membrane changed from hydrophilic to hydrophobic, the water contact angle increasing from 33.8° to 112.6° (Supplementary Fig. 8). Thermogravimetric analysis (TGA) (Supplementary Fig. 9) shows a large weight loss (~23%) at 100 °C for the (LDH/FAS)$_{25}$ membrane, indicating a highly hydrated state. Membranes with different numbers of assembly layers were also measured, these samples showed negligible % differences in weight loss from room temperature to 100 °C (Supplementary Fig. 10), indicating a similar presence of water content in (LDH/FAS)$_n$ membranes with different values of $n$. In contrast, the (LDH/FAS)$_{25}$-PDMS membrane only displayed ~2% weight reduction under the same conditions but does show a significant weight loss when heated above 120 °C. The inhibition of water desorption from the (LDH/FAS)$_{25}$-PDMS membrane is ascribed to a high water vapour barrier property of the hydrophobic PDMS coating. We found the retention of water within the (LDH/FAS)$_n$-PDMS membrane was an important attribute for the CO$_2$ separation performance, which will be discussed in the following sections.

**Fig. 1 Assembly of membranes.** Schematic representation for the fabrication of (LDH/FAS)$_n$-PDMS membranes.

**Fig. 2 Characterisation of LDH nanosheets and LBL assembly of (LDH/FAS)$_n$ membranes.**

- **a** XRD patterns of MgAl(CO$_3$)-LDH and MgAl(NO$_3$)-LDH.
- **b** SEM images of MgAl(NO$_3$)-LDH.
- **c** Tapping-mode AFM image and height profiles of single-layer MgAl-LDH nanosheets.
- **d** UV-Vis absorption spectra of the (LDH/FAS)$_n$ membranes (inset: the approximately linear relationship between absorbance at 272 nm and bilayer number $n$).
Gas separation performance. The permeance of individual gases through the (LDH/FAS)$_n$-PDMS membranes with different bilayer numbers ($n = 5 - 25$) was investigated. The permeance of H$_2$, N$_2$, CO$_2$ and CH$_4$ were measured, as these are the main components of natural gas, syngas, and flare gas from cracking. The gas transmission rate of an untreated poly(tetrafluoroethylene) (PTFE) substrate is $10^8$ GPU ($1$ GPU $= 1 \times 10^{-6}$ cm$^3$(STP) cm$^{-2}$ s$^{-1}$ cm Hg$^{-1}$), illustrating this substrate is almost fully permeable to these gas molecules. After deposition of the (LDH/FAS)$_n$-PDMS membranes, the transmission rates for H$_2$, N$_2$, CO$_2$ and CH$_4$ were all dramatically reduced with increasing $n$ from 5 to 25 (Fig. 4a) due to the introduction of a physical barrier$^{37,38}$. With $n = 5$, gas transmission rates were in the order H$_2$ > CO$_2$ > N$_2$ > CH$_4$. This indicates the gas transmission shows size-dependent selectivity when the membrane is thin, by considering the diameters of these gas molecules (H$_2$: 0.289 nm, CO$_2$: 0.33 nm, N$_2$: 0.364 nm, CH$_4$: 0.38 nm)$^9$. The CO$_2$ transmission rate (CO$_2$TR) of the (LDH/FAS)$_{25}$-PDMS membranes decreases at a lower rate than those of other gases when the bilayer number exceeds 10, because of the selective permeance of CO$_2$ molecules. The (LDH/FAS)$_n$-PDMS membranes with $n = 25$ shows high selectivity for CO$_2$ transport, with a CO$_2$TR of 7748 GPU that is remarkably higher than H$_2$TR (180 GPU), N$_2$TR (91 GPU) and CH$_4$TR (124 GPU) (green line in Supplementary Fig. 11).

The CO$_2$ selectivity for the (LDH/FAS)$_n$-PDMS membranes was evaluated by computing a relative selectivity factor (SF) (Eq. 1):

$$SF(CO_2/other\,gas) = \frac{CO_2TR}{GTR}$$ (1)

where CO$_2$TR is the CO$_2$ transmission rate, and GTR is the transmission rate of other gases (H$_2$, N$_2$ and CH$_4$). Upon increasing $n$ from 5 to 25, the (LDH/FAS)$_n$-PDMS membrane exhibits an enhanced SF(CO$_2$/H$_2$), SF(CO$_2$/N$_2$) and SF(CO$_2$/CH$_4$) from 0.6, 0.9 and 0.8 to 43, 86 and 62, respectively (Fig. 4a).

The separation performance of the (LDH/FAS)$_{25}$-PDMS membrane for CO$_2$/N$_2$ (Fig. 4b) and CO$_2$/CH$_4$ (Fig. 4c) is shown in the Robeson upper bound (2008) diagrams$^{31}$. Owing to the lack of Robeson upper bound in the CO$_2$/H$_2$ system, a permeability/selectivity map reported by Freeman et al.$^{39}$ in 2006 was applied to evaluate the CO$_2$/H$_2$ separation performance of our membrane (Fig. 3d). Comparison of these upper bound lines and with other membrane materials in the literature$^{40-46}$, the CO$_2$ permselectivity of (LDH/FAS)$_{25}$-PDMS membrane outperforms most of the reported systems and is higher than the Robeson or Freeman upper bound limits. These results reveal that the (LDH/FAS)$_{25}$-PDMS membrane overcomes the “trade-off” between permeability and selectivity, as so provides the basis for an efficient CO$_2$ separation material for industrial gas mixtures. Upon further increasing the bilayer number greater than 25, a downward trend in the permeance was observed. A bilayer number of 25 seems to strike the optimum balance between permeability and selectivity.

When a 1:1:1:1 mixture of H$_2$, N$_2$, CH$_4$ and CO$_2$ (25% by partial pressure) was exposed to the (LDH/FAS)$_n$-PDMS membranes the permeance for all these gases was lower than that for individual pure gas (brown line in Supplementary Fig. 11), due to the competitive adsorption of different gases$^{47,48}$. In spite of this, the (LDH/FAS)$_n$-PDMS membranes exhibited excellent CO$_2$ permselectivity for the four mixed gas systems. As shown in Fig. 5a, when the number of bilayers is low ($n = 5$), in the membrane transported gas was 33.1%, 22%, 25.2% and 19.7% for H$_2$, N$_2$, CH$_4$ and CO$_2$ respectively. With increasing membrane thickness, the penetration for all the gases decreases (Fig. 5b), similar to the results in pure gas. However, the permeance of H$_2$, CH$_4$ and N$_2$ decreases at much faster rates than
for CO$_2$, so overall the CO$_2$ selectivity increases (Fig. 5c) and the proportion of CO$_2$ in the filtered gas is far larger when $n = 25$. Upon increasing the bilayer number from 5 to 25, the proportions of H$_2$, N$_2$ and CH$_4$ decrease stepwise to 2.3%, 1.2% and 1.6%, respectively. In contrast, the proportion of CO$_2$ in the membrane filtered gas increases rapidly from 19.7% to 94.9% to ultimately give outstanding CO$_2$ selectivity. The (LDH/FAS)$_{25}$-PDMS membranes also show acceptable CO$_2$ permeance (1938 GPU) when $n = 25$.

**Gas separation mechanism.** Solubility and diffusivity are two key parameters for gas separation performance. An affinity for CO$_2$ for the membrane favours increased solubility selectivity. Preferential adsorption of the (LDH/FAS)$_{25}$-PDMS membrane was investigated using a mixture of CO$_2$/N$_2$. A typical adsorption isotherm is shown in Fig. 6a, which exhibits a much larger CO$_2$ adsorption than that of N$_2$. In addition, the CO$_2$ temperature programmed desorption (TPD) profile (Supplementary Fig. 12) of MgAl-LDH shows two maximum adsorption peaks at 158 °C and 176 °C, attributed to weak (hydroxyl groups on the LDH surface) and medium intensity (Mg$_2$(dobdc)) coordination) basic sites, respectively. The affinity between CO$_2$ and membrane was further confirmed by Fourier-transform infrared (FT-IR) spectroscopy (Supplementary Fig. 13), which shows $\delta$(CO$_2$)$_{oop}$ adsorption band at 835 cm$^{-1}$ (ascribed to the bicarbonate species) when the membrane was exposed to CO$_2$ atmosphere. These results indicate that LDH has a certain CO$_2$ adsorption capacity and can reversibly interact with the acidic CO$_2$, so that the CO$_2$ molecules can preferentially accumulate on the LDH nanosheets and move freely and quickly within the hybrid membrane.

We believe that sub-nanometre channels within the membrane can serve as sieving pathways for these gases, allowing only molecules smaller than the height of the channels to permeate. The alternate stacking of the LDH nanosheets and FAS yields a layer spacing of 0.34 nm, this creates a permeation cut-off when the molecular dynamic diameter of the gas is bigger than this value (CH$_4$ and N$_2$ in this study). In addition, the interlocked layered structure containing nanochannels parallel to the substrate is beneficial to reduce the out-of-plane defects and inhibits the diffusion of larger gas molecules. To provide further support for a size-sieving function for these 2D nanochannels, a pure LDH nanosheet stacked membrane was prepared using a vacuum filtration method (Supplementary Fig. 14). This membrane displays selectivity (Supplementary Fig. 15) for H$_2$ permeation using mixtures of either H$_2$/N$_2$ or H$_2$/CH$_4$. The ability of these LDH membranes to allow the permeation of H$_2$ but rejection to N$_2$ and CH$_4$ is entirely consistent with the free distance of 0.30 nm for these LDH membranes. This value lies so between the dynamic diameter of H$_2$ and N$_2$ or CH$_4$. Furthermore, we performed CO$_2$ separation performance experiments on a disordered NO$_3$-LDH/FAS-PDMS membrane and found that such membrane showed CO$_2$ permeability but poor CO$_2$/N$_2$ selectivity (Supplementary Fig. 16), which further indicates that the regular nanochannels between LDH layers are essential to achieve high-efficiency CO$_2$ separation.

The solution/diffusion coefficients of CO$_2$ and N$_2$ in the hybrid LDH/FAS membranes were investigated via the time-lag method. While the solubility coefficient and so penetration for CO$_2$ increases as the number of bilayers within the membrane increases (Supplementary Fig. 17) due to the accumulation of CO$_2$-philic LDH nanosheets. There is also a competing tortuosity/barrier effect, arising from horizontally oriented
LDH nanosheet. Therefore, the diffusion coefficients for both CO₂ and N₂ decrease (Supplementary Fig. 18) with increasing \( n \) due to the creation of an increased physical barrier of LDH nanosheets. However, the CO₂/N₂ diffusion coefficient ratio increases, because the nanosheets do not restrict the diffusion of the smaller CO₂ as much.

As discussed earlier, the transmission rate for CO₂ is much higher than that of H₂ when the number of bilayers within the membrane exceeds 10, in spite of the smaller molecular size of H₂. This counterintuitive behaviour suggests other factors may be facilitating CO₂ transport. We believe FAS can act as an effective CO₂ carrier because of the reversible reaction between the amidine groups and CO₂ in aqueous solution\(^5\)\(^4\)\(^-\)\(^6\), as shown in Equation 2 below:

\[
\text{FAS} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{FAS} \cdot \text{HCO}_3^- + \text{H}_2\text{O}
\]

To probe the role of FAS for CO₂ transport, we studied the interaction between CO₂ and the thin membrane. In situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was used to monitor the membrane during CO₂ diffusion. Figure 6b shows the intensity of the absorption bands due to the protonated C=\( N \) group (1652 cm\(^{-1}\)) and bicarbonate (1599 cm\(^{-1}\))\(^3\)\(^5\) increase when CO₂ is exposed to the membrane. In addition, the intensities of two broad absorption bands assigned to bidentate carbonate and bicarbonate at 1310 and 1190 cm\(^{-1}\) derived from the CO₂ adsorption onto the LDH\(^5\)\(^7\)\(^,\)\(^8\), also increased. When He was introduced instead of CO₂, the intensities of these peaks gradually returned to the original intensities. These results indicate that the amidine groups within the membrane are reactive to CO₂ with high reversibility, and these groups actively contribute to the high-efficiency of the membrane for CO₂ separation. In addition, Supplementary Fig. 19 shows the CO₂ permeance of the (LDH/FAS)\(_n\)-PDMS membrane decreases with the increase of feed pressure and the decreasing trend slows down under high pressure, further confirming the permeation of CO₂ follows facilitated transport mechanism due to the reversible reaction as shown in Equation 2.

In order to further probe the apparent CO₂-facilitated transport through these (LDH/FAS)\(_n\)-PDMS membranes, we conducted temperature-dependent permeation at 27 kPa. The
adsorption and subsequent He adsorption (within 2 min) transport of CO2. As discussed above, the reversible reaction structure with PDMS plays an important role in the selective using the LBL process, the subsequent coating of this hybrid layer temperature. These results indicate an increase in CO2 perme-

Fig. 6 Study on CO2 selective transmission mechanism. a Pure-component CO2 and N2 adsorption in (LDH/FAS)25-PDMS membrane. b In situ DRIFTS spectra of (LDH/FAS)25-PDMS membrane upon CO2 (within 0–2 min) adsorption and subsequent He adsorption (within 2–5 min).

effect of temperature on CO2 permeability and CO2/N2 selectivity is shown in Supplementary Fig. 20, we also investigated the activation energy for CO2 permeation. The permeability of CO2 increases exponentially with increasing temperature and follows an Arrhenius relationship, indicating activated diffusion of CO2 in the membrane. The activation energy for CO2 diffusion in the (LDH/FAS)25-PDMS membrane is at least 8.0 kJ mol⁻¹ higher than that of N2 (see Supplementary Information), which results in the trend of increasing selectivity of CO2/N2 with increasing temperature. These results indicate an increase in CO2 permeability caused by the facilitated transport is much faster than the increase in N2 permeability induced by thermally activated diffusion rates.

Following the construction of alternating (LDH/FAS)n layers using the LBL process, the subsequent coating of this hybrid layer structure with PDMS plays an important role in the selective transport of CO2. As discussed above, the reversible reaction between CO2 and FAS requires water, and so the PDMS coating plays a key role as a moisture vapour-blocking layer, inhibiting diffusion loss of water within the membranes. Without PDMS coating, the (LDH/FAS)n membranes would rapidly dehydrate when heated at ~50 °C for 30 min (the same drying condition to obtain PDMS coated membranes).

To investigate the influence of water content on the separation performance of the (LDH/FAS)n membranes, a series of (LDH/FAS)n membranes with different degrees of hydration were prepared by controlling the drying temperature (Supplementary Table 2). Upon decreasing the membrane water content (25–0%), the CO2 permeance drops dramatically from 7748 to 217 GPU. These results confirm that the presence of water is a key component in facilitating transport in these membranes.

The gas transport behaviour of a fully dehydrated (LDH/ FAS)25 membrane for H2, N2, CH4 was also investigated. We find that this membrane still shows a molecular sieving effect (Supplementary Fig. 21). The temperature dependence (25–80 °C) of the selectivity of CO2 vs. N2 for the fully dehydrated (LDH/FAS)25 membrane did not change whereas the permeability of CO2 and N2 doubled (Supplementary Fig. 22). In the absence of water, gas permeability is thought to be just thermally activated.

Although (LDH/FAS)n-PDMS membranes are thermally robust, heating to 150 °C for 30 min results in decreased membrane performance (Supplementary Fig. 23). (LDH/FAS)n-PDMS membranes can retain the necessary degree of hydration within the membrane structure and so can effectively operate with a dry gas feed. Typically, the presence of water vapour in feed gas condenses on membrane surfaces or pores, which deteriorates the permeability or selectivity of membrane materials. Pure PDMS membranes exhibit high gas permeance but low permselectivity for CO2 (Supplementary Fig. 24), which further supports the suggestion that the primary function of PDMS is preventing water evaporation from the hydrated membrane without unduly affecting the gas permeation.

The selective transmission of CO2 is ascribed to be based on the synergy of solubility selectivity, diffusivity selectivity and reaction selectivity. For larger molecules, such as CH4 and N2, their transmission is selectively blocked by the sub-nanometre channels and the barrier effect imposed by the LDH nanosheets. As a result, their transmission follows the classic solution-diffusion mechanism. For H2 with a smaller size than the height of channels, it is not adequately blocked by the sub-nanometre channels and LDH nanosheets, and some H2 penetrates the membrane. Facilitated transport, as introduced by FAS provides reaction selectivity of CO2. Taking into consideration these different factors, high-efficiency CO2 separation is achieved using (LDH/FAS)n-PDMS membranes.

In order to investigate the potential practical applications of (LDH/FAS)n-PDMS membranes, a series of operational stability tests were conducted. Supplementary Fig. 25 illustrates that the (LDH/FAS)n-PDMS membrane maintains the high separation performance of CO2/H2, CO2/N2 and CO2/CH4 during a 120 h operational test. Meanwhile, the membrane does not exhibit obvious surface damage (Supplementary Fig. 26) after continuous gas permeation for 120 h, indicating good chemical compatibility and high mechanical stability. Even treated under a higher temperature of 80 °C, the (LDH/FAS)n-PDMS membrane is still intact without defects and the building units are well-bonded with each other without falling off, demonstrating good thermal stability (Supplementary Fig. 27). The remarkable stability may be attributed to the creation of strong electrostatic anion-layer interactions by partial deprotonation of the FAS. However, to achieve industrial application, the energy consumption and environmental impacts for the separation process should be evaluated using life cycle assessment and energetic analysis method. The regeneration of fouled membranes should also be considered, such as by thermal regeneration or chemical regeneration techniques. To provide further support to the significant role of the electrostatic interaction between the building units in these 2D heterostructures, new membranes were prepared by using graphene oxide (GO) instead of the LDH
nanosheets via the same fabrication method to give (GO/FAS)\(_n\)-PDMS.

The XRD of the (GO/FAS)\(_n\)-PDMS membranes displayed a Bragg reflection corresponding to a d-spacing of 0.76 nm (Supplementary Fig. 28). By subtracting the thickness of a GO layer (0.35 nm) we can estimate the interlayer channel thickness. The channel thickness in (GO/FAS)\(_n\)-PDMS is larger (0.41 nm) than that of (LDH/FAS)\(_n\)-PDMS (0.34 nm). We attribute this to the absence of any significant electrostatic interactions between GO and FAS (Supplementary Fig. 29 and Table 3). We also find that (GO/FAS)\(_n\)-PDMS membranes exhibit poor stability during long-term gas permeation tests (Supplementary Fig. 30). Furthermore, very small differences between the permeation of H\(_2\), CO\(_2\), N\(_2\), and CH\(_4\) through (GO/FAS)\(_n\)-PDMS membranes are observed.

In conclusion, we show that single-layer LDH nanosheets and FAS superlattice structures fabricated by LBL assembly can be effective CO\(_2\) separation membranes. The membrane performance was optimised by controlling the balance between gas barrier and transmission. The PDMS coated membrane, (LDH/FAS)\(_n\)-PDMS exhibits excellent CO\(_2\) preferential permeability over either N\(_2\), CH\(_4\), or H\(_2\). Furthermore, the (LDH/FAS)\(_n\)-PDMS membranes are mechanically robust and maintain their high separation performance during long-term operational testing. By considering the building units are all cheap industrial raw materials, and the membranes are easy to prepare on various substrates, it is possible to realise large-scale membrane manufacture.

We believe these hybrid lamellar membrane heterostructures hold great potential for CO\(_2\) capture and separation.

**Methods**

**Reagents and materials.** Formamidine sulfonic acid (FAS) and poly(dimethylsiloxane) (PDMS) with a molecular weight of ~50,000 were purchased from Aladdin (Beijing, China). PTFE substrates (thickness: ~200 µm; average pore size: ~220 nm) were obtained from Sigma-Aldrich company. Single-layered graphene oxide (GO) (Beijing, China). Deionized water was used in all the experiments.

**Synthesis of MgAl-LDH nanoplates.** MgAl(CO\(_3\))\(_2\)-LDH nanoplates were synthesised by an urea-assisted hydrothermal method\(^{25}\). Typically, Al(NO\(_3\))\(_3\), Mg(NO\(_3\))\(_2\), urea, and water were mixed and stirred under the N\(_2\) gas flow for 24 h. The resulting MgAl(NO\(_3\))\(_2\)-LDH nanoplates were centrifuged, washed, and vacuum-dried.

**Exfoliation of LDH nanoplates into monolayer nanosheets.** In all, 0.1 g MgAl(NO\(_3\))\(_2\)-LDH was strongly agitated in 100 mL formamide for 48 h. A colloidal suspension of positively charged and unilaminar MgAl-LDH membrane was successfully prepared with a concentration of 1 g L\(^{-1}\).

**Fabrication of the (LDH/FAS)\(_n\)-PDMS membrane.** The layer-by-layer (LBL) deposition and spray-coating techniques were adopted to fabricate the (LDH/FAS)\(_n\)-PDMS membranes. Quartz glass and silicon wafer were used as substrates for UV–Vis spectra, SEM and AFM characterisation, respectively. The PTFE substrate was chosen for the other measurements. Prior to deposition, quartz glass and silicon wafer were washed in ethanol, acetone, and deionized water for 15 min, respectively. The PTFE substrate was washed using deionized water for 5 min. The glucose monomethoxypyruvate was used as the polymerization substrate and the substrates were dipped in the resulting MgAl(NO\(_3\))\(_2\)-LDH colloidal suspension (1 mg mL\(^{-1}\)) for 10 min followed by washing thoroughly, and then the substrate was immersed into FAS aqueous solution (2.0 L\(^{-1}\)) for 10 min. The (LDH/FAS)\(_n\)-PDMS membranes were fabricated by alternating deposition of LDH nanosheets and FAS for n cycles. The as-prepared (LDH/FAS)\(_n\)-PDMS membranes were dried at room temperature (~25 °C) for 1 h unless otherwise stated. Ultimately, a thin layer of PDMS was deposited on the (LDH/FAS)\(_n\)-PDMS membrane surface using an airbrush style spray-gun (3 applications) and a spin-coater (1000 rpm, 1 min). The obtained (LDH/FAS)\(_n\)-PDMS membranes were dried at 50 °C for 30 min.

**Fabrication of the disordered NO\(_3\)-LDH/FAS-PDMS membrane.** FAS aqueous solution (2.0 g L\(^{-1}\)) was added into MgAl(NO\(_3\))\(_2\)-LDH suspension (1.0 g L\(^{-1}\)) with a volume ratio of 1:1, followed by stirring at room temperature for 12 h. Then the NO\(_3\)-LDH/PDMS dispersion was cast on PTFE substrate to prepare composite membranes. The NO\(_3\)-LDH/PDMS membrane was dried at room temperature (~25 °C) for 1 h. Ultimately, a thin layer of PDMS was deposited on the NO\(_3\)-LDH/PDMS membrane via spray and spin coating steps.

**Fabrication of pure LDH membrane.** The LDH membrane was prepared by depositing a colloidal suspension of MgAl(NO\(_3\))\(_2\)-LDH (1 g L\(^{-1}\)) on PTFE substrates using vacuum-assisted suction filtration. The as-prepared LDH membranes were dried at room temperature (~25 °C) for 1 h.

**Fabrication of (GO/FAS)\(_n\)-PDMS membranes.** A similar method combining LBL deposition and spray-coating was applied to prepare (GO/FAS)\(_n\)-PDMS membranes for comparison study, using GO colloidal suspension (1 g L\(^{-1}\)), FAS aqueous solution (2 g L\(^{-1}\)), and PDMS solution.

**Characterisation techniques.** XRD patterns were recorded by a Rigaku XRD-6000 diffractometer, using Cu Ka radiation (λ = 0.1342 nm) at 40 kV, 30 mA. The UV–Vis absorption spectra were collected in the range 200 – 800 nm on a Shimadzu UV-3000 spectrophotometer. The morphology was investigated using a scanning electron microscope (SEM; Zeiss SUPRA 55) with an accelerating voltage of 20 kV, a FEI Cs-corrected Titan 80–300 high-resolution transmission electron microscope (HRTEM) operated at 300 kV and a NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments. The FT-IR spectra were performed using a Vector 22 (Bruker) spectrophotometer with 2 cm\(^{-1}\) resolution. In situ DRIFTS of CO\(_2\) and N\(_2\) was performed on a VERTEX 70 (Bruker Company) spectrometer equipped with MCT narrowband detector and an in situ reaction cell. The pre-processing and testing details are as follows. Firstly, the membrane was carefully placed onto the support sheet of the reaction cell. Secondly, the sample was pre-processed in a He flow (50 mL min\(^{-1}\)) at 80 °C with a heating rate of 5 °C min\(^{-1}\), followed by 20 min of purification (50 mL min\(^{-1}\)) for 1 h and cool to 25 °C. Subsequently, CO\(_2\) was introduced into the cell, and then DRIFTS was collected every 30 s until the CO\(_2\) adsorption signal remained unchanged. Finally, the gas flow was switched to high-purity He to collect desorption spectra every 30 s. Thermogravimetric analysis (TGA) was performed with a HCT-1 differential thermal gravimetric analyser (Beijing Herwen Scientific Instrument Factory, Beijing, China). The particle size distribution of LDH nanoparticles was measured with a Malvern Mastersizer 2000 analyser (Malvern Instruments Ltd., Malvern, UK). The gas (H\(_2\), N\(_2\), CO\(_2\), and CH\(_4\)) transmission rates were measured using a VAC-V2 gas transmission rate testing system (Lablink Instruments Co., Ltd, Jinan, China). Solution/diffusion coefficients were obtained by Basic 201 gas transmission rate testing system (Lablink Instruments Co., Ltd., Jinan, China) via the time-lag method\(^{25}\).

**Data availability**

The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files.
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Author contributions
J.H. conceived the concept. X.X. and J.W. conducted the experiment and analysed the results. A.Z., S.D., B.L. and K.S. assisted in gas separation measurement. X.X. and J.H. wrote the paper and prepared the figures. All authors discussed the results. D.O’H co-supervised the research and revised the manuscript.

Competing interests
The authors declare no competing interests.

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