Metal Confined in 2D Membranes for Molecular Recognition and Sieving towards Ethylene/Ethane Separation

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Membranes with nanochannels have exhibited great potential in molecular separations, while it remains a great challenge to separate molecules with very close physical properties and kinetic diameters (e.g., ethylene/ethane) owing to the lack of size-sieving property and specific affinity. Herein, a metal confined 2D sub-nanometer channel is reported to successfully discriminate ethylene over ethane via molecular recognition and sieving. Transition metal cations are paired with polyelectrolyte anions to achieve high dissociation activity, forming reversible complexation with ethylene. Aberration-corrected transmission electron microscopy observes that the metals with size of \( \approx 0.44 \text{ nm} \) are uniformly confined in graphene oxide (GO) interlayer channels with average height of \( \approx 0.44 \text{ nm} \), thereby cooperating the size-sieving effect with a molecular recognition ability toward ethylene and stimulating its selective transport over ethane. The resulting ultrathin (=60 nm) membrane exhibits superior ethylene/ethane separation performance far beyond the polymeric upper-bound. Density functional theory (DFT) and molecular dynamic simulations reveal that the metal@2D interlayer channel provides a molecular recognition pathway for selective gas transport. The proposed metal confined in 2D channel with molecular recognition and sieving properties would have broad application in other related fields such as single-atom catalysis, sensor and energy conversion.

1. Introduction

In the recent decade, 2D materials, including graphene and derivatives,[1] transition metal carbide/nitride (MXene),[2] metal-organic framework (MOF),[3] and covalent organic framework (COF)[4] nanosheets, have emerged as prominent building blocks for high-performance separation membranes.[5] By manipulating the size and functionality of nanochannels, 2D-material membranes have exhibited extraordinary performance in molecular separations including water purification[6] and gas separation.[7] Nevertheless, it remains a grand challenge for 2D-material membranes to separate mixtures of molecules with extremely close physical properties and kinetic diameters owing to the lack of size-sieving properties and specific affinity of the 2D nanochannels. For instance, towards ethylene/ethane separation, the current distillation technology is very energy-consuming and concurrently increases carbon dioxide emissions.[8] It is considered as one of the seven chemical separations that if improved can reap great global benefits.[9]

The most widely investigated membrane material for ethylene/ethane separation is a carbon molecular sieve (CMS), which possesses ultramicropores with molecular sieving properties.[10] However, the relatively low mechanical strength and aging problem might restrict its development. An alternative is developing ethylene or ethane-selective adsorbent,[11] which is based on designing specific interactions towards targeted molecules. Until now, there is no reported membrane material having both molecular sieving and specific interaction properties for efficient ethylene/ethane separation.

Molecular recognition is some of the most significant features of chemical and biological systems.[12] The recognition effect stems from specific noncovalent interactions, including hydrogen bonding, metal coordination, van der Waals forces, and \( \pi-\pi \) interactions. The most common recognition motif is between antibodies and aptamers,[13] where the key lies in a unique structure formed by a folded and constrained bioheteropolymer that creates a binding pocket/interface able to recognize a specific molecule. Such exquisite molecular complementarity between antibodies and aptamers inspires us to mimic their structure and feature to construct 2D channels with optimized geometry and chemistry configurations for gaining improved molecular discrimination properties.

Herein, we design novel metal-confining 2D sub-nanometer channels with molecular recognition and precise size-sieving for discriminating ethylene over ethane (Scheme 1). Graphene oxide (GO) nanosheets are assembled into 2D channels with precisely controlled sub-nanometer interlayer height to discriminate planar ethylene (4.84 Å \( \times 4.18 \text{ Å} \times 3.28 \text{ Å} \)) over stereoscopic ethane (4.82 Å \( \times 4.08 \text{ Å} \times 3.81 \text{ Å} \)) by the size difference of 0.53 Å along the c axis (Figure S1 and Table S1, Supporting
Information). Meanwhile, transitional metal ions, which serve as the binding sites and could efficiently recognize ethylene with unsaturated C=C bonds via reversible π complexation, are confined in the size-sieving 2D sub-nanometer channels, thereby further stimulating the ethylene transport over ethane.

Constructing such hypothetical ethylene-selective channels faces two main challenges: i) The interlayer sub-nanometer channels with size-sieving properties would be easily destroyed as introducing metal cations into 2D sub-nanometer channels due to the strong cation-π interaction with GO[14] and the formation of metal salt nanocrystals.[15] Single metal atom has been successfully anchored on the 2D base plane of graphene for catalytic applications.[16] Nevertheless, to the best of our knowledge, anchoring atomic-level metal in 2D confined sub-nanometer channels have not yet been reported. ii) It remains elusive for metal cations to establish efficient reversible π complexation to stimulate ethylene transport because it depends on both orbital property of cations and binding energy of their counter ions.[17] The orbital property of cations would influence the molecular orbital of cation-ethylene complex and thus the strength of π complexation. Moreover, the high binding energy between cations and counter ions would suppress the dissociation of cations and sacrifice the recognition capability.

To address the abovementioned challenges, in this work, we introduce the polyelectrolyte as the medium between GO and metal to construct highly ordered metal-confining 2D channels. The metal cations were rationally paired with polyelectrolyte counter ions having weak electrostatic interaction rather than strong ionic bonds in commonly used metal salt, thereby promoting the dissociation of cations to recognize ethylene molecules via reversible π complexation. Meanwhile, by various molecular interactions (Scheme 1), the polyelectrolyte bridging GO and metal cations enabled the cations to be atomic-level decorated on GO nanosheets, thereby preserving the sub-nanometer structure and size-sieving property of 2D channels. By establishing the synergistic effect of size-sieving and molecular recognition, the metal@GO sub-nanometer channels can efficiently discriminate ethylene over ethane during the continuous membrane separation process.

2. Results

2.1. Morphology

Ag@GO membrane was fabricated on polyether sulfone (PES) substrate (Figure S2, Supporting Information) via ion exchange combined with vacuum filtration method (Figure S3, Supporting Information). The GO solution for membrane fabrication exhibited a Tyndall effect due to light scattering of GO nanosheets uniformly dispersed in water (Figure S4a, Supporting Information). AFM image and particle size distribution via dynamic light scattering (DLS) showed that the lateral size of GO nanosheets was ≈1 µm (Figure S4b,c, Supporting Information), and the thickness of nanosheets was ≈1 nm. Importantly, we paired Ag⁺ with the polyelectrolyte, polystyrene sulfonate (PSS, Figure S5a, Supporting Information), instead of commonly used BF₄⁻ with two advantages: i) It contributes to the highly ordered GO laminates because the anchoring property of SO₃⁻ suppresses the aggregation of silver nanoclusters into large nanocrystals. ii) it is beneficial to the atomic-level distribution of silver ions, maximizing the efficiency of Ag@GO channels for recognizing and transporting ethylene. These two points would be confirmed by following aberration-cor-

Scheme 1. Metal confined in 2D sub-nanometer channel for stimulating ethylene transport over ethane. The magnified areas demonstrate the size-sieving property and the molecular recognition effect of 2D channels, which are enabled by the bridging effect of polyelectrolytes. The blue, green, and red dash lines correspond to cation–π interaction, hydrogen bonding, and electrostatic interaction, respectively. The blue, red, yellow, and white spheres correspond to metal, O, S, and H, respectively.
rected transmission electron microscopy (AC-TEM) images. As a control, AgBF₄ was selected to fabricate AgBF₄/GO membrane via directly mixing and filtration. However, this method leads to the generation of large AgBF₄ nanocrystals in membranes, leading to disordered and non-selective GO channels (Figure 1a). AC-TEM images of AgBF₄/GO membrane from different spots showed the GO laminates aligned in various orientations (Figure 1b and Figure S6, Supporting Information), which would sacrifice the sieving property. By contrast, pairing Ag⁺ with PSS contributed to highly ordered GO laminates with an interlayer height of ≈0.44 nm in Ag@GO membranes. It exactly lies between the molecular kinetic dimeters of ethylene.

![Diagram](image)

**Figure 1.** Distribution state of metal in 2D channels. a,f) Schematics of disordered and non-selective GO channels (a) and highly ordered and C₂H₄-selective GO channels (f). b,g) AC-TEM images of GO channels with various orientations in AgBF₄/GO membrane (b) and highly ordered GO channels with one orientation (g). The yellow dashed arrows are eye-guiding lines indicating the orientations of GO. c) AC-TEM image, d) HAADF image of aggregated AgBF₄ nanocrystals, and e) corresponding EDS mapping of Ag element in AgBF₄/GO nanocomposite. h) AC-TEM image, i) HAADF image of silver nanoclusters, and j) corresponding EDS mapping of Ag element in Ag@GO nanocomposite. k) Digital photos of PES-supported Ag@GO membrane, and the inset shows the membrane bent by tweezers. l) Surface and m) cross-sectional SEM images of Ag@GO membrane.
(0.416 nm) and ethane (0.444 nm) and thus could discriminate ethylene over ethane.

The distribution state of silver ions within 2D sub-nanometer channels is critical to realizing the efficient recognition towards ethylene. As shown in Figure 1c and Figure S7, Supporting Information, silver ions tended to aggregate and form nanocrystals on GO nanosheets in the AgBF₄/GO sample. The lattice fringe was 0.223 nm, corresponding to (220) lattice plane of AgBF₄ phase. The HAADF image and corresponding EDS mapping (Figure 1d,e and Figure S8, Supporting Information) showed many light spots assigned to the high-number-element silver, indicating a non-uniform distribution of AgBF₄ nanocrystals in the AgBF₄/GO membrane. The nanocrystals could form a strong interaction force with GO nanosheets and generate non-selective defects in the GO lamimates. In terms of the complexation effect toward ethylene, the ionically bonded AgBF₄ nanocrystals could possess relatively little dissociated Ag⁺ compared with the electrostatically paired Ag⁺ in Ag@GO membrane, leading to the poor reversible interaction toward ethylene.

Interestingly, by replacing BF₄⁻ with PSS chain, the uniform distribution of silver nanoclusters in membranes was achieved. As shown in Figure 1h, silver nanoclusters with size of ~2–3 nm were attached to the typical honeycomb structure of the graphitic region, confirming the existence of Ag@GO architecture. Moreover, the HAADF image and corresponding EDS mapping of Ag@GO sample further confirmed the atomic-level distribution of silver nanoclusters (Figure 1i,j). The above results demonstrate that the metal@GO strategy realized the homogeneous distribution of silver nanoclusters confined in 2D sub-nanometer channels, which is beneficial to recognizing ethylene and stimulating its transport.

The morphology of Ag@GO nanochannel membrane was further characterized. The digital photos of Ag@GO membrane showed a brown separation layer uniformly distributed on the substrate (Figure 1k). The bent membrane maintained its structural integrity, indicating the membrane flexibility and good adhesion between the ~60 nm membrane layer with a smooth surface (Figure 1l,m) and substrate. To explore the distribution of silver nanoclusters inside the membrane, a thicker Ag@GO membrane (~330 nm) layer was fabricated (Figures 9 and S10, Supporting Information), showing an ordered laminar structure. EDS mapping images of the selected area demonstrated a uniform distribution of Ag, S, C, and O elements in the Ag@GO membrane. In addition, the polarized light image (Figure S11, Supporting Information) demonstrated a more regular orientation of GO nanosheets within Ag@GO membrane than AgBF₄/GO membrane, again confirming the formation of highly ordered 2D sub-nanometer channels.[38] The results suggest that the strategy of Ag@GO is critical to reducing the aggregation of silver nanoclusters and contributes to the well-defined 2D channels for ethylene/ethane separation.

2.2. Physico-Chemical Properties

We characterized the interlayer height of 2D channels, the structural property, and the functional group of GO and Ag@GO membranes. XRD patterns of the membranes and the corresponding interlayer height calculated based on Bragg equation[19] are shown in Figure 2a. With the introduction of silver into the interlayer channels of GO membranes, the d-spacing of Ag@GO membrane was nearly maintained at 0.78 nm, indicating the introduction of silver would not affect the ordered structure of 2D sub-nanometer channels. The flexibility of GO nanosheets could allow a portion of interlayer channels to be sub-nanometer.[19d] Since graphene thickness (0.34 nm) accounts for a part of the d-spacing, the height of empty space between GO nanosheets (interlayer height) was calculated to be 0.44 nm, which was consistent with the previous TEM characterization. The interlayer heights of PSS/GO and AgBF₄/GO membranes slightly expanded to 0.45 and 0.46 nm, respectively, corresponding to the sacrificed size-sieving property. The pattern of AgBF₄/GO membrane showed the highest FWHM (full width at half maximum) of 1.74° (Table S2, Supporting Information), corresponding to the disordered nanostructure stemming from large AgBF₄ nanocrystals.[20]

The FTIR spectra demonstrated the peak shift of the asymmetric vibration absorption of SO₃⁻ in Ag@GO membranes (Figure 2b), confirming the existence of hydrogen bonding between SO₃⁻ groups and oxygen-containing groups of GO nanosheets.[21] In the XPS spectra (Figure S12, Supporting Information), new peaks corresponding to S 2p region and C=S bond were observed in the spectrum of Ag@GO membrane, confirming the introduction of PSS containing SO₃⁻ into the membrane. Moreover, as shown in Figure 2c, the binding energies of Ag 3d₃/2 and Ag 3d₅/2 of Ag@GO membrane shifted toward higher positions (374.66 and 368.66 eV) compared with those of AgBF₄/GO membrane (374.14 and 368.14 eV). This result suggests an enhancement of positive charge density of silver nanoclusters by substituting PSS for BF₄⁻, which would be beneficial to the reversible complexation and more efficiently recognize ethylene.[22] The peak assigned to C=O bond shifting from 286.8 to 286.5 eV (Figure S13, Supporting Information) confirmed the hydrogen bonding between hydroxyl groups from GO nanosheets and SO₃⁻ groups from PSS chain,[21] which was consistent with FTIR spectra (Figure 2b).

The structural properties of membranes were further characterized by Raman spectroscopy, which is sensitive to distinguishing ordered and disordered carbon structures. By comparing the Raman spectra of membranes fabricated by different methods (Figure 2d and Figure S14, Supporting Information), it suggests that the vacuum filtration method employed for Ag@GO membranes contributes to less defects in membranes.[24] Comparing the digital images (Figure S15, Supporting Information), SEM and AFM images (Figure S16, Supporting Information) of these membranes, the Ag@GO membrane showed the most ordered laminar structure and smoothest membrane surface (Table S3, Supporting Information), which is beneficial to the construction of sub-nanometer channels for ethylene-selective permeation.

2.3. Gas-Transport Properties

The permeation of gas molecules with different kinetic diameters (H₂, CO₂, N₂, CH₄, C₂H₆, and C₃H₈) through AgBF₄/GO and Ag@GO membranes was evaluated (Figure 3a). It
demonstrated that both the permeation rates of CO₂ and C₂H₄ molecules were higher in Ag@GO membrane owing to the effective recognition by dissociated silver ions. Moreover, the effects of GO deposition amount (Figures S17 and S18, Supporting Information) and silver loading (Figure 3b, Tables S4 and S5, Supporting Information) on the ethylene/ethane separation performance were investigated to optimize 2D channels of Ag@GO membranes. We found Ag@GO membrane containing 34 wt% silver (Ag@GO-34) exhibited the highest performance with ethylene permeance of 46.7 GPU and ethylene/ethane separation factor (SF) of 12.3. To understand the critical role of metal@GO structure, we further compared the ethylene/ethane separation performance of pristine GO membranes, AgBF₄/GO membranes fabricated by different methods, and Ag@GO membranes (Figure 3c). It suggests that the ethylene/ethane SF of GO membrane was undesirable, although the interlayer height of 2D channels ideally could discriminate ethylene over ethane. The result implies the great challenge that even tiny defects in 2D channels would sacrifice the size discrimination property,[25] especially for the ethylene/ethane gas pair with only 0.28 Å difference in molecular kinetic diameters. For comparison, the ethylene permeance of layer-by-layer AgBF₄/GO and post-treated AgBF₄/GO membranes was quite high while the SF is ≈1, which was attributed to large defects on the membranes (Figure S16, Supporting Information) owing to the strong cation-π interaction and generation of large salt crystals. The AgBF₄/GO membrane exhibited both low ethylene permeance and SF, which could be attributed to non-selective wrinkles from the electrostatic interaction between AgBF₄ nanocrystals and GO nanosheets and the low dissociation degree of Ag⁺ in aggregated nanocrystals (Figure S16, Supporting Information, and Figure 1c).

It is worth mentioning that the Ag@GO membrane with a smooth surface possessed prominently enhanced separation performance (ethylene/ethane SF > 12) owing to the uniform distribution of atomic-level silver (Figure 1i,j) and easier...
Figure 3. Membrane \( C_2H_4/C_2H_6 \) separation performance. a) Gas-transport properties of AgBF\(_4\)/GO and Ag@GO membranes. The inset shows ethylene/ethane separation performance of two membranes, and the GO deposition is 0.2 mg. b) Effects of mass fraction of silver in membranes on the ethylene/ethane separation performance of Ag@GO membranes. c,d) Effects of various membrane fabrication methods (c) and different kinds of metal cations/counter ions (d) on the ethylene/ethane separation performance of membranes. The GO deposition is 0.6 mg. e) Continuous operation test of Ag@GO-34 membranes over 100 h. f) Comparison of ethylene/ethane separation performance of different kinds of membranes with the polymeric upper-bound. The upper-bound lines are drawn based on the literature\cite{26} by converting permeability to permeance assuming the membrane thickness of 300 nm (solid line) and 1 \( \mu \)m (dashed line) \cite{27}. The separation performance of these membranes is listed in Table S6, Supporting Information.
dissociation of silver ions in 2D channels. The important roles of PSS chains and silver nanoclusters on the ethylene/ethane separation performance of Ag@GO membranes were further revealed (Figure 4). The composition of PSS/GO membranes was optimized to achieve the ethylene/ethane SF was improved to 1.65, which was =65% higher than the Knudsen diffusion selectivity of =1, demonstrating the size-sieving effect in PSS/GO membranes. It confirmed that introducing PSS stimulated the ordered stacking of GO and highly enhanced the size-sieving property of GO membrane. On the basis of PSS/GO membranes, silver nanoclusters were introduced for the molecular recognition of ethylene, prominently increasing the ethylene/ethane SF to 12.3 (Figure 4b). In contrast, although directly introducing AgBF$_4$ nanocrystals might theoretically achieve the molecular recognition effect, it generated non-selective defects in GO laminates (Figure S16j, Supporting Information) and sacrificed the size-sieving property of GO membrane. On the basis of PSS/GO membranes, silver nanoclusters were introduced for the molecular recognition of ethylene, prominently increasing the ethylene/ethane SF to 12.3 (Figure 4b). In contrast, although directly introducing AgBF$_4$ nanocrystals might theoretically achieve the molecular recognition effect, it generated non-selective defects in GO laminates (Figure S16j, Supporting Information) and sacrificed the size-sieving property of GO membrane. It suggests that achieving the highly ordered GO channels with size-sieving property is the prerequisite for realizing the molecular recognition effect, and both the molecular sieving and recognition effects are crucial to the construction of ethylene-selective channels.

Moreover, we understood the role of counter ions on the ethylene/ethane transport through the metal@GO membrane. Another polyelectrolyte containing sulfonate groups, Nafion (Figure S5b, Supporting Information), was employed as an alternative to PSS. The as-fabricated membrane was referred to Nafion-Ag@GO membranes. SEM and AFM images (Figure S22, Supporting Information) showed the surface of Nafion-Ag@GO membrane was dense, while the membrane thickness (1.25 µm) was higher than that of Ag@GO membranes (330 nm) at the same GO deposition, stemming from the longer polymeric chains of Nafion than PSS. The introduction of Nafion could also contribute to the uniform distribution of silver in membranes, which was confirmed by EDS mapping (Figure S23, Supporting Information). The separation performance of membranes with BF$_4$, Nafion, or PSS as counter ions was also compared in Figure 3d. Both Nafion and PSS contribute to prominently enhanced ethylene/ethane SF, further demonstrating the key role of polyelectrolytes in constructing ordered laminates with few defects. In addition, compared with Nafion-Ag@GO membrane, the thinner separation layer of Ag@GO membrane gained much higher ethylene permeance.

We further demonstrated the universality of metal@GO strategy by varying metal cations (Ag$^+$, Mg$^{2+}$, and Ni$^{2+}$) (Figure 3d). Compared with filtrated Mg(NO$_3$)$_2$/GO and Ni(NO$_3$)$_2$/GO membranes fabricated by directly mixing metal salts and GO solution, aggregation of nanocrystals can be avoided in Mg@GO and Ni@GO membranes (Figures S19–S21 and Table S7, Supporting Information). As shown in Figure 3d, the ethylene/ethane SF of membranes containing Mg$^{2+}$ and Ni$^{2+}$ is 2.3–3.6 times higher than that of pristine GO membrane, demonstrating the universality of the metal@GO strategy. Meanwhile, Ag@GO membrane showed the highest ethylene permeance and ethylene/ethane SF among the three kinds of membranes. To demonstrate the superiority of Ag, the strength of $\pi$ complexation interaction between three cations and ethylene was investigated and compared via theoretical calculations (Section 2.4).

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The stability of silver ions in membranes was concerned with practical application. Strategies including the use of polarized silver nanoparticles and introducing ionic liquids have been proposed to address the issue. In this work, we proposed to employ the 2D confined channels to anchor silver nanoclusters (Scheme 1), efficiently enhancing the stability of silver. The continuous operation test over 100 h (Figure 3e) demonstrated the stability of silver nanoclusters and thus the stable ethylene/ethane separation performance (ethylene permeance: 43.9 GPU, ethylene/ethane SF: 10.7) of Ag@GO-34 membranes. More systematic stability tests will be conducted to further evaluate the separation performance of Ag@GO membranes in our future work. As the ethylene concentration in the feed decreased, the ethylene permeance and ethylene/ethane SF simultaneously increased (Figure S24, Supporting Information), highlighting the importance of sufficient silver for recognizing ethylene and stimulating...
its transport over ethane. The transport mechanism behind would be investigated and strategies for improving the separation performance at the feed stream of high ethylene concentration would be developed in future work. The feed composition of 1:99 (volume ratio) ethylene/ethane was employed to simulate the process of recovering ethylene in the retentate stream with low ethylene concentration. In addition, it suggests that the high humidity of feed and sweep streams played an important role in the high ethylene/ethane separation performance of Ag@GO membranes (Figure S25, Supporting Information). Higher water content in membranes would further stimulate the dissociation of silver ions \[28,30\] and intensify the molecular recognition effect, accelerating the transport of ethylene.

The membrane performance of this work was compared with the ethylene/ethane polymeric upper-bound (Figure 3f). Considering the thickness of compared membranes is \(=330\) nm (Figure S9, Supporting Information), two lines corresponding to the polymeric upper-bounds conserved at the membrane thickness of 300 nm and 1 \(\mu m\) were drawn respectively. The 300 nm line was above the 1 \(\mu m\) one, indicating much higher permeance must be achieved to surpass the upper-bound (300 nm) compared with the upper-bound (1 \(\mu m\)) without sacrificing the selectivity. The ethylene/ethane separation performance of the Ag@GO membranes in this work far exceeded the upper-bound (300 nm), demonstrating great potential for ethylene purification. The separation performance of Ag@GO membranes remained to be improved compared with that of ILS/GO membranes with ethylene permeance of 72.5 GPU and ethylene/ethane selectivity of 215.\[13\] In addition, the reported ILS/boron nitride (BN) membranes exhibited attractive ethylene permeance of 138 GPU and ethylene/ethane selectivity of 128, and a comprehensive performance comparison was given.\[32\] Although high selectivity was observed in the ILS/nanosheet composite membranes, the high viscosity of ILS led to micrometer thick membranes, and the ILS-based membranes generally face the loss of ILS under high transmembrane pressure difference, leading to the decrease of separation performance. In this work, for the first time, we proved the feasibility of employing 2D confined channels for discriminating ethylene and ethane. To advance the separation performance, the uniformity of 2D channel size could be further improved, and the structure of counter ions can be designed for more easily dissociated cations and thus enhanced recognition capability towards ethylene in the future. Moreover, the scale-up fabrication of Ag@GO membranes could be realized via blade-coating or slot-die coating methods, and the effect of operation parameters (e.g., stage-cut, testing temperature, and pressure) on the separation performance would be systematically investigated in our following work.

### 2.4. Molecular Insights into Transport Mechanism

Density functional theory (DFT) calculations were employed to reveal the complexation interaction (\(\Delta E_{\text{int}}\)) between cations and ethylene.\[31\] Generally, more negative \(\Delta E_{\text{int}}\) value corresponds to stronger binding energy and more stable cation/ethylene complex. The computed \(\Delta E_{\text{int}}\) for \(\text{Ag}^+\)/ethylene, \(\text{Mg}^{2+}\)/ethylene, and \(\text{Ni}^{2+}\)/ethylene complexes are \(-25.1, 2.3, \) and \(-977\) kcal mol\(^{-1}\), respectively. It indicates that \(\text{Ni}^{2+}\) binds to ethylene very strongly while \(\text{Mg}^{2+}\) tends to leave away from ethylene. Relatively, \(\text{Ag}^+\) moderately binds to ethylene, indicating an intermediate interaction and there might be more reversible complexation with ethylene.

To reveal the nature of the interaction in the complexes, the electron density difference maps exhibiting electron transfer and polarization due to the formation of the complexes were plotted (Figure 5a–c).\[34\] All the three cations induced \(\pi\) electrons in ethylene to be polarized in their directions, with the order of polarization degree of \(\text{Mg}^{2+}/\text{ethylene} < \text{Ag}^+/\text{ethylene} < \text{Ni}^{2+}/\text{ethylene}\). This is coincident with the interaction strength of cations with ethylene, indicating that the induction effect plays an important role in the stabilization of complexes. The superposition map of the electrostatic potential (ESP) colored van der Waals (vdW) surfaces\[35\] for the metal ion and ethylene molecule in dimer structures is shown in Figure 5d–f. It can be observed that cation and ethylene are combined in an evident electrostatic complementary manner. The positive ESP of cations directly interacts with the C=C bond of ethylene having negative ESP. The mutual penetration extents of vDW surfaces of various metal ions with ethylene follow this order: \(\text{Mg}^{2+} < \text{Ag}^+ < \text{Ni}^{2+}\). The result agrees with the interaction strength of cations with ethylene, implying that the electrostatic interaction also contributes to the stabilization of complexes.

As is shown in Figure 5g–i, density-of-states (DOS) plots\[36\] were drawn to explore the electronic structural nature of complexes. The frontier orbitals gap, that is the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is 6.5, 8.3, and 3.6 eV for \(\text{Ag}^+\)/ethylene, \(\text{Mg}^{2+}\)/ethylene, and \(\text{Ni}^{2+}\)/ethylene, respectively. The relatively larger HOMO–LUMO gap indicates that it is more difficult for electron transfer and polarization to happen. The result is consistent with the electron density difference analysis which depicts the strongest polarization between \(\text{Ni}^{2+}\) and ethylene and ethylene with the lowest HOMO–LUMO gap. Figure 5g–i demonstrates it is mainly the orbitals of C atoms and cations that contribute to the HOMO and LUMO of all the three complexes. The orbital composition analysis was performed through the C-squared Population Analysis (SCPA).\[37\] As is shown in Figure 5j–l, the fractional contributions of various orbitals from ethylene and cations to HOMO and LUMO of three cation-ethylene complexes were compared, suggesting that the contribution of atomic orbitals of metal ions to frontier orbitals of complexes is in the order of \(\text{Mg}^{2+} < \text{Ag}^+ < \text{Ni}^{2+}\).

According to the calculation results above, the complexation interaction strength of cations with ethylene follows the order of \(\text{Mg}^{2+} < \text{Ag}^+ < \text{Ni}^{2+}\). The interaction between \(\text{Ni}^{2+}\) and ethylene is very strong, leading to hard decomposition when ethylene hops from one \(\text{Ni}^{2+}\) site to another. Nevertheless, for \(\text{Mg}^{2+}/\text{ethylene}\) complex, the complexation interaction is quite weak, which retards the formation of the complex and thus impairs the capability of reversible interaction. In contrast, \(\text{Ag}^+\)/ethylene complex shows the intermediate interaction strength with ethylene, maximizing the molecular recognition capability of Ag@GO channels. Correspondingly, Ag@GO membrane achieved the highest ethylene/ethane separation performance.
To gain molecular insights into the ethylene/ethane transport through 2D sub-nanometer channels with recognition capability, molecular dynamic (MD) simulation was employed. As shown in Figure 6a, the oxygen atoms of SO$_3^-$ groups tended to align along the outside of PSS chains, and Ag$^+$ was distributed in a bilayer manner, providing two consecutive pathways for recognizing ethylene. The orientation of SO$_3^-$ groups was attributed to rich hydrogen bonds between oxygen-containing groups from GO and SO$_3^-$ groups. Accordingly, Ag$^+$ was brought to the outside of PSS chains by SO$_3^-$ groups primarily owing to the electrostatic interaction between Ag$^+$ and SO$_3^-$ groups, contributing to the bilayer pathway for recognizing and transporting ethylene molecules. The 2D view of the simulated system might cause doubt on whether there were enough free spaces for gas transport. As shown in Scheme 1, ethylene can freely transport through metal@GO channels in 2D sub-nanometer channels by the direction perpendicular to the GO nanosheet. Figure 6b demonstrates most of the PSS chains were assigned to the center of the interlayer while Ag$^+$ was distributed along two sides of PSS chain, which is consistent with the distribution in Figure 6a. For comparison, Ag$^+$ was randomly distributed in the AgBF$_4$/GO system (Figure S27, Supporting Information), which would sacrifice the efficiency of reversible interaction. Moreover, based on radial distribution functions (RDFs) (Figure 6c), interactions between silver ions and counter ions (BF$_4$ or PSS) in AgBF$_4$/GO and Ag@GO systems were compared. Usually, the value of the first peak corresponds to the interaction strength between the selected two components. Here the RDF of Ag–BF$_4$ is higher than that of Ag–PSS, indicating a weaker interaction in Ag–PSS pair, corresponding to highly dissociated Ag$^+$ and thus more efficient complexation with ethylene in Ag@GO membrane. Therefore, the counter ion of silver ions would influence the chemical environment of silver nanoclusters in 2D channels and thus the recognition efficiency. Based on the above results, silver nanoclusters in Ag@GO membrane possessed highly dissociated Ag$^+$ and more easily recognized ethylene, thereby promoting the ethylene transport.

3. Conclusion

We have created metal confined in 2D sub-nanometer channels to discriminate ethylene over ethane. The successful construction of highly ordered 2D sub-nanometer channels with
≈0.44 nm height contributes to the size-sieving of ethylene and ethane. More importantly, employing polyelectrolyte as a counter ion contributes to the atomic-level distribution of silver in 2D sub-nanometer channels and the highly dissociated cations with an enhanced positive charge, maximizing the efficiency of recognizing and transporting ethylene. The Ag@GO membranes exhibited ethylene permeance of 46.7 GPU and ethylene/ethane SF of 12.3, surpassing the polymeric upper-bound. MD simulations revealed that a bilayer transport pathway for molecular recognition was created in 2D sub-nanometer channels. The nanostructure of metal confined in 2D channels could be of interest in a variety of applications including molecular separation, single-atom catalysis, sensor, and energy conversion.

4. Experimental Section

Materials: GO was synthesized by the typical modified Hummers’ method and supplied by Nanjing JCNANO Tech Co., Ltd. Sodium PSS and Nafion 117 were purchased from Sigma-Aldrich. Metal salts, including AgBF4, Mg(NO3)2, and Ni(NO3)2, were provided by Macklin Co., Ltd. PES substrates with a diameter of 47 mm and pore size of ≈220 nm were purchased from Haining Zhongli Filtering Equipment Co., Ltd. H2, CO2, N2, CH4, C2H6, C3H8, and Ar with a minimum mole fraction of 99.99% for gas separation performance test were provided by Nanjing Special Gases Company. Deionized water was used in all the experiments. All of the materials were used without further purification.

Membrane Preparations: In this work, four methods, including layer-by-layer spin-coating (Method 1), spin-coating and salt immersion (Method 2), direct mixing and filtration (Method 3), and ion-exchange and filtration (Method 4), were employed to fabricate metal-ion-incorporating GO membranes (Figures S3 and S14, Supporting Information). For Method 1, GO solution and AgBF4 solution were successively spin-coated on the PES substrate, which was considered as one cycle. After several cycles, the membrane was fabricated, which was named as layer-by-layer AgBF4/GO membrane. For Method 2, GO solution was first spin-coated on the substrate to fabricate the pure GO membranes, followed by the immersion process in AgBF4 solution. The as-fabricated membrane was named as post-treated AgBF4/GO membrane. For Method 3, GO solution was mixed with the AgBF4 solution, and the mixture was filtrated through the PES substrate. The as-fabricated membrane was named as filtrated AgBF4/GO membrane (referred to AgBF4/GO membrane for short). For Method 4, the AgBF4 solution was first mixed with PSS to replace sodium with silver ions. The obtained Ag+ -PSS solution was then mixed with GO solution, followed by vacuum filtration to obtain the Ag@GO membrane (Figure S3, Supporting Information). For the control experiment, the PSS/GO membrane was prepared by the filtration of the mixture of PSS and GO solution. In addition, the pristine GO membrane was fabricated by the filtration of pure GO solution. All membranes were dried at room temperature for 24 h before the gas separation test. The AgBF4/GO and Ag@GO nanocomposites for TEM characterization were fabricated by dropping the corresponding membrane solution on the copper mesh, followed by drying at room temperature.
Layer-by-layer AgBF₄/GO membranes (Method 1) were prepared with GO solution of 0.25 mg mL⁻¹ and AgBF₄ solution of 5 mg mL⁻¹, and 6 spin-coating cycles. Post-treated AgBF₄/GO membranes (Method 2) were prepared with GO solution of 0.25 mg mL⁻¹ and 6 spin-coating cycles, followed by the immersion process in AgBF₄ solution of 10 mg mL⁻¹ for 8 h. AgBF₄/GO membranes (Method 3) were prepared at the GO deposition of 0.6 mg and the AgBF₄/GO mass ratio of 9.4 and 188.8. The resulting membranes were referred to as AgBF₄/GO-X membranes, where X represented the mass fraction (wt.%) of the silver ion in AgBF₄/GO membranes. Based on the elemental analysis of the X-ray photoelectron spectroscopy (XPS), the silver mass fractions were calculated as 34, and the membrane was named as Ag@GO-34. Other PSS/GO mass ratio of 10:1. Based on the XPS result, the deposition of 0.6 mg and the AgBF₄/GO mass ratio of 9.4 and 188.8. The resulting membranes were referred to as AgBF₄/GO-X membranes, where X represented the mass fraction (wt.%) of the silver ion in AgBF₄/GO membranes. For instance, an Ag@GO membrane was prepared at the Ag'/Na⁺ molar ratio of 10:1 and the PSS/GO mass ratio of 10:1. Based on the XPS result, X was calculated as 34, and the membrane was named as Ag@GO-34. Other Ag@GO membranes were named in the same way. To demonstrate the universality of the strategy, Ni(NO₃)₂ and Mg(NO₃)₂ were employed as an alternative to AgBF₄ to fabricate GO membranes containing magnesium and nickel based on the fabrication process similar to that of Ag@GO membranes. Moreover, Nafion was employed as an alternative to PSS to fabricate Nafion–Ag@GO membranes.

Characterizations: The morphology of AgBF₄/GO and Ag@GO membranes was observed by field-emission scanning electron microscopy (FESEM, S4800, Hitachi, Japan) and polarizing microscopy (BM-57XCD, Shanghai BM Optical Instruments Manufacture Co., Ltd). The size distribution of GO nanosheets was analyzed by Zetasizer Nano ZS90 (Malvern Panalytical, UK). TEM and AC-TEM images were obtained by JEM-2100F (Japan Electron Optics Laboratory Co., Ltd, Japan) and Themis Z (Thermo Fisher Scientific, USA) with an accelerating voltage of 200 kV. The surface roughness of membranes was obtained by atomic force microscopy (AFM, XE-100, Park SYSTEMS, Korea) operated in the non-contact mode. The interlayer height of GO membranes was characterized by X-ray diffraction (XRD, Smartlab 3 kW, Rigaku, Japan) in the range of 5° ≤ 2θ ≤ 40° with a step width of 0.05° and a scan rate of 0.2° s⁻¹ at room temperature. The chemistry attributes of membranes were analyzed by XPS (Thermo ESCALAB 250, USA) and Fourier transform infrared (FTIR) spectra (Thermo, Nicolet Nexus 470 spectrometer, USA) with the range of 500–4000 cm⁻¹. Raman spectroscopy (LabRAM HR Evolution, HORIBA, France) was carried out with 532 nm wavelength incident laser light in the range of 500–2550 cm⁻¹. The mass fraction of silver nanoclusters in membranes and the percentage of Na⁺ exchanged by Ag⁺ in PSS were determined by XPS. During the fabrication process of Ag@GO membranes, the molar ratio of AgBF₄ to Na⁺ in PSS and the mass ratio of PSS to GO were varied. The atomic fractions of different elements in these membranes were determined by XPS (Table S4, Supporting Information), and then the mass fraction of silver nanoclusters and Na⁺-exchanged percentage of different membranes were calculated and listed in Table S5, Supporting Information. In addition, these membranes were named according to the naming rule mentioned above.

Gas Permeation Experiments: Based on the Wicke–Kallenbach method,[38] single gas and mixed gas permeation tests were carried out to evaluate the gas separation performance of membrane samples. For the single gas permeation test, the feed gas was humidified H₂, CO₂, N₂, CH₄, C₂H₆, or C₂H₄ with a flow rate of 30 mL min⁻¹, and humidified Ar with the flow rate of 5 mL min⁻¹ was chosen as the sweep gas (Figure S28, Supporting Information). The pressure of the permeate side was 1 atm and there was no pressure drop between the sides of the membranes. The operating temperature of the permeation test was 25 °C. The component of the targeted gas in the permeate side was detected by gas chromatography (Agilent 7820A, USA). When the system reached steady-state, the gas permeance was calculated from the average value of test results calculated by the following equation:

\[
P = \frac{1}{\Delta P} \frac{A}{d} \left( \frac{dV}{dt} \right)
\]

where \( P \) is the gas permeance (1 GPU = 10⁻⁶ cm³ (STP) cm⁻² s⁻¹ cmHg⁻¹), \( \Delta P \) is the effective area of membrane, \( \Delta P \) is the transmembrane pressure (atm), \( P_{\text{gas}} \) represents the atmospheric pressure (atm), \( T \) is the testing temperature (°C), and \( dV/dt \) represents the volumetric displacement rate in the bubble flow meter. The ideal selectivity, \( \alpha \), was calculated by the ratio of the permeance of the individual gases which can be expressed as follows:

\[
\alpha = \frac{P_1}{P_2}
\]

During the mixed gas permeation test, a humidified mixture of C₂H₄ and C₂H₆ (1:99, vol%) was employed as the feed gas with a total flow rate of 60 mL min⁻¹ (the volume ratio of C₂H₄ to C₂H₆ was variable when investigating the effect of feed composition), while humidified Ar with the flow rate of 10 mL min⁻¹ was chosen as the sweep gas. The relative humidity (RH) of gas streams was controlled by saturated salt solutions that were magnesium chloride (33%), sodium chloride (75%), and pure water (85%).[39] The mixed gas permeation test was measured at atmospheric pressure and 25 °C. The SF can be calculated as follows:

\[
\alpha_{AB} = \frac{y_A}{y_B} \frac{x_A}{x_B}
\]

where \( x \) and \( y \) are the volumetric fraction of the one component in the feed and permeate side, respectively.

Molecular Simulations: To get a deep understanding of the metal cation (Ag⁺, Mg²⁺, Ni²⁺)/ethylene interacting complex, the DFT calculations were conducted. All calculations were accomplished by the ORCA package.[40] The hybrid functional PBE0 was applied for the electron exchange correlation, which was a commonly used function for systems including transition metals.[41,42] The def2-TZVP basis set was applied for geometry optimization and frequency calculations. The RIJCOSX technique was enabled for accelerating the calculations. The aqueous solution was simulated using the implicit CPCM polarizable continuum model. The Grimme’s correction employing B-J damping (D3(BJ)) was used to account for the dispersion interaction. All the wavefunction analysis was performed by using the MultiwfN program.[39] The geometrically converged structures of Ag⁺/ethylene, Mg²⁺/ethylene, and Ni²⁺/ethylene without imaginary frequencies are shown in Figure S29, Supporting Information. It can be seen that the metal cation locates over the C=C bond of ethylene for all three complexes. The Mg²⁺/ethylene complex has the largest cation–C distances, by contrast, the Ni²⁺/ethylene complex has the shortest metal–C distances.

The interaction energy between the metal ion and the ethylene molecule (\( \Delta E_{\text{int}} \)) was calculated using the double hybrid density functional PW91 along with the D3(BJ) correction and the def2-TZVP basis set based on the following equation:

\[
\Delta E_{\text{int}} = E_{\text{complex}} - E_{\text{ethylene}} - E_{\text{cation}}
\]

where \( E_{\text{complex}} \) is the energy of metal ion/ethylene complex, \( E_{\text{ethylene}} \) is the energy of the isolated ethylene molecule, and \( E_{\text{cation}} \) is the energy of the isolated metal cation.

The electron density difference between the metal cation and the ethylene molecule (\( \Delta \rho \)) was calculated as follows:

\[
\Delta \rho = \rho_{\text{complex}} - \rho_{\text{ethylene}} - \rho_{\text{cation}}
\]
where $\rho_{\text{complex}}$ is the electron density of metal cation/ethylene complex, $\rho_{\text{ethylene}}$ is the electron density of the isolated ethylene molecule, and $\rho_{\text{metal}}$ is the electron density of the isolated metal cation.

To explore the nanostructure and molecular interaction within the membranes, MD simulation was performed by Materials Studio 6.0 in Forcite module. Two lamellar GO nanosheets with the dimensions of 3.5 × 3.5 nm² were parallel arranged, where the oxygen-containing groups were randomly grafted on their internal face. After optimization, the interlayer distance was 0.8 nm, which was similar to the experimental result. The equimolar compounds of PSS and Ag⁺ (or BF₄⁻ and Ag⁺), comprising 50 molecules, were randomly inserted into the GO interlayer. First, the system was subjected to energy minimization by smart method with 10 000 iterations, and then it was further equilibrated by canonical ensemble (NVT) with 1 ns. Subsequently, another 3 ns NVT calculations with a time step of 1 fs were implemented for production runs. The system temperature was maintained at 313.15K by the Nose method. The simulation models were described by the universal force field, which was wildly applied to calculate the 2D nanosheet-based membrane. Periodic boundary condition was applied in all directions. The bonded interaction ($E_{\text{bonded}}$) was calculated as follows:[1][2][3]

$$E_{\text{bonded}} = E_{\text{stretching}} + E_{\text{bending}} + E_{\text{torsional}}$$

where $E_{\text{stretching}}$, $E_{\text{bending}}$, and $E_{\text{torsional}}$ correspond to the bond stretching, bending, and torsional potentials, respectively. The nonbonded interaction ($E_{\text{nonbonded}}$) involved Lennard-Jones (LJ) and ESPs, which was calculated as follows:

$$E_{\text{nonbonded}} = \sum_{ij} 4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^12 - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 + \sum_{i} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

where $r_{ij}$ is the distance between atoms $i$ and $j$, $\sigma_{ij}$ and $\varepsilon_{ij}$ are the well depth and collision diameter, $q_i$ and $q_j$ are the atomic charges of atoms $i$ and $j$, and $\varepsilon_0 = 8.8542 \times 10^{-12}$ C² N⁻¹ m⁻² is the permittivity of vacuum. The total energy ($E$) was composed of bonded interactions and nonbonded interactions:

$$E = E_{\text{bonded}} + E_{\text{nonbonded}}$$

After reaching the equilibrium state, the interaction energy ($\Delta E$) between BF₄⁻-paired Ag⁺ and GO and that between PSS-anchored Ag⁺ and GO were calculated as follows:

$$\Delta E = E_{ij} - E_i - E_j$$

where $E_{ij}$ is the total energy of the whole system of $i$-$j$ and $E_i$ and $E_j$ are the energies of the isolated $i$ and $j$, respectively. The distribution probabilities of Ag⁺ and PSS along GO interlayer in the PSS-anchored Ag⁺/GO system were calculated to provide molecular insights into the microstructure of Ag@GO membranes. In addition, the interaction of PSS or BF₄⁻ towards Ag⁺ in the individual system was evaluated by RDF using:

$$g_i(r) = \frac{N_i(r)V}{4\pi r^2 \Delta N_j}$$

where $V$ is the cell volume, $r$ refers to the distance between atoms $j$ and $i$, $N_i(r)$ is the number of atom $j$ and $N_j(r)$ is the number of atom $j$ within a shell from $r$ to $r + \Delta r$. The hydrogen bonds between SO₃⁻ and oxygen-containing groups from GO nanosheets were examined based on these two geometrical criteria: 1) $r(H\cdotsO) \leq 0.35$ nm; 2) $\alpha(O\cdotsH\cdotsO) \leq 30^\circ$.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
L.C. and G.P.L. conceived the idea. L.C. conducted the experiments and wrote the manuscript. L.C., R.H.L., and X.C. performed the characterizations. L.C., Y.N.G., and Q.L. designed and analyzed the theoretical calculations. H.Z. took the digital photos. L.C., Y.N.G., and G.P.L. analyzed the data and prepared the graphs. L.C., G.Z.L., G.P.L., and W.Q.J. discussed the results and commented on the manuscript. The manuscript was written through the contributions of all authors. All authors have given approval for the final version of the manuscript.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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