Graphdiyne is a novel two-dimensional material deriving from graphene that has been recently synthesized and featuring uniformly distributed sub-nanometer pores. We report accurate calculations showing that graphdiyne pores permit an almost unimpeded helium transport which can be used for its chemical and isotopic separation. Exceptionally high He/CH$_4$ selectivities are found which largely exceed the performance of the best membranes used to date for extraction from natural gas. Moreover, by exploiting slight differences in the tunneling probabilities of $^3$He and $^4$He, we also find promising results for the separation of the fermionic isotope at low temperature.
Membranes using nanoporous two-dimensional (2D) materials are emerging as attractive candidates for applications in molecular separations and related areas. In particular, graphene-based materials exhibit vantage points with respect to conventional 3D materials, by virtue of their thermal and chemical stability as well as a low molecular weight and efficient transport capability. Graphene sheets do not have pores for molecular sieving and the introduction of sub-nanometer pores is required to obtain sufficient molecular permeance. This can be obtained by means of “top-down” fabrication methods able to create holes in suspended graphene sheets, which, however, are in general not sufficiently controllable. “Bottom-up” assembly processes represent a valuable alternative and have permitted the synthesis of new 2D materials characterized by regular and uniformly distributed sub-nanometer pores. The most promising examples are graphdiyne and 2D polyphenylene honeycomb (2DPPH). In the former, peculiar triangular pores arise from carbon chains formed by two conjugated C-C triple bonds that link adjacent benzene rings. In the latter, the resulting structure is instead similar to that of graphene but with one missing hexagon per unit cell which is passivated by hydrogens, leading to almost circular openings (see Fig. 1.a). The successful synthesis of these materials has led to important theoretical studies devoted, firstly, to their application as effective single-layer membranes for gas separation and water filtration technologies and, secondly, to the tailoring of related porous 2D structures by changing pore shape and size through the incorporation of functional groups.

In this work we want to assess the capability of the recently synthesized graphdiyne and 2DPPH materials as efficient membranes for helium separation applications. As it is well known, the growing demand for helium in a variety of industrial and scientific applications, together with ongoing production deficiencies, has recently led to shortages of this element. Additionally, $^3$He is crucial for large neutron-scattering facilities and the depletion of its stockpiling might also affect fundamental research in ultracold physics and chemistry. Natural gas remains the richest and most accessible source of helium even if its concentration is less than 1.5% in most of the helium-producing wells. Existing methods for performing both the chemical separation of He from natural gas and
the separation of He isotopes require energetically costly techniques, such as cryogenic distillation and pressure-swing adsorption. In principle membrane-based gas separation have a much lower thermodynamic cost and recent theoretical works have proposed the use of 2D membranes for the chemical and isotopic separation of He gas. In particular, studies on He permeability through 2DPPH membranes were already addressed but, to our knowledge, the graphdiyne capability for He separation has not been investigated yet. Moreover, in our opinion, the reliability of the He–2DPPH penetration barriers, obtained by means of the density functional theory (DFT) and second-order Møller-Plesset perturbation (MP2) methodology, might need a deeper analysis.

In Fig. 1.a we report the molecular structures that can be considered as the smallest precursors of graphdiyne and 2DPPH and which are here used to study their pores. It can be seen that, inside the pores, smaller black figures are also depicted. Their area corresponds to the effective pore size which has been estimated by considering the van der Waals (vdW) radii of the acetylenic carbon bonds, for graphdiyne, and of the inner hydrogen atoms, for 2DPPH (∼ 1.6 Å and 1.3 Å, respectively). The side length of the the inner triangle is 3.9 Å, for graphdiyne, and the diameter of the inner circle is 0.8 Å for 2DPPH. In the same way, the helium vDW diameter is 2.6 Å (represented by a double-headed arrow in Fig. 1.a) and it is smaller than the graphdiyne pore side but larger than the diameter of the 2DPPH circular opening. This comparison already suggests that He penetration should be easy in graphdiyne pores and more difficult when passing through the 2DPPH smaller pore.

A more quantitative assessment comes from electronic structure calculations. The prototypical systems of Fig. 1 are small enough to allow the use of the high level (and computationally expensive) “coupled” supermolecular second-order Møller-Plesset perturbation theory (MP2C) approach. The accuracy of this method, which is particularly suited to recover non-covalent weak interactions, has been recently assessed by extensive calculations of rare gas–fullerene and -coronene interaction energies. In Fig. 1.b we report the calculated potential energy profiles for one helium atom perpendicularly approaching the 2D structures. In particular, $z$ is the distance between helium and the geometric center of the pores. It can be seen that the penetration barrier
(defined as the energy difference between \( z=0 \) and \( \infty \), \( E_{PB} \)) is high (about 0.516 eV) for 2DPPH but becomes much lower (about 0.033 eV) for graphdiyne.

The He–2DPPH penetration barrier was previously obtained by means of MP2 and DFT calculations and found to be 0.523\(^8\) and 0.430\(^7\) eV, respectively. Our estimation is in between the previous calculations and closer to the MP2 value. Present value should be considered as the reference one since, to our knowledge, the employed dispersion corrected DFT approach\(^7\) has not been sufficiently tested on this specific system. In addition, the MP2 estimation\(^8\) lacks the correction included in the MP2C method\(^22\) which is indeed much needed to improve the description of non-covalent interactions.\(^23\) As for the He–graphdiyne system, it should be stressed that the calculated barrier of few tens of meV not only is much lower than that for 2DPPH, but also represents an energy gap comparable with other proposed 2D materials which, however, have not been fully synthesized yet. They include partially nitrogen functionalized porous graphene\(^12\) (about 0.025 eV) and porous graphene-E-stilbene-1\(^13\) (about 0.050 eV).

Barrier heights could be further reduced if the optimization of the position of the atoms defining the pores is taken into account. In fact, related additional calculations at the density functional level of theory (DFT) have been performed by considering the full “periodic” structure of a single graphdiyne layer and we have found that the barrier can lower by about 15% due to the deformation of the pores (see Fig. S1).

To examine the efficiency of the two kinds of pores for helium permeation in more detail, we have considered a simple Arrhenius behavior for the diffusion rate \( D \) as a function of the temperature \( T \): \( D(T) = A_0 e^{-\frac{E_{PB}}{kT}} \), where \( E_{PB} \) is the computed penetration barrier. As it is customary in this context\(^7\),\(^14\),\(^18\) we have taken the same diffusion prefactor \( A_0=10^{11} \text{s}^{-1} \) for both pores. The related diffusion rates are reported in Fig. 1.c and it can be seen that graphdiyne exhibits a much higher permeability than 2DPPH in an ample range of temperature, being the difference of about eight orders of magnitude at room temperature. These results clearly show that, due to its “ad hoc” pore size, a graphdiyne membrane is much more suited than the 2DPPH one for helium permeation and in the following we will focus on the former, analyzing in detail its separation capabilities.
In order to investigate the separation of helium from natural gas, we have considered neon and methane as limiting cases of the complex mixture of alkanes and rare gases therein usually present. Thus, additional accurate energy profiles are reported in Fig. 2 (upper panel) and compared with that of helium. It should be pointed out that methane is considered as a pseudo-atom, so that the reported energy profile is actually an average of different potential curves (see Supp. Inf. and Fig. S2). We have found that the penetration barrier $E_{PB}$ (also reported in Table 1) for Ne and CH$_4$ increases up to 0.106 and 1.460 eV, respectively, suggesting a high impediment to the passage of methane.

To assess the separation capability of the graphdiyne pores, we have computed transmission probabilities for the passage of these species by means of time-dependent wave packet simulations. A new force field, optimized on the benchmark MP2C electronic structure results, has been obtained to this end. It provides the basic features of the interaction in the full configuration space, and therefore it is suitable for performing molecular dynamics simulations. Specifically, its formulation involves the Improved Lennard-Jones (ILJ) pair potential function$^{25}$ (see Eq. 1 of Supp. Inf.), here used for describing the non-covalent interaction between the rare gas (and methane in the pseudo-atom limit) and the carbon atom forming the graphdiyne net structure. Additional MP2C energy curves for approaches of the atom (molecule) to different sites of the graphdiyne pore have been computed (see Fig. S3) to further test and improve the proposed force fields. The values of the optimized ILJ parameters are reported in Table 1. In the upper panel of Fig. 2 we present a comparison between MP2C and ILJ curves and a very good agreement can be observed which confirms the reliability of the proposed force fields.

For simplicity we have just considered a one-dimensional transmission of the atom through the center of a graphdiyne pore, where the interaction potentials have been obtained by summing up ILJ pair potentials between the atom (molecule) and the neighboring carbon atoms of a graphdiyne sheet until convergence. Values of the penetration barriers obtained in this way are reported in Table 1. Thermally weighted transmission probabilities $P(T)$ have been computed and used to estimate selectivities of the different molecular combinations $X/Y$, defined as the probability ratios
\( S = \frac{P^X}{P^Y} \). The temperature dependence of these selectivities is presented in the lower panel of Fig. 2. Exceptionally high selectivities can be noticed for He/CH\(_4\) and Ne/CH\(_4\) combinations in a wide range of temperatures and they are about \(10^{24}\) and \(10^{23}\), respectively, at room temperature. As for the He/Ne combination, the corresponding selectivity is about 27 at room temperature, suggesting a less efficient capability for the separation of these species, but in any case larger than 6, the value considered acceptable for industrial applications.\(^\text{26}\)

Present results clearly indicate that the combination of a very high He diffusion rate (Fig. 1) and very high He/CH\(_4\) and Ne/CH\(_4\) selectivities (Fig. 2) makes graphdiyne a very promising material for the separation of He and Ne from the hydrocarbons contained in natural gas (higher alkanes, also present in natural gas, are expected to have even smaller transmission probabilities due to their larger size). As a matter of fact, due to the very low He and Ne concentrations in most of the natural gas reservoirs, very high selectivities (about \(1000^{27}\)) are required. This stringent requirement is indeed largely overcome by present estimations and, to our knowledge, not approached by the polymeric membranes up to date proposed for this purpose (corresponding selectivities are about \(100^{28}\)).

The high permeability that we have found for He-graphdiyne has encouraged us to study the possibility of separation of its isotopic variants. In particular, the separation of \(^3\)He and \(^4\)He could be achieved by taking advantage of slight differences in the tunneling probabilities of the two isotopes and by exploiting them in multistage processes,\(^\text{20}\) which involve the passage of the gas through some graphdiyne layers. To this end we have computed transmission probabilities for \(^3\)He and \(^4\)He as functions of kinetic energy. The results are given in the upper panel of Fig. 3. It can be seen that, for kinetic energies lower than the classical barrier (see last column of Table 1), the \(^3\)He transmission probability is significantly higher than that of \(^4\)He, while the opposite occurs for higher kinetic energies. For this reason, it makes sense to keep the gas temperature as low as possible in order to exploit the low energy side of the transmission curve.

Thermally weighted transmission probabilities as well as the corresponding \(^3\)He/\(^4\)He selectivity\(^29\) as a function of temperature are reported in Fig. 3 (lower panel). We have obtained that the
selectivity at 77 K (liquid nitrogen temperature) is about 1.04 and increases rapidly at low temperatures reaching the acceptable reference value of 6\textsuperscript{26} at about 20 K. However, as the temperature drops, the transmission probabilities considerably decrease, as well as the He flux. In fact at 20K the \(^3\)He transmission probability, even if larger than that of \(^4\)He and of the classical limit (see lower panel of Fig. 3), is quite low and in the range of 10\(^{-9}\). The overall flux is the transmission probability multiplied by the frequency of gas collisions with the pore, which, according to the kinetic theory of gases, is \(P/\sqrt{2\pi mkT}\) where \(P\) is the pressure of the species, \(m\) its the molecular mass, \(T\) the temperature and \(k\) the Boltzmann constant. If we assume a 100% porous sheet, ideal gas conditions and a pressure of 3 bar we can estimate an upper-bound\textsuperscript{30} of the total helium flux: at 77K it is about 3.7\(\times\)10\(^{-3}\) moles cm\(^{-2}\) s\(^{-1}\) while at 20K is about 1.5\(\times\)10\(^{-8}\) moles cm\(^{-2}\) s\(^{-1}\), a value leading to a permeance\textsuperscript{31} equal to 1.5\(\times\)10\(^{-8}\) moles cm\(^{-2}\) s\(^{-1}\) bar\(^{-1}\) which is slightly lower than the limit of 6.7\(\times\)10\(^{-8}\) moles cm\(^{-2}\) s\(^{-1}\) bar\(^{-1}\)\textsuperscript{26} considered acceptable for industrial applications.

**Conclusions**

In summary, by means of electronic structure MP2C computations, we have shown that graphdiyne is much more suited than 2DPPH for helium permeation since it involves a much lower penetration barrier (of the order of few tens of meV). Additional calculations of the interaction of neon and methane with a graphdiyne pore have allowed us to setup reliable full force fields which have been used to compute quantum mechanical probabilities and selectivities for the passage of gases through the openings. We have found exceptionally favorable He/CH\(_4\) and Ne/CH\(_4\) selectivities in a wide range of temperatures which largely exceed the performance of the best membranes used for helium chemical separation. Thermally weighted helium tunneling calculations have been also performed to show selective transmissions of \(^3\)He versus \(^4\)He. For temperatures below 100K the \(^3\)He/\(^4\)He selectivity becomes appreciably larger than 1, reaching an acceptable value of 6 at about 20K. We thus propose that, in addition to its promise for hydrogen\textsuperscript{9} and water\textsuperscript{11} purification, a graphdiyne based membrane can be efficiently used for helium separation applications addressed
to filtering natural gas and, possibly, isotopic mixtures. On the basis of this work, we assume that graphdiyne pores should also provide favourable selectivities for He/Ar, He/Kr and He/N$_2$ gas combinations which could permit optimal separation of helium from heavier rare gases and hydrothermal spring gases, the latter primarily composed of nitrogen.

A full assessment of the capability of graphdiyne for helium isotopic separation would actually require three-dimensional simulations in order to better estimate the helium permeance at low temperatures and to take into account for zero-point energy effects due to in-pore vibrational modes. Work in this direction, by using the ILJ full force field, is in progress.

**Computational methods**

All MP2C calculations have been performed by using the Molpro2012.1 package. The geometry of the pores are obtained considering the following bond lengths: 1.431 Å for the aromatic C-C, 1.231 Å for triple C-C, 1.337 Å for the single C-C between two triple C-C bonds, 1.395 Å for the single C-C connecting aromatic and triple C-C bonds and 1.09 Å for C-H bonds. The aug-cc-pVTZ basis set was employed for the pore structures, while the aug-cc-pV5Z basis has been used for rare gases and methane molecule. All considered molecular structures are treated as rigid bodies. The obtained interaction energies have been corrected for the basis set superposition error by the counterpoise method of Boys and Bernardi. Transmission probabilities for the passage of the atom/molecule through the pores were obtained by means of time-dependent wave packet calculations. The time-dependent Schrödinger equation was solved for an initial one-dimensional Gaussian wave packet. The coordinate grid is set up from $z = -L$ to $z = L$ ($L$ is a sufficiently large distance) and the interaction potential $V(z)$ for negative $z$’s has been built as an specular image of $V(z)(z > 0)$. The stationary wave function was obtained from the Fourier transform of the time-dependent wave packet and with this, the time-independent flux through the barrier ($z = 0$) and the energy dependent transmission probability, $P(E)$, are obtained. Finally, the temperature-dependent transmission probability, $P(T)$, was computed from numerical integration of $P(E)$, weighted by a
one-dimensional Maxwell-Boltzmann distribution of molecular velocities.

**Supporting Information**

Supporting Information is available from the Wiley Online Library: it includes additional figures reporting periodic DFT calculations as well as intermolecular potentials related to different configurations used for graphdiyne pore–methane computations and for the optimization of the obtained force fields.

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Figure 1: a) Molecular structures used to study the nano-pores of graphdiyne(1) and 2D polyphenylene honeycomb (2). The black triangle and circle depicted inside the pores represent their effective available area to be compared with the van der Waals diameter of the He atom (red double-headed arrow). b) Energy profiles obtained at the MP2C level of theory for He perpendicularly approaching the geometric center of graphdiyne and 2DPPH pores. c) Rates for He diffusion through the pores as functions of temperature (see text).

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Figure 2: Upper panel: Energy profiles obtained for helium, neon and methane perpendicularly approaching the geometric center of the graphdiyne pore. In the case of methane the resulting curve is the average of four limiting configurations (see Fig. S2). Red dots refer to the MP2C level of theory results while solid curves represent estimations obtained with optimized Improved Lennard Jones (ILJ) force fields (see text). Lower panel: Selectivities for different molecular combinations as functions of temperature (see text).

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Figure 3: Upper panel: Quantum mechanical and classical transmission probabilities of He through graphdiyne pore as a function of kinetic energy. Lower panel: $^3\text{He}/^4\text{He}$ selectivity (red line) and thermally weighted quantum transmission probabilities (solid and dashed black lines for $^3\text{He}$ and $^4\text{He}$, respectively) as functions of temperatures. Classical transmission probability is reported as a dotted line.

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Table 1: Penetration barrier ($E_{PB}$) for He, Ne and CH₄ passage through graphdiyne pores. Parameters for the rare gas (methane)-carbon Improved Lennard Jones (ILJ) pair potential (see Eq. 1), used to obtain the full force fields, are also reported, together with the resulting penetration barriers after a pair-wise summation over a graphdiyne sheet. $E_{PB}$ and $\varepsilon$ are in meV, $R_m$ in Å , and $\beta$ is dimensionless.

|       | $E_{PB}$(MP2C) | $R_m$  | $\varepsilon$ | $\beta$ | $E_{PB}$(ILJ) |
|-------|----------------|--------|---------------|---------|---------------|
| He    | 33.90          | 3.595  | 1.209         | 7.5     | 36.92         |
| Ne    | 105.76         | 3.671  | 2.388         | 7.5     | 109.17        |
| CH₄   | 1460.31        | 4.046  | 7.763         | 7.5     | 1454.70       |

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(29) For simplicity we assume a (classical) Boltzmann distribution for kinetic energies of both isotopes instead of the intrinsic quantum statistics of fermionic $^3$He and bosonic $^4$He atoms. However, if a mixed nonideal quantum gas was considered, an even larger $^3$He/$^4$He selectivity would be expected since the Fermi-Dirac distribution is broader than the Bose-Einstein one.

(30) We assume that any particle reaching the surface will always encounter a pore and that it will experience a potential energy barrier equals to that normal to the plane of the pore. In a more realistic simulation the helium flux is expected to be lower.

(31) Permeance ($Q$) is defined as the ratio between the flux and pressure drop across the pore, $Q = \frac{\text{Flux}}{\Delta P}$. In the present case we are assuming $\Delta P = 1$ bar.

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