



# Ultrathin Reduced Graphene Oxide/Organosilica Hybrid Membrane for Gas Separation

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**ABSTRACT:** Here, reduced graphene oxide (r-GO) nanosheets were embedded in an organosilica network to assemble an ultrathin hybrid membrane on the tubular ceramic substrate. With the organosilica nanocompartments inside the r-GO stacks and the intensified polymerization, r-GO sheets endow the as-prepared hybrid membranes with high H<sub>2</sub> and CO<sub>2</sub> separation performance. The resulting selectivities of H<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> are found to be 223 and 55, respectively, together with gas permeance of approximately  $2.5 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> for H<sub>2</sub> and  $6.1 \times 10^{-8}$ mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> for CO<sub>2</sub> at room temperature and 0.2 MPa. To separate larger molecules from H<sub>2</sub>, the H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub>/*i*-C<sub>4</sub>H<sub>10</sub> selectivities are as high as 1775 and 2548, respectively. Moreover, at 150 °C and 0.2 MPa, the hybrid membrane retains high separation



performances with ideal selectivities higher than 200 and 30 for  $H_2/CH_4$  and  $CO_2/CH_4$ , respectively, which are attractive for gas separation and purification of practical applications.

KEYWORDS: graphene oxide, organosilica, ultrathin membrane, hybrid membrane, gas separation

## **INTRODUCTION**

Membrane-based separation is very promising in terms of economy and energy-saving for many industrial separation processes, due to the characteristics of no phase-change involvement, easier operation, modularity, and environmental benignity.<sup>1-6</sup> For gas separation, the membranes act as filters to sieve gas molecules on the basis of molecule size and polarity.7 Therefore, membranes are critical for effective separation of different gas molecules, especially in the case of separating small gases under harsh conditions of high temperature and high pressure. Synthesizing membranes with high gas permeances and high separation selectivity is desirable but challenging due to the small gas molecule size differences at the subangstrom scale and requires rational designs and optimizations on membrane materials and the preparation procedure. $^{8-11}$  Generally, the membrane performance is limited by the trade-off effect; that is, the gas permeance of a membrane inversely correlates to its thickness, but the high selectivity closely relies on the high membrane quality which is normally positively related to membrane thickness.<sup>12</sup> A robust, thin, but high quality (small and ultranarrow pore size distribution) membrane is expected to break the trade-off and achieve the high permeance and high selectivity simultaneously, and it would largely facilitate its application in practical separations.<sup>13</sup>

Organosilica membrane, hybrid, organically linked silicabased membrane derived from organoalkoxysilanes, is a highly promising membrane candidate for molecules separation.<sup>14,15</sup> Similar to the pure silica membranes, it can be prepared by a facile sol-gel procedure that allows coating of a thin layer on various porous supports and, thus, has great potential for largescale preparation of these membranes. In the meanwhile, the connected inorganic siloxane groups and the incorporation of alkylene bridging groups between the two silicon atoms, which repels water and shields the siloxane group from hydrolysis, therefore, bring the essential stability for the hybrid network under harsh conditions.<sup>16,17</sup> Organosilica membranes have been widely used for pervaporation and gas separation. The preparation of organosilica membrane basically consists of the hydrolysis step, that produces reactive groups of terminal silanol, and subsequently the polymerization (or condensation) step, in which the precursor molecules are cross-linked forming the siloxane bonds via the dehydration of aforementioned terminal silanol groups and/or condensation of the silanol and parent ethoxyl silicate groups under relatively high temperatures  $(100-600 \ ^{\circ}C)$ .<sup>16</sup> The pores are the spaces within the silica networks that contain multimembered siloxane rings.

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© 2021 The Authors. Published by American Chemical Society Controlling the length of the siloxane rings<sup>18</sup> and the crosslinking sites<sup>19</sup> is normally the critical principle to manipulate the membrane nanostructure and pore size. Prevailing methods, such as employing different types of alkylene bridging groups,<sup>14,20</sup> incorporating a second or third alkoxysilane precursors for co-condensation,<sup>21,22</sup> and controlling the sol-gel processing parameters,<sup>17,19</sup> had been demonstrated for effectively controlling the pore size and improving the separation performances of prepared membranes. In addition, other strategies, such as adding appropriate metals in the networks that partially block the pore size and/or improve the affinity of specific molecules to a membrane layer, were also proposed to enhance the gas selectivity.<sup>23,24</sup>

The successful preparation of nanosheet materials, such as zeolite nanosheets,<sup>25</sup> metal-organic framework nanosheets,<sup>26,27</sup> graphitic carbon nitride  $(g-C_3N_4)$  nanosheets,<sup>28</sup> MoS<sub>2</sub> sheets,<sup>29<sup>1</sup></sup> and graphene-based laminates,<sup>30</sup> has offered many options and opportunities to membrane scientists for fabricating ultrathin membranes with promising separation results, breaking the trade-off effect between membrane selectivity and membrane permeance. Membrane quality and separation performances had undergone a tremendous increase. Among the numerous two-dimensional (2D) materials, graphene oxide (GO) has gained much attention because of its single-atomic thickness and good chemical and mechanical stability.<sup>31,32</sup> In addition, the hydroxyl, carboxyl, and epoxide groups on the edge of the carbon-carbon plane render the GO hydrophobic and hydrophilic,<sup>33</sup> enabling GO's good dispersion in the precursor solution and excellent compatibility with the hydrophobic-hydrophilic hybrid organosilica matrix.

In this study, as shown in Figure 1, we propose a facile, novel strategy, using the high-surface-area 2D nanosheets, reduced



Figure 1. Schematic illustration of r-GO/organosilica hybrid membrane on a tubular ceramic substrate for gas separation.

graphene oxide (r-GO) specifically, as space confining agents to locally intensify the polymerization of the hydrolyzed precursor molecules to prepare ultrathin hybrid r-GO/ organosilica membranes. The well-dispersed GO laminates constructed interconnected nanocompartments in the pre-

cursor solutions and contained the precursor molecules inside these nanocompartments after drying out the solvent molecules. Subsequently, in the polymerization step, due to the steric hindrance of GO flakes, the silanol groups preferentially react with the relatively closer reactive groups within the nanocompartments, compared with the cases of pure organosilica membranes, generating relatively denser membrane nanostructure locally inside these nanocompartments and reducing the pores size. The high surface area of GO laminates maximized such a space-confining effect and, therefore, the polymerization intensifying effect in each nanocompartment. The large amount of r-GO and r-GO constructed nanocompartments populated the locally polymerization-intensified organosilica throughout the membrane matrix. As a result, the ultrathin (25 nm) r-GO/orgnaosilica hybrid membranes exhibited very high gas selectivity of  $H_2/$  $CH_4 = 223$ ,  $CO_2/CH_4 = 55$ . In this study, we use the 1,2bis(trienthoxisilyl)ethane (BTESE) derived organosilica membrane as the base membrane and ceramic hollow fiber as supports to demonstrate the feasibility of this strategy.

## EXPERIMENTAL SECTION

## Preparation of Organosilica Sol and GO/Organosilica Coating Solutions

The organosilica polymer sol was prepared from the hydrolysis and polymerization of 1,2-bis(trienthoxisilyl)ethane (BTESE, 96%, J&K Scientific Ltd.) in ethanol (AR, Sinopharm) with hydrochloric acid (36-38%, Sinopharm) as the acid catalyst, according to our previous work.<sup>34</sup> Briefly, BTESE was first added to ethanol with an established ratio at room temperature, then a mixture of water and hydrochloric acid was added to the solution under stirring. The final solution molar ratio of BTESE/ethanol/H2O/HCl was 1:46:60:0.1. After stirring for 5 h, the weight percent of the precursor BTESE was diluted 10 times via ethanol as a solvent for use. Graphene oxide (GO) was purchased from Nanjing XFNANO Materials Tech. Co. Ltd. GO sheets were added to the polymer sol under ultrasonication for at least 1 h and were stirred every 30 min during ultrasonication until GO/ organosilica coating solutions were obtained. In this work, a series of GO/organosilica coating solutions were prepared. The various weight ratios of GO to organosilica were 1/2, 1/1.5, 1/1, 1.5/1, and 2/1.

## Fabrication of r-GO/Organosilica Membrane

Large pores of the porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic tubes ( $\phi_{outer} = 3.5$  mm,  $\phi_{inner} = 1.5 \text{ mm}, l = 60 \text{ mm}, \text{ nominal pore size} = 100 \text{ nm}, \text{ purchased}$ from Hyflux Ltd. Co.) were modified by industrial colloidal silica (particle size is 12 nm, Ludox SM-30, Sigma-Aldrich) in advance, as the intermediate layer. The supports were preheated to 140 °C before being coated with colloidal silica and then were calcined at 550 °C for 20 min. The modified substrate was kept at 120 °C for at least 30 min with both ends sealed, and then it was vertically put into the asprepared coating solution. After a period of 30 s, the substrate was pulled out slowly at a rate of  $1 \text{ mm} \cdot \text{s}^{-1}$  so that it had been coated with the precursor solution on its outer surface. After this hot dip-coating process, the substrate was dried at 80 °C for 15 min and calcined at 300 °C under argon atmosphere for 5 h to obtain the GO incorporated organosilica membranes. Five GO/organosilica coating solutions with different weight ratios of 1:2, 1:1.5, 1:1, 1.5:1, and 2:1 of GO to organosilica were prepared to fabricate GO/organosilica membranes as GO-Si1/2, GO-Si1/1.5, GO-Si1/1, GO-Si1.5/1, and GO-Si2/1, respectively. The pristine organosilica membranes were prepared with the same process as the control.

#### Characterization

The membrane of pure organosilica and r-GO/organosilica prepared by calcination at 300  $^{\circ}$ C were characterized by Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Company). The morphologies of hybrid membranes were characterized by field emission scanning electron microscopy (FESEM, S-4800, Hitachi) and transmission electron microscopy (TEM, Talos F200X). The sample used for TEM was obtained on a double beam scanning electron microscope (FIB, Helios-G4-CX). The d-spacing of GO sheets was investigated by X-ray diffraction (XRD). XRD patterns were collected on a Bruker AXS D8 Advance diffractometer using Cu K $\alpha$  radiation at a voltage of 40 kV and 40 mA. The thickness of GO sheets was measured by atomic force microscopy (AFM, Dimension 3100, Vecco). X-ray photoelectron spectroscopy (XPS) was carried out on an AXIS ULTRA X-ray photoelectron spectrometer using Mg K $\alpha$  radiation. Small-angle X-ray scattering (SAXS) was performed by using the NanoSTAR SAXS camera (Bruker-AXS). The scattering intensity I(q) was given as a function of q, which is the scattering vector, and obtained as  $q = 4\pi \sin \theta / \lambda$ , in which  $2\theta$  is the scattering angle. The zeta potential of the organosilica sol and GO/organosilica sol were tested on Nano ZS (Malvern Instruments Ltd., England). All the GO/organosilica powders for tests were prepared by the same process with no supports.

#### **Gas Permeance Tests**

The tested pure gases  $(H_2, CO_2, N_2 \text{ and } CH_4)$  were fed to the outside of the membranes which were sealed in a permeation module with silicone O-rings. For single component gases, the feed stream was pressurized to measure gas permeation with downstream at atmospheric pressure and the gas flux was determined by a soap film bubble flow meter. The gas permeance (*P*) is calculated from the following equation in an SI unit:

$$P = Q/(\Delta pS)$$

where Q is the gas molar flow rate (mol·s<sup>-1</sup>),  $\Delta p$  is the transmembrane pressure drop (Pa) between input and output sides, and S is the membrane area (m<sup>2</sup>).

The ideal selectivity  $(\alpha_{1,2})$  is calculated from

 $\alpha_{1,2} = P_1 / P_2$ 

where  $P_1$  and  $P_2$  are the permeance for gas 1 and gas 2, respectively. Mixture gas permeation was carried out by feeding gas mixtures  $(H_2/CH_4 \text{ and } CO_2/CH_4)$  with equal molar ratios on the outside of the membrane in a module under the atmospheric feed pressure with a flow rate of 50 mL/min for each gas and argon as the sweep downstream with a flow rate of 120 mL/min. The concentration of mixed gases on the permeate side were recorded by using a calibrated gas chromatograph with a TCD detector. The gas mixture selectivity( $\alpha_{i,i,mixed}$ ) is defined by the following expression:

$$\alpha_{i,j,\text{mixed}} = \frac{x_i/x_j}{y_i/y_i}$$

where x is the molar fraction of the components (gas i or j) in the permeate side and y is the molar fraction of the components (gas i or j) in the feed side.

## RESULTS AND DISCUSSION

After ultrasonicating the mixture of GO and the organosilica polymer sol with mole compositions of BTESE/ethanol/ water/hydrochloric acid of 1:46:60:0.1 for 1 h, the GO flakes with planar size > 500 nm (Figure S1) were well dispersed in the precursor sol in a wide range of weight ratios of GO/ organosilica (1/2, 1/1.5, 1/1, 1.5/1, 2/1). Accordingly, the transparent organosilica sol turned to be dark black after the adding of large amount of GO flakes (Figure S2a, GO/ organosilica = 1:1). Compared with the organosilica sol, the zeta potential would drop from 22.1 to -7.52 mV when adding GO into the sol solution (Figure S2b). This indicates that the GO/organosilica is not stable. Therefore, the GO/organosilica coating solutions should be kept stirred before use. In this study, we finished the dip-coating within a short period of 2 min so that there was no condensation of GO/organosilica. In previous literature, the GO or modified GO laminates had been added to the polymer matrix for enhancing the quality and separation performance of the resultant GO/polymer composite membranes. However, their GO concentrations were very low, less than 10 wt % of GO to polymer matrix,<sup>35–37</sup> because of the incompatibility of GO with organic polymer precursors. In this regard, the organosilica membranes can potentially act as a platform to explore the influences of GO laminates on enhancing the separation performance of a GO/organosilica membrane in a wide range of GO/organosilica weight ratios.

Prior to the coating of the GO/organosilica layer on the support, the support was dipped into an industrial silica gel. This helps to decrease the support surface roughness and reduce the effective pore size, which had been proven to be beneficial for a high quality organosilica membrane.<sup>38</sup> A hot dip-coating method<sup>34</sup> was employed to coat the well-mixed precursor sol onto the simply modified support surface. The coated supports were then dried at 80 °C for 15 min. Polymerization was carried out at 300 °C for 5 h in argon atmosphere, and a light black colored hybrid membrane (Figure S2b, membrane with coating of GO/organosilica = 1/1) was obtained, indicating the successful preparation of GO-containing membranes. Field emission scanning electron microscopy (FESEM) images of the as-prepared membranes, as shown in Figures 2a,b and S3, showed a continuous and



**Figure 2.** SEM images of the (a) surface and (b) cross section. (c) TEM, (d) HRTEM, and (e) HAADF-STEM, as well as the corresponding EDX mapping images of the cross section of the GO-Si1/1 hybrid membrane.

smooth layer on the outer surface of the support. With the increasing ratio of GO/organosilica, the membrane surface began to show some wrinkles. This is, probably, because the large amount of GO laminates made the GO sheets difficult to spread out in the hybrids and the relatively smaller portion of organosilica precursors cannot fully cover the GO laminates in the membrane layer, thus exposing one side of GO laminates to the atmosphere. The thicknesses of the GO/organosilica layers were in the range of 20-34 nm. To the best of our knowledge, these are the thinnest organosilica-based membranes among those in the literature. Figure 2c and d displays the TEM and high-resolution TEM (HRTEM) images of the cross-section of the GO-Si1/1 hybrid membrane. HRTEM reveals that the hybrid membrane with a thickness of approximately 25 nm tightly adhered to the predeposited SiO<sub>2</sub> layer on the support. However, the lattice fringes of GO sheets cannot be clearly observed even in the HRTEM image. On the other hand, the high-angle annular dark-field scanning TEM (HAADF-STEM) and the corresponding energydispersive X-ray (EDX) mapping images (Figure 2e) clearly

depict the C-rich and Si-rich regions, corresponding to the membrane layer and the  $SiO_2$  intermdiate layer, respectively.

During the polymerization process, the GO incorporated in the organosilica matrix was expected to undergo a thermal reduction process and became reduced GO (r-GO) which was evidenced by the XRD (Figure S4) profiles of the prepared membranes. The characteristic peaks significantly shifted from 13.15° of pristine GO to 23.35° of the membrane samples, which corresponded to an interlayer distance decrease from 0.67 nm to only 0.38 nm, according to Bragg's law. It should be noted that the r-GO *d*-spacing is very close to the thickness of the graphene layer, <sup>39,40</sup> which means that there is little effective space left for molecules to transport between the adjacent r-GO sheets. In other words, the r-GO sheets interspersed with organosilica polymer have a blocking effect on gas molecules transporting across the membrane, thus leaving the pores of the organosilica matrix as the main permeation pathway for the molecules. And this blocking effect is positively correlated with the size of gas molecules, thus realizing the molecular sieving effect of the as-prepared membrane for gas separation, which will be discussed later.

The SAXS data were collected to investigate the dispersion and structral features of r-GO in the r-GO/organosilica hybrids. As shown in Figure S5, compared with the organosilica sample, the r-GO/organosilica sample had a lower intensity at low q ( $q < 0.15 \text{ nm}^{-1}$ ). When q was greater than 0.15 nm<sup>-1</sup>, the r-GO/organosilica hybrids showed higher intensity than the pristine organosilica, owing to the higher electron density accumulated in the r-GO/organosilica.<sup>41</sup> The broad shoulder around  $q = 0.1 \text{ nm}^{-1}$  in the SAXS of the r-GO/ organosilica could be attributed to the correlated r-GO sheets in the lamellar phase, with a corresponding spacing  $(d = 2\pi/q)$ of 63 nm.<sup>42</sup> The information of the aggeregation state of the r-GO layers could be obtained from the fractal dimension  $(d_m)$ , which is related to the slope of the SAXS curves in the log-log scale at low q.<sup>43</sup> The different  $d_m$  values are determined by fractal geometry. In this study, the loose structure of the organosilica sample formed a surface fractal. After the incorporation of r-GO into organosilica, the mass fractal structures appeared in the hybrid sample.

In order to further understand the nanostructure of the hybrid r-GO/organosilica membranes, they were subjected to FT-IR characterization. As shown in Figure S6a, the presence of the characteristic peaks at 1728 cm<sup>-1</sup> was associated with the C=O stretching vibration from r-GO planes.<sup>44–47</sup> The intensive peaks at 1000 and 453 cm<sup>-1</sup>, originating from Si–O– Si asymmetric stretching and rocking vibrations,<sup>48-51</sup> and the peaks at 772 cm<sup>-1</sup>, assigned to Si-C stretching vibrations,<sup>52</sup> indicated that the sol-gel reactions successfully took place in the hybrids. However, the peak of Si-O-Si was not found in the spetra of the GO/organosilica hybrids before treated at 300 °C for 5h. Compared with pure organosilica membrane, the hybrid r-GO/organosilica membranes showed dramatically weaker silanol (Si–OH) peaks at around 920, 1640, and 3440  $\rm cm^{-1}$ , <sup>48,49,53</sup> indicating a smaller amount of silanol groups within the hybrid membranes. Furthermore, the peak of the C=C stretching vibration of the membranes showed a redshift from 1627 to 1569  $cm^{-1}$  after the polymerization process. We speculated that the adjacent r-GO stacks formed nanocompartments and confined many silanol groups inside these nanocompartments. The cross-linking reactions between these silanol groups were intensified due to the space confinement effect of these r-GO stacks and resulted in a

higher degree of cross-linking. The detection of a subtle peak at 1385 cm<sup>-1</sup> (Figure S6b), corresponding to Si-O-C=O,<sup>54</sup> in r-GO/organosilica membranes indicated the occurrence of reaction between organosilica silanol groups and GO carboxyl groups during the hydrolysis or thermal annealing steps. Based on the absorption intensity of Si-C of the r-GO/organosilica membranes, the confinement effect on silanol groups with r-GO was quantitatively described by the ratio of the absorption intensity of Si-C. As expected, the increased GO concentration in the membranes produced the higher degree of polymerization between GO and organosilica, with 1.6%, 2.3%, 2.7%, 3.6%, and 5.3% for GO-Si1/2, GO-Si1/1.5, GO-Si1/1, GO-Si1.5/1, and GO-Si2/1, respectively.

In order to understand the nanostructure of the r-GO/ organosilica hybrid membrane, XPS was performed to analyze the elements within the membrane (Figure S7). The highresolution C 1s spectrum of pure GO sheets revealed four carbon peaks: C=C bonds at the binding energy of 284.4 eV, C-C bonds at 285.0 eV, C-O bonds at 286.9 eV, and O-C= O bonds at 288.5 eV. As for the membrane samples with different GO/organosilica mass ratios, the C-O bond intensity decreased significantly while that of C=C bonds increased remarkably, which further confirmed the reduction of GO flakes during the polymerization. With regard to silicon, the hybrid membrane samples shifted 0.6 eV to lower bonding energies compared with the pure organosilica membrane; this probably due to the existence of the less electronegative r-GO in membranes.<sup>55</sup> Deconvolution of the high-resolution Si 2p spectra of pristine organosilica showed that there existed two peaks at 102.6 and 103.1 eV. The lower binding energy peak most likely corresponded to the SiO<sub>3</sub>C in the organosilica powders, and the higher binding energy peak was identified as the inorganic moieties SiO<sub>4</sub>. By increasing the r-GO, the SiO<sub>4</sub> content in the membranes decreased from 46.6% to 20.3%, while the RSiO<sub>3</sub> content increased from 53.4% to 79.7%, clearly indicating the increment of carbon content in membranes and the reduction of Si-O-Si formed by Si-OH.

To evaluate the separation performances of the hybrid r-GO/organosilica membranes, single gas permeation measurements at a pressure difference of 0.2 MPa and room temperature were carried out. As illustrated in Figure S8a, compared with the pure organosilica membrane, upon the incorporation of GO stacks into the organosilica networks, the gas permeance underwent a dramatic decrease, although the hybrid r-GO/organosilica membranes were even thinner (Figure S3). This is contrary to the literature results that the enhanced gas permeance after the adding of GO flakes was observed, resulting from the introduction of straight and fast transport channels (GO *d*-spacing).<sup>37</sup> In this study, the thermal reduction of GO during the high temperature polymerization step decreased the size of *d*-spacing, which is, therefore, blocked for gas molecules. Consequently, the gas molecules must bypass these micrometer-sized r-GO stacks to permeate through the membrane layer in a more tortuous way (Figure S9), resulting in the lower gas permeances, compared with the pure organosilica membrane. Furthermore, the larger the molecule, the more tortuous it is to pass through, so the gas permeance decreases are dependent to gas molecules and larger molecules exhibited larger decrease. For example, the smallest  $H_2$  (0.289 nm) underwent a decrease by a factor of 21, from 5.73  $\times$  10<sup>-6</sup> mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> for pure organosilica membrane to  $2.66 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> for the GO/Si1/2 membrane, followed by  $CO_2$  (0.33 nm) by a factor of 26 and  $N_2$  (0.346 nm) by a factor of 57. The largest  $CH_4$  (0.38 nm) decreased by a factor of 79, from  $4.35 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> for pure organosilica membrane to  $5.48 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot$  $Pa^{-1}$  for the GO/Si1/2 membrane. This could be attributed to the pore size decrease of the hybrid r-GO/organosilica membrane. As mentioned above, the space confining effect of the GO stacks is speculated to intensify the cross-linking of the organosilica network and decrease the pore size of the hybrid membranes. From the obtained gas permeances, the pore size of the hybrid membrane is between the size of CO<sub>2</sub> (0.33 nm) and N<sub>2</sub> (0.346 nm). As a result, compared with pure organosilica membrane, the hybrid r-GO/organosilica membranes showed much higher gas ideal selectivities (Figure S8b). The ideal gas selectivities increased with increasing GO fractions in the hybrid membranes with the highest ideal selectivities of  $H_2/N_2$ ,  $H_2/CH_4$ ,  $CO_2/N_2$ , and  $CO_2/CH_4$  being  $120 \pm 11, 223 \pm 14, 29 \pm 5$ , and  $55 \pm 7$ , respectively, obtained by the hybrid r-GO/Si = 1/1 membrane. This membrane also exhibits extraordinary selectivity of H<sub>2</sub> and CO<sub>2</sub> over molecules larger than 0.4 nm, such as C<sub>3</sub>H<sub>8</sub> (0.446 nm) and *i*-C<sub>4</sub>H<sub>10</sub> (0.51 nm), with the ideal selectivities of  $H_2/C_3H_{81}$   $H_2/i$ - $C_4H_{101}$  $CO_2/C_3H_{8i}$  and  $CO_2/i-C_4H_{10}$  being 1775, 2548, 463, and 664, respectively (Figure S10). Higher GO/Si ratios represent stronger a confining effect and, subsequently, larger degree of cross-linking and smaller pore size, decreasing the resultant membrane pore size toward the size of the CO<sub>2</sub> molecule. Further increasing the r-GO/Si ratio to 2/1, the gas permeances increased and the ideal selectivities decreased, suggesting the existence of cracks on the hybrid membranes. That is probably because the amount of organosilica precursors trapped in the GO nanocompartments was limited and the organosilica matrix could not form a continuous layer within the nanocompartments. This was consistent with the SEM observation of the hybrid r-GO/Si = 2/1 membrane in which GO wrinkles can be detected, as shown in Figure S3. Table S1 lists the H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> permeances and the ideal selectivities  $(H_2/CH_4 \text{ and } CO_2/CH_4)$  of three tested membranes (r-GO/organosilica = 1/1) prepared with the same procedures, as a proof of the reproducibility of membranes. The values of gas permeance and the ideal selectivity scattering within  $\pm 11\%$  revealed the good reproducibility of the hybrid membranes.

The coating solution with a GO/Si ratio of 1/1 was also diluted by a factor of 2 and 4 to prepare the hybrid membranes, trying to further reduce the membrane thickness and enhance the gas permeability. As shown in Figure S11, the diluted solution indeed led to thinner hybrid membranes (~16-22 nm). However, the corresponding organosilica matrix layers seem too thin to fully cover the GO nanosheets, resulting in many defects on the surfaces. Herein the transport for all gases is effectively accelerated (Figure S12a). The large molecules undergo a greater degree of increase in permeance as they can leak through the defects, yielding reduced ideal selectivities of H<sub>2</sub> and CO<sub>2</sub> over larger gas molecules. In particular, the membrane prepared with the 4-fold dilute solution exhibited a remarkable drop for the selectivities (Figure S11b and c).

One of the advantages of the organosilica membranes is the stability at higher temperatures; therefore, we investigated the separation performance of the hybrid membranes at 150 °C. For single gas permeation, compared with those at 25 °C, the permeance of H<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> showed a slight increase, probably resulting from the enhanced diffusivity of those

molecules at higher temperature. However, the  $CO_2$ permeance showed a slight decrease. It is well accepted that adsorption plays a vital role in the separation performance. We have thus comparatively measured the adsorption isotherms of CO<sub>2</sub> and CH<sub>4</sub> on the r-GO/organosilica powder at 25 and 150  $^{\circ}$ C. Note that the adsorption of H<sub>2</sub> and N<sub>2</sub> on r-GO/ organosilica powders is negligible at both temperatures and no CH<sub>4</sub> adsorption is detected at 150 °C. As shown in Figures S13, the adsorption capacity of  $CO_2$  is significantly higher than that of CH<sub>4</sub> at 25 °C. The corresponding adsorption selectivity of CO<sub>2</sub> over CH<sub>4</sub> was calculated to be about 5.4 (Figure S14) based on the initial slope of the gas uptake, implying the preference of CO<sub>2</sub> transport within the membrane at 25 °C. Compared with the heat of adsorption for CO<sub>2</sub> on the neat organosilica sample (23.7 kJ/mol), the r-GO/organosilica sample showed a slightly lower value (20.1 kJ/mol). In contrast, the heat of adsorption for CH4 was significantly increased from 12.31 kJ/mol on the pristine organosilica to 29.67 kJ/mol on the r-GO/organosilica, indicating that the organosilica materials present enhanced affinity to CH44 but reduced affinity to  $CO_2$  after the incorporation of r-GO.

With the temperature increased to 150 °C, the adsorption of  $CO_2$  is drastically weakened to a negligible level. Correspondingly, the  $CO_2$  permeance was nearly halved. In other words, the advantage of high adsorption for  $CO_2$  molecules is offset. As a result, an obvious decay for  $CO_2/N_2$  and  $CO_2/CH_4$  selectivities is found in both single gas and equimolar binary mixture measurements (Figure 3). Interestingly, the weak  $CH_4$  adsorption has some profound influence on the permselectivity



**Figure 3.** (a) Ideal selectivities of  $H_2/CH_4$ ,  $H_2/N_2$ ,  $CO_2/CH_4$ , and  $CO_2/N_2$  (inset: corresponding permeance of single gases); and (b) selectivities of binary gases mixtures of the GO-Si1/1 hybrid membrane at 25 and 150 °C ( $\Delta p = 0.2$  MPa).

properties of  $H_2/CH_4$  mixtures. As shown in Figure 3, the  $H_2/$ CH<sub>4</sub> selectivity in the gas mixture measurement drops by approximately 50% compared to the calculated single-gas selectivity at 25 °C. The CH<sub>4</sub> in the gas mixture may be preferentially adsorbed on GO nanosheets and thus impede the transport of nonadsorptive H<sub>2</sub> molecules. Similar results have also been observed on the ZIF-8@GO membrane, in which the  $H_2/CH_4$  selectivity was decreased by about 30%, compared with the ideal single-gas selectivity.<sup>56</sup> Although the ideal selectivities underwent a slight decrease at 150 °C, the values of  $H_2/CH_4$ ,  $H_2/N_2$ ,  $CO_2/CH_4$ , and  $CO_2/N_2$ selectivities were still over 200, 95, 30, and 15, respectively, and by far exceeded the corresponding Knudsen selectivities (2.8, 3.7, 0.6, and 0.8), suggesting that the r-GO/organosilica membrane still possesses high separation performances at high temperature. Moreover, the mixture separation values of  $H_2/$  $N_2$ ,  $CO_2/N_2$ , and  $CO_2/CH_4$  of the r-GO/organosilica hybrid membrane at room temperature were found to be 92, 24, and 47, respectively, comparable to the ideal selectivities in single gas test, further confirming the outstanding quality of the asprepared hybrid membrane. Moreover, the CO<sub>2</sub>/CH<sub>4</sub> binary mixture through the r-GO/organosilica membrane was tested over 24 h at room temperature, and both gas permeances and the  $CO_2/CH_4$  separation performance kept approximately stable with slight fluctuations, indicating the high long-time stability of the rGO-organosilica membrane (Figure S16). The CO<sub>2</sub>/CH<sub>4</sub> binary mixture passed through a water cell before feeding to the r-GO/organosilica membrane to investigate the hydrothermal stability. As shown in Figure S17, the membrane could remain hydrothermally stable under continuous feeding gases for at least 4 h. Further, the separation performance of CO<sub>2</sub>/CH<sub>4</sub> from the equimolar mixture through the rGOorganosilica membrane with the gas (CO<sub>2</sub> or CH<sub>4</sub>) pressure drop increasing from 0.1 to 0.4 MPa revealed that the asprepared membrane did not contain macroscopic defects and kept its high gas permselectivity (Figure S18).

As shown in Figure 4, the separation performance of our optimized r-GO/organosilica membrane measured at room temperature and 0.2 MPa for separating H<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/ CH<sub>4</sub> is compared with other reported membranes. A detailed comparison with the literature is also summarized in Tables S2 and S3. The relative low permeances of  $H_2$  and  $CO_2$  are ascribed to the blocking effect of r-GO with its reduced dspacing, while the selectivity increase of the membrane could also be explained by this point due to the positive correlation between the molecular size and blocking effect. Compared to the highly oriented  $Zn_2(bIm)_4$  nanosheet membrane guided by GO supported on a porous tube reported by Zhang's group,<sup>5</sup> our membrane gave a lower performance for  $H_2/CH_4$  but much higher performance for  $CO_2/CH_4$  (Tables S2 and S3). The r-GO/organosilica membrane exhibited higher  $CO_2/CH_4$ selectivity than most GO-based membranes, except for the GO-PEGDA (poly(ethylene glycol) diamines) membrane reported by Jiang's group,<sup>58</sup> which mainly resulted from the introduction of CO<sub>2</sub>-philic nanodomains. Nevertheless, the asprepared hybrid membrane for separating either H<sub>2</sub>/CH<sub>4</sub> or CO<sub>2</sub>/CH<sub>4</sub> gas couples is beyond most GO/rGO-based and organosilica-based membranes as well as MOF-polymer mixed matrix membranes (MMMs), because the collaborative advantages of r-GO and organosilica endow the hybrid membrane with the appropriate transportable spacing that can effectively screen out the gas molecules that are larger than CO<sub>2</sub>. Moreover, in contrast to the reported GO-based



Figure 4. Comparison of the (a)  $H_2/CH_4$  and (b)  $CO_2/CH_4$  separation performance of reported representative membranes, including GO/rGO-based membranes, organosilica/silica-based membranes, and MOF-polymer MMMs. Closed symbols are the data from single-gas permeation test, and half-open symbols are data from the binary-gas separation test. More detailed data are listed in Tables S2 and S3.

membranes, our r-GO/organosilica membranes were easily fabricated on large-scale tubular substrates by hot dip-coating, which is advantageous in reducing waster and feasible in practical applications.

## CONCLUSIONS

In conclusion, we have successfully prepared ultrathin hybrid r-GO/organosilica membranes on hollow fiber supports. The organosilica precursors were trapped inside of the GO stack constructed nanocompartments, and their polymerization was therefore intensified in the polymerization step. The resulting ultrathin hybrid membrane displays high H<sub>2</sub>- and CO<sub>2</sub>-selective separation performance owing to the enhanced cross-linking and reduced pore size. At 25 °C and 0.2 MPa, the ideal selectivities of GO-Si1/1 for H<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> are calculated to be 223 and 55, respectively. Even when heated to 150 °C, the excellent separation performance of the hybrid membrane can be well maintained. The simple and efficient preparation strategy of r-GO/organosilica membranes indicates great potential for gas separation in practical processes.

## ASSOCIATED CONTENT

## **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.0c00073.

Detailed experimental characterization and comparison with literature (PDF)

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## Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Dong, G.; Zhang, Y.; Hou, J.; Shen, J.; Chen, V. Graphene oxide nanosheets based novel facilitated transport membranes for efficient CO<sub>2</sub> capture. *Ind. Eng. Chem. Res.* **2016**, 55 (18), 5403–5414.

(2) Lin, L.-C.; Grossman, J. C. Atomistic understandings of reduced graphene oxide as an ultrathin-film nanoporous membrane for separations. *Nat. Commun.* **2015**, *6*, 8335.

(3) Ma, J.; Ping, D.; Dong, X. Recent developments of graphene oxide-based membranes: A review. *Membranes* **2017**, 7 (3), 52.

(4) Yang, E.; Ham, M.-H.; Park, H. B.; Kim, C.-M.; Song, J.-h.; Kim, I. S. Tunable semi-permeability of graphene-based membranes by adjusting reduction degree of laminar graphene oxide layer. *J. Membr. Sci.* **2018**, *547*, 73–79.

(5) Zhan, Y.; Wan, X.; He, S.; Yang, Q.; He, Y. Design of durable and efficient poly(arylene ether nitrile)/bioinspired polydopamine coated graphene oxide nanofibrous composite membrane for anionic dyes separation. *Chem. Eng. J.* **2018**, 333, 132–145.

(6) Zhang, J.; Schott, J. A.; Li, Y.; Zhan, W.; Mahurin, S. M.; Nelson, K.; Sun, X.-G.; Paranthaman, M. P.; Dai, S. Membrane-based gas

separation accelerated by hollow nanosphere architectures. Adv. Mater. 2017, 29 (4), 1603797.

(7) Du, N.; Park, H. B.; Dal-Cin, M. M.; Guiver, M. D. Advances in high permeability polymeric membrane materials for  $CO_2$  separations. *Energy Environ. Sci.* **2012**, *5* (6), 7306–7322.

(8) Jiang, J.; Lu, Z.; Zhang, M.; Duan, J.; Zhang, W.; Pan, Y.; Bai, J. Higher symmetry multinuclear clusters of metal-organic frameworks for highly selective  $CO_2$  capture. *J. Am. Chem. Soc.* **2018**, *140* (51), 17825–17829.

(9) Li, W.; Su, P.; Li, Z.; Xu, Z.; Wang, F.; Ou, H.; Zhang, J.; Zhang, G.; Zeng, E. Ultrathin metal-organic framework membrane production by gel-vapour deposition. *Nat. Commun.* **2017**, *8* (1), 406. (10) Ma, X.; Kumar, P.; Mittal, N.; Khlyustova, A.; Daoutidis, P.; Mkhoyan, K. A.; Tsapatsis, M. Zeolitic imidazolate framework membranes made by ligand-induced permselectivation. *Science* **2018**, 361 (6406), 1008–1011.

(11) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. Porous materials with optimal adsorption thermodynamics and kinetics for  $CO_2$  separation. *Nature* **2013**, 495 (7439), 80–84.

(12) Park, H. B.; Kamcev, J.; Robeson, L. M.; Elimelech, M.; Freeman, B. D. Maximizing the right stuff: The trade-off between membrane permeability and selectivity. *Science* **2017**, *356* (6343), eaab0530.

(13) Kim, H. W.; Yoon, H. W.; Yoon, S.-M.; Yoo, B. M.; Ahn, B. K.; Cho, Y. H.; Shin, H. J.; Yang, H.; Paik, U.; Kwon, S.; Choi, J.-Y.; Park, H. B. Selective gas transport through few-layered graphene and graphene oxide membranes. *Science* **2013**, *342* (6154), 91–95.

(14) Castricum, H. L.; Paradis, G. G.; Mittelmeijer-Hazeleger, M. C.; Kreiter, R.; Vente, J. F.; Ten Elshof, J. E. Tailoring the separation behavior of hybrid organosilica membranes by adjusting the structure of the organic bridging group. *Adv. Funct. Mater.* **2011**, *21* (12), 2319–2329.

(15) Chai, S.; Du, H.; Zhao, Y.; Lin, Y.; Kong, C.; Chen, L. Fabrication of highly selective organosilica membrane for gas separation by mixing bis(triethoxysilyl)ethane with methyltriethoxysilane. *Sep. Purif. Technol.* **2019**, 222, 162–167.

(16) Ren, X.; Tsuru, T. Organosilica-based membranes in gas and liquid-phase separation. *Membranes* **2019**, *9* (9), 107.

(17) Yu, X.; Nagasawa, H.; Kanezashi, M.; Tsuru, T. Improved thermal and oxidation stability of bis(triethoxysilyl)ethane (BTESE)-derived membranes, and their gas-permeation properties. *J. Mater. Chem. A* **2018**, *6* (46), 23378–23387.

(18) Kanezashi, M.; Yoneda, Y.; Nagasawa, H.; Tsuru, T.; Yamamoto, K.; Ohshita, J. Gas permeation properties for organosilica membranes with different Si/C ratios and evaluation of microporous structures. *AIChE J.* **2017**, *63* (10), 4491–4498.

(19) Niimi, T.; Nagasawa, H.; Kanezashi, M.; Yoshioka, T.; Ito, K.; Tsuru, T. Preparation of BTESE-derived organosilica membranes for catalytic membrane reactors of methylcyclohexane dehydrogenation. *J. Membr. Sci.* **2014**, 455, 375–383.

(20) Li, G.; Kanezashi, M.; Tsuru, T. Preparation of organicinorganic hybrid silica membranes using organoalkoxysilanes: The effect of pendant groups. J. Membr. Sci. 2011, 379 (1–2), 287–295. (21) Meng, L.; Kanezashi, M.; Wang, J.; Tsuru, T. Permeation properties of BTESE-TEOS organosilica membranes and application

to O<sub>2</sub>/SO<sub>2</sub> gas separation. J. Membr. Sci. 2015, 496, 211–218. (22) Yu, L.; Kanezashi, M.; Nagasawa, H.; Guo, M.; Moriyama, N.;

Ito, K.; Tsuru, T. Tailoring ultramicroporosity to maximize  $CO_2$  transport within pyrimidine-bridged organosilica membranes. ACS Appl. Mater. Interfaces **2019**, 11 (7), 7164–7173.

(23) Qi, H.; Chen, H.; Li, L.; Zhu, G.; Xu, N. Effect of Nb content on hydrothermal stability of a novel ethylene-bridged silsesquioxane molecular sieving membrane for  $H_2/CO_2$  separation. J. Membr. Sci. 2012, 421–422, 190–200.

(24) Ten Hove, M.; Nijmeijer, A.; Winnubst, L. Facile synthesis of zirconia doped hybrid organic inorganic silica membranes. *Sep. Purif. Technol.* **2015**, *147*, 372–378.

(25) Jeon, M. Y.; Kim, D.; Kumar, P.; Lee, P. S.; Rangnekar, N.; Bai, P.; Shete, M.; Elyassi, B.; Lee, H. S.; Narasimharao, K.; Basahel, S. N.; Al-Thabaiti, S.; Xu, W.; Cho, H. J.; Fetisov, E. O.; Thyagarajan, R.; Dejaco, R. F.; Fan, W.; Mkhoyan, K. A.; Siepmann, J. I.; Tsapatsis, M. Ultra-selective high-flux membranes from directly synthesized zeolite nanosheets. *Nature* **2017**, *543* (7647), 690–694.

(26) Peng, Y.; Li, Y.; Ban, Y.; Jin, H.; Jiao, W.; Liu, X.; Yang, W. Metal-organic framework nanosheets as building blocks for molecular sieving membranes. *Science* **2014**, *346* (6215), 1356–1359.

(27) Rodenas, T.; Luz, I.; Prieto, G.; Seoane, B.; Miro, H.; Corma, A.; Kapteijn, F.; Llabrés I Xamena, F. X.; Gascon, J. Metal-organic framework nanosheets in polymer composite materials for gas separation. *Nat. Mater.* **2015**, *14* (1), 48–55.

(28) Wang, Y.; Li, L.; Wei, Y.; Xue, J.; Chen, H.; Ding, L.; Caro, J.; Wang, H. Water transport with ultralow friction through partially exfoliated g-C<sub>3</sub>N<sub>4</sub> nanosheet membranes with self-supporting spacers. *Angew. Chem., Int. Ed.* **2017**, *56* (31), 8974–8980.

(29) Achari, A.; Sahana, S.; Eswaramoorthy, M. High performance  $MoS_2$  membranes: effects of thermally driven phase transition on  $CO_2$  separation efficiency. *Energy Environ. Sci.* **2016**, *9* (4), 1224–1228.

(30) Yang, E.; Karahan, H. E.; Goh, K.; Chuah, C. Y.; Wang, R.; Bae, T.-H. Scalable fabrication of graphene-based laminate membranes for liquid and gas separations by crosslinking-induced gelation and doctor-blade casting. *Carbon* **2019**, *155*, 129–137.

(31) Li, D.; Qiu, L.; Wang, K.; Zeng, Y.; Li, D.; Williams, T.; Huang, Y.; Tsapatsis, M.; Wang, H. Growth of zeolite crystals with graphene oxide nanosheets. *Chem. Commun.* **2012**, *48* (16), 2249–2251.

(32) Xu, W. L.; Fang, C.; Zhou, F.; Song, Z.; Liu, Q.; Qiao, R.; Yu, M. Self-assembly: A facile way of forming ultrathin, high-performance graphene oxide membranes for water purification. *Nano Lett.* **2017**, *17* (5), 2928–2933.

(33) Hu, R.; He, Y.; Zhang, C.; Zhang, R.; Li, J.; Zhu, H. Graphene oxide-embedded polyamide nanofiltration membranes for selective ion separation. *J. Mater. Chem. A* **2017**, *5* (48), 25632–25640.

(34) Kong, C.; Du, H.; Chen, L.; Chen, B. Nanoscale MOF/ organosilica membranes on tubular ceramic substrates for highly selective gas separation. *Energy Environ. Sci.* **2017**, *10* (8), 1812–1819.

(35) Dong, G.; Hou, J.; Wang, J.; Zhang, Y.; Chen, V.; Liu, J. Enhanced  $CO_2/N_2$  separation by porous reduced graphene oxide/ Pebax mixed matrix membranes. J. Membr. Sci. **2016**, 520, 860–868.

(36) Li, X.; Cheng, Y.; Zhang, H.; Wang, S.; Jiang, Z.; Guo, R.; Wu, H. Efficient  $CO_2$  capture by functionalized graphene oxide nanosheets as fillers to fabricate multi-permselective mixed matrix membranes. *ACS Appl. Mater. Interfaces* **2015**, 7 (9), 5528–5537.

(37) Shen, J.; Liu, G.; Huang, K.; Jin, W.; Lee, K. R.; Xu, N. Membranes with fast and selective gas-transport channels of laminar graphene oxide for efficient  $CO_2$  capture. *Angew. Chem., Int. Ed.* **2015**, *54* (2), 578–82.

(38) Yang, X.; Du, H.; Lin, Y.; Song, L.; Zhang, Y.; Gao, X.; Kong, C.; Chen, L. Hybrid organosilica membrane with high  $CO_2$  permselectivity fabricated by a two-step hot coating method. *J. Membr. Sci.* **2016**, *506*, 31–37.

(39) Lee, S. E.; Jang, J.; Kim, J.; Woo, J. Y.; Seo, S.; Jo, S.; Kim, J.-W.; Jeon, E.-S.; Jung, Y.; Han, C.-S. Tunable sieving of small gas molecules using horizontal graphene oxide membrane. *J. Membr. Sci.* **2020**, *610*, 118178.

(40) Su, Y.; Kravets, V. G.; Wong, S. L.; Waters, J.; Geim, A. K.; Nair, R. R. Impermeable barrier films and protective coatings based on reduced graphene oxide. *Nat. Commun.* **2014**, *5*, 4843.

(41) Mianehrow, H.; Lo Re, G.; Carosio, F.; Fina, A.; Larsson, P. T.; Chen, P.; Berglund, L. A. Strong reinforcement effects in 2D cellulose nanofibril-graphene oxide (CNF-GO) nanocomposites due to GOinduced CNF ordering. *J. Mater. Chem. A* **2020**, *8* (34), 17608– 17620

(42) Xu, Z.; Gao, C. Graphene chiral liquid crystals and macroscopic assembled fibres. *Nat. Commun.* **2011**, *2*, 571.

(43) Chouhan, D. K.; Kumar, A.; Rath, S. K.; Kumar, S.; Alegaonkar, P. S.; Harikrishnan, G.; Umasankar Patro, T. Laponite-graphene oxide

hybrid particulate filler enhances mechanical properties of crosslinked epoxy. J. Polym. Res. 2018, 25 (2), 60.

(44) Acik, M.; Mattevi, C.; Gong, C.; Lee, G.; Cho, K.; Chhowalla, M.; Chabal, Y. J. The role of intercalated water in multilayered graphene oxide. *ACS Nano* **2010**, *4* (10), 5861–5868.

(45) Hontorialucas, C.; Lopezpeinado, A. J.; Lopezgonzalez, J. D. D.; Rojascervantes, M. L.; Martinaranda, R. M. Study of oxygencontaining groups in a series of graphite oxides - physical and chemical characterization. *Carbon* **1995**, 33 (11), 1585–1592.

(46) Liu, J.; Bai, H.; Wang, Y.; Liu, Z.; Zhang, X.; Sun, D. D. Selfassembling TiO2 nanorods on large graphene oxide sheets at a twophase interface and their anti-recombination in photocatalytic applications. *Adv. Funct. Mater.* **2010**, *20* (23), 4175–4181.

(47) Stankovich, S.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. *Carbon* **2006**, *44* (15), 3342–3347.

(48) Pang, Y. X.; Hodgson, S. N. B.; Weglinski, B.; Gaworska, D. Investigations into sol-gel silica and silica hybrid coatings for dielectromagnetic soft magnetic composite applications. *J. Mater. Sci.* **2006**, *41* (18), 5926–5936.

(49) Sadeghi, M.; Semsarzadeh, M. A.; Moadel, H. Enhancement of the gas separation properties of polybenzimidazole (PBI) membrane by incorporation of silica nano particles. *J. Membr. Sci.* **2009**, 331 (1–2), 21–30.

(50) Wang, J.; Kanezashi, M.; Yoshioka, T.; Tsuru, T. Effect of calcination temperature on the PV dehydration performance of alcohol aqueous solutions through BTESE-derived silica membranes. *J. Membr. Sci.* **2012**, *415*, 810–815.

(51) Wu, Q.; Gong, L.-X.; Li, Y.; Cao, C.-F.; Tang, L.-C.; Wu, L.; Zhao, L.; Zhang, G.-D.; Li, S.-N.; Gao, J.; Li, Y.; Mai, Y.-W. Efficient flame detection and early warning sensors on combustible materials using hierarchical graphene oxide/silicone coatings. *ACS Nano* **2018**, *12* (1), 416–424.

(52) Xu, R.; Kanezashi, M.; Yoshioka, T.; Okuda, T.; Ohshita, J.; Tsuru, T. Tailoring the affinity of organosilica membranes by introducing polarizable ethenylene bridges and aqueous ozone modification. ACS Appl. Mater. Interfaces **2013**, 5 (13), 6147–6154.

(53) Kim, J. H.; Lee, Y. M. Gas permeation properties of poly(amide-6-b-ethylene oxide)-silica hybrid membranes. *J. Membr. Sci.* 2001, 193 (2), 209–225.

(54) Dalagan, J. Q.; Enriquez, E. P. One-step synthesis of mesoporous silica-graphene composites by simultaneous hydro-thermal coupling and reduction of graphene oxide. *Bull. Mater. Sci.* **2014**, *37* (3), 589–595.

(55) Wahab, M. A.; Kim, I.; Ha, C.-S. Bridged amine-functionalized mesoporous organosilica materials from 1,2-bis(triethoxysilyl)ethane and bis[(3-trimethoxysilyl)propyl]amine. *J. Solid State Chem.* **2004**, *177* (10), 3439–3447.

(56) Huang, A.; Liu, Q.; Wang, N.; Zhu, Y.; Caro, J. Bicontinuous zeolitic imidazolate framework ZIF-8@GO membrane with enhanced hydrogen selectivity. *J. Am. Chem. Soc.* **2014**, *136* (42), 14686–14689.

(57) Li, Y.; Liu, H.; Wang, H.; Qiu, J.; Zhang, X. GO-guided direct growth of highly oriented metal organic framework nanosheet membranes for  $H_2/CO_2$  separation. *Chem. Sci.* **2018**, 9 (17), 4132–4141.

(58) Wang, S.; Xie, Y.; He, G.; Xin, Q.; Zhang, J.; Yang, L.; Li, Y.; Wu, H.; Zhang, Y.; Guiver, M. D.; Jiang, Z. Graphene oxide membranes with heterogeneous nanodomains for efficient  $CO_2$  separations. *Angew. Chem., Int. Ed.* **2017**, *56* (45), 14246–14251.