Carbon quantum dots enabled tuning of the microphase structures of poly (ether-*b*-amide) membrane for CO₂ separation

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ABSTRACT: In this study, molecular-level of mixed matrix membranes are prepared by incorporating two types of carbon quantum dots (QDs), polymer-like QDs (PQD) and graphene oxide QDs (GQD) into Pebax[®], a poly (ether-*b*-amide) copolymer. PQD is shown to destroy part of the intrinsic crystalline structure of Pebax as typical fillers do. By comparison, GQD has fewer functional groups and causes an interesting enhancement of the microphase separation of Pebax[®]. The polyether domains become more segregated and more available for the selective CO₂ permeation. As a result, the gas separation performance of the membranes is evidently enhanced. GQD outperforms PQD as filler and the encouraging enhancement occurs at lower loading. The membrane with 0.05 wt% GQD loading shows the optimal gas separation property while it is 1 wt% for PQD-doped membranes. A possible mechanism is tentatively proposed based on the findings of this study.

1. INTRODUCTION

Membrane-based separation technologies offer a wide range of opportunities in efficient CO₂ capture.¹⁻² Among various materials, polymers are widely used in the preparation of membranes due to their low cost, easy fabrication and scaling-up.³⁻⁴ However, pure polymer membranes often suffer from a trade-off between permeability and selectivity,^{2, 5-6} which places further restrictions on their practical application. Mixed matrix membranes (MMMs), fabricated by doping inorganic fillers into a polymer matrix, are perceived as a promising solution due to the compromise between membrane processability and separation capacity.^{2,7-8} Significantly, MMMs can borrow the latest achievements of inorganic and polymer materials, as well as the state-of-the-art understanding of the polymer–inorganic interface.

In the multiphase MMMs, inorganic fillers usually play pivotal roles and represent the novelty of the designed MMMs. The diversity in filler size, shape, porosity and surface chemistry is known to bring about various effects on membrane structures and gas transport properties.⁹⁻¹⁰ As a typical example, the particle size has long been of great interest due to its impact on the filler dispersion and polymer–filler interfacial morphologies.¹¹⁻¹² From this perspective, nanosizing fillers tends to improve the properties of MMMs.^{4,13-14} Nanoscale fillers can be more favorable to fabricate thin film composite (TFC) membranes for practical application, because the ultra-thin active layers requires much smaller filler than the film thickness.^{8,15-16} Nanoscale fillers can also produce high polymer-filler interface area.¹⁴ In this way, the interfacial adhesion or compatibility is essential.¹⁷ More importantly, fillers have more chances to interact with polymer chains, so as to manipulate the mobility and the packing manner of polymer chains around them.^{14,17-18} Especially, if the filler size approaches molecular level, a small amount of fillers may trigger a substantial alteration of the membrane structures.¹⁹ For instance, Liu et al.²⁰ reported that metal-organic polyhedral (MOP, average 9 nm in diameter) could enlarge the *d*-spacing of a polyimide matrix, and a low doping amount (1.6 wt%) imparted a 40% increase of CO₂ permeability without sacrificing the selectivity. Therefore, developing nanosized (usually less than 20 nm) or molecular level fillers is a crucial component for the next-generation MMMs. However, until now, only a handful of fillers of this size are reported in the preparation of MMMs, such as beta-cyclodextrin,²¹ polyhedral oligomeric phenethyl-silsesquioxanes (POSS),¹⁹ calixarene,²² and the aforementioned MOP, etc., because of the limited content of nanofillers “soluble” in a solvent without the aid of surfactant.

Recently, carbon quantum dots (QDs) with molecular-level size (2-10 nm), biocompatibility, chemical stability and designable properties,²³⁻³⁴ have harvested the interests of membrane researchers. QDs have versatile surface groups, which are convenient to modulate their solubility in desired solvent systems,²⁵ and effectively form molecular-level MMMs. In a previous work,²⁶ we reported a molecular-level hybrid NafionTM/QDs MMMs for enhanced proton conduction, in which QDs with controllable hydrophobicity could spontaneously and selectively assemble in ionic or backbone nanophases of NafionTM. In this way, the microstructures of ionic or backbone phases can be independently regulated. These results confirm that QDs are ideal for microstructure regulation to improve MMMs.

Herein, we developed QDs-doped mixed matrix membranes for CO₂ capture. Two types of QDs, polymer-like QDs (PQD) and graphene oxide QDs (GQD), were facilely synthesized *via* one-step microwave-assisted pyrolysis and used as fillers (Scheme. 2). The block copolymer Pebax[®] MH 1657 (Scheme. 1), composed of soft polyether and rigid polyamide 6 (PA6) segments, was selected as matrix due to its preferential CO₂ solubility, commercial availability and, significantly, incomplete microphase separation structures, which are expected to be tuned by the two types of QDs with different hydrophilicity. The differences between GQD and PQD in chemical structures were demonstrated, and further correlated with the differences between microphase structures and gas transport properties of the corresponding MMMs, respectively. In addition, a series of TFC membranes with about 220 nm thick selective layers were successfully prepared, by taking advantage of the matched size of QDs.

Scheme. 1. Chemical structure of Pebax® MH 1657 (weight ratio of PA6 to PEO: about 40:60).

2. EXPERIMENT

2.1 Materials

Citric Acid Anhydrous (99.5 wt% purity) and diethylenetriamine (DETA, 99 wt%) were purchased from Shanghai Aladdin biochemical technology. Glycerol (99 wt%) and dopamine hydrochloride (DA) were obtained from Shanghai Macklin Biochemical Co., Ltd. Pebax® MH 1657 copolymer was supplied by Arkema Co., Ltd. Poly (dimethylsiloxane) (PDMS, hydroxy terminated), ditin butyl dilaurate (DBD) and tetraethyl orthosilicate (TEOS) were supplied by Sigma-Aldrich. Anhydrous ethanol and heptane were purchased from Tianjin Fengchuan Reagent Technologies Co., Ltd. The PVDF support membrane with a molecular weight cut-off (MWCO) of 100,000 g mol⁻¹ was obtained from Zhongkeruiyang Membrane Engineering & Technology Co., Ltd (Beijing, China). The ultraviolet lamp (300 nm) system was homemade. All chemicals were used as purchased. Deionized (DI) water was used throughout.

2.2 Synthesis of carbon quantum dots

QDs were prepared by one-step microwave-assisted pyrolysis of citric acid and diethylenetriamine based on a previously reported procedure (Scheme. 2).²⁷ The QDs with different degrees of carbonization can be obtained by varying the water content of the reaction system. Typically, QDs with low degrees of carbonization were synthesized as follows. Citric acid (1 g)

and diethylenetriamine (560 μL) were dissolved in the DI water (2.0 g) entirely under ultrasonic-bathing, then the prepared solution was transferred into a microwave oven and heated at 750 W for 5 min. The products were washed with anhydrous ethanol for three times to remove unreacted small molecules. The remaining solid was dispersed in DI water and freeze-dried for 48 h. The as-prepared QDs are referred here as PQD. QDs with higher degrees of carbonization were prepared by the same method, while the DI water (2.0 g) in the system was replaced by mixture of DI water (1.0 g) and glycerol (1.0 g). The as-synthesized QDs are referred here as GQD.

Scheme. 2. Schematic of formation of QDs

2.3 Preparation of the membranes

All dense membranes were prepared by solution casting. Pebax[®] 1657 was dissolved in an ethanol/water (70/30 wt%) mixed solvent under 80 °C refluxing for 2 h to obtain a 3 wt% Pebax[®] 1657 solution. The purified QDs were then dispersed in the same solvent with ultrasonic treatment for 4 h. Afterwards, the suspension was mixed with the Pebax[®] solution, followed by further

sonication and stirring for 4h and 8h, respectively. The solution containing the QDs was cast into a Teflon petri dish and dried in a vacuum oven at 30 °C for 48 h, and these membranes were further dried at 50 °C for 24 h to remove the residual solvent. The resultant membranes were then labelled as Pebax-PQD-X and Pebax-GQD-Y, where X and Y respectively represent the PQD and GQD content relative to the weight of Pebax®.

TFC membranes were prepared by dip-coating. PDMS was used as gutter layer; Pebax®, Pebax-PQD-1 and Pebax-GQD-0.05 coating solution as selective layer. For the gutter layer, PDMS, DBD and TEOS (2/1/1 by weight) were dissolved in *n*-heptane, followed by magnetic stirring for 5 min and standing for 30 min at room temperature. PVDF support was coated with PDMS firstly by dip-coating, and dried at 50°C for at least 12 h. Then, the surface of the gutter layer was modified with dopamine, according to the literature.²⁸ After drying, the modified support was coated with Pebax®, Pebax-PQD-1 and Pebax-GQD-0.05 coating solutions and dried at room temperature for 12h. These as-prepared TFC membranes were denoted as Pebax/PVDF, Pebax-PQD/PVDF and Pebax-GQD/PVDF, respectively.

2.4 Characterization of the QDs and membranes

The QDs and MMMs were imaged by transmission electron microscopy (TEM) on a FEI Talos™ F200S equipment. The MMMs and TFC membranes cross-sections, as well as the surfaces of MMMs, were imaged by scanning electron microscopy (SEM) on a JSM-7500F equipment. The chemical composition of QDs and membranes were detected by X-ray photoelectron spectroscopy (XPS) on a multifunctional imaging electron spectrometer (XPS, Thermo ESCALAB 250XI, Thermo Scientific, USA). The Fourier transform infrared (FTIR) spectra were recorded on a

PerkinElmer Spectrum Two instrument with a resolution of 4 cm⁻¹ at room-temperature. A Bruker Dimension FastScan™ microscope was employed to record atomic force microscopy (AFM) images of membranes and QDs in contact and non-contact modes. Size distribution of the QDs in water was measured by using dynamic light scattering (DLS) (Malvern Zetasizer Nano ZS90). Differential scanning calorimetry (DSC) was conducted over a temperature range from -70 to 250 °C with a heating rate of 10 °C/min to investigate the thermal properties of membranes. The crystalline properties of membranes and QDs were probed by X-ray diffractometry (XRD) (Bruker D8 Advance ECO, Germany) in the ranges of 5–70° at the scanning speed of 5°/min. Thermogravimetric analysis (TGA) of QDs and membranes was conducted by TGA-50 SHIMADZU from 30 to 800 °C at 5 °C min⁻¹ under nitrogen-atmosphere. An Instron Mechanical tester (Testometric 350 AX) was employed to measure the mechanical properties of the membrane at an elongation rate of 2 mm min⁻¹ under room temperature. The tested membrane size was 1.0 cm × 4.0 cm. In addition, the water content of the membranes in binary gas experiences was measured. After testing, the membranes were weighted as m_1 (mg), then they were placed in a vacuum oven at 100 °C for 12 h and further dried at 150°C for another 6 h. The weight was measured as m_0 (mg). The water content of the membranes was calculated by the following equations and the relative error was controlled to be less than 4%.

$$W_c = (m_1 - m_0) / m_0 \times 100\% \quad (1)$$

2.5 Gas permeation experiments

Binary mixed gas (10 vol% CO₂ + 90 vol% N₂) and single gas (CO₂, N₂) permeability values were determined based on a constant pressure/variable volume method and

constant-volume/variable pressure, respectively. In the binary mixed gas separation experiments, according to demand, the feed gas and sweep gas could be saturated by bubbling through a tank before they entered membrane cell, and the tank was heated in order to achieve the best humidification effect. The composition of the percolated gas was measured by using a gas chromatographer (GS-101, Ripuli). The permeability of the membranes was calculated by the following equation:

$$P_i = \frac{Q_i l}{\Delta p_i A} \quad (2)$$

where the P_i is the permeability of the “ i ” gas, in Barrer, 1 Barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹. Q_i is the volumetric permeation flow rate of the gas “ i ” (cm³/s) at standard temperature and pressure (STP), l is the thickness of membranes (cm), Δp_i (cmHg) is the transmembrane partial pressure difference of gas i , and A is the effective membrane area (15.9 cm²). In the single gas permeation experiments, the permeability, and the diffusion coefficient, D , of the corresponding gas were probed by the time-lag method. The relevant equations are (3-5):

$$D = \frac{l^2}{6\theta} \quad (3)$$

$$S = \frac{P}{D} \quad (4)$$

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (5)$$

where l is the membrane thickness, and θ (s) is the diffusivity time lag. S was calculated by the equation (4). The formula (5) of selectivity (α_{ij}) is applied for both binary gas and single gas experiments, where P_i and P_j are the permeability of gas “ i ” and “ j ”, respectively.

In the gas permeation experiences of TFC membranes, the same method as for the binary mixed gas experiences was used, but the feed and sweep gases were directly introduced into membrane

cell and the percolated single gas permeance was showed by an ADM flow meter (G6691A, Agilent) or bubble flow meter. The permeances (P_i/l and P_j/l) and selectivity of TFC membranes to gases “ i ” and “ j ” were calculated by the equations 2 and 5. The permeances are reported in GPU (gas permeation unit), $1 \text{ GPU} = 10^{-6} \text{ cm}^3 (\text{STP}) \text{ cm}^{-2} \text{ s cmHg}^{-1}$.

3. RESULTS AND DISCUSSTION

3.1 Characterizations of QDs

Two types of QDs with different degrees of carbonation were synthesized via one-step microwave-assisted polycondensation of citric acid and DETA. The solvent of reaction system was either water or water/glycerol, varying the reaction temperature in the polycondensation procedure. PQD (Fig S1a) with -OH, -CO₂H, -NH/-NH₂ functionalization was synthesized using water as solvent, which ensures a carbonization-free condensation. In contrast, GQD (Fig S1b) was synthesized with the mixed solvent, which enables a higher reaction temperature (exceeding 100 °C). Not only dehydration condensation takes place, but also desamidization, deamination and further carbonization.²⁷ In addition, like other QDs, their aqueous solution exhibited intense fluorescence under ultraviolet light (Fig. S1c-d).

The TEM and AFM images (Fig. 1a-b and Fig. S2) show that both GQD and PQD have a typical zero-dimensional nanostructure with the size of 1-5 nm, implying their molecular-level size.²³ Dynamic light scattering (DLS) analysis (Fig. S3) shows the similar results. They also reveal that the CDs have an evenly dispersion without any aggregation. The XRD (Fig. S4) patterns for both QDs display broad diffraction peaks due to their small size and the different d -spacing results from the different amount of remaining groups. Furthermore, the FTIR and XPS spectra reveal the

difference between their chemical structures. The FTIR (Fig. 1c) spectra has bands at 1635 and 1540 cm^{-1} for both kinds of QDs, attributed to C=O and N-H, respectively. For PQD, they are more intense. Furthermore for PQD, there are additional bands at 1040, 2850-2950 and 3270 cm^{-1} attributed to C-N, C-H and O-H, respectively, which suggest additional functionalization groups. The XPS spectra (Fig. S5) of PQD has stronger peaks for O 1s and N 1s but a weaker peak for C 1s. The deconvolution of the C 1s band (Fig. 1d) for GQD possesses sp^2 (C=C) at binding energy 284.7 eV, sp^3 (C-C) at 285.6 eV and C-O-C at 287.2 eV, implying the Graphene Oxide-like structure, which has been reported elsewhere.²⁹ In contrast, sp^2 (C=C) was not found in PQD, like other common polymers which only shows various groups due to carbonization-free condensation.^{23,26} Meanwhile, the C-N and C-OH bands were not detected in GQD, which agrees well with FTIR. Such results demonstrate that PQD has more functionalization groups than GQD, because the majority of O-containing groups were consumed at higher reaction temperatures, as revealed by the TGA analysis (Fig. S6).

Fig. 1. (a) TEM image and (b) AFM topographic image of GQD. (c) FTIR and (d) XPS C 1s spectra of QDs.

3.2 Membrane characterization

QDs-incorporated Pebax[®] membranes were prepared *via* solution casting. An intense fluorescence was observed under ultraviolet light (Fig. S7) for Pebax-QDs solutions and the corresponding membranes, suggesting that QDs were successfully introduced into the Pebax[®] matrix. The TEM images (Fig. S8a-b) reveal that GQD (0.05 wt%) and PQD (1 wt%) are evenly distributed and there is no visible aggregation in the Pebax[®] matrix. However, when the loading increases above 0.3 wt%, GQD tends to agglomerate (Fig. S8c). The SEM cross-sectional images (Fig. S9) of the MMMs display minor changes compared to the pristine membrane and the doped QDs cannot be distinguished, due to its molecular-size distribution. When the surface of the membranes was probed by AFM and SEM (Fig. 2), as revealed by Pebax-GQD-0.05 membrane (Fig. 2b and e), a typical mikado-like polyamide nanophase (the brighter regions) can be seen dispersed in the continuous PEO phase, resulting from the block copolymer self-assembly, similar to what has been reported before for Pebax[®] and PolyActive[™] membranes with other additives.²⁹⁻³⁰ The quantity and size of the “mikado” reflect the crystallization degree of the polyamide nanophase, and further the contrast with the adjacent PEO nanophase reflects the microphase separation. Compared with the pristine membrane, the polyamide nanophase becomes more prominent after loading GQD. An opposite trend was observed for the PQD-embedded membrane. This unveils two different behaviors promoted by the addition of GQD and PQD, corresponding to intensified microphase separation and collapse of the intrinsic structure in the Pebax[®] matrix, respectively.

Fig. 2. (a-c) AFM and (d-f) SEM micrographs of Pebax[®], Pebax-GQD-0.05 and Pebax-PQD-1 membranes.

The interactions between the QDs and the copolymer chains were initially analyzed by FTIR (Fig. S10). Obviously, the peak of Pebax-QDs membranes around at 1542 cm^{-1} has a higher frequency shift than the peak around at 1099 cm^{-1} , particularly for PQDs, as illustrated in Fig. S10b and c. The XPS C 1s spectra of membranes (Fig. 3a) further reflects this interaction. Both the C-N and C=O in the PA6 blocks have a lower frequency shift, while the $\text{CH}_2\text{-CH}_2\text{-O}$ of PEO blocks gives a lower frequency shift only in PQD-doped membrane, implying GQD prefers to interact with PA6 blocks. This shift suggests the formation of hydrogen bonds between different filler functionalization and the Pebax[®] amide blocks.^{17,31} That also enhances the thermostability of MMMs (Fig. S11). Another evidence for these interactions is the variation of the Pebax[®] glass transition temperature (T_g) relative to the PEO block, as shown in Fig. 3d and Table S1. The T_g relative to the PA6 segments would be expected around 47°C , which is the value for the analog homopolymer. However, it could not be detected. A partial miscibility with PEO would reduce T_g bringing it to a lower temperature range. It could then be masqueraded by other transitions, like the

melting of the PEO. The T_g of PEO phases in Pebax-PQD membranes is higher than that of the pristine membrane, varying from -55.4 °C to -49.1 °C, while that of Pebax-GQD membranes only have a slight increase, from -55.4 °C to -54.2 °C. For all MMMs, the increased T_g value can be ascribed to the interactions between fillers and matrix, which restrict the segment flexibility. The more abundant groups of PQD result in a stronger interaction, probably in the form of hydrogen bonding, corresponding to a larger increase of T_g . Hydrogen bonding is probably the primary cause for the disorder of the microphase structures in the case of membranes with PQDs as fillers. Without strong preferential interactions, the GQDs act primarily as nuclei for the crystallization.

Fig. 3. (a) XPS C 1s spectra of Pebax, Pebax-GQD-0.05 and Pebax-PQD-1 membranes, (b) XRD patterns, and (c-e) DSC results of Pebax® and Pebax-QDs membranes.

The crystallinity and order of the membranes were further investigated by XRD, as shown in Fig. 3b. It could be seen that GQD and PQD change the crystallinity of the Pebax® matrix in opposite ways. The peak relative to the Pebax® polyamide block³² (the gray area) becomes stronger with the addition of GQD while it is weakened when PQD is added, indicating that the polyamide nanophase becomes more ordered in the presence of GQD membranes, but it is disrupted by the

PQD. The crystallinity of Pebax[®] and Pebax-QDs membranes could be better quantified by using DSC (Fig. 3c, e and Table S1). More than a confirmation of the XRD observation, the DSC results allowed to distinguish between the thermal properties of each copolymer block and how they are affected by the fillers. The crystallinity relative to the polyamide phase in the pristine membrane is 13.01%, indicating a large content of non-crystallized segments.³³ The amorphous PA6 segments can interact with the PEO blocks, leading to a partial miscibility. The NH groups, which are responsible for the hydrogen bonds with the C=O groups in a pure crystalline PA6 phase, can then alternatively form hydrogen bonds with the oxygens of the polyether blocks.³⁴ For the CO₂ transport in Pebax[®] membranes, a Lewis acid-base interaction with the same oxygen groups is fundamental. The Lewis acidity of the CO₂ is a result of the carbon atom electropositivity, which has an electron density deficiency, compared to the oxygen in the same molecule.³⁵ The oxygen atoms of the polyether groups in Pebax[®] have unpaired electrons available for a strong Lewis acid-base interaction with CO₂, contributing for its solubility in the polymer matrix. However, if part of the ether groups will be compromised by forming hydrogen bonds with the NH groups of the amorphous polyamide segments, fewer groups will be available to interact with CO₂. It is then expected that fillers that promote the segregation between the polyether and polyamide blocks, which causes the increased polyether domains and therefore enhances the CO₂ solubility and transport. Compared with the pristine membrane, the crystallinity of the polyamide nanophase measured by DSC is enhanced in the case of Pebax-GQD membranes but reduced for the Pebax-PQD membranes. This agrees with the results of XRD. As mentioned above GQD might promote the nucleation of the Pebax[®] crystalline phases, acting as nuclei or crystallization initiators,

as previously observed for other fillers, such as one-dimension halloysite.³⁶ GQDs do not add a significant number of functional groups to the system, compared with PQD.

The effect observed for PQD is quite different and much more connected to its functional groups. In general, a reasonable amount of hydrogen bonds between fillers and segments will lead to a re-arrangement of chain.³² PQD reduced both the PA6 and PEO crystallinity. The incorporation of PQD might directly and efficiently interrupt the ordered chain packing of both PA6 and PEO segments. Such inference agrees well with AFM and SEM results.

Table 1. Mechanical properties of Pebax[®] and Pebax-QDs membranes (25 °C).

Membranes	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Toughness (kJ/m ³)
Pebax [®]	115 ± 19	13 ± 0.5	387 ± 8.7	4.1 ± 0.23
Pebax-GQD-0.05	63 ± 7.5	13 ± 0.3	816 ± 14.1	7.2 ± 0.35
Pebax-GQD-0.15	63 ± 9.8	13 ± 0.4	644 ± 10.3	6.0 ± 0.17
Pebax-PQD-1	112 ± 21	15 ± 0.5	772 ± 9.5	8.2 ± 0.41
Pebax-PQD-2	61 ± 4.6	16 ± 0.7	994 ± 12.3	10.6 ± 0.45

The alteration of microphase structures due to QD addition can be also reflected by the mechanical properties, as shown in Table 1 and Fig. S12. Compared to the pristine membrane, the Young's Modulus of Pebax-PQD membranes decline with the increasing of PQD content, which agrees with the disruption of the crystalline PA6 phase as revealed by XRD. Meanwhile, the strong interaction between PQD and polymer can be responsible for the sharp improvement of both tensile strength and elongation at break. However, interestingly, the elongation at break of Pebax-GQD-0.05 membrane is much better than pristine Pebax[®] membrane and Pebax-PQD-1 membrane. The latter even exhibits stronger polymer-filler interactions (revealed by the higher T_g). Therefore, the increase of elongation at break cannot be totally ascribed to the strength of the

filler-polymer interfacial interactions. It appears not reasonable for conventional polymers, while for Pebax[®] — a typical block copolymer — there is a rational explanation that the “soft” PEO nanophase might become more continuous due to the enhanced microphase separation, which further results in largely improved toughness. Besides, it should be noted that the incorporation of GQD is expected to affect the interconnectivity of PA6 domains due to low compatibility, and therefore the Young’s Modulus of Pebax-QD membranes reduces although the crystallinity of PA6 was enhanced, which is very similar with previous reports.^{37,38}

3.3 Gas separation performance test

3.3.1 Effect of fillers on gas separation performance

The detailed single gas test of selected membrane samples was carried out to correlate with the membrane structures changes. The relevant parameters are listed in Table S2. Pristine Pebax[®] membranes have a CO₂ permeability of 93.0 Barrer and CO₂/N₂ selectivity of 44.3. Comparing all membranes investigated in this work, Pebax-PQD-1 and Pebax-PQD-2 membranes had the best CO₂ permeability and CO₂/N₂ selectivity, respectively. Meanwhile, we realized that membranes with higher solubility (*S*) also had higher diffusivity (*D*). This parallel trend is not unusual for PEO-based membranes.³⁸⁻³⁹ In addition, the CO₂/N₂ selectivity of the membranes with PQD continuously increased with the filler content. This can be understood, since by loading PQD two concomitant effects occur: (1) the polymer chain mobility is restricted due to additional interactions with the filler functional groups, and (2) the additional groups also interact with CO₂, changing its solubility.

For Pebax-GQD membranes, both the optimal CO₂ permeability and CO₂/N₂ selectivity are

observed 0.05% filler, and also S and D are maximum under this condition. This is because large amount of PEO chains become more flexible due to the enhanced microphase separation, which increases the availability of CO₂-philic sites and decreases the resistance to the transport.⁴⁰⁻⁴² A decline of CO₂ permeability occurs when the GQD loading increase to 0.15 wt%, which may be caused by aggregation of GQD. Also, such findings hint that GQD has weak interactions with the PEO segment, reflected by increased diffusivity coefficient. Along with the membrane characterization results, it can be further inferred that GQD mainly interacts with PA6 segment while PQD interacts with PEO and PA6 segments simultaneously, which may be the key that determines the sharply different results for the two kinds of MMMs. Together, these results demonstrate that QDs with tailored structures could tune the microstructures of Pebax[®] more precisely than other fillers used for molecular-level hybridization.

In addition, the binary mixed gas (10 vol% CO₂ + 90 vol% N₂) permeation test under humidification was performed for all membranes, and the corresponding results are shown in Fig. 4a. The gas separation performance of all MMMs transcends the upper bound reported in 2008 (Fig. 4c). Particularly, the Pebax-GQD-0.05 membrane displays a CO₂ permeability of 668 Barrer and CO₂/N₂ selectivity of 101, 155% and 130% higher than that of the pristine membrane. Obviously, water plays an important role in such an excellent performance. The water-driven plasticization effect could enlarge the d -spacing of polymer chains and further increase CO₂ permeability,⁴³ as revealed by the comparison of gas separation performance between humidified and dry membranes (Fig. S13). In order to clearly understand the effect of water, the corresponding water content was recorded and shown in Fig. 4b. Evidently, Pebax-GQD membranes exhibit higher water content

than Pebax-PQD membranes, with a peak value of 38% for Pebax-GQD-0.05 membrane. Therefore, a stronger swelling effect can be obtained for Pebax-GQD membranes, as well as higher gas permeability. Such results can also be interpreted by the difference of microstructures between the two types of membranes. Compared to Pebax-PQD membranes, more amorphous PEO nanophase within Pebax-GQD membranes affords more space to sorb and retain water.

Fig. 4. (a) Gas separation performance of membranes with different filler contents (binary gas, humidified, 1bar, 25°C). The error of CO_2/N_2 selectivity controls with the area of symbol. (b) Water content of Pebax® and Pebax-QDs membrane. The top and bottom x-axis represent the content of PQD and GQD, respectively. (c) Comparison of CO_2/N_2 separation performances (binary gas, 25°C, 1bar) of Pebax-PQD and Pebax-GQD membranes with the Robeson's upper bound.

3.3.2 Effect of the operation pressure on the gas separation performance

The effect of the operation pressure on the gas separation performance was subsequently conducted to investigate the gas transport mechanism in the presence of water. Pebax-GQD-0.05

and Pebax-PQD-1 membranes were selected due to their higher CO₂ separation performance, with Pebax[®] membrane as control. The operation pressure was varied between 1 to 6 bar. The results are shown in Fig. 5. It is obvious that the CO₂ permeability decreases for both Pebax[®] and Pebax-PQD-1 membranes with increasing pressure and the CO₂/N₂ selectivity slightly increases, which could attribute to the membrane compression. However, to our surprise, the Pebax-GQD-0.05 membrane displays a relatively sharp decline for both CO₂ permeability and CO₂/N₂ selectivity with enhanced feed gas pressure. In general, for facilitated transport membranes, the CO₂ permeability and CO₂/gas selectivity will show an obvious decline with the increase of feed gas pressure due to the well-known “carrier saturation effect”.⁴⁴ This suggests Pebax-GQD membranes partially follow the characteristics of facilitated transport mechanism at relatively low pressure. As the gas feed pressure exceeds 3 bar, the CO₂/N₂ selectivity begins to slowly increase like the Pebax[®] and Pebax-PQD-1 membranes, suggesting that the contribution of facilitated transport is restricted beyond 3 bar. Such difference between Pebax-GQD and Pebax-PQD membranes might be related to the relatively high water content of Pebax-GQD, which provides better environment for facilitated transport.

Fig. 5. Effect of feed gas pressure on gas separation performances for Pebax[®], Pebax-PQD-1, Pebax-GQD-0.05 membranes (binary mixed gas, humidified, 25°C).

3.3.3 A summary of the loading-dependence characteristics of Pebax-based MMMs

In the discussion above, an interesting is that the optimal PQD loading (0-2 wt%) far exceeds the GQD loading (0-0.15 wt%). Pebax-PQD membranes with filler loading as low as Pebax-GQD membranes were also prepared, but the gas separation performance only shown a negligible increase compared with the pristine membrane and Pebax-GQD membrane with the same loading (Fig. S14). In fact, the phenomenon is common for Pebax-based MMMs according to the literature (Table 2). There is a broad filler optimal-loading range from 0.025 wt% to 20 wt%, but most of them show an optimal loading below 2 wt%. In many cases this is due to aggregation above this limit. In this sense, the filler dispersed in Pebax[®] membrane is more likely to function as a structural modifier rather than an efficient separator, which is thought to be highly related to the partial microphase separation and the controlled separation mechanism of Pebax[®]. According to this study, even the fillers with the optimal loading below 2 wt% can be further divided into two categories. For type I, the optimal loading is extremely low (0-0.2 wt%). The examples of type I fillers include GO, ionic liquid modified GO, MoS₂, HNT, and even porous covalent triazine piperazine polymer. This type of fillers shows a common feature: they generally contain few active hydrogen atoms (hydrogen bond donor sites). In this way, they are not expected to form hydrogen bonds with PEO. In this work they have a physical effect, nucleating and therefore enhancing the PA6 crystallization and blocks segregation. For type II, the optimal loading falls in the range of 0.2-2 wt%, with typical examples of fillers like aminosilane-functionalized GO, imidazole-functionalized GO, amino-modified porous organosilicon nanotubes, COF-5, and POSS. The majority of this type (especially for the non-porous ones) is highly functionalized with more

Table 2. The comparison of permeability and selectivity values between different Pebax®-based membranes with optimal filler loadings.

Filler	Optimal CO ₂ permeability (Barrer) / filler loading (wt%)	Optimal CO ₂ /N ₂ selectivity / filler loading (wt%)	Test pressure and temperature (bar / °C)	Ref.
GO (1-2 μm)	96 / 0.1	92 / 0.2	3 / 25	17
POSS-OH (CO ₂ /H ₂)	119 / 2	8.7 ^a / 2	2 / 35	
POSS-COOH (CO ₂ /H ₂)	127 / 1	8.8 ^a / 1	2 / 35	19
GO	100 / 0.1	91 / 0.1	3 / 25	31
HNTs	80.4 / 0.1	290 / 0.1	2 / 35	36
COF-5	493 / 0.4	48.3 / 0.4	1 / 30	39
GO	113 / 0.05	72.4 / 0.05	4 / 25	
Ionic liquid modified GO	143 / 0.2	79.4 / 0.2	4 / 25	40
Aminosilane-functionalized GO	174 / 0.5	45.2 / 0.7	2 / 35	41
PEG / GO	695 / 0.06	55.8 / 0.3	1 / 35	47
Porous covalent triazine piperazine polymer	81 / 0.1	79 / 0.025	4 / 20	48
Dopamine/polyethyleneimine-grafted TiO ₂	66.7 / 3	101 / 3	3 / 20	49
MoS ₂	64 / 0.15	93 / 0.1	2 / 30	50
MXene	21.6 ^b / 0.15	72.5 / 0.15	2 / 25	51
aminated partially reduced GO	47.5 / 0.1	105.6 / 0.1	4 / 25	52
<i>p</i> -tert-Butylcalix[4]arene	265.18 / 0.75	109.16 / 0.75	10 / 35	53
surface functionalized NaX	287.76 / 1.5	288.86 / 1.5	6 / 25	54
C60(OH) ₂₄	338 ^b / 1	41 / 1	5 / 35	55
N-doped few-layer graphene	239.8 / 4	95.5 / 4	1 / 25	56
Amino-modified porous organosilicon nanotubes	148.6 / 0.5	23 / 0.5	2 / 30	57
Imidazole functionalized GO	64 / 0.8	90.3 / 0.8	4 / 25	58
PEG-PEI-GO	145 / 10	62 / 10	1 / 25	59
ZIF-8	145 / 8	97 / 34	3.75 / 20	60
UiO66-NH ₃	123 / 20	80 / 10	3 / 20	
UiO66	135 / 20	58 / 7.5	3 / 20	61
Polydopamine / PEG composite microcapsules	270 / 1	73 / 1	2 / 25	62
PQD	367 / 1	68 / 1	1 / 25	This work
GQD	668 / 0.05	101 / 0.05	1 / 25	This work

a. The selectivity was measured for CO₂/H₂ separation.

b. No available permeability and hence the permeance data are shown here with the unit of GPU.

hydrogen bond donors. Therefore, the effect of type-II fillers is based on their chemical functionalization and the capacity of more strongly interacting with both PEO and PA6 segment simultaneously.

3.3.4 Fabrication of thin film composite membranes

Developing TFC membranes is of great significance for industrial applications of gas separation membranes. In this study, the pristine Pebax[®], Pebax-GQD-0.05 and Pebax-PQD-1 were fabricated into selective layers of TFC membranes. With the same coating procedure, the thin film thickness of all membranes was around 220 nm, prepared on porous PVDF supports coated with a PDMS gutter layer, as shown in Fig. S15. The separation performance was measured with single gas and listed in Table S3. The trend for the TFC membranes is similar to that observed for the corresponding dense self-standing membranes reported in the first part of this work. The TFC membrane prepared with Pebax/GQD selective layers exhibited high CO₂ permeance (310 GPU) and CO₂/N₂ selectivity of 47, in which the support membrane—PVDF covered by PDMS— shows a CO₂ permeance of 2178 GPU and a CO₂/N₂ selectivity of 9.9. These are promising results for practical application.

4. CONCLUSIONS

In summary, we utilized two types of QDs, graphene oxide QDs (GQD) and polymer-like QDs (PQD), as fillers to regulate the microphase structures of Pebax[®] membrane. The introduction of PQD and GQD result in different microphase structures. With high content of functional groups, PQD disrupts the crystalline structures of both the polyether and polyamide domains of Pebax[®]. The relatively strong interactions between PQD and the polymer matrix restrict the flexibility of

the polymer chains. In contrast, GQD possesses fewer functional groups and enhances the microphase separation of Pebax[®]. Therefore, more amorphous PEO nanophases available for CO₂ transport is expected, resulting in enhanced CO₂ permeability and selectivity. In binary mixed gas test, gas separation performance data of all the MMMs lie beyond the upper bound reported in 2008. Especially, the Pebax-GQD-0.05 membrane respectively showed a 155% and 130% increase of CO₂ permeability and CO₂/N₂ selectivity, compared with the pristine membrane. Moreover, the reasons for the observations were tentatively elucidated: PQD interacts with both PEO and PA6 chains, while GQD prefers to interact with PA6 chains to a large extent. The different kinds of interactions determine the different microphase behaviors and the respective optimal filler loading. Accordingly, such interesting results could open new avenues to understanding molecular-level hybridization and designing Pebax-based MMMs.

■ ASSOCIATED CONTENT

● Supporting Information

Images of PQD and GQD, as well as their aqueous solution under daylight and UV. XPS spectra, TGA curves and DLS of PQD and GQD. Images of Pebax[®], Pebax-GQD and Pebax-PQD solution under daylight and UV, and corresponding membranes under UV. TEM images of PQD, Pebax-GQD-0.05, Pebax-PQD-1 and Pebax-GQD-0.3. Cross-section images of Pebax[®], Pebax-PQD-1 Pebax-GQD-0.05 and TCFMs. XPS, TGA and mechanical properties of Pebax[®], Pebax-CDs membranes. Binary gas separation property under dry and humidified state of dense membrane and single gas transport property of

TCFMs. Comparison of gas separation properties between PQD-doped membranes with low PQD loading and Pebax-GQD membranes.

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Notes

The authors declare no competing financial interest.

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