1. Introduction

Demand for clean freshwater is increasing as the consequences of climate change continue to take its toll around the world and more and more contaminants are finding their way into water sources. There has been great potential to improve the performance of semi-permeable membranes to filter water as a portion of...
the nanoparticles studied before had shown to be not very compatible nor have good dispersibility in the polyamide (PA) layer of thin film nanocomposite (TFN) membranes[1-19]. TFC membranes, the precursor to TFN membranes before quantum dot (QD) loading, can be formed through the interfacial polymerization method using both trimesoyl chloride (TMC) and piperazine (PIP). CQDs, GQDs, or GOQDs, are generally found to be synthesized through the direct pyrolysis or heating of citric acid (CA) and would then be incorporated onto TFC membranes at differing weight percentages to determine the effectiveness of the newly-formed TFN membranes regarding a variety of factors compared to the initial TFC membranes.

TFN membranes can be used in water purification by a variety of membrane separation processes including forward osmosis reverse osmosis. Forward osmosis has the benefit of being a natural process where the water flows through the membrane because of a natural concentration gradient, but the effectiveness in the solute separation from pure water could be lower than reverse osmosis. Reverse osmosis has the benefit of being able to force water through a membrane to separate it from the solutes initially dissolved in it regardless of concentration gradient, but it requires high pressure; thus, it requires much more energy than forward osmosis processes. After the incorporation of QDs onto membranes for a certain membrane separation process, the performance of the membrane generally improved. To give an example, for an ultrafiltration (UF) process, one type of QDs, GOQDs, was shown to act as good nanofillers based on the antifouling capability, permeability, and hydrophilicity on polysulfone (PSF) UF membranes after GOQD loading[30]. Additionally, by changing the process in which CQDs are made, the size and the functional groups of CQDs can differ, making them have different properties. According to which properties are desired for a certain application, one can adjust the synthesis process to get the desired size and properties of CQDs. The incorporation of quantum dots into the PA layer has shown unique characteristics in changing the properties of the membrane, such as decreasing the roughness of the surface, increasing hydrophilicity of the PA layer, increasing the water flux, and displaying improved antifouling performance overall when graphene quantum dots (GQDs) are incorporated into the membrane, indicating the potential of quantum dots in this area[19]. Functionalizing CQDs with Na+ ions were shown to have even better pure water permeability and water flux than regular CQDs while maintaining a similar percentage of salt rejection.

QDs are so versatile that they are finding applications in other areas besides water filtration. Not only can QDs be used in water treatment, but when applied to TFN hollow fiber membranes in pressure retarded osmosis (PRO), it has displayed better osmotic power generation[20]. Greater power density was reported for TFC membranes incorporated with Na-CQDs than ones without them. QDs also found application in solvent-resistant nanofiltration for the separation of organic mixtures and in direct methanol fuel cells (DMFCs) to improve their performance. DMFCs with CQDs showed increased peak power density, electro-chemical selectivity, proton conductivity, and more compared to their counterparts without CQDs. One category of QDs, GOQDs, have polar functional groups that are oxygenated, and can be even used for dehydration[21]. Loading silver ions (Ag+) with GOQDs onto a PA layer was also shown to improve the bactericidal property of the membrane [22], even though incorporation of QDs already made the membrane less prone to antifouling.

2. Quantum Dots

Quantum dots are 0D nanoparticles that are less than 10 nm in size and exhibit novel properties.

2.1. Graphene quantum dots

For the synthesis of GQDs that would be incorporated into TFN membranes, CA was decomposed thermally by putting it into a crucible and heating it for 15 min at 200°C in an electric oven[19]. The solid citric acid turned into liquid during thermal treatment and GQDs formed through certain forces operating at the nano-
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Fig. 1. Schematic diagram of the quantum dots embedded thin film composite membrane.

scale from the molecules that were decomposed from citric acid. For the membranes, initially poly(ether sulfone) support membranes were prepared through non-solvent induced phase separation (NIPS). These membranes were then turned into several different PIP - TMC TFN membranes with varying levels of GQD incorporation through the method of interfacial polymerization. This method of polymerization was done at the interface of PIP and TMC to create a PA layer. More specifically, the support membranes were first immersed into aqueous solutions that had 0.1% PIP by weight percentage (wt) and varying amounts of GQDs. Then, the membranes were taken out and any excess liquid was removed. After this, the membranes were dipped in a 0.1 wt% TMC/n-heptane solution for two minutes, forming a polyamide layer. To evaporate the n-heptane fully and

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### Table 1. Summary of Membrane

<table>
<thead>
<tr>
<th>Thin layer of TFC</th>
<th>Monomer (Diamine)</th>
<th>Monomer (Acid chloride)</th>
<th>Filler</th>
<th>Pristine polymer water flux (L/m² · h)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide</td>
<td>PIP</td>
<td>TMC</td>
<td>GQDs</td>
<td>15.0</td>
<td>[19]</td>
</tr>
<tr>
<td>Polyamide</td>
<td>MPD</td>
<td>TMC</td>
<td>CQDs and Na⁺ functionalized CQDs</td>
<td>66.59 when P = 0</td>
<td>[20]</td>
</tr>
<tr>
<td>Sodium alginate (SA)</td>
<td>-</td>
<td>-</td>
<td>GOQDs</td>
<td>149,644 (g m⁻² h⁻¹)</td>
<td>[21]</td>
</tr>
<tr>
<td>Polyamide</td>
<td>MPD</td>
<td>TMC</td>
<td>GOQDs loaded with silver phosphate</td>
<td>25.8</td>
<td>[22]</td>
</tr>
<tr>
<td>Polyamide</td>
<td>MPD</td>
<td>TMC</td>
<td>GQDs</td>
<td>15 ~ 20 for 0.5 draw solution concentration</td>
<td>[23]</td>
</tr>
<tr>
<td>Polyamide</td>
<td>PEI</td>
<td>TMC</td>
<td>GQDs</td>
<td>6 ~ 7.5</td>
<td>[24]</td>
</tr>
<tr>
<td>Tannic acid (TA)</td>
<td>-</td>
<td>-</td>
<td>GOQDs</td>
<td>15.81 ± 0.2 (0.2 MPa driven pressure)</td>
<td>[27]</td>
</tr>
<tr>
<td>Polyamide</td>
<td>PIP</td>
<td>TMC</td>
<td>GOQDs</td>
<td>110.3 (Na₂SO₄), 110.4 (MgSO₄), 115.5 (NaCl), 112.5 MgCl₂ all for 100 psi</td>
<td>[28]</td>
</tr>
<tr>
<td>Amino modified polyvinylidene fluoride</td>
<td>-</td>
<td>-</td>
<td>GOQDs</td>
<td>(7.07 ± 0.24) × 10³ L m⁻² h⁻¹ bar⁻¹ (pure water permeability coefficient)</td>
<td>[29]</td>
</tr>
<tr>
<td>Polysulfone (PSF)</td>
<td>-</td>
<td>-</td>
<td>GOQDs</td>
<td>82.52 LMH bar⁻¹</td>
<td>[30]</td>
</tr>
<tr>
<td>Polymer</td>
<td>PEI</td>
<td>TMC</td>
<td>CDs</td>
<td>16.1 (ethyl acetate), 8.0 (acetone), 5.9 (toluene), and 4.2 (n-heptane) for 4 bar</td>
<td>[31]</td>
</tr>
<tr>
<td>Polyamide</td>
<td>MPD</td>
<td>TMC</td>
<td>CQDs and Na-CQDs</td>
<td>24,252.80 at 15 bar, 39,223.62 at 23 bar</td>
<td>[32]</td>
</tr>
<tr>
<td>Polyamide</td>
<td>PIP</td>
<td>TMC</td>
<td>Carboxylic CQD (CCQD), amino CQD (NCQD), and sulfonated CQD (SCQD)</td>
<td>18.0 at 0.6MPa</td>
<td>[33]</td>
</tr>
</tbody>
</table>

Trimesoyl chloride (TMC); m-phenylenediamine (MPD); piperazine (PIP); polyethylenimine (PEI); graphene quantum dots (GQDs); carbon quantum dots (CQDs); graphene oxide quantum dots (GOQDs), carbon dots (CDs); carbon quantum dots (CQDs)
for more polymerization, the membranes were then air-dried for 15 min. in an oven at 60°C. Characterization of the GQDs was done via TEM, FTIR was used to determine functional groups located on the surfaces of the membranes, XPS was used to analyze surface elemental compositions of the membranes, and the morphology was seen through SEM. When looking at the XPS results, the O/C ratios of the GQDs/PIP-TMC TFN membrane were higher than that of PIP-TMC nanofiltration (NF) membranes without any GQDs, and a possible explanation for this is the contribution of oxygen-containing functional groups from GQDs and changes in the number of interconnecting groups in the PA active layer. Looking at the SEM, the PIP-TMC NF membrane had a surface that was rugged and dense, while the GQDs/PIP-TMC membranes were smoother. The incorporation of GQDs in TFN membranes was shown to have the effect of increasing water flux with the GQDs/PIP-TMC membrane having a water flux of 102.0 L/(m² h), 6.8 times higher compared to the pristine membrane of PIP-TMC NF [15.0 L/(m² h)]. The easy fabrication process, eco-friendliness, high NF efficiency, and good properties for preventing the accumulation of materials on surfaces in water regarding these membranes makes this study of potential use in applications of water treatment.

Forward osmosis is another important area for water desalination. In this work, GQDs were incorporated to the TFNs for potential applications in wastewater treatment and desalination by studying their bactericidal properties and effect on forward osmosis (FO)[23]. GQDs were produced through the pyrolysis of CA, and the interfacial polymerization process between 1,3-phenyldiamine (MPD) and TMC was used to prepare TFC/TFN membranes for FO on substrates made up of polyethersulfone (PES). ATR-FTIR spectra of TFC and TFN membranes were taken, and after increasing the amount of GQDs on the membranes, there was an effect of considerably lowered intensity of peaks with some peaks disappearing completely. In general, nanomaterials that are carbon-based have great antimicrobial properties because of their mechanisms that are harmful to cells. Included in this category are GQDs, and their incorporation onto TFNs made the selective layer more hydrophilic, which had the effect of lowering the contact angle as the TFC membrane had a contact angle of 72.9° while for the TFN membrane it was 51°. This is strategically beneficial to lower adhesion of foulants, thus improving the antifouling property of the membrane. It was also shown that incorporating a higher concentration of GQDs to the TFN membrane made the polyamide selective layer thicker than before while also creating a denser layer than the pristine TFC membranes, making the membrane much less permeable and creating a blockage of the surface. Permeability of water increased at the beginning, with 29% permeability for TFN-0.05 and 49% for TFN-0.1, but then went down as the concentration of GQDs increased to TFN-0.5. Additionally, TFN-0.5 showed greater than 90% bacterial inactivation for E. coli and greater than 95% bacterial inactivation for S. aureus compared to a pristine TFC membrane. The reason for this was because of the uniform dispersion that the GQDs had with a low tendency to form clusters, as well as increasing the number of active edges on the membrane surface, leading to increased surface cytotoxicity.

Compared to RO and other energy-intensive desalination and water treatment processes, FO has benefits of needing a smaller amount of energy to run, good water recovery, and low fouling levels as it only uses the osmotic pressure difference that occurs naturally between the high and low saline solutions separated by a semipermeable membrane[24]. However, the main issue with FO processes is the problem of internal concentration polarization (ICP). ICP can make the water flux much lower by lowering the osmotic pressure gradient by having solute molecules aggregate near the active and support layer. Through the study, it was found that incorporating GDQs into the membranes improved water permeability and MgCl2 rejection compared to the pure TFC-0 membrane. GQDs were synthesized through the direct pyrolysis of GQDs through the utilization of a “bottom-up” approach. Interfacial polymerization was used to prepare TFC membranes by putting
polyacrylonitrile (PAN) substrates that were hydrolyzed in a 2.0M NaOH solution immersion (H-PAN) into an aqueous monomer solution. These substrates were then dried in air and then also put in a 0.20 w/v% TMC/n-hexane organic monomer solution, allowing for the synthesis of a PA layers on the surface of the H-PAN substrates. FTIR showed that the created GQDs had an aromatic rings, and TEM imaging showed no visible agglomeration of GQDs, showing instead GQDs that were dispersed well and a structure of 2D sheets. Going more in detail, the diffusion resistance went down as the content of GQDs went up to 0.050 wt%, indicating that the addition of GQDs enhanced mass transfer, leading to lower ICP. Increasing GQD wt% past 0.050, the diffusion resistance went up gradually, signaling a gradual increase of ICP, and this may have been caused by the accumulation of GQDs. Additionally, at 0.050 wt%, the membrane demonstrated best performance regarding separation and the highest flux at 12.9 L m⁻² h⁻¹. Water flux increased 22.0% and reverse salt flux went down 32.2% compared to the pure TFC-0 membrane.

Nanofiber membrane are another kind of filtering membrane, and a process of incorporating GDQs in the PAN nanofibers will be discussed. GDQs were synthesized by treating pyrene with nitrate so that it could convert into 1,3,6-trinitropyrene. This mixture was then subjected to dilution with deionized water (DI) and filtration through a nylon membrane. After ultrasonication in a DI solution with ammonia and hydrazine hydrate, the suspension was placed into an autoclave and heated for 8h at 200°C. Nanofibrous membranes were prepared through an electrospinning process. Imaging from TEM and AFM seemed to indicate that the GQDs were made up of 2–5 layers. With a wide range of potential applications in the environmental and biological field, GQDs have garnered interest to function as sensors. Over the surface of the membrane, GQD-PAN membranes had uniform dispersion of GQDs. Even under light irradiation that was ongoing, luminescence levels of immersed and dry GQD-PAN membranes were shown to have high stability for the duration of two months. Regarding the decrease of the intensity of light emission of the membrane from free chlorine, the process was rapid and conspicuous in a visual manner when placed below UV light. The photoluminescence (PL) quenching by GQDs that is not able to be reversed makes the related sensing platforms only able to be used once, but the concentration of chlorine in real-time found in networks for water distribution may still be measured through the filtering membranes that were fabricated by electrospinning.

Solvent-resistant nanofiltration (SRNF), also known as organic solvent nanofiltration (OSN), is a technique that at the molecular level can separate mixtures of organic substances. These membranes can potentially be used when separating substances containing organic compounds from organic solvents. However, the main problem holding back the effectiveness of SRNF membranes is the low solvent resistance of these membranes. The study examines a new TFN membrane that is based on polyimide (PI), which demonstrated better solvent resistance than previous findings. Regarding the synthesis of GQDs, a solution containing GQDs was passed through the PAN UF membrane to remove any impurities that may have been in the solution with a size that was greater than 10.0 nm. To prepare the making of nanocomposite membranes that would be doped with GQDs, the PI substrate was affixed to a glass plate and a MPD solution was then poured on top. Then, the 1,2,4,5-Benzenetetracarboxylic acyl chloride (BTAC) solution was applied on top to form a polyamic acid (PAA) active layer with GQDs embedded into it. Based on the thickness of the GQDs that were observed (0.8–2.0 nm), it was hypothesized that the GQDs were made up of 1–3 layers of graphene. In addition, TEM imaging showed an average GQD size of 1.9 nm, and such a small size allowed for a greater water flow because of additional pathways from an increase in specific surface area. The SRNF membranes that were prepared, named (PI-GQDs-50/PI)ₓ, was shown to have almost a 50% higher permeability of ethanol compared to membranes without any GQDs with identical prepa-
2.2. Graphene oxide quantum dots

Zhang et al. fabricated GOQDs through direct pyrolysis of CA where using a heating mantle, 2 g of CA was heated at a temperature of 200°C[27]. The fabrication of GOQDs was able to be confirmed after the CA changed its phase from a solid to a liquid and its color as a liquid changed from being colorless to a pale yellowish color, later turning into orange, all within a period of 30 minutes. After undergoing dialysis to get rid of excess CA, GOQDs were able to be obtained through freeze-drying the solution. GOQDs can be applied in areas such as low-pressure NF, UF, microfiltration, pervaporative dehydration, and water treatment through incorporation onto preexisting membranes to improve hydrophilicity, antibiofouling and bactericidal performance, and water permeability, to give a few examples.

GOQDs were used to enhance NF performance[27]. GOQDs were formed through the method of direct pyrolysis. Interfacial polymerization was utilized to form TA/GOQDs TFM membranes. Findings that were reported using FTIR showed that through covalent linking, GOQDs were able to be incorporated successfully into the separation layer made of tannic acid (TA). GOQDs were spread throughout a TA film on TFN membranes for NF at low pressure. Compared to the pure TA TFC membrane, the membrane with GOQDs had improved antifouling properties and a maximum pure water flux of 23.33 L/m² h at 0.2 MPa, 1.5 times more compared to the membrane without GOQDs. Rejection of Congo Red was established at 99.8% and methylene blue at 97.6%. Normally, NF processes are very susceptible to being fouled and having low permeability, as well as being expensive in general. As a result, developing NF membranes with good antifouling properties under low pressure is important. Several dyes were tested in this study, and the rejection rate was the highest for Congo Red and lowest for methylene blue, which can be explained by the Donnan exclusion theory that states that as water molecules permeate across the membrane because of the pressure applied, the membrane surface with TA/GOQDs will be electrostati-
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Fig. 4. (a) Preparation process of TA/GOQDs TFN membrane. (b) Scheme of reaction mechanism among TA, GOQDs, and IPDI (Reproduced with permission from Zhang et al., 27, Copyright 2017, American Chemical Society).

Fig. 3. Synthesis of GOQDs (Reproduced with permission from Zhang et al., 27, Copyright 2017, American Chemical Society).

Fig. 5. (a) Raman spectra of as-prepared GOQDs, (b) XRD patterns of GOQDs, (c) TEM image of as-prepared GOQDs, (d) the corresponding size distribution of GOQDs shown in panel c, (e) AFM image of GOQDs, and (f) the corresponding height profile along the black line shown in panel e (Reproduced with permission from Zhang et al., 27, Copyright 2017, American Chemical Society).

Fig. 6. Schematic illustration of the separation process for TA/GOQDs TFN membrane (Reproduced with permission from Zhang et al., 27, Copyright 2017, American Chemical Society).

cally attracted to methylene blue as it is positively charged and electrostatically repulsed to Congo Red. These rates of rejection went up as the concentration of GOQDs increased up to a concentration of 0.5g/L. As for the stability of these TA/GOQDs TFN membranes long-term, TA/GOQDs-0.5 TFN membranes exhibited no clear degradation in water flux and rejection of Na₂SO₄, indicating good durability and stability.

Li et al. focused on the antibacterial properties of thin films that are used in RO processes. Considerable efforts have been undertaken to incorporate metallic nanoparticles onto TFC membranes, such as Fe, TiO₂, and Ag nanoparticles, and these can control microorganisms’ growth[22]. Silver phosphate (AP) is another substance that can be considered in this category of antibacterial nanoparticles, and it is becoming more widely known because of its good photo-oxidation and great quantum efficiency in the presence of visible light. A drawback of AP, however, is that because of its morphology that cannot be controlled and low stability, it tends to lump together. This prevents uniform dispersion on the surface of the membrane, lowering the membrane’s separation performance. To overcome this, a nanocomposite of GOQD and AP may be used,
as lots of negative charges on GOQD can be used as sites of reaction for Ag\(^+\) to control the initial growth and morphology of AP for synthesis, improving distribution of AP on the membrane while improving the antibacterial property of the membrane. GOQD/AP was found to improve the permeability of water across the membrane and have low adsorption of contaminants that were hydrophobic because of the many hydrophilic groups on the TFN membrane, such as carboxyl and hydroxyl groups. Regarding the antibacterial property of the membranes, the synergistic effect between AP and GOQD led to the significantly higher prevention of bacterial growth. Results showed that GOQD/AP incorporation could improve the TFN membrane’s antifouling property from raised surface electronegativity. Regarding the fabrication of GOQDs, a heterogeneous mixture containing GOQDs was treated with ultrasonic waves to make it into a homogeneous mixture. Then, in order to place Ag\(^+\) onto the surface of the GOQDs, which were negatively charged, AgNO\(_3\) solution was added drop by drop into the mixture while the mixture was being mixed magnetically. After continued magnetic stirring even after adding Na\(_2\)HPO\(_4\) \(\cdot\) 12H\(_2\)O, the precipitate was washed and freeze-dried to produce GOQD/AP. Interfacial polymerization was used to create the TFC and TFN membranes incorporated with GOQD/AP nanocomposites. After looking at SEM images of the surface and cross sections of the membrane, structures resembling valleys and ridges were observed, indicating a complete reaction between MPD and TMC.

A filtration method assisted by pressure was used to physically coat GOQDs onto TFN NF membranes to enhance permeability of water and the rejection of salts and dyes[28]. At a pressure of 100 psi with room temperature, aqueous solutions that had a concentration of 500 ppm of Na\(_2\)SO\(_4\), MgSO\(_4\), NaCl, and MgCl\(_2\) were used to test the effectiveness of GOQDs on the separation of ions of NF membranes. With the coating of GOQDs, water flux went up by approximately 15 LMH for all the salt aqueous solutions. Permeability of water increased from the improved surface attraction to water that led to the increase of water solubilization. The effect of different Na\(_2\)SO\(_4\) solutions for ion separation was also studied, and it was observed that with increasing concentration, the salt rejection as well as the water flux decreased, owing to greater osmotic pressure and greater polarization of concentration. Compared to the pure NF membranes, the GOQD/NF membranes had better salt rejection and water flux. Additionally, with GOQDs, rejection of methyl orange went up to 97% from 89.2% while rejection of methylene blue went down to 71% from 75.4%. Regarding potential changes in antifouling properties with the addition of GOQDs, no blatant difference was found, and the NF membranes were shown to have good antifouling properties in general. The GOQD coating and NF membrane were also shown to have good stability with only low fluctuations of salt rejection and water flux over time. For this study, the coating of the GOQDs to make the salt/dye rejection and permeability of water better was made through a method of pressure-assisted filtration. TEM imaging of GOQDs showed near spherical shapes of GOQDs and a good crystalline structure as clear lattice outer edges could be seen. After coating the surface of NF membranes that had a total area of 14.6 cm\(^2\) with 50 µg of GOQDs, SEM imaging displayed a much rougher membrane surface for these membranes compared with NF membranes without any GOQD coating. The GOQD coated membranes were free of any spots not having the GOQD coating.

A new type of membrane with improved antibiofouling and antibacterial properties has been observed through the incorporation of GOQDs into amino modified polyvinylidene fluoride (PVDF) membranes[29]. Here, instead of pyrolysis, a hydrothermal oxidation process was used to synthesize GOQDs from carbon black. In order to create a GOQDs-PVDF membrane, the surface of the PVDF membrane was first hydroxylated and then administered with 3-aminopropyl-trimethoxysilane (APTMS). SEM imaging indicated uniform dispersion of nanoparticles on the surface of PVDF, which suggested GOQDs were immobilized. After a filtration time of 10 hours, the relative flux decrease of GOQD/PVDF was 23%, much lower than pure PVDF.
at 86% and graphene oxide (GO)-sheet modified PVDF at 62%. Owing to the uniform dispersion and structure of GOQDs, GOQD/PVDF showed good antibiofouling, and the modified membrane had stability and durability over a long period of time thanks to strong covalent forces that exist between GOQDs and PVDF. 0D GOQDs bonded to PVDF were also shown to have better antibacterial properties compared to previous studies with 2D GO sheets and polymer membranes with 1D carbon nano-tubes. After the addition of GOQDs onto PVDF, hydrophilicity increased as the water contact angle went down to 34.3° as the water contact angle of pure PVDF was 118.5°. Over a filtration time of 12 hours, the decrease of flux was 24.3% for GOQD/PVDF while flux decreased 88.4% for pure PVDF, suggesting that PVDF incorporated with GOQDs has much better antibiofouling properties compared with pure PVDF. Additionally, even past 10 hours of filtration, the value of permeation was stable for GOQD/PVDF. Regarding the proliferation of S. aureus and E. coli, after being attached to GOQD/PVDF for one hour, the metabolic activity for E. coli cells decreased 88.9%, but for the PVDF membrane modified with 2D GO, it decreased by only 69.2%.

For all the membranes that were fabricated in this study, a phase-inversion method, which gets rid of a liquid polymer solution to form a solid polymer membrane that is porous, was used for their fabrication[30]. PSF membranes incorporated with GOQDs for the purpose of UF at various weight percentages of 0.1~0.5 were created. For background, UF is a process utilized for the filtration of water and is useful for its simplicity in operation, effectiveness of cost, high efficiency, and no detectable production of harmful byproducts. PSF is a membrane with good chemical, mechanical, and thermal stability that is commonly used in UF. Unfortunately, as PSF is hydrophobic in nature, the membrane fouls severely and pores are blocked off, lowering water flux. The materials that cause fouling that lead to a severe decrease of flux were observed to accumulate in the troughs of membrane surfaces that were characterized to be rougher. At 0.5 wt%, irreversible fouling was at 10.3% and flux recovery ratio at 89.7%, the lowest out of all the GOQD-incorporated PSF membranes. Interestingly, at 0.1 and 0.3 wt% of GOQDs, porosity of the membranes went up, while at an increased wt% of 0.5 the porosity went down. Comparing pure PSF membrane porosity with the GOQD enhanced membranes, the former had 55.7% porosity and the latter

Fig. 7. SEM images for normal E. coli cells at the surface of pristine PVDF membrane (a,b) and GOQDs-PVDF membrane (c,d) (Reproduced from Zeng et al., 29).

Fig. 8. SEM images of (a,b) pristine PVDF, (c) PEG modified PVDF, (d) APTMS modified PVDF, (e) GOQDs-PVDF and (f) GOQDs-PVDF membranes after 15 min ultrasonication treatment (Reproduced from Zeng et al., 29).
85.9% porosity. Water flux at 0.3 wt% was 130.54 LMH bar⁻¹ while at 0.5% it was lower at 85.79 LMH bar⁻¹. The increased porosity for the membrane with 0.1 and 0.3 wt% had more space in which water could flow through and lowered the resistance for the flow of water, whereas a 0.5 wt% resulted in a denser structure with less permeability than the lower wt% membranes. XPS results indicated that the number of functional groups on GO sheets is much lower than GOQDs, and this can be explained through edge effects found in GOQDs. Additionally, increasing the weight percentage of GOQDs led to a significant increase of viscosity, which had the effect of the membrane structure being denser and thicker.

A new nanocomposite membrane was developed by incorporating GOQDs into a sodium alginate (SA) matrix for the dehydration of ethanol for application in pervaporative dehydration.[21] The synthesis of GOQDs involved the direct pyrolysis of CA, and the SA-GOQDs nanocomposite membranes had their preparation done on dry PAN substrates through a spin-coating method. TEM imaging indicated that the GOQDs were uniformly distributed quite fairly and dispersed nicely. SEM imaging showed smooth surface structures of the SA-GOQDs/PAN membranes at the microlevel, thanks to the GOQDs being nanosized. This smooth surface structure at the microlevel was similar for the SA/PAN membrane as well. Because of the nanoscale size and the high attraction to water of the GOQDs, the membrane showed good performance regarding ethanol dehydration that was 60% higher compared to a pure alginate membrane, as the membrane achieved 2432 ± 58 g m⁻² h⁻¹ of total permeation flux at 2 wt%. A “bottom-up” method was utilized in the synthesis of GOQDs through the pyrolysis of citric acid. For the preparation of nanocomposite membranes, GOQDs were incorporated into SA. SA has excellent performance when it comes to dehydration separation. At higher loadings of GOQDs, the permeation flux goes down as the separation factor remains nearly constant. Results showing an increase in permeation flux suggests that shorter and less winded pathways through stacks of GOQDs favor the transport of water.

3. Carbon Quantum Dots

CQDs were produced by heating CA in fine powder form for 3 h at 180 in a container made of class that was loosely covered[32]. After heating, the material was then brought down to room temperature. Dissolving this material in water, it was then dialyzed against DI water and then freeze-dried to obtain the CQDs. CQDs can be functionalized with Na⁺ ions, and upon incorporation to a PA membrane, it was found to increase the pure water permeability while maintaining a high NaCl rejection percentage of 97.7%. CQDs show promise in applications of both membrane separation and power generation through osmosis.

NF is also one important technique for the purpose of organic solvent nanofiltration (OSN)[31]. Here, CQDs with differing degrees of carbonation were prepared using pyrolysis that was microwave-assisted. CQDs of smaller sizes than 5 nm with different degrees of carbonation were able to be made by altering the amount of ultra-purified water that CA was dissolved in. The higher the amount of ultra-purified water, the lower the carbonation degree. H-PAN had a mixture of homogeneous polyethyleneimine-carbon dots (PEI-CDs) cast onto it. After removing excess PEI-CDs solution, a solution of n-hexane and TMC was cast on top of the PEI-CDs layer. SEM imaging suggested a homogeneous and smooth PAN/PEI surface that was free of apparent defects or voids. The networks of PEI were cross-linked, and they conferred onto composite membranes great solvent resistance and rejection of solute. CDs on these membranes functioned to accelerate solvent molecules across the membrane. CDs that were carbonated without glycerol with water as the solvent even achieved an increase for solvent flux of 54.3% and an increase of 40.5% for solvent uptake. However, the adsorption and permeability of non-polar solvents was lowered when using these CDs, improving the permeation when it came to polar solvents as a result.

Gai et al. reported on TFN membrane containing
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Functionalized carbon quantum dots[32]. Carbon quantum dots are prepared by finely grinding citric acid powder and heated at 180°C for 3 h in air. This product was then cooled to room temperature and placed in deionized water to dissolve. The desired solute was separated by the difference in permeability with other solutes through a semipermeable membrane and then freeze dried to make the CQDs. Regarding the fabrication of the membrane, interfacial polymerization was used to place a PA layer on each substrate’s inner surface. TFN membranes incorporated with CQDs are one kind of these membranes to create PA layers without any defects. For the use of desalination of brackish water, CQDs functionalized with sodium ions were used in a hollow fiber configuration as opposed to a flat sheet. TEM images showed spherical CQDs and Na-CQDs with sizes from 2–6 nm that did not aggregate in clumps, but instead were dispersed well. Compared to a regular TFC membrane, it was found that the membrane with Na-CQDs incorporation had a 47.1% increase in the permeability of pure water. This increase may have resulted because of a decrease in membrane thickness, increase in space among PA chains, higher effective surface area, and a greater number of hydrophilic groups that have oxygen. The optimal membrane was found to be TFN membranes incorporated with 1% wt Na-CQDs, 57.65 ± 3.26 LMH as the measured water flux, and a salt rejection percentage of 98.6% when the feed solution had 2000 ppm NaCl.

Three different CQDs were synthesized by Sun et al. For carboxylic carbon quantum dots (CCQDs), they were prepared through direct pyrolysis of citric acid[33]. Amino carbon quantum dots (NCQDs) were formed through pyrolysis at low temperature of citric acid with branched polyethyleneimine (BPEI) around. Sulfonated carbon quantum dots (SCQDs) were synthesized through pyrolysis of citric acid and poly(sodium 4-styrene sulfonate) (PSS). The interfacial polymerization method was utilized in the formation of TFC/TFN membranes incorporated with the various types of CQDs, and through TEM imaging, the NCQD and SCQD sizes were found to be larger than CCQD and all of the CQDs were found to be dispersed well and have a near spherical shape. The synthesized three different functionalized CQDs were added to TFN membranes, more specifically the PA layer. The addition of these different CQDs onto TFN membranes gave these membranes differing properties according to which group they were functionalized with. Among these groups, the TFN-SCQD membrane exhibited the highest water flux at 42.1 L m⁻² h⁻¹ with rejection percentage of Na₂SO₄ at 93.6%. The membrane with SCQD also had the best antifouling effect. The lowest water flux was attributed to the TFN-NCQD membrane at 31.5 L m⁻² h⁻¹. For all the membranes incorporated with these groups, the water flux measurement linearly increased with the pressure applied, but it is of note that the CQD’s functional groups do have a role in determining the TFN membrane permeability.

Gai et al. reported power generation through the PRO process using thin film composite membranes[20]. CQDs were prepared by heating citric acid powder that was ground for 3 h at 180°C in order to make original CQDs (O-CQDs) that were altered at the surface with carboxyl groups. Using the method of interfacial polymerization, a polyamide selective layer was formed in the hollow interior surface of the PES fiber substrates. Through TEM characterization, the structures of O-CQDs and CQDs functionalized with Na⁺ were seen to be spherical with sizes around 3–9 nm, with all three categories of CQDs having great hydrophilic properties because of the small size of CQDs and the presence of groups with Na and O, allowing for good CQD dispersion in the medium of aqueous solutions. Having set a mixture of deionized water and 1.0 M NaCl as the feed solution, the study was able to generate a maximum power density of 34.20 W/m² at a pressure of 23 bar with a novel TFC membrane, and this power density was the highest to be reported in literature, according to the authors. Because water flows from higher concentration to a lower concentration across a semipermeable membrane because of chemical potential difference, power can be generated by using the hydrostatic potential. This study incorporated CQDs
onto PA layers and tested these layers for their performance regarding PRO. Some films were incorporated with Na\(^+\) functionalized CQDs at 1% wt and at a pH of 5 and 9. The highest water flux was obtained with the TFC-(Na-CQD-5)-1, which stands for Na\(^+\) functionalized CQDs incorporated onto TFC with 1% wt and at a pH of 5. The study determined the increased power density and water flux CQDs with Na\(^+\) functionalization to be because of a lower thickness of the PA layer in TFC-(Na-CQD-5)-1 and TFC-(Na-CQD-9)-1, more groups of oxygen that were hydrophilic in the PA layers, greater surface area, and a PA network that was looser. Ultimately, TFC-(Na-CQD-9)-1 was found to be the most optimal, in terms of high-power density and water flux and low reverse salt flux.

Prathiban et al. reported the applicability of CQDs in direct methanol fuel cells (DMFCs)[33]. This study investigated the functionality of CQDs to reduce methanol transport from the anode to the cathode in DMFCs by potentially acting as an inorganic filler. DMFCs have been garnering interest as a possibly better alternative to Li-ion batteries because of its great specific energy density to power electronic devices. However, a major problem of DMFCs is methanol crossover, and in order to reduce this, many polymer electrolyte membranes have been proposed, including Nafion composite membranes, which were found to be the best among all others because of high proton conductivity and the high stability of Nafion. Adding CQDs to Nafion could enhance ionic conductivity from hydrogen bonding between hydrophilic groups in CQDs and sulfonic acid groups in Nafion. The preparation of CQDs was achieved by mixing 1.8 g Gelatin with 80 mL of water, and this was then placed in an autoclave. To produce a hydrothermal process, the autoclave was put into a furnace for 3 h at 200°C. To make the hybrid membrane of Nafion-CQDs, a mixture of CQDs and 5 wt% of Nafion ionomer that was mechanically mixed for 4 h and ultrasonically dispersed for 1h was cast in a petri dish made of glass and underwent drying in a vacuum. Upon looking at the pattern of X-ray diffraction, the experimenters were able to see indications of the amorphous nature of GQDs, and this is from the abundant functional groups that can be found within CQDs. This combined membrane was found to have 33% lower methanol crossover and around 30% greater proton conductivity compared to the pure Nafion membrane. Using it in a DMFC, 113 mW cm\(^{-2}\) of maximum power density was achieved at 70°C under ambient pressure, which performance-wise was around 75% greater than the pure Nafion membrane under the same conditions. The optimal content of the Nafion-CQDs as a filler in the study was discovered to be at 1.5 wt%.

4. Conclusions

QDs have generally been shown to improve membrane performance for applications in water reclamation, osmotic power generation, direct methanol fuel cells, sensing technology, and more. The QDs that have been studied were made up of a couple of different materials depending on the study, including carbon, graphene, or graphene oxide. These QDs can also be functionalized with Ag\(^+\), Na\(^+\), or various amino acid groups onto different types of membranes, such as hollow fiber membranes, nanocomposite membranes, etc., to exhibit better desired properties compared to the original membrane. The superb hydrophilicity, antifouling property, and other great properties of QDs combined with their low cost, environmental friendliness, low toxicity, and ability to be applied in various applications makes the study of QDs very appealing for the future of membrane technology. In this review, the utility of different quantum dots in composite membrane were discussed.

References

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