



# Novel thin film composite hollow fiber membranes incorporated with carbon quantum dots for osmotic power generation

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## ABSTRACT

By means of carbon quantum dots incorporation, we have developed novel thin film composite (TFC) membranes for osmotic power generation. The newly developed TFC membrane exhibits a peak power density as high as 34.20 W/m<sup>2</sup> at 23 bar using 1.0 M NaCl and deionized water as the feed pair. To our best knowledge, this is the highest ever power density reported in the literature. The carbon quantum dots (CQDs) are a new class of carbon nanomaterials with advantages of excellent hydrophilicity, low toxicity, environmental friendliness, easy synthesis and low cost. The CQDs are incorporated into the polyamide selective layers via the conventional interfacial polymerization reaction. The effects of incorporating different CQDs and their loadings on membrane morphology, properties and PRO performance have been examined. It is found that the addition of Na<sup>+</sup>-functionalized CQDs not only increases the existence of hydrophilic oxygen-containing groups and surface area of the polyamide layer, but also changes the morphology with a looser and thinner polyamide network. The TFC membrane comprising 1 wt% Na-CQD-9 has the optimal performance. Compared with the control, the water flux and power density at 23 bar increase from 44.52 to 53.54 LMH and 28.44 to 34.20 W/m<sup>2</sup> respectively, while the reverse salt flux remains unchanged.

## 1. Introduction

Global energy demand has expanded dramatically over the last decades due to the rapid growth of world population and economy [1]. The total primary energy consumption worldwide was about 160,310 million MWh in 2014, and would reach around 240,318 million MWh in 2040 [2]. The search for renewable energy has received substantial attention in recent years because it may not only provide sustainable energy for the future but also mitigate the greenhouse gas emissions from fossil fuels [2,3].

Osmotic energy, also known as salinity gradient energy, is increasingly acknowledged as one of the promising renewable and sustainable energy sources [4–8]. Currently, reverse electrodialysis (RED) and pressure retarded osmosis (PRO) are the two main techniques that aim to harvest the osmotic energy from two solutions with different salinities [6–13]. Different from RED which uses ionic exchange membranes, PRO employs semi-permeable membranes between these two solutions. Since water spontaneously diffuses across the semi-permeable membranes from the low concentration side (i.e., feed solution) to the pressurized high concentration side (i.e., draw solution) due to the chemical potential difference, it results in a higher pressure or higher volume in the draw solution compartment. One can therefore convert

the hydrostatic potential via hydro-turbines or pressure exchangers for power generation [11–15]. Integrations between PRO and seawater reverse osmosis (SWRO) desalination as well as membrane distillation (MD) have been proposed and demonstrated recently from both academia and industries [11,14–18]. The performance of hybrid systems and the amount of energy saving for SWRO are strongly dependent on (1) the performance of PRO membranes, (2) the energy to water price ratio and (3) feed quality and compositions [11,14,19–26].

The heart of PRO process is the semi-permeable membrane, which determines the overall power generation, plant size, capital costs and profitability. According to the experience of Statkraft, who built the first commercial PRO prototype in the world, the employment of high performance PRO membranes is crucial for the commercialization of the PRO technology [24,27]. The energy generated from PRO must be sufficiently higher than the energy consumption for pretreatments of the feed pair and feed pumps in order to have positive economical values. Therefore, intensive efforts have been focused on the development of high performance PRO membranes [8,22,28–32]. Among them, thin film composite (TFC) membranes made from interfacial polymerization have received most attention because they have (1) superior permeation properties compared with traditional phase inversion ones and (2) flexibility to optimize the substrate and the polyamide selective

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layer separately. Several strategies have been implemented to improve the mechanical strength and to mitigate the internal concentration polarization (ICP) of the TFC membranes, such as (1) modifying the physicochemical properties of the substrate by pre-compression and polydopamine (PDA) cross-linking [33,34], and (2) molecularly engineering the substrate with different morphology and structures by controlling the phase inversion process [33–36]. Meanwhile, many other approaches have been employed to improve the water permeability of the TFC membranes by appropriate modifications of the polyamide selective layers, such as (1) using additives or surfactants in the monomer solution, and (2) post-treating the nascent polyamide selective layer with chloride, alkaline, alcohol etc. [37–39].

Various nano-materials, such as zeolites, inorganic salts, graphene oxide (GO), carbon nanotubes (CNTs), zeolitic imidazolate frameworks (ZIFs) and metal–organic frameworks (MOFs), have also been employed to tailor the polyamide selective layer with improved separation performance [40–47]. Significant performance enhancements have been reported with a reasonable loading of these nanoscale materials. Carbon quantum dots (CQDs) are a new class of carbon nanomaterials discovered in the last decade. In addition to optical properties, they have unique features such as excellent hydrophilicity, low toxicity, environmental friendliness and low cost [48,49]. They are currently used in chemical sensing, nano-medicine and photo-catalysis [48]. To our best knowledge, there is no exploration to include them in the polyamide layer during interfacial polymerization. Therefore, the first objectives of this study are to (1) explore if CQDs can be incorporated into the polyamide layer during interfacial polymerization and (2) produce novel TFC membranes for PRO applications with a much enhanced power density. Various CQDs would be synthesized and embedded into the polyamide layer using an aqueous mixture of *m*-phenylenediamine (MPD) and CQDs during interfacial polymerization. The second objectives of this work are to investigate (1) the fundamentals of performance enhancement and (2) the effects of CQDs chemistry and loading on membrane morphology and PRO performance. This study may provide new insights and open up novel strategies to design better PRO membranes for osmotic power generation.

## 2. Experimental section

### 2.1. Materials

Veradel® 3100P polyethersulfone (PES, Solvay Specialty Polymers), *N*-methyl-2-pyrrolidone (NMP, 99.5%, Merck), polyethylene glycol 400 (PEG, *M<sub>w</sub>* = 400 g/mol, Acros Organics) and glycerol (Industrial grade, Aik Moh Pains & Chemicals Pte. Ltd.) were purchased to fabricate and post-treat PES hollow fiber substrates for the TFC membranes. 1,3,5-benzenetricarbonyl trichloride (TMC, 98%, Sigma-Aldrich), hexane (99.9%, Fisher Chemicals), *m*-Phenylenediamine (MPD, 98%, T.C.I.) and sodium dodecyl sulfate (SDS, 99%, Sigma-Aldrich) were employed in the interfacial polymerization process to fabricate the polyamide selective layers of the TFC membranes. Citric acid (99.5%, Sigma-Aldrich) and sodium hydroxide (98%, Sigma-Aldrich) were utilized to synthesize and functionalize the CQDs. Sodium chloride (NaCl, 99.5%, Merck) was acquired to prepare all the saline solutions in this work. The deionized (DI) water used in this work was produced by a Milli-Q ultrapure water system (Millipore, USA). All chemicals were used as received without further purification.

### 2.2. Syntheses and characterizations of carbon quantum dots (CQDs)

The original CQDs (O-CQD) and Na<sup>+</sup>-functionalized CQDs (Na-CQD) were synthesized as illustrated in Fig. 1, following the method reported by Guo et al. with some modifications [50]. Firstly, the grinded citric acid powders were put into a glass container covered with a glass slide and then heated in air at 180 °C for 3 h to form O-CQD passivated with carboxyl groups. Subsequently, the product containing

O-CQD was dispersed in DI water, and then dialyzed with Slide-A-Lyzer G2 Dialysis Cassettes (2 K MWCO) until there was no significant variation of conductivity in the surrounding DI water. After the dialysis process, a portion of the resultant O-CQD aqueous solution was freeze dried directly to get the O-CQD product, while the other portion was neutralized with a NaOH solution of 5.0 M to pH = 5 and 9. During the neutralization process, the carboxylic acid groups of O-CQD reacted with hydroxyl groups to form neutralized Na-CQD. Afterwards, the Na-CQD aqueous solution was also freeze dried to produce two Na-CQD products, which are referred to as Na-CQD-5 and Na-CQD-9 for respective CQDs solutions of pH = 5 and 9.

The synthesized O-CQD, Na-CQD-5 and Na-CQD-9 were characterized by high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100F), Fourier transform infrared spectroscopy (FT-IR, Vertex 70, Bruker, USA) with a wavenumber range of 4000–500 cm<sup>-1</sup> and an X-ray photoelectron spectrometer (XPS, Kratos AXIS Ultra<sup>DL</sup>D spectrometer, Kratos Analytical Ltd) with a mono Al K<sub>α</sub> X-ray source.

### 2.3. Fabrication of PES hollow fiber substrates

The commercial PES polymer, which had been dried at 60 °C under vacuum overnight, was dissolved in a mixture of NMP and PEG (NMP/PEG = 1:1) by stirring at 60 °C first, and then DI water was added dropwise into the polymer solution after it was cooled down to room temperature. Subsequently, the polymer solution was stirred slowly for about 24 h, then the prepared homogenous polymer solution (polymer concentration = 21 wt%) was further degassed under vacuum before spinning.

A dry-jet wet spinning process utilizing the co-extrusion technique through a dual layer spinneret was employed to prepare the PES hollow fiber membranes as the substrates for the TFC membranes. DI water, polymer solution and NMP were pumped into the dual layer spinneret through the inner, middle and outer channels, respectively, to fabricate the inner-selective hollow fiber substrate. The details of the spinning process were similar to the previous reports [36,51]. The as-spun PES hollow fiber substrates were immersed in tap water for 2 days before being post-treated by a 50% glycerol aqueous solution for another 2 days followed by air dry for 2 days. Finally, small lab-scale modules were made and each module consisted of three PES hollow fiber substrates.

### 2.4. Fabrication of PES TFC hollow fiber membranes

The polyamide selective layer was synthesized on the inner surface of the PES hollow fiber substrates by interfacial polymerization. First, a 2 wt% MPD aqueous solution containing (1) 0.1 wt% SDS and (2) one of the synthesized O-CQD, Na-CQD-5 and Na-CQD-9 at 0–2 wt% was pumped into the lumen side of the lab-scale module for 3 min at a flow rate of 4.25 mL/min. Then compressed air was purged into the lumen side of the module for 5 min to remove the excessive MPD solution. Subsequently, a 0.15 wt% TMC in hexane solution was pumped into the lumen side of the module at a flow rate of 2.50 mL/min for 5 min to react with the MPD solution saturated on the membrane surface. To remove the excessive TMC solution, the module was purged with air again through the lumen side for 1 min. All prepared lab-scale modules consisting of TFC membranes were kept in air overnight and then soaked in DI water for at least one day before tests or characterizations. The TFC membranes inside the modules were denoted as TFC-0 (control), TFC-(O-CQD)-1, TFC-(Na-CQD-5)-1, TFC-(Na-CQD-9)-0.5, TFC-(Na-CQD-9)-1 and TFC-(Na-CQD-9)-2, respectively, where 0.5, 1 and 2 refer to the weight percentages of CQDs in the MPD solutions.

### 2.5. Membrane characterizations

To study the effects of CQDs on the polyamide selective layer, various characterization techniques were employed in this work. To

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