



# Carbon dots-incorporated composite membrane towards enhanced organic solvent nanofiltration performance



Zhijie Yuan<sup>a,1</sup>, Xiaoli Wu<sup>a,1</sup>, Yanjun Jiang<sup>b</sup>, Yifan Li<sup>a</sup>, Jiajia Huang<sup>a</sup>, Lan Hao<sup>a</sup>, Jie Zhang<sup>a</sup>, Jingtao Wang<sup>a,\*</sup>

<sup>a</sup> School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, PR China

<sup>b</sup> School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, PR China

## ARTICLE INFO

### Keywords:

Carbon dots  
Tunable carbonation degree  
Composite membrane  
Organic solvent nanofiltration  
Selective accelerator

## ABSTRACT

Herein, a series of composite membranes hybridized by sub-5 nm carbon dots (CDs) in polymer active layer were fabricated for organic solvent nanofiltration. The CDs with tailored functional groups were facily synthesized and embedded into polyethyleneimine (PEI) matrix, and then dip-coated on polyacrylonitrile support to prepare composite membranes through interfacial polymerization. The resultant membranes were characterized by scanning electron microscopy, atomic force microscopy, fourier transform infrared spectroscopy, contact angle, thermal gravity analysis and tensile testing. The nanofiltration performances of membranes were evaluated by solvent uptake behavior, solvent flux and solute rejection, confirming that hybridization of small-sized CDs could well exert the advantages of PEI and CDs: the completely cross-linked PEI networks assured excellent solvent resistance and solute rejection ability, whilst CDs worked as selective nano-accelerators for solvent transfer via their functional groups. Carbonation degree acutely governed the acceleration ability of CDs for different solvents. And for instance, lowly carbonated CDs could efficiently adsorb polar solvents by the hydrophilic groups, thus providing a 54.3% permeance increase for isopropanol to  $42.6 \text{ L m}^{-2} \text{ h}^{-1}$ . Meanwhile, this kind of CDs also suppressed the transport of non-polar solvents and thereby enhanced membrane selectivity. In contrast, obvious increase of non-polar solvent uptaking and permeation was achieved by high-carbonation-degree CDs via their hydrophobic domains.

## 1. Introduction

Zero-dimensional (0D) materials, with many exceptional properties such as large specific surface area [1] and novel size effect [2], have garnered intense interests for many promising applications, especially in photoelectricity [3] and bio-medicine [4]. Among 0D materials, carbon dots (CDs) have triggered increasing attention since its first report in 2004 by Scrivens et al. [5]. Superior to many similar-size materials [6,7], the non-porous CDs were synthesized through an environmental-friendly and energy-saving approach – one-step microwave-assisted pyrolysis of citric acid and ethylenediamine [8–14]. In such a way, monodisperse sub-5 nm CDs with ultrahigh surface-to-volume ratio and different loadings of groups (–OH, –NH<sub>2</sub> and –CO<sub>2</sub>H) were obtained, rendering them great potential in the fabrication of high-performance nanocomposites [15]. For example, despite being rarely reported, CDs might be distinct reinforcers for separation membranes by providing uniform-dispersed, selective transport sites, while

large-sized fillers fall to do so.

On the other hand, in industrial process of pharmaceuticals, petrochemicals and foods, organic solvents (e.g., alcohols, esters, ketones, alkanes, aromatics) are the indispensable chemicals [16], the usage of which is just lower than that of water. Different from the natural resource of water, organic solvents are produced through energy-intensive and harsh-environment processes. Therefore, the separation and recycling of organic solvents are crucially important issues for saving resources and avoiding pollution [17,18]. Compared with the traditional flash chromatography [19], distillation [20] and extraction [21], organic solvent nanofiltration (OSN) which employs a solvent-permeable and solute-blocking membrane might be one promising candidate as it can save energy and chemical to a certain extent [22]. For OSN, the properties of nanofiltration membrane are of vital significance, and high flux is highly needed to deal with a large volume of solvent solution. The low-cost, prominent processibility, and rejection ability make polymeric OSN membrane state-of-the-art at present [23].

\* Corresponding author.

E-mail address: [jingtaowang@zzu.edu.cn](mailto:jingtaowang@zzu.edu.cn) (J. Wang).

<sup>1</sup> These authors contributed equally to the preparation of the manuscript.

However, polymeric membranes usually suffer from trade-off effect between permeation and rejection because of the wide distribution of free volume cavities of polymer chains. To overcome this inherent shortcoming, cross-linking and hybridization techniques have been utilized to adjust polymer chain free volume via covalent bonds or weak interactions, thus enhancing the sieving transfer ability [24]. By comparison, hybridizing nanofillers into polymer matrix is more attractive and universal since various materials can be employed for tunable free-volume regulation, and can provide additional transport carriers for solvent, which are difficult to be realized by cross-linking method [25].

For polymer-filler hybrid membrane, the nanostructure and component of fillers are critical in performance enhancement of OSN [26]. To sum up, nano-size to micro-size particles (MOFs [27], silica [28], zeolite [29]) and sheets (graphene oxide [30], MXene [25]) have been incorporated into the active layer of OSN membrane. The presence of nanochannels within the filler or facilitated transport sites on filler surface can accelerate solvent migration. For instance, Wu and co-workers created alcohol-selective pathways along MXene surface using the –OH groups, facilitating the isopropanol flux by 30.2% [25]. Together with the physical rejection of sheets on solutes, the resultant hybrid membrane readily overcame the trade-off effect in OSN membrane. However, the fabrication of desirable hybrid membrane that can well retain and combine the advantages of polymer and filler is still a challenge due to the following facts. The large-sized fillers (most > 100 nm, especially nanosheets) would segment polymer bulk, sacrificing its inherent transfer ability and also making the membrane brittle [31]. Secondly, thick membrane (most > 1  $\mu\text{m}$ ) is required to avoid defects due to the possible aggregation of fillers; however, thick membrane results in high membrane resistance and limited solvent flux. Considering size effect, small fillers at polymer-chain size scale (like CDs) might be more attractive because of their good compatibility and dispersion as well as ultrahigh surface-to-volume ratio [32]. Up to now, there is no report on CDs-based nanofiltration membranes, except for the paper by Li et al. for anticounterfeiting [33].

Herein, we reported a kind of polymer-CDs hybrid membrane and its application in organic solvent nanofiltration. Sub-5 nm CDs with tunable carbonation degree, i.e. surface groups, were synthesized facilely as nanofillers. And polyethyleneimine (PEI) was selected as polymer matrix due to its excellent solvent resistance and film-forming ability. Cross-linked PEI-CDs layer was coated on hydrolyzed polyacrylonitrile (PAN) support to obtain thin and defect-free composite membrane. The physicochemical properties and microstructures of membranes were investigated systematically. The OSN performances in terms of solvent resistance, solvent flux and solute rejection were evaluated in detail.

## 2. Experimental

### 2.1. Materials

PEI ( $M_w$  20,000 Da) was purchased from Alfa Aesar (Tianjin, China) without any post-treatment. TMC was supplied by Jianglai biochemical reagent Co., Ltd (Shanghai, China). PAN support with the molecular weight cutoff ( $MWCO$ ) of 50,000 Da was supplied by Zhongkeruiyang Membrane Engineering & Technology Co., Ltd (Beijing, China), which was hydrolyzed by sodium hydroxide before utilization. Diethylenetriamine (DETA) and citric acid (99.5 wt% purity, without water) were obtained from Aladdin biochemical technology Co., Ltd (Shanghai, China). Organic solvents used to prepare membranes and for filtration experiments (*n*-hexane, glycerol, *n*-heptane, acetone, toluene, isopropanol, and ethyl acetate) were obtained from Tianjin Kewei Chemistry Co., Ltd. Polyethylene glycol oligomers (PEG,  $M_w$ s 200, 400, 600, 800, 1000, 1500 and 2000 Da) were supplied by Aladdin biochemical technology Co., Ltd (Shanghai, China). Deionized water was used throughout the experiment.

### 2.2. Synthesis of CDs with different carbonation degrees

CDs with different carbonation degrees were prepared by one-step microwave-assisted pyrolysis according to the literature [13], which was tuned by changing the composition of reaction solvents and thus the reaction temperature. Typically, citric acid (0.96 g) was dissolved in the mixture of ultra-purified water (0.5 g) and glycerol (1.5 g). After citric acid being dissolved completely, DETA (540  $\mu\text{L}$ ) was loaded in the above solution. The mixture was treated by ultrasonic for 5 min at room temperature followed by heating in a 750 W microwave oven for another 5 min. During the reaction process, the color of the solution changed from colorless to yellow and then to black. Subsequently, the products were purified by washing with ethanol for three times to remove residual small molecules, and then dispersed in water. After centrifugation, CDs1 with the highest carbonation degree were yielded from the aqueous solution through freeze drying for 48 h. CDs with lower carbonation degree were prepared by the same method with the amount of ultra-purified water increasing to 1.0 g, 1.5 g, and 2.0 g, respectively, meanwhile the corresponding amount of glycerol decreased to 1.0 g, 0.5 g, and 0 g, respectively. The resultant CDs were named as CDs $M$ , where  $M$  ( $M = 1, 2, 3,$  and  $4$ ) represented the successively decreased carbonation degree.

### 2.3. Preparation of the composite membranes

The support (PAN) was tailored into disc with a diameter of 9.0 cm and then immersed in NaOH solution (1 M) for 1 h at 50 °C. The residual NaOH was removed by washing with water until the pH of the rinsed water reached about 7.0. The hydrolyzed PAN support was stored in water for its subsequent use.

A certain amount of CDs were dispersed into water (26.0 g) by stirring for 1 h at room temperature. PEI (4.0 g, 50 wt%) aqueous solution (24.0 g) was prepared and stirred for 1 h. Afterwards, the above solutions were mixed and stirred for a homogenous PEI-CDs solution (50.0 g). Then, the mixture was cast onto the surface of hydrolyzed PAN support and kept for 10 min. After removing the excess solution, the solution of TMC (0.5 g) and *n*-hexane (50.0 g) was cast onto PEI-CDs layer and kept for 2 min to perform the cross-linking reaction. Then, the membrane was dried firstly in the air for 20 min, and then at 60 °C for 2 h in the oven to evaporate residual *n*-hexane as well as complete cross-linking reaction. The filler content of 10 wt% CDs $M$  was utilized to ensure a close thickness of active layer (Fig. S1 and Table S1), and the resultant composite membranes were named as PAN/PEI-CDs $M$ -10. Three other membranes prepared by embedding CDs2 were collectively named as PAN/PEI-CDs2- $X$ , where  $X$  ( $X = 2, 5,$  and  $30$ ) represented the filler content.

### 2.4. Characterization of CDs and composite membranes

Fourier transform infrared spectroscopy (FTIR) of the membrane samples was recorded on a zinc selenium/diamond plate of a Nicolet (MAGNA-IR560) instrument with a resolution of 4  $\text{cm}^{-1}$  in the range of 4000–670  $\text{cm}^{-1}$  at room temperature. Transmission electron microscopy (TEM) of CDs was performed on a FEI model TECNAI G2-TEM operated at 200 kV. The samples were prepared by immersing 400-mesh carbon-coated copper grids into the water solutions of CDs, followed by drying under vacuum. Thermal gravity analysis (TGA) was conducted by TGA-50 SHIMADZU from 30 to 800 °C at a heating rate of 10 °C  $\text{min}^{-1}$  under nitrogen atmosphere. The distribution of component within CDs and membranes was analyzed by the energy dispersive spectroscopy (EDS) on a scanning electron microscope (SEM, JSM7500F) instrument after freeze-fractured in liquid nitrogen and followed by sputtering with gold under the vacuum degree of 5 Pa. Also, the surface and cross-sectional images of membranes were observed on this SEM. The crystalline structures of CDs were performed by a wide X-ray diffractometry (WXRD) using a RigakuD/max2500 v/PC

Download English Version:

<https://daneshyari.com/en/article/7020179>

Download Persian Version:

<https://daneshyari.com/article/7020179>

[Daneshyari.com](https://daneshyari.com)