

Hierarchically Porous Carbon Membranes Derived from PAN and Their Selective Adsorption of Organic Dyes^{*}

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Abstract Porous carbon membranes were favorably fabricated through the pyrolysis of polyacrylonitrile (PAN) precursors, which were prepared with a template-free technique-thermally induced phase separation. These carbon membranes possess hierarchical pores, including cellular macropores across the whole membranes and much small pores in the matrix as well as on the pore walls. Nitrogen adsorption indicates micropores (1.47 and 1.84 nm) and mesopores (2.21 nm) exist inside the carbon membranes, resulting in their specific surface area as large as 1062 m²/g. The carbon membranes were used to adsorb organic dyes (methyl orange, Congo red, and rhodamine B) from aqueous solutions based on their advantages of hierarchical pore structures and large specific surface area. It is particularly noteworthy that the membranes present a selective adsorption towards methyl orange, whose molecular size (1.2 nm) is smaller than those of Congo red (2.3 nm) and rhodamine B (1.8 nm). This attractive result can be attributed to the steric structure matching between the molecular size and the pore size, rather than electrostatic attraction. Furthermore, the used carbon membranes can be easily regenerated by hydrochloric acid, and their recovery adsorption ratio maintains above 90% even in the third cycle. This work may provide a new route for carbon-based adsorbents with hierarchical pores *via* a template-free approach, which could be promisingly applied to selectively remove dye contaminants in aqueous effluents.

Keywords: Carbon membranes; Polyacrylonitrile; Thermally induced phase separation; Methyl orange; Selective adsorption.

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INTRODUCTION

Dyes and pigments are very common in our daily life, and approximately 0.7 million tons have been produced annually for textiles, package, plastics, rubber, and cosmetics^[1]. However, beyond 10% are discharged into water bodies as waste contaminants, many of which are identified to be carcinogen and mutagen, and may severely damage humans and aquatic biota^[1]. Several techniques by far have been developed to treat dyes in effluents. Among others, adsorption has been found to be the most effective procedure in practical applications^[2]. Dyes will be transferred from aqueous effluent to a solid phase by adsorbents, and they are subsequently regenerated or stored not in direct contact with the environment. Various adsorbents were explored for these applications and porous carbon materials are accepted as a successful and attractive one for the removal of dye contaminants. It is

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because they possess high specific surface area, excellent chemical stability, low density, good biocompatibility, and high cost effectiveness from various low-cost precursors^[3]. Moreover, their sorption capacity or selectivity can be modulated by chemical modification and pore architecture designation^[4]. Recently, carbon materials with hierarchically porous structure are attracting much attention for adsorption and separation^[5]. Those hierarchical pores not only endow the carbon materials good mass transport through the large pore channels, but also maintain a favorable specific surface area based on their fine pores.

It is well known that templating method is the most capable one for constructing mesoporous, macroporous, and hierarchically structured porous materials, which depends on the framework of hard- or soft-templates^[6–8]. A number of inorganic materials were usually used as hard-templates, such as silica, aluminosilica, zeolites, anodic alumina oxide membrane, colloidal particles and colloidal crystals^[9]. The hard-templating technique involves first the creation of a sacrificial template, followed by the impregnation of an appropriate carbon source, then carbonization and subsequent removal of the template. As a result, the carbon products will inversely replicate the architecture of the parent templates. It is conceivable that precursors with high viscosity are difficult to completely diffuse into all space of templates^[10], and defects will unexpectedly emerge in final carbon materials. On the other hand, soft-templating strategy is developed through phase separation of polymer blends or block copolymers, and then carbonization to eliminate sacrificial components^[11]. The microdomains from the sacrificial components will be selectively transferred into ordered pores *via* pyrolysis, so their morphology and scale must be bound to confine the pore structures of carbon materials. Nevertheless, it is not easy to synthesize block copolymers for a satisfactory phase separation. For instance, polyacrylonitrile (PAN), as an important precursor for carbon materials^[12], has high melting point and viscosity that make the direct templating process unavailable. Besides, PAN-based block copolymers are rarely reported and their phase behaviors still need to be understood further. Therefore, template-free techniques are necessary to fabricate porous carbon materials from the view of time-saving and low cost.

Recently, a priori preparation of porous polymer precursors followed by pyrolysis has been found to be a useful way to design pore structures of carbon^[13–16]. For example, Okada *et al.* used thermally induced phase separation (TIPS) process to prepare porous PAN precursors and then pyrolyzed into mesoporous carbon monolith^[15]. Actually, TIPS is a well-known method for polymer membranes and microcellular foams with excellent mechanical properties^[17–21]. In a TIPS process, an appropriate diluent will be chosen to induce a thermo-driven phase separation for a polymer, and the morphology of diluent phase usually determines the final pore architectures. Generally, cellular, lacy, and bi-continuous pores are resulted from liquid-liquid phase separation, whereas spherulitic or metallic pores are often formed as polymer or diluent crystallizes during solid-liquid or liquid-solid phase separation. We previously chose dimethyl sulfoxide (DMSO) as a crystallizable diluent to prepare PAN membranes^[20, 21] and foams^[22] with honeycomb- or channel-like pores by TIPS method. Moreover, the PAN foams were used as a priori precursor for macroporous carbon monoliths *via* pyrolysis. Nevertheless, the resulted carbon monolith has a very low specific surface area that is not suitable for adsorption application.

Herein, carbon membranes with hierarchical pores were fabricated through the pyrolysis of PAN membranes with cellular-like pores, which were made *via* TIPS process using DMSO and glycerol as mixing diluents beforehand. These hierarchical pores, including cellular-like macropores and mesopores, endow the carbon membranes very high specific surface area (1062 m²/g). Furthermore, they can be used as dye adsorbents and even exhibit selective adsorbing behavior towards methyl orange. We detailedly investigated the oxidation and carbonation processes of PAN membranes, and the adsorption behaviors of porous carbon membranes. This work may provide a new route for carbon-based adsorbents with hierarchical pores *via* a template-free approach, which could be promisingly applied to selectively remove dye contaminants in aqueous effluents.

EXPERIMENTAL

Polyacrylonitrile (PAN, $M_n = 115000$, $M_w = 251000$, MWD = 2.19) was kindly supplied by Anqing Petroleum Chemical Corporation of China. It is a copolymer of acrylonitrile (AN) and vinyl acetate (VA), and the molar ratio of AN:VA is 24:1. It was dried overnight in vacuum oven before use. Dimethyl sulfone (DMSO2, 99%) was purchased from Dakang Chemicals Co., China. Glycerol in AR grade was a commercial product. Methyl orange (MO), Congo red (CR), and rhodamine B (RB) were purchased from Aladdin Chemistry Co. Ltd. and used as received.

Porous carbon membranes were prepared by oxidation and carbonization of PAN precursor membranes. PAN membranes were fabricated *via* TIPS method according to our previous work^[20]. PAN, DMSO2 and glycerol were chosen as the ternary system to form PAN membranes, and their typical ingredients were 12%, 61.6% and 26.4%, respectively. The ternary mixture was heated at 160 °C to obtain homogeneous solution, followed by degassing the air bubbles. Then the solution was quickly transferred to a stainless steel mould (thickness ~200 μ m) that was preheated in an oven at 160 °C. Afterwards, the whole mould was quenched into a water bath at 30 °C to induce phase separation, and the solution was totally solidified. Finally, a nascent membrane was taken out of the mould and immersed in deionized water for 24 h at 40 °C to form a wet PAN membrane. After drying, the PAN membranes were cut into round shape with the diameter of 25 mm.

The pyrolysis process was conducted in high-temperature tube muffle furnace (SGL-1700, Shanghai Daheng Optical Precision Machinery Co., Ltd., China). In the oxidation step, the PAN membranes were firstly put into corundum crucible, and then heated to 200–250 °C at a rate of 0.5–2 K/min and held for 0.5–2 h in air. Subsequently, they were cooled to 100 °C at a rate of –5 K/min, and the oxidized membranes were obtained. In the carbonization step, the stabilized membranes were reheated to 700–900 °C at a rate of 1–4 K/min, and held for 0.5–2 h. The final carbon sheets were followed by cooling to 100 °C at a rate of –5 K/min and further cooled to room temperature naturally. The whole carbonization step was under N₂ atmosphere. Table 1 lists the specific conditions for each sample.

Table 1. Oxidation and carbonization conditions, C $\equiv$ N fraction of polyacrylonitrile for each oxidized sample, and weight loss after carbonization

Sample	Temperature (°C)	Heating rate (K/min)	Holding time (min)	C $\equiv$ N fraction (%)	Weight loss (wt%)
Oxid-1	200	1	60	77.5	2.8
Oxid-2	250	1	60	19.2	5.9
Oxid-3	300	1	60	32.4	11.9
Oxid-4	250	0.5	60	48.6	7.9
Oxid-5	250	2	60	72.6	11.1
Oxid-6	250	1	30	30.1	4.4
Oxid-7	250	1	120	12.8	6.5
Oxid-8	250	0.5	120	42.2	10.7
Carb-1	700	2	60	–	46.1
Carb-2	800	2	60	–	65.4
Carb-3	900	2	60	–	75.3
Carb-4	800	1	60	–	51.2
Carb-5	800	4	60	–	57.9
Carb-6	800	2	30	–	58.9
Carb-7	800	2	120	–	70.9

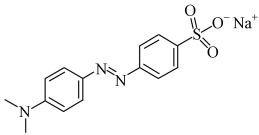
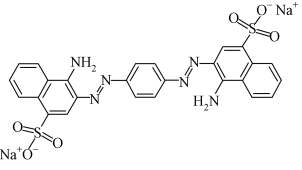
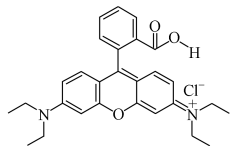
In the carbonization step, all the samples were firstly oxidized by heated to 250 °C at a rate of 0.5 K/min and held for 2 h.

Fourier transform infrared spectra (FTIR, Bruker Vector 22, Switzerland) were taken by 32 scans at a nominal resolution of 4 cm^{–1} using a Nicolet 6700 spectrometer. Wide-angle X-ray diffraction (WAXD) was performed in a range of 10°–40° on a Rigaku D/Max-2550PC X-ray diffractometer (Panalytical, Netherlands) with CuK α ($\lambda = 0.154$ nm) radiation. Raman spectra were obtained with inVia-Reflex spectroscopy (Renishaw, England) at room temperature. Field emission scanning electron microscopy (FESEM, Sirion-100, FEI, USA)

was employed to investigate the morphologies of the carbon membranes. Average pore size of each sample was determined from the SEM image by an image analysis software according to the reported method^[23]. Nitrogen adsorption technique with Brunauer-Emmett-Teller (BET) method was applied to get information of specific surface area, and pore size distribution of porous carbon membranes was conducted by an automated gas sorption analyzer (AUTOSORB-IQ-MP, Quantachrome, USA).

The aqueous solutions of MO, CR and RB with concentration of 50 mg/L were used for the adsorption studies. The adsorption behaviors of porous carbon membranes were investigated according to the following procedure. Typically, sample with weight of 10 mg was added into 10 mL of aqueous solution (50 mg/L), and the mixture was then shaken at 25 °C for 24 h. The mixture solution was filtered through a syringe-driven filter with pore size of 0.45 μm for further characterizations. The residual concentration of organic dyes in the filtered solution was measured by UV-Vis spectroscopy (UV 2450, Shimadzu, Japan) at their UV adsorption wavelengths (Table 2). To study the reusability, the used carbon membranes were recovered by washing in hydrochloric acid for 48 h, and then rinsed by ethanol and deionized water.

Table 2. Molecular structure and physical properties of the used dyes

Dye	Structure	Type	Molecular weight (g/mol)	UV adsorption wavelength (nm)
Methyl orange		Anionic dye	327	463
Congo red		Anionic dye	696	497
Rhodamine B		Cationic dye	479	554

RESULTS AND DISCUSSION

Chemical and Structural Evolution during Carbon Membranes Formation

PAN or its copolymers are the most suitable precursors for carbon fibers because they have considerable carbon yield, high melting point, and relatively cheap price^[13]. Generally, the fast pyrolysis of PAN generating a graphitic structure undergoes two stages of thermal treatment that are oxidation and carbonization. The chemical and structural changes during carbon formation at each stage play an imperative role in achieving the ultimate product quality. Therefore, we detailedly investigated the effects of several parameters of oxidation and carbonization on the chemical and structural changes, such as temperature, heating rate, and holding time (Table 1).

Oxidation is the most important stage for PAN-based carbon, which can transfer linear PAN molecular chains to aromatic ladder structure at low temperatures^[24]. Figure 1 illustrates FTIR spectra exhibiting the chemical structures of the pristine PAN membranes and oxidized samples under different conditions. After oxidation, the absorption peak at 2243 cm^{-1} ($\nu_{\text{C}\equiv\text{N}}$) presents a significant reduction in sharpness and intensity, which indicates the loss of linear pendent cyanide in PAN chains. A weak band appears at 2195 cm^{-1} assigned to the nitrile group attached to the olefinic chain as a result of cyclization. Meanwhile, a pair of new bands at 1610 cm^{-1} and 1590 cm^{-1} occurs and increases as a function of holding time, which is assigned to a mix

vibration of C=N, C=C, N-H and out-plane bending of C=C-H, respectively^[13]. They reveal the appearance of ladder structures, and represent the dehydrogenation and cyclization during oxidation process^[25]. The extent of cyclization can be calculated by the following formula according to the literature^[26]. Table 1 lists the data of C≡N fraction unreacted for each oxidized sample. It is clear that these values decrease as holding time prolongs. Moreover, samples of Oxid-1 and Oxid-5 show the highest C≡N fraction values, indicating that low temperature or high heating rate is not suitable for cyclization.

$$\text{CN fraction unreacted} = \frac{\text{ABS}(2243)}{\text{ABS}(2243) + f \times \text{ABS}(1595)}$$

where ABS(2243) and ABS(1595) mean the absorbance of C≡N groups and C=N groups, respectively. f represents the ratio of C≡N and C=N group absorptivity constant, here it equals to 0.29.

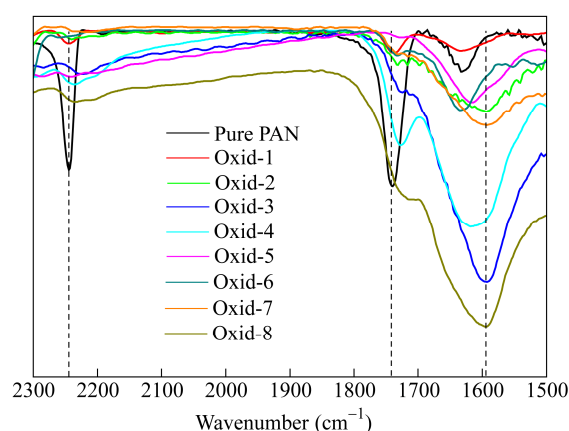


Fig. 1 FTIR spectra of PAN powder and oxidized PAN membranes.

SEM was carried out to display the evolution of pore structure inside the membranes through pyrolysis. As shown in Fig. 2(a), obvious shrink has taken place for pores across the membranes, and even collapse happens in the samples of Oxid-5 and Oxid-7. Comparing the thickness and pore sizes of the membrane samples (Fig. 2b), it is clear that the membrane deformation aggravates with the enhancement of temperature, heating rate and holding time during the oxidation process. Among others, the heating rate has the most significant effect on the pore deformation. When the heating rate increases from 0.5 K/min to 2 K/min, the pore size will decrease from 2.3 μm to 1.1 μm . This is consistent with other reports^[27].

Considering the chemical and structural changes of oxidized membranes, we finally chose an appropriate oxidation route, that is, PAN membranes are heated to 250 $^{\circ}\text{C}$ at 0.5 K/min and then held for 2 h. This process can ensure the oxidized samples with stable structure and enough oxidation extent, and subsequently obtain excellent carbon membranes. Similarly, we studied the effects of the carbonization temperatures (700–900 $^{\circ}\text{C}$), heating rates (1–4 K/min), and holding times (0.5–2 h) on the chemical components and structures of carbon membranes. The specific parameters have also been listed in Table 1. FTIR spectra show that most adsorption peaks either disappear or dramatically decrease after carbonization (Fig. S1 in Supporting Information), which indicates the occurrence of carbonization. Moreover, C-H peaks at 2850 and 2926 cm^{-1} and wide peaks at 1700–1000 cm^{-1} suggest a large amount of irregularly amorphous carbon but little aromatic structure in the carbon membranes^[28]. This could be one reason for the low strength of our carbon membranes, but it can be improved by increasing the carbonization temperature, heating rate, or holding time.

Compared to the oxidation process, little deformation has occurred on the pore structure of carbon membranes (Fig. 3a). All samples show cellular pores with large size closed to surfaces and small size in the middle. Their average sizes decrease with the increasing carbonization temperature and holding time, or slowing

down the heating rate (Fig. 3b). Similar variation tendency has been found for the thickness of membranes. Given the formation effectiveness, we at last chose 800 °C, 4 K/min and 1 h as appropriate carbonization parameters. On the other hand, the PAN membranes turn from white to dark brown under oxidation and then change to black after carbonization. Their weight losses are slight in the former step but dramatic in the latter one (Table 1). After pyrolysis, the diameter of membrane decreases from 25 mm to 14 mm (Photo in Fig. 3a), because the density of carbon ($1.5\text{--}2.0\text{ g/cm}^3$) is larger than that of PAN (1.14 g/cm^3). Nevertheless, it should be pointed out that the carbon membranes can keep the planar appearance well like PAN membranes, which ascribes to the homogeneous pore structures produced *via* TIPS method. In addition, both WAXD technique and Raman spectrometry have been applied to confirm the carbon structures of the obtained carbon membranes (Fig. S2 and Fig. S3 in Supporting Information).

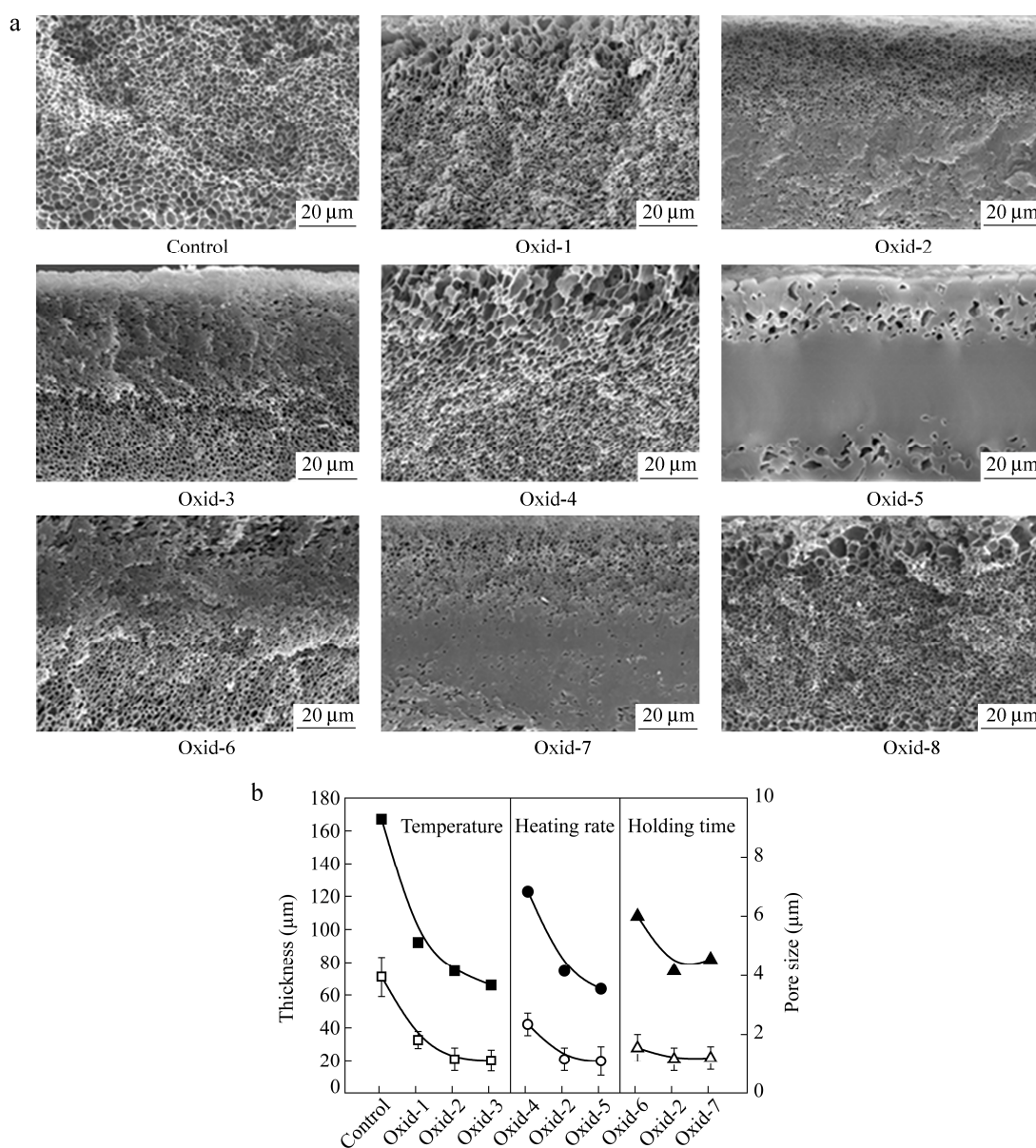


Fig. 2 (a) SEM images for PAN membranes before and after oxidation; (b) Thickness (solid symbols) and pore size (hollow symbols) of PAN membranes before and after oxidation

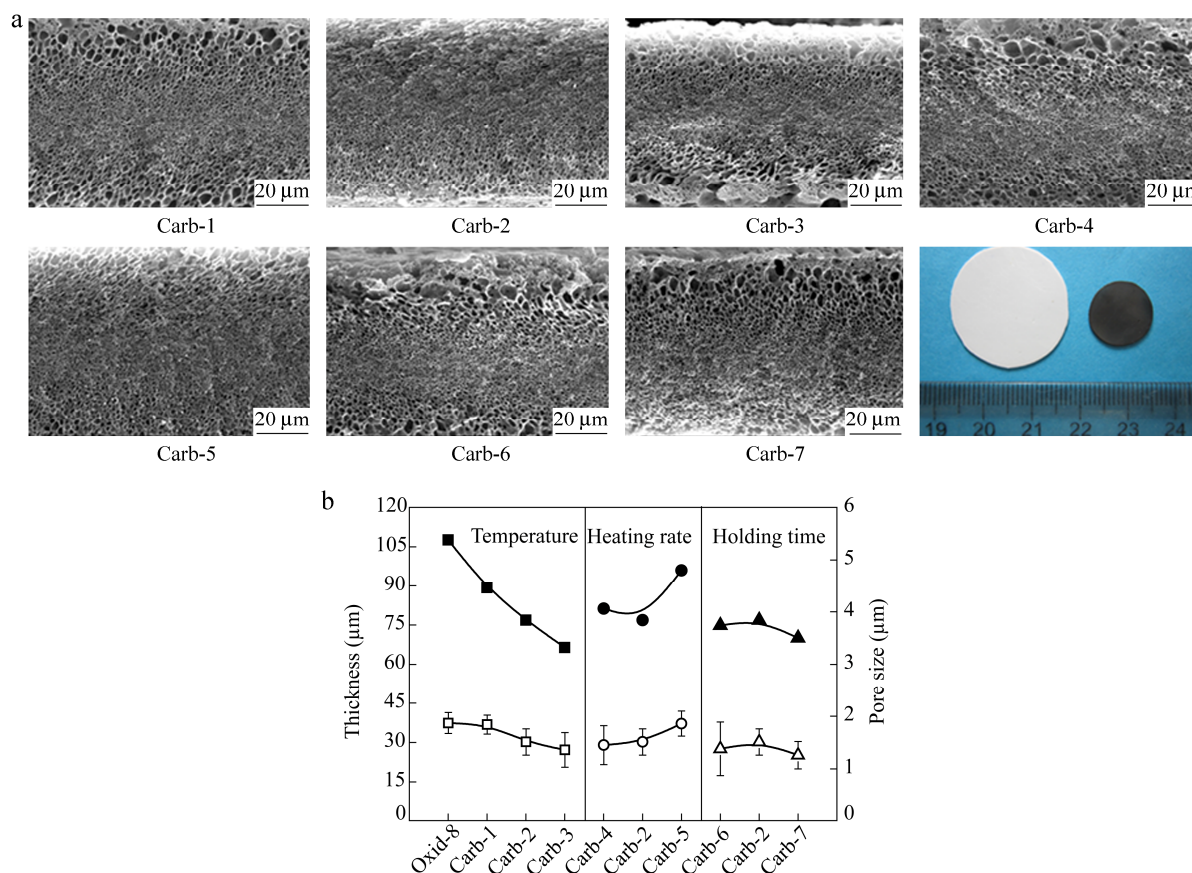


Fig. 3 (a) SEM images for the carbon membranes, and photographs of the membranes before and after carbonization; (b) Thickness (solid symbols) and pore size (hollow symbols) of PAN membranes before and after carbonization

Hierarchical Pores in Porous Carbon Membranes

From the magnified SEM images (Fig. 4), we can see that the carbon membranes possess hierarchical pores: cellular macropores across the whole membranes and much small pores inside the matrix and on the pore walls. The rough pore walls in the carbon membranes are different from the smooth pore walls in the carbon monoliths we prepared previously^[22]. Moreover, such a kind of rough pore walls is rarely reported before. Yang *et al.* fabricated carbon foams with smooth surfaces by coaxial electrohydrodynamic atomization^[27]. We think the rough surfaces in our carbon membranes may be due to the evaporation of the residual diluents (dimethyl sulfone and glycerol) from PAN membranes during oxidation and carbonization processes.

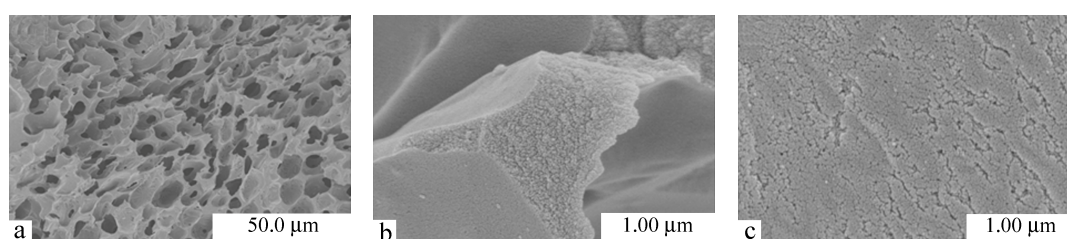


Fig. 4 SEM images for the carbon membranes prepared under the optimal parameters: (a) cross-section of membrane; (b) cross-section of pore wall; (c) surface of pore wall

Nitrogen adsorption technique has been carried out to further confirm the hierarchically porous structure. Figure 5 shows a nitrogen adsorption-desorption isotherm of carbon membranes by BET method. According to the IUPAC classification^[29, 30], the resulted carbon membrane exhibits the form of type I isotherm, and its general shape suggests a wide distribution of pore sizes. At low relative pressures ($P/P_0 < 0.2$), the isotherm has a steep increase, indicating the existence of pore sizes closing to the micropore range. Meanwhile, the small slope at the medium relative pressure denotes the mesoporosity. The corresponding pore size distribution was calculated based on density functional theory (DFT) method. We can see that the carbon membrane has a pore size distribution in microporosity range (< 2 nm), and the pore width is mainly centered at 1.47 and 1.84 nm. There also exists mesopores with size of 2.21 nm. It is particularly noteworthy that the BET surface area of the carbon membranes is as large as 1062 m²/g, which is larger than many other PAN-based porous carbon materials reported before^[31–33]. Such a large surface area is based on the hierarchical pores inside the carbon membranes. Among others, the cellular macropores are constructed by TIPS process, while the mesopores and micropores mainly existing on the pore walls may be attributed to the evaporation of the residual diluents from PAN membranes during pyrolysis. Such a large surface area is really beneficial for molecule adsorption.

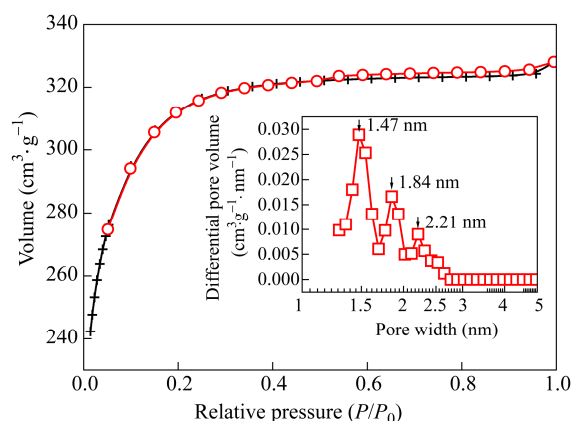


Fig. 5 A nitrogen adsorption-desorption isotherm of the carbon membrane: (Inset) Pore size distribution calculated by DFT method

Adsorption of Organic Dyes

The above results indicate that the carbon membranes may have potential applications in the separation of organic dyes from aqueous solutions based on their advantages of large specific surface area and hierarchical pore structures. The adsorption behaviors of the carbon membranes have been explored to adsorb three model dyes, methyl orange (MO), Congo red (CR), and rhodamine B (RB). Table 2 lists the molecular structures and several physical properties of these dyes. It is clear that both MO and CR are anionic dyes with respective molecular weights of 327 and 696 g/mol, while RB as a cationic dye has a molecular weight of 479 g/mol.

As shown as Fig. 6, MO (50 mg/L, 10 mL) can be completely adsorbed by 10 mg carbon membranes in 8 h, illustrating an average MO adsorption rate of 150 mg per gram of carbon membranes per day. This equilibrium amount of MO adsorbed is much larger than those of carbon sorbents reported by Mohammadi *et al.*^[34] and Singh *et al.*^[35]. Meanwhile, the orange MO aqueous solution fades into colorless after adsorption. However, the same carbon sample displays very weak adsorption behaviors for CR and RB with concentration of 50 mg/L and contacting times of 24 h. Their corresponding adsorption percentages are 23% and 11%, and the adsorption capacities are as low as 11.5 mg/g and 5.5 mg/g, respectively. It is very interesting that the carbon membranes show up a selective adsorption towards MO. As regards the selectivity, electrostatic attraction and steric structure matching are commonly two key factors affecting the adsorption capability of adsorbents^[36–38]. However, we can firstly rule out the effect of electrostatic attraction, because both MO and CR possess anions but present prodigious difference on adsorption behaviors. After treated by sulfuric acid, the carbon membranes can be oxidized and carboxylized (Fig. S3 in Supporting Information). Therefore, the adsorption capacity for RB

is significant enhanced to 49 mg/g, which is attributed to the electrostatic interaction between the cation of RB and the derived carboxyl groups on the carbon membranes.

In previous researches, the molecular size of organic dyes were studied both from the aspects of experimental determination and theoretical calculation. Costantino *et al.* calculated the van der Waals dimensions of a single MO molecule by Hydrochem Program, which has a axial length of 1.67 nm and a maximum width of 0.61 nm^[39]. Huang *et al.* also reported that the theoretical sizes of MO and CR are 1.19 nm × 0.68 nm × 0.37 nm and 2.29 nm × 0.82 nm × 0.60 nm, respectively, that were calculated by Gaussian 03^[40]. Actually, dye molecules, especially for ones possessing hydrogen bonds or benzene rings, always tend to form aggregates that are associated with solution concentration, temperature and pH value^[41]. Lendel *et al.* found that the size of CR aggregates become as large as 40 nm when its concentration is 1 mmol/L^[41]. RB has a molecular size of 1.8 nm, but it is easy to form into dimer with a space of 1.9–2.3 nm, especially when pH is higher than 4^[42]. It is clear that MO molecule has a smaller size than RB and CR, and the latter ones are much easier to be dimer than the former one due to their benzene rings under the solution concentration of 0.15 mmol/L and pH of 7. Therefore, MO molecule preferentially transfers into the micropores and mesopores, resulting in the adsorption selectivity of the carbon membranes. Besides, the large cellular pores endow the carbon membranes good mass transport.

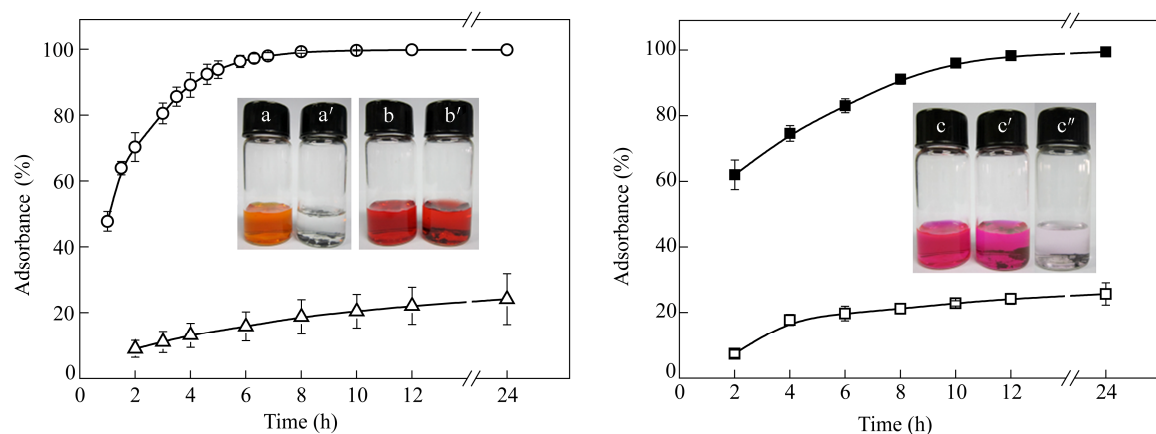


Fig. 6 Time dependent adsorption of methyl orange (○), Congo red (Δ), rhodamine B (□) on carbon membranes, and rhodamine B (■) on the carboxylated carbon membrane. Insets are photographs of methyl orange solution (a, a'), Congo red solution (b, b') and rhodamine B solution (c, c') before (a–c) and after adsorption (a'–c') on the carbon membranes. Inset (c'') is the photograph of rhodamine B solution after adsorption on the carboxylated carbon membrane.

To further confirm the selective adsorption towards MO, the as-prepared carbon membranes were directly put into an aqueous solution including both solutes of MO and RB with concentration ratios of 4:1 or 3:2. We can see from Fig. 7(a) that as time extends to 22.5 h, the UV adsorption intensity of the peak at 463 nm is significantly reduced by 83.3%, whereas the one at 554 nm shows a decrease of 25%. As increasing the RB content in the mixing solution, the adsorption for MO can be as high as 90%, and that for RB is lower than 20% (Fig. 7b). This result obviously reveals that MO in the aqueous solution can be preferentially and selectively adsorbed by the carbon membranes.

After adsorbing MO, the used carbon membranes can be regenerated by immersing into hydrochloric acid for 48 h. It is because MO molecule is anionic dye, which can easily desorb from adsorbents by using protic acid. Figure 8 shows that the first-regenerated carbon membranes maintain 96% adsorption property for MO (50 mg/L, 10 mL) in cycle 2, during which the adsorption time is 10 h. Similarly, the second-regenerated carbon membranes still can adsorb 93% MO (50 mg/L, 10 mL) in cycle 3.

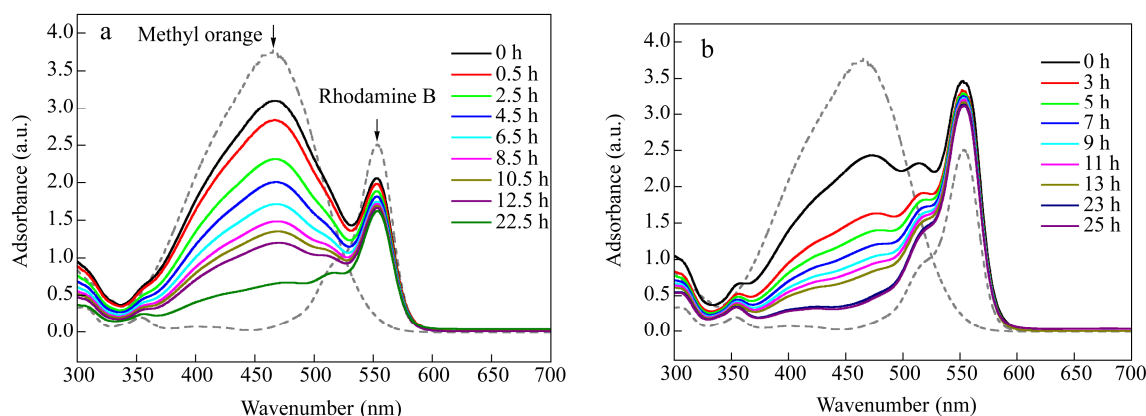


Fig. 7 UV-Vis absorption curves of the mixture of methyl orange and rhodamine B on the carbon membranes in a variation of adsorption time (Concentration ratios of methyl orange and rhodamine B are (a) 4:1 and (b) 3:2.)

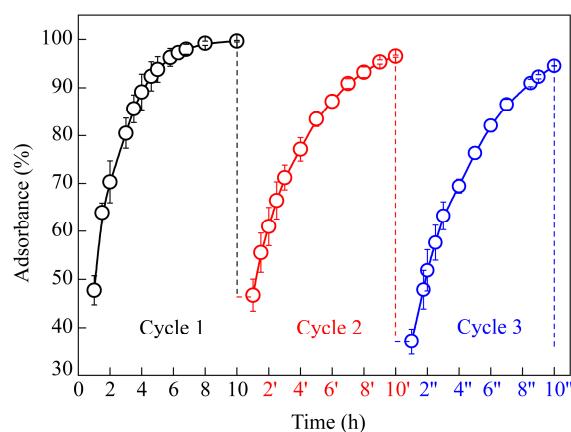


Fig. 8 Time dependent adsorption of methyl orange on the carbon membranes in three cycles

CONCLUSIONS

Carbon porous membranes have been successfully fabricated by the pyrolysis of polyacrylonitrile (PAN) precursors, which were priorly prepared *via* thermally induced phase separation (TIPS). The carbon membranes with planar appearance and uniform pores can be formed under an appropriate pyrolysis condition, that is, oxidized by heating to 250 °C at 0.5 K/min and then holding for 2 h, and subsequently carbonized under parameters of 800 °C, 4 K/min and 1 h. As a result, hierarchically porous structures are constructed including cellular macropores with average size of 1.5 μm , mesopores with size of 2.21 nm, and micropores with sizes of 1.47 and 1.84 nm. Notably, the specific surface area of the carbon membranes can be as large as 1062 m^2/g . Moreover, the carbon membranes present a selective adsorption towards methyl orange (1.2 nm) rather than Congo red (2.3 nm) and rhodamine B (1.8 nm), which is attributed to the steric structure matching between the molecular size and pore structure. The used carbon membranes can be easily regenerated by hydrochloric acid, and their recovery adsorption ratio maintains above 90% even in the third cycle.

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