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Facile and controllable route for nitrogen doping of carbon nanotubes composite membranes by catalyst-free chemical vapour deposition

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ABSTRACT

In this study, we present a facile approach that makes it possible to finely and selectively dope with nitrogen the structure of carbon nanotubes (CNTs) composite membranes. CNTs were grown inside nanoporous anodic alumina membranes (NAAMs) by a catalyst-free chemical vapour deposition (CVD) approach using different precursor mixtures containing carbon and nitrogen at different ratios. Different precursors were used to fabricate undoped and N-doped CNTs-NAAMs, with nitrogen content ranging from 0 to 7%. The morphology and chemical composition of the prepared composite membranes were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The obtained results reveal that the C/N ratio in the precursor source plays a crucial role in the doping process and incorporation of nitrogen into the structure of CNTs. It was found that a minimum threshold of 5:1 C/N ratio is required to obtain N-doped CNTs structures. This fabrication route does not compromise the morphology and graphitic structure of doped CNTs, making it an optimal process to tune the properties of these composite membranes for different applications, including catalysis, molecular separation and sensing. In this work, the molecular transport properties of N-doped CNTs-NAAMs with different level of doping were assessed by studying the diffusion of two model molecules with different hydrophilic-hydrophobic and charge properties. The obtained results show that the diffusional flux of a particular dye molecule was significantly affected by the nitrogen content of CNTs deposited inside NAAMs, confirming that the transport properties and chemical selectivity of CNTs-NAAMs composites can be controlled by nitrogen doping. This approach presents a new avenue to tune the properties of CNTs-NAAMs composites membranes, opening new opportunities for these membranes to be used in separation applications.

1. Introduction

Typical structures of carbon nanotubes (CNTs) are chemically inert as they present a chemistry based only on sp^2 carbon. However, some applications such as electronics, catalysis, sensing, transport and separation require CNTs to have specific properties (e.g. conductivity, catalytic reactivity, surface chemistry, hydrophobicity/hydrophilicity, etc.) in order to achieve optimal performances. So far, different surface modification approaches aiming to tailor the chemical properties of CNTs have been explored [1–4]. Among the various approaches, chemical oxidation, covalent immobilisation and doping with foreign atoms are the most widely employed routes to modify CNTs. The structure of CNTs can be doped with different atoms such as N, P, S, etc. which are integrated into the hexagonal sp^2 carbon structure by substitution of C atoms. Nitrogen doping of CNTs structure is particularly attractive and favourable because N has close atomic size to that of carbon (i.e. nitrogen contains one additional electron as compared to carbon) and thus nitrogen-doped CNTs structure could exhibit novel electronic and catalytic properties [5]. Nitrogen doping of CNTs has been explored for tunning and enhancing their physical, chemical and catalytic activity properties [6–8].

CNTs-based composite membranes have been recently attracting much attention due to the outstanding features of CNTs with smooth hydrophobic graphitic walls, ordered and vertically aligned structures with high aspect ratio, chemical stability, mechanical robustness and ease of chemical functionalization. These features

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make CNTs-based composite membranes unique candidates to mimic protein channels in biological membranes [9,10] and have spread the applicability of CNTs-based composite membranes across a broad range of applications, such as water desalination, chemical separation, catalysis, drug delivery, sensing and energy storage [11–13]. For the most of these membranes, their properties and applications are dependent on the properties and chemical composition of inner nanotube surface. In the case of membrane separation applications, fluids and gases flow through the internal tubular structure of CNTs and therefore the transport property of these membranes is of great importance for achieving optimal performances for advanced processes (e.g. detection of chemical composition of complex mixtures, separation of chemical pollutants in contaminated water, removal of ions in desalination, etc.). So far, several molecular dynamics simulations and experimental studies have successfully demonstrated the outstanding transport properties and chemical selectivity of CNTs membranes for a broad range of gases and molecules [14–18].

Structurally, two configurations of CNTs-based composite membranes have been explored for separation/transport applications: namely; i) membranes with randomly distributed bundles of CNTs and ii) membranes featuring vertically aligned arrays of CNTs grown inside different templates. The latter configuration enables an extremely fast and controllable transport of molecules through CNTs, which increases their efficiencies in separation/filtration processes as compared to the former type [14,19]. Template-assisted synthesis method is the most widespread route for preparing composite membranes featuring vertically aligned arrays of CNTs. Among the different templates, silicon nitride, polymer matrices [20,21] and nanoporous anodic alumina membranes (NAAMs) produced by electrochemical anodization of aluminium have been demonstrated as unique platforms to produce CNTs membrane with precisely controlled geometric features. These templates can be fabricated with precisely engineered nanopores, which are perfect moulds to grow CNTs with vertically aligned nanotubular structure [22–27]. Direct template synthesis of CNTs by catalyst-free chemical vapour deposition (CVD) in these templates is of particular interest since this approach overcomes the inherent drawbacks of traditional fabrication methods used to prepare CNTs.

As mentioned above, doping CNTs with nitrogen could open new opportunities to explore and understand the influence of the chemical structure of CNTs on the transport performance of CNTs composite membranes, which is of critical importance for advancing the properties of these membranes for separation applications. So far, many studies have reported on the doping of CNTs with nitrogen [28–34]. Most of these studies are based on catalyst-based CVD processes using ferrocene as metal catalyst. It is worthwhile to note that nitrogen doping of CNTs using catalyst-based CVD approach results in CNTs with periodic interlinked structures inside the nanotubes (i.e. bamboo-like structure), which are not suitable for transport and separation applications [30,31]. Moreover, significant changes in the dimensions of N-doped CNTs were observed [28,29]. Therefore, to develop a facile route to dope the structure of CNTs with dopant atoms in a selective fashion without affecting their geometric features still remains challenging. To the best of our knowledge, the nitrogen doping of CNTs membranes by a catalyst-free CVD process has not been explored yet. Recently, we demonstrated that the transport and selectivity properties of composite membranes based on CNTs and nanoporous anodic alumina membranes (NAAMs) can be finely tuned by engineering the dimensional features of CNTs and the surface chemistry of their inner surface by post-oxidation treatment [35].

Herein, we present a facile synthesis method aiming to dope the structure of CNTs composite membranes with nitrogen atoms using a catalyst-free CVD approach. CNTs composite membranes were prepared by growing vertically aligned multi-walled carbon nanotubes (MWCNTs) inside the nanopores of NAAMs, which were used as templates. The role of C/N ratio of carbon and nitrogen precursor in the formation and nitrogen content of N-doped CNTs-NAAMs was determined by using different mixtures of precursors including *N*,*N*-dimethylformamide (DMF), pyridine and their mixtures with toluene and ethanol. The critical C/N atomic ratio required for preparation of N-doped CNTs composite membranes was established for the first time. A schematic illustration of the CVD fabrication process of undoped and N-doped CNTs-NAAMs composite membranes and the selective doping of CNTs structure are shown in Fig. 1.

The selective nitrogen doping of the inner and outer surfaces of CNTs during the synthesis step is characterized by a set of techniques in order to establish a solid and comprehensive rationale towards understanding and tailoring the properties of CNTs for different applications. Furthermore, the transport performance and chemical selectivity of the resulting composite membranes (i.e. undoped and N-doped CNTs-NAAMs composite membranes) is assessed by a series of experiments, revealing the importance of nitrogen doping on this property of CNTs.

2. Experimental details

2.1. Materials

High purity aluminium (Al) foils (thickness 0.32 mm, purity 99.999%) were obtained from Goodfellow Cambridge Ltd, UK. Copper chloride ($CuCl_2$), oxalic acid ($H_2C_2O_4$), chromium trioxide (CrO_3), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), ethanol 99.7% (C_2H_6O), toluene 99.8% (C_7H_8), *N*,*N*-Dimethylformamide (DMF) (C_3H_7NO), pyridine (C_5H_5N), hydrofluoric acid (HF), Rose Bengal ($C_{20}H_4Cl_4I_4O_5$ – $(RosB)^{2-}$) and Tris(2,20-bipyridyl) dichlororuthenium(II) hexahydrate ($C_{30}H_{24}Cl_2N_6Ru \cdot 6H_2O$ – $(Ru(BPY)_3)^{2+}$) were purchased from Sigma Aldrich (Australia) and used as received. High purity deionized (DI) water (resistivity 18.2 M Ω cm) from a Milli-Q water purification system was used to prepare all the solutions used in this study.

2.2. Fabrication of nanoporous anodic alumina membranes (NAAMs)

Nanoporous anodic alumina membrane templates were prepared by a two-step electrochemical anodization process using high purity Al foils following a previously reported method [22,36,37]. Briefly, circular Al chips with a diameter of 1.5 cm were first cleaned under sonication in ethanol and water for 10 min followed by electro-polishing in a mixture of $HClO_4$ and C_2H_6O 1:4 (v:v) at 20 V and 5 °C for 3 min and then dried under nitrogen stream. The electro-polished Al foils were anodized in 0.3 M aqueous oxalic acid electrolyte at 40 V and 6 °C using a two electrode electrochemical reactor equipped with temperature controller. The first anodization step was carried out for 20 h and the resulting nanoporous layer was selectively removed in a mixture of H_3PO_4 (0.4 M) and H_2CrO_7 (0.2 M) at 70 °C for 3 h in order to obtain hexagonally organized pits on the Al surface. The second anodization step was performed for 15 h to specifically obtain NAAMs with pore lengths of 50 ± 2 μm and pore diameter 40 ± 5 nm. The remaining aluminium substrate was removed in a saturated solution of HCl and $CuCl_2$. Finally, the oxide barrier layer at the bottom of NAAMs was chemically opened in 5 *wt* % H_3PO_4 at 35 °C. This process was performed by monitoring the current over time in a U-cell in order to have a precise control over the pore opening step and prevent the membranes from undesired pore