



# Novel application of graphene oxide to improve hydrophilicity and mechanical strength of aramid nanofiber hybrid membrane

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## ABSTRACT

The synergy effect of nano-materials with composite membrane has provided numerous opportunities to strengthen the performance of the membrane in all-around research territories. Previous studies have demonstrated that bulk aramid macroscale fibers can be effectively split into aramid nanofibers (ANFs) by dissolution in dimethylsulfoxide (DMSO) in the presence of potassium hydroxide (KOH). Addressed herein is a facile and low-cost approach to endow hydrophobic Kevlar nanofiber membranes with reliable hydrophilicity and improved mechanical strength. Introduction of Graphene oxide (GO) into the structure of ANFs membranes was realized through  $\pi$ - $\pi$  stacking interactions and aramid nanofiber-graphene oxide (ANFGs) hybrid membranes contained gradient concentrations of GO with enhanced hydrophilicity and mechanical strength were synthesized. The structure, composition and mechanical properties of hybrid membranes were characterized by FT-IR, XRD, SEM and Universal pull machine. Within the range of GO loadings assessed in this work, it was found that the ANFGs with GO 0.75 wt.% and 1.0 wt.% provide optimal potentiation both on tensile strength ( $377 \pm 3$  MPa) and Young's modulus ( $18.36 \pm 0.87$  GPa). The hydrophilicity of the ANFGs membranes was assessed by water contact angle measurements which showed that medium GO content (1 wt.%) result in the most hydrophilic coating with the lowest contact angle of  $53 \pm 0.4^\circ$ . ANFGs hybrid membranes offered not only remarkable mechanical performance, but also better hydrophilicity which should be due to abundant functional groups in GO, indicating great potential of such membranes in water industry.

## 1. Introduction

Membrane technology science has attracted numerous attention over the past several decades because of its extensive applications in various industrial fields such as water desalination, ultrapure water production, refuse reclamation and effluent treatment [1]. Among the maturely developed polymer-based membranes, Kevlar-nanofiber membranes have attracted tremendous interest on account of its superior properties, including outstanding mechanical properties, good thermal stability, and excellent chemical resistance to incursive reagents such as organic solvents and acids. Kevlar fiber (also called aramid fibers) consist of long molecular chains which is produced from PPTA between which there are inter-chain bonds making the material extremely strong and stiff with a tensile strength of 3.6 GPa and a Young's modulus of 90 GPa [2,3]. It is a widely known high-strength polymer, which has been used for a variety of applications, including bullet-proof vests, protective clothing and high-performance composites for aircraft and automotive industry [4–6]. However, the low

surface to volume ratio of macro-fiber is at risk of limiting its potential applications by the lack of weak adhesion between fibers and inorganic nanometer-scale components. Inspiringly, Kotov's group take the lead in reporting that the dissolution of Kevlar threads or fabrics in DMSO by controlled deprotonation with KOH can effectively split the bulk aramid macroscale fiber into aramid nanoscale fibers (ANFs) [7].

ANFs membranes have already been extensively studied in various domains, while one of the major defects of ANFs membrane is the hydrophobicity in nature, which causes severe membrane fouling and permeability decline, as well limits their application in water and wastewater treatments. Also in general suffering from fouling lead to low life cycle of the membrane. While fouling is due primarily to low surface hydrophilicity, improvement in membrane hydrophilicity seems to be an efficient technique to overcome the membrane fouling problems. To overcome these disadvantages, developing a facile and economical approach to prepare membrane materials with enhanced hydrophilicity as well as mechanical strength should be of significant importance.

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Graphene oxide (GO), a partially oxidized form of natural graphite, is capturing much more interests in the fields of material research due to its high surface area, outstanding electron transport and mechanical properties. The incorporation of these atomically thin carbon sheets into a polymer matrix can significantly improve physical properties such as the mechanical strength of the host polymers at a very low additive amount [8–10]. Generally, GO is invoked as a reinforcement filler to enhance the mechanical properties [11]. Besides, the presence of functional groups such as carboxyl and hydroxyl groups on the surface also makes GO an ideal additive to enhance the hydrophilicity of membranes, because it can take up water effortlessly [12]. In short, GO is more fitting for fabricating organic-inorganic-blended ultrafiltration membranes.

Recently, to improve hydrophilicity of the membrane with GO has attracted considerable attention [13]. Inspired by the studies of combining GO and cellulose-nanofibers [14], the main purpose of our work hammer at integrating two ultra-strong materials, namely ANFs and GO, into one GO-functionalized ANFs hybrid composite membrane labeled as ANFGs membrane to improve the hydrophilicity and mechanical strength compared with that of pristine ANFs membrane.

Much researches have been investigated to tailor the performance of composites hybrid membranes [15,16], among various modification techniques, blending modification has the benefit of easy preparation by phase inversion. Introducing hydrophilic polymers or nanoparticles into nanofiber membranes through common blending method has been demonstrated as an effective strategy to enhance the hydrophilicity of membranes.

Herein, we report a promising strategy to improve hydrophilicity and mechanical strength of the mixed membranes by blending GO in ANFs. The mechanical stability and hydrophilicity of the membranes, which are always used to be the two sides of a coin, while they are simultaneously increased over the pristine ANFs membrane by the  $\pi$ - $\pi$  stacking of GO in this system.

## 2. Materials and methods

### 2.1. Materials

The Kevlar-29 brand yarn (136 dtex) was obtained from DuPont, USA. Graphite powders (100 meshes, 99.999%) were purchased from Alfa-Aesar Co., Ltd. Concentrated sulfuric acid (95–98%), concentrated hydrochloric acid, sodium nitrate (99.5%) and potassium permanganate ( $\text{KMnO}_4$ ) were purchased from Sigma Aldrich. Potassium hydroxide (KOH) and Dimethyl sulfoxide (DMSO) were provided by Aladdin. All chemicals were used as received without further purification. Nylon filtration membrane with 0.1  $\mu\text{m}$  pore diameter (Filtration Equipment Factory Co., Ltd., Haining, China) was utilized in this study.

### 2.2. Preparation of ANFs/DMSO dispersion

The aramid nanofiber (ANFs)/DMSO dispersion was prepared employing the method described previously by Kotov's group [7]. In a nutshell, accurately weighing of 1.0 g Kevlar-29 yarn and 1.5 g KOH before adding them into 500 ml of DMSO. After constant magnetic stirring for 5–7 days at room temperature, a crimson and viscous ANFs/DMSO dispersion was obtained successfully with the concentration of 2 mg/ml as displayed inset of Fig. 2d.

### 2.3. Preparation of GO/DMSO dispersion

Graphene oxide (GO) was prepared from graphite powder using a modified Hummer's approach. The graphite oxidation was carried out by mixing concentrated  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$  (320 ml: 80 ml) and graphite powder (3g) under vigorous stirring conditions for 12 h. Subsequently, 18 g of potassium permanganate ( $\text{KMnO}_4$ ) was added slowly over a 12 h period. The resulting mixture stirred continuously for 24 h to permit the

oxidation of graphite, during which the color of the mixture changed from dark purplish green to dark brown. The oxidation process was quenched by adding moderate 3 ml  $\text{H}_2\text{O}_2$  (30%) solution, monitored by the change of color to a bright yellow. Next, the reaction mixture was filtered and the residue was washed with 5% HCl aqueous solution. Furthermore, this residue was dispersed in deionized water and cleaner residue with neutral pH was separated by centrifugation. This oxidized material was then ultra-sonicated in water to get sufficiently exfoliated graphene oxide. After drying in vacuum at 60 °C, the ultimate product was used for further characterization and membrane preparation.

For the preparation of GO/DMSO dispersions, a 10 mg amount of dried GO product obtained above was first ground sufficiently with a mortar and pestle and then added into 100 ml DMSO before sonication for 2 h, forming a homogeneous GO/DMSO solution which remain steady even two weeks later. The solid content of graphene oxide in the dispersion was calculated to be 0.1 mg/ml.

### 2.4. Characterization of GO

A series of characterization tools were adopted in order to confirm the successful synthesis of GO samples. FT-IR spectra was measured on a Perkin Elmer Spectrum One spectrometer (Nicolet Nexus 670, USA) in the spectral region of 4000–500  $\text{cm}^{-1}$ . Raman spectroscopy were adopted to determine the chemical structure of GO products in the form of solid-state powder. Scanning electron microscope (SEM- Hitachi S-4700) and transmission electron microscope (TEM- JEOL 2000 FX) were employed to observe the nanoscale morphology of GO samples by drying a drop of dilute GO/DMSO solution on substrate completely. XRD measurement was performed by a D/man-rBX X-ray generator operated at 30 mA and 40 kV to identify the stacking in GO powders. Thermo-gravimetric analysis of GO solid-phase powder (1.354 mg) was employed by TGA (TA Q500) using a heating rate of 10 °C/min from 30 to 800 °C in the atmosphere of nitrogen.

### 2.5. Fabrication of ANFs/GO hybrid membranes

GO and ANFs DMSO dispersion were blended with a given ratio followed by a desired amount of DI water to improve protonation. Specifically, 5 ml of as-obtained ANFs/DMSO dispersion (2 mg/ml) was diluted to 30.0 ml by the additional DMSO. Then GO/DMSO solutions (0.1 mg/ml) of different volumes (0, 0.25, 0.50, 0.75, 1.01, 2.04 and 4.17 ml) were added dropwise with vigorous stirring, creating membrane samples with designated names of ANFGs-0.25, ANFGs-0.5, ANFGs-0.75, ANFGs-1, ANFGs-2 and ANFGs-4 for membranes with GO loadings 0.25%, 0.50%, 0.75%, 1.0%, 2.0% and 4.0%, respectively. After that, 4.0 ml of DI water was further added dropwise under vigorous stirring for all mixtures, which led to the formation of a gel-like state, then the ANFs/GO/DMSO mixture was stirred vigorously for 2 h to achieve a homogeneous dispersion. The obtained dispersions were vacuum filtrated using nylon membranes and the production was soaked in DI water for 12 h to eliminate any residual solvent followed with air drying. Finally, the bone dry nylon membrane was soaked in DI water again for another 10 min to make the composite membrane fall off integrally, subsequently with air drying to obtain pure ANF membrane and ANFGs hybrid membranes as shown in Fig. 2c and e.

### 2.6. Characterization and performances study of ANFGs hybrid membranes

ATR-FTIR studies were performed to investigate the functional groups of membrane surfaces and the presence of GO. XRD measurement was carried out by D/man-rBX X-ray generator operated at 30 mA and 40 kV to study the crystalline structure and distribution of the GO. The size and morphology of as-prepared ANFs were distinguished by using a transmission electron microscope (TEM). The surface and cross-section morphology of hybrid membranes was analyzed using scanning electron microscopy (SEM). Surface hydrophilic behavior of ANFGs

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