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A porous graphene composite membrane intercalated by halloysite nanotubes for efficient dye desalination

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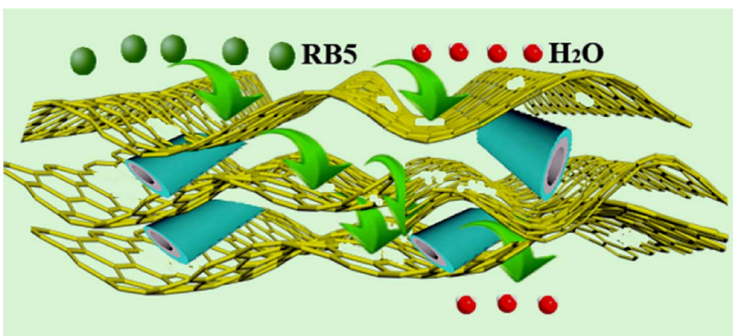
GRAPHICAL ABSTRACT



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ABSTRACT

Porous reduced graphene oxide (PRGO) was obtained by making pores on graphene oxide layers. Halloysite nanotubes, modified by Poly (sodium-p-styrenesulfonate) (PSS), were used to enlarge the interlayer spacing of PRGO. These two materials were immobilized on membrane surface through a time-saving, facile solvent evaporation method. The sandwich structure, formed through solvent evaporation process, provided additionally continuous pathway for water and salts, thus improving the water permeability of the composite membranes. Comprehensive characterizations of the materials were characterized by FT-IR, TEM, Raman, EDS and XRD. The composite membranes were characterized by SEM, FT-IR and EDS. The composite membranes exhibited a higher separation effect for salts and dye (i.e. 4.7% for $MgSO_4$, 4.7% for $MgCl_2$, 6.8% for NaCl, and 14.3% for Na_2SO_4; up to 97.9% for Reactive Black 5). The pure water permeation of composite membranes could reach as high as 8.8 L/(m^2 h bar). Hence, the graphene-based hybrid membranes presented a potential application in separation for salts and dyes.

1. Introduction

Nanostructured carbon materials, such as carbon nanotubes and graphene oxide, are receiving heightened concern for their novel application in photocatalysis [1–3], gas sorption [4] and electricity [5–11]. And of which, extensive researches have been conducted on graphene-based materials for their outstanding properties [12], basically including exceptionally high mechanical strength [13,14], unique

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Table 1
Different HNTs-PSS contents of PRGO/HNTs-PSS hybrid membranes.

	M-1	M-2	M-3	M-4	M-5	M-6
PRGO(μL)	50	50	50	50	50	50
HNTs(μL)	0	25	50	100	200	800
PVA(μL)	100	100	100	100	100	100

conductivity [14,15], strong antimicrobial activity [16]. Hence, it can provide potential applications in catalysis [17,18], lithium ion batteries [19], supercapacitor [20–22], etc. More recently, graphene oxide (GO), deemed as hydrophilic nanosheets, has led to many proposals in water treatment because of its large specific surface [23] and molecular sieving effect [24]. Moreover, the presence of hydrogen bond and van der Waals force between GO nanosheets typically result in a severe aggregation [25], further inevitably imposing the limitations in its environmental application. For instance, aggregation blocks the channel for water transferring, and leads to a lower water permeability of GO-based mixed matrix membrane. Enlarging the intercalating space and making pores on GO surface are superior alternatives to solve this problem.

So far, porous reduced graphene oxide (PRGO) in aqueous dispersion has drawn extraordinary attention in view of its wide application in desalination [26–31], sensor [32], catalyst [33] and nanofiltration [34], etc. Furthermore, PRGO are extensively used to remove dyes [35–37]. These studies for removing dyes with PRGO have been developed based on degradation-adsorption mechanism. GO and PRGO are also introduced to separate dyes and salts [35,38,39]. Chen et al. [35] fabricated hybrid membranes by coating (PRGO–carbon nanotubes) onto an anodic aluminum oxide with high permeability and separation performance for dyes. Sheath & Majumder [38] showed that filtration membranes fabricated by capillary-force-assisted self-assembly enabled promising rejection properties and high water permeation. Li et al. [40] reported a facile approach for large-scale production of aqueous graphene dispersions without the aid of surfactant stabilizers, which provided a useful strategy to achieve homogeneous graphene distribution in aqueous solution. Numerous studies for the design of PRGO have emerged in recent years [26,32–34,41,42]. To date, PRGO can be obtained via steam etching [32], thermal annealing [42], base and acid treatment [33,41]. In our work, PRGO was obtained by a facile method of alkaline treatment and followed by hydrochloric acid treatment at room temperature. Graphene is reported to be relatively smooth owing to the sp^2 hybridization of carbon atoms in graphene. However, reduced graphene oxide has a tendency to be corrugated on account of the existence of some sp^3 hybridizated carbon atoms [43]. Reduced GO nanosheets are inclined to aggregate due to $\pi-\pi$ interaction when dispersed into water [44]. It has been reported that the addition of polymer could not only strengthen the adhesion between PRGO and substrate but also weaken the reaction among the layers of PRGO. Polyvinyl alcohol (PVA) is an ideal candidate for its particular properties. That is to say, hydrogen bonding had been proved to be formed between PVA and GO sheets [25]. Pourjavadi and coworker [45] found that hydrogen bonding was formed between PVA and functionalized reduced graphene oxide because reduced graphene oxide had some oxygen-containing groups. In this work, Water was used as solvent for both PRGO and PVA to obtain a homogeneous dispersion of PRGO.

Halloysite nanotubes (HNTs), the economical clay materials, are able to be modified due to its structure of positively charged $Al(OH)_3$ inner lumen and negatively charged SiO_2 outer surface [46–51], and widely used for water treatment [52]. Nevertheless, the bad dispersion of HNTs will lead to uneven surface of the hybrid membrane resulting in a low rejection effect. Thus, it is crucial to improve the dispersibility of HNTs. Some researchers reported that Poly (sodium-p-styrenesulfonate) (PSS) could be employed to improve the dispersibility of HNTs by adsorbing PSS to the lumen of HNTs via compensating for the internal positive charges [52,53]. The surface charge of the nanotubes could be enhanced by modifying the inner lumen with anionic surfactants in aqueous solutions [54]. The Zeta potential of the nanotubes increased and the colloids became stable after modifying. For water treatment, series of methods have been used, including photocatalysis [55–57], adsorption [58] and membrane technology [59]. Membrane technology has been regarded as one of the most promising method because it is energy-saving and clean. It is widely used in wastewater treatment, especially the dye removal. HNTs were employed in separation for dye and salts by some researchers [53,60,61]. Zhu et al. fabricated membranes by blending HNTs-poly(sodium 4-styrenesulfonate) (HNTs-poly(NASS)) composites via phase inversion method and obtained a high rejection for dyes [60]. Qin et al. prepared oriented HNTs hybrid membranes via a facile evaporation-induced method [53].

Taken these conditions into account, PRGO/HNTs-PSS composite materials were immobilized on the surface of Polyacrylonitrile (PAN) membrane by immersing PAN membrane into the mixture of PRGO, HNTs and PVA. Safarpour et al. [62] prepared the membranes by interfacial

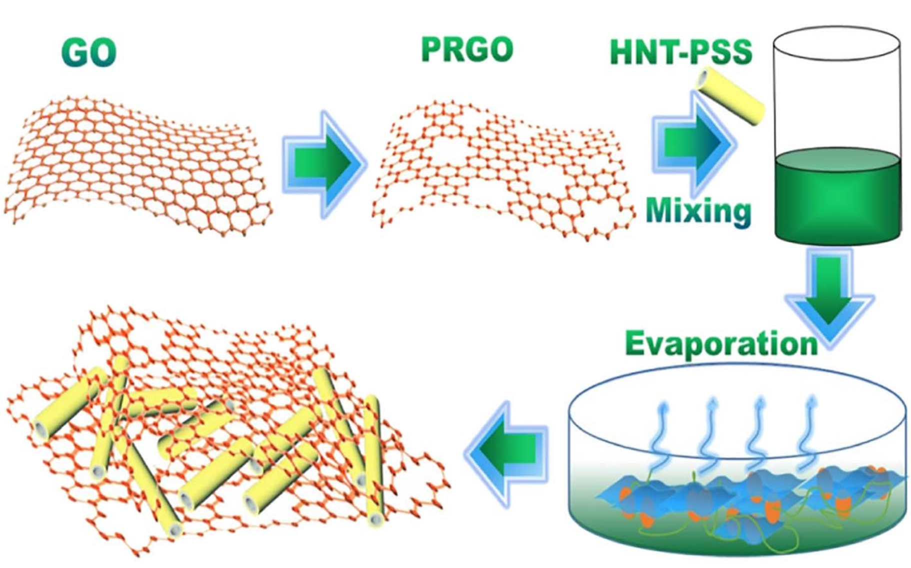

Fig. 1. Fabrication process of sandwich-like, HNTs intercalated PRGO membrane.