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Synergistic effects of CNT and GO on enhancing mechanical properties and separation performance of polyelectrolyte complex membranes

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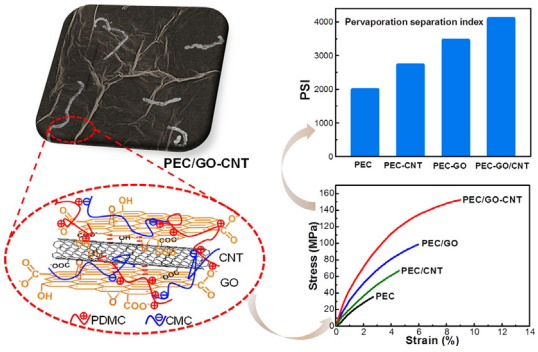
HIGHLIGHTS

- Solution-processable PECs incorporated with CNT and GO were prepared.
- Synergistic effects on enhancing mechanical property of PECM were achieved.
- Pervaporation separation index was enhanced by introducing GO and CNT.

GRAPHICAL ABSTRACT



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ABSTRACT

High strength polyelectrolyte complex (PEC) nanocomposite membranes were prepared via synergistic ionic complexation between graphene oxide/carbon nanotubes nanofillers (GO/CNT) and oppositely charged polyelectrolytes of sodium carboxymethyl cellulose (CMC) and poly(2-methacryloyloxy ethyl trimethylammonium chloride) (PDMC). Ultraviolet-visible, Raman spectroscopy and microscopies results demonstrated that the combination of one-dimensional CNTs and two-dimensional GO nanosheets lead to an integrated three-dimensional network through π-π interaction with GO distributed parallel to the surface of PEC membranes. Besides, CNTs and GO nanosheets are tightly encapsulated by PEC matrix through electrostatic interactions. The tensile strength of PEC/GO-CNT nanocomposite membrane containing 3 wt% GO-CNT (1:1, w/w) was 155.4 MPa, showing 2.3 and 1.6 times as high as that of PEC/CNT and PEC/GO membranes, respectively. Moreover, PEC/GO-CNT membranes showed improved separation performance and operation stability with introduction of the three-dimensional network constructed by GO and CNT.

1. Introduction

The electrostatic complexation between oppositely charged polyelectrolytes yields polyelectrolyte complexes (PECs) [1], a large family of polymer composites with applications ranging from flocculation [2],

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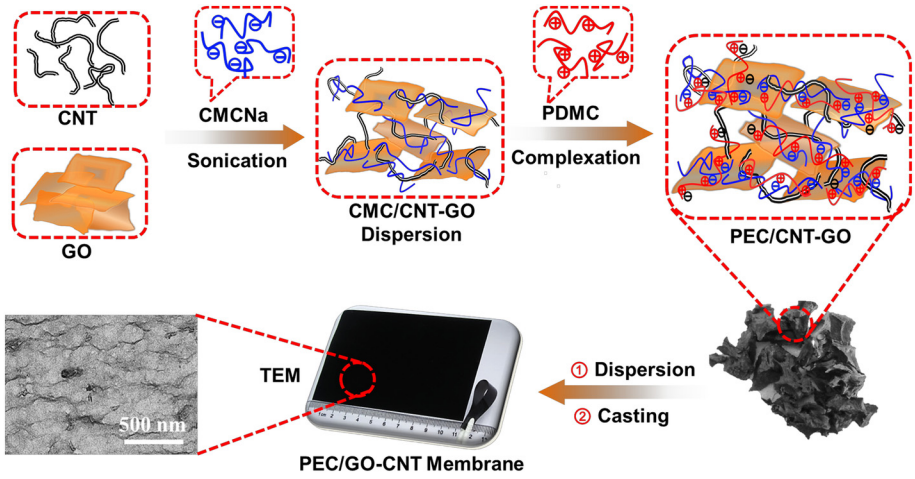

Fig. 1. Schematic illustration of the preparation of PDMC-CMC PEC/GO-CNT membranes.

biomedicine [3–6], catalysis [7], smart materials [8], wet adhesion [9] to molecule separation [10,11]. Among the many materials properties of PECs, a high mechanical property is particularly required for applications such as separation membranes [12], fibrous scaffolds [13], and paper reinforcements etc. [14]. PECs made from strong ionic pairs feature higher mechanical properties than that prepared from weak polyelectrolytes, but they suffer from even lower processability (i.e., insolubility and infusibility) due to the stronger electrostatic interaction [15,16]. Alternatively, the incorporation of inorganic additives into PEC matrix is a promising solution to improve mechanical properties of PECs [17–19].

Carbon nanotubes (CNTs) and graphene oxides (GO) are recognized as idea nanofillers for polymer reinforcement attributed to their high aspect ratios, large specific surface area (>2000 $m^2\ g^{-1}$), and high conductivities [20–22]. Polymer nanocomposites filled with either CNT or GO have been well-documented in literature, with some of them even found practical successes already [23,24]. Recently it appears that the one-dimensional (1D) and two-dimensional (2D) geometries of CNT and GO could offer extra opportunities in terms of the so-called synergistic effects [25–28]. Proofs of concept have been reported in literature that a higher enhancement was achieved when both the CNT and GO were exploited simultaneously instead of being used alone. For example, Li et al. improved the tensile strength of chitosan films by 139% (from 69.1 to 147.8 MPa) through incorporating the chitosan modified reduced GO and CNT concurrently [29]. The combining of small amount (<5%) of 1D CNT with 2D GO generated a versatile three dimensional (3D) structure through π-π interaction and yield more interactions with the matrix, hence lead to synergic properties [30–32].

However, most of the synergistic effects of CNT/GO reported so far were achieved with neutral polymers or single-component polyelectrolytes. When it comes to PECs that contain oppositely charged polyelectrolytes, it remains elusive to accomplish the synergistic effect. First, PECs are normally insoluble and infusible, thus both the solution blending and thermal blending methods for single-component polymers do not easily apply to PECs. Moreover, the strong interaction between oppositely charged polyelectrolytes could shield the interaction between polymer matrix and nanofillers, thus offsetting the mechanical enhancement effect of nanofillers [19]. Self-assembled multilayer films might host the synergistic enhancement of CNT and GO through hierarchical brick-and-mortar microstructures, but this labor-demanding method is not suitable for bulk materials engineering. In our previous work, these problems were partially touched by the "acid-protection" method which we proposed to incorporate CNTs and copper ions (Cu^{2+}) [19]. This method was shown to facilitate the synergistic effect in terms of mechanical strength. However, the divalent Cu^{2+} also resulted in excessive crosslinking of anionic polyelectrolytes, thus the nanocomposite membrane suffer from a 50% loss of permeability in separation 10 wt% isopropanol-water mixture at 40 °C. In addition, the ~3 orders of magnitude size mismatch of copper ions and CNT does not favor the maximum synergistic improvements in multiple aspects of separation membranes.

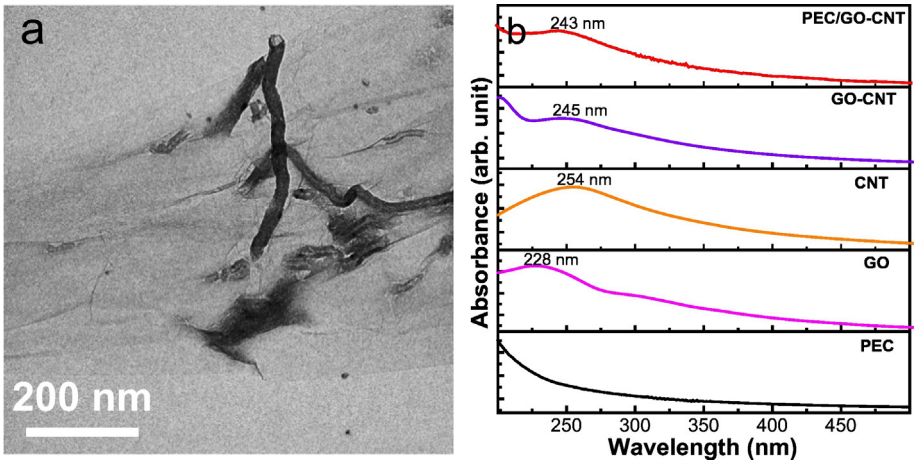

Fig. 2. (a) TEM image of GO-CNT dispersion (0.1 mg mL^{-1}), (b) UV–vis curves of CNT, GO, GO-CNT, PEC and PEC/GO-CNT dispersions (0.1 mg mL^{-1}).