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3D Printed Janus membranes Polycaprolactone/graphene flakes/zeolite based for oil-water separation

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Abstract

Janus interface materials are two-dimensional and three-dimensional porous materials exhibiting asymmetrical properties on each face, stemming from distinct structures and components with hydrophobic/hydrophilic characteristics. Emphasizing the importance of unidirectional liquid transportation in separation or collection processes, the manipulation of microfluidics offers practical solutions to diverse challenges, such as oil-water separation, among others. In recent years, there has been an increase in research focused on the application of Janus hybrid membranes in oil-water emulsion separation. Due to their asymmetric surface engineering, which influences surface wettability, layer thickness, and pore structure, Janus membranes exhibit superior mass transport capabilities compared to conventional membranes [1]. Janus membranes have shown great promise in separating water and oil due to their distinct properties on each side. Typically, the hydrophilic side of the membrane attracts water, facilitating its passage, while the hydrophobic side repels water and retains oils. This arrangement enables efficient separation between the two liquids without requiring chemicals or energy-intensive methods. Consequently, these membranes have broad applicability, from treating contaminated water to recovering oil in industrial processes [2]. However, membrane technology faces limitations such as fouling and structural degradation despite its potential. To overcome these limitations, graphene flakes (GF) incorporated into the polymeric matrix can enhance the water flux and suppress the fouling of the membranes by controlling surface charge. Among the various techniques employed in membrane production, 3D printing stands out due to its capability to manufacture materials with nearly limitless geometric constraints. It enables the creation and assembly of intricate designs in a single step, offering a distinct advantage over conventional manufacturing processes. In this work, Janus hybrid membranes were manufactured by 3D-printing technology, which has shown great potential to fabricate membranes with hierarchical porosity and designed configuration through successive layer-deposition of optimized inks [3]. Given this context, the primary aim of this study was to assess the permeance of a Janus hybrid membrane comprised of a polymeric Polycaprolactone (PCL) layer containing graphene flakes (GF) constructed on an inorganic zeolite (ZEO 13X) substrate by additive manufacturing. PCL/GF-inks were prepared by mixing a PCL 30% (wt./vol) concentrated solution and a 1.0% (wt./vol) GF solution previously dissolved in $CHCl_3$, which both solutions were homogenized under magnetic stirring for 24h [4]. Afterward, some thickener additives (MC, methylcellulose, ranging from 0.5 to 2.5 wt.%) and lubricants (PEG, poly(ethylene glycol, ranging from 1 to 5 wt.%), were added under mechanical stirring at 300rpm for 10 min. In addition, inorganic ZEO 13X-inks were prepared by mixing ZEO 13X powder into 3 wt.% alginate hydrogel containing 0.01 wt.% of deflocculant, a plasticizer (MT, montmorillonite nanoclay 2.5 to 6.5 wt.%), MC and PEG, respectively [5]. The optimized inks were characterized by targeting rheological properties to obtain suitable slurries. Both organic and inorganic optimized inks were printed according to a 3D model designed by solidworks®2019 SP5. Further, three-dimensional inorganic membranes were dried at ambient conditions for 24 h and then fired in a Muffle-type furnace in two steps: (i) at 600 °C for 30 min at a heating rate of 5 °C/min for debinding; (ii) at 1000°C for 60 min at a heating rate of 10 °C/min. Afterward, the individual PCL/GF organic membrane, ZEO 13X inorganic membrane, and attached Janus hybrid membrane were characterized by scanning electron microscopy (SEM, Tescan, VEGA3 LMU, Czech Republic). Furthermore, the contribution of each membrane component to oil/water separation in a membrane module was also evaluated. The results obtained for the morphological characterizations of the Janus membrane and the isolated components are shown in Fig.1. It is noted that the pores of the PCL-GF layer and the ZEO 13X zeolite particles are approximately 2 µm, which provides a pleasant morphology for Janus-type membranes. The PCL-GF layer is hydrophobic and offers flexibility, while the zeolite-containing layers offer high porosity and selective adsorption capacity. Therefore, this combination allows Janus membranes to perform selective separation processes efficiently. Furthermore, the alternating layers provide a porous structure that facilitates the selective diffusion of molecules. Other support geometries will be printed to compare and evaluate the most efficient oil/water separation system. This study provides new insights into applying Janus membranes obtained through additive manufacturing.

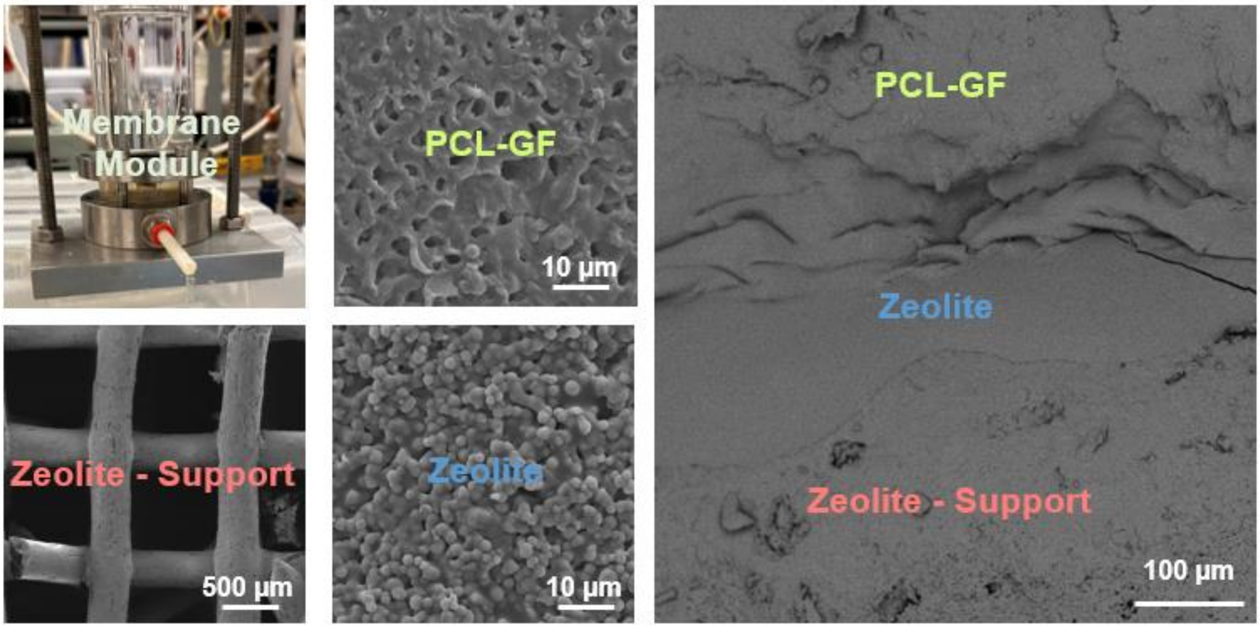

Fig. 1. Scanning electron microscopy (SEM) of the Janus membrane and each component.

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