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Hydrophobic PVDF/graphene hybrid membrane for CO_2 absorption in membrane contactor

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ABSTRACT

Graphene nanosheets were incorporated into polyvinylidene fluoride (PVDF) membrane in order to improve the membrane hydrophobicity. The hybrid membrane was prepared using the non-solvent induced phase separation method, and used in a membrane contactor for CO_2 absorption. The incorporation of graphene induced the PVDF crystal transformation from γ-form to α-form, and resulted in a more open and loose sub-layer structure. The hydrophobicity of the hybrid membrane was enhanced compared to the pristine PVDF membrane. However, the increase in the contact angle values with the graphene concentration only occurred for the bottom surface (i.e., the surface of the substrate interface). The CO_2 absorption performance with water as the absorption solution was dependent on the membrane orientation. When the bottom surface of high roughness faced the absorption solution, the hybrid membrane exhibited a faster CO_2 transfer. Due to the improvement in the membrane hydrophobicity, the wetting problem was significantly mitigated, and a long term run with high CO_2 absorption efficiency could be guaranteed. Our results demonstrated that the incorporation of graphene is a promising approach to obtain hydrophobic PVDF membrane for gas membrane absorption.

1. Introduction

CO_2 is widely known as greenhouse gas and believed to be responsible for global warming; therefore, its emission control and reduction have received great attention [1]. In anthropogenic emission sources, more than one-third of CO_2 emissions come from the combustion of fossil fuels in power plants [2]. Many techniques have been employed for CO_2 capture from the flue gas; among them, the packed absorption column based on the gas-liquid contactor is the most common configuration. However, on an industrial scale, the absorption columns require large footprint and high cost, and suffer from a variety of operational problems, such as liquid channeling, flooding, entrainment and foaming [3].

Membrane contactor with microporous membrane between the flue gas and the absorption solution is an emerging technology for CO_2 absorption [4,5]. Highly packed membrane modules probabilize large and stable gas/liquid contact area; therefore, the equipment size is significantly reduced and the scale-up is easy. Thanks to the independent gas and liquid flows, membrane contactor successfully overcomes the above-mentioned operational problems in the packed absorption column [4,6].

In the membrane contactor the gas transport across the membrane is based on the gas diffusion inside the membrane pores [7]. In order to prevent the absorption solution from entering into the membrane pores, i.e., membrane wetting, and maintain a high absorption efficiency, hydrophobic membranes with small pore sizes are generally desired [6]. Polymeric materials with intrinsic hydrophobicity, such as polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidene fluoride (PVDF), are often used to prepare microporous membranes for gas absorption in the membrane contactor [6,8]. Hydrophobic PTFE and PP membranes are now commercially available [8,9]. Since PTFE and PP are insoluble in most common solvents at ambient temperature, these membranes are often fabricated using the melting and stretching method [10,11]. As a result, the porosity is generally low and the gas transfer resistance is high [9]. PVDF are soluble in several organic solvents that are miscible with water, such as N,N-dimethylformamide (DMF) and 1-methyl-2-pyrrolidinone (NMP). Therefore, PVDF membranes can be fabricated using the non-solvent induced phase separation (NIPS) method, which is simple and flexible [6]. The pore size and distribution, porosity, and pore structure of the PVDF membranes can be well regulated and

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controlled by the conditions of the phase inversion [12]. The PVDF membranes of microfiltration and ultrafiltration have been widely employed in water treatment. Since the hydrophobicity is not as good as that of PTFE and PP membranes, PVDF membranes suffer from serious wetting problems in the membrane contactor for gas absorption, especially in long-term runs [13]. Therefore, the improvement of the hydrophobicity of the PVDF membranes is crucial for their use in the gas membrane absorption.

Many attempts have been made to obtain PVDF membranes with strong hydrophobicity, such as changing the coagulation bath composition [14], blending hydrophobic polymers [15], grafting hydrophobic macromolecules [16], creating hydrophobic coating, etc. [17]. The incorporation of inorganic nanoparticles into the doping solution of PVDF is another attractive method for membrane modification due to its simplicity and diversity. The well dispersed SiO_2, montmorillonite, or clay nanoparticles significantly changed the surface morphology of PVDF membrane as well as its pore structure, and enhanced membrane hydrophobicity [18–20].

Graphene is a monolayer of carbon atoms, arranged in a honeycomb network or an unrolled single-walled carbon nanotube [21]. Its extraordinary electronic, thermal, and mechanical properties have been well studied since 2004 [22]. Graphene nanosheets have been successfully used as additive in polymers in order to reinforce the electronic conductivity, thermal conductivity, optical property, and mechanical strength [23]. As intrinsic hydrophobic nanosheets, the incorporation of graphene can also enhance the hydrophobicity of the polymer, and produce even superhydrophobic materials. For example, the polyvinyl chloride (PVC) fibers embedded with 4 wt% graphene achieved a superhydrophobic surface with a water contact angle of 166.3° [24]. This hybrid fiber can be used to produce self-cleaning photoelectrodes in the photovoltaic cells. The addition of graphene into PVDF could also produce gels with surface contact angle higher than 150° [25].

The PVDF/graphene hybrid membrane has been barely prepared, and its application in membrane contactor for CO_2 absorption has not been investigated. In this study, hybrid PVDF membranes incorporated with different concentrations of graphene were prepared using the NIPS method. Since the prepared membranes were asymmetric, both surfaces were comprehensively characterized. The effect of membrane orientation was considered for the CO_2 absorption test and its wetting resistance was also discussed. Our results demonstrated that the addition of graphene intensified the asymmetry of the prepared PVDF membranes in terms of hydrophobicity. Compared with the membrane surface of the coagulation bath interface, the membrane surface of the substrate interface exhibited much higher hydrophobicity due to the graphene addition. As a result, the CO_2 absorption rate as well as its long term performance was strongly dependent on the membrane orientation of the prepared hybrid membrane.

2. Experiments

2.1. Materials

The PVDF polymer (Solef 1010, $Mw=3.52\times10^5$ g/mol, Mw/Mn=2.3) was purchased from Solvay Specialty Chemicals (Belgium). 1-Methyl-2-pyrrolidone (NMP, $>99.5\%$) and polyethylene glycol 400 (PEG-400, $>99.5\%$) was purchased from Tianjin Guangfu Chemical Co., China. Graphene (≥99.5, 300–500 nm, 1–5 layers) was purchased from Nanjing SCF Nanotech, Co., Ltd, China. All the above chemicals for membrane preparation were used as received. CO_2 was commercial cylinder gas with purity higher than 99% (Tianjin Dongxiang gas Co., China). Monoethanolamine (MEA) with 99.5% purity was purchased from Tianjin Guangfu Chemical Co., China.

2.2. Membrane preparation

PVDF polymer pallets and graphene were vacuum dried at 60 ± 2 °C for 24 h before use. 15 wt% PVDF and 5 wt% PEG-400 were dissolved in NMP with different concentrations of graphene (0, 1, 3, and 7 wt%, which were labeled as M-0, M-1, M-3, M-7, respectively). The prepared dope solution was stirred homogeneously at 60 °C for 24 h and then degassed for more than 12 h at room temperature.

Asymmetric flat sheet PVDF membranes were prepared via the NIPS method using an Elcometer 4340 motorized film applicator (Elcometer Asia Pte Ltd., UK). The degassed dope solution was cast on a glass plate at room temperature with a knife gap of 200 μm. The cast membrane was exposed in air for 30 s and subsequently immersed into a coagulation bath of tap water. The membrane surface of the substrate interface, i.e., the surface directly contacting with the glass plate, was referred to the bottom surface, while the other surface was referred to the top surface. The prepared membrane was transferred into fresh tap water and kept for 3 days to remove the residual solvent. Finally, it was dried in air at room temperature before use.

2.3. Membrane characterization

The membrane was vacuum dried at 40 °C for 10 h before analysis.

2.3.1. Membrane morphology

The morphology of both surfaces of the prepared hybrid membranes as well as the cross section fractured in liquid nitrogen was characterized by a Nanosem430 field emission scanning electron microscope (FEI, USA).

2.3.2. Surface roughness

Membrane surface roughness was measured by atomic force microscopy (AFM) in tapping mode (Dimension ICON, Bruker, Germany). The measurements were carried out with a silicon nitride probe (NP-O10, Shanghai, China) at a scan rate of 1 Hz over an area of 100 μm^2. The collected data were analyzed using nanoscope controller software (Version 1.40r3, Bruker, Germany) and the root mean square roughness for each sample was calculated.

2.3.3. Static contact angle

The hydrophobicity of both surfaces of the prepared membrane was determined based on the static contact angle measurement with contact angle goniometer (JC2000C, Shanghai, China) at room temperature. At least five contact angle data at different locations on one surface were averaged to get a reliable value.

2.3.4. Wide angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) analysis was conducted using an X-ray diffractometer (D-MAX2500, Rigaku, Japan) with a Cu Kα radiation source (1.54 Å). The generator was operated at 40 kV and 150 mA at room temperature. Samples were scanned from 5° to 60° (2θ) with a step of 0.02°.

2.3.5. Pore size

The average pore size of the membrane was determined using an automatic mercury porosimeter (AutoPore IV-9500, Tektronix, USA).

2.3.6. Porosity

Three sample pieces were cut from randomly selected spots of a piece of prepared membrane and subjected to porosity measurements. The samples were immersed in ethanol for 24 h. Then they were wiped with blotting paper and immediately weighed to