



# A facile method to functionalize engineering solid membrane supports for rapid and efficient oil–water separation



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## ABSTRACT

A facile and low-cost method is developed to functionalize engineering metal membrane supports, such as stainless steel (SS), with epoxy-containing polymer poly(glycidyl methacrylate) (PGMA) to produce a versatile and universal platform for subsequent surface modification. With a PGMA anchoring layer, we have demonstrated that hydrogel particles, such as polyacrylamide-co-poly(acrylic acid) (PAM-co-PAA), can be subsequently grafted to form functional polymer membranes for rapid and efficient oil–water separation. By contact angle and AFM measurement, we have confirmed that PAM-co-PAA hydrogel particle layer grafted on a PGMA-modified SS surface exhibits excellent selectivity as required for liquid–liquid separation, showing high affinity to water but not to oils as an ideal membrane for oil–water separation. To evaluate the separation efficiency, a simple flow-through device is employed to separate free-floating oil from water in the mixture of varied initial oil volume fraction and oil composition. Under substantially high pump flow rate up to 1.3 L/min, PAM-co-PAA hydrogel treated SS mesh can achieve excellent separation efficiency with less than 5% oil or water in the respective filtrate at the flux of as high as  $540 \text{ m}^3/(\text{m}^2 \cdot \text{h})$  and retentate at the flux of  $1.95 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ . This separation efficiency is better than, or comparable to, the maximal performance achieved using conventional gravity methods at much lower flow rate. Similar approach could be also adapted to graft superhydrophobic and superoleophilic polymer membranes with PGMA-treated engineering support to separate water from oil.

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## 1. Introduction

Developing functional membrane supports for efficient and rapid oil–water separation has attracted more attentions in the recent decade and becomes in urgent need since *Deepwater Horizon* oil spill in 2010. As the largest oil spill accident in the US history, it has resulted in continuous and extensive damage to the environment around the Gulf of Mexico [1–4]. The lasting damage of the oil spill is in part due to the lack of suitable filtration technologies for oil recovery – only 17% of leaked oil has been recovered in the *Deepwater Horizon* spill [5]. Additionally, oil–water membrane separation could also be applied in many conventional industries such as oil refinery [6], produced water treatment [7], pre- and

post-treatment of food oils [8], and emerging fields including biodiesel separation and purification [9], which has spawned a huge market. For instance, on the treatment of onshore produced water alone, the current total value of the global market is estimated to be ~\$59 billion and is expected to increase substantially over the next eight years [10]. However, most widely applied gravity methods including API separator require large occupancy space, long retention time, and high operating cost, all of which greatly restrict their applications at the state of emergency and also in small and medium platforms [11–13]. Instead, membrane filtration has broader application fields because it is efficient, small space occupying, and low operating cost, but it is often expensive in membrane material cost and requires high pressure or electric field in operation [14]. To lower the material cost by improving the separation efficiency and extending the service life of membranes, various functional polymers have been explored to modify engineering mesh supports [15–18]. However, the binding of polymers with mesh supports is often very weak, mainly by van der Waals

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interaction, and thereby significantly reduces the durability and separation efficiency of polymer membrane. To improve the binding strength between polymers and a mesh support, building chemical bonds between them is a commonly considered approach. However, practically it is often very difficult for widely used stainless steel (SS) mesh supports due to the lack of functional groups on their surfaces. In this work, we have successfully developed a facile and economic method to functionalize engineering mesh supports with a universal anchoring and reactive polymer coating that allows subsequent grafting of functional polymers or particles as separation filters. Such grafted polymer membranes on SS mesh support can afford rapid and efficient separation of free-floating oil from water without extra pressure.

Due to the lack of functional groups on SS surface, it is necessary to first introduce some functional groups by coupling agents for subsequent polymer coating. Currently used coupling agents, including silanes [19,20], catechol [21], alkanolic acids [22], alkylthiols and alkylamines [23], and poly(ethylenimine) [24] for SS surface modification are not multifunctional; thus more than one couple agent is required to accommodate the grafting of functional polymer membrane, which could significantly increase both material and processing cost. In this work, we have selected a highly-reactive epoxy-containing polymer, poly(glycidyl methacrylate) (PGMA), as a universal anchoring layer covalently bound on the SS mesh support to allow subsequent surface modification. PGMA has been proven as a universal platform for chemical treatment of various substrates including polymer and inorganic materials, but it has not been applied on metal surface yet [25,26]. Also importantly, PGMA is environmental stable and reusable, which can help lower its manufacturing cost and further broaden its application. Compared with the most widely used silane-based self-assembly method, our approach is of low cost to produce multifunctional groups for subsequent surface modification because epoxy groups could react with many groups such as alcohols, carboxylic acids and their derivatives, ammonia and amines, and metal halide at mild conditions [27,28]. In this work, we have demonstrated that PGMA can be easily grafted to SS surface by simple thermal treatment. To apply it for oil–water separation, we subsequently graft PGMA-treated SS surface with one of the cheapest water-soluble polymers available in the market, polyacrylamide-co-poly(acrylic acid) (PAM-co-PAA) hydrogel particle, which is superoleophobic in aqueous media similar to polyacrylamide hydrogel [15]. Another advantage of using hydrogel as separation membranes is that it can be easily regenerated by copious wash using detergents for repeatable separation processes, thereby exhibiting additional economical and environmental benefits. The performance of PAM-co-PAA coated SS mesh to separate free-floating oil from water, for which the volume fraction of oil in the mixture is typically greater than 5%, is examined against flow rate and oil composition.

## 2. Experimental section

### 2.1. Materials

Glycidyl methacrylate (GMA) is purchased from Sigma–Aldrich and purified by basic alumina column before use. Polyvinylpyrrolidone ( $M_w = 40,000$  g/mol) (PVP40), acetone, ethanol, isopropanol (IPA), acrylamide (AM), acrylic acid (AA), N,N'-Methylenebisacrylamide (MBAM), 2,2'-Azobis(2-methylpropionitrile) (AIBN), sulfuric acid, hydrogen peroxide, acetone, 1,2-dichloroethane, sodium benzenesulfonate (SDBS), Reactive Orange 16 and Rhodamine B are all purchased from Sigma–Aldrich and used directly. Dodecane and rapeseed oil are purchased from VWR and used directly. Stainless steel (SS) (Alloy type 316) wire mesh with pore width,  $w = 43$  and  $74$   $\mu\text{m}$  and mirror-like SS sheet are

purchased from McMaster and cleaned by being sonicated in acetone for 10 min first and soaked in the piranha solution at room temperature ( $\sim 22$  °C) for 5 min to produce hydroxyl-terminal rich surface before further chemical treatment by hydrogel particles.

### 2.2. Synthesis of PGMA

Dispersion polymerization is used for the synthesis of PGMA [29]. Typically, 30 g GMA and 0.675 g PVP40 are dissolved in the mixture of 162 mL ethanol and 8 mL deionized water (Barnstead Nanopure II). After being purged with nitrogen for 30 min, 0.6 g AIBN is added to the solution and the solution is heated and kept at 70 °C in nitrogen atmosphere under stirring at a speed of 350 rpm for 12 h for polymerization. At the end of polymerization, the product of PGMA polymer is centrifuged and washed by ethanol for three times to remove excess GMA and other chemicals in the supernatant, and dried at 40 °C in vacuum for 24 h. The molecular weight,  $M_w$  of PGMA is measured to be 23,000 g/mol ( $M_w/M_n = 6.4$ ) by gel permeation chromatography (GPC) (Waters) with dimethylformamide (DMF) as the solvent. For the treatment of SS mesh, PGMA is dissolved in chloroform at a concentration of 5 g/L.

### 2.3. Synthesis of PAM-co-PAA hydrogel particle

PAM-co-PAA hydrogel particle is synthesized by dispersion polymerization. Typically, 35 g monomer mixture including AM, AA and crosslinker MBAM at a respective weight ratio, 40: 40:20 or 47.5:47.5:5, is dissolved in the mixture of 200 mL IPA and 200 mL ethanol under the purging of nitrogen for 30 min. Subsequently, 0.16 g AIBN is added to the solution and the entire mixture is heated and kept at 60 °C under continuous stirring at a speed of 500 rpm for 12 h in nitrogen atmosphere. After being centrifuged and washed by copious ethanol to remove excess monomers and crosslinker, the product of PAM-co-PAA polymer is dried at 40 °C in vacuum for 24 h. The diameter,  $d$  of PAM-co-PAA hydrogel particle in water is measured by dynamic light scattering (ZetaPlus, Brookhaven Instruments) to be 2.0  $\mu\text{m}$  with a polydispersity (PDI) of 0.360 for 20% MBAM crosslinker-to-monomer (CM) ratio and 364 nm with a PDI of 0.264 for 5% MBAM CM ratio. The hydrogel particle is dispersed in deionized water at a concentration of 100 g/L to be used for the surface modification of SS mesh.

### 2.4. Modification of SS substrates

The scheme of chemical modification process of SS substrates is shown in Fig. 1. In this work, the SS substrates are all treated by PGMA polymer first, then by PAM-co-PAA hydrogel particles. To graft PGMA to the mesh surface, the hydroxyl-terminal rich SS mesh after immersion in piranha solution is dipped into the PGMA solution for 5–10 s and taken out quickly. The residual PGMA solution in mesh pores could provide sufficient PGMA coating on SS wire surface because the PGMA chloroform solution can completely wet and spread on hydroxyl-terminated SS surface, which also offers a rapid yet efficient approach to chemically modify the SS mesh. After air-drying in a fume hood, the PGMA-coated SS mesh is baked at  $T = 110$  °C in vacuum for 1 h to enhance the binding of PGMA to the mesh surface as suggested for the case on silica surface [30]. Afterwards, the mesh is sonicated in acetone for 10 min to remove excess unattached PGMA. The subsequent grafting of PAM-co-PAA hydrogel particles to the PGMA-modified mesh is similar to the grafting process of PGMA to the mesh by dip-coating and subsequent thermal treatment at  $T = 150$  °C in vacuum for 12 h to form covalent bonds of PAM-co-PAA with PGMA on the SS surface. Finally, the polymer-coated SS mesh is sonicated in water at least

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