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Ultralight Free-Standing Reduced Graphene Oxide Membranes for Oil-in-Water Emulsions Separation

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We report a facile and environmental friendly route to fabricate ultralight free-standing RGO membranes. Such a membrane is capable of separating multiple types of surfactants stabilized oil-in-water emulsions with oil droplet in nano/sub-micrometer size, as well as displays high separation efficiency and excellent anti-fouling property, making it a highlighted alternative for water remediation.

Oil plays a significant role in the modern daily life and social development, yet simultaneously in turn brings about severe environment pollution.[1-2] Process for emulsified oil-in-water that act as a universal and intractable pollution source, is an urgent and challenging worldwide subject because of its serious threat to environment and human health.[3-4] Filtration membrane techniques have been extensively employed for removing emulsified oil from water with an acceptable permeation flux and relatively simple procedure than other technologies.[5-7] Nevertheless, the inevitable fouling by oil droplets or absorbed surfactants has been a crucial issue to limit its widespread application.[8-10] Inspired by the water-repellent property of lotus leaf[11] and oil-repellency of fish scales in water[12], superwetting materials with superhydrophobic-superoleophilic[13-24] or superhydrophilic-superoleophobic[25-30] properties via rational combination of surface chemistry and structure roughness have sparked tremendous excitements in the scientific community given their wide applications in environmental remediation, oil-water separation etc. Most of these materials are, however, burdened with the invalidity for removing nano/sub-micrometer-sized oil droplets stabilized in emulsions.[20,26,31] Therefore, it is highly desirable to develop new underwater superoleophobic materials and thus achieve anti-fouling capacity to separate oil-in-water emulsions efficiently.

Graphene has moved into the spotlight in recent years for its promising applications in fields such as physics, chemistry, and materials science, among others.[32] At present, the most easily and potential method for large-scale produce of graphene is reduction of graphene oxide (GO)[33], which covered with hydroxyl, carboxyl, epoxy and other oxygen containing groups. The common reductants used for reduction of GO, such as hydrazine hydrate[34], hydroquinone[35], and sodium borohydride[36] etc, are always hindered by their intrinsic poisonous or hazardous nature. Accordingly, it is anticipated to explore milder reduction methods for access to graphene-based materials. Although reduced graphene oxide (RGO) materials have been widely proposed for applications[37] that range from conductive thin films[38], nanofiller materials[39] to versatile platforms for anchoring functional polymers[40-43], etc, few efforts have been devoted to incorporate them into emulsified sewage treatment fields to date.[44]

In this work, we report the fabrication of RGO membranes for anti-fouling oil-in-water emulsions separation by a facile environmental friendly route. Benefiting from the fascinating properties of dopamine serving as both benign reductant and self-polymerized capping agent simultaneously, the prepared polydopamine coated RGO membrane (PDA-RGO) is endowed with superhydrophilic and underwater superoleophobic wetting behaviors. Impressively, the membrane exhibits free-standing property with ultralight weight, to the best of our knowledge, which is the first time to form the free-standing RGO materials for oil/water separation. Furthermore, the membrane is capable of separating multiple types of surfactants stabilized oil-in-water emulsions with oil droplet in nano/sub-micrometer size, and displays high separation efficiency with all extremely low oil content in filtrates. As a consequence, this approach may provide a forward outlook for graphene-based materials in applications of industrial

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emulsified wastewater treatment, domestic sewage purification and so on.

Fig. 1 Schematic illustration of preparing the free-standing RGO membranes and vacuum filtration process, and showing the separation capacity of oil-in-water emulsion.

The inspiration of using dopamine in conjuction with GO is based on its physicochemical properties of adhesion and self-polymerization. In parallel, the fascinating reducing capacity at weak alkaline pH has made dopamine interesting as a milder and nontoxic reducing agent, which ensures dopamine to be chosen for one-step reaction whereby GO is reduced and decorated by dopamine at the same time. As schematically shown in **Fig. 1**, the GO dispersion was first produced and then an aqueous solution of dopamine-hydrochloride with Tris buffer (pH 8.5) was added under stirring at room temperature to obtain the PDA coated RGO suspension. The RGO membrane was subsequently formed through vacuum filtration of a certain volume of the obtained suspension onto a commercial mixed cellulose ester (MCE) filter membrane. Taking into consideration the existence of abundant hydrophilic functional groups of PDA such as catechol groups and amine groups as well as the high surface roughness, the as-prepared membrane displayed superhydrophilic and underwater superoleophobic properties, which was perceived to be used for separating oil-in-water emulsions.
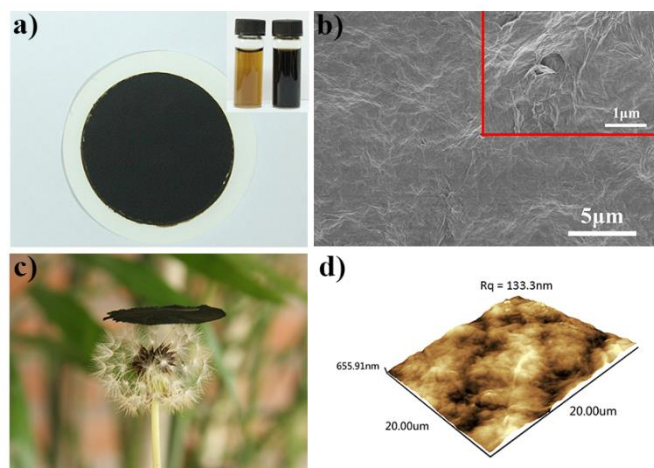

Fig. 2 a) Photograph of the filtered RGO membrane, the inset are the photographs of aqueous suspensions of GO before and after reaction with dopamine. b) FESEM image of RGO membrane showing a fluctuant and porous structure in which PDA-RGO nanosheets are overlapped with each other, the inset is the high magnification view of the porous RGO membrane. c) Photograph of a piece of free-standing RGO membrane standing on a dandelion,

indicating the ultralight property of the membrane. d) AFM image of the free-standing RGO membrane.

The PDA coated RGO suspension was produced by mixing an aqueous dispersion of GO flakes with a solution of dopamine-hydrochloride. After magnetically stirring for 24 h at room temperature, the yellow brown GO suspension turned into a black solution (inset in **Fig. 2a**), which exhibited a visible change in color. The RGO membrane was obtained under vacuum filtration onto a MCE filtration membrane support (**Fig. 2a**). Field emission scanning electron microscope (FESEM) was performed to investigate the microstructures of the MCE support and free-standing RGO membrane. The MCE support exhibited an abundant porous structure consisting of a polymer framework with a fairly smooth surface (**Fig. S1**). **Fig. 2b** showed that the resultant membrane was built from self-corrugated RGO flakes during deposition to form a fluctuant and continuous surface with a roughness on nanoscale wherein distributed many pores in micrometer sizes, constructing a micro- and nanoscale hierarchical composite structure. The membrane could peel from the support easily by itself after dried at ambient condition for several minutes and a piece of free-standing RGO membrane (~4.5 mg) could effortlessly stand on a dandelion (**Fig. 2c**), demonstrating the scalable possibility of fabricating ultralight RGO membrane. In addition, AFM image in **Fig. 2d** presented that the membrane had a root-mean-squared roughness (Rq) of 133.3 nm, which was in good agreement with the FESEM results.
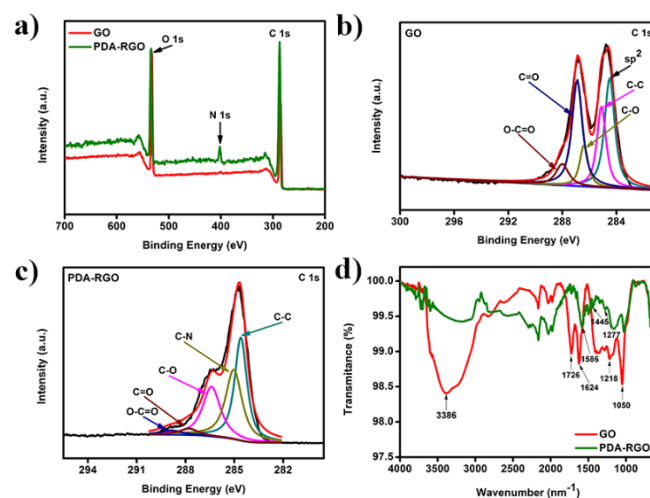

Fig. 3 a) XPS survey spectra of GO (red) and PDA-RGO (green). XPS spectra for C 1s of GO (b) and PDA-RGO (c). d) FTIR spectra of GO before and after reaction with dopamine.

The composition change of GO before and after reaction with dopamine was examined by X-ray photoelectron spectroscopy (XPS) and presented in **Tab. S1**. The peaks of C 1s and O 1s were observed in GO and PDA-RGO, while a new peak of N 1s emerged in PDA-RGO, which should arise from PDA on the resultant membrane (**Fig. 3a**). The C 1s core level spectra of GO was shown in **Fig. 3b** and could be deconvoluted into five peak components with binding energies at about 284.5, 285.1, 286.4, 286.9 and 288.0 eV, attributable to the sp^2-hybridized carbon, C-C, C-O, C=O and O-C=O species, respectively. Although the C 1s spectrum of PDA-RGO also exhibited the majority of same peaks, the peak associated with C-C became dominant (**Fig. 3c**). Additionally, the notable decrease in intensities

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of C=O and O-C=O species and the appearance of C-N peak component indicated that dopamine had been successfully reduced and capped on the GO. The incorporation of PDA in the RGO membrane was further confirmed by FTIR spectroscopy (**Fig. 3d**). Peaks at 1586 and 1277 cm^{-1} were assigned to the amide N-H shearing vibration and stretching vibration of the phenolic C-OH group, respectively. The band at 1445 cm^{-1} corresponded to C-C vibration of the benzene ring moiety. These results strongly confirmed the presence of PDA on the RGO sample. The disappearance of C-OH vibration at 3386 cm^{-1} and C=O peak at 1726 cm^{-1} due to GO provided a solid evidence for dopamine reducing GO to RGO. It is also worth noting that peaks due to C-OH and C-O stretching modes at 1218 and 1050 cm^{-1} of GO were not detected in the spectrum of PDA-RGO, suggesting that GO was reduced by one-step dopamine self-polymerization.
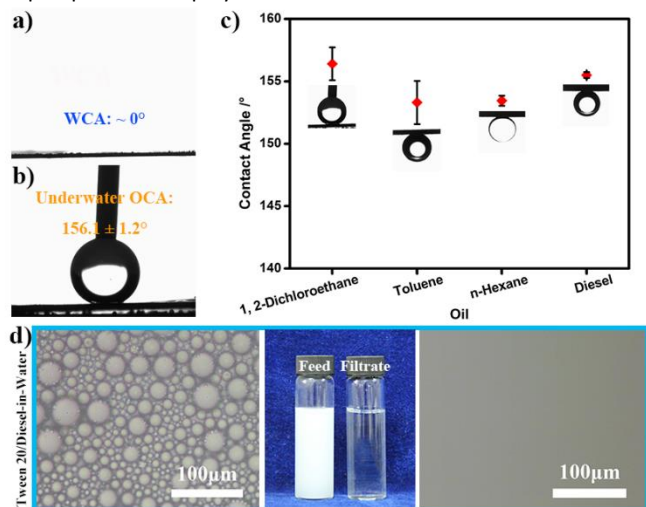

Fig. 4 Photographs of a water droplet on the RGO membrane in air (a) and an oil droplet on it underwater (b). c) Superwetting behavior of the membrane in oil/water/solid systems for sundry oils. d) Photographs of Tween 20-stabilized diesel-in-water emulsion before and after filtration.

The aforementioned SEM images told us that the randomly overlapping and self-corrugation of hydrophilic PDA coated RGO nanosheets formed the free-standing membrane with micro- and nanoscale composite structure, which is crucial for achieving superwetting behavior according to the Cassie model arisen from Young's equation.[45] **Fig. 4a**-**4b** showed the wetting behavior of water and oil on the membrane more detailedly. When a water droplet was placed on the membrane surface in air, it spread instantaneously within 3 s and a water contact angle (WCA) of nearly zero was gained. Therewith, the membrane exhibited superoleophobicity with oil contact angle (OCA) of 156.1 ± 1.2° when an oil (1, 2-dichloroethane was taken as an example) droplet was placed on the surface underwater. Analogously, the OCAs of various oils underwater were measured and shown in **Fig. 4c**. The result that all OCAs were larger than 150° verified the superwetting property of the as-prepared membrane, which was expected to be advantageous to separate oil-in-water emulsions.

To evaluate mechanical properties of our free-standing RGO films quantitatively, tensile test was further performed. The typical strain-stress curve of the RGO film was shown in **Fig. S2**. The tensile

strength and toughness of the film are up to 55 MPa and 0.39 MJ cm^{-3}. These values are comparable with that of pure GO films in previous studies.[46] The satisfactory mechanical performances endow our film with well practicality during oil-water separation application.

A series of sundry surfactants stabilized oil-in-water emulsions have been prepared to test the separation capacity of the membrane. Despite the free-standing RGO membrane was not functioning so well when applied an external pressure, the MCE filter membrane with pore sizes of 0.22 μm average diameter was introduced as a bottom support to solve the problem. The membrane was fixed into the separation apparatus (**Fig. S3**). The as-prepared emulsions were poured onto the membrane and the separation was driven by a vacuum filtration system at ~0.1 MPa. **Fig. 4d** and **Fig. S4** gave the separating results of diesel-in-water emulsions stabilized with Tween 20, CTAB and SDS surfactants, respectively, as examples. Compared to the original milky white feed emulsion in either case, all the collected filtrates were clear and transparent. Optical microscopy was conducted to clearly see the difference of composition between the feed and the corresponding filtrate at low magnification. Not a single oil droplet was observed in the image of collected filtrate in comparison with the whole view composed of closely packed droplets before filtration, implying that diesel in emulsions had been successfully removed. To check the effect of MCE filter membrane on separation efficiency, the same separation process of Tween 20-stabilized diesel-in-water emulsion was also carried out by using two layers of MCE filter supports (**Fig. S5**). Wherein, the upper layer was as a control sample to simulate the as-prepared free-standing RGO membrane. The collected filtrate (in the middle) was translucent and opaque, indicating that only oil droplets with size larger than that of MCE support (~220 nm) could be blocked. Since the average droplet size of emulsion was mainly distributed around 100nm (Fig. 5a), therefore, the MCE filter membrane has minimal effect on separation efficiency. The fluxes of the membrane for separating three types of surfactant stabilized oil-in-water emulsions were calculated by measuring the time for a certain volume of emulsions to permeate through, as shown in **Fig. S6**. It was clearly seen that the fluxes of Tween 20 stabilized emulsions were generally lower than that of the other two surfactants stabilized emulsions. The possible deduction will be clarified in **Fig. 5e-5f** and **Fig. S8**. Notably, the fluxes of diesel-in-water emulsions were lower than other emulsions, which probably due to the intrinsic high viscosity of diesel consuming demulsification time.
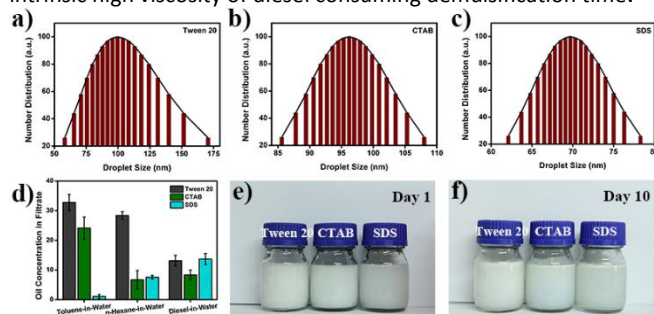

Fig. 5 a)-c) DLS curves of the oil droplet size distribution of the diesel-in-water emulsions stabilized with different types of

surfactants. d) Oil concentration in corresponding filtrate for toluene-in-water, n-hexane-in-water and diesel-in-water emulsions stabilized with different surfactants. e) and f) with 0.5 mg mL^{-1} of Tween 20, CTAB and SDS in three diesel-in-water emulsions, the emulsions keep stable at least for 10 days.

The oil droplet size distribution of different types of surfactants stabilized emulsions (diesel-in-water emulsions were taken as examples) before filtration was further accurately measured using dynamic light scattering (DLS). As can be seen in **Fig. 5a**, the feed of Tween 20 stabilized emulsion was mainly distributed around 100 nm, showing a phase composition in sub-micrometer size. Moreover, the average droplet size distributions of CTAB- and SDS-stabilized emulsions were all less than 100 nm (**Fig. 5b-5c**). These results indicated that 1 % of diesel had been evenly dispersed in continuous water phase with the aid of surfactant under magnetically stirring. The oil concentration in the feed and correspondingly collected filtrate after one time separation was analyzed by the infrared spectrometer oil content analyzer and summarized in **Tab. S2** and **Fig. 5d**. Concentration of each oil in either case was the average value of at least three measurements with different samples. The oil concentration of all filtrates were lower than 35 mg L^{-1}, which was in good accordance with the regulations drafted by the US Environmental Protection Agency (EPA) that the maximum discharge of oils in their effluents is limited to 42 mg L^{-1} for any one day. Strikingly, the oil concentration of the separated SDS-stabilized toluene-in-water emulsion was even low to 2 mg L^{-1}. The high separation efficiency of the membrane with all water purity in corresponding filtrate higher than 99.6 % (**Fig. S7**) is mainly owing to its "oil-repellency" property, thus water can infiltrate and trap into the superhydrophilic structure surface and build a passing barrier for oil at the same time. With regard to Tween 20-stabilized emulsions, the value was in general higher than that of CTAB- and SDS-stabilized emulsions, which was considered to be caused by the intrinsic feature of Tween 20. As a common non-ionic surfactant, Tween 20 displays the superior capability of emulsifying oil/water and being inert to high concentration of electrolytes, pH variation and light irradiation etc. This deduction was verified by examining the diesel-in-water emulsions stability separated in this work as shown in **Fig. 5e-5f**. The concentration of three types of surfactants in each emulsion was kept at 0.5 mg mL^{-1}. After maintained for 10d without any disturbance, the Tween 20-stabilized emulsion was almost constant without any visible change, whereas the CTAB- and SDS-stabilized emulsions turned into shallow and translucent in color. The major difference between each sample was also tested by optical microscopy (**Fig. S8**). The Tween 20-stabilized emulsion was composed of dense packed oil droplets in whole view, which keeps stable performance without visible variation compared to that of freshly prepared emulsion. By contrast, the CTAB- and SDS-stabilized emulsions tend to self-demulsification with tiny oil droplets impacting with each other to form larger clusters.
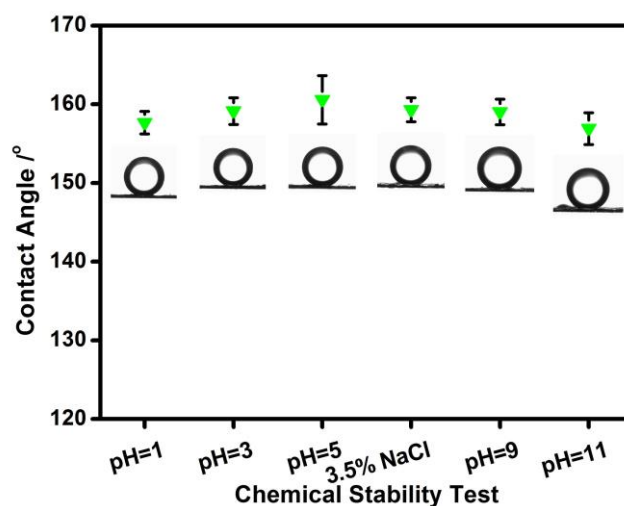

Fig. 6 Chemical stability test of the membrane toward 1, 2-dichloroethane under water after immersing in the solutions with different pH values and concentrated salt.

Wetting behavior toward water in air and 1, 2-dichloroethane under water as well as microstructure of the RGO membrane after cycles of emulsion separation tests have been measured and presented in **Fig. S9**. The results that the membrane maintains its superhydrophilicity and underwater superoleophobicity with randomly distributing protuberant RGO flakes indicate the excellent anti-fouling property of RGO membrane. The chemical stability of the membrane was evaluated by characterizing its pH and concentrated salt resistance. **Fig. 6** gives the underwater OCA (1, 2-dichloroethane was taken as an example) of the membrane after being immersed in different pH solutions and concentrated salt solution for 2 h. It can be seen that the membrane keeps underwater superoleophobicity with > 150° OCA for pH ≤ 11 and concentrated salt condition. For pH > 11, however, the PDA layer would be removed in alkaline solution and the RGO membrane dissolved completely. Thus, our membrane exhibits superior stability against acidic, concentrated salt and weak alkaline conditions.

Conclusions

In conclusion, we have developed a novel anti-fouling RGO membrane with superhydrophilicity and underwater superoleophobicity. The resultant membrane presents splendid free-standing property with ultralight weight, which has been rarely reported in literature about graphene-based materials for oil/water separation up to now. This membrane applies to multiple types of surfactants stabilized oil-in-water emulsions with oil droplet in nano/sub-micrometer size, and displays spectacular separation efficiency that in good consistent with the EPA regulations. More importantly, the membrane exhibits superior chemical stability against acidic, concentrated salt and weak alkaline conditions. Therefore, we expect our membranes will highlight a forward outlook for graphene-based materials in practical applications for emulsified water remediation produced in industry and daily life.

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Acknowledgements

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Ultralight free-standing RGO membranes are capable of separating multiple types of surfactants stabilized oil-in-water emulsions with high separation efficiency.