SPECIAL TOPIC: Graphene Oxides towards Practical Applications

Interface-enhanced distillation beyond tradition based on well-arranged graphene membrane

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ABSTRACT Traditional distillation (TD) is generally an energy-intensive and inefficient process for separation and purification of liquids in chemical industries. Herein, we developed an interface-enhanced distillation (IED) by employing a well-arranged membrane of reduced graphene oxide (rGO) sheet arrays embedded with silicon dioxide nanofibres (rGO/SiO₂) as the evaporation intermediate layer on the liquid surface. This IED enlarges the evaporation surfaces and weakens the intermolecular forces on the liquid/solid/gas interfaces, realizing the fast and even low temperature fraction collection with less energy consumption. The IED delivers evaporation rates 200%–300% times that of TD, meanwhile having an energy saving of 40%–60% and a time saving of 50%–70% for diverse liquid feeds. In atmospheric IED manner, high boiling point and perishable organics can be collected with high quality at a temperature lower than their boiling points. This IED provides an innovative strategy for highly efficient distillation in chemical industries.

Keywords: interface-enhanced distillation, enlarged evaporation surfaces, weakened intermolecular forces, fast evaporation, energy and time savings

INTRODUCTION

Distillation is key technology in chemical industry to purify and separate liquids from mixtures of components with different boiling points, which is widely utilized in petrifaction, chemical engineering, light industry and so on [1–4]. Traditional distillation (TD) process involves the thermally driven conversion from liquid to gas state at the liquid/gas interface by breaking the intermolecular

forces including hydrogen bonds, van der Waals force, and electrostatic energy, and then the condensation of vapor for fraction collection [5–8]. However, TD is an energy-inefficient process with only 5%–20% thermal conversion efficiency and relies heavily on non-renewable energy [9,10], which accounts for more than 50% energy consumption of the world's chemical industries [11], concomitantly causing severe energy and environmental crisis [12–14]. It has been put in a quandary for effectively improving the distillation efficiency and minimizing the energy consumption.

The evaporation in TD is limited at the planner liquid/gas interface (Fig. 1a, b), and the escape of vapor must overcome the intensely intermolecular forces within bulk liquid (Fig. 1c) [15–18]. Currently, a variety of previous studies have demonstrated that by rational design of the material structure and management of the interaction between molecules and materials, the evaporation rate can be tailored [15,19]. Yu's group [15] demonstrated that a hierarchically nanostructured gel enabled rapid water diffusion pumping of micron channels and a reduced vaporization enthalpy due to the intermolecular interaction between water molecules and polymeric meshes. Such features endow this hierarchically nanostructured gel with a record high evaporation rate. Zhu's group [20] reported a carbonized mushroom with umbrella-shaped black pileus and porous structure, providing a large surface area for evaporation and minimizing the heat loss for fast evaporation. Herein, we demonstrate an interface-enhanced distillation (IED) based on a well-arranged membrane with reduced graphene oxide (rGO) sheet

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arrays embedded with silicon dioxide nanofibres (rGO/SiO₂) as the evaporation intermediate layer on the liquid surface (Fig. 1d), realizing the fast and even low temperature fraction collection. The rGO/SiO₂ membrane allows the adsorptive liquid transport along the aligned lamellar walls (Fig. 1e), inducing the formation of liquid/solid/gas interfaces and thus greatly enlarging the available area in favor of evaporation compared with TD (Movie S1, an animation showing the IED process). Meantime, the intermolecular forces on liquid/solid/gas interfaces are obviously weakened that facilitates the escape of molecules with a lower energy consumption. As one example shown in Fig. 1c, f, the bulk water mainly possesses long-range, strong hydrogen bonding interactions [21–23]. After water transports along rGO/SiO₂ lamellar walls with rough surfaces, the increased distance and angle with adjacent water molecules on vertically aligned rGO/SiO₂ wall will cause relatively weak hydrogen bonding interactions [24–26]. As expected, the IED delivers evaporation rates about 200%–300% as high as that of TD with the energy and time savings of up to about 60% and 70% for common solvents and specific compounds, respectively. By virtue of atmospheric IED,

better-quality fractions are collected from high-boiling-point and perishable organics at a temperature lower than their boiling points. This innovative IED is expected to largely reduce the energy consumption of global chemical industries.

RESULTS AND DISCUSSION

Preparation and characterization of the rGO/SiO₂ membrane

The well-arranged rGO/SiO₂ membrane with aligned lamellar walls was prepared by a directional freeze-drying method [27,28], in which the flexible SiO₂ nanofibres with diameters of 300–400 nm were synthesized by an electrospinning method (Fig. 2a–c) [29]. As shown in Fig. 2d, a monolith rGO/SiO₂ membrane with a size of 0.5 m×0.4 m can be easily manufactured. Cross-sectional scanning electron microscopy (SEM) image shows the long-range vertically aligned lamellar walls of rGO/SiO₂ (Fig. 2e). During the directional freeze-drying process, one-dimensional (1D) flexible SiO₂ nanofibres are anchored on graphene sheets, assembling into the 2D aligned lamellar walls with tunable channel width from

Figure 1 Conceptual diagram. (a, b) Schematic representation of the TD process associated with thermally driven evaporation at the liquid/gas interface. (c) Illustration of the long-range, strong hydrogen bonding interactions in bulk water. (d, e) Schematic representation of the IED process using rGO/SiO₂ membrane with aligned lamellar walls as the evaporation medium layer, which is relevant to the surface-enlarged evaporation at the liquid/solid/gas interfaces with continuous heat supply. (f) The weakened hydrogen bonding interactions on rough rGO/SiO₂ wall surfaces for easy escape of water molecules with lower energy consumption.

Figure 2 Preparation and characterization. (a) GO solution is homogeneously mixed with SiO₂ nanofibres. (b) The GO/SiO₂ solution is subjected to directional freeze-casting to obtain the GO/SiO₂ hydrogel. (c) After freeze-drying and reduction under the vapor of hydrazine hydrate, the rGO/SiO₂ membrane with aligned lamellar walls is obtained. (d) Photograph of a large-scale rGO/SiO₂ membrane with a size of 0.5 m×0.4 m. (e) Cross-sectional SEM image of rGO/SiO₂ with long-range vertically aligned lamellar walls. (f) The 1D SiO₂ nanofibres are embedded in the 2D aligned lamellar walls, forming the firm bonding points. (g) Photographs of rGO/SiO₂ membrane subjected to the deformations of bending and twisting. (h) Stress-strain curves of rGO/SiO₂ at different set strains from 50% to 90% in water. (i) Cyclic stress-strain curves of rGO/SiO₂ (=80%) for 100 cycles in water.

60 to 150 μm (Fig. S1a–e). More significantly, the SiO₂ nanofibres are well interconnected with the aligned walls to form the strong bonding points, thus effectively endowing the main framework of rGO/SiO₂ membrane with mechanical stability (Fig. 2f) [30]. As a result, the rGO/SiO₂ membrane can be bent, twisted and even compressed to a large degree (Fig. 2g). The rGO/SiO₂ membrane is able to sustain a strain (ϵ) deformation of 90% and keep structural stability after 100 cycles at $\epsilon=80\%$ in water (Fig. 2h, i). For pure rGO and SiO₂ membranes prepared under the same conditions, irrecoverable deformations occurred at the set strain of 50% (Fig. S2a, b).

Performance of the IED

This robust rGO/SiO₂ membrane works as the evaporation intermediate layer on the liquid surface to induce the

formation of the liquid/solid/gas interfaces for highly efficient IED (Fig. S3). We first investigated the basic evaporation behavior for common solvents with different latent enthalpies of the liquid-vapor phase change (H_{LV}), saturated vapor pressure (P_V), boiling point (T_{bp}) and polarity (δ) at the ambient condition (temperature=25°C, relative humidity=70%), such as *N,N*-dimethylformamide (DMF), water, chlorobenzene, and ethanol [31]. The evaporation rate is defined by the Equation (1):

$$V = \Delta m / \rho t A, \quad (1)$$

where V (L m⁻² h⁻¹) is the evaporation rate, Δm is the loss of liquid, ρ (kg m⁻³) is the density, t (h) is the time of evaporation and A (m²) is the evaporation area. Impressively, by using rGO/SiO₂ membrane as the intermediate layer, all the average evaporation rates are 215%–412% times of those absent of intermediate layers

Figure 3 IED performance investigation. (a) Surface evaporation rates of various pure liquids in TD manner and IED mode using rGO/SiO₂ membrane at ambient condition with the temperature of 25°C and relative humidity of 70%. Inset percentages in (a) are the evaporation rate increases on rGO/SiO₂ membrane compared with pure liquid. (b) Water evaporation rates in TD and IED modes under different temperatures from 25 to 100°C. (c) Ethanol evaporation rates in TD and IED modes at temperatures from 25 to 78°C. (d) Evaporation rate increases of various pure liquids in IED manner, such as water, ethanol, and toluene in contrast with TD at their T_{bp} . (e) Energy and time saving of diverse pure solvents and compounds in the IED mode compared with TD to collect the same amount of products at T_{bp} .

(Fig. 3a). The evaporation rate increases for DMF, chlorobenzene and toluene are higher than other liquids, implying the negative impact of P_v , δ and H_{LV} (Table S1 and detailed analyses in Supplementary information) [32]. In this IED mode, the rGO/SiO₂ membrane remains stable in various organic matters for a few months (Fig. S4). The chemical stability of rGO/SiO₂ in IED for solvents (e.g., ethanol, ethyl acetate and DMF) was also verified by energy-dispersive X-ray spectrum (EDS) survey, Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) spectrum (Fig. S5 and the detailed analyses in SI).

These typical solvents and compounds including alkanes, alcohols, ketones and benzenes were tested with IED under different temperatures. The laboratory-built IED system includes a container, an electrical heating sleeve as the heating source, an electronic balance to

measure the mass loss and an electricity meter to record the energy consumption (Fig. S6). As temperature varies from 25°C to the corresponding T_{bp} , all the evaporation rates for different liquids in IED are much higher than that of TD (Fig. 3b, c), which also means that the IED will allow the effective product collection at a temperature lower than T_{bp} (dotted line in Fig. 3b, c). The interfacial temperature of the rGO/SiO₂ membrane is almost the same with the temperature of liquid body in the IED mode measured by thermometer (Fig. S7), and the average evaporation rates of diverse liquids in IED increase to 195%–312% compared with TD at T_{bp} (Fig. 3d). The largely accelerated evaporation rate in IED facilitates the faster fraction collection, as well as much less energy and time consumptions. To obtain the same yield of fractions at T_{bp} (Table S2), the IED can cut down the expenditure of energy for 40.6%–60.2% and save 48.9%–

67.9% period of time for the tested solvents and compounds (Fig. 3e). Note that the electricity consumptions of the TD and IED systems are carefully recorded to calculate the energy savings (see SI for detailed analyses).

Mechanism exploration

The highly efficient IED is mainly ascribed to the enlarged evaporation surfaces and weakened intermolecular forces at the liquid/solid/gas interfaces. Here we chose three representative solvents including water, ethanol and *n*-hexane as examples to explore the mechanism of IED. The optimized water transport channel width of the rGO/SiO₂ membrane is 120 μm defined by experimental tests (Fig. S8). The axisymmetric geometric COMSOL model is shown in Fig. 4a, where the phase field method was used to simulate the liquid transport behavior on the channels of rGO/SiO₂ membrane. The amphiphilic rGO/SiO₂ allowed liquid to transport along the aligned lamellar walls and induced the formation of liquid/solid/gas interfaces (Fig. S9). Only part of the channels were filled with liquid and most of the available air space between the aligned lamellar walls of rGO/SiO₂ membrane was effectively exposed for evaporation. In the COMSOL simulations,

the agglomerative state of water on the rGO/SiO₂ lamellar walls is larger than that of ethanol and *n*-hexane due to the stronger δ , which is also in accordance with the optical microscopy observations with larger amount of adsorptive water on the rGO/SiO₂ surface (Fig. 4b and Figs S10, S11).

On the other hand, the molecular dynamics (MD) simulation reveals the intermolecular force within liquid in TD and IED modes [33–38]. After equilibration at T_{bp} , the rGO/SiO₂ was hydrated and surrounded by liquid molecules (Fig. 4c and Figs S12–S14). The intermolecular energy of liquid ($E_{inter}(l)$), including hydrogen bonds, van der Waals force, and electrostatic energy, was defined by Equation (2) [36]:

$$E_{inter}(l) = \sum_{i < j} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}, \quad (2)$$

where ϵ_{ij} , σ_{ij} , r_{ij} and ϵ_0 are the Lennard-Jones (LJ) energy parameter, LJ size parameter, the distance between atoms i and j , and the vacuum permittivity, respectively. Benefiting from the enlarged rough evaporation surfaces and oxygen-containing functional groups of rGO/SiO₂, the

Figure 4 Mechanism exploration of IED. (a) COMSOL simulation results of water transport pathway in the channel of the rGO/SiO₂ membrane. The modeled structure is built according to the axisymmetric geometric principle with the optimized channel width of 120 μm. (b) Optical microscopy images of water on the rGO/SiO₂ membrane. (c) Snapshots of water, ethanol and *n*-hexane evaporation in the IED mode after equilibration at T_{bp} in the MD simulation. The IED shows enlarged evaporation surface. (d) The decreased intermolecular energy ($E_{inter}(l)$) of liquids on the rGO/SiO₂ surface in IED mode compared with bulk liquid in the TD system after equilibration in the MD. (e) The slopes (ΔS) of evaporation curves versus time for water, ethanol and *n*-hexane vapor molecules in TD and IED modes after equilibration at T_{bp} in the MD simulations, respectively. $\Delta S1$ and $\Delta S2$ are named for bulk liquid in TD and liquid on the rGO/SiO₂ membrane in the IED mode.

consecutive network of the intermolecular forces in liquid on rGO/SiO₂ is disturbed and the r_{ij} of the molecules on rGO/SiO₂ surface is increased [5,39,40], resulting in the decreased intermolecular energy (Fig. 4d). Especially for water with strong hydrogen bonding interactions, the number of hydrogen bonds in bulk water is 2.49 times as high as that of water on the rGO/SiO₂ membrane (Fig. S15). The H_{LV} of liquid is mainly related to the intermolecular energy, which is written as Equation (3) [15,36]:

$$H_{LV} = -E_{\text{inter}}(1) + Nk_{\text{B}}T, \quad (3)$$

where N is the number of liquid molecules and k_{B} is the Boltzmann constant. Consequently, the decreased intermolecular energy of liquids on the rGO/SiO₂ surface induces reduced H_{LV} compared with bulk liquid. As demonstrated in differential scanning calorimetry (DSC), the H_{LV} of liquids on rGO/SiO₂ was lower than that of bulk liquids for water, ethanol and *n*-hexane, respectively (Table S3), promoting fast liquid evaporation in the IED mode. In the MD simulation (Movies S2–S7), the slopes of evaporation curves *versus* time indicate the evaporation rates named as $\Delta S1$ and $\Delta S2$ for bulk liquid in TD and liquid on the rGO/SiO₂ membrane in the IED mode (Fig. S16). Notably, water on the rGO/SiO₂ surface possesses higher agglomerative state and stronger intermolecular force compared with ethanol and *n*-hexane. After equilibration at T_{bp} , the $\Delta S2$ in IED is 185%, 211% and 294% times of $\Delta S1$ in TD mode (Fig. 4e), respectively, demonstrating similar increase trend with the experimental results.

In the IED system, the well-arranged rGO/SiO₂ membrane with aligned lamellar walls works as the macroporous intermediate layer on liquid surface for accelerated evaporation. The rGO/SiO₂ is rich in oxygen-containing functional groups [41] and favorable for liquid spreading to form the enlarged liquid/solid/gas interfaces, in which the intermolecular forces cannot persist to the extent as found in bulk liquid [42,43]. Optical microscopy images of DMF, toluene and ethyl acetate reveal the similar enlarged evaporation surface on the rGO/SiO₂ membrane (Fig. S17), and the corresponding evaporation rates in IED are 203%–308% as high as that in TD mode (Fig. 3d). The enlarged evaporation surface and weakened intermolecular forces at the liquid/solid/gas interfaces function together to accelerate the evaporation in IED. By contrast, the cellular-structured rGO/SiO₂ film was measured in IED with a lower evaporation rate than that of the rGO/SiO₂ membrane with vertically aligned lamellar walls (Fig. S18a) [44]. The vapor escape route was

blocked on the cellular-structured rGO/SiO₂ film as shown in the optical microscopy observation (Fig. S18b, c). Similarly, the IED performance by using the well-arranged rGO/SiO₂ membrane is better than that of other porous materials with cellular or layer-by-layer structures, such as polyimide (PI) film, carbonized polyurethane (PU) foam and rGO film (Fig. S19).

Separation and purification of liquid mixtures

The IED system was then investigated to separate and purify liquid mixtures with different T_{bp} , such as polar mixtures (e.g., ethanol/water, water/DMF, and 1,4-dioxane/chlorobenzene), high-boiling-point solutions (e.g., DMF/dimethyl sulfoxide (DMSO), DMSO/*N,N*-dimethyl formamide (NMP), and ethylene glycol/NMP) and perishable organics (e.g., ethyl acetoacetate/DMSO and partially oxidized aniline) for fast fraction collection. We designed an open IED apparatus (250 mL) that allowed the rGO/SiO₂ intermediate layer (diameter=70 mm, thickness=2 mm) standing above the liquid surface (Fig. 5a and Fig. S20). As expected, at the steam temperature of T_{bp} , the IED exhibited evaporation rates about 187%–284% as high as TD for fraction collection from all the mixtures (Fig. 5b and Fig. S21a, b). The resulting energy and time saving for the separation and purification mixtures in IED at T_{bp} are 40.6%–57.2% and 46.0%–64.8%, respectively (Fig. S21c and Table S4). This effective IED based on the well-arranged rGO/SiO₂ membrane indeed enables fast distillation with much less energy and time.

Remarkably, at a steam temperature lower than their T_{bp} in IED, there is the same amount of fraction collection with an 11–39°C temperature decrease compared with TD (Fig. 5c, d and Fig. S22). The saturated vapor pressure (P_{V}) at different temperatures was defined by the Clausius-Clapeyron equation, which is written as [5]:

$$\frac{d \ln P_{\text{V}}}{d(1/T)} = \frac{-H_{LV}}{RZ_{LV}}, \quad (4)$$

where R is the universal gas constant (8.314 J K^{−1} mol^{−1}), and Z_{LV} is the compressibility factor difference between saturated vapor and liquid. In Equation (4), Z_{LV} can be approximated as a constant for the same liquid and the P_{V} is mainly influenced by H_{LV} . The latent enthalpies of the liquid-vapor phase change of pure liquid and liquid on rGO/SiO₂ are named as H_{LV1} and H_{LV2} , respectively. In the IED mode, the weakened intermolecular force of liquids on the rGO/SiO₂ membrane induces the reduced H_{LV2} . As shown in the DSC measurement, the H_{LV2} in IED is 7%–29% lower than H_{LV1} in TD for the tested

Figure 5 IED for the separation and purification of liquid mixtures. (a) Laboratory-built IED system using the rGO/SiO₂ membrane as the evaporation medium layer on liquid surface and electrical heating sleeve as the heater. (b) The water yield in TD and IED from the water/DMF mixture (4:1, v/v). (c, d) The DMF and aniline yield fractions from high-boiling-point solutions (DMF/DMSO, 4:1, v/v) and partially oxidized aniline reagent by TD and IED under different temperatures. (e) The content of the targeted solvents and compounds in original liquid mixtures, and the collected fractions by TD at T_{bp} and IED at temperature lower than T_{bp} , respectively. Expect for partially oxidized aniline solution, the volume ratio of the liquid mixture (m/n) is 4:1, where m is the targeted substance and n is the other solvent. (f) Energy saving for separation and purification of various liquids in IED at the temperature lower than their T_{bp} when compared with TD. (g) The scaling up IED system of 0.4 m×0.4 m×1.3 m. (h) The ethanol yields by TD and IED from ethanol/water mixture (4:1, v/v) in the large scale IED system at T_{bp} (78°C).

liquids, such as ethanol, water, 1,4-dioxane, and DMF (Fig. S22 and Table S5). According to Equation (4), the reduced H_{LV2} will largely increase the P_V on the rGO/SiO₂ surface in IED compared with TD, which also mean that at a temperature lower than their T_{bp} in the TD mode, the P_V in the IED system can reach to the value close to the atmospheric pressure, thus realizing the low temperature fraction collection (Fig. S23).

This low-temperature IED presents great potential for high-quality fraction production with much less energy

consumption, especially for the separation and purification of high- T_{bp} liquid mixture and perishable organics. For example, the collection of ethyl acetoacetate or aniline by IED is at the steam temperature of 137 or 145°C, which are 43 and 39°C lower than their T_{bp} in TD system of 180 and 184°C, respectively. As a result, the purity of ethyl acetoacetate or aniline in IED is 97.6% and 98.4%, much higher than that in TD with the value of 90.3% and 92.8% confirmed by gas chromatography (Fig. 5e and Figs S24, S25). Moreover, the purity of other products

collected at the temperature lower than T_{bp} in IED also exhibits comparable purity with TD mode (Figs S26–S31). This low-temperature and highly efficient IED do a favour to save ca. 10.9%–30.8% energy consumption for all of the mixture distillation (Fig. 5f). More importantly, the fraction collection at a temperature lower than T_{bp} in the IED system also shows the importance to reduce heat loss, improve energy conversion efficiency, as well as cut down the cost of equipment investment. Notably, the rGO/SiO₂ membrane presents excellent mechanical property in liquid. After long-term cyclic tests, it can still maintain structural stability in organic media (Fig. S32).

The scaled-up IED system was also manufactured to demonstrate the feasibility for high output of product from the ethanol/water mixtures (4:1, v/v). The rGO/SiO₂ membrane with the diameter of 0.35 m was used with the initial liquids of 65 L in the open distillation reactor (Fig. 5g). Under continuous condensation, ca. 44.7 L m⁻² ethanol was obtained within 5 h in the IED system at the steam temperature of 78°C, about 2.1 times of that in TD with the output of ca. 21.1 L m⁻² (Fig. 5h), well proving the effectiveness and durability of IED in large scale for the separation of liquid mixtures.

CONCLUSIONS

In summary, we demonstrated an efficient IED by using the well-arranged rGO/SiO₂ membrane as the evaporation intermediate layer on the liquid surface. Unlike TD model, the IED takes full use of enlarged evaporation surfaces and weakened intermolecular forces on the liquid/solid/gas interfaces, thus accelerating about 200%–300% evaporation rates of diverse solvents and compounds. The concomitant energy and time consumption in the IED system can be decreased by up to about 60% and 70%, respectively. More importantly, the developed IED system realizes the production of better quality for high-boiling-point and perishable organics at a temperature lower than their T_{bp} . Such efficiently and widely applicable IED strategy shows great potential to boost the development of other distillation systems, such as rectification, flash distillation or multistage distillation processes with great global merits of energy and time savings.

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Author contributions Qu L and Zhang P designed the experiments; Zhang P, Liao Q, Yao H and Wang D performed the experiments; Xu Q, Ma T and Liao Q conducted the computational studies; Cheng H, Li C, Yao H and Geng H gave advice on experiments; Qu L supervised the entire project. All authors discussed the results and reviewed the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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基于排列有序石墨烯膜材料的界面增强蒸馏

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摘要 用于化学工业中液体分离和纯化的传统蒸馏是一种高能耗、低效率的方法。本文制备了排列有序的石墨烯膜材料作为液体表面的蒸发层用于界面增强蒸馏。该界面增强蒸馏增大了蒸发面积, 削弱了溶液中分子在石墨烯膜材料表面(液/固/气界面)的分子间作用力, 从而可加快蒸发速率, 降低能耗, 节约时间, 甚至实现了低于沸点温度下馏分的收集。