1. Introduction

Amphiphiles substances are substances with a hydrophilic group at one end and a hydrophobic group at the other end, such as fatty acids, fatty alcohols, fatty amines, and fatty aldehydes. On the one hand, these substances are widely present in nature. For example, fatty acids can be obtained in large quantities from the plants which are renewable or generated from the life activity of microorganisms. On the other hand, they are also synthesized in large quantities in industries. It was reported that their use has been growing since the 1980s, from the 1.7 million tons used in 1984 and the 15.93 million tons used in 2014 to the expected 24.19 million tons used in 2022. The global annual output is growing fast at a rate of 4–5%. For example, the world market for only detergent alcohols exceeds 2.7 million tons with an annual average growth rate of 3.7% predicted for 2021. Due to their amphiphilic characteristics, these substances are widely used in various fields such as daily chemical, textile, mining, and paper industries. After their use, thousands of tons of surfactants are directly discharged into water bodies. Their concentration at the air–water interface is much higher than that of the bulk phase due to the interfacial concentration effect and further causes adverse effects on the ecosystem. For example, concentrated fatty acids and fatty amines are able to acidify or alkalize the water body locally and even cause deterioration of the water body. Moreover, the concentrated amphiphilic substances enable enriching of highly toxic substances such as phenols, cyanides and heavy metals at the air–water interface or changing their reaction pathways to produce more toxic intermediates in water, thus posing higher risk to the environment. Most importantly, these interfacial amphiphiles have been reported to release volatile organic compounds (VOCs) under sunlight irradiation, leading to wider air pollution and global climate change. In regard to these problems, various technologies especially for the oxidation methods including UV irradiation, ozonation and advanced
oxidation processes (AOPs) generated by hydroxy radicals (·OH) have been developed to remove this type of organic waste;\textsuperscript{5,16,17} the products of these oxidation procedures are human-benign but worthless. Therefore, some resource-based methods have received increasing attention. For example, physical methods such as adsorption and air flotation have been used to recover these substances.\textsuperscript{17,18} However, it is still difficult to efficiently separate the products, since the properties of amphiphilic substances are maintained during the process of recycling and they remain mixed with other substances or impurities in the same phase. Other resource conversion technologies, such as chemical catalysis\textsuperscript{19–22} enzyme catalysis,\textsuperscript{23–25} photo-enzyme catalysis\textsuperscript{24,26} and photocatalysis,\textsuperscript{27,28} can change the properties of the products to be significantly different from those of the starting chemicals, and therefore may promote the possibility of effective separation. The encountered problem is that the related systems usually use organic solvents as the reaction media to make the resulting products directly dissolve in the solvent, so that the formed homogeneous system requires tedious, difficult and high-cost posttreatment.

In contrast, the widely existing air–water interface is considered as a new promising catalytic conversion venue due to its inherent advantages of the solvation effect, concentration effect and easy separation of generated products from the interface.\textsuperscript{29–31} The catalytic conversion occurs independent of any catalysts under the environmental conditions.\textsuperscript{7} In our previous work, we have found that the amphiphilic substance at the gas–water interface can undergo effective resource conversion upon photoinitiation from liquid to gaseous hydrocarbons\textsuperscript{28} and solid fluorescent nanomaterials (FNs),\textsuperscript{32,33} respectively. Here, value-added hydrocarbons are commonly used for fuels and basic chemical raw materials, including the precursors of masks, protective clothing, lubricants, detergents and polymer materials.\textsuperscript{23,34,35} FNs, owing to their attractive optical properties, small size, low cost, and biocompatibility,\textsuperscript{36} have emerged as promising materials that are applied in cell imaging,\textsuperscript{17–19} analyte detection,\textsuperscript{40,41} and light-emitting devices.\textsuperscript{12} Despite some achievements, the mechanism of how to achieve efficient automatic separation of the converted resource products has not yet been explored. This understanding plays a crucial role in regulating the products and promoting the technology to the industrial scale. Meanwhile, whether the photochemical behavior of other substances with different parent structures has similar or different resource conversion behaviors needs to be further explored.

With these problems, in this work, four representative amphiphiles including nonanol, nonanal, NA and nonyl amine were firstly dispersed in water, respectively, and they automatically gathered at the air–water interface due to the interfacial concentration effect.\textsuperscript{4} To our surprise, all four model amphiphiles selected showed strong reactivity under interfacial photochemistry. After photoradiation ($\lambda > 254$ nm) for 2 hours, their accumulative gaseous products were collected using a micro-syringe and analyzed by GC-MS. The results showed that their gaseous products were mainly composed of alkanes, linear alpha-olefins (LAOs) and nonanal (Fig. 1a and Fig. S2†), but their selectivity was different. Specifically, the gas products from nonanol showed selectivity of up to 99% for olefins and 1% for alkanes; the gas products from nonyl amine showed selectivity of up to 50% for olefins and 50% for alkanes; the gas products from NA showed selectivity of up to 86% for alkenes, 2% for alkanes and 12% for other substances; and the gas from nonyl amine showed selectivity of up to 66% for alkanes, 33% for olefins, and 1% for other gases (Fig. 1c). The difference in selectivity could be attributed to their different photochemical pathways caused by their different functional groups. The details will be further discussed in the mechanism section later. The selectivity for olefins is outstanding, following the trend of nonanol (99%) > NA (86%) > nonyl amine (66%) > nonanal (50%). In particular, the selectivity of the first two is much higher than that of previous olefins obtained under harsh or complex conditions, which often involved expensive catalysts or high-temperature and high-pressure environments.\textsuperscript{29,43} This indicates a good application prospect of the technology based on the air–water interface. It is worth mentioning that the selectivity for the production of olefins via the decarboxylation route of fatty acids is relatively low because of the more favorable decarboxylation pathway.\textsuperscript{29} Obviously, the method based on interfacial photochemistry can overcome this difficulty well. Furthermore, Fig. 1b shows that the gas yield per unit concentration (/mM) followed the trend of nonanal > nonyl amine > NA > nonanol. This trend may be related to their photochemi-
cal activity. As known, optical excitation energy including vertical excitation energy (VEE) and adiabatic excitation energy (AEE) is an effective indicator for photochemical activity and can be calculated by DFT. Smaller optical excitation energy indicates higher photoactivity and thus higher gas yield. According to our DFT calculations for the first VEE and AEE, and excitation energy from S₀ to T₁ (TEE) of the four amphiphiles, their photoactivity followed the same trend of nonanal > NA > nonyl amine > nonanol (Fig. 1d, Fig. S12 and Table S1†). This trend was consistent with that of both the conversion rate (Fig. 1e) and absorption efficiency for light (λ > 254 nm, Fig. S3†), demonstrating the rationality and accuracy.
of our DFT calculations. Therefore, the difference in their photoactivity basically explains the trend of their gas production. We note that NA is more photoactive than nonyl amine, but shows a lower gas production. This is because in addition to the shared nonanal-mediated pathways, nonyl amine is able to produce gas directly (Fig. 1f; more details will be provided in the mechanism section later). Additionally, nonanal with the highest photochemical activity was detected in nonanol, nonyl amine and NA-involved systems, indicating that nonanal is a key intermediate for the further production of high value-added alkenes and alkanes.

Based on the above analysis and combined with literature reports,\textsuperscript{4,30} we proposed the possible mechanism of photochemical resource conversion of the four amphiphiles to value-added gaseous products (Fig. 1f). Some key reactions were verified by DFT calculations (Table S2\textsuperscript{†}). The results show that all these four precursors produce value-added products i.e., olefins and/or alkanes (products 3–6, abbreviated as P3–6) through the generation of the key intermediate nonanal first and followed by its photocleavage reactions of Norrish type I and II. To be more specific, nonanol was transformed into nonanal (P1) by oxidation of O\textsubscript{2} apart from the directly absorbed light for the reaction owing to its relatively low photoactivity. This oxidation process is supported by DFT calculations (\(\Delta G = -561.14 \text{ kJ mol}^{-1}\)). The generated nonanal acts as a photosensitizer\textsuperscript{31} to undergo the hydrogen abstraction reaction with one nonanol (\(\Delta G = -41.53 \text{ kJ mol}^{-1}\)) and further generates two nonanol \(\alpha\)-carbon free radicals (\(\Delta G = -117.24 \text{ kJ mol}^{-1}\)). These carbon free radicals undergo addition with oxygen and then undergo pyrolysis with a bond dissociation energy of 9.21 kJ mol\textsuperscript{-1} to generate two nonanal and \(\cdot\text{OH}\), possibly followed by the production of \(\text{H}_2\text{O}_2\) by \(\cdot\text{OH}\) recombination (Fig. S5\textsuperscript{†}). The generation route of \(\cdot\text{OH}\) was further clarified by ESR, presenting the typical 1:2:2:1 quartet lines after capture by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) (Fig. S4\textsuperscript{†}). Therefore, the yield of nonanal could be increased with prolonged illumination time. For the concentrated NA at the air–water interface, it was converted into nonanal (P1) by direct photocleavage into \(\cdot\text{OH}\) and nonyl radicals after NA was excited to NA* upon photoirradiation, and then nonanal underwent Norrish type II reaction to give rise to linear alpha-olefins (LAOs) C\textsubscript{7–9}-LAO. Additionally, NA was also able to produce olefins directly.\textsuperscript{30} The existing two reaction pathways render the selectivity (86\%) of olefins obtained from NA higher than that of pure nonanal (50\%). For the concentrated nonyl amine at the air–water interface, it can effectively absorb the light provided according to its UV-vis spectrum (Fig. S3\textsuperscript{†}), and then be excited to the excited state. The excited nonyl amine* underwent photolysis of the C–N bond to produce the nonane free radical (P7). The photocleavage energy of this reaction is 303.02 kJ mol\textsuperscript{-1}, which can be provided by our light (<471.04 kJ mol\textsuperscript{-1}, calculated by \(E = 1240/\lambda, \lambda > 254 \text{ nm}\), and then the nonane free radical underwent reox reactions to give rise to nonanal (P1)\textsuperscript{30} (more details can be found in Fig. S5\textsuperscript{†}). Meanwhile, the nonane free radical would undergo further C–H homolysis (photocleavage energy calculated to be 374 kJ mol\textsuperscript{-1}) to produce the nonane biradical (P9), which then self-coupled into C\textsubscript{9}-LAO (P10, Fig. 1a). These multiple processes for the hydrocarbons resulted in a gas yield from nonyl amine higher than that of NA, even though it possesses lower photoactivity than NA. Overall, nonanal acts as a key intermediate for the conversion of four substances containing different functional groups into value-added hydrocarbons under interfacial photochemistry. Functional groups are the key factors affecting the photochemical activity (\(\cdot\text{CHO} > \cdot\text{COOH} > \cdot\text{NH}_2 > \cdot\text{OH}\)), which leads to the difference in the amount of the intermediate nonanal produced. The cumulative amount and selectivity of gaseous products were determined by both the yield of nonanal and photolysis pathway of the surfactants.

Finally, considering the coexistence of various surfactants in real environments, we added the four surfactants into one quartz cell, called a mixed system, with a total volume ratio of 1% (v/v), which is the same as the individual surfactants. The GC-MS results (Fig. S8a\textsuperscript{†}) showed that the gas products of the mixed system are still C\textsubscript{4}–C\textsubscript{8} olefins and C\textsubscript{7}–C\textsubscript{9} alkanes, and its total gas production is second only to the highest nonanal. This result suggested that the technology of interfacial light conversion also shows strong applicability in complex mixed systems, demonstrating strong application potential.

2.2 Photoconverting different amphiphiles into liquid double-tailed surfactants

After analyzing the value-added gaseous products from amphiphiles under interfacial photoirradiation, their corresponding liquid products were identified by GC-MS. Results show that 8-heptadecanol (P15) was detected in all the amphiphiles (Fig. 2a), which means these different amphiphiles underwent the same photochemical pathway. Apart from 8-heptadecanol, C\textsubscript{16}–alkane (P18) and 8-heptadecane (P19), the NA–NA dimer (P21) and 9-octadecylamine (P24) were respectively detected from nonanal, NA and nonyl amine-containing systems. Therefore, their possible mechanisms were proposed as follows (Fig. 2b): first, all amphiphiles produced nonanal after photoirradiation followed by generating the C\textsubscript{8}–octane radical (P11) through the Norrish type I reaction. Then, the C\textsubscript{8}–octane radical further coupled with \(\cdot\text{OH}\) to form octanol (P13). The formed octanol, similar to nonanol, suffered hydrogen abstraction from the excited nonanal to generated the octanol radical (P14), which then coupled with the produced C\textsubscript{9}–octane radical to form 8-heptadecanol at the air–water interface. For the concentrated nonanal at the interface, it moved to an excited state after light absorption. Subsequently, it underwent two possible ways of photocleavage to produce the nonanal radical (P16) and C\textsubscript{9}–octane radical. Due to the interfacial concentration effect, both of them would form C\textsubscript{16}–alkane (P18) and 8-heptadecane (P19) through self-coupling and cross-coupling, respectively; for the concentrated NA, it became an excited NA* upon photoirradiation.\textsuperscript{4,32,44} Acting as a photosensitizer, NA* directly underwent the hydrogen abstraction reaction with ground NA to generate NA free radicals (P20). Due to the high concentration at the interface, these radicals directly underwent self-coupling into a double-tailed surfactant – the NA–NA
dimer (P21); for the concentrated nonyl amine, it could be excited according to the obvious overlap between its UV-vis absorption spectra and the light provided (Fig. S3†).

Afterwards, the excited nonyl amine underwent C–N and C–H photolysis to form nonane radical (P23) and nonyl amine radical (P22), respectively, and followed by the formation of 9-octadecylamine (P24) through cross-coupling. Overall, the formation of double-tailed surfactants produced by light-induced radical coupling mainly results from the concentration effect of the air–water interface, since it concentrates the generated free radicals at the interface and greatly increases the probability of collision between each other.14,45,46 Due to the better performance of the obtained double-tailed surfactants such as lower critical micelle concentration (CMC) value,45 it showcases higher practical value in oil displacement, soil remediation and other fields,32 so as to successfully achieve the goal of waste-to-resource conversion. Overall, the four amphiphiles can generate double-tailed surfactants with higher value through self-coupling and cross-coupling of intermediate radicals. In this work, the two-tailed surfactants in situ formed the vesicle microreactor, offering a unique site for further conversion of intermediates to solid products.

2.3 Photoconverting different amphiphiles into solid fluorescent nanomaterials

After identification of gaseous and liquid products, solid products were verified by MS firstly. Different from the result before illumination, the three amphiphiles excluding nonanol presented typical cluster peaks after illumination (Fig. 3a). This possibly meant the formation of FNs.33 Furthermore, TEM was employed to observe their morphologies. The results showed that no particles were observed in the nonanol-containing system after irradiation, while the solid products from both nonanal and nonyl amine after irradiation displayed the traditional spherical appearance. Their diameters were 4.42 and 4.35 nm, respectively and showed amorphous morphologies. This finding was in line with MS results. After dispersing in ethanol solution and exposed to a UV 365 nm lamp, the solid products from nonanal and nonyl amine presented bright blue fluorescence. All these results demonstrated that the solid products were FNs, which was highly consistent with previous literature reports.32,47,48 Similar with our reported NA system,32 white vesicles were also observed in the aqueous solution of nonanal and nonyl amine upon photoirradiation (Fig. S7†). This suggested that FNs obtained from nonanal and

![Fig. 2 Analysis of liquid products obtained from different amphiphiles under air–water interfacial photoirradiation: (a) identification of liquid products; (b) the mechanism of converting amphiphiles into value-added double-tailed surfactants.](image-url)
nonyl amine should be formed by a similar photo-polymerization and self-assembly (PISA) approach as that of NA.\textsuperscript{32} These findings highly demonstrated that amphiphiles can be photoconverted to widely used FNs. It is worth noting that the absolute fluorescence quantum yield (AFQY) is an important parameter of FNs in practical applications. Since nitrogen can effectively inhibit non-radiative transitions, FNs obtained from nonyl amine theoretically possess the highest AFQY. As expected, the AFQY of FNs reached as high as 44.35\%, which was about 15 folds higher than that of NA (2.80\%) and even higher than that of nitrogen-doped FNs obtained from harsh reaction conditions.\textsuperscript{49–51} This indicates that photoconverting N-containing surfactants will have great practical application value. Overall, except nonanol with the lowest photoactivity, the other three amphiphiles can generate value-added FNs through PISA in the microreactor of vesicles, which provides nanoconfined and reduction effects.\textsuperscript{33,36} Among them, the FNs obtained from nitrogen-containing precursors exhibit superior fluorescence performance. Surprisingly, more FNs were formed in the mixed system compared to that in the individual system (Fig. S8b†), indicated by the darker yellow color showing under room light and fluorescence quenching effects\textsuperscript{52} under 365 nm UV light. The phenomenon illustrated the existing significant synergistic effect among the four surfactants, and the related synergistic mechanism is worth further study in the future.

2.4 Shared mechanism and principal differences of the easily separable value-added products and their regulation

Based on the aforementioned discussion, all four types of amphiphiles could be photoconverted into gaseous, liquid and solid value-added energy substances and functional nano-
materials at the air–water interface. In particular, gaseous olefins and/or alkanes were produced through the generation of the key intermediate nonanal from amphiphiles followed by its photolysis reactions of Norrish type I and II; liquid double-tailed surfactants are generated by photoinduced free radicals coupling at the air–water interface; FNs are formed by PISA aided by the vesicle microreactor, which is formed by the double-tailed surfactants (Fig. 4a).

To reveal the efficient separation mechanism of interface light-induced products, Henry’s constant ($H^P$) and dipole moment were firstly calculated to explain the highly separable products generated in the gas–liquid two phases. In detail, $H^P$ is defined as the proportionality factor of compounds between the air and liquid. This constant can well describe the distribution ability i.e. separation coefficient of compounds in the gas–liquid two-phase systems. A lower $H^P$ value means that the substance possesses a higher ability to allocate to the gas phase. The dipole moment refers to the product of the magnitude of the charge and the distance between the centres of positive–negative charges. It is a physical quantity that

![Image](https://example.com/image.png)

**Fig. 4** (a) Shared mechanism and principal differences of photoconverting different amphiphiles into gas–liquid–solid three-phase products by cross-media transformation (the larger values represent their higher propensity); Henry’s constant, dipole moment and photoactivity of (b) amphiphiles and (c) their products calculated by DFT; mass flow analysis of (d) amphiphiles to gaseous and solid and (e) their distribution of the gas category (the labeled values and the thickness of the lines indicate their degree of propensity). The effect of system pH on the (f) yield and selectivity of gaseous products from (g) nonanal and (h) nonyl amine after photoirradiation for 2 h.
measures the polarity of a molecule. A lower dipole moment value usually indicates a weaker interaction force with polar water molecules, thus promoting their distribution towards the gas phase. Results show that the Henry’s constants of the gas products (C₆₋C₁₀-LAOs and C₆₋C₁₀-alkanes) was distributed between 10⁻⁴ and 10⁻² mol m⁻³ Pa⁻¹ (Fig. 4c III). Such values were far lower than that of their parent substances (10⁻¹⁻¹⁰⁶ mol m⁻³ Pa⁻¹, Fig. 4b). The considerable differences make the product easy to separate automatically. This trend was highly in line with the results calculated by the COSMOthermX software (Fig. S9†). Also, the dipole moments (<1 Debye) of gaseous olefins (Fig. 4c III) and alkanes is far less than that of their parents (2–6 Debye, Fig. 4b), indicating the significantly reduced polarity and water solubility.53 Secondly, in addition to these changes of the two constants, the unique gas–water interface also plays an important role in the efficient separation of gas products. This is attributed to the interface reaction venue with water molecules only on the one side and gas atmosphere on the other side. If gas molecules are generated at the interface, only one side of the material produced at the interface is likely to be bound by water molecules, making the binding force far less than when it is bound by water in all directions in the bulk phase. Therefore, the two-dimensional air–water interface can considerably facilitate the escape of gaseous substances into the gas atmosphere. In summary, the abovementioned considerably lower HF₃, lower dipole moment of products compared to their parents and the presence of the air–water interface collectively explain the reason for the transformation of these products into the gas phase automatically.

Meanwhile, Henry’s constant of the double-tailed surfactants was spread in the range of 2.84 × 10⁻¹⁻3.83 × 10², which was 1–6 orders of magnitude higher than that of the gas products, and their large dipole moment (2–5 Debye) elucidated their distribution in the liquid phase (Fig. 4c II). Compared to the gaseous hydrocarbons, the formation of hydrogen between the heteroatom (N/O)-containing functional groups contained in the liquid products and water increased their solubility in water.

To quantify the conversion propensity of the four types of amphiphiles, gas–solid two-phase material flow analysis was performed. Specifically, as shown in Fig. 4d, their propensity towards the gas phase followed the trend nonanal (7.9) > nonyl amine (0.48) > NA (0.183) > nonanol (0.1). Specifically, nonanol and NA were inclined to produce olefins while nonyl amine was inclined to generate alkanes (Fig. 4e). Nonanal was inclined to generate alkanes (Fig. 4e). Nonanal was nonanol and NA were inclined to produce olefins while nonyl amine mainly presented in the form of nonyl amine (C₉-NH₃⁺) under alkaline conditions, while nonyl amine mainly presented in the form of nonyl amine cations (C₉-NH₃⁺) under acidic conditions (Fig. S13†). Based on this, it was initially speculated that their ionic forms possessed higher photoactivity, leading to higher gas production. However, this speculation was not supported by the DFT calculations,56 NA mainly existed in the form of NA anions (C₈-COO⁻) under alkaline conditions, while nonyl amine mainly presented in the form of nonyl amine cations (C₉-NH₃⁺) under acidic conditions (Fig. S13†). Based on this, it was initially speculated that their ionic forms possessed higher photoactivity, leading to higher gas production.

Among the gas–liquid–solid three-phase products, the gaseous products can be quickly and automatically separated, which is attributed to their lower Henry’s constant, lower dipole moment and the presence of the unique air–water interface, and also the high selectivity. These advantages place the technology close to possible practical application. To achieve their regulation, we further investigate the effects of the system photosensitizer and pH on gas yield and selectivity. Nonanal and nonyl amine with the highest total gas production were selected as the model surfactants. As shown in Fig. S10†, humic acid only slightly enhanced the gas production of the NA system and even inhibited the gas production from nonanal and nonyl amine upon interfacial illumination. In particular, NA enriched humic acid with higher photoactivity at the air–water interface,44 and thus excited humic acid could much more effectively photosensitize NA than NA* to promote gas production; for nonanal, humic acid inhibited nonanal gas production due to the competitive absorption of light with the highly photoactive nonanal; for nonyl amine, humic acid and nonyl amine underwent acid–base neutralization to greatly reduce the interfacial nonyl amine, resulting in a reduction of gas production to about 30% (Fig. S10a†). In addition, humic acid has a limited effect on the selectivity of gas products (Fig. S10b†). As a comparison, pH has a great impact on the gas production and selectivity. Firstly, in term of total gas production, upon adjusting the pH from acidic to alkaline (from 3 to 11), the gas production from nonanal increased while the gas production from nonyl amine decreased apparently (Fig. 4f). The opposite trend may be highly related to the morphologies of the two surfactants in different pH distributions. Note that nonanal is easily oxidized to NA in water upon photoirradiation (Fig. S11†). The trend of pH values in nonanal solution being consistent with that in NA solution also supported this conclusion (Fig. S12†). In that case, the –COOH functional group is more sensitive to pH due to its high dissociation capacity compared to –CHO. Therefore, the effect of pH on the nonanal system is mainly demonstrated by affecting the morphology of the formed NA. According to the CurTiPot software calculations,56 NA mainly existed in the form of NA anions (C₈-COO⁻) under alkaline conditions, while nonyl amine mainly presented in the form of nonyl amine cations (C₉-NH₃⁺) under acidic conditions (Fig. S13†). Based on this, it was initially speculated that their ionic forms possessed higher photoactivity, leading to higher gas production. However, this speculation was not supported by the DFT calculations, because first vertical excitation energy of the NA anion (C₈-COO⁻) and nonyl amine cation (C₉-NH₃⁺) were 6.1659 eV and 8.896 eV, respectively, and both higher than that of neutral NA (5.8032 eV, C₈-COOH) and neutral nonyl amine (6.949 eV, C₉-NH₃) (Fig. S14†). Other plausible reasons should be further explored. According to the literature,57 the solubility of NA anions and nonyl amine cations in water is higher than in their neutral molecular states, which causes the molecular layer of NA and nonyl amine molecules to be thinner at the air–water interface. This state maximizes the numbers of the hydrogen bond between interfacial surfactants and the water molecules to decrease their reaction activation energy barrier under photolysis,8,10 thereby promoting gas production.
Apart from the regulation of gas production, the selectivity of gaseous products can be further optimized by adjusting pH. When adjusting the pH from alkaline to acidic conditions, the selectivity of olefins from the nonanalsystem increased from 60–70% (Fig. 4g); however, on adjusting the pH from both alkaline and acidic to neutral conditions, the selectivity of alkane from nonyl amine increased from 60–70% to about 80% (Fig. 4h). According to our proposed mechanism (Fig. 1f), the generation of alkanes is controlled by the Norrish type I reaction, while olefins are controlled by the Norrish type II reaction. Therefore, the selectivity of gas products regulated by pH may be achieved by manipulating the proportion of the Norrish type reaction. Altogether from the above discussion, we can say that desirable yield and selectivity of the gaseous products from the amphiphiles can be realized by simply adjusting the system pH.

2.5 Preliminary economic assessment

Since fatty acids are the most widely and easily obtained raw materials among the four amphiphiles,\(^{12,58,59}\) we conducted a preliminary economic evaluation on the laboratory scale based on NA. In the economic evaluation, we selected 1 ton of NA wastewater for the generation of C₇-LAO as the basis of calculation. Its costs mainly included key reagent cost and energy cost that was calculated based on the electricity used. The unit price is mainly determined based on the average value of market price, and all the data involved in the calculation came from our experiments and literature studies.\(^{4,12,60–64}\) Compared to the operating cost of conventional chemical heterogeneous catalysis (\(1144.3–1500\) \$ per m\(^3\)) and chemical homogeneous catalysis (\(1658.6–1731.5\) \$ per m\(^3\)) and enzymatic catalysis (\(>9890\) \$ per m\(^3\)), the cost of air–water interfacial photoirradiation ranges from 511.14 to 800 \$ per m\(^3\) (Table S3†), showing an overwhelming economic advantage. This result indicated that the methodology could be much more promising for industrial applications in the future.

3. Experimental methods

3.1 Chemicals

Nonanol (98%) and nonanal (98%) were purchased from Aladdin. NA (≥97.5%) was provided by Sinopharm Chemical Reagent Co., Ltd. Nonyl amine (99%) was obtained from J&K Scientific. Dichloromethane (DCM), chloroform and triethylamine were obtained from Thermo Fisher Scientific Co., Ltd (HPLC grade). Potassium permanganate, ethanol, and petroleum ether were obtained from Beijing Chemical Works. Acetonitrile used in this study was of Optima LC/MS grade and was available from Fisher Scientific (Fair Lawn, NJ). Humic acid was obtained from XiLong SCIENTIFIC (Guangdong, China). DMPO was purchased from Sigma-Aldrich. All other reagents used were obtained commercially and used without further purification. Deionized water (18 MΩ cm) was used throughout the experiments.

3.2 Generation and analysis of gaseous and liquid products

The various surfactants (1%, v/v) including nonanol, nonanal, NA and nonyl amine were respectively dispersed in four sealed quartz cells (inner diameter of 2.8 cm and length of 15 cm, creating a 6.1544 cm\(^2\) air–water interface), which were filled with 50 mL of water. After ultrasound for 10 min, these samples were irradiated by means of a 500 W high-pressure mercury lamp (\(\lambda > 254\) nm, light intensity = 12 mW cm\(^{-2}\)) with magnetic stirring (Fig. S1†). These reactions were not deoxygenated and were maintained at ambient temperature using a low-temperature water pump (ZL-500). The gaseous products in the sealed quartz cells were extracted with a 1 mL syringe at predetermined time points and immediately injected into the gas-sampling loop of the GC-MS (QP2020 NX, Shimadzu, Japan, column: Rtx-5MS) for qualitative and quantitative analysis. The corresponding liquid phases were extracted with a certain amount of DCM and 1 μL was injected into the same GC-MS. Helium was used as the carrier gas for the quantification of the hydrocarbons. The photochemical experiments were carried out in duplicate from two distinct samples unless indicated otherwise. The hydroxyl radical (OH) that originated from nonanol and nonyl amine aqueous solution after photoirradiation was detected with a quasi-in-situ ESR (E500, Bruker, Germany) equipped with a light source. DMPO was used as a spin trapping agent.

3.3 Purification and physico-chemical characterization of solid products upon photoirradiation

Corresponding solid samples produced from nonyl mine and nonanal were obtained by using a freeze-drier (FD-IC-50, Beijing Biocool, China) to remove water and other impurities. The obtained solid solution was dissolved in acetonitrile and detected by ESI-TOF-MS (micrOTOF II, Bruker Daltonics, Germany) under negative mode. Subsequently, solid samples were further separated and collected using a thin layer chromatography silica gel plate and separated by 0.22 μm microporous membrane to remove impurities. Petroleum ether, chloroform and triethylamine were applied as the eluents (v/v/v = 12:2:1). UV-vis absorption was measured on a UV-vis spectrophotometer (Agilent Technologies, USA) using 1 cm quartz cuvettes. Fluorescence images of solids were obtained under a 365 nm UV lamp (10 W, mercury lamp) under excitation at 365 nm. AFQY was performed by using a NanoLog infrared fluorescence spectrometer (Nanolog FL3-2iHR, France) with a calibrated integrating sphere on a Varian FLR025 spectrometer.

3.4 Theoretical calculations

The calculations were carried out using Gaussian 16.\(^{65}\) For the excitation energy including VEE, AEE and TEE, the ground state (S\(_0\)), first singlet state (S\(_1\)) and first triplet state (T\(_1\)) of surfactants were respectively optimized in the water using density functional theory (DFT), time-dependent DFT (TD-DFT) and unrestricted DFT (UDFT) at the M062X/def2TZVP level.\(^{66}\) For the differences in the Gibbs free energy of key reactions, their
reactants and corresponding products were computed using DFT at the M06-2X/def2TZVP level. All their frequencies were calculated at the same level and performed with a polarized continuum model (PCM) model and D3BJ correction.\textsuperscript{57}

For the Henry's law constant and dipole moment calculations of the gaseous and liquid products, all involved molecules were completely optimized using DFT at the M06-2X/6-31G* level. Their frequencies were calculated at the same level and performed with a solute electron density (SMD) model and D3 correction.\textsuperscript{68} Subsequently, Henry's law constant can be calculated from the following formulae:\textsuperscript{53,69}

\[
\ln K_{\text{solv}} = \frac{-\Delta G_{\text{solv}}^0}{RT}
\]

(1)

\[
K_{\text{solv}} = H^F = \left[ \frac{J}{P_f} \right] = \frac{e^{-\Delta G_{\text{solv}}^0}}{P_f}
\]

(2)

\[
\Delta G_{\text{solv}}^0 = G_{\text{water}}^1 - G_{\text{gas}}^1
\]

(3)

\[
\Delta G_{\text{solv}}^0 = G_{\text{water}}^1 - G_{\text{gas}}^1 + 1.89 \text{ kcal mol}^{-1}
\]

(4)

where $\Delta G_{\text{water}}^0$ represents the standard-state free energy of solvation of the organic molecule, which can be calculated by the difference of $E$ (single point energy) in water and vacuum.\textsuperscript{51,69} The use of eqn (1) implies that the liquid phase provides an ideally dilute solution, and as a consequence, $K$ is the Henry's law constant (referred to as $H^F$, eqn (2)). The Henry’s law constant calculated by using eqn (1) is dimensionless, and the conversion to SI units, mol m$^{-3}$ Pa$^{-1}$, is made by division with $R \times T$. $R$ is the universal gas constant, $R = 8.314462618$ J K$^{-1}$ mol$^{-1}$ and $T$ is the temperature (298.15 K). $J$ represents any chemical species and $P_f$ the partial pressure of gaseous $J$. It is noted that the standard-state Gibbs free energy of solvation i.e. the Gibbs free energy of transferring of a species from the gas phase at a solute partial pressure of 1 bar to a 1 M ideal solution. Therefore, 1.89 kcal mol$^{-1}$ of free energy change should be added to the calculated free energy of solvation, which was calculated according to the above method corresponding to the free energy of the process of moving from the 1 M gas phase state to the solvent to become the 1 M solvation state.\textsuperscript{70}

Additionally, dipole moment can obtained after their structure optimization, and thermodynamic properties were evaluated at 298.15 K and under 1.0 atm.

4. Conclusion

In this work, the in situ air–water interface is employed to convert four waste surfactants into high value-added products upon photoirradiation under ambient conditions. The results show that four representative amphiphiles with different functional groups can be directly transformed into automatically separated hydrocarbons and fluorescent nanoparticles (FNs) in gas and solid phases respectively. Such an excellent separation performance is attributed to the fact that the Henry's law constant and dipole moment of the products are significantly reduced relative to those of their parents and the unique two-dimensional (2D) interface further accelerates their separation. In particular, the optimal selectivity of olefins is up to 99%, and the fluorescence quantum yield of FNs can reach as high as 44.35%. The experimental results combined with theoretical calculations revealed that the four surfactants share similar resource conversion mechanisms, but their functional groups significantly affect the degree of conversion due to the differences in their photoactivity. Compared to the conventional chemical catalysis (1144.3–1731.5 $\text{S per m}^3$) and enzymatic catalysis (>9890 $\text{S per m}^3$), air–water interfacial photoirradiation (511.14–800 $\text{S per m}^3$) shows an obvious economic advantage. Therefore, this work of waste-to-resource conversion with high performance mitigates not only urgent environmental pollution but also the energy crisis, therefore providing a promising approach for the sustainable development of human society.

Conflicts of interest

There are no conflicts to declare.

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