Formation of surface protic ionic liquid nanodroplets for nanofabrication

Haitao Yu^{a,1}, Brendan P. Dyett^{a,1}, Sachini Kadaoluwa Pathirannahalage^a, Miaosi Li^b, Calum J. Drummond^{a,*} and Tamar L. Greaves^{a,*}

^a School of Science, College of Science, Engineering and Health, RMIT University, Victoria, Australia

^b School of Engineering, College of Science, Engineering and Health, RMIT University, Victoria, Australia

¹ H. Y. and B. P. D. contributed equally to this work.

* Corresponding authors: calum.drummond@rmit.edu.au; tamar.greaves@rmit.edu.au;

Abstract

Femtoliter droplets at solid interfaces attract significant interest as the basic units in many physical and biological processes. One challenge in the application of these tiny droplets is their fast evaporation rate in air due to their large surface-to-volume ratio. Ionic liquids with low volatility present an opportunity to overcome this challenge. The advanced properties of ionic liquids (ILs) have seen them widely applied in chemical reactions, biopolymers, molecular self-assembly and separations. At interfaces the wettability of ILs is pursued in next-generation lubricants and battery technology. Previously IL droplets at solid surfaces have been prepared by nano dispensing, micropipette, and solvent evaporation. Here we have extended the solvent exchange protocol to yield protic ionic liquid droplets at the interface with controlled size, distribution, location and stability in both liquid and air surroundings. During growth, the droplets demonstrated an interesting dewetting dynamic. To our knowledge, this behaviour has not been observed for molecular liquids during solvent exchange and suggests interesting interfacial dynamics of the ionic liquid. One proof-of-concept application of using surface nanodroplets of the protic ionic liquid ethylammonium nitrate for compartmentalized reactions and templating SiO₂ nanostructures has been demonstrated. This work broadens and intertwines the opportunities of ILs and nanodroplets.

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1. Introduction

Nanoscope droplets at the interface draw a great deal of interest as the basic units in lab-on-chip devices, biomedical diagnostics, liquid-liquid micro-extraction, and material synthesis.^{[1],[2],[3],[4],[5],[6]} These surface nanodroplets offer a robust and highly reproducible platform for research on compartmentalized reactions, drug release, single-cell analysis and screening at the femtoliter (fL), single cell, or single molecule level. Various technologies have been developed to produce surface nanodroplets with tailored sizes and distributions, such as inkjet printing,^{[7],[8]} deposition by microfluidic robots,^{[5],[9]} dewetting a thin film,^[10] and solvent exchange.^{[11],[12],[13]} Among them, solvent exchange is a simple, flexible, and scalable bottom-up approach for nanodroplets production and versatile for extensive liquids, including water on a hydrophilic substrate in organic phase and oils with viscosities ranging from 0.6 cSt to 1000000 cSt on a hydrophobic substrate in water phase.^[14] Driven by the oversaturation pulse at the mixing front where a good solvent of oil (or water) is displaced by a poor solvent, nanodroplets will nucleate and grow on appropriate substrates. Meanwhile, the droplet size can be controlled at the femtoliter (fL) scale by the flow conditions, solution composition, and interfacial properties.^{[11],[12],[15],[16]} Specifically, the volume per unit area (V_{area}) of surface nanodroplets produced by a solvent exchange process follows the scaling law: $V_{\text{area}} \sim h^3 \text{Pe}^{3/4}$, where h and Pe describe the channel height and Peclet number of the flow. However, due to the large surface-to-volume ratio of surface droplets in fLs, the evaporation rate can be extremely rapid. This typically limits the surface nanodroplets to remain confined within another immiscible liquid and thus significantly narrows the applications of surface nanodroplets in air phase, especially so for water droplets. Ionic liquids however may provide an opportunity to overcome this as an alternative solvent to water.

Ionic Liquids (ILs) are salts with poorly coordinated ions which cannot pack efficiently leading to melting points below 100 °C. ILs can be tailored to have highly beneficial properties, such as high conductivity, tailorable viscosity and thermal stability, and low vapour pressure at room temperature.^[17] ILs have been widely applied in chemical reactions, biopolymers, molecular self-assembly, and separations.^{[18],[19],[20]} Various solvent features

such as polarity, cation alkyl chain length, anion nucleophilicity, hydrophobicity, pH, salt kosmotropicity and ionicity can be tailored for a specific application by changing the structure of the cation and the anion.^[21] ILs can be separated into two broad categories; aprotic ionic liquids (AILs) and protic ionic liquids (PILs). The ILs of interest in this project are PILs produced through proton transfer from a Brønsted acid to a Brønsted base. The main advantage of using PILs is the low cost and simplicity of the synthesis process, in comparison to AILs.^[22] The extra proton available in PILs also allow for a hydrogen bonded network, akin to water.^[23,24]

The use of ILs at interfaces is pursuant to many surface processes.^[25] These include the development of next generation lubricants.^[26] Likewise, the wettability of ionic liquids with electrode materials such as graphite/graphene is highly relevant for battery applications.^{[27],[28]} The low volatility of ionic liquids has also seen them exploited as probes to study the behaviour of soft virus particles^[29] and featuring in designs for functional thin films with controlled wettability.^[30] ILs have also been prepared as free emulsion systems as microemulsions^[31] or in microfluidic devices.^[32] Previously, IL droplets at solid surfaces have been prepared by nano dispensing,^[29] micropipette,^[30] and solvent evaporation.^[25]

Here we have extended the solvent exchange protocol to yield ionic liquid droplets at an interface. This approach produced ethylammonium nitrate (EAN) nanodroplets on a glass substrate with controlled size, distribution, location and stability in both liquid and air surroundings. One proof-of-concept application of using dual-component surface nanodroplets as a droplet-based platform for compartmentalized reactions and templating nanostructures at the femtoliter scale was demonstrated. This work advances the prospective opportunities for ionic liquids and nanodroplets in chemistry and biology applications.^[33]

2. Results and Discussions

2.1. Dewetting phenomenon during nanodroplet growth

The growth of EAN droplets occurred on the glass substrate as a result of the solvent exchange process. Exchanging ethanol by EAN saturated cyclohexane initiated the start of the solvent exchange process, and led to oversaturation of the EAN. In turn, this led to the nucleation of EAN droplets nucleated on the glass substrate, which then gradually grew,

shown in **Figure 1**, for a flow rate of $200 \mu\text{L min}^{-1}$. The time of nucleation was defined as 0 s. At 2 s, tiny EAN droplets of irregular shape first appeared, and these then gradually became larger revealing the droplet nucleation and growth mechanism, as well as the obvious pinning from nanoroughness of the glass substrate. These droplets then kept growing until 6 s where the lateral diameter decreased until finally reaching the stable state at 100 s. The growth over time of these droplets is shown in Figure 1. This series has a variable contrast to facilitate visualization. The same snapshots with a constant contrast are also shown in Figure S1. During this process, the initially pinned and varied morphology of droplets transferred into a round shape, dominated by the capillary force.

These processes were captured quantitatively through the probability density function (PDF), mean diameter and surface coverage of droplets plotted in **Figure 2a-c**. PDF of EAN droplets at different timesteps from 1.5 s to 100 s during the growth was demonstrated, in which, the droplet size distribution range increased from only $3 \mu\text{m}$ at 1.5 s to about $10 \mu\text{m}$ at 10 s. Then, the range gradually reduced from 10 s to 100 s, resulting in a size distribution range of $5 \mu\text{m}$ and peak located between $2 \mu\text{m}$ and $3 \mu\text{m}$ at the final state of formation. This suggests that a dewetting phenomenon of droplet lateral size occurred during the EAN droplet formation. On the other hand, the mean diameter dramatically increased to the maximum value of $\sim 3 \mu\text{m}$ in approximately 10 s and then gradually reduced and stabilized at $\sim 2.6 \mu\text{m}$ at 100 s. The surface coverage illustrated a similar trend: increasing to 38% in the first 10 s and decreasing back to 23% at the end. The reduction in surface coverage was more pronounced than expected for a continual nucleation and growth, which is limited by the competition and continual coalescence between droplets.^[34] To further examine the dynamic growth process of an individual droplet, which is identified by a yellow arrow in Figure 1, has been tracked. Its diameter increased to the maximum value of $6.2 \mu\text{m}$ at about 8 s, and then dropped down to about $4.4 \mu\text{m}$ at 80 s, shown in **Figure 2d**. However, its maximum intensity (**Figure 2e**) kept increasing from 0 s to 80 s, corresponding to the increased contrast in the timeseries. In Total internal reflection fluorescence microscopy (TIRF), the evanescent wave will penetrate into the solution yielding an expected excitation depth of a few hundred nanometers. When the droplet first nucleates, its height is small, thus having a low number of fluorescent molecules in the excitation pathlength. As the droplet increases in height, more fluorophores are in the pathlength and are excited. Based on this, the intensity increase shown in Figure 2e indicates the droplet height has increased as the lateral diameter was receding.

Under the EAN oversaturation pulse created in the solvent exchange process, EAN nucleates on the glass surface forming small, film-like droplets. Then small EAN droplets grew further and merged with other droplets. The EAN droplets transfer to a spherical-cap shape, driven by the surface energy relationship amongst EAN, cyclohexane, and the glass substrate according to Young's equation. This increase in contact angle (CA) during growth is contrary to the typical formation of water and other organic oils where the surface droplet growth process on a homogeneous substrate is always at a constant contact angle.^{[35],[36]} However, this dynamic CA process is consistent with the dewetting process observed with amphiphiles, and shares an interesting parallel with previous simulations which revealed that ionic liquid droplets increased in contact angle as the droplet increased in size.^[28]

The droplet dewetting phenomenon observed in the whole droplet growth process of about 60 s resembles the autophobic observed for droplets of amphiphile solutions on a substrate, where structuring of the amphiphile at the substrate induces a spontaneous dewetting.^[37] The structuring of the IL droplets, which are also amphiphilic in nature, can be inferred by earlier work on the forces between mica surfaces. It has been demonstrated that surfaces act to orientate IL bulk structure^[38] and this IL exhibits ordered layers at the solid interface. Here it would be expected that the cation, EA⁺, binds to the negatively charged silica surface. The subsequent layering gradually decays to bulk properties, which is sensitive to minute presence of water, for example.^[39] The conditions during the solvent exchange process are nominally dry, however ethanol, the co-solute could play a similar role on the surface properties. It is not expected that ethanol will have a large influence on the bulk structure of the IL.^[40] Earlier studies have also revealed ordering of hydrocarbon liquids at solid interfaces, particularly for cyclohexane, which is the bulk solvent used here.^[23] The dewetting may be linked to the competition of layers at the interface as ethanol is gradually exchanged by cyclohexane. The final contraction on the contact line could be rationalized by the hydrogen bonded network/high cohesion of the bulk ionic liquid.^[23,41]

In addition, the relatively high viscosity (28 cP) of EAN and strong surface-ion force between the glass substrate and ionic liquid, led to a strong pinning effect, and reduced dynamic rate of dewetting to a spherical shape, especially after the droplet merging during the growth process. The dimensionless Ohnesorge number (Oh) of one EAN droplet with a diameter of 1 μm in air, describes the relative importance of viscous to surface tension effects, and can be calculated by the equation 1:^[42–44]

$$Oh = \mu/\sqrt{\rho\gamma L} = 4.7 > 1, \quad (1)$$

where viscosity $\mu = 28$ cP, density $\rho = 1.261$ kg L⁻¹, surface tension between EAN and cyclohexane $\gamma_{EAN-CH} = 29.0 \pm 0.8$ mN m⁻¹ (measured by pendant EAN drop in cyclohexane), and lateral diameter $L = 1$ μ m. This suggests that the dynamic growth process of EAN surface nanodroplets could be dominated by more viscous dissipation effects than surface tension.

We also observed that the dewetting phenomenon was more pronounced after the merging. As sketched in **Figure 3**, two EAN droplets are on the glass substrate with contact angle θ at the initial state before merging. As they keep growing during the solvent exchange process, and eventually touch each other, they will merge into one droplet at a transient state with a dynamic contact angle θ' . With an increasing volume, the final CA after merging equals θ_f , which is larger than the initial CA, θ . Because $\theta' < \theta < \theta_f$, this merging drop will keep dewetting during the growth and finally self-transfer into a final state with the contact angle increasing to θ_f . This merging mode is in good agreement with our experimental results: footprint dewetting, and intensity increase of droplets shown in **Figure 2**.

2.2. Growth at various flow rates

The dynamic growth processes of droplets at different flow rates are presented in supporting videos S1-4. Representative images for the final EAN surface droplets produced at different flow rates, ranging from 50 μ L min⁻¹ to 400 μ L min⁻¹ are shown in **Figure 4a**. It clearly shows that larger droplets were produced at a faster flow rate (Q). To determine the volume of the droplets, the contact angle of EAN droplets on the glass substrate in cyclohexane was measured to be $\sim 44^\circ$ by confocal microscopy. The V_{area} was 0.009, 0.023, 0.045, and 0.078 $\mu\text{m}^3 \mu\text{m}^{-2}$ with the assumption of $\theta_f = \theta = 44^\circ$ at $Q = 50, 100, 200$, and 400 $\mu\text{L min}^{-1}$, respectively. The droplet volume per unit area (V_{area}) and probability density function (PDF) for each flow rate are plotted as **Figure 4b** and **4c**, respectively. **Figure 4b** demonstrates that $\log(V_{\text{area}})$ is proportional to $\log(Q)$ with the fitting slope of 1, which suggests a scaling law: $V_{\text{area}} \sim Q$. The exponent of Q in this scaling law equals 1, instead of 3/4 reported in ref.^[11]. This enhancement of the exponent comes from the prominent dewetting phenomenon during

growth. In addition, according to Figure 4c, for low flow rates the size distribution was relatively uniform and became increasingly broader as the flow rate increased. At the slowest flow rate of $50 \mu\text{L min}^{-1}$, its PDF shows a peak at about $1.6 \mu\text{m}$ and a range from $1 \mu\text{m}$ to $3 \mu\text{m}$. As a comparison, the peak of PDF at the fastest flow rate of $400 \mu\text{L min}^{-1}$ shifts to about $2.2 \mu\text{m}$. The coalescence of droplets prompts the appearance of larger droplets with a diameter over $5 \mu\text{m}$ which broadens the distribution range. Monodisperse droplet size could be potentially controlled by using prepatterned substrates with hydrophilic domains and hydrophobic surroundings as a promising template for material synthesis.^{[12],[35]}

At a higher Q , a larger transient EAN oversaturation level was created at the mixing front between solutions A and B during the solvent exchange process, which contributes a larger and faster droplet growth. More droplets merge with other droplets during the growth process, which drives a more pronounceable dewetting phenomenon as introduced before. This can be noticed in supporting video S1-4. The dewetting phenomenon during droplet growth is obvious at fast Q (200 and $400 \mu\text{L min}^{-1}$), but hard to be observed at slow Q (50 and $100 \mu\text{L min}^{-1}$). As the dynamic CA (θ') is smaller than the final CA (θ_f) during the dewetting process, it results in a larger surface area for the diffusion growth of droplet with same volume, and thus finally enhances the droplet volume at final status. Therefore, the droplets grow larger at a faster flow rate Q , which contributes to the increase of the exponent of Q in the volume scaling law from $3/4$ to 1 .

2.3. Stable surface EAN nanodroplets in air

It was observed that the surface EAN nanodroplets produced in cyclohexane could be continuously transferred into the air phase because of their high viscosity and low vapour pressure at room temperature, despite their large surface-to-volume ratio and associated surface energy transformations. From **Figure 5a** and **5b**, we can observe that the distribution and locations of EAN nanodroplets on the glass substrate was not significantly altered by the movement of the three-phase contact line between cyclohexane, air, and the substrate. The CA of EAN in air was $53 \pm 3.3^\circ$ which is larger than that in the cyclohexane phase (44°). As a result, the decrease in lateral diameter of EAN nanodroplets was reasonable. These surface EAN nanodroplets in air were very stable. There was no variation of these EAN nanodroplets for several days in our experiments at room temperature. When we shifted our view close to the channel wall where some cyclohexane remained, we observed that the three-phase contact line (CL) of cyclohexane, air, and glass substrate was at a static state touching with EAN

nanodroplets, which is marked with blue dashed line in **Figure 5c**. These results match the theoretical analysis of the coalescence of two different three-phase contact lines which are EAN-cyclohexane-substrate CL and cyclohexane-air-substrate CL, reported in Ref. ^[45].

The spreading coefficient of EAN at the cyclohexane-air interface can be defined as $S = \gamma_{air-CH} - \gamma_{EAN-CH} - \gamma_{air-EAN}$. Here, γ_{air-CH} , γ_{EAN-CH} , and $\gamma_{air-EAN}$ are the surface energy between air and cyclohexane, EAN and cyclohexane, and air and EAN, respectively. As $\gamma_{air-CH} = 25.0 \text{ mN m}^{-1}$, $\gamma_{EAN-CH} = 29.0 \text{ mN m}^{-1}$ and $\gamma_{air-EAN} = 48.5 \text{ mN m}^{-1}$, thus $S = -52.5 \text{ mN m}^{-1} < 0$, which suggests that it is energetically favourable for EAN droplets to remain on the glass substrate when they are transferred from the cyclohexane phase into the air phase. This builds a theoretical base for obtaining surface nanodroplets of EAN in the air phase.

Once exposed to air, it has been demonstrated that EAN exhibits ordering at the air interface such that the hydrophobic alkyl groups shield the more polar components of the IL.^[40] It is noted that the ILs are hygroscopic and will interact with atmospheric water. For hydrophobic ILs water may partition to the air interface which is associated with re-orientation of ILs as well as a reduction in the interfacial surface tension.^[46] In the context of IL nanodroplets, a reduction in interfacial surface tension may result in a gradual spreading of the droplet with time. As to EAN in this case, EAN also adsorbed atmospheric water in air as the surface tension of a 30 μL EAN drop in air increased from 50.8 ± 0.7 to $51.7 \pm 0.5 \text{ mN m}^{-1}$ in 24 hrs. The plot of surface tension as a function of time is shown in **Figure S2**. The negligible change in surface tension suggests that the morphology of the EAN should remain stable over the time frame used in these experiments. At the final state, water adsorption by EAN droplet and the water evaporation should reach a balance. As to our surface EAN nanodroplet with a volume in fLs, the large surface-to-volume ratio greatly enhances the water evaporation rate, and thus the water amount in EAN droplets in air should be small.

2.4. SiO₂ nanostructures based on nanodroplets

As a demonstration of a potential application of these IL nanodroplets, they were then used as nanoreactors to produce variable SiO₂ nanostructures. To achieve this, we produced the binary droplets that were functionalised by two components, namely h-TEOS and EAN at different ratios. Our previous study work explains how the ratio of the component in the

binary droplets can be effectively tuned by adjusting the ratio of the components in their original liquid solution.^[13]

The dual-component h-TEOS/EAN droplets exhibit the tuneable features as compartmentalized “nanoreactor”, which enabled the formation of a variety of SiO₂ nanostructures due to the different functions of two components. In particular, the dehydration of h-TEOS in the nanodroplets produces SiO₂, while the EAN works as a solvent and templating agent during the reaction.^[47] When the SiO₂ nanostructure formation was completed, the water-miscible EAN was easily removed by solvent extraction with water, enabling the further characterization of the remaining SiO₂ structure on the surface.

When the nanodroplets contained pure h-TEOS, the dehydration of the droplets produced SiO₂ aggregates packed at the rim of the droplet, with a defect at the middle (the dark region surrounded by the SiO₂ rim in white) due to the unstable surface tension forces at the pinning edge, as shown in **Figure 6a**. The addition of EAN into the nanodroplets greatly altered the structure of SiO₂, as shown in **Figure 6b-d**. Specifically, SiO₂ nanostructures were obtained in a flat lens shape from the droplets containing 75%h-TEOS/25%EAN, which could be due to the higher hydrophilicity of h-TEOS than EAN (Figure 6b). The SiO₂ nanostructure then exhibits a thick and spherical cap shape when the EAN ratio increased to 50%, i.e, 50%h-TEOS/50%EAN, attributed to the larger CA of the droplets with increased proportion of EAN, as shown in Figure 6c. When EAN was further increased to 75% (25%h-TEOS/75%EAN), the reduced concentration of h-TEOS leads to insufficient precursor for the formation of the SiO₂ to support the spherical cap shape. As a result, a hollow structure of SiO₂ is clearly observed in Figure 6d. This tuneable surface SiO₂ nanostructure formation achieved by the dual-component IL droplets demonstrates the possibility to produce compartmentalized reactions with this surface nanodroplet-based platform, which is potentially controllable by the exact components in femtoliter droplets.

3. Conclusion

Solvent exchange has been demonstrated to yield ionic liquid droplets at the surface of an inert substrate. The droplets formed by nucleation and growth, with eventual sizes ranging between 0.2 – 10 μm, which can be tailored by flow and solution conditions. During the nucleation and growth process, IL droplets demonstrated an interesting dewetting dynamic.

Upon reaching a peak lateral size, the contact line of the droplet receded giving rise to an increase in contact angle. We believe that this behaviour has not been observed previously for molecular liquids during solvent exchange and suggests interesting interfacial dynamics of the ionic liquid. The technique is universal and can be utilized to prepare nanodroplets of many types of ionic liquids. The ionic liquids also demonstrated resilience to contact angle destabilization and could maintain their size and spatial distribution while being transferred from the oil to air phases. As a proof of concept, EAN surface nanodroplets were utilized as nanoreactors to yield silica nanostructures which were templated by the ionic liquid.

4. Materials and Methods

4.1. Reagents

Ethylamine (97% , Sigma), nitric acid (70% , Univar), ethanol (absolute, Univar), cyclohexane (>99.9%, Sigma), tetraethoxysilane (98%, Sigma), hydrochloric acid (32%, RCI Labscan) were used as received without further purification.

4.2. Ionic Liquid Synthesis

The protic ionic liquid used in this experiment, ethylammonium nitrate (EAN), was prepared via a slow-paced acid-base reaction using equal mole ratios of ethylamine with nitric acid. ^[48]

This reaction was highly exothermic and needed to be performed at a slow pace. An ice bath was used to ensure the temperature of the reaction was maintained below 10 °C throughout the reaction. The obtained ionic liquid was dried using a rotary dryer for 12 hours before being freeze dried for 60 hours. A Karl Fischer titration was then performed to measure the remaining concentration of water. The water content of the IL was measured to be 0.03 wt%.

4.3. Solvent exchange process

As sketched in Figure 7, the home-made microfluidic channel (Height: 350 μm, Width: 15 mm, Length: 50 mm) was used to produce EAN nanodroplets on the hydrophilic glass substrate. The flow channel was first filled with solution A (2 vol% EAN in ethanol) and then exchanged with solution B (EAN saturated cyclohexane). The flow rate was 50, 100, 200, and 400 μL min⁻¹, controlled by a syringe pump (NE-1000, PumpSystems Inc.). The glass

substrates (26 × 60 mm, No. 1.5H, Marienfeld) were rinsed by ethanol and dried by N₂ flow prior to use. After EAN nanodroplets were produced in cyclohexane, they were continuously transferred into the air phase by injecting air at 100 μL min⁻¹.

4.4. h-TEOS/EAN-based SiO₂ nanostructure

Tetraethoxysilane (TEOS) was first hydrolysed in water with molar ratio of 1:4 TEOS to water, and then brought to pH = 2 with hydrochloric acid. This hydrolyzation process took about 2 days, resulting in the dual-phase solution becoming a transparent single-phase, namely hydrolysed TEOS (h-TEOS), [49],[50].

0.2 mL mixture of h-TEOS and EAN at different ratios of 1:0, 3:1, 1:1, and 1:3 were dissolved in 10 mL ethanol as solution A, labelled as samples: h-TEOS, 75%h-TEOS/25%EAN, 50%h-TEOS/50%EAN, and 25%h-TEOS/75%EAN correspondingly. After the h-TEOS/EAN nanodroplets were produced on the glass substrate by solvent exchange process, they were continuously transferred into air phase and heated at 85 degrees for 6 hrs on a hot plate to promote condensation of h-TEOS; $Si(OH)_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$. This yielded a mixture of SiO₂ and EAN on the glass substrate. By rinsing the samples with water, and then drying them, a three-dimension SiO₂ nanostructure was obtained on the glass substrate.

4.5. Total internal Reflection Fluorescence Microscopy (TIRF)

TIRF was performed on a Nikon N-Storm super resolution confocal microscope (TIRF 100×, 1.49 NA objective lens). Solution A was dyed with Nile red. The fluid cell was mounted and illuminated by a 561 nm continuous wave (CW) laser. Within the NIS-Elements AR software, the TIRF mirror position was adjusted until achieving TIR, determined by the appearance of interference patterns of the substrate. The region of interest was collected by an Andor iXon DU-897 EMCCD camera, with a pixel calibration of 158 nm per pixel. Image analysis was performed using home-built python codes utilizing the open source PIMS, scikit, and TrackPy packages for Python.

4.6. Scanning Electron Microscopy (SEM)

Following washing and heat treatment the silica structures were cut and mounted onto SEM stubs and subjected to a high vacuum environment overnight. The stubs were sputter coated by a thin ~ 3.5 nm Pt coating (Gatan, Precision Etching and Coating System). Scanning

electron microscopy was performed at high vacuum on a FEI VERIOS 460L at 3kV, 50 pA and a working distance of 4 mm.

Supporting Information

Figure S1 shows the representative snapshots of EAN droplets nucleation and formation over time in a constant contrast. Figure S2 shows surface tension measurement of a 30 μL EAN drop in air as a function of time. Supporting video S1-4 shows the formation of EAN surface nanodroplets by solvent exchange protocol at different flow rates (50, 100, 200, and 400 $\mu\text{L min}^{-1}$), respectively. The play speed of supporting video S1 (50 $\mu\text{L min}^{-1}$) is at $4\times$ real time. And the play speeds of other supporting videos S2-4 are at real time.

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Author contributions

H.Y., B.P.D., T.G. conceived and designed the research. H.Y., B.P.D., S.K.P. performed experiments. H.Y. and B.P.D. analysed the results. All authors contributed to the manuscript preparation and results interpretation.

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Figure 1. Representative snapshots of EAN droplets nucleation and formation process on a glass substrate by solvent exchange process at the flow rate of $200 \mu\text{L min}^{-1}$. Scale bar: $10 \mu\text{m}$.

Figure 2. EAN droplets formation by solvent exchange process at the flow rate of 200 $\mu\text{L min}^{-1}$. (a) Probability density function (PDF) of EAN droplets at the corresponding timesteps of Figure 1 from 1.5 s to 100 s, (b, c) Mean diameter and surface coverage of surface EAN nanodroplets growth as a function of time on glass substrate during solvent exchange process. (d, e) Dynamic variation of diameter and the maximum intensity of an individual EAN nanodroplet on the glass substrate, indicated by the yellow arrow in Figure 1.

Figure 3. A schematic of the droplets merging process during droplet growth. The static CA of EAN droplet on the glass substrate in cyclohexane is defined as θ . The dynamic CA when merging happens is defined as θ' and CA at the final state after merging is θ_f . With a larger volume at the final state, $\theta_f > \theta$. As $\theta' < \theta < \theta_f$, an obvious dewetting phenomenon of droplet diameter is observed during droplet growth.

Figure 4. Surface EAN droplets formation under different flow rates. (a) Representative TIRF images of droplets produced at different flow rates: 50, 100, 200, and 400 $\mu\text{L min}^{-1}$. Scale bar is 10 μm . (b) The log-log plot of droplet volume per unit area (V_{area}) as a function of flow rate (Q). The red dashed line shows the fitting slope of 1, which suggests the scaling law: $V_{\text{area}} \sim Q$. (c) The plot of PDF at different flow rates versus droplet diameter.

Figure 5. Surface nanodroplets of EAN on the glass substrate (a) in cyclohexane and (b) in air phase. (c) Stable three-phase CL among cyclohexane, air, and substrate touching with EAN nanodroplets marked by blue dashed line. The region above CL shows EAN droplets left in cyclohexane phase and the region under CL shows EAN droplets transferred into air phase. Scale bar: 10 μm .

Figure 6. SEM images of SiO_2 nanostructure fabricated based on the nanodroplets of h-TEOS and EAN at different ratios: (a) 1:0, (b) 3:1, (c) 1:1, and (d) 1:3.

Figure 7. Schematic diagram of EAN nanodroplets formation in femtoliters on the glass substrate by solvent exchange process in cyclohexane phase and air phase. The microfluidic channel is first filled with solution A (EAN-rich) and then exchanged by solution B (low EAN solubility).

Protic ionic liquid ethylammonium nitrate nanodroplets at the interface can be formed by solvent exchange with controlled size, distribution and stability in both liquid and air surroundings. These surface EAN nanodroplets were used as compartmentalized nanoreactors for templating SiO_2 nanostructures. This work advances and intertwines the opportunities of ionic liquids and nanodroplets.

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Author/s:

Yu, H;Dyett, BP;Pathirannahalage, SK;Li, M;Drummond, CJ;Greaves, TL

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