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Unusual Dual Superlyophobic Surfaces in Oil–Water Systems: The Design Principles

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Studying of surface interaction with water and oil is not only of fundamental importance to understand complex multiphase fluid phenomena,^[1-6] but also enhances our ability to control surface wetting properties in oil-water systems, which is crucial for a variety of technical applications including marine antifouling,^[7,8] oil recovery,^[9,10] phase-transfer catalysis,^[11,12] emulsion separation,^[13,14] nanoparticle self-assembly,^[15] and microfluidics.^[16] In a solid-oil-water system, the water contact angle (CA) against oil ($\theta_{w/o}^*$) and oil CA against water ($\theta_{o/w}^*$) in principle sum up to 180° as they are supplementary to each other. Consequently, a surface that is oleophobic under water is generally hydrophilic under oil (Figure 1a), and a surface that is hydrophobic under oil is oleophilic under water (Figure 1b). Underwater oleophobicity and underoil hydrophobicity have thus been understood as contradictory properties. This is especially true when it comes to underwater superoleophobicity $(\theta_{o/w}^*)$ larger than 150°) and underoil superhydrophobicity ($\theta_{w/o}^*$ larger than 150°), and these two properties are not expected to appear on the same surface (Figure 1c). In fact, the former property generally demands textured surfaces of high surface energy, which is referred to as the "fish-scale effect",[7,17] whereas the latter requires coatings of low surface energy, similar to the well-known "lotus effect" except that air is replaced with oil.^[18,19] Contrasting the general knowledge, here we show that judicious design allows surfaces that are both superhydrophobic under oil and superoleophobic under water (i.e., dual superlyophobic in oil-water systems). The successful design is based on two principal criteria, namely, the liquid filling criterion and the steady solid-oil-water composite interface criterion, and key parameters turn out to be a well-defined intermediate surface chemistry and re-entrant topography.

From a thermodynamic point of view, the underwater superoleophobic state and the underoil superhydrophobic state cannot both be energetically favorable for a given surface. Depending on competitive affinity interactions to the surface between oil and water, either water replaces oil (Figure 1a) or vice versa (Figure 1b), and only one state might be

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thermodynamically favorable. Generally, surfaces of high surface energy have stronger affinity to water than oil, whereas surfaces of low surface energy show stronger affinity to oil instead. This is why underwater superoleophobicity occurs on high energy surfaces,^[7,17] while underoil superhydrophobicity occurs on low energy ones.^[19,20] Although a lot of surfaces have been reported that exhibit either of the above two properties, surfaces that possess both properties are extremely rare. To our knowledge, only two exceptions have been reported.^[14,21] However, in both of these cases, the underlying mechanism regarding thermodynamic contradiction between the two wetting states remains unclear. More importantly, how to rationally create such dual superlyophobic surfaces, i.e., the key design principle, is far from known.

Metastable states offer access to novel wetting phenomena. Such states have been widely investigated in ambient air environment to understand various wetting transition behaviors^[22-24] as well as to create liquid-repellent surfaces.^[25-28] Employing metastable states in solid-oil-water systems by judiciously designing surface topography and chemical composition can provide us a way to circumvent the thermodynamic contradiction and create surfaces that combine underoil superhydrophobicity and underwater superoleophobicity, where the two wetting states feature Cassie-Baxter-type (henceforth Cassie-type) composite interfaces^[29]—submerged droplets (water or oil) are suspended by a composite interface of solid and the other liquid (oil or water)-and at least one or even both wetting states are metastable. In this study, we demonstrate the above concept with microfabricated post structures because well-defined topographies allow such surfaces to be designed in a highly rational manner as well as better understanding of the phenomena. We consider the surfaces need to meet two design criteria (Figure 2a): i) the microstructures must be readily filled by water and oil without trapped air layer when submerged in one of the two liquids; ii) the submerged microstructures can support steady oil-water interfaces when the second liquid is introduced, or in other words, the second liquid can be suspended by the texture rather than that it intrudes into the texture. The first criterion would create a water or oil film trapped within the texture and the second one guarantees the trapped liquid film not to be displaced by the other suspended liquid. Under the above two criteria, Cassie-type composite interfaces can be obtained in both water-in-oil and oil-in-water situations, and moreover large apparent CAs (i.e., $\theta_{w/o}^*$ and $\theta_{o/w}^*$) are able to be induced, both of which are important for liquid repellency^[23]—repelling of the second liquid by the first liquid in oil-water systems.

To ensure ready filling of the microstructures by water or oil, the liquid should be able to displace air within the texture effortlessly when submerging the surface. Here, we only

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Figure 1. Wetting in oil-water systems. a) An oleophobic surface under water is generally hydrophilic under oil, and b) a hydrophobic surface under oil is oleophilic under water. c) A surface that is both superoleophobic under water and superhydrophobic under oil (i.e., dual superlyophobic) is not expected from a thermodynamic point of view.

need to consider the water filling criterion, which is a sufficient condition for oil filling since oil has lower surface tension and thus generally fills the texture easier than water. For a micropost-structured surface, the criterion of water filling can be expressed as (see Figure S1, Supporting Information)':

$$\theta_{\rm w} < \theta_{\rm c} = \max[\varphi, \arctan(L/2H)] \tag{1}$$

where θ_w is the intrinsic water CA on the planar surface, φ the local geometric angle at the upper corner of posts (90° for vertical posts), *L* the pitch, and *H* the post height. The above equation is obtained by considering the condition that allows free liquid entrance into the texture, from either the top or the lateral side of the post array. This leads to two critical CAs for liquid filling, i.e., φ and arctan(*L*/2*H*), and the final θ_c is the maximum of them.

To meet the second criterion of supporting the oil–water interfaces, the posts need to provide an outward suspension force in both water-in-oil and oil-in-water cases: the oil–water interfaces would bend toward the solid side (Figure 2a). It thus requires the intrinsic water CA in oil $\theta_{w/o}$ as well as the intrinsic oil CA in water $\theta_{o/w}$ to exceed φ :

$$\theta_{\rm w/o} > \varphi, \quad \theta_{\rm o/w} > \varphi$$
 (2)

From Equation (2) it is known that $\theta_{w/o} + \theta_{o/w} > 2\varphi$. As $\theta_{w/o}$ and $\theta_{o/w}$ add up to 180° for ideal surfaces, φ has to be less than 90°.

This suggests that the posts should possess re-entrant (i.e., local negative slope) geometric characteristic in principle.

To facilitate the prediction of surface chemistry that simultaneously meets Equation (1) and (2), we need to be aware of the relationship between $\theta_{w/o}$, $\theta_{o/w}$, and θ_{w} . According to Bartell–Osterhof equation,^[30] which is derived from Young's equation, the following relationship holds: $\gamma_w \cos \theta_w = \gamma_o \cos \theta_o + \gamma_{ow} \cos \theta_{w/o}$, denoting γ_o , γ_{ow} , and θ_o as oil surface tension, water–oil interfacial tension, and intrinsic oil CA, respectively. Using a linear assumption and considering the endpoint consistence, van Dijke and Sorbie rewrote it as follows:^[31] $\cos \theta_w = \left[\frac{1-(\gamma_o - \gamma_{ow})/\gamma_w}{2}\right] \cos \theta_{w/o} + \left[\frac{1+(\gamma_o - \gamma_{ow})/\gamma_w}{2}\right]$, the validity of which was verified by experimental investiga-

the validity of which was verified by experimental investigations.^[32] Thus Equation (2) can be expressed as:

$$\theta_{w/o} = \arccos\left[\frac{2(\cos\theta_{w} - 1)}{1 - (\gamma_{o} - \gamma_{ow}) / \gamma_{w}} + 1\right] > \varphi$$

$$\theta_{o/w} = 180^{\circ} - \arccos\left[\frac{2(\cos\theta_{w} - 1)}{1 - (\gamma_{o} - \gamma_{ow}) / \gamma_{w}} + 1\right] > \varphi$$
(3)

From the above analyses, it is clear that re-entrant structures are needed for preparing dual superlyophobic surfaces in oilwater systems, and moreover the surface chemistry (i.e., θ_{w}) should satisfy two requirements as defined by Equation (1) and (3). We fabricated a series of surfaces of hexagonally arrayed posts with re-entrant characteristic by structuring SU8 photoresist using photolithography (see Supporting Information). As shown in Figure 2b, the posts show an overhang geometry with $\varphi \approx 76^\circ$, and the upper and lower diameters are $D_{\rm u} \approx 15$ and $D_{\rm b} \approx 13 \ \mu m$, respectively. The post height is $H \approx 24 \ \mu m$, and the pitch L is systematically varied in different samples, from 25 µm (P1) and 35 µm (P2) to 60 µm (P3). Next, we resolve how to match surface chemistry with the microstructures to create dual superlyophobic surfaces under water and oil. From Equation (1), θ_c is calculated to be 76° for all the three fabricated samples. Thus, the criterion that ensures water and oil filling is:

$$\theta_{\rm w} < 76^{\circ}$$
 (4)

Using hexadecane as a model oil, γ_w , γ_o , γ_{ow} are 72.8, 27.5, and 39.0 mN m⁻¹, respectively. Hence from Equation (3) we get the requirement for establishing the solid–oil–water composite interfaces:

$$\theta_{w/o} = \arccos\left(\frac{\cos\theta_{w} - 0.421}{0.579}\right) > 76^{\circ}$$

$$\theta_{o/w} = 180^{\circ} - \arccos\left(\frac{\cos\theta_{w} - 0.421}{0.579}\right) > 76^{\circ}$$
(5)

The surface chemistry criterion can be obtained by solving Equation (4) and (5) graphically, as shown in Figure 2c. The red and blue curves show how $\theta_{w/o}$ and $\theta_{o/w}$ vary with θ_{w} , respectively. Under the above requirements, it is deduced that θ_w needs to be within the range of 56–74°, highlighted by the green area in the graph.

The above estimation provides a highly useful guideline for screening appropriate surface chemistries. We tested two surface



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Figure 2. Design of dual superlyophobic surfaces in oil–water systems. a) Schematic of oil–water interfaces supported by micropost structured surfaces. $\theta_{w/o}$ and $\theta_{o/w}$ are the intrinsic water-in-oil and oil-in-water CAs, respectively, φ the local geometric angle of posts, *L* the pitch, *H* the post height, and D_u and D_b the upper and lower diameters of posts, respectively. b) Top and side views of three fabricated surfaces composed of hexagonally arrayed microposts with $\varphi \approx 76^\circ$, $H \approx 24 \,\mu$ m, $D_u \approx 15 \,\mu$ m, and $D_b \approx 13 \,\mu$ m. *L* is about 25 μ m for P1, 35 μ m for P2, and 60 μ m for P3. c) Theoretical search of appropriate surface chemistry (i.e., intrinsic water CA θ_w). Applicable θ_w is estimated to be within 56–74°.

chemistries with θ_w located between 56° and 74°, including the 3-cyanopropyltrichlorosilane monolayer coating (CPTS) ($\theta_w = 57^\circ$, see Figure S2, Supporting Information for silanization details) and native SU8 coating ($\theta_w = 72^\circ$) (see Figure S3, Supporting Information for surface elemental analyses). Indeed, these surfaces were able to induce dual superlyophobicity under water and oil. The wetting properties of CPTS-coated surfaces are shown in **Figure 3** (wetting properties of SU8 surfaces are shown in Figure S4, Supporting Information). We first evaluate the robustness of solid–oil–water composite interfaces, which characterizes the ability of the composite interface to withstand pressure of the suspended liquid. Similar to the case in ambient air,^[25,33] we quantify it with a robustness factor: $RF = P_c/P_{ref}$, where P_c is the critical pressure for the suspended liquid to break through the texture, and $P_{\rm ref}$ is a characteristic reference pressure which is close to the minimum pressure difference across the composite interface exerted by droplets on a highly lyophobic surface. Thus, *RF* must be much larger than 1 to ensure steady composite interfaces; otherwise the suspended liquid would disrupt the composite interface and drive away the other liquid film trapped within the texture. For our hexagonally arrayed posts, *P*_c

scales as $\frac{\pi\gamma_{ow}D_u\sin(\theta-\varphi)}{\sqrt{3}L^2/2-\pi D_u^2/4}$, here θ represents $\theta_{w/o}$ or $\theta_{o/w}$. In oil–water systems, P_{ref} is expressed as $2\gamma_{ow}/l_{cap}$ (see Figure S5, Supporting Information), where $l_{cap} = \sqrt{\gamma_{ow}/(\rho_w - \rho_o)g}$ is the capillary length in oil–water systems, and ρ_w , ρ_o , and g are water density, oil density, and gravitational acceleration, respectively. Hence we get the robustness factor



Figure 3. Wetting properties of the prepared surfaces in oil–water systems. a) Relationship between robustness factor and θ (i.e., $\theta_{w/o}$ and $\theta_{o/w}$). b) Relationship between apparent CA θ^* (i.e., $\theta^*_{w/o}$ or $\theta^*_{o/w}$) and θ . The hollow symbols in (a) and (b) show the calculated robustness factor and θ^* of the surfaces coated by 3-cyanopropyltrichlorosilane (CPTS) ($\theta_w = 57^\circ$), respectively. The solid symbols in (b) show the experimental θ^* . c) Droplet profiles on the CPTS-coated surfaces. Upper row: water droplet in oil; lower row: oil droplet in water. Thin oil or water cushion is clearly observed between droplets and the surface P3. d) Both water and oil droplets (10 µL) can easily move away from the slightly inclined CPTS-coated P3 in oil–water systems. The inclination angles are labeled on the left schematics.

$$RF = \frac{\pi D_u \sin(\theta - \varphi)}{\sqrt{3}L^2 - \pi D_u^2/2} l_{cap}$$
(6)

Figure 3a shows the relationship between *RF* and θ for the three fabricated structures. Experimentally measured $\theta_{w/o}$ and $\theta_{o/w}$ of CPTS coating are 88° and 121°, respectively (Figure S6, Supporting Information), a little higher than van Dijke and Sorbie's prediction. The sum of the two CAs is accordingly

larger than 180°, which could be explained by CA hysteresis existing widely on real surfaces^[34] and in fact adds extra stability to solid–oil–water composite interfaces. The robustness factors of the CPTS-coated surfaces are much greater than unity for all the three samples, as indicated in Figure 3a. Even for the most sparsely structured sample P3, the *RF* is 7.3 for water in oil and 24.7 for oil in water. Therefore the CPTS-coated samples are able to support steady Cassie-type composite interfaces.

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We further calculate apparent CAs of the samples (Figure 3b) according to the Cassie model:^[29]

$$\cos\theta^* = f_s \cos\theta - (1 - f_s) \tag{7}$$

where θ^* represents $\theta^*_{w_0}$ or $\theta^*_{o/w}$, and f_s indicates the solid fraction occupied by posts, which is 0.33, 0.17, and 0.06 for P1, P2, and P3, respectively. Due to its lowest solid fraction, CPTS-coated P3 gives the largest theoretical $\theta_{w/o}^*$ and $\theta_{o/w}^*$, both of which are well above 150°, and is thus expected to be ideal for achieving dual superlyophobicity under water and oil. CA measurement results are shown in Figure 3c. All samples show very high apparent CAs, which are slightly larger than Cassie's prediction and vary from 145° to greater than 150°. Especially, the $\theta^*_{w/o}$ and $\theta^*_{o/w}$ of CPTS-coated P3 are as high as 164° and 169°, respectively; that is, it exhibits remarkable superlyophobicity under both water and oil. Moreover, a thin oil or water cushion can be clearly observed between the submerged droplets and the surface benefiting from the large pitch of P3, confirming the Cassie-type wetting states. This fact is highly important as it provides the direct and convincing evidence that the oil or water thin film trapped within the texture accounts for the dual superlyophobicity, whereas in previous reports^[14,21] it was not clear whether Cassie-type composite interfaces were present for both wetting states. Our design criteria ensure the steady trapping of oil or water films between the droplets and the surface, which is essential for its remarkable wetting properties. Due to the extremely low solid fraction of P3, droplets can be regarded as sitting on another liquid film with minimum contact with the solid. Hence droplets are highly mobile on the surface, as demonstrated in Figure 3d (and Movie S1 and S2, Supporting Information), where droplets of 10 µL can easily slide down the slightly inclined surfaces (with a slope of 24° for water droplet in oil and 18° for oil droplet in water, respectively). Note that the driving force for droplet sliding here is much less than that in common liquid-air systems due to small density difference between the two liquids (1.00 and 0.77 g cm^{-3} for water and hexadecane, respectively). By considering the force balance parallel to the surface, we can obtain that the hysteresis force (i.e., lateral adhesion force) is no more than $9 \,\mu\text{N}$ for the water droplet in oil and $7 \,\mu\text{N}$ for the oil droplet in water, respectively.

The dual superlyophobicity was also confirmed to work not only in the hexadecane-water system, but also in various other oil–water systems. This was demonstrated with CPTS-coated P3 by using petroleum ether, silicone oil, dodecane, and octane as model oils (Figure S7, Supporting Information).

We also investigated the effect of different surface chemistries with θ_w outside the range of 56–74°, i.e., those do not meet the criteria of Equation (1) and (2). As shown in **Figure 4**a, when treated with more hydrophilic chemistry, including O₂ and H₂ plasma treatment ($\theta_w = 6^\circ$) and polydopamine coating ($\theta_w = 48^\circ$) (see Figure S3, Supporting Information), the surfaces exhibited Cassie-type underwater superoleophobicity with $\theta_{o/w}^*$ above 170°. However, these surfaces were not superhydrophobic under oil, and they showed $\theta_{w/o}^*$ of 48° and 107°, respectively, indicating a Wenzel-type wetting state^[35]—water displaces oil and penetrates into the texture. On the other hand, when treated with more hydrophobic chemistry, including octadecyltrichlorosilane (ODTS) ($\theta_w = 90^\circ$) and 1H,1H,2H,2H.



perfluorooctyltrichlorosilane (FOTS) ($\theta_w = 110^\circ$) (see Figure S2 and S3, Supporting Information), the surfaces possessed Cassie-type underoil superhydrophobicity with $\theta_{w/o}^*$ of 178° and 175°, respectively. However, an air plastron layer was sustained when these surfaces were submerged under water due to failure of the water filling criterion. Consequently, an oil droplet spread completely within the air layer, and simultaneously displaced air out of the texture, leading to formation of an air bubble aside, as indicated by the arrows in Figure 4a. The wetting properties of the surfaces with various surface chemistries are summarized in **Table 1**.

Figure 4b illustrates the three different wetting modes observed above. With a very hydrophilic surface chemistry $\theta_{\rm w} \leq 56^\circ$, $\theta_{\rm w/o}$ is not large enough to support a composite solid– oil-water interface for water droplet in oil, hindering underoil superhydrophobicity. With a very hydrophobic surface chemistry $\theta_{\rm w} > 76^\circ$, $\theta_{\rm w}$ is not small enough for water filling and elimination of air plastron, and meanwhile, $\theta_{o/w}$ is too small to support a composite interface for oil droplet in water, thus causing oil spreading within the air layer. Another possible wetting mode theoretically corresponding to $74^{\circ} \le \theta_{w} \le 76^{\circ}$, where water can fill the texture but $\theta_{0/w}$ is still too small to support underwater superoleophobicity, is schematically shown in Figure S8 (Supporting Information), though not observed in this study. Only intermediate surface chemistries that satisfy Equation (1) and (2) $(56^\circ \le \theta_w \le 74^\circ)$ can guarantee Cassie-type wetting states for both water-in-oil and oil-in-water cases, thus inducing both underwater superoleophobicity and underoil superhydrophobicity. It is worth mentioning that the applicable range of θ_{w} is structure-dependent, and could shift toward more hydrophilic region with reduced φ .

We also analyze the thermodynamic characteristic of the wetting states. Theoretical curves regarding Cassie and Wenzel state CAs are plotted in Figure 4c. Wenzel CAs were calculated with: $\cos\theta^* = r\cos\theta$,^[35] where r = 1.36 is the surface roughness of surface P3. The transition from Wenzel state to Cassie state occurs at $\theta_t = 136^\circ$, only above which thermodynamically stable Cassie states are obtained. Plasma and polydopamine treated surfaces exhibited thermodynamically stable underwater superoleophobicity, whereas ODTS and FOTS treated surfaces exhibited thermodynamically stable underoil superhydrophobicity. By contrast, for the CPTS and SU8 coated surfaces, both underwater superoleophobicity and underoil superhydrophobicity are in the metastable Cassie regime. The appearance of metastable state is virtually inevitable since dual stable Cassie states would require both $\theta_{w/o}$ and $\theta_{o/w}$ to be larger than $\theta_t = \arccos[(f_s - 1)/(r - f_s)] > 90^{\circ,[23]}$ which defies the fact that the two intrinsic CAs are supplementary in principle. The metastable characteristic explains why two thermodynamically contradicting states can appear on the same surface, as at least one or both states are not energetically favorable.

Besides appropriate surface chemistry, the re-entrant structure is also crucial. For surfaces without re-entrant characteristic, such as vertical posts, no surface chemistry could simultaneously satisfy Equation (1) and (2) (Figure S9, Supporting Information). Vertical posts (or positively sloped posts) may support either a Cassie-type water droplet in oil or oil droplet in water, but do not support both, especially when the robustness of composite interfaces is considered. Indeed,

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a controlled sample of vertical posts with structural parameters similar to P3 does not show dual superlyophobicity in oil–water systems (Figure S10, Supporting Information).

Different from previous reports,^[14,21] our dual superlyophobic surfaces (including CPTS- or SU8-coated P3) are not superamphiphilic (i.e., superhydrophilic and superoleophilic) in air. Though both surfaces are superoleophilic in air, they show water CA of 72° and 83°, respectively (Figure S4 and S11, Supporting Information). This indicates that superamphiphilicity is not a prerequisite for dual superlyophobicity under water and oil. Moreover, a superamphiphilic surface may not lead to dual superlyophobicity under water and oil, as evidenced by the plasma-treated P3, which is superamphiphilic in air (Figure S12, Supporting Information), but remains

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Table 1. Wetting properties of P3 with hydrophilic (plasma and PDA), hydrophobic (ODTS and FOTS) and desirable intermediate (CPTS and SU8) surface chemistries.

Surface chemistry	$ heta_w^{a)}$ [°]	θ _{w/o} ^{a)} [°]	$ heta_{o/w}{}^{a)}$ [°]	$ heta_{ m w/o}^{ m *}{}^{ m a)}$ [°]	$ heta_{o/w}^{\star}{}^{a)}$ [°]
Plasma	6 ± 2	46 ± 4	155 ± 3	48 ± 5	174 ± 5
PDA	48 ± 3	71 ± 3	139 ± 4	107 ± 4	170 ± 5
CPTS	57 ± 2	88 ± 4	121 ± 4	164 ± 2	169 ± 2
SU8	72 ± 2	120 ± 4	85 ± 3	169 ± 3	160 ± 4
ODTS	90 ± 3	171 ± 4	3 ± 2	178 ± 2	0 ^{b)}
FOTS	110 ± 2	150 ± 3	55 ± 3	175 ± 5	0 ^{b)}

^{a)}The θ symbols without * are intrinsic CAs on planar surfaces, and the ones with the * are apparent CAs on structured surfaces; ^{b)}Oil spreads within air plastron, showing an apparent CA of zero.

hydrophilic in oil (Figure 4). The key to achieve dual superlyophobicity under water and oil lies in the two principal criteria we proposed.

Our work demonstrates that by the combination of reentrant topography and delicately matched surface chemistry dual superlyophobic surfaces under water and oil can be prepared. We reveal the principal design criteria and identify the key role of metastable states in this unusual wetting phenomenon. Our understanding and design strategy provide a solid basis for developing dual superlyophobic materials in oil-water systems, which could bring unique applications in various fields involving multiphase fluids, such as marine antifouling, oil-water separation, and microfluidic devices. On the other hand, the unique dual superlyophobicity can be understood as a path-dependent phenomenon, where one surface shows two dramatically different wetting properties dictated by its history (whether it enters into water or oil first). Therefore, our study also emphasizes the importance of taking into careful consideration their history when studying behaviors of various solid-oil-water systems (e.g., oil recovery, particle phase transfer, liquid-liquid interface assembly, etc.).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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