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Robust Bijels for Reactive Separation *via* Silica-Reinforced Nanoparticle Layers

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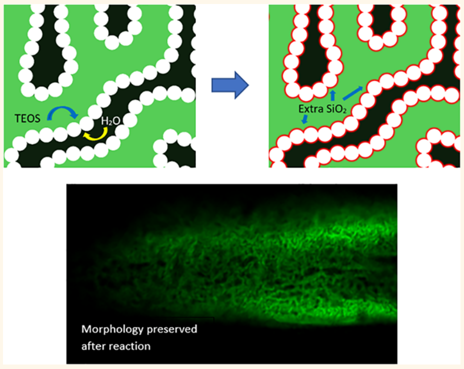
Supporting Information

ABSTRACT: Pickering emulsions have been successfully used as media for catalysis and separation. However, simultaneous reaction and separation cannot be performed in a continuous mode in these systems, because reagents cannot be readily loaded into or recovered from the dispersed phase. Bicontinuous interfacially jammed emulsion gels (bijels), in which the oil and water phases are continuous throughout the structure, have potential as media for simultaneous reaction and separation in a continuous mode. In this work, we take a major step toward realizing this vision by demonstrating the ability of bijels to be used in reactive separation performed in a batch fashion. To perform effectively, bijels must maintain their morphology and interfacial mass transfer properties during reaction. To strengthen the bijels, we modify the solvent transfer-induced phase separation (STRIPS) method to make bijels resistant to mechanical stresses and prevent detachment of nanoparticles from the oil/water interface due to pH changes by chemically fusing the interfacial nanoparticles. The reinforced bijel is successfully tested in base-catalyzed hydrolysis of esters and remains robust under these challenging conditions.



KEYWORDS: *biphasic reaction, catalysis, emulsions, separation, interface, Pickering, microfluidics*

Biphasic media for catalysis, featuring adjacent oil and aqueous phases, provide significant advantages, including facile handling of water and oil soluble reagents and products, easy separation based on polarity, and significantly enhanced conversion.[1−9] These concepts of simultaneous chemical conversion and separation have been successfully demonstrated using Pickering emulsions.[10−15] However, conventional Pickering emulsions have nonideal features that impede their use as biphasic reaction media. Each Pickering droplet, dispersed in the external phase, acts as a discrete, batch microreactor. Once reagent within the droplet reactors is exhausted, or droplet absorbers become saturated with a product, regeneration of reagent and product retrieval become complex issues. Furthermore, interfacial area is limited, and the discrete nature of the drop phase significantly impedes the development of a continuous biphasic process.

The recent development of bicontinuous biphasic mixtures, known as bijels, provides a potential avenue to transform the field of biphasic reactive separations.[16−22] In bijels (bicontinuous interfacially jammed emulsion gels), continuous domains of oil in contact with continuous domains of water pervade the structure, with significant interfacial area stabilized *via* the jamming of interfacially trapped nanoparticles. This distinct morphology provides a possible route for enhanced interphase mass transfer and could potentially allow for the continuous supply of reagents, reaction interfacial catalysis, and partitioning and separation of products, allowing for continuous reactive separation. In this work, we describe the use of bijels made *via* solvent transfer-induced phase separation (STRIPS) as media for catalytic reactive separation performed in a batch fashion, a key step forward to realizing this broader vision. Importantly, we show that it is critical to stabilize bijels against mechanical and chemical degradation to enable such a scheme. As-synthesized, bijels are fragile and lose their integrity under changes of solution conditions and mechanical agitation required to drive reactions of interest, for example, base-catalyzed hydrolysis reactions of esters. By locally fusing interfacially trapped nanoparticles *via* silica deposition *in situ*, we show that STRIPS bijels can be used as effective media for

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biphasic reactive separations under these more challenging conditions.

RESULTS AND DISCUSSION

We have previously introduced the solvent transfer induced phase separation (STRIPS) method for the continuous manufacture of bijel fibers, particles, and planar membranes.[23−25] The STRIPS process is described in Figure 1.

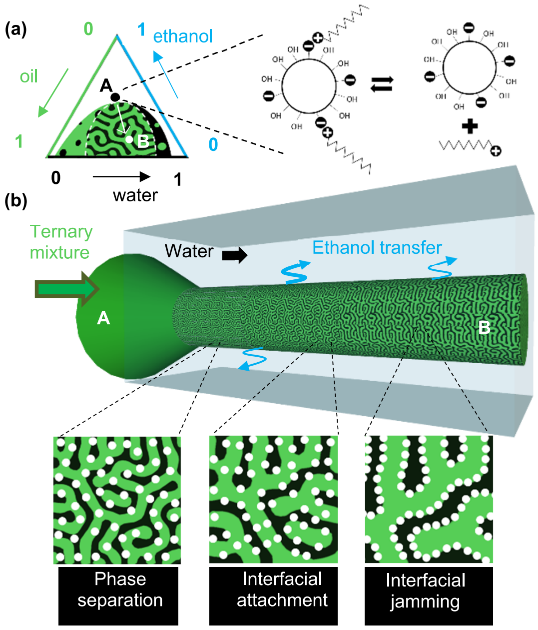

Figure 1. Formation of bijel fiber by STRIPS. (a) A silica suspension in water (Ludox TMA), cetyltrimethylammonium bromide (CTAB) solution in ethanol, and oil (*e.g.*, hexanediol diacrylate) are mixed together to form a ternary mixture. (b) The ternary mixture is introduced in a coflow configuration with a water−CTAB solution in two coaxial capillaries; upon contact between the two streams, ethanol transfers into the water steam triggering phase separation of the ternary mixture stream.

STRIPS bijels are prepared by mixing an aqueous suspension of silica (Ludox TMA), oil (*e.g.*, hexanediol diacrylate), and surfactant doped ethanol solution, such that the mixture becomes homogeneous (point A in the ternary phase diagram in Figure 1), with ethanol acting as the cosolvent. We use cetyltrimethylammonium bromide (CTAB) as the surfactant, which interacts with silica nanoparticles to facilitate their interfacial attachment and jamming during bijel formation. The resulting suspension (referred to henceforward as the ternary mixture for the primary oil, water, and cosolvent components) is exposed in a coflow configuration to a water−CTAB solution using two coaxial capillaries, with a ternary mixture in the inner capillary and the surfactant solution in the external one. Upon contact, ethanol from the ternary mixture diffuses into the surrounding water stream, triggering the oil−water phase separation.

As-produced, STRIPS bijels can be used as reactive separation media for reactions that do not involve significant changes in solution conditions. For example, it is straightforward to induce noncatalytic hydrolysis of acetic anhydride by adding the reactant in the oil phase (hexanediol diacrylate) and trigger the reaction and separation of product upon the formation of STRIPS bijels (see SI). However, many industrially relevant homogeneously catalyzed reactions require more challenging reaction conditions such as changes in the solution pH or temperature, as well as mechanical stirring.[6,15]

Although the attachment energy of nanoparticles to interfaces can be very large,[26] nanoparticles can nevertheless rearrange and even detach from the interface if solution conditions such as pH are altered.[27] This can disrupt the jammed layer of nanoparticles that stabilizes the interfaces throughout the bijel structure, resulting in a loss of bicontinuous morphology as shown in Figure 2a. In this image, upon increasing the solution pH to 9, the bicontinuous (striped) configuration transforms into a structure with discrete domains of water in oil. We believe the increased surface charge of the silica nanoparticles leads to the adsorption of additional CTAB, which makes the nanoparticles preferentially wet the oil phase (see SI).

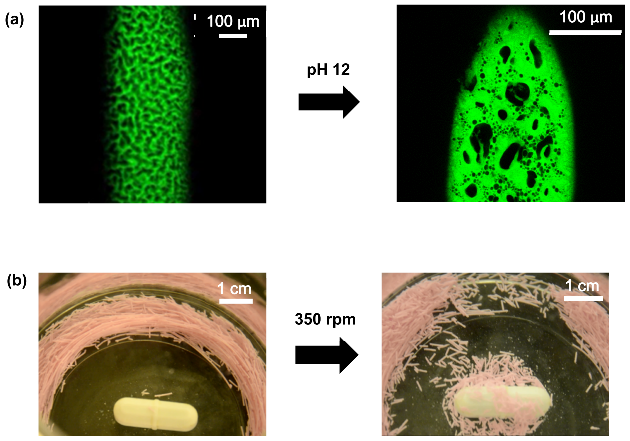

Figure 2. Chemical and mechanical fragility of STRIPS bijels. (a) The bicontinuous morphology is lost after pH change to pH 12. (b) A 2.5 cm long stir bar is placed in an 8 cm diameter container filled with 3 g of bijel fibers and 315 g of water. Stir bar velocity is increased up to 350 rpm, which leads to the breakup of the fibers.

Another critical weakness of STRIPS bijel fibers is their mechanical fragility. Even mild stirring can easily disrupt their integrity as shown in Figure 2b. Moreover the integrity of the jammed nanoparticle layer relies on interfacial tension and therefore on the presence of the oil−water interface itself. Thus, the addition of ethanol or amphiphiles, which increase oil−water miscibility, can disrupt the nanoparticle layers at the interface. Such issues have impeded the adoption of bijels as reactive separation media in industrially relevant reactions.[6,15]

We propose a room temperature treatment that overcomes these shortcomings. We are inspired by previous reports that demonstrated reinforcement of particle-stabilized emulsions *via* the addition of a silane agent.[28,29] By induction of a condensation reaction of the silane and deposition of silica on nanoparticles attached to interfaces, particles at the oil−water interface could be partially and locally fused to each other *via* silica bridges. We use an analogous procedure to induce such local fusion between interfacially jammed nanoparticles at the oil−water interface of the STRIPS bijel. Tetraethyl orthosilicate (TEOS) is added to the ternary mixture. Upon phase separation, TEOS partitions in the bijel oil phase and reacts with the surrounding water to generate thin silica layers that bridge the SiO_2 nanoparticles, locking them in place in the jammed interfacial layer, as schematically shown in Figure 3a.

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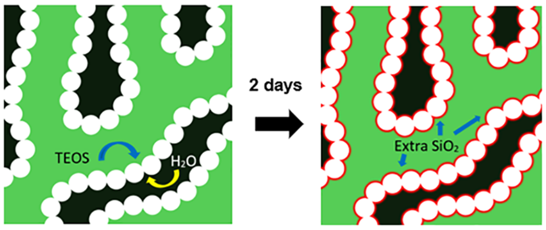


Figure 3. Silica reinforced bijel formation schematics by STRIPS. Tetraethyl orthosilicate (TEOS) is added to the ternary mixture; upon phase separation, it partitions in the oil phase and reacts with the surrounding water to create silica bridges interfacially locking the silica nanoparticles. Fibers are stored for 2 days to ensure complete TEOS conversion.

We perform this treatment at different temperatures (30 and 40 °C), and the bicontinuous morphology is preserved. Moreover this treatment is not limited to fiber-shaped bijels; it is possible to reinforce STRIPS bijel in other geometries as we demonstrate for planar membranes (see SI).

Room temperature silica reinforcement of the bijel imparts robustness to the structure against changes in the solution pH and application of mechanical stresses. The silica-reinforced bijels maintain their macroscopic integrity under the stirring conditions that led to disintegration of STRIPS bijel without the reinforcement as shown in Figure 4a. Also, when the solution pH is changed to pH 13, silica reinforced bijel fibers maintain their bicontinuous microstructure (Figure 4b).

Further proof of the superior mechanical properties of reinforced bijels can be observed by simply inducing mixing and removal of the two fluid phases by multiple ethanol washing cycles followed by evaporation of ethanol itself (Figure 4c,d). The silica-reinforced bijel shell maintains its structure despite the loss of the oil−water interface and evaporation of the liquid mixture. This implies that the structure can withstand the capillary stresses generated during ethanol evaporation, indicating the presence of percolating silica bridges throughout the entire structure. Absent reinforcement, STRIPS bijels completely disintegrate upon the addition of ethanol.

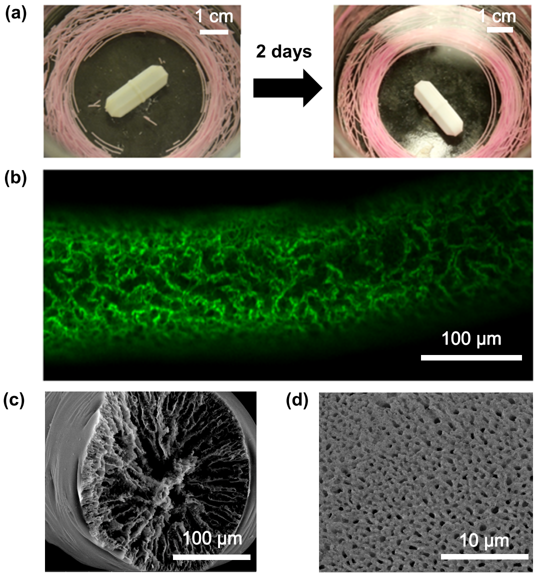


Figure 4. Robust bijel characterization. (a) Silica reinforced bijel mechanical robustness. They can withstand stirring that would destroy as-prepared STRIPS bijels. The experimental conditions are the same as in Figure 2b. (b) Silica reinforced bijel chemical robustness. The bicontinuous morphology is preserved after pH change from 3 to 13. (c) SEM micrographs of silica of cross-section and (d) surface of reinforced bijels; the silica scaffold survives solvent evaporation and the porous structure is retained.

An important concern is that the reinforcement process *via* the deposition of thin silica layers could render the interface impermeable. That is, the silica layers may block the interstices between the jammed nanoparticles and impede transport between oil and water essential to biphasic reaction schemes. We confirm that the porosity of the interfacial layer is retained and that interphase transport can occur, by extracting the oil phase from a bijel. The silica suspension with oil, water, and ethanol in a single phase (*i.e.*, the bijel precursor solution) is stained with a hydrophobic dye, Sudan Red. Fibers are extruded into a water bath (see Figure 1). Ethanol is then added to the water bath, and the entire system is stirred. Subsequently, the ethanol−water mixture is replaced with fresh ethanol multiple times. After 140 min, the fibers lose their red color and turn white, indicating that the oil phase has been removed, likely through the interstitial pores of the reinforced nanoparticles layer (see SI).

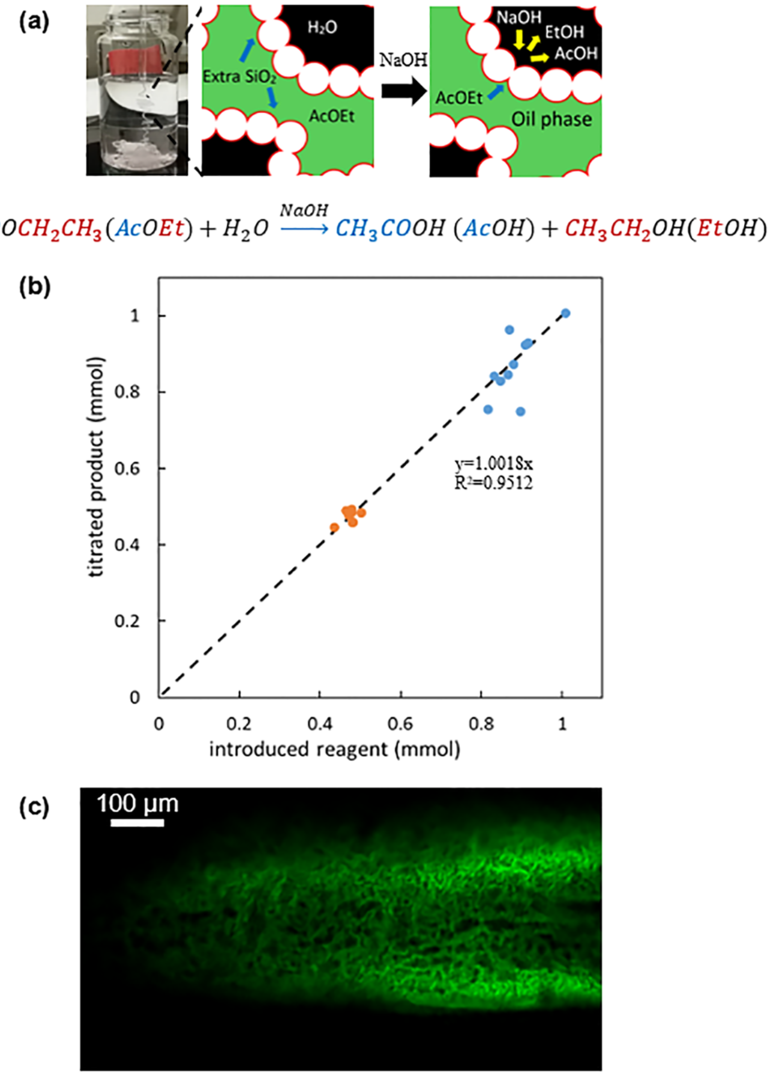
The influence of TEOS content on bijel interfacial morphology is characterized by Brunauer−Emmett−Teller (BET) measurement of samples (see Table 1 and SI). The extra silica network generated by TEOS hydrolysis decreases the pore diameter and increases the average surface area, indicating that the silica shell deposits within the pores, and that the deposited silica network itself is porous. As summarized in Table 1, the change in pore size or thickness of the silica reinforcing shell depends on the concentration of TEOS. Permeation experiments demonstrate that the pores remain open up to TEOS concentration of 10%.

Table 1. Properties of Reinforced Bijel Samples from Nitrogen Adsorption Isotherms

sample	S_{BET}[a] (m^2/g)	pore diameter (nm)
2%TEOS	106	12.4
5%TEOS	127	6.5
10%TEOS	134	6.1

[a] Surface area.

The mechanical and chemical integrity of STRIPS bijels opens the possibility to enable reactive separations that require changes in the solution conditions. To demonstrate this concept, we choose the base-catalyzed hydrolysis of ethyl acetate as such homogeneously catalyzed reactions are often performed in the chemical industry. To ensure that the oil phase does not participate in the reaction and remains stable, we use a mixture of inert cyclohexanone and bromobenzene as the oil phase. To induce the hydrolysis reaction, the reagent, ethyl acetate, is added to the ternary mixture together with TEOS. Upon phase separation, ethyl acetate partitions into the oil domains. After the TEOS reaction has occurred, the solution pH is increased by the addition of base (NaOH) to trigger the reaction (pH 13 and 13.5 depending on the amount of reagent used). Bijels fibers within a container are placed in an oil bath at 40 °C for 2 days, as shown in Figure 5a. The reaction releases an acid as a product (see reaction equation in Figure 5), which reduces the solution pH; therefore, the



$$CH_3COOCH_2CH_3(AcOEt) + H_2O \xrightarrow{NaOH} CH_3COOH\ (AcOH) + CH_3CH_2OH(EtOH)$$

Figure 5. Reactive separation with homogeneous catalyst in STRIPS bijel fiber. (a) Description of reactive separation process. The ternary mixture is kept at 0 °C to avoid any unwanted reaction prior to bijel formation. The reagent is loaded in the ternary mixture and upon phase separation partitions in the oil phase. After TEOS reaction, pH is increased to the reaction value, and the fibers are placed in an oil bath at 40 °C for 2 days. (b) Reaction conversion measurement by titration. The moles of product are plotted against the moles of reagent introduced, their molar ratio equals the ratio between the product and reagent stoichiometric coefficients, which indicates total conversion has been achieved. Blue markers represent reactions performed with a starting pH of 13.5, whereas the orange markers represent reactions performed with a starting pH of 13. (c) Confocal image of bijel fiber after reaction that shows morphology retention.

reaction conversion can be determined by measuring the change in the solution pH. The water solution after reaction is titrated using a commercial solution of 1 N HCl, the difference between the recorded moles of base before and after the reaction corresponds to the product generated by the reaction. In Figure 5b, the moles of product are plotted against the moles of reagent introduced. Their ratio equals the stoichiometric coefficients ratio, which indicates complete conversion and recovery of products for both conditions (see also SI). The bijel fibers also retain their bicontinuous morphology as shown in Figure 5c. We also confirm the bicontinuous morphology based on a fluorescent dye diffusion experiment (see SI).

CONCLUSIONS

This current work focuses on the reinforcement of STRIPS bijels to make them chemically, mechanically, and thermally robust, which is a key step toward realizing continuous reactive separation. We have demonstrated that silica-reinforced STRIPS bijels can be used for simultaneous reactive separation in batch fashion, accessing the entire pH spectrum, a task impossible for untreated bijels. This reinforcement treatment is very versatile, allowing the incorporation of different functionalities on bijels while retaining the essential features for bijels such as bicontinuous morphology and interphase mass transfer capability. To further advance the long-term goal of realizing continuous reactive separation, we have performed preliminary experiments in a flow-through reactor and have confirmed that continuous reactive separations can be achieved with the TEOS-reinforced robust STRIPS bijel (see SI). We will be developing a thorough study of this system in our future work, with a focus on systems of relevant industrial and scientific interest like condensation reaction of biomass-derived oxygenates[30] and formation of oleo-furan surfactants.[31] Moreover, by using catalytically active oxides such as alumina and titania as the reinforcing materials, it will be possible to induce reactive separations based on heterogeneous catalysis, which we are also currently exploring.

METHODS

Most chemical reagents are purchased from Sigma unless otherwise noted. For bijel fabrication, Ludox TMA colloidal silica (SiO_2, 34 wt % suspension in water), cetyltrimethylammonium bromide (CTAB, BioUltra >99%), diethyl phthalate (DEP, 99.5%), ethanol (100%, Decon Laboratories), Nile Red (Technical grade), Sudan Red (95%), bromobenzene (ReagentPlus, 99%), cyclohexanone (ACS reagent, >99%), 1,6-hexanediol diacrylate (HDA, 99% Alfa Aesar), tetraethyl orthosilicate (TEOS, reagent grade, 98%), ethyl acetate (99.9%, Fisher Scientific), acetic anhydride (99.7%,Fisher Scientific, Ac_2O), 0.1 N HCl solution (Fisher Scientific) are used. Round glass capillary (outer diameter 1.0 mm, inner diameter 0.58 mm) and square capillary (outer diameter 1.5 mm, inner diameter 1.05 mm, length 150 mm) are obtained from World Precision Instruments and AIT Glass, Inc., respectively. The diameter of tip for the round glass capillary is narrowed to be 20−300 μm. The round capillary is inserted into the square capillary and aligned concentrically to fabricate the device for STRIPS bijel fabrication. The capillaries are coated with poly(diallydimethylammonium chloride) (PDADMAC) to avoid undesirable adsorption of extruded bijel fibers. The syringe pumps are purchased from Harvard Apparatus.

Preparation and Application of STRIPS Bijels for Homogeneous Catalyzed Reactive Separation. We use 7 components: (i) bromobenzene, (ii) cyclohexanone, (iii) pure ethanol, (iv) solution of hexadecyltrimethylammonium bromide (CTAB) in ethanol (0.2 M), (v) suspension of silica nanoparticles in water (Ludox TMA, pH = 3), (vi) ethyl acetate, and (vii) tetraethyl orthosilicate (TEOS). Components i−vi are mixed and placed in an ice bath. The following proportions are used for the pH 13 (13.5) hydrolysis: 1 (0.95) g (i), 0.8 (0.75) g (ii), 1.22 g (iii), 0.51 g (iv), 1.32 g (v), and 0.125 (0.25) mL (vi). After roughly 30 min, 0.125 mL of TEOS is added. A water solution of 1 mM CTAB at pH 3 (continuous phase) is prepared; such mixtures are injected through round and square glass capillaries, respectively.[23] The syringe used for flowing the seven component mixture (henceforward reactive mixture) is placed in an ice jacket to prevent any unwanted hydrolysis during bijel formation (see SI). The extruded reactive mixture is collected in a container filled with a continuous phase solution. Generally, approximately 1.8 g of mixture is injected in a container filled with approximately 15 g of water. Therefore, we have roughly 0.47 (0.85) mmol of reagent. After 2 days, sodium hydroxide is added to bring the pH to 13 (13.5), and the fibers are placed in an oil bath at 40 °C for 2 days. The water phase surrounding the fiber is titrated using a commercial solution of HCl, 0.1 N, to measure the concentration of acetic acid released by the reaction.

Preparation and Application of STRIPS Bijels for Imaging. HDA or DEP can be used instead of i and ii as oil. After fabrication of bijel fiber, the bicontinuous structures are imaged by using a confocal microscope (laser excitation at 488 nm and emission at 500−600 nm) with Nile red staining. Sudan Red is used as a contrast agent when confocal microscopy is not performed.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b05718.

- Confocal microscopy of bijels and reaction conversion results (PDF)
- STRIPS bijel imaging *via* confocal microscopy (AVI)
- STRIPS bijel morphology change after pH change to pH = 9 (AVI)
- Robust bijel morphology retention after pH change to pH = 11 (AVI)
- Robust bijel morphology retention after pH change to pH = 13(AVI)
- Robust bijel morphology retention after reaction with associated thermal and chemical stresses (AVI)
- Robust bijel retention of morphology after reaction dye permeation experiment (AVI)
- Robust bijel membrane with 2% TEOS (AVI)
- Robust bijel fiber reacted with 5% TEOS (AVI)
- Robust bijel fiber reacted with 10% TEOS (AVI)
- Confocal scans of reinforced bijel manufactured at 40°C (AVI)
- Confocal scans of reinforced bijel manufactured at 30°C (AVI)
- Stirring of STRIPS bijels illustrating fragility of STRIPS bijel under mechanical agitation (AVI)
- Stirring of robust bijels illustrating retention of morphology and physical integrity under mechanical agitation (AVI)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Jarrousse, J. Influence Dun Chlorure Dammonium Quaternaire Sur Des Reactions Entre Composes a Hydrogene Mobile et Derives Chlores. *C R Chim* **1951**, *232*, 1424−1426.

(2) Duynstee, E. F. J.; Grunwald, E. Organic Reactions Occurring in or on Micelles. Reaction Rate Studies of the Alkaline Fading of Triphenylmethane Dyes and Sulfonphthalein Indicators in the Presence of Detergent Salts. *J. Am. Chem. Soc.* **1959**, *81*, 4540−4542.

(3) Menger, F. M.; Donohue, J. A.; Williams, R. F. Catalysis in Water Pools. *J. Am. Chem. Soc.* **1973**, *95*, 286−288.

(4) Joó, F. Aqueous Biphasic Hydrogenations. *Acc. Chem. Res.* **2002**, *35*, 738−745.

(5) Cole-Hamilton, D. J. Homogeneous Catalysis–New Approaches to Catalyst Separation, Recovery, and Recycling. *Science* **2003**, *299*, 1702−1706.

(6) Manabe, K.; Iimura, S.; Sun, X.-M.; Kobayashi, S. Dehydration Reactions in Water. Brønsted Acid−Surfactant-Combined Catalyst for Ester, Ether, Thioether, and Dithioacetal Formation in Water. *J. Am. Chem. Soc.* **2002**, *124*, 11971−11978.

(7) Tundo, P.; Perosa, A. Multiphasic Heterogeneous Catalysis Mediated by Catalyst-Philic Liquid Phases. *Chem. Soc. Rev.* **2007**, *36*, 532−550.

(8) Minakata, S.; Komatsu, M. Organic Reactions on Silica in Water. *Chem. Rev.* **2009**, *109*, 711−724.

(9) Yang, X.; Wang, X.; Qiu, J. Aerobic Oxidation of Alcohols over Carbon Nanotube-Supported Ru Catalysts Assembled at the Interfaces of Emulsion Droplets. *Appl. Catal., A* **2010**, *382*, 131−137.

(10) Crossley, S.; Faria, J.; Shen, M.; Resasco, D. E. Solid Nanoparticles That Catalyze Biofuel Upgrade Reactions at the Water/Oil Interface. *Science* **2010**, *327*, 68−72.

(11) Faria, J.; Ruiz, M. P.; Resasco, D. E. Phase-Selective Catalysis in Emulsions Stabilized by Janus Silica-Nanoparticles. *Adv. Synth. Catal.* **2010**, *352*, 2359−2364.

(12) Ruiz, M. P.; Faria, J.; Shen, M.; Drexler, S.; Prasomsri, T.; Resasco, D. E. Nanostructured Carbon-Metal Oxide Hybrids as Amphiphilic Emulsion Catalysts. *ChemSusChem* **2011**, *4*, 964−974.

(13) Zhang, W.; Fu, L.; Yang, H. Micrometer-Scale Mixing with Pickering Emulsions: Biphasic Reactions without Stirring. *ChemSusChem* **2014**, *7*, 391−396.

(14) Yang, H.; Zhou, T.; Zhang, W. A Strategy for Separating and Recycling Solid Catalysts Based on the PH-Triggered Pickering-Emulsion Inversion. *Angew. Chem., Int. Ed.* **2013**, *52*, 7455−7459.

(15) Zhang, M.; Wei, L.; Chen, H.; Du, Z.; Binks, B. P.; Yang, H. Compartmentalized Droplets for Continuous Flow Liquid−Liquid Interface Catalysis. *J. Am. Chem. Soc.* **2016**, *138*, 10173−10183.

(16) Stratford, K.; Adhikari, R.; Pagonabarraga, I.; Desplat, J.-C.; Cates, M. E. Colloidal Jamming at Interfaces: A Route to Fluid-Bicontinuous Gels. *Science* **2005**, *309*, 2198−2201.

(17) Herzig, E. M.; White, K. A.; Schofield, A. B.; Poon, W. C. K.; Clegg, P. S. Bicontinuous Emulsions Stabilized Solely by Colloidal Particles. *Nat. Mater.* **2007**, *6*, 966−971.

(18) Cates, M. E.; Clegg, P. S. Bijels: A New Class of Soft Materials. *Soft Matter* **2008**, *4*, 2132.

(19) Lee, M. N.; Mohraz, A. Bicontinuous Macroporous Materials from Bijel Templates. *Adv. Mater.* **2010**, *22*, 4836−4841.

(20) Lee, M. N.; Mohraz, A. Hierarchically Porous Silver Monoliths from Colloidal Bicontinuous Interfacially Jammed Emulsion Gels. *J. Am. Chem. Soc.* **2011**, *133*, 6945−6947.

(21) Tavacoli, J. W.; Thijssen, J. H. J.; Schofield, A. B.; Clegg, P. S. Novel, Robust, and Versatile Bijels of Nitromethane, Ethanediol, and Colloidal Silica: Capsules, Sub-Ten-Micrometer Domains, and Mechanical Properties. *Adv. Funct. Mater.* **2011**, *21*, 2020−2027.

(22) Reeves, M.; Stratford, K.; Thijssen, J. H. J. Quantitative Morphological Characterization of Bicontinuous Pickering Emulsions *via* Interfacial Curvatures. *Soft Matter* **2016**, *12*, 4082−4092.

(23) Haase, M. F.; Stebe, K. J.; Lee, D. Continuous Fabrication of Hierarchical and Asymmetric Bijel Microparticles, Fibers, and Membranes by Solvent Transfer-Induced Phase Separation (STRIPS). *Adv. Mater.* **2015**, *27*, 7065−7071.

(24) Haase, M. F.; Sharifi-Mood, N.; Lee, D.; Stebe, K. J. *In Situ* Mechanical Testing of Nanostructured Bijel Fibers. *ACS Nano* **2016**, *10*, 6338−6344.

(25) Haase, M. F.; Jeon, H.; Hough, N.; Kim, J. H.; Stebe, K. J.; Lee, D. Multifunctional Nanocomposite Hollow Fiber Membranes by Solvent Transfer Induced Phase Separation. *Nat. Commun.* **2017**, *8*, 1234.

(26) Levine, S.; Bowen, B. D.; Partridge, S. J. Stabilization of Emulsions by Fine Particles I. Partitioning of Particles between Continuous Phase and Oil/Water Interface. *Colloids Surf.* **1989**, *38*, 325−343.

(27) Poulichet, V.; Garbin, V. Ultrafast Desorption of Colloidal Particles from Fluid Interfaces. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 5932−5937.

(28) Liu, Y.; Chen, X.; Xin, J. H. Silica Nanoparticles-Walled Microcapsules. *J. Mater. Sci.* **2006**, *41*, 5399−5401.

(29) Wang, H.; Zhu, X.; Tsarkova, L.; Pich, A.; Möller, M. All-Silica Colloidosomes with a Particle-Bilayer Shell. *ACS Nano* **2011**, *5*, 3937−3942.

(30) Zapata, P. A.; Faria, J.; Pilar Ruiz, M.; Resasco, D. E. Condensation/Hydrogenation of Biomass-Derived Oxygenates in Water/Oil Emulsions Stabilized by Nanohybrid Catalysts. *Top. Catal.* **2012**, *55*, 38−52.

(31) Park, D. S.; Joseph, K. E.; Koehle, M.; Krumm, C.; Ren, L.; Damen, J. N.; Shete, M. H.; Lee, H. S.; Zuo, X.; Lee, B.; Fan, W.; Vlachos, D. G.; Lobo, R. F.; Tsapatsis, M.; Dauenhauer, P. J. Tunable Oleo-Furan Surfactants by Acylation of Renewable Furans. *ACS Cent. Sci.* **2016**, *2*, 820−824.

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