Electronic Supplementary Information

for

Particle-stabilised non-aqueous systems

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Experimental

Materials:

Fumed silica nanoparticles were produced by the introduction of volatile chlorosilanes into an oxyhydrogen flame and consist of ultrapure amorphous silicon dioxide. The nanoparticles had a mean primary particle diameter of approximately 20 nm and were coated to different extents with dichlorodimethylsilane (DCDMS). Particle wettability was characterised in terms of the measured percentage of unreacted SiOH groups remaining on the surface using a base titration method.[1] This ranged from 100% (most hydrophilic) to 14% (most hydrophobic). The coated silica nanoparticles with measured values of %SiOH were kindly supplied by Wacker-Chemie (Germany). Although the primary particle diameter was 20 nm, the powder also contained fused aggregates of multiple primary particles and larger agglomerates of the fused aggregates.

Laponite (RD) clay nanoparticles was provided by (Southern Clay Products Texas, USA). According to the manufacturer, Laponite RD is a fully synthetic clay similar in structure and composition to natural hectorite of the smectite group. It has an empirical formula of $Na^{0.7+}$ $[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{0.7-}$, where Na is an interlayer exchangeable cation, and a charge deficiency of 0.7 per unit cell. It is comprised of six octahedral magnesium ions sandwiched between two layers of four tetrahedral silicon atoms. Isomorphous substitution of magnesium with lithium in the central sheet creates a net negative charge compensated by intralayer sodium ions located between adjacent layers in a stack. It contains 59.5% SiO_2, 27.5% MgO, 0.8% Li O, and 2.8% Na_2O and has a specific surface area of 370 m^2 g^{-1}, and cationic exchange capacity (CEC) of 7.3 x 10^{-4} mol g^{-1}. The dimensions of the elementary platelets are as follows: diameter 30 nm and thickness 0.1 nm. In the dry state or in organic solvents, the platelets are pilled up, forming 2-3 layers thick tactoïds held together by long-range attractive forces. Reactive silanols, corresponding to structural defects, are located at the broken edges of these stacks while MgOH groups are contained into the internal space of the individual clay sheets. Natural kaolinite sample was collected from local area and grounded to fine powder.

Iron (III) chloride ($FeCl_3$, anhydrous, 97%), Ethyl alcohol and acetone were purchased from Fisher Chemicals. Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$, 98%), ammonia solution (33 wt.%), ethylene glycol (>95%), n-hexane (> 99%), benzene (> 99%), were purchased from BDH Chemicals UK). Castor oil, oleic acid, paraffin light oil from Avonchem Limited (UK). Dimethyl sulfoxide DMSO (> 99%), dimethylformamide DMF (> 99%) and 1-chlorohexadecane (> 98%) were purchased from Fluka. Glycerine (> 99%) and acetonitrile (> 98%) were purchased from Winlab chemicals. Pure corn oil and pure virgin olive oils were purchased from local stores. Formamide (> 98.5%), carbon tetrachloride (>99%) were purchased from Merck. Clove oil was purchased from Alan Pharma (UK). Petroleum ether (60-80 °C) was purchased from Qualikems (India). Styrene (99.5%), thermal initiator 2,2′-Azobis(2-methylpropionitrile) (AIBN) (98%), toluene, Divinylbenzene (DVB), Cetyltrimethylammonium bromide (CTAB) (99.99%), Rhodamin B (95%) and cyclohexane (>98%) were purchased from Sigma-Aldrich. Styrene was de-inhibited by passing through neutral aluminium oxide column or by washing with 10% NaOH solution and dried.

Modification of Laponite (RD) nanoparticles:

In a round bottom flask 20 g of laponite clay were dispersed in 500 ml distilled water containing 6 g, 65 x 10^{-4} M of CTAB, which caused complete cation exchange, at room temperature then the temperature was increased to 80 °C under vigorous stirring for 6–8 hrs with a condenser. The resulting modified laponite clay was separated by filtration and washed several times with distilled water to remove any free surfactant (checked by $AgNO_3$ solution) then vacuum dried at 60 °C for 24 hrs and kept in a sealed container until use.

Preparation of oleic acid coated magnetite nanoparticles:

We have used a classical co-precipitation of Fe^{3+} and Fe^{2+} with NH_4OH to prepare the magnetite (Fe_3O_4) nanoparticles.[2] The method involves co-precipitation from Fe^{2+} and Fe^{3+} aqueous salt solutions by addition of a base. The chemical reaction may be written as follows:

$$Fe^{2+}+2Fe^{3+}+8OH^{-} \rightarrow Fe_3O_4+4H_2O \quad (1)$$

According to this reaction an initial molar ratio of Fe^{3+}:Fe^{2+} =2:1 is needed for the production of Fe_3O_4. The required amount of $FeCl_3$ and $FeCl_4.4H_2O$ were dissolved in 40 ml of Milli-Q water. The solution was heated at 80 °C for 1 hour while being stirred. Then 12 ml of NH_4OH (33% w/w) and 1g oleic acid were quickly added. The resulting suspension is vigorously stirred for another 1 hour at the same temperature and then cooled to room temperature. The precipitated particles were washed five times with water and ethanol, separated by magnetic decantation and dried in oven at 80 °C.

Preparation of Pickering non-aqueous simple o/o and double o/o/o emulsions:

Simple o/o emulsions were prepared by dispersing a known mass of the solid particles into one liquid which we expect to be the continuous phase of the formed emulsion. The second oil phase was added with the desired volume fraction to the solid particle dispersions. Note that the particle mass is based on the oil in which they disperse in while the phase volume fraction is based on the total volume of the system. There was no rule of selecting which oil or solvent will be a good medium for dispersing either the very hydrophobic silica of 23% SiOH, or the relatively hydrophobic 50% SiOH silica. In other words, 23% SiOH silica can be easily dispersed in polar aprotic solvents like DMF, DMSO or formamide as well as in nonpolar solvents like hexane or benzene. The mixture was then homogenised using a DI-25 basic Yellow-line, IKA (Germany) homogeniser (rotor-stator) with an 18 mm head operating at 13,000 rpm for 2-3 minutes. The oil phase of the primary o/o emulsion can be loaded, as required, with magnetite nanoparticles with a known mass based on this phase or AIBN initiator and 1 wt.% DVB (based on oil mass) if polymerisation is required. Stability against coalescence of all emulsions was monitored by following observation of any free layer or the phase started to form either on top or bottom of the emulsion. Since, we used various oils with different densities and refractive indices, careful must be taken when determining the emulsion type and whether it creams upwards or sediments downwards. The emulsion continuous phase was determined by measurement by observation of what happened when a drop of emulsion was added to a volume of each of the pure liquid phases. The emulsions only dispersed in the liquid when its continuous phase matched the liquid to which it was added.

Generally, we found that double o/o/o emulsions are better stabilised by a single silica particle type at either interface, namely the hydrophobic silica. Hydrophilic silica particles with 80% SiOH are not good candidate for stabilising such emulsions even if they initially dispersed in some polar oils like formamide (which is the nearest example of water in terms of high polarity). Nevertheless, still we cannot adapt general rules here for selecting which couple of solvents in combination of which silica particles can make an emulsion, which require other experimental investigations based on particle contact angle and surface and interfacial tensions of the various oils used here which are under investigation. Double o/o/o emulsions were prepared in two-stage method. Stage 1 involved the preparation of a simple emulsion as shown above. In stage 2, the primary o/o emulsion, just prepared in stage 1, is re-emulsified into another immiscible oil phase containing a known mass (expressed in wt.% of continuous phase) of solid nanoparticles. Most of double o/o/o emulsions were formed by hand shaking the primary o/o emulsions in the outer oil phase. However, in some cases the second homogenisation step was performed using a homogeniser working at 8,000 rpm for 10 seconds. Selecting the volume fraction of the primary emulsion $\phi_{o/o}$ in the final o/o/o emulsions is crucial for the structure and morphology of the resulted materials since double emulsions showed catastrophic phase inversion at higher $\phi_{o/o}$, say between 0.4-0.6. Usually, double emulsions formed between these values exhibited unique porous structure when the middle oil phase was subsequently polymerised.

Images and video-recorded by optical and fluorescence microscopy using (Olympus BX-41 fitted with DP70 digital camera) and applying the Rhodamine TRITC filter set. Images and videos were processed using Corel Paintshop pro X4 software processed using Image-pro v.6.0 software. Average emulsion drop diameters were obtained from the optical images by measuring a minimum of 20 drops from each slide. Digital images were taken by a personal Samsung galaxy smart phone S1.

Preparation of Pickering porous polyMIPEs:

Pickering polyMIPE formed by polymerisation of a pre-made (50:50) glycerine-in-styrene non aqueous o/o emulsion stabilised by 2 wt.% of 50% SiOH silica nanoparticles at 75 °C for 24 hours. Pickering polyMIPE prepared via polymerisation of a styrene-in-glycerine-in-styrene (o/o/o) non-aqueous double emulsion, stabilised by 3 wt.% of 50% SiOH silica in the inter s/g interface and 2 wt.% of the same type of silica in the outer g/s interface $\phi_s = 0.2$, $\phi_{s/g} = 0.5$. For both simple and double emulsions, 2 wt.% of AIBN (based on monomer mass) was added to the outer oil phase for simple o/o emulsions and to both inner and outer oil phases of the double o/o/o emulsions. Polymerisation of double o/o/o emulsions were prepared in similar way but with different liquids, such as formamide-in-styrene-in-water, formamide-in-styrene-in-formamide or even triple non-aqueous emulsion of the type formamide-in-styrene-in-formamide-in-styrene (o/o/o/o) which is under structure analysis.

Polymeric materials (microparticles or porous monoliths) were characterised by Jeol SEM (JSM-6380 LA). Around 0.5 cm^3 or solid dry sample was fixed in the SEM sample holder by a double-sided carbon black sticker. All samples were Pt coated before examined by SEM. Pore size was measured as an average of around 30 pores in the sample.

Foam and liquid marbles preparation and characterisation:

Homogeniser or hand shaking methods were used to generate foams with either ethylene glycol or glycerol. The desired mass of silica particles was added to a known mass of the oil and the layer of silica powder usually formed on top of either liquid. The density of the foam were measured gravimetrically for selected samples by measure the mass and volume of part of the upper creamed foam layer and hence calculate the density. Volume fraction of the foam was measured by dividing the height in “cm” of the foam by the total height of the system (foam and separated clear liquid layer). Foam microstructures were examined using optical microscope shown above. Foam height remained fixed for weeks with no coalescence or disproportionation. Liquid marbles of glycerine-in-air were stabilised by silica of 23% SiOH only. Liquid marbles were generated by simple roll small drops of the liquid on a bed of silica particles. Some dyes were used as Congo red, methylene blue, Rhodamin B and model drug Isatin. Since glycerine has relatively high surface tension (64 mN/m at 20 °C) and low vapour pressure, the liquid marbles formed were very stable for weeks in open air.

Table 1 Summary of selected Pickering non-aqueous systems.

Syst. no.	Oil or gas phase			particle type	wt.% of particles	Emulsion type	Stability[a]	Notice
	inner	middle	outer					
1	glycerine		styrene	50% SiOH silica	1 in styrene	g/s	stable	C.P.I[b], ϕ_{g}(0.6-0.7)
2	styrene		glycerine	80% SiOH silica	1 in glycerine	s/g	unstable	
3	styrene	glycerine	styrene	50% SiOH silica	3 in glyc., 2 in styr.	s/g/s	stable	polyMIPDE
4	acetonitrile		corn	23% SiOH silica	1 in corn	ac/cor	stable	C.P.I, ϕ_{ac}(0.3-0.4)
5	glycerine		clove	50% SiOH silica	1 in clove	g/clo	stable	
5	clove	glycerine	clove	50% SiOH silica	1 in glyc, 2 in clo	clo/g/clo	stable	can be magnetic
7	glycerine	clove	glycerine	50% SiOH silica	1 in clo, 2 in glyc	g/clo/g	stable	
8	e. glycol		styrene	50% SiOH silica	1 in styrene	eg/s	stable	C.P.I, ϕ_{eg} (0.6-0.7)
9	acetonitrile		paraffin	23% SiOH silica	1 in paraffin oil	ac/par	metastable	~ ϕ_{ac} 0.2-0.3
10	glycerine		castor	50% SiOH silica	1 in castor	g/cast	stable	C.P.I, ϕ_{g} (0.5-0.6)
11	glycerine	castor	glycerine	50% SiOH silica	1 in cast, 1 in glyc	g/cast/g	stable	translucent
12	glycerine		olive	23% SiOH silica	1 in olive	g/oli	stable	C.P.I, ϕ_{g} (0.7-0.8)
13	glycerine		olive	50% SiOH silica	1 in olive	g/oli	sable	C.P.I, ϕ_{g} (0.6-0.7)
14	glycerine		olive	organo-laponite	1 in olive	g/oli	stable	
15	glycerine		olive	80% SiOH silica	1 in olive	no	unstable	
16	formamide		pet. ether	23% SiOH silica	1 in pet.ether	fa/pe	stable	no inversion
17	formamide		pet. ether	50% SiOH silica	1 in pet.ether	fa/pe	stable	multiple at ϕ_{fa} 0.4
18	formamide		styrene	50% SiOH silica	1 in styrene	fa/s	stable	C.P.I, ϕ_{fa} (0.6-0.7)
19	formamide	styrene	formamide	50% SiOH silica	2 in sty, 2 in fa	fa/s/fa	stable	fluorescent, magn.
20	n-hexane		formamide	50% SiOH silica	1 in formamide	hex/fa	stable	can be magnetic
21	CCl4		formamide	50% SiOH silica	1 in formamide	ct/fa	stable	C.P.I, ϕ_{eg} (0.4-0.5)
22	air		e. glycol	23% SiOH silica	1,3 in e. glycol	air/eg	stable	(NAF) Foam
23	air		e. glycol	50% SiOH silica	1 in e. glycol	no		dispersion
24	air		glycerine	23% SiOH silica	1,3 in glycerine	air/g	stable	(NAF) Foam
25	air		glycerine	50% SiOH silica	1,3 in glycerine	air/g	stable	foam/liquid
26	benzene		formamide	50% SiOH silica	1 in formamide	b/fa	stable	
27	styrene		formamide	organo-laponite	1 in formamide	s/fa	stable	HNP
28	styrene + OCMNs		formamide	organo-laponite	1 in formamide		stable	HNP
29	formamide	styrene	glycerine	50% SiOH silica	2 in sty, 2 in glyc	fa/s/g	-	Under test
30	styrene		formamide	50% SiOH silica	1 in styrene	s/fa	stable	C.P.I, ϕ_{s} (0.4-0.6)
31	paraffin		DMSO	50% SiOH silica	1 in DMSO	parf/dmso	stable	stable up to ϕ_{par} 0.6
32	DMSO		paraffin	23% SiOH silica	1 in DMSO	dmso/parf	stable	C.P.I, ϕ_{dm} (0.5-0.6)
33	1-chloro hexadecane		e. glycol	50% SiOH silica	1 in e. glycol	chex/eg	stable	C.P.I,ϕ_{chex} (0.6-0.7)
34	DMF		cyclohexane	23% SiOH silica	2 in c.hexame	dmf/chx	stable	C.P.I,ϕ_{dmf} (0.4-0.5)
35	cyclohexane		DMF	23% SiOH silica	2 in DMF	chx/dmf	stable	viscous translucent
36	formamide		paraffin	50% SiOH silica	1 in paraffin	fa/parf	stable	gel like at $\phi_{fa} = 0.5$
37	DMF		hexane	50% SiOH silica	1 in either	no	unstable	phase separation
38	DMF		hexane	23% SiOH silica	2 in c.hexame	dmf/hex	stable	C.P.I,ϕ_{dmf} (0.4-0.5)
39	DMSO		hexane	23% SiOH silica	1 in hexane	dmso/hex	stable	
40	glycerine		silicon oil	50% SIOH silica	1 in silicon oil	g/so	stable	C.P.I,ϕ_{g} (0.6-0.7)
41	silicon oil		glycerine	natural kaolinite	1 in glycerine	so/g	stable	C.P.I,ϕ_{so} (0.6-0.7)
42	glycerine	silicon o	glycerine	50% SIOH silica	1 in silicon,1 in g	g/so/g	stable	multiple
43	silicon oil	glycerine	silicon oil	50% SIOH silica	1 in g, 1 in silicon	so/g/so	stable	multiple
44	castor		silicon oil	23% SIOH silica	1 in silicon oil	g/so	stable	C.P.I,ϕ_{g} (0.6-0.7)
45	formamide		ionic liquids	both	-	-	-	Under test
46	liquid crystals		oils	any	-	-	-	planned

[a] Refers to stability against coalescence, [b] C.P.I (catastrophic phase inversion). HNP (hybrid non-aqueous particles), NAF (non-aqueous foam)

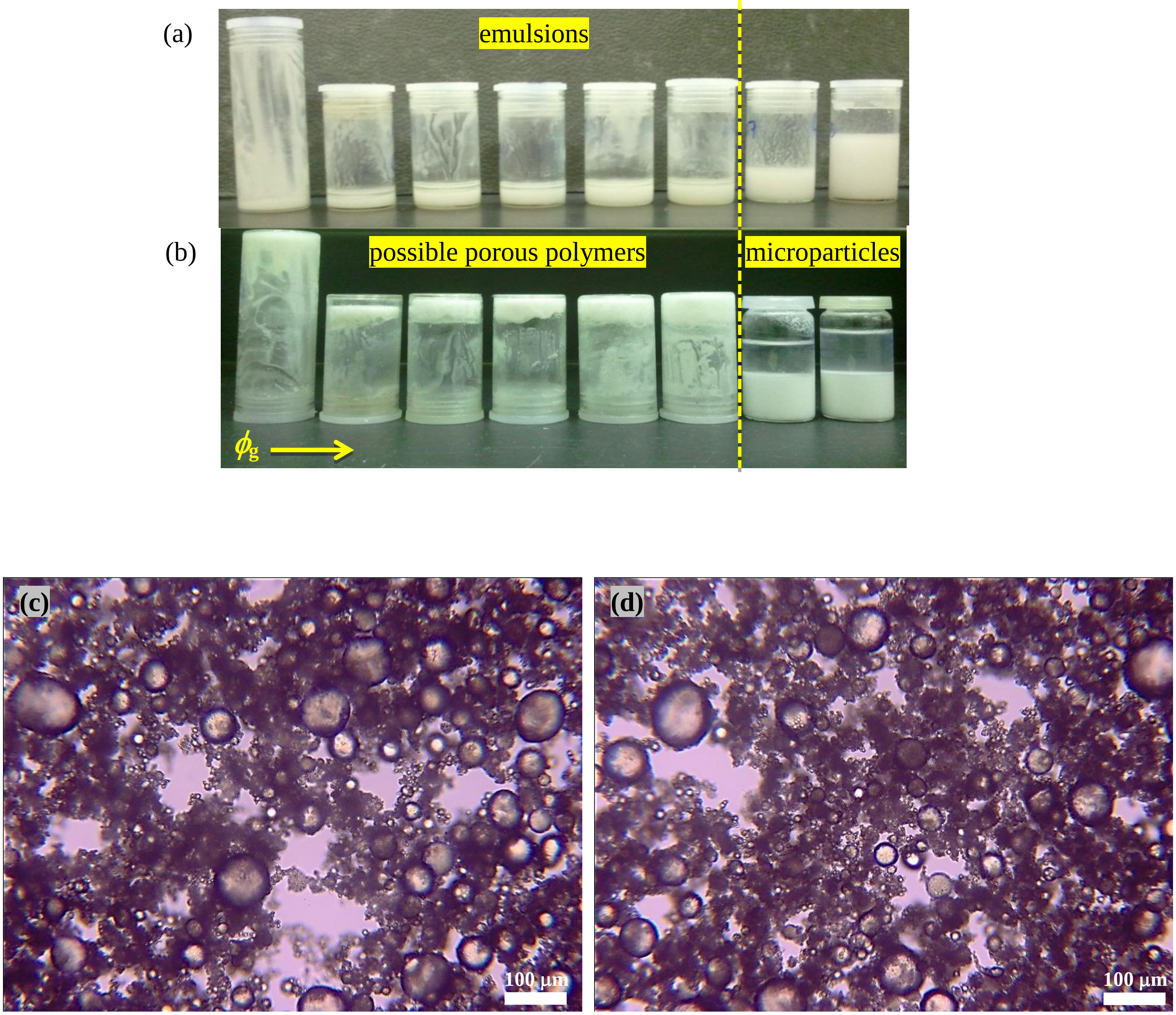

Fig.S1. (a) Digital image for glycerine-in-styrene (g/s) non-aqueous emulsions as a function of volume fraction of glycerine, ϕ_g, from left to right (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8). The emulsions were stabilised by **1** wt.% of 50% SiOH silica nanoparticles dispersed initially in styrene containing 2 wt.% of AIBN initiator. (b) Polymeric materials formed after suspension polymerisation of corresponding emulsions shown in “a”. Optical micrographs polystyrene microparticles formed by polymerisation of the inverted s/g emulsions at (c) ϕ_g = 0.7 and (d) ϕ_g = 0.8.

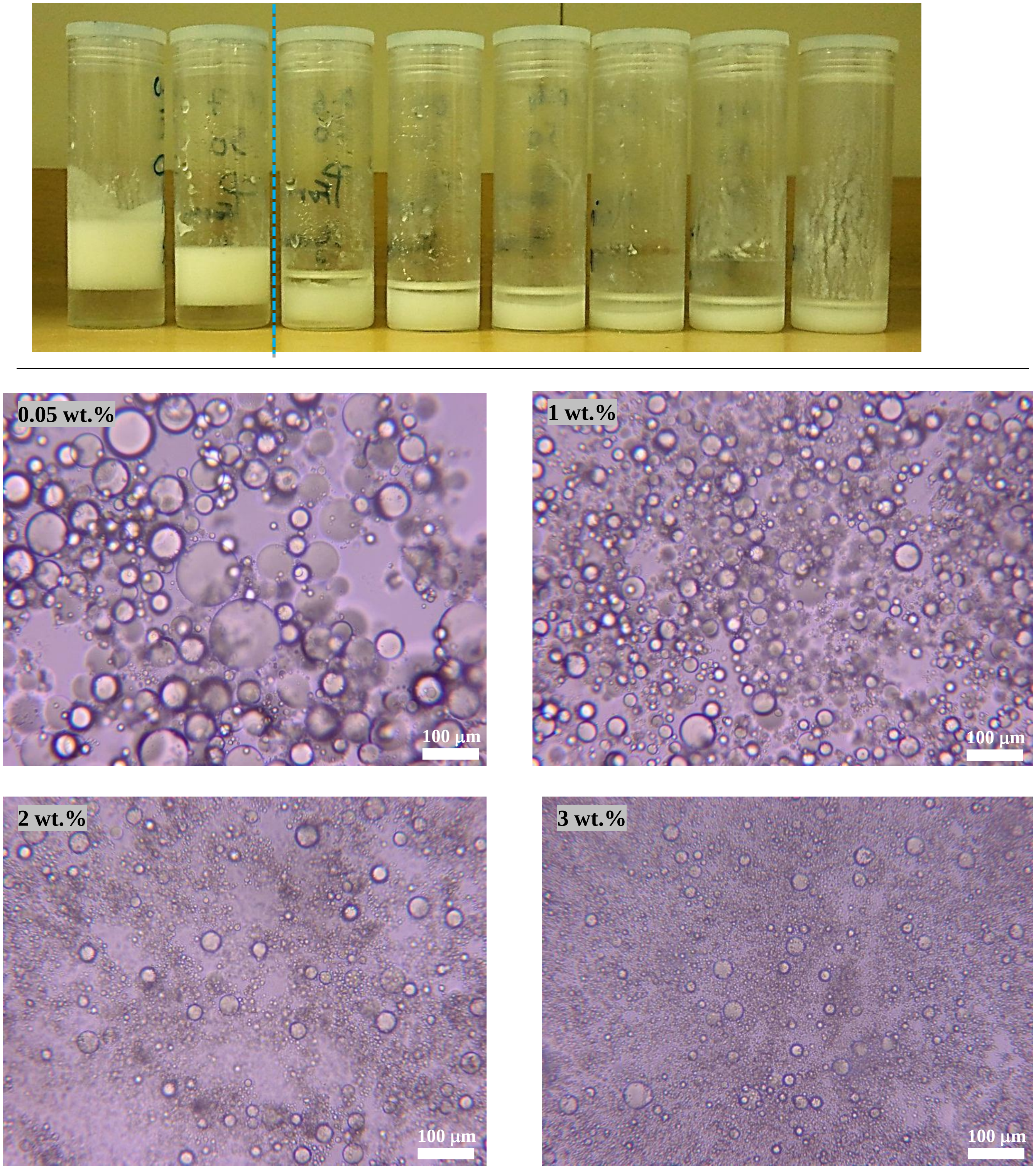

Fig.S2. (top) Digital images for an emulsion system of fa/s (system 18 in Table 1) stabilised by 1 wt.% of 50% SiOH silica dispersed initially in styrene. (bottom) optical images for the emulsion formed with fixed ϕ_{fa} = 0.2 and at different concentrations of silica particles (given). The volume fractions of internal phases are from right to left is 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8. Notice the reduction in drop sizes with wt.% of silica.

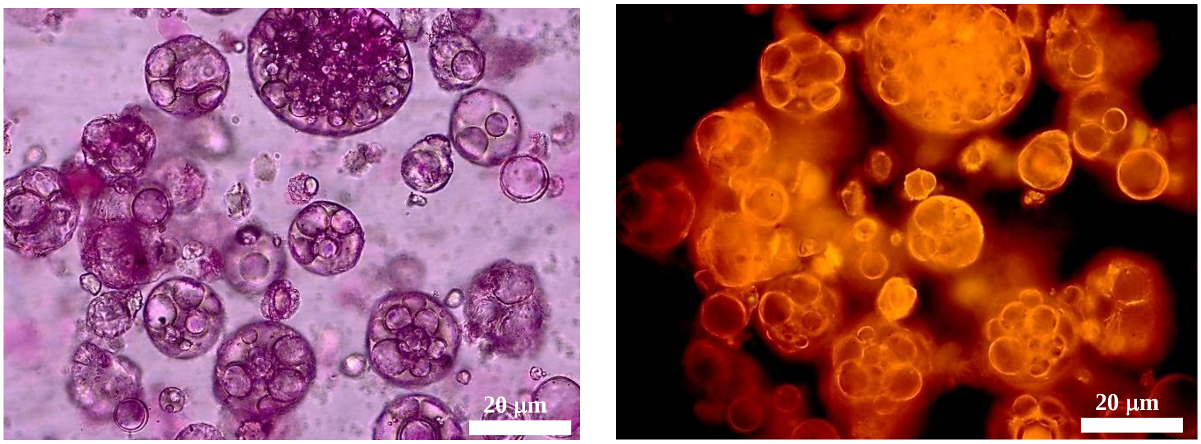

Fig.S3. Optical (left) and fluorescent (right) images for (three components) double o/o/o emulsion of systems of formamide-in-styrene-in-formamide fa/s/fa stabilised by 2 wt.% of 50% SiOH silica dispersed initially in styrene with ϕ_{fa} = 0.2. Inner formamide drops were loaded with 3 wt. % of unmodified magnetite particles and 0.2 wt.% Rhodamine b. Middle styrene phase contains 1 wt.% DVB and 2 wt.% AIBN. The $\phi_{fa/s}$ in the final double emulsion was 0.4. The outer formamide phase contains 2 wt.% of 50% SiOH silica nanoparticles. The emulsion was polymerised and polymeric hollow materials were formed, which replicate the same original structure of the emulsion before polymerisation after releasing the large internal formamide drops. Note that the second stage of producing this double emulsion involved hand shaking only.

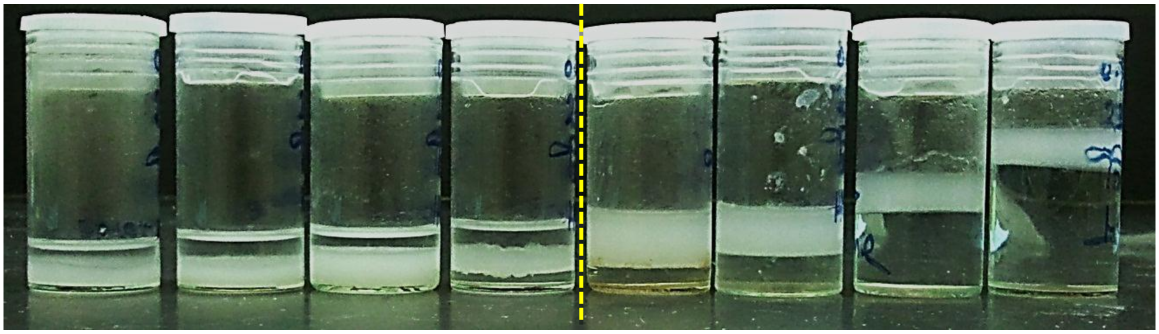

Fig.S4. Digital images for an emulsion system of dmf/hex (system 38 in Table 1) stabilised by 2 wt.% of 23% SiOH silica particles. The volume fractions of internal phases are from left to right: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8. This system underwent complete phase separation when stabilised by 23% SiOH silica particles.

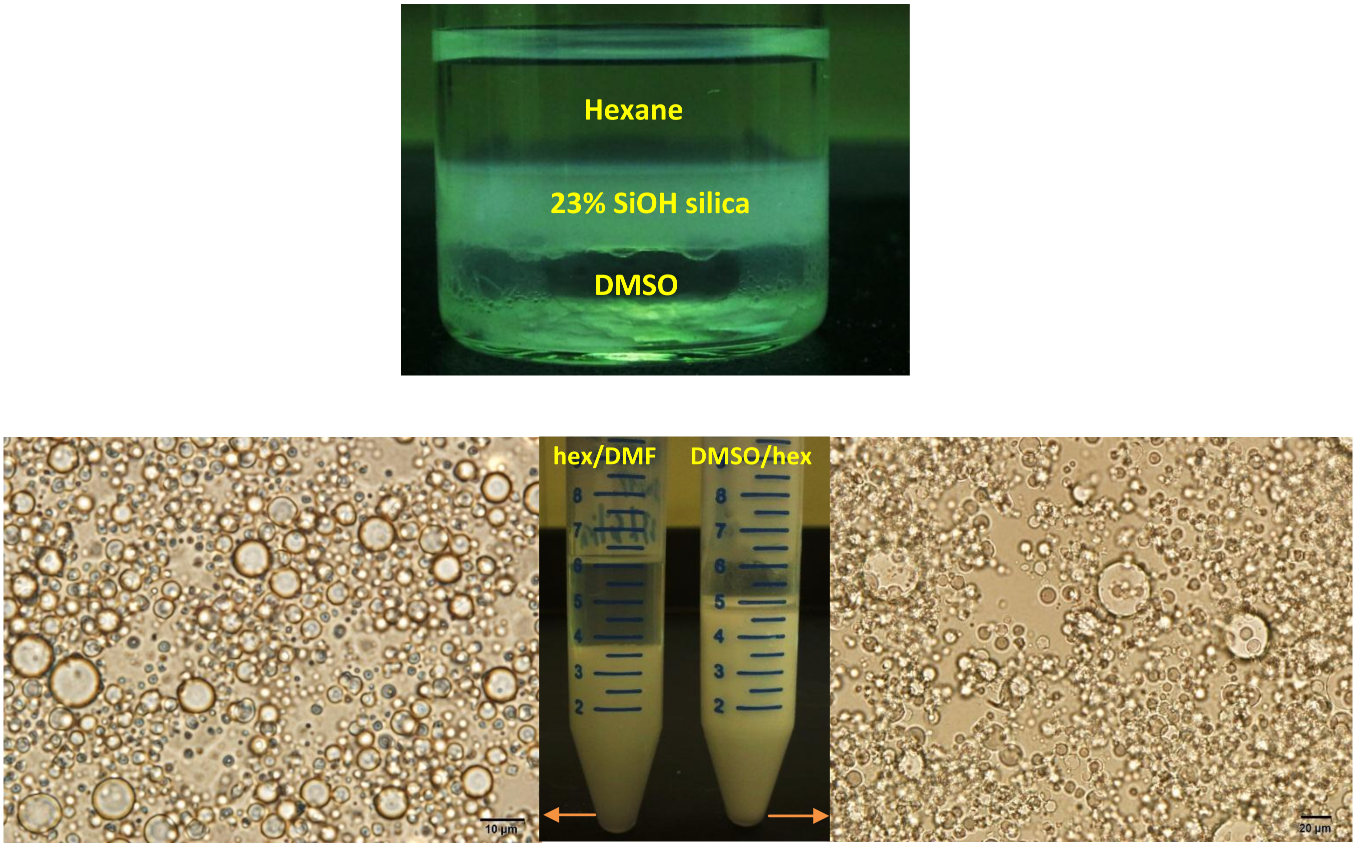

Fig.S5. (upper) digital image for an emulsion components before homogenisation which contains hexane with sedimented silica top and middle layers, respectively, and DMSO phase at the bottom layer. (lower) emulsions of hex/DMF and DMSO/hex stabilised by 3 wt.% of 23% SiOH silica particles with fixed volume fraction of internal phase (0.3).

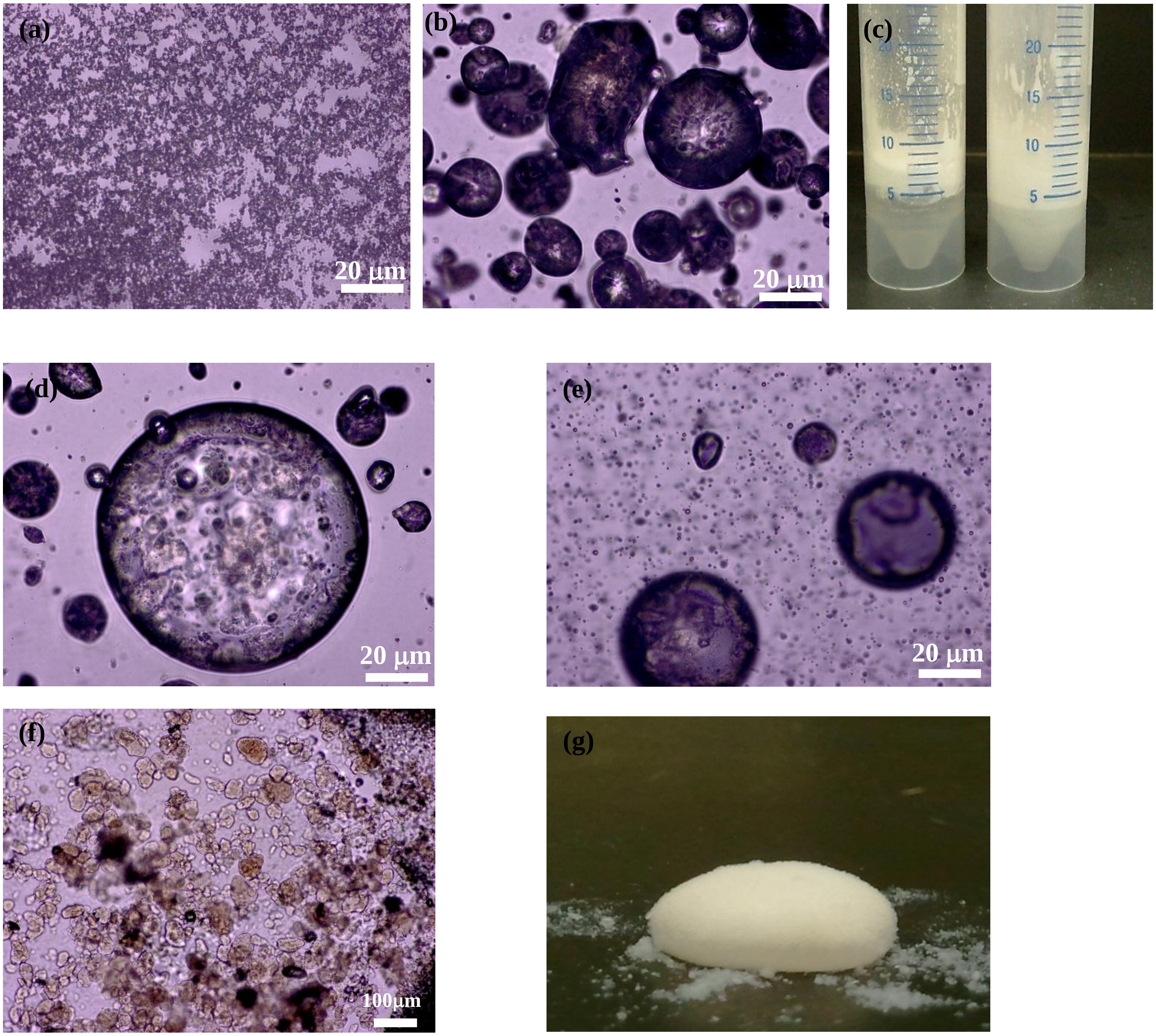

Fig.S6. Optical micrographs of microstructure of glycerine foams. (a) Foam stabilised by 1 wt.% of 23% SiOH silica, volume fraction of foam after 7 days was ϕ_f = 0.37. (b) Foam stabilised by 3 wt.% of 23% SiOH silica after 7 days, ϕ_f = 0.55. (c) A digital image showing the difference in foam heights shown in "a" and "b" 7 days after preparation. (d) A single foam capsule as in "b" at a higher magnification showing the entrapped silica aggregates inside the capsule. (e) Foam stabilised by 1 wt.% of 50% SiOH after homogenisation for 1 min. (f) Large silica aggregates observed in glycerine foam with excess of 23% SiOH silica particles. (g) An image for glycerine foam when using an excess of silica, foam generated by hand shaking.

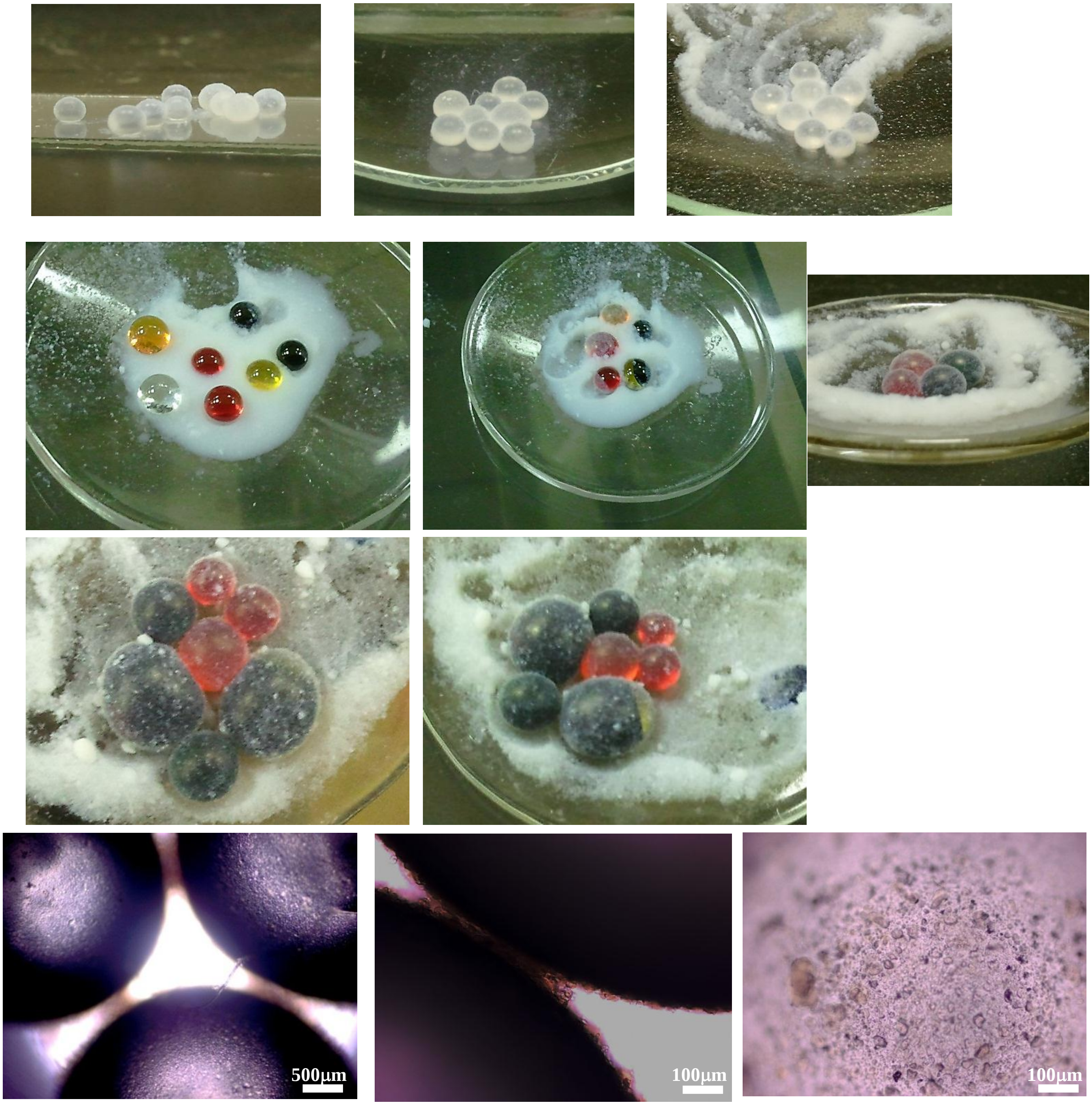

Fig.S7. Digital and optical images of glycerine-in-air liquid marbles (25 μl) in air stabilised by 23% SiOH silica particles. Liquid marbles can be easily transferred, and still stable, to clean glass clock once they are fully covered with silica aggregates. During rolling liquid marbles can coalesce as seen in the dye-treated ones. Dyes used are Congo red, methylene blue, sodium fluorescein and Isatin. Optical images show the bridging contact between adjacent marbles and the morphology of their surface which is composed mainly of large silica aggregates, which provide mechanical stabilisation of the glycerine, drops in air.

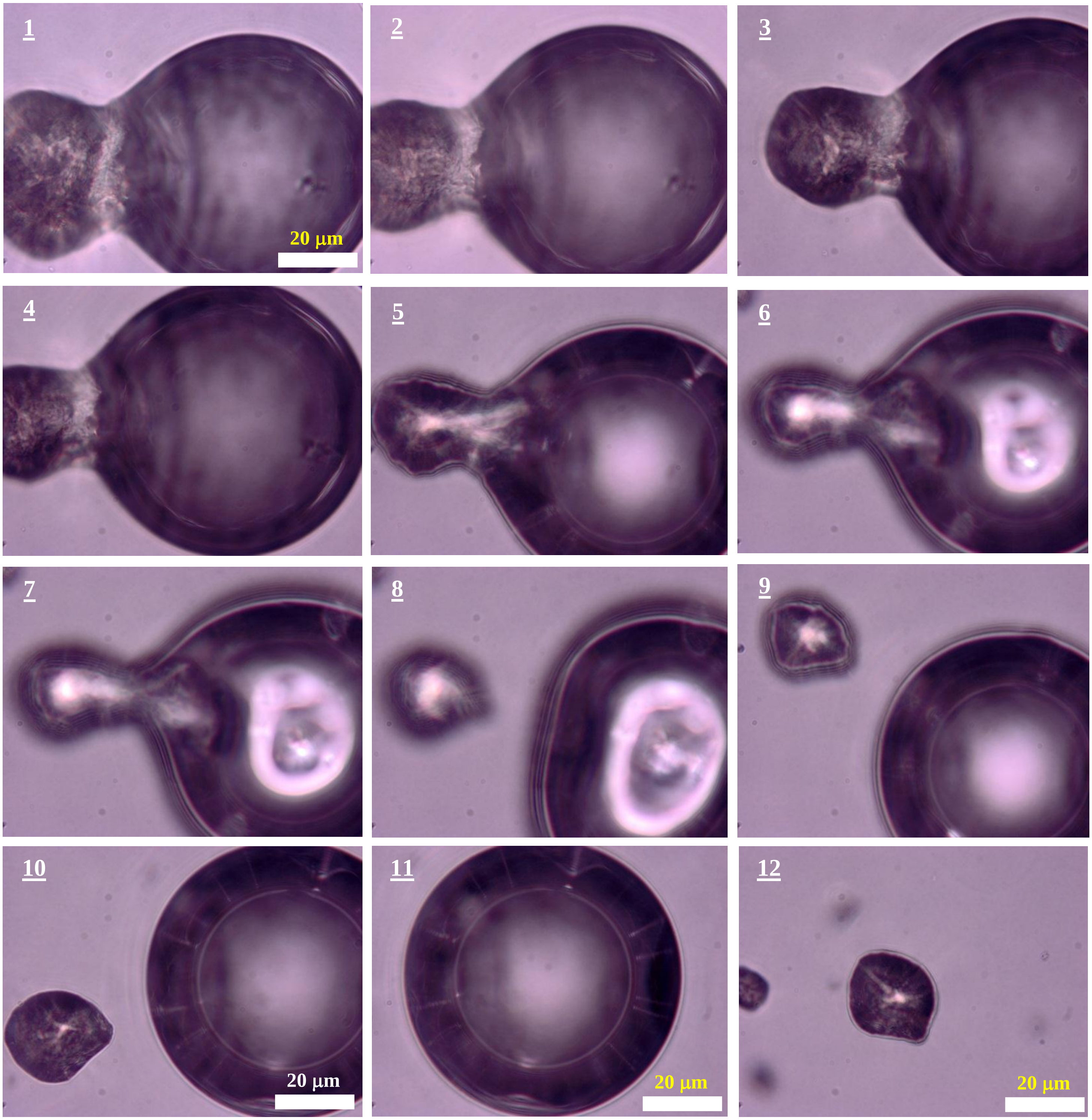

Fig.S8. Optical images describing a time course for a sequential of release of one single air bubble which was trapped inside a single foam colloidosome capsule formed from 1 wt.% of 23% SiOH DCDMS-modified silica nanoparticles when foaming in ethylene glycol. Time scale between each image is about 5 seconds as this was done by pressing the 100X objective lens of the microscope on the cover slip to promote the release the air from the capsule. This is indicative of extremely stable and flexible foams were formed.

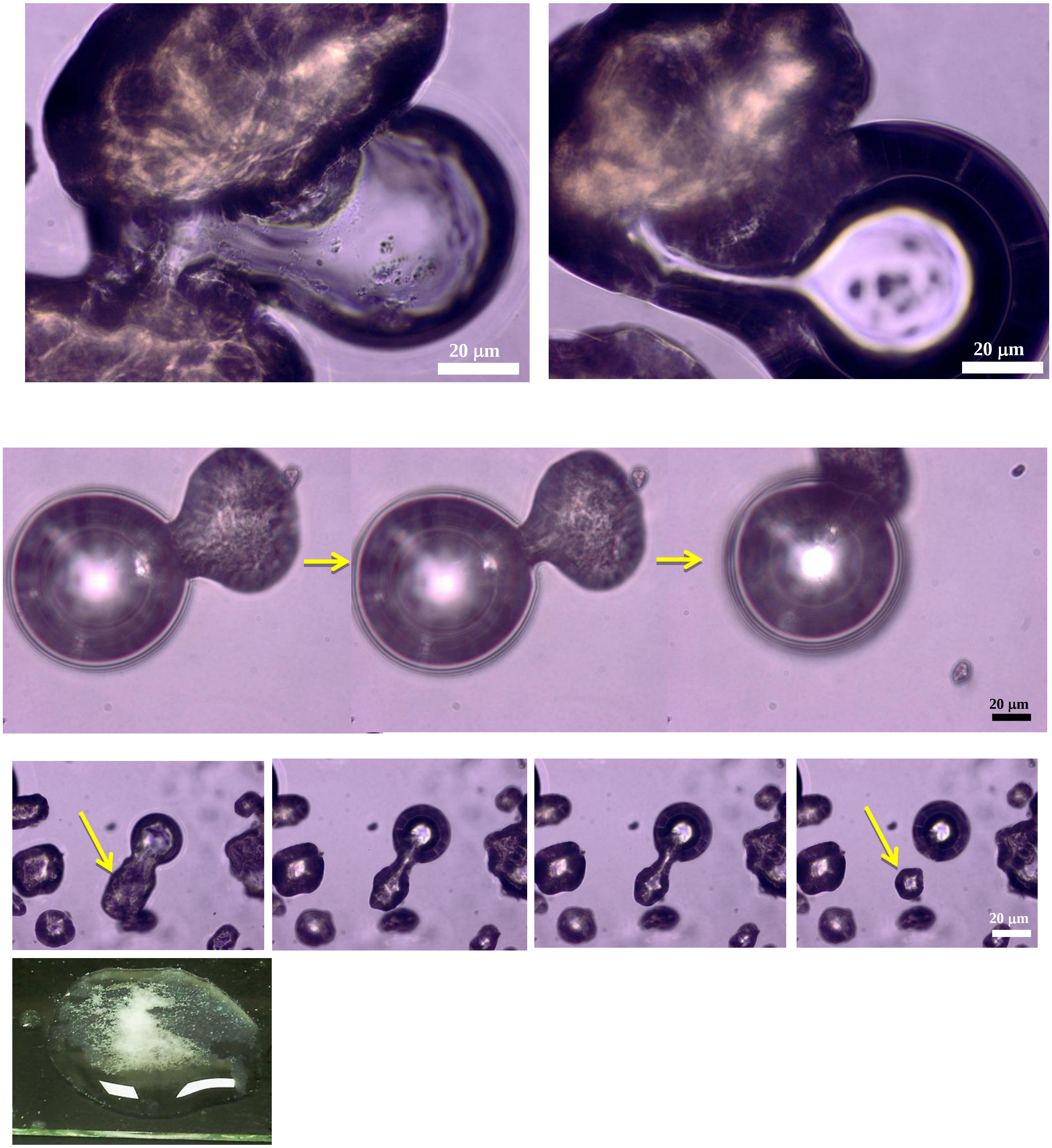

Fig.S9. Optical images for ethylene glycol foams shown in Fig.S24 showing the release of air bubbles from different foam capsules. Notice the two foam capsules which are connected by air bubble and eventually separated. Notice also the reduction of foam capsules by around the third fold after releasing the air, indicative again of unique flexibility and deformability of these foams which are fully covered by rough silica layers that provide exceptional stability to this system. The digital image shows that we can transfer the foam into a water surface.

References:

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2 L. E. Euliss, J. A. DuPont, S. Gratton and J. DeSimone, *Chem. Soc.Rev.*, 2006, **35**, 1095.