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Aquivion®-carbon composites *via* hydrothermal carbonization: Amphiphilic catalysts for solvent-free biphasic acetalization

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ELECTRONIC SUPPORTING INFORMATION

FIGURE AND TABLE CAPTIONS

Fig. S13. Macroscopic appearance and evolution profile of C_{12}-aldehyde/EG emulsions stabilized by Aq-guar and Aq-cell at low particle weight loading. Emulsification conditions: 45 ^{o}C, 10 mmol C_{12}-aldehyde, 20 mmol EG, 0.1 wt.% catalyst loading, homogenization at 13,000 rpm for 5 min.

Experimental

Materials

Aquivion® PFSA in both suspension and powder form (i.e. Aq-PW98-S, elementary particle size = 50 nm; acid loading = 1.0 mmolH$^+$/g) was provided by Solvay Specialty Polymers (Italy). Guar gum (natural-type, food purity) was provided from Solvay China. Cellulose (99%) was purchased from Sigma-Aldrich. Ethyleneglycol (EG, >99%), dodecyl aldehyde (C_{12}-aldehyde, 92%), tetrahydrofuran (THF, >99%) and 1,2-dichlorobenzene (>99%), all supplied by Sigma-Aldrich, were used for carrying out the acetalization reactions. Finally, 1,2-dichlorobenzene (>99%, Aldrich) was used as internal standard in the GC analytical tests. Sulfuric acid (H_2SO_4, 95%-98%, Sinopharm) was used for the preparation of carbons by hydthermal carbonization. P-toluenesulfonic acid monohydrate (PTSA, 99%, Dow Chemical), HZSM-5 (supplied by East China Normal University) and H-Resin (732 cation exchange resin, Sinopharm) were used as reference and benchmark catalysts, respectively. All the materials were used as received without further purification.

Preparation of polysaccharide-derived Aquivion®-carbon composites

A suspension of Aq-PW98-S was first prepared by adding 1 g of the powder to 20 mL of deionized water at 50 ^oC under stirring. Subsequently, 1 g of guar gum or cellulose was added slowly into the suspension at the same temperature under vigorous stirring. In the former case, the initial suspension generated a light yellow viscous gel within few minutes. In both cases, the Aquivion® and polysaccharide suspension was kept under stirring at 50 ^oC for 2 h. Then, the mixture was sealed in a 50-mL Teflon®-lined autoclave and submitted to hydrothermal carbonization (HTC) at 180 ^oC for 24 h. After this period, the autoclave was quenched to room temperature and the resultant solid was filtered, washed with deionized water until neutral pH, and dried at 100 ^oC overnight under vacuum. The final composites, termed as Aq-guar and Aq-cell, respectively, showed in each case black and brown colors (Fig. S3).

Preparation of polysaccharide-derived carbons

The polysaccharide-derived carbon materials were prepared from guar gum or cellulose as carbon precursor using the same protocol reported above for the Aquivion®-carbon composites, but in the absence of Aq-PW98-S. The as-obtained carbon materials were termed as C-guar and C-cell, respectively.

Characterization methods

Sulfur elemental analysis was carried out by inductively coupled plasma (ICP-AES) on LECO CHNS-932 analyzer. In a typical analysis, 1 mg sample was placed in a Ag crucible and burned at 1050 °C under pure O_2 atmosphere. The resulting CO_2, H_2O and SO_2 gases were quantified by FTIR spectroscopy, while N_2 was determined by differential thermal conductivity.

Acid-base titration was performed using a Metrohm 794 Basic Titrino system. Prior to titration with NaOH (0.01 M), the samples were subjected to ion exchange with a NaCl solution (0.5 M) at room temperature during 24 h.

The solid-state ^{13}C-NMR MAS spectra were recorded on a Bruker AVANCE III 600 WB spectrometer operating at 600 MHz resonance frequency and equipped with a 4-mm standard probe spinning at 25 kHz. The chemical shifts were referenced to adamantane (δ_{CH2}=38.5 ppm) and 3-(trimethylsilyl)-1-propane sodium sulfonate (δ=0.0 ppm), respectively. The ^{19}F-NMR MAS spectra were recorded on a Bruker AVANCE III 400 WB spectrometer at 400 MHz resonance frequency and equipped with a 4-mm standard probe spinning at 25 kHz. The chemical shifts were referenced to $CFCl_3$.

Fourier transform infrared (FT-IR) spectra were recorded on powders dispersed in KBr (2 mg sample in 300 mg KBr) using a Perkin Elmer One FT-IR spectrometer with a resolution of 4 cm^{-1} and operating in the range of 400-4000 cm^{-1} with 10 scans per spectrum.

X-ray diffraction (XRD) was performed using a Rigaku D/Max-2200/PC diffractometer provided with Cu Kα radiation (λ = 1.5418 Å) and a beam voltage of 45 kV. The patterns were registered in the 2θ domain 0-70° with a measured step of 0.02° and a time integration of 0.5 s.

X-ray photoelectron spectroscopy (XPS) was carried out under ultrahigh vacuum on a Perkin–Elmer PHI 5000C ESCA system provided with Al Kα radiation. The binding energy shift due to the surface charging was adjusted by a reference to the C1s line at 284.8 eV.

The textural properties of the samples were measured from N_2 adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2010 surface area analyzer. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method from the adsorption branch in the relative pressure range $0.05 < P/P_0 < 0.25$, while the pore volumes were measured at $P/P_0 = 0.99$. The Barrer-Joyner-Halenda (BJH) method was used for measuring intercrystalline mean pore sizes using the adsorption data from the adsorption branch. Prior to the sorption measurements, the samples were degassed at 150 °C for 3 h.

Thermogravimetric analysis (TGA) was used to assess the thermal stability of the samples. The measurements were carried out on a TA SDT Q600 Instrument by heating the samples from room temperature to 900 °C at a rate of 10 °C/min under air atmosphere (100 mL(STP)/min).

The morphology of Aquivion®-carbon particles was inspected by scanning electron microscopy (SEM) using a JEOL JSM-6360LV microscope operating at 60 kV.

The particle size distributions (PSD) were measured on a Malvern Mastersizer 3000 (range lens, 300RF mm; beam length, 2.40 mm; size range from 0.01 to 3500 μm). In a typical measurement, 0.50 ± 0.01 g sample was added to 50 mL deionized water in a 100 mL beaker. The resulting suspension was dispersed by ultrasonication for 10 min at room temperature. Then the suspension was added into the sample unit under stirring conditions (2,400 r.m.p). The samples were added to the sampler for an obscurantation <10%.

Catalytic tests

The biphasic acetalization reaction of dodecyl aldehyde (C_{12}-aldehyde) and ethyleneglycol (EG) was carried out in a batch reactor. In a typical test, C_{12}-aldehyde (10 mmol), EG (20 mmol) and the catalyst (with an equivalent amount affording 10 μmolH^+) were sealed in a glass reactor (50 mL) and then stirred at 45 ^{o}C for 1 h. After the reaction, tetrahydrofuran (THF, 4.5 g) was added to form one sole phase. Then, the heterogeneous catalyst was separated by centrifugation (12,000 rpm, 15 °C) for 10 min and the supernatant solution was recovered (ca. 1.0 g) using a syringe and 1,2-dichlorobenzene (0.1 g) was introduced as an internal standard. The solution was then analyzed by gas chromatography using an Agilent 7890 GC equipped with a FID detector and a HT-5 capillary column (length 30 m, i.d. 0.25 mm, film thickness 0.25 mm). The different products were identified by GC-MS (Aglient 6890N/5973). Mass balances were accurate to within 5% in all the catalytic tests. The catalyst productivity (*P*) was defined as the number of moles of cyclic acetal (C_{12}-G) produced per mole of H^+.

A reusability test was carried out on Aq-guar and Aq-Si1 composites to assess their catalytic stability. In this tests, the sample was washed with ethanol (30 mL) four times and centrifuged out from the solution (12,000 rpm). After drying at room temperature, the catalyst was reused for the next run.

Emulsification studies

Preparation of C_{12}-aldehyde/EG emulsions: The C_{12}-aldehyde/EG emulsions were prepared according to the following method. First, the given catalyst with an equivalent loading providing 10 µmolH^+ or a loading of 0.1 wt.% combined with C_{12}-aldehyde (10 mmol) were placed in a 20-mL beaker and ultrasonicated (Julabo) at room temperature for 20 min to ensure proper wetting of the particles. Later on, EG (20 mmol) was added to reach a C_{12}-aldehyde/EG molar ratio of 1:2 (weight ratio of 5:3) as in the catalytic tests. The final dispersion was then homogenized at 45 ^oC for 5 min using an ultra-turax Fluko FA25 homogenizer with a 10-mm dispersing tool operating at 13,000 rpm. After the preparation, the emulsified mixture was kept static at 45 ^oC for 1 h min to assess the stability of the emulsified phase.

Emulsion volume and droplet size: The emulsion volume was measured by direct inspection of the C_{12}-aldehyde/EG emulsion using a Nikon D300s camera equipped with a macro lens (AF-S Macro Nikon 105 mm 1:2.8G ED) and NK remote software. The continuous phase was appraised using the dilution method by dropping one droplet of the emulsion into C_{12}-aldehyde and EG separately. The droplet size was measured with an Olympus IX-51 light transmission microscope equipped with x10 ocular, x4, x10, x40 and x100 objectives and DP2-BSM software. Visilog software was used to analyze the droplet size.

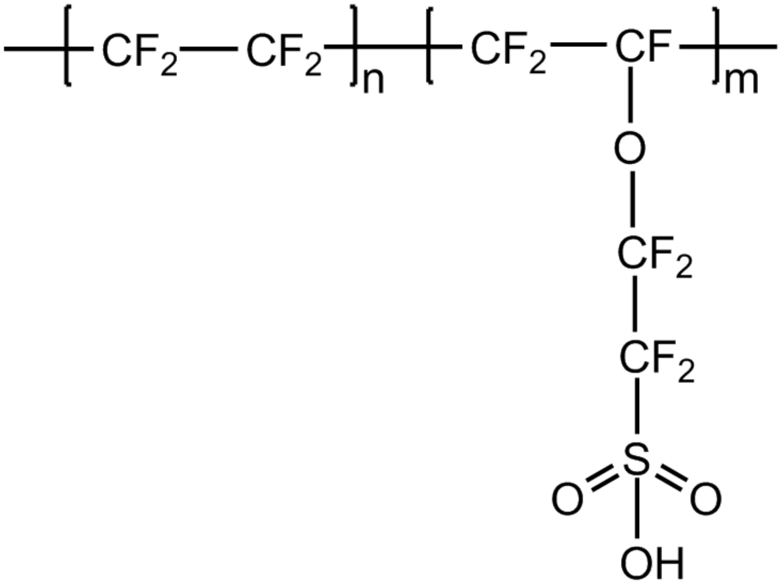

Fig. S1. Molecular formula of Aquivion® PFSA.

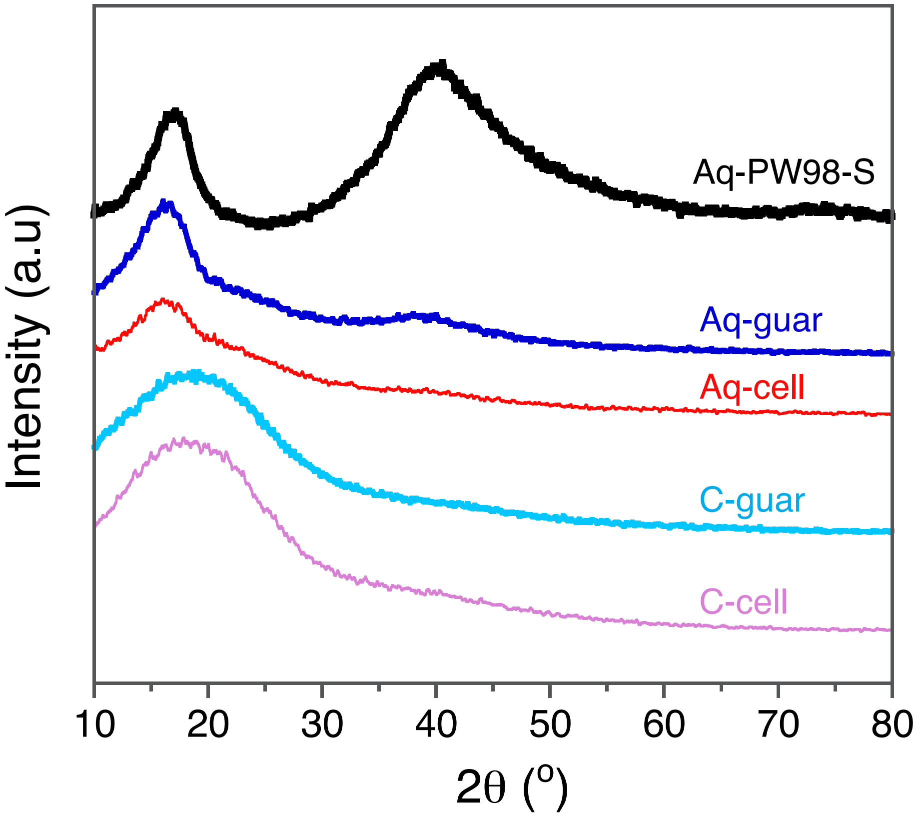

Fig. S2. XRD patterns of Aq-PW98-S, Aq-guar, Aq-cell, C-guar and C-cell.

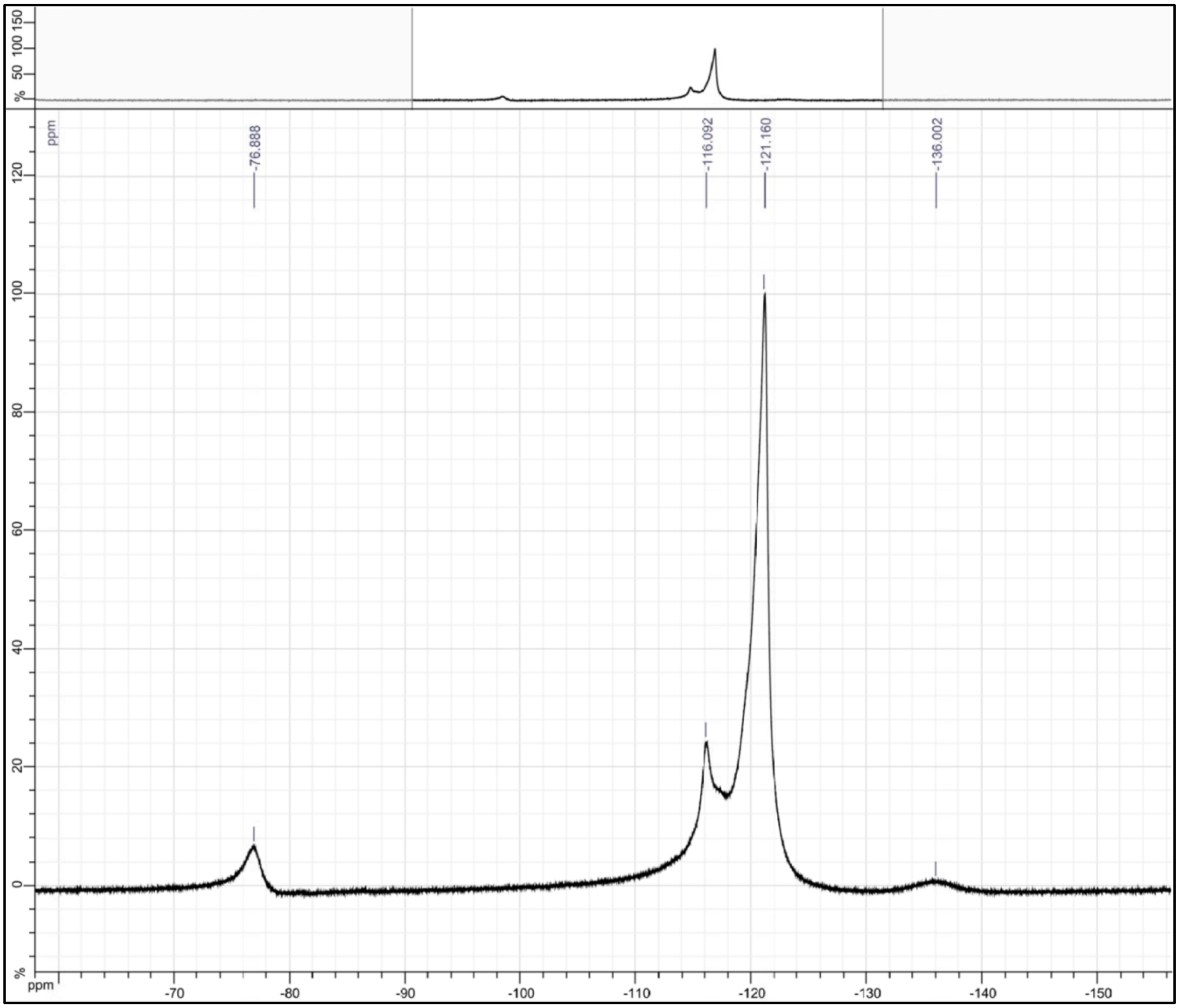

Fig. S3. ^{19}F NMR spectrum measured on Aq-PW98-S.

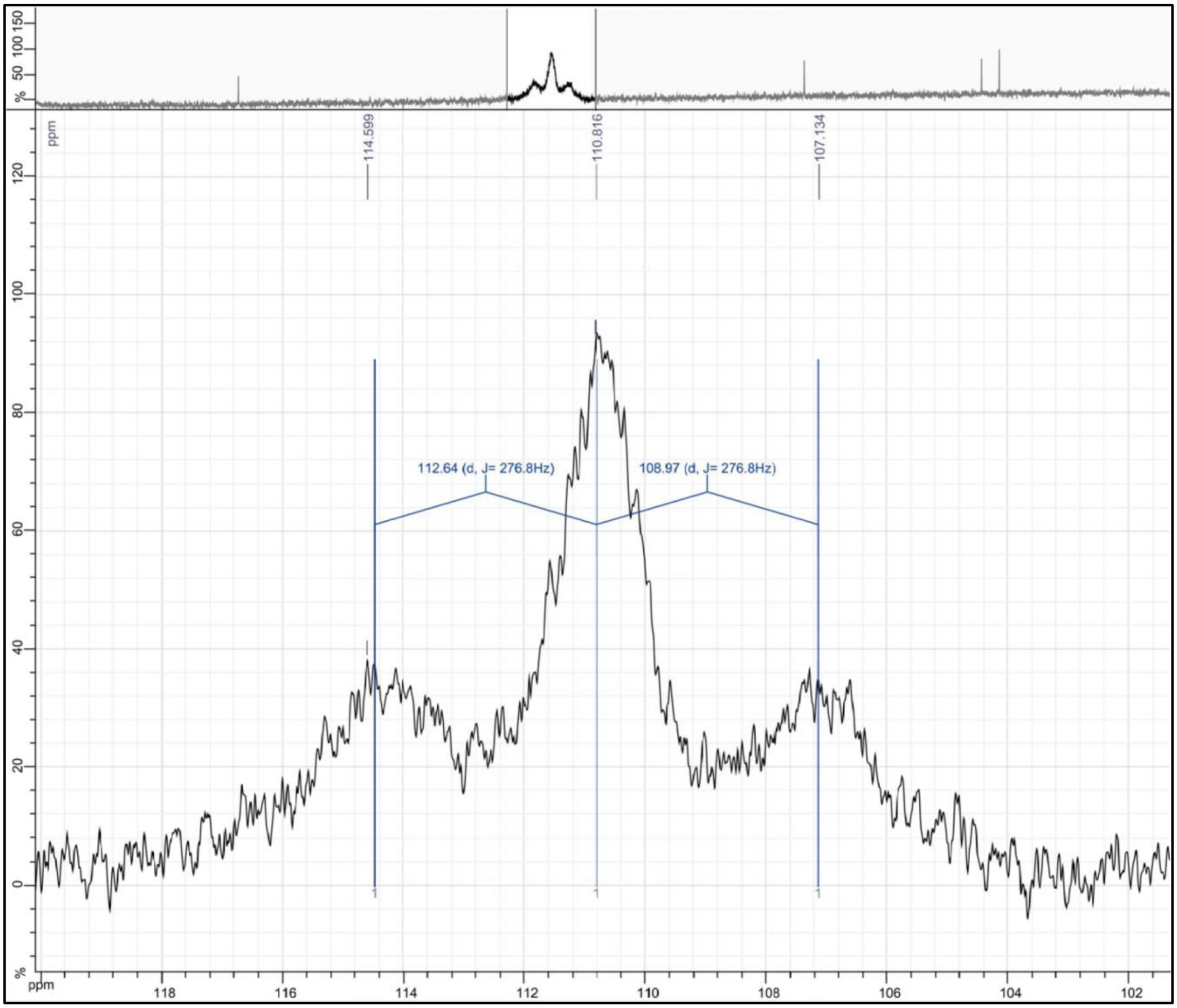

Fig. S4. ^{13}C NMR spectrum measured on Aq-PW98-S.

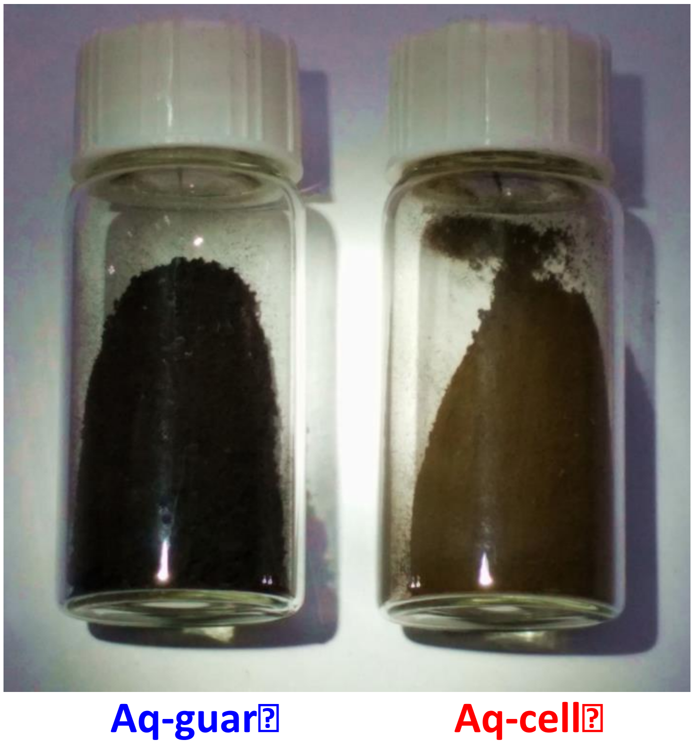

Fig. S5. Macroscopic appearance of Aq-guar and Aq-cell composites.

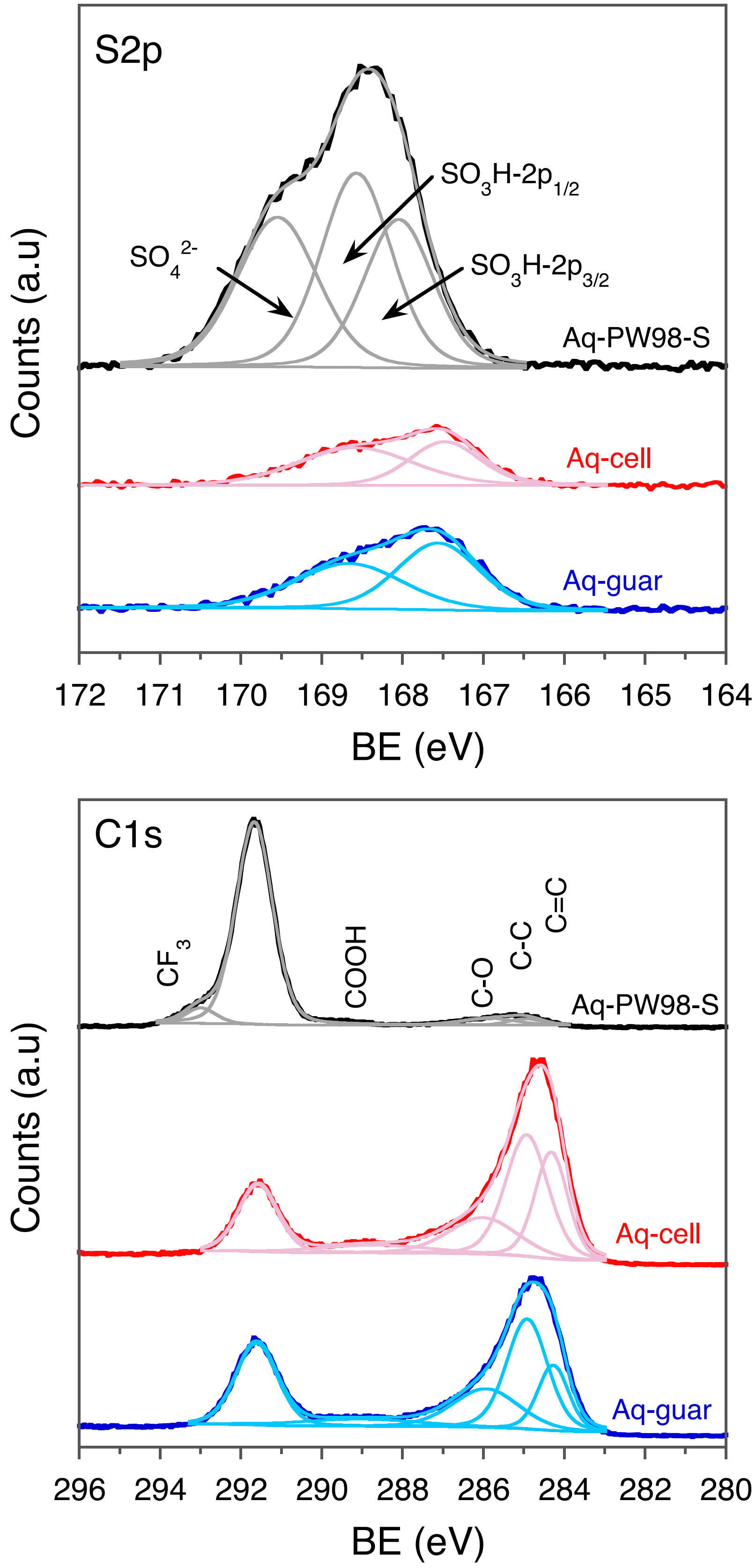

Fig. S6. S2p (top) and C1s (bottom) XPS spectra of Aq-PW98-S, Aq-guar and Aq-cell.

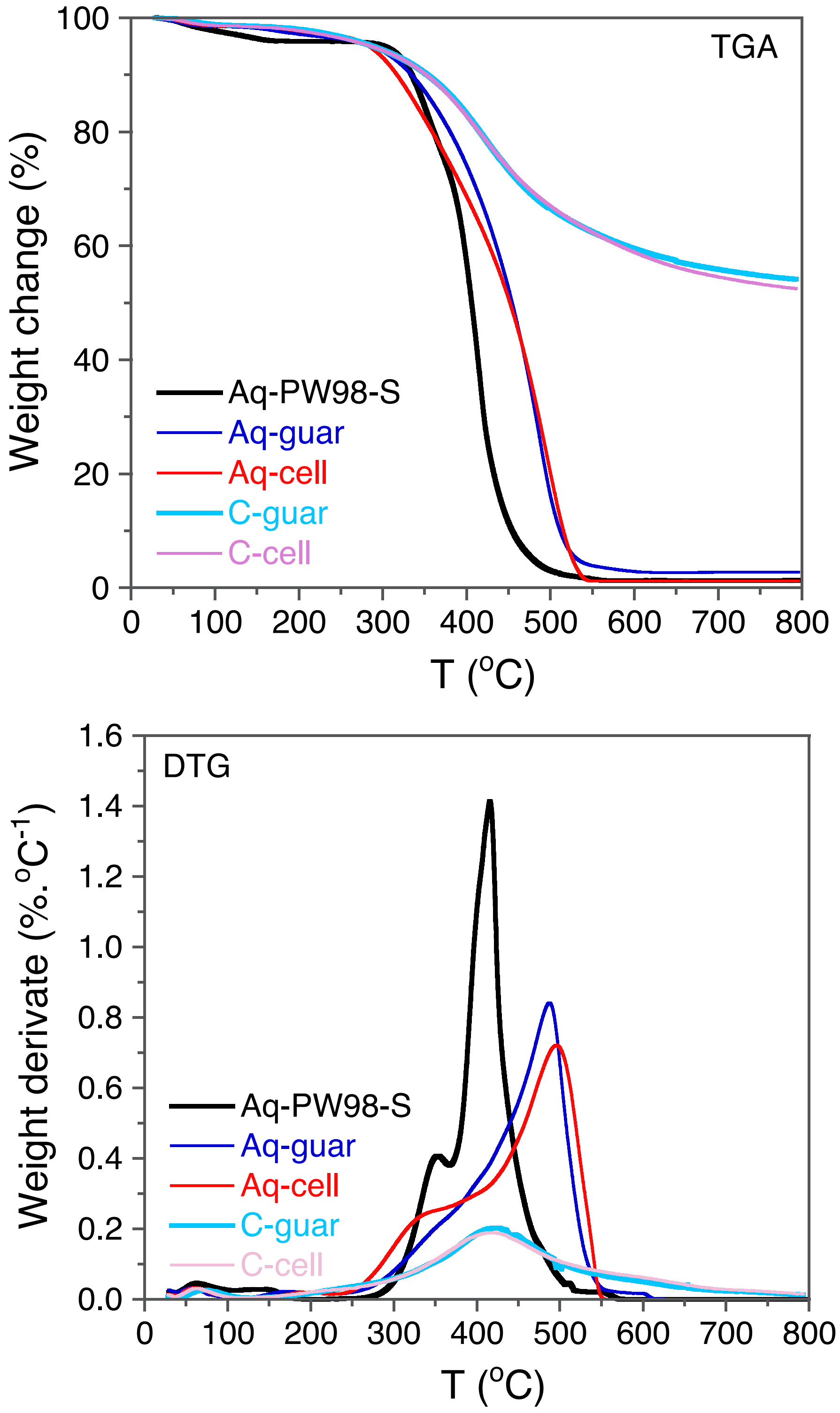

Fig. S7. TGA / DTG profiles for Aq-PW98-S, Aq-guar and Aq-cell.

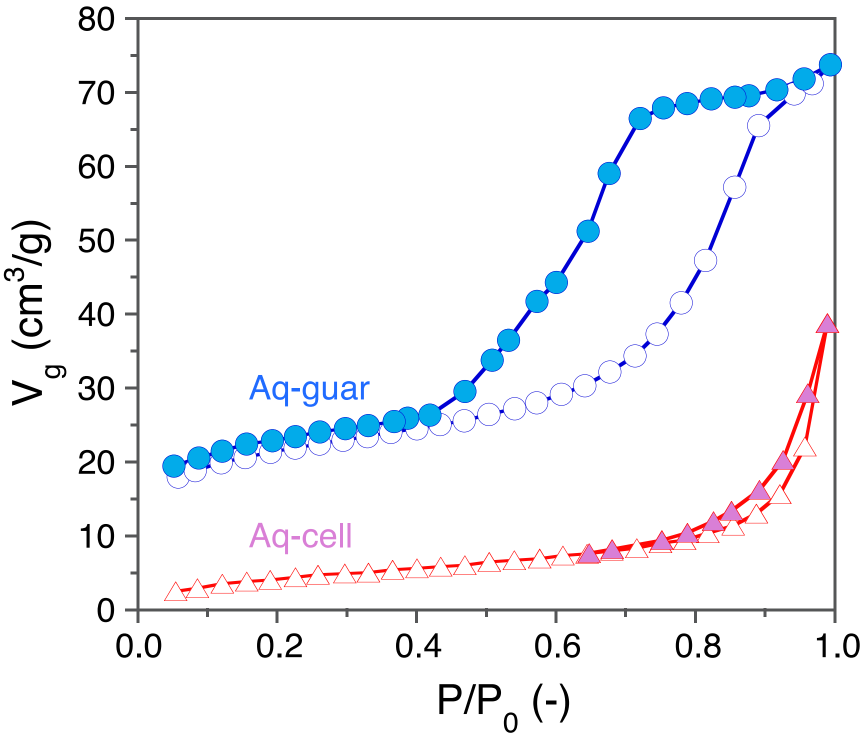

Fig. S8. N_2 adsorption/desorption isotherms at 77 K for Aq-guar and Aq-cell.

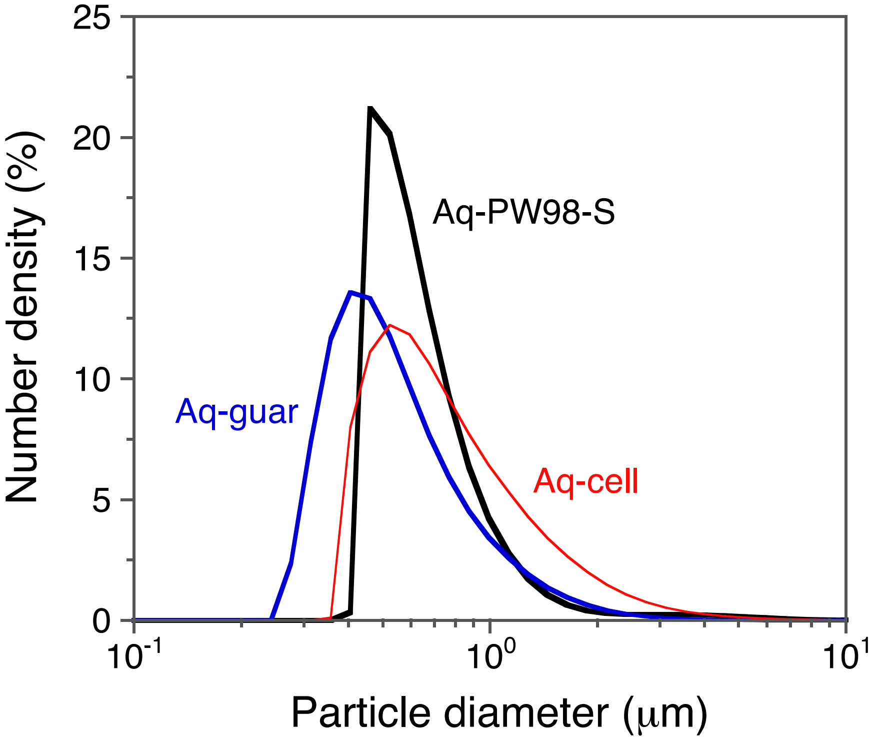

Fig. S9. Particle size distributions (PSDs) of Aq-PW98-S, Aq-guar and Aq-cell (supernatant phase).

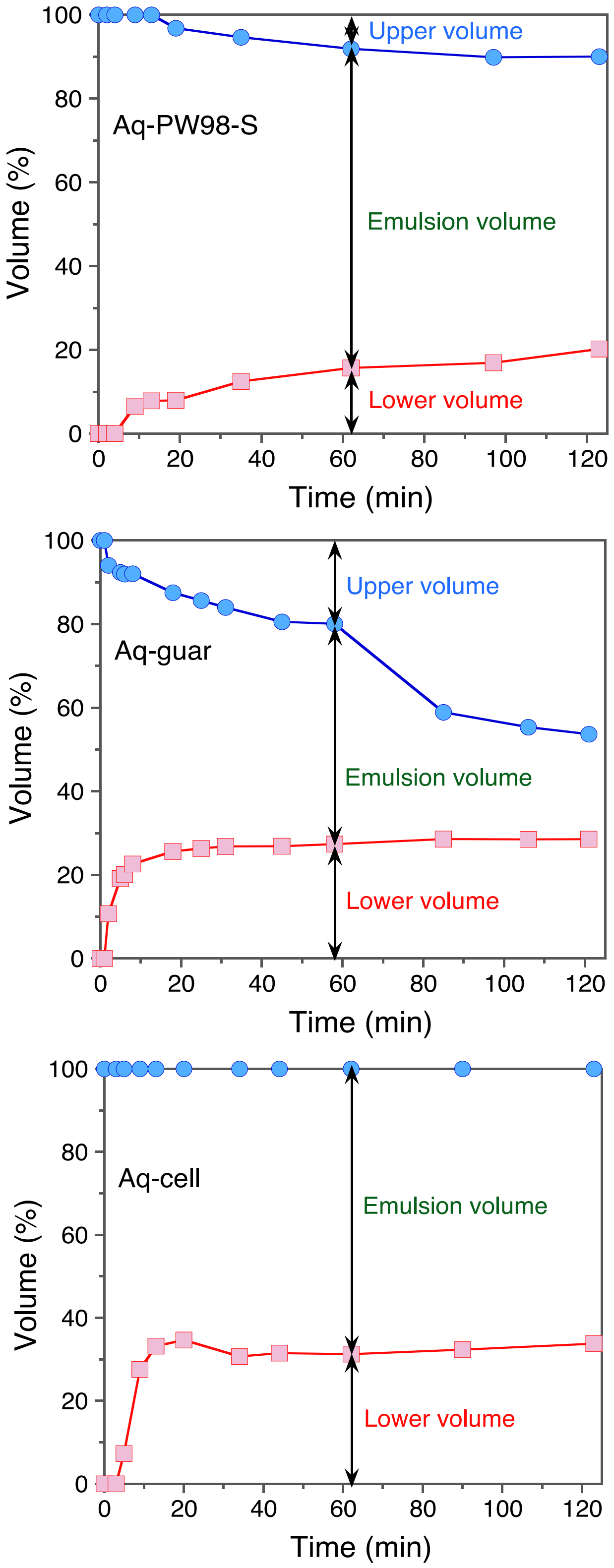

Fig. S10. Time-evolution of the emulsion volume for the C_{12}-aldehyde/EG system stabilized by Aq-PW98-S, Aq-guar and Aq-cell. Emulsification conditions: 45 ^{o}C, 10 mmol C_{12}-aldehyde, 20 mmol EG, catalyst loading providing 10 µmolH^{+}, homogenization at 13,000 rpm for 5 min.

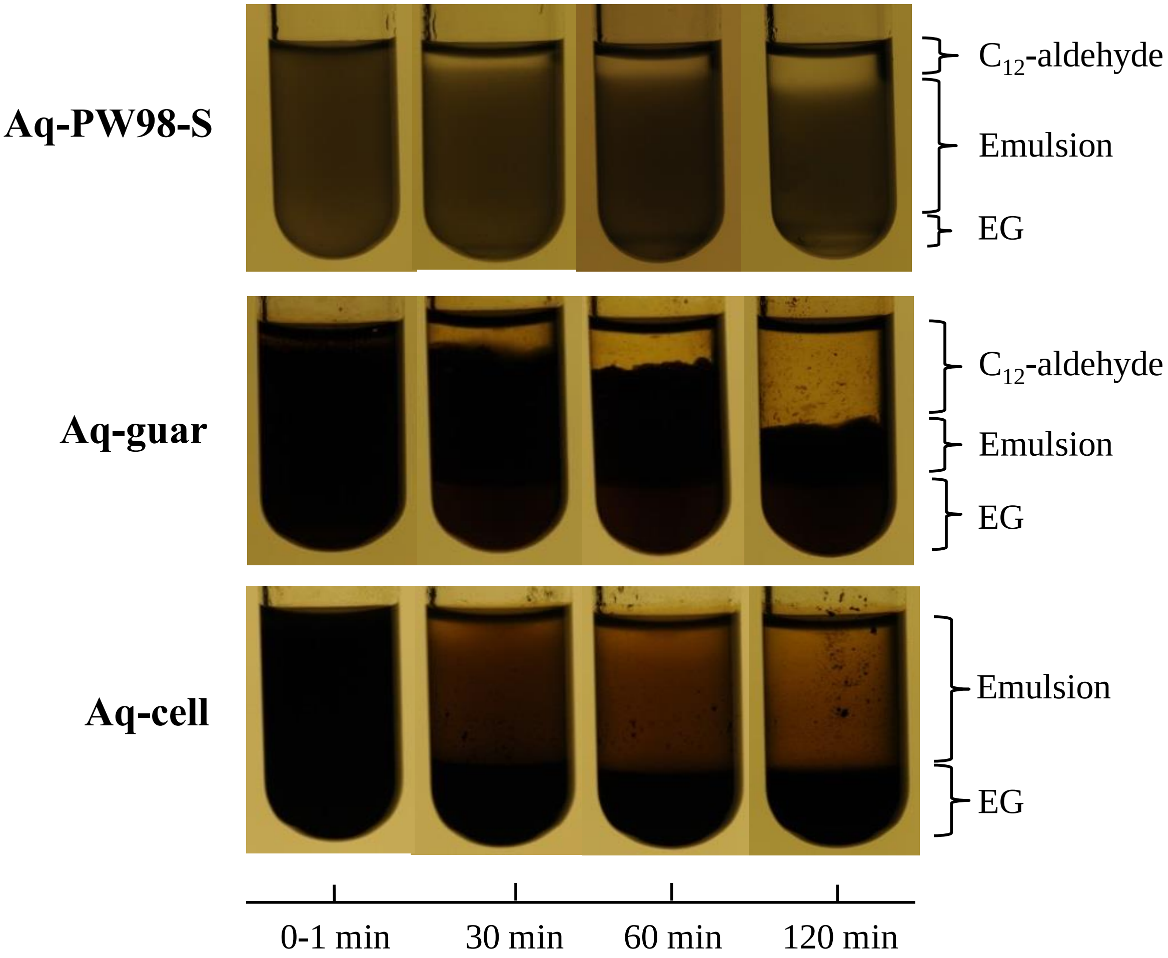

Fig. S11. Macroscopic appearance and evolution profile of C_{12}-aldehyde/EG emulsions stabilized by Aq-PW98-S, Aq-guar and Aq-cell. Emulsification conditions as in Fig. S10.

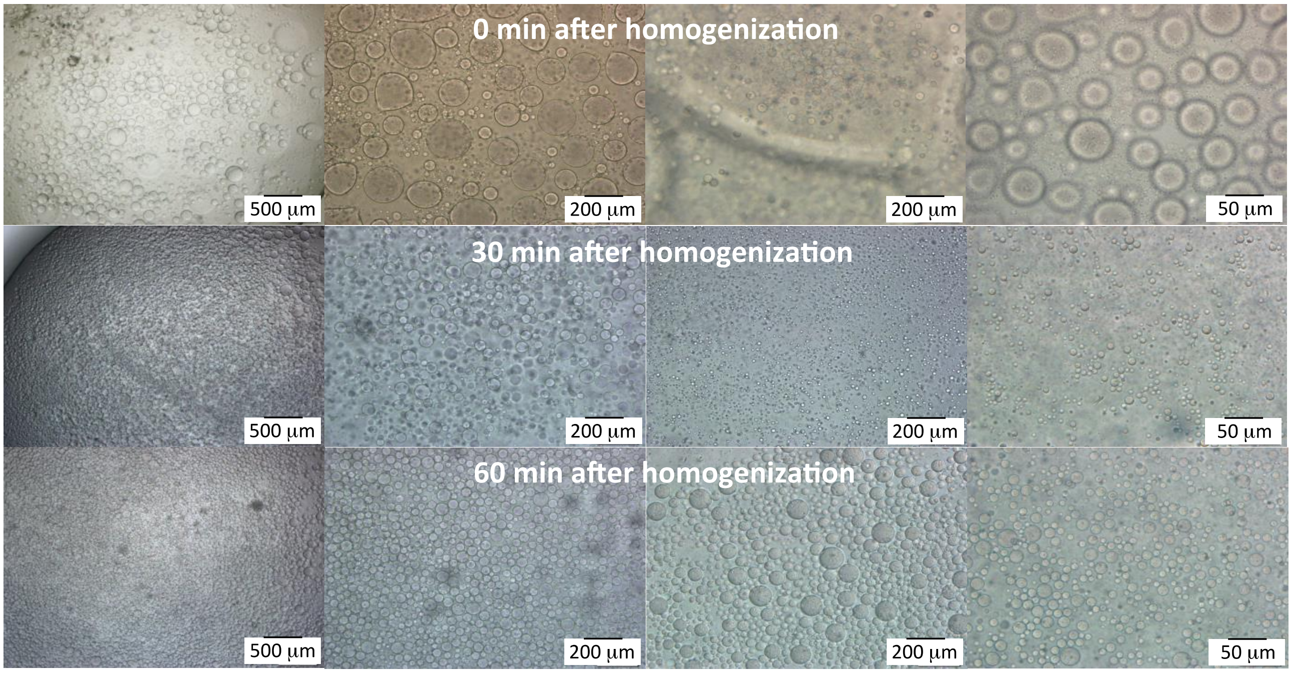

Fig. S12. Microscopic appearance and evolution profile of C_{12}-aldehyde/EG emulsions stabilized by Aq-PW98-S. Emulsification conditions as in Fig. S10.

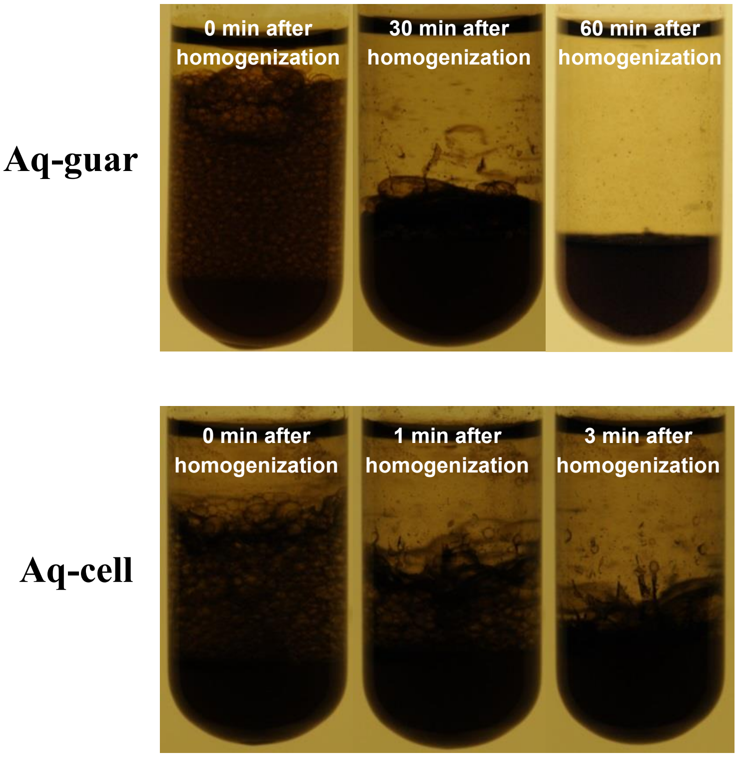

Fig. S13. Macroscopic appearance and evolution profile of C_{12}-aldehyde/EG emulsions stabilized by Aq-guar and Aq-cell at low particle weight loading. <u>Emulsification conditions</u>: 45 °C, 10 mmol C_{12}-aldehyde, 20 mmol EG, 0.1 wt.% catalyst loading, homogenization at 13,000 rpm for 5 min.