

Supporting information

Phase diagram studies

When selecting the surfactant its stability should be taken into account. For instance, Na-AOT is unstable and dimerizes when N_2H_4 , commonly used reducing agent, is used. Also, platinum nanoparticle formation does not happen in Br-containing surfactants, CTAB and DDAB, due to anion exchange between surfactant and the precursor, and the precise nature of formed complexes is still unclear.¹

Phase diagrams of four different microemulsion systems were studied in this work, the fifth, DDAB, phase diagrams is available from the literature.² All microemulsions were prepared by mechanical vortexing and by sonication of the mixture of surfactant, water and oil. Table S1 gives the microemulsion compositions for each surfactant studied in this work:

Table S1 Microemulsion compositions used for the phase diagram study.

Surfactant to oil ratio	1/9	2/8	3/7	4/6	5/5	6/4	7/3	8/2	9/1
Water concentration / %	10	20	30	40	50	60	70	80	90

After mixing, the microemulsions were examined visually. An example of the series of Na-AOT/Heptane/Water microemulsion samples is given on Figure S2. We observed that at the s/o ratio of 6/4 at lower water content samples (10 - 60 %) single-phase microemulsions are formed. With increase of water content viscosity is also increasing and at 70 % single-phase gel is formed, but with further increase of water phase-separation occurs.

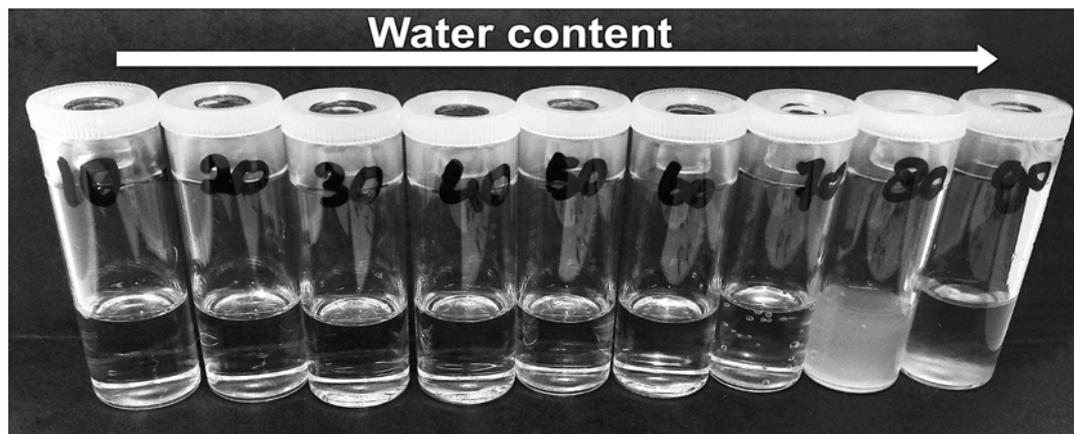


Figure S1 Na-AOT/Heptane/Water microemulsions with s/o ratio 6/4 and water contents from 10 to 90wt%.

Based on similar visual observations for all samples of all systems the following phase diagrams were built (Figure S3). Only stable microemulsions, which are single-phase and clear, can be later used for the synthesis of the metal nanoparticles.

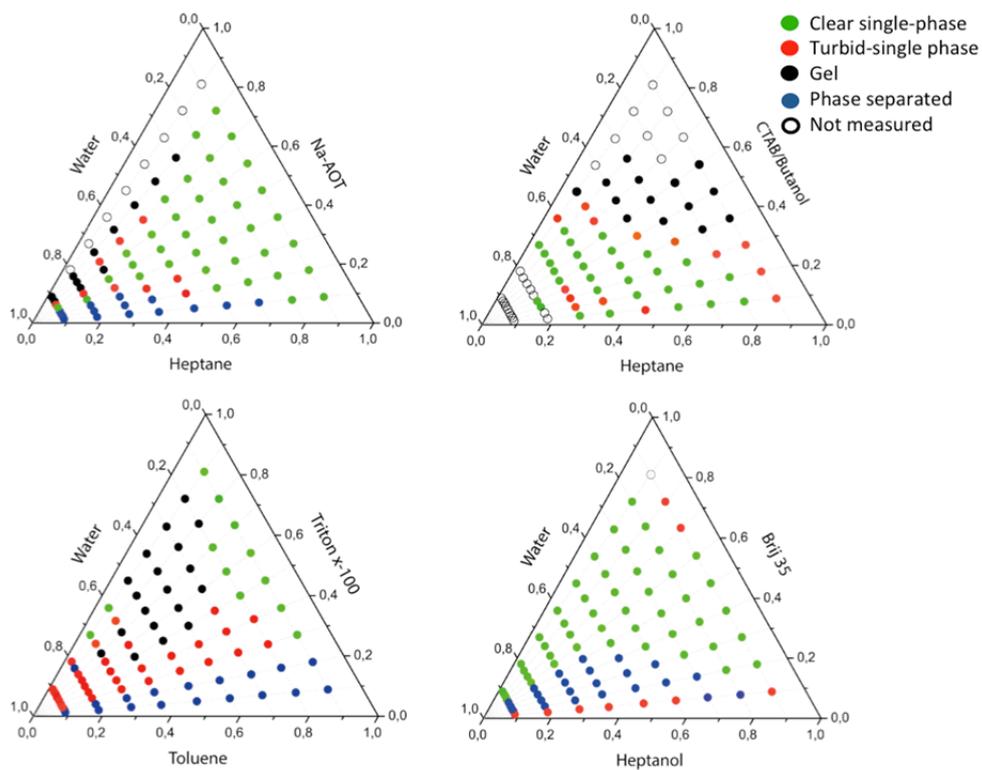


Figure S2 Phase diagrams of Na-AOT/heptane/water; Triton X-100/toluene/water; Brij 35/heptanol/water microemulsions and CTAB/ heptane/water-butanol microemulsions.

Next, the phase diagrams of the microemulsions have been investigated by conductivity measurements in order to identify the phase transition regions and regions with water continuous structures, such as the bicontinuous phase. Based on the measurements of the electrical conductivity phase diagrams for four different systems were constructed (Figure S3).

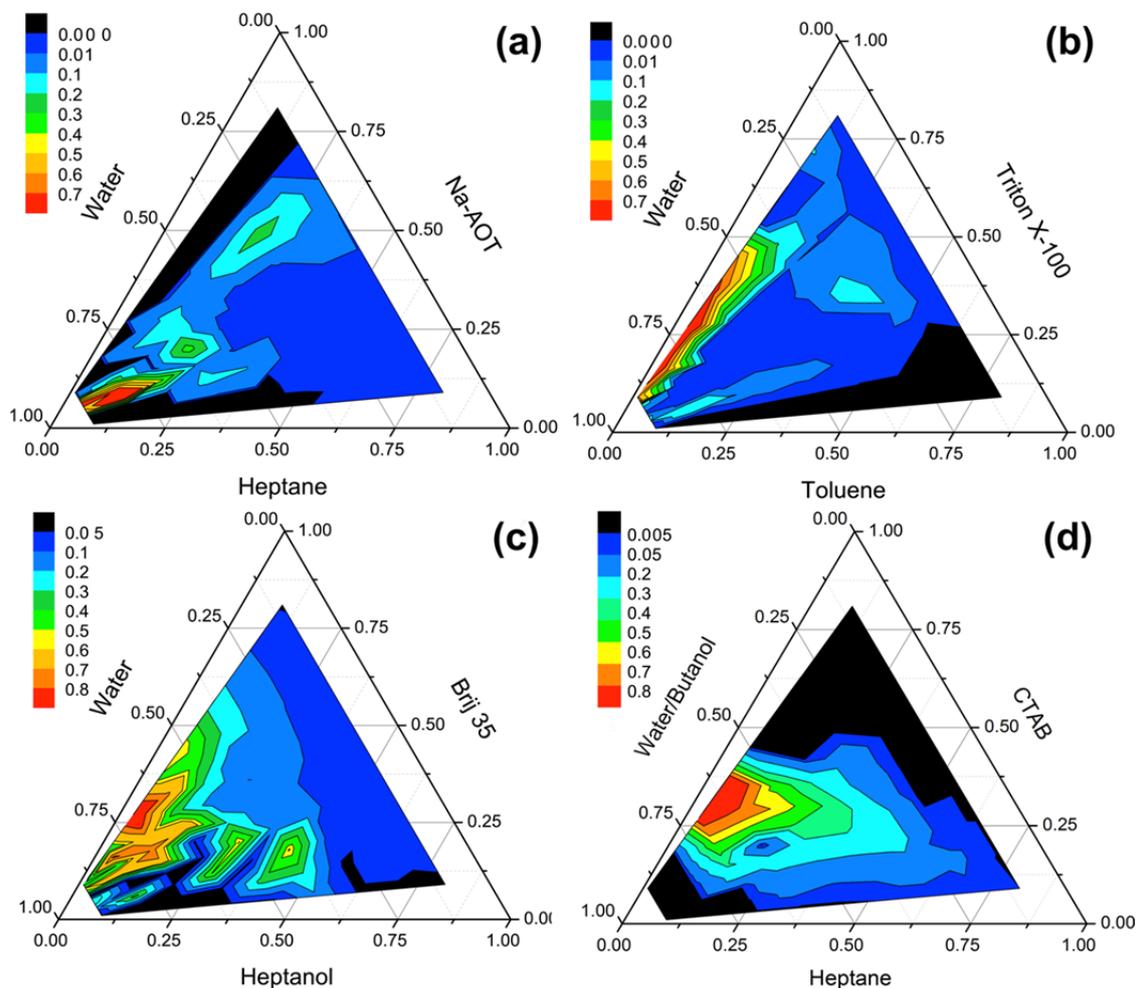


Figure S3 Phase diagrams of Na-AOT/heptane/water; Triton x-100/toluene/water; Brij 35/heptanol/water microemulsions and CTAB/heptane/water-butanol microemulsions built based on electrical conductivity measurements. The color map is based on relative electrical conductivity; white regions were not measured, and black regions represent phase-separated samples.

Synthesis of metal nanoparticles

The microemulsions used for the synthesis of the metal nanoparticles consisted of a surfactant – in the case of CTAB/heptane/water a co-surfactant, butanol, was added – oil and water phases. Two microemulsions of the same nature and compositions were prepared: the first containing the metal precursor in the water phase and the second containing a reducing agent. As a metal precursors solution 20 mM H_2PtCl_6 was used, and 200 mM NaBH_4 was used as a reducing agent except when otherwise specified. For the synthesis of gold nanoparticles 5 to 15 mM HAuCl_4 and 10 times excess of NaBH_4 were used. Only limited amounts of precursor can be solubilized in the water phase of microemulsion because otherwise destabilization of the microemulsion system due to ionic strength occurs (Table S2). The yield of the synthesis is the ratio of metal synthesized to the weight of the template.

In table S2 theoretical yields of the synthesis are presented for 20 wt% water content are given, however, for several systems such as Na-AOT and Triton x-100, the water content was increased up to 40 % giving us opportunity to double the

yield. Ten times excess of reducing agent was used in all the synthesis procedures, therefore 100 % conversion can be assumed after the reaction time of 1 day.

Table S3 lists the microemulsion compositions used in this work.

Once, both microemulsion are stabilized and appeared homogenous single-phase they were gently mixed. It is important to note here, that the microemulsions should be mixed in such a way that no foaming occurs while NaBH_4 is present, otherwise larger nanoparticles can form. Immediately after mixing the initially yellow colored mixture slowly became dark black in the case of Pt and dark red for gold NPs, implying that platinum (or gold) nanoparticles were formed. In order to make sure that the reaction is completed, nanoparticles are only extracted after one day.

The example of the reduction reaction is given on the Figure S5.

Table S2 Maximum precursor (H_2PtCl_6 , HAuCl_4) concentration at STP for a stable microemulsion formulation and the related theoretical synthesis yields (for 20 wt% water content).

ME system	Precursor concentration (mM)	Yield (wt%)
Na-AOT/heptane/water	350	1.37*
Triton X-100/toluene/water	500	1.95*
Brij 35/heptanol/water	500	1.95
CTAB/heptanol/water	15	0.06
CTAB/heptane/water-butanol	15	0.06
DDAB/decane/water	15	0.06

* Yield is doubled when 40 wt% compositions are used.

Table S3 Microemulsion compositions used for the synthesis of platinum and gold nanoparticles. The remaining part for all systems was water phase composition.

Microemulsion	Composition / Wt%		
	Surfactant	Oil	Water
Na-AOT/heptane/Water	54	26	20
	47	23	30
Triton X-100/toluene/Water	56	24	20
	62	24	14
Brij 35/heptanol/Water	56	24	20
	49	21	30
DDAB/decane/water	40	40	20
CTAB/heptanol/water	30	50	20
CTAB/heptane/water-butanol	30	20	50

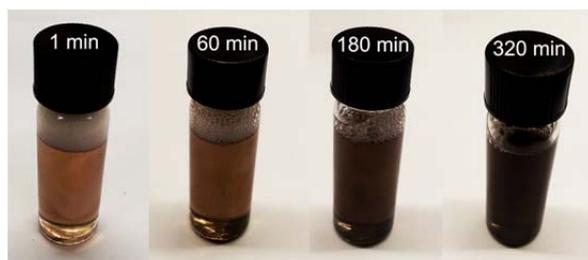


Figure S4 Reduction of H_2PtCl_6 with NaBH_4 in microemulsion of 56 % Triton X-100/24 % toluene/20 % water.

The reaction kinetics were monitored by UV-Vis. The absorbance of platinum precursor, H_2PtCl_6 , at 260 nm is not observed due to disturbance of the signal by hydrogen bubbles formed during the reduction. However, it was possible to monitor the formation of the nanoparticles by tracking the turbidity of the solution. Therefore, the absorbance at of the background, at 650 nm, where no reagent/product peaks exist, was monitored and recorded to measure reaction kinetics (Figure S6). Different reaction rates for reduction reaction are characterized for various microemulsion systems. For instance, the fastest is the reaction in Brij 35, which completes in 2.5 hours, whereas for Na-AOT and Triton X-100 it takes roughly 5 hours to complete the reaction (Figure S6).

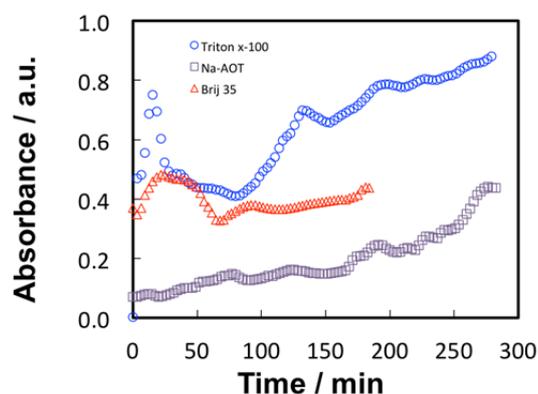


Figure S5 UV-Vis absorption spectra at 650 nm to observe rate of formation of the platinum nanoparticles in the systems of 54% Triton X-100/26 % toluene/20 % water, 54 % Na-AOT/26 % heptane/20 % water and 56 % Brij 35/24 % heptanol/ 20 % water.

For gold nanoparticle synthesis when ionic surfactant is used the reaction completes very fast for CTAB and goes much slower for Na-AOT and DDAB systems (Figure S7). However, when non-ionic surfactant is used first small nanoparticles are formed and then they grow in size, which is observed by a color change from red to blue. The reason for that is that there is much weaker affinity of non-ionic surfactants to the gold surface compared to platinum, and therefore, non-ionic surfactants can not stabilized gold (Figure S8).

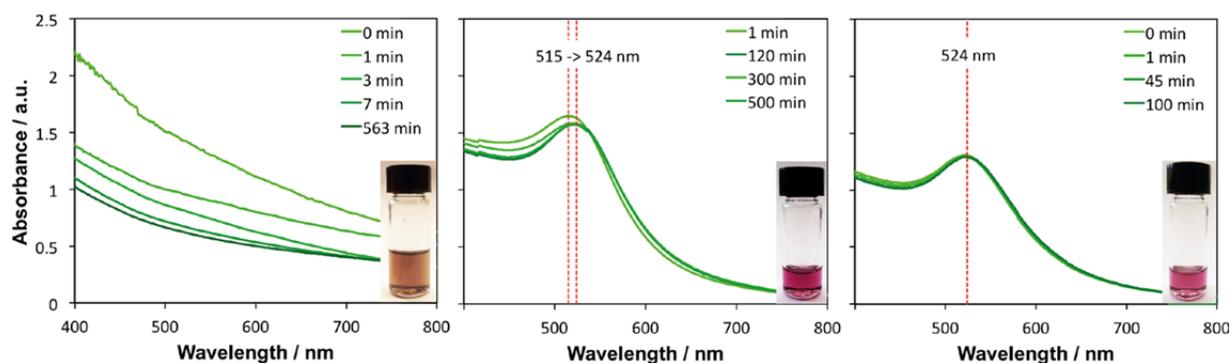


Figure S6 UV-Vis absorption spectrum of Au NPs synthesized in microemulsions of Na-AOT, DDAB and CTAB (from left to right). The inset picture is the photograph taken the day after synthesis completion.

As it was mentioned above the non-ionic surfactants cannot stabilize gold, however, it was possible to quench the reaction by stabilizing the particles with a strong capping agent: 11-mercapto-1-undecanol, which has a thiol group and it can covalently bind gold nanoparticles and stabilize them. 1 ml of ME was removed from a big batch during the synthesis every 5 - 10 minutes, then the solution of 0.2 ml of heptanol solution of 1wt% 11-mercapto-1-undecanol was added to the sample to quench the growth reaction. As a result, it nanoparticles of various sizes where produced by controlling the residence time (Figure S8).

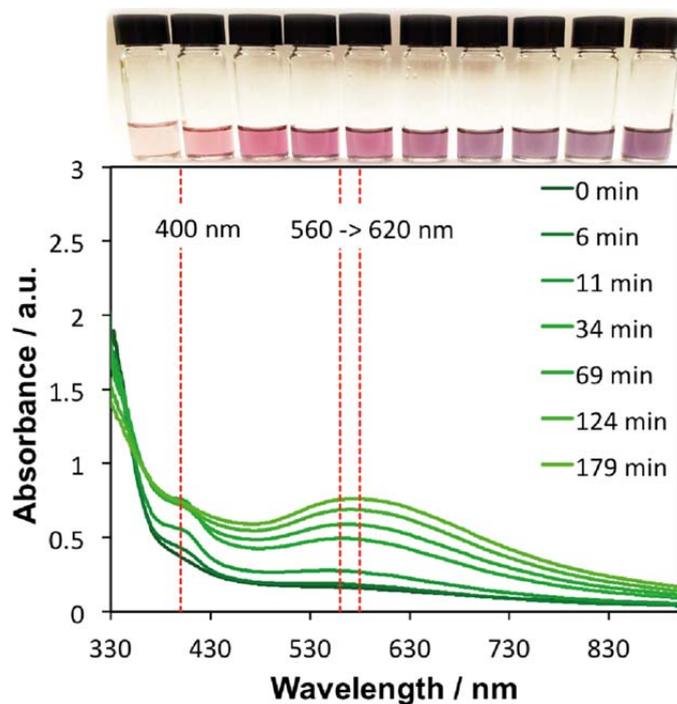


Figure S7 UV-Vis absorption spectra Au NPs produced in Triton X-100 microemulsion. The top picture is the photograph of the quenched samples next day after the synthesis.

Proposed mechanism of the reduction reaction in the bicontinuous dense microemulsions

Two microemulsions, one with reducing agent and the second with metal precursor in the water phase, are mixed together. The reactants react in the water phase of the bicontinuous microemulsion and metal is reduced to form nanoparticles (Figure 8). Detailed mechanism of nanoparticle formation in bicontinuous microemulsion can be found in a previous publication.³

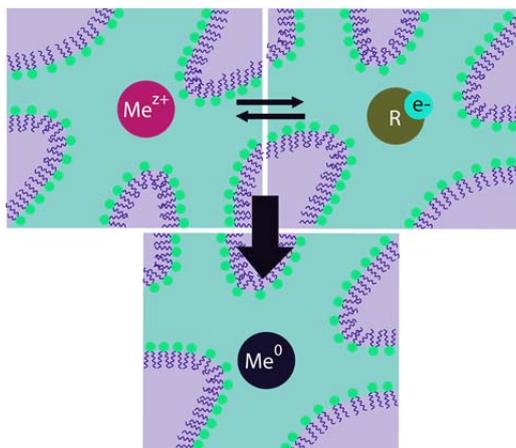


Figure S8 Simplified illustration of formation of nanoparticles in bicontinuous microemulsion.

Effective surfactant chain length

The effective surfactant length in a microemulsion cannot be easily determined but it is roughly equal to the critical chain length. This critical chain length sets a limit on how far the chains can be extended and shows a maximum length beyond which the hydrocarbon chain cannot be considered as a fluid. It is of the same order, but somewhat less than the fully extended molecular length of the chain L_{max} .⁴ The maximum chain length can be calculated with the following equation:⁵

$$L \leq L_{max} \approx (0.154 + 0.1265n), \quad (\text{Eq. S1})$$

where n is number of carbon atoms. L and L_{max} in nm.

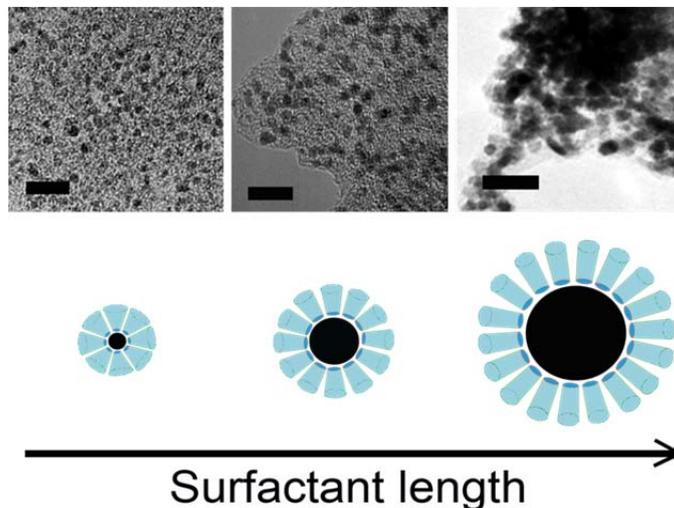


Figure S9 Sketch of dependence of the size of the nanoparticles on the surfactant parameter (scale bar 10 nm).

Extraction of the nanoparticles and surfactant removal

For the extraction, carbon black support Vulcan XC-72 was added to the microemulsion and then the mixture was sonicated for one hour. Afterwards THF was added to the mixture drop-wise while mixing in order to break the microemulsion. Then the resulted solution was centrifuged for 15 minutes at 7000 rpm. The transparent filtrate solution was separated and nanoparticle coated carbon were washed several times with a sequence: THF, 0.1 M HClO₄ (40 - 50 °C), Millipore water (70 °C), THF, Millipore water. Extracted and carbon-supported platinum nanoparticles were dried at 100 °C. The last step of the cleaning was an electrochemical treatment of the catalyst in order to activate by desorbing final traces of the surfactant. The procedure involved application of dynamic voltage from 0.05 - 1.45 V, 10 cycles in 0.1 M HClO₄ at 25 °C and scan rate of 50 mV s⁻¹. Figure S10 shows the voltammograms taken before and after cleaning or electrochemical activation. It can be observed that the peaks for hydrogen adsorption and desorption (0.05 - 0.40 V) appeared after the cleaning, which means the surface area of platinum is clean and available for hydrogen adsorption/desorption.

The electrochemical surface area (ECSA) of the catalyst was calculated by integrating the charge passing through the electrode during hydrogen adsorption/desorption, and then it was corrected for double layer non-faradaic currents. The charge required to oxidize a hydrogen monolayer is known to be 0.21 mC cm⁻², which corresponds to 1.3 × 10¹⁵ Pt atoms per cm². The ECSA was 50 - 60 m² g⁻¹, which is high compared to literature values.⁶

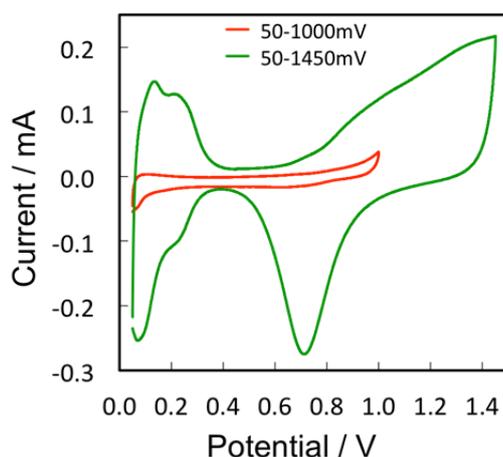


Figure S10 The voltammogram of the catalyst before (in red) and after cleaning (green) taken in 0.1 M HClO₄ at 25 °C at 50 mV s⁻¹ scan rate.

Another way of the extraction was burning of the surfactant molecules by oxidizing them in air at high temperatures, which is the most common procedure in the literature.⁷ Therefore, in order to check this possibility we heat-treated our catalyst at relatively mild heat-treatment temperature of 250 °C for 3 hours. Surfactant removal left unprotected nanoparticles to agglomerate at these elevated temperatures and we observed agglomeration of the nanoparticles (Figure 11).

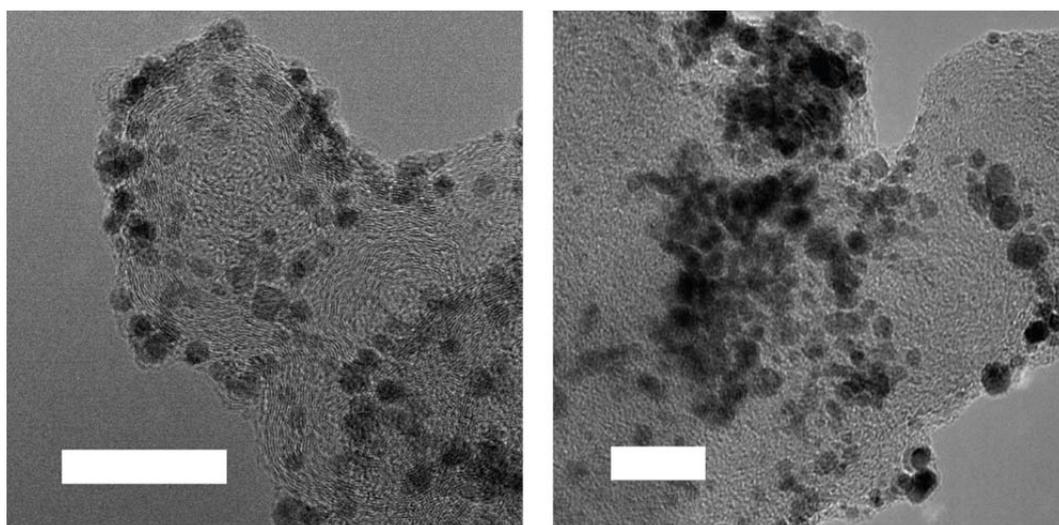


Figure S11 Effect of the heat treatment on the nanoparticles for the surfactant removal, before and after heat treatment (scale bar 20 nm). Nanoparticles synthesized in Na-AOT/heptane/water ME.

Dispersion of Pt nanoparticles functionalized with various surfactants on carbon supports

After the synthesis, the Pt nanoparticles were extracted and dispersed on carbon support (Vulcan XC-72R). Traces of the surfactant were still present on the platinum, which determined the dispersion of the nanoparticles on the support (Figure S13). Pt functionalized with Brij 35 were clustered and did not disperse well on the hydrophobic carbon support due to the surfactant nature which has large hydrophilic domains of PEG (Figure S1). However, Pt functionalized with Na-AOT and Triton X-100 dispersed well over whole carbon support due to presence of long aliphatic chains in case of AOT and aromatic groups in case of Triton X-100 (Figure S1).

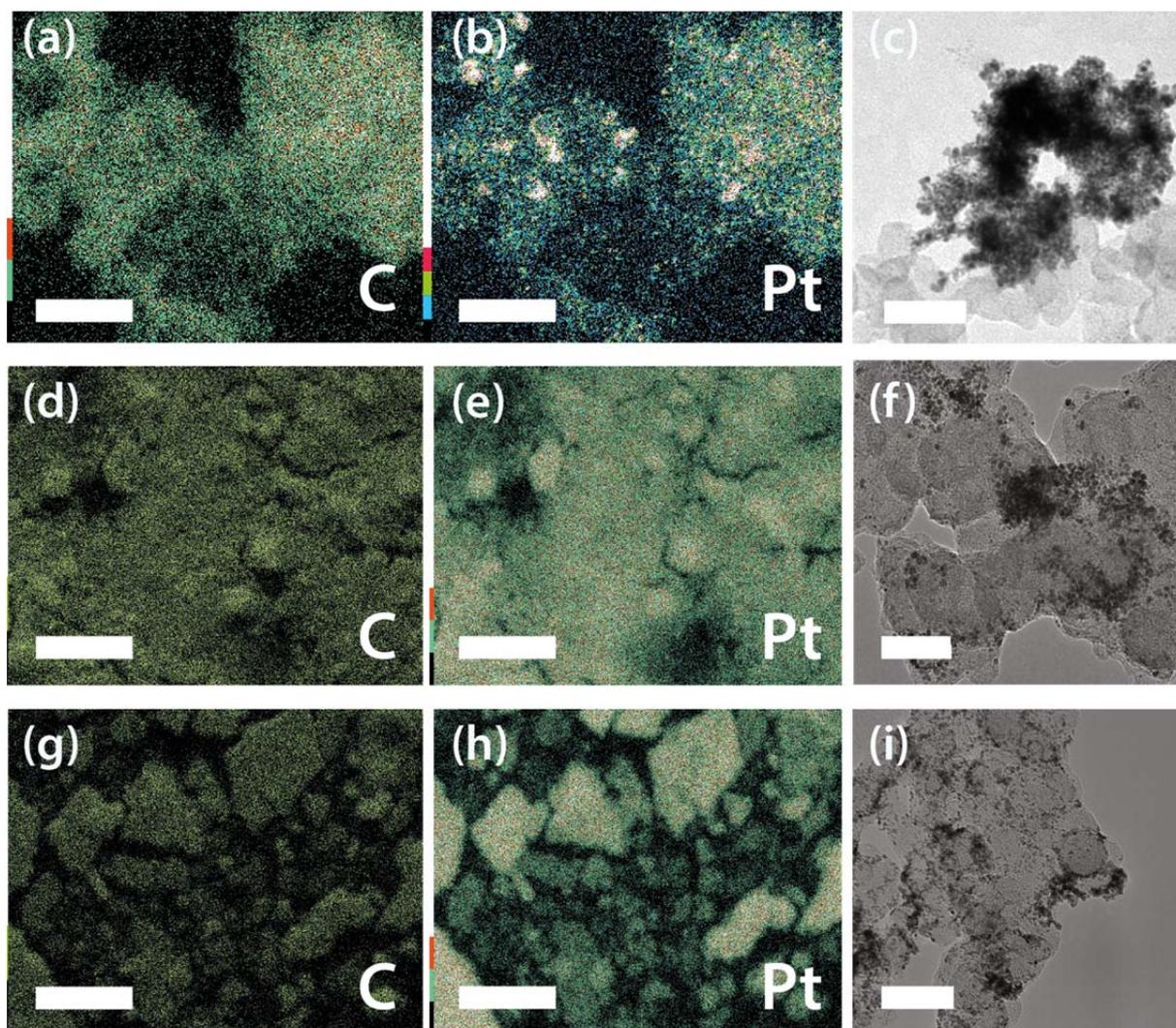


Figure S12 EDS mapping of the Pt supported on carbon Vulcan XC72 (scale bar 3 μ M) and related TEM micrographs (scale bar 50 nm). Pt nanoparticles were functionalized by the surfactant Brij 35 (a-c), Na-AOT (d-f) and Triton X-100 (g-i).

Size and morphology of the nanoparticles

Table S4 summarizes the size of the nanoparticles synthesized in various microemulsion systems from TEM measurements. For platinum, H_2PtCl_6 and NaBH_4 are used, whereas for gold HAuCl_4 and NaBH_4 .

Table S4 Microemulsion compositions and the size of the nanoparticles synthesized in them.

Microemulsion system				Size / nm
54 % Na-AOT/	26 % heptane/	20 % water	(Pt)	2.4 ± 0.4
56 % Triton X-100/	24 % toluene/	20 % water	(Pt)	2.7 ± 0.6
56 % Brij 35/	24 % heptanol/	20 % water	(Pt)	4.0 ± 1.1
54 % Na-AOT/	26 % heptane/	20 % water	(Au)	4.1 ± 1.2
40 % DDAB/	40 % decane/	20 % water	(Au)	6.2 ± 0.9
30 % CTAB/	50 % heptanol/	20 % water	(Au)	6.7 ± 1.6

Platinum nanoparticles synthesized in different microemulsion systems

Platinum nanoparticles were synthesized in microemulsions of the same surfactant but different compositions. The TEM micrographs of platinum nanoparticles from microemulsions of various compositions are given on Figures S14-16.

Figure S14 shows that the size of the nanoparticle did not change with the change of the composition of the Na-AOT/Heptane/Water microemulsion. However, in this particular case N_2H_4 was used as a reducing agent instead of $NaBH_4$. It was observed that the size of the nanoparticles increased, due to modification (dimerization) of the surfactant by hydrazine.

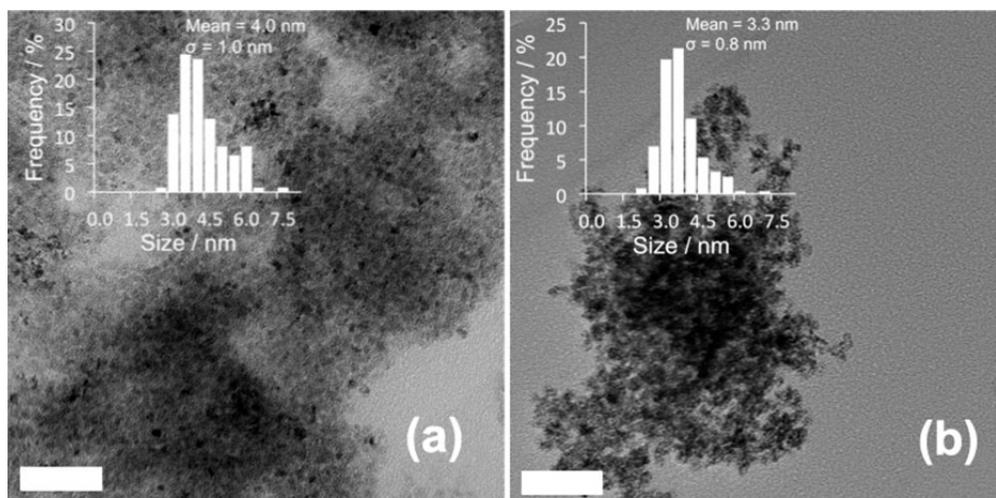


Figure S13 Size of the nanoparticles synthesized in 54 % Na-AOT/26 % heptane/20 % water (a) and 47 % Na-AOT/23 % heptane/30 % water (b), scale bar 20 nm.

Size of the platinum nanoparticles also did not change significantly with the change in composition of the other microemulsion systems (Figures S15, S16).

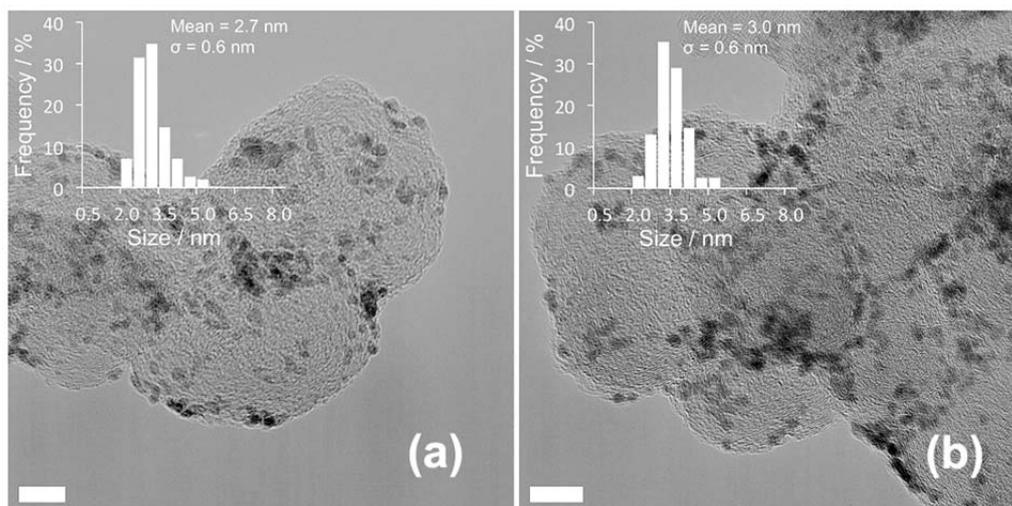


Figure S14 Electron micrograph and size distribution of nanoparticles synthesized in 56 % Triton X-100/24 % toluene/ 20 % Water (a) and 62 % Triton x-100/18 % toluene/ 20 % water (b), scale bar 10 nm.

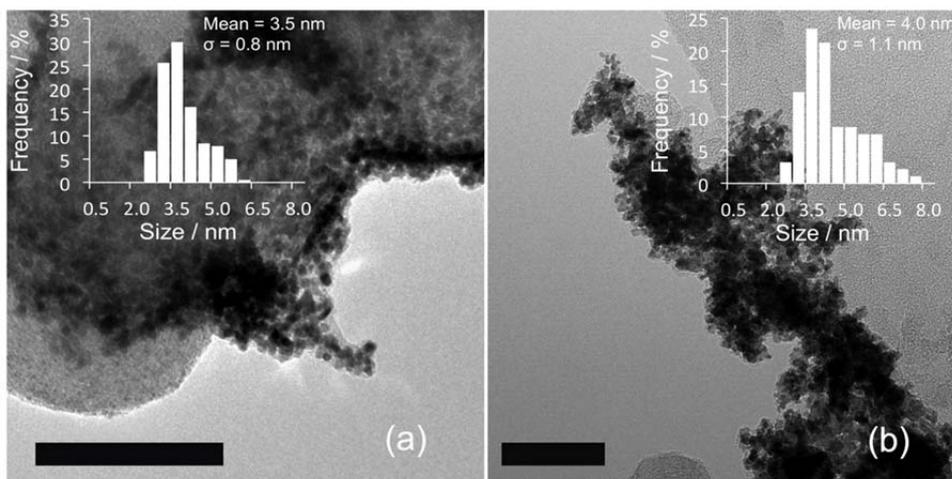


Figure S15 Electron micrograph and size distribution of nanoparticles synthesized in 49 % Brij 35/21 % heptanol/30 % water (a) and 56 % Brij 35/24 % heptanol/20 % water (b); scale bar 50 nm.

Other metals

Other metals (Fe, Cu, Ru, Pd, *etc.*) and metal alloys (Pt-Ru, Pt-Co, Pt-Ru-Co) were synthesized in dense microemulsion systems. Examples are given on the figures S-17 (Pd nanoparticles) and S18 (Pt-Ru-Co alloy).

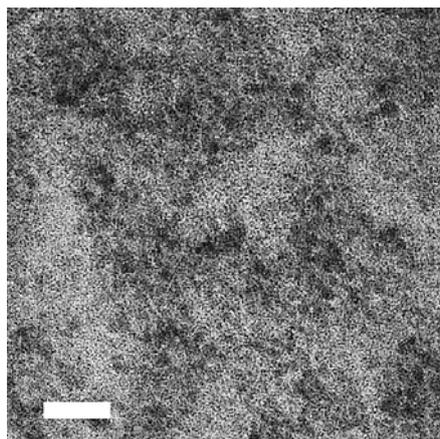


Figure S16 Electron micrograph of palladium nanoparticles synthesized in 54 % Na-AOT/26 % heptane/ 20 % water; scale bar 20 nm.

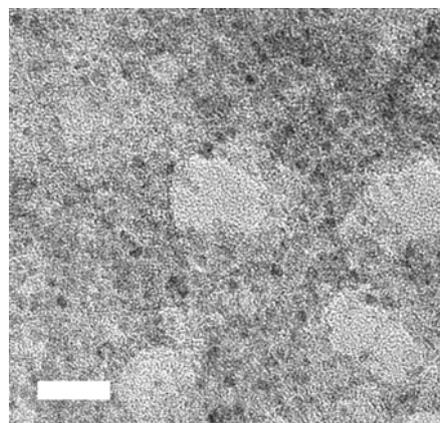


Figure S17 Electron micrograph of tri-metallic Pt-Ru-Co alloy nanoparticles synthesized in 54 % Na-AOT/26 % heptane/ 20 % water; scale bar 20 nm.

XRD measurements

The platinum nanoparticles synthesized in various microemulsions, extracted and deposited on the carbon were subsequently analyzed with XRD. The X-ray diffraction patterns of the platinum nanoparticles synthesized in the three different microemulsion system are shown in Figure S19. The diffraction peaks at Bragg angles of 46.5° , 54.3° and 80.3° correspond to the (111), (200) and (220) platinum crystal facets with predominantly FCC (111) crystal phase. These patterns are with a good agreement with the reference data for platinum.⁸ No shape effects or difference in crystal structures were observed for the nanoparticles synthesized with different surfactants.

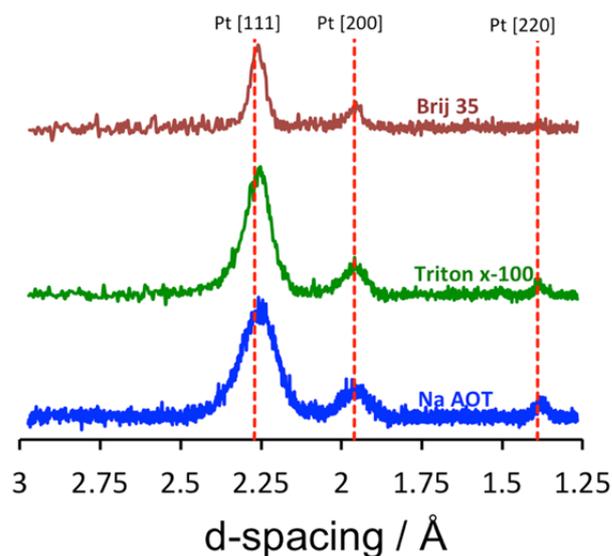


Figure S18 XRD patterns of platinum nanoparticles synthesized in: Na-AOT/heptane/water, Triton X-100/toluene/water and Brij 35/heptanol/water microemulsions.

Stability of the Na-AOT surfactant studied by NMR

NMR measurements showed that the surfactant was not affected during the synthesis procedure and remained chemically inert (Figure S20, 21). The spectrum was also compared to the literature and did not show a difference.⁹ No change in chemical structure of other surfactants is expected. Only for Br⁻ containing surfactants (CTAB and DDAB) anion exchange occurs between the surfactant and the metal precursor (H_2PtCl_6 , $HAuCl_4$).

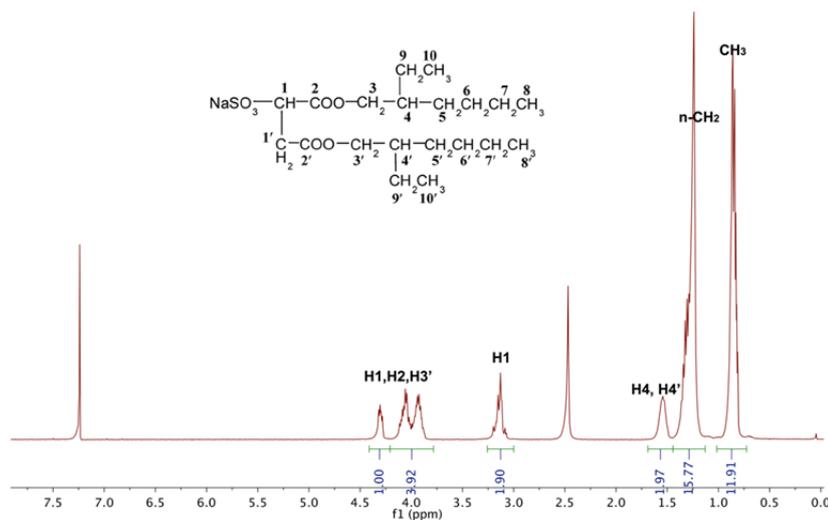


Figure S19 NMR spectrum of Na-AOT before synthesis of the Pt nanoparticles.

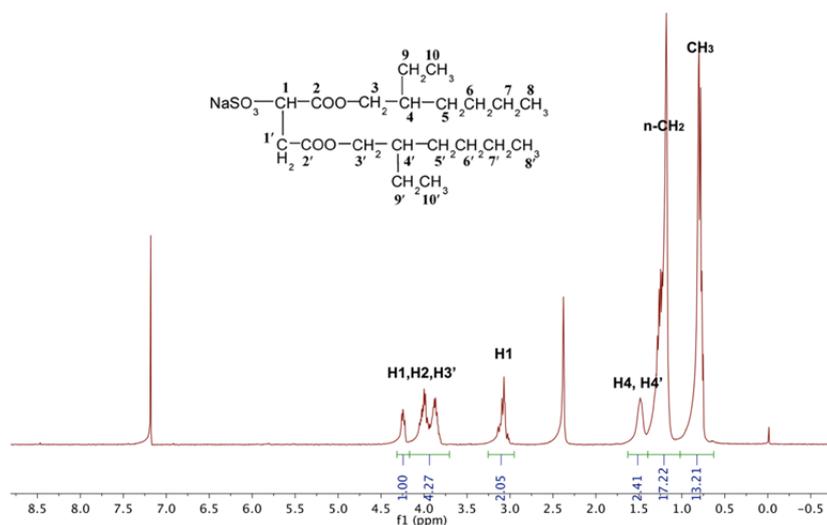


Figure S20 NMR spectrum of Na-AOT after synthesis of the Pt nanoparticles.

References

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