Electronic Supplementary Information (ESI)

S1 Experimental Section

The preparation of metallic nanoparticles (NPs) via w/o-microemulsions is described elsewhere[16]. Bimetallic NPs were prepared at different overall mass fractions of the aqueous phase (w_A). The compositions of the samples and the preparation conditions are presented in Table S1 (See Supporting Information). The characterization of the w/o-microemulsions which contain the metal salt and the reducing agent as well as the time evolution of the particle formation and growth in w/o-microemulsion was studied by small-angle X-ray scattering (SAXS) as described in Supporting Information. For particle characterization, HRTEM images and SAED patterns were collected on a JEOL 4000 FX operating at 400 keV. EDX was done on the Zeiss SESAM using an EDAX detector. All experiments were conducted at room temperature and ambient pressure. The nanoparticles were dissolved in ethanol and then deposited on thin holy carbon films (Plano, 300 mesh - *Artikel S147-3*). HRTEM images and SAED patterns were recorded on a 2kx2k CCD camera (Gatan UltraScan). For data analysis the Gatan DigitalMicrograph software was used. Lattice spacings were obtained from HRTEM images by linescans across lattice fringes. The diameter of diffraction rings was obtained by using the DiffTools package [23]. For calibration diffraction patterns of pure Si were used.

S1.1 Nanoparticle Preparation

Table S1: Compositions of samples and preparation temperature used for the synthesis of Pt:Pb nanoparticles at different mass fractions of the aqueous phase w_A. γ_b represents the mass fraction of Brij30 and 1-octanol in the oil phase; δ is the mass fraction of 1-octanol in the mixture of 1-octanol and Brij30; T_{wefb} is the phase transition temperature between the 1- and $\bar{2}$ -phase region (*wefb*).

Aqueous phase / mM	w_A	γ_b	δ	T_{wefb} / °C	Sample
13 mM H_2PtCl_6 : 13 mM $Pb(NO_3)_2$	0.10	0.114	0.37	28.0	1
160 mM $NaBH_4$	0.10	0.095	0.24	28.0	
13 mM H_2PtCl_6 : 13 mM $Pb(NO_3)_2$	0.08	0.114	0.37	30.5	2
160 mM $NaBH_4$	0.08	0.095	0.24	30.5	
13 mM H_2PtCl_6 : 13 mM $Pb(NO_3)_2$	0.06	0.114	0.37	34.0	3
160 mM $NaBH_4$	0.06	0.095	0.22	34.0	
13 mM H_2PtCl_6 : 13 mM $Pb(NO_3)_2$	0.04	0.114	0.37	35.0	4
160 mM $NaBH_4$	0.04	0.095	0.21	35.0	

S1.2 Materials

The oil *n*-octane (99.5%) was purchased from Fluka. The alcohol 1-octanol (99%) and the surfactant Brij30 were purchased from Sigma Aldrich. Brij30 contains an average of four ethylene oxide groups and a linear alkyl chain of $C_{12}H_{25}$. The metal salts hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, 99.9%), lead (II) nitrate ($Pb(NO_3)_2$, 99.999%), and the reducing agent sodium borohydride ($NaBH_4$, 99%) were also supplied by Sigma Aldrich. Ethoxylated polyethylene imine (referred to as PEI20EO), with a molecular weight of about 13 000 g mol^{-1}, was kindly provided by BASF (80 wt.% aqueous solution). The polymer originated from a hyperbranched PEI of a molecular weight ~600 g mol^{-1} and the substitutable hydrogens on the primary and secondary nitrogens were replaced by ethoxylated chains containing on average 20 repeat units. All chemicals were used without further purification. The water was taken from a Millipore-Q water purification system.

S1.3 Techniques for nanoparticle characterization

The SAXS measurements were performed on a SAXSess high-flux small-angle X-ray scattering instrument (Anton Paar, Austria), attached to a PW3830 X-ray generator (PANalytical) with a sealed-tube anode (Cu Kα wavelength of 0.1542 nm). The generator was operated at 40 kV and 50 mA. Vacuum-tight refillable quartz capillaries (1 mm diameter, sample volume ≤ 100 μL) were used in order to determine the size and shape of the w/o-microemulsions containing the metal salts and the reducing agent, respectively. For kinetic studies, a vacuum-tight refillable quartz capillary in the flow cell unit was used. The w/o-microemulsion containing the metal salts was drawn into a syringe, which was then placed at one end of the flow cell sample holder, while the w/o-microemulsion containing the reducing agent was drawn into a syringe, which was placed at the other end of the flow cell sample holder. An exposure time of 0.5 seconds was used. The experiment started when the quartz capillary was filled with the w/o-microemulsion containing the metal salt. After measuring this sample for 10 s, the w/o-microemulsion containing the reducing agent was carefully and slowly injected via the syringe thus mixing the two reacting microemulsions. All experiments were performed at T_{wefb}. The sample temperature was controlled with a thermostatted sample holder unit (TCS 120, Anton Paar). The 2-D scattered intensities were recorder on a CCD detector (Princeton Instruments) and were converted via SAXSQuant software (Anton Paar) to one dimensional scattering curves as a function of the magnitude of the scattering vector $q = (4\pi/\lambda) sin(\theta/2)$, where θ is the total scattering angle. All intensities were transmission-calibrated by normalizing the attenuated primary intensity at q = 0 to unity and were corrected by subtracting the background scattering from the capillary and the solvent (octane). The size of the microemulsions droplets were determined via Guinier analysis (extrapolation to zero angle, q = 0.06 – 0.4 nm^{-1}) assuming the droplets as homogeneous spheres. Data were fitted with $\ln(I) = \ln(I_0) - (R_G^2/3)q^2$, where R_{G} is the radius of gyration. The particle radius R can be obtained by assuming that the particles are spheres., *i.e.* $R^2 = (5/3) R_G^2$.

S2. Results

Table S2. Atomic composition of samples 1, 2, 3 and 4 (see Table S1) determined via EDX.

Sample 1 / nm^2	**Pt:Pb atomic ratio**	**Sample 2 / nm^2**	**Pt:Pb atomic ratio**
20	73 : 27	20	8 : 92
15	70 : 30	200	72 : 28
15	73 : 27	20	68 : 32
10	65 : 35	20	74 : 26
10	68 : 32	10	69 : 31
20	4 : 96	20	66 : 34
Sample 3 / nm^2	**Pt:Pb atomic ratio**	**Sample 4 / nm^2**	**Pt:Pb atomic ratio**
20	75 : 25	100	71 : 29
20	72 : 28	10	65 : 35
15	77 : 23	10	76 : 24
10	71 : 29	10	62 : 38
20	75 : 25	15	69 : 15
10	68 : 32	20	73 : 27
20	6 : 94	20	8 : 92

Table S3. Diameters d of the w/o-microemulsions containing the two metal salts H_2PtCl_6 and $Pb(NO_3)_2$ in a 1:1 molar ratio determined by SAXS, the mean number of Pt and Pb atoms per droplet and the calculated particle diameter d_{calc} of PtPb NPs; d_{calc} was calculated assuming no exchange of materials among droplets and using the equation $d = \sqrt[3]{\frac{6}{\pi}\left(N_{Pt}v_{Pt} + N_{Pb}v_{Pb}\right)}$, where N_{Pt} and N_{Pb} are the number of Pt and Pb atoms per nucleus, respectively, and v_{Pt} = 0.01551 nm^3 and v_{Pb} = 0.03136 nm^3 are the volumes of a single Pt(0) and Pb(0) atom, respectively; the atomic volume was calculated from the atomic mass (M_{Pt} = 195.08 g mol^{-1}, M_{Pb} = 207.2 g mol^{-1}), the density (ρ_{Pt} = 21.45 g cm^{-3}, ρ_{Pb} = 11.34 g cm^{-3}) and the Avogadro number as $v = M_{Pt}/\rho_{Pt}N_A$.

w_A	**w/o-µe** (H_2PtCl_6 + $Pb(NO_3)_2$) **d / nm**	**Pt,Pb atoms per droplet**	**NPs d_{calc} / nm**
0.10	29.9 ± 0.8	110,110	2.14
0.08	26.1 ± 0.8	73,73	1.87
0.06	21.6 ± 0.4	41,41	1.55
0.04	17.2 ± 0.1	21,21	1.23

S3. References

23. D. R. Mitchell, *Microscopy research and technique*, 2008, **71**, 588-593.