Supplementary Information - A One-pot Route To Stable Pickering Emulsions Featuring Nanocrystalline Ag and Au

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Experimental Details:

Silver Chloride (AgCl), chloro(triphenylphosphine)gold (Au(PPh$_3$)Cl), sodium hydroxide (NaOH), tetrakis(hydroxymethyl)phosphonium chloride (THPC), triphenylphosphine (PPh$_3$) were all purchased from Sigma-Aldrich and used as received. The solvents dichloromethane (CH$_2$Cl$_2$), pentane (C$_5$H$_{12}$), toluene (C$_7$H$_8$) were purchased from Fisher Scientific and deionised water was attained from an Elga Purelab DI reservoir.

Synthesis of chlorotris(triphenylphosphine)silver(I):

Ag(PPh$_3$)$_3$Cl was prepared using a method previously reported.[1] Briefly: to a continuously stirred dispersion of AgCl (1.430 g, 10 mM) in 150 mL of dichloromethane a solution of triphenylphosphine (10.97 g, 40 mM) in 50 mL dichloromethane was added drop-wise. The stirring was continued for a further 60 minutes by which time all solids had dissolved. The solution was left to evaporate until the volume had halved (75 mL). The contents of the vessel were then filtered and diluted with 10 mL of pentane. Solid Ag(PPh$_3$)$_3$Cl crystallized upon cooling the pentane-dicholoromethane mixture. The product was filtered *in-vacuo* and re-crystallized from pentane. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.23 (m, 45H, 9 x C$_6$H$_5$), 1.65 (s, 2H, CCl$_2$H$_2$), ^{13}C NMR (CDCl$_3$) δ 133.90 (d, J = 17.2 Hz), 129.69 (s), 128.72 (d, J = 8.8 Hz), 77.22 (s). Elemental analysis (%) found: C, 69.45; H, 4.84; Cl, 4.23; P, 9.69; Ag, 11.02. Calcd: C, 69.71; H, 4.84; Cl, 3.82; P, 10.00; Ag, 11.62.

Preparation of Pickering emulsions:

Five millilitres of a 0.6445 mM solution of Ag(PPh$_3$)$_3$Cl in toluene was carefully stood atop 1.0 mL 18.43 mM NaOH in water. Aqueous tetrakishydroxymethylphosphonium chloride (50 mM, 0.12 mL, THPC) solution was then injected into lower water layer. The vial was immediately introduced into a water bath held at 15 °C attached to a ultra-sonic horn (Sonorex RK31 model, stated power rating: 40 W nominal; 160 W peak). The irradiation was continued for 60 minutes over the course of which the water bath temperature was maintained between 15-20 °C.

Similarly, five millilitres of a 0.6445 mM solution of Au(PPh$_3$)Cl in toluene was layered atop 1.0 mL 18.43 mM NaOH in water. Aqueous THPC (50 mM, 0.12 mL) solution was then injected into lower water layer. Again the vial is introduced to the water bath with ultra-sonic agitation as described above for 60 minutes, with the bath temperature held at between 15-20 °C.

The Pickering emulsions made as described above were stored in sealed vials in a dark cupboard at ~ 15 °C for the duration of the monitoring process (up to 3 months). Images of the droplets were taken over a period of 3 months after preparation using the on-board microscope setup on the BioForce NanoeNabler molecular printing system with optical magnification up to 700x. Droplets were imaged in this equipment by taking a drop of emulsion from the storage vial, and then being sandwiched

between two microscope slides for imaging. A video is included below of a 2 week old Pickering emulsion prepared with Ag nanoparticles, of toluene droplets (~1-2 μm diameter) freely moving within the majority water phase.
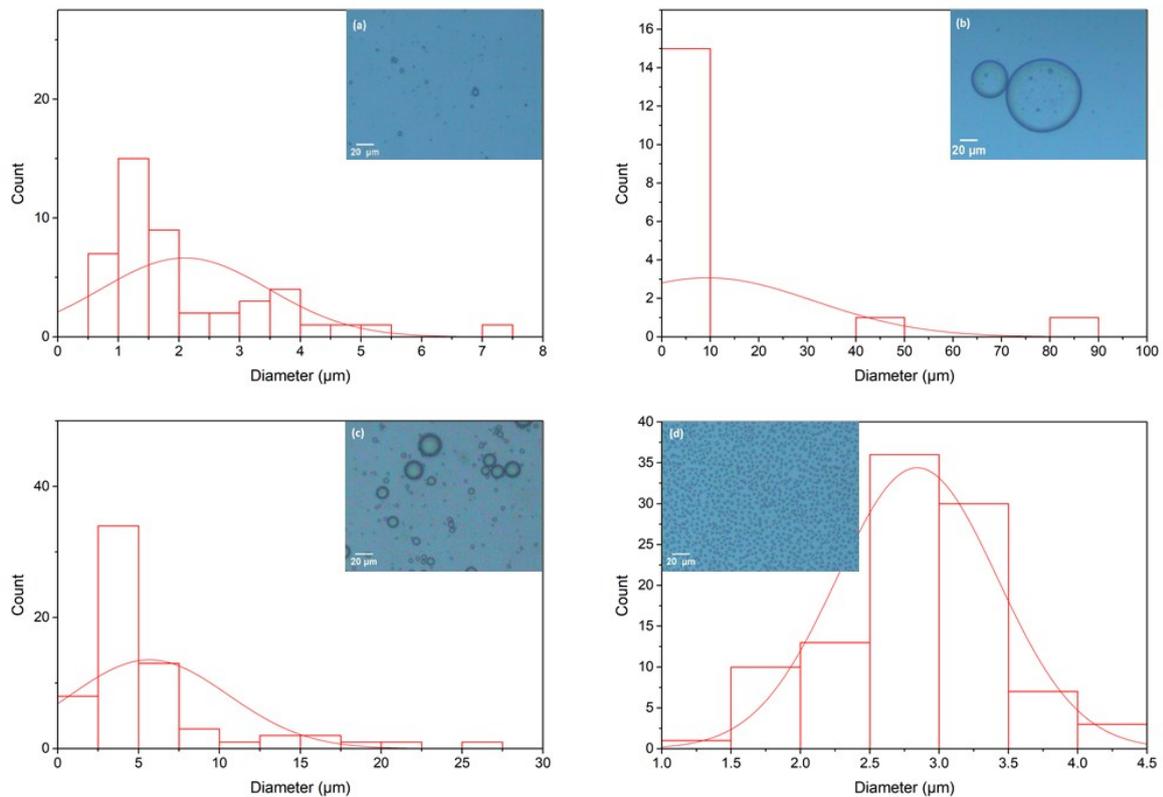
vid 31-8-18 of PE1
water layer 15-8-18.a

Figure 1: Shown in this figure are size distribution histograms of measured droplets of their respective microscope images, seen in the main paper in Figure 3. The size distributions are typical and were verified with 4 (or more) images obtained from distinct areas of the sample.
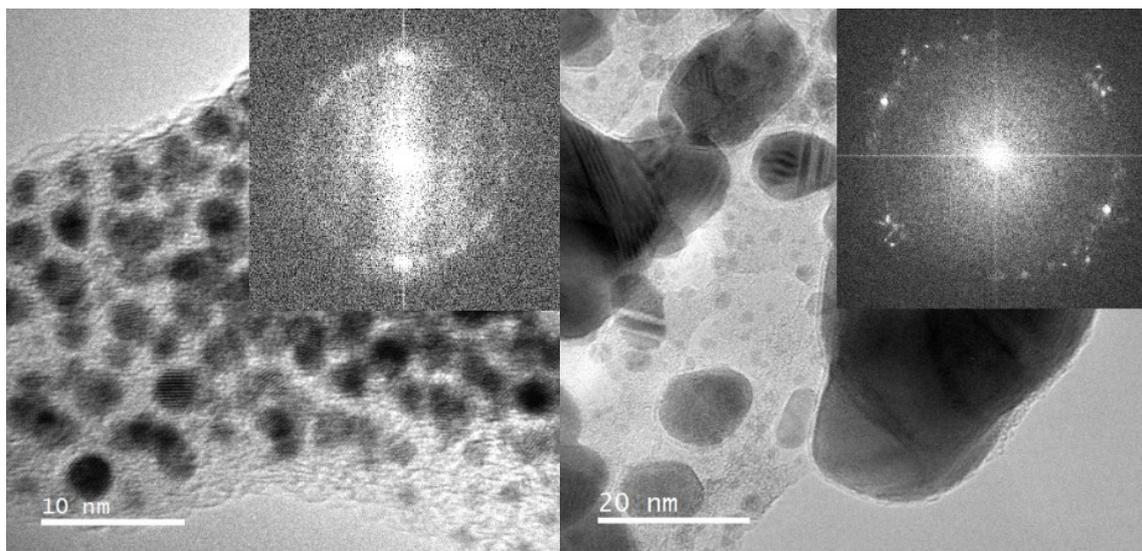
Figure 2: HRTEM images of Au and Ag nanoparticles synthesised in situ-of Pickering emulsion preparation. Image a. shows freshly prepared Au nanoparticles with inset FFT, while image b. shows Ag nanoparticles from a 3 month old Pickering emulsion with inset FFT.

Fourier transform plots of lattice resolved Au and Ag nanoparticles seen in HRTEM, yield spots consistent with those expected from the (111) spacing of face centered cubic Au and Ag crystallites. Additionally, the aged Ag nanoparticles (from the 3 month old emulsion) shows lattice with separation of around 0.210 nm, possibly indicating (200) spacing expected with separations of 0.204 nm. Also seen is the 0.165 nm lattice spacing, attributed to Ag (211) lattice.

Ag nanoparticles prepared at the interface of toluene and water have been studied using H1 NOSEY NMR technique, where through the Overhauser effect between proton spins on protons in close proximity to each other, whether the surface ligands PPh_3 and THPO are existing as mixed surfactants or in spate regions can be established. For proton spins of less than 5 Å distance from each other, the presence of off-diagonal peaks should be present in the NOSEY spectra. We could find no presence of any off-diagonal peaks for this sample agreeing with analysis published previously for nanoparticles prepared at the toluene-water interface.[2]

We also used NOSEY NMR to observe Ag nanoparticles prepared with the same reducing agents, disperse however in a mix of CH_3OH and H_2O, resulting in nanoparticles of comparable size and shape. This spectra was also absent of any off-diagonal peaks, again indicating that opposing surface ligands are not within close proximity to each other. This goes counter to our assumptions based on the principle of this technique, as with the nanoparticles synthesised in this system an equally dispersed coverage of the two surface ligands would be expected on the nanoparticle surface and hence cross-coupling between protons.
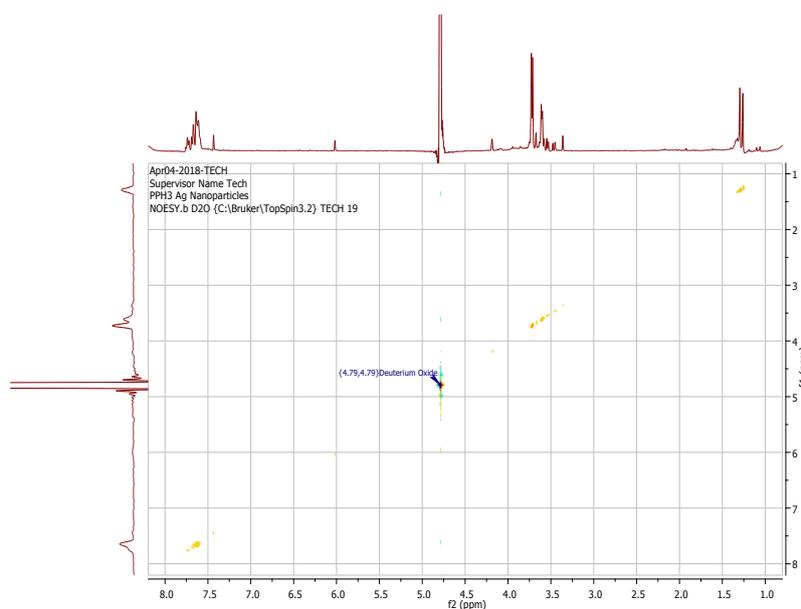
Figure 3 : ^{1}H NOSEY 2D NMR spectra of (a.) silver nanoparticles produced at the interface of Toluene and water, and (b.) silver nanoparticles synthesised with the same reducing agents, however instead solvent in a mix of CH_3OH and H_2O

Acknowledgements:

References:

1. D. V Sanghani, P. J. Smith, D. W. Allen and B. F. Taylor, *Inorganica Chim. Acta*, 1982, **59**, 203–206.

2. K. Luo, C. Hu, Y. Luo, D. Li, Y. Xiang, Y. Mu, H. Wang and Z. Luo, *RSC Adv.*, 2017, **7**, 51605–51611.