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Chemical Communications

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Cite this: DOI: 10.1039/xxxxxxxxxx

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

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Accepted Date

DOI: 10.1039/xxxxxxxxxx

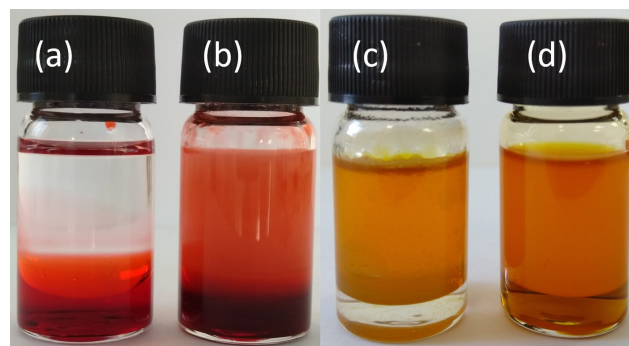
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**A simple, one-pot reaction scheme leading to water-in-toluene- and toluene-in-water type Pickering emulsions solely stabilized by nanocrystals of Ag and Au is described. Sol properties- ageing and ability to disperse substances are studied. The nature of the solid surfactants and their surface structure is ascertained by transmission electron microscopy and nuclear magnetic resonance spectroscopy.**

Pickering emulsions consist of fine liquid droplets, ensclosed by microscopic solids, dispersed in a non-miscible fluid.<sup>1-7</sup> Such water-in-oil or oil-in-water colloids have been studied for over a hundred years<sup>8</sup> and are well known for their remarkable stability, particularly against ageing.<sup>3,9,10</sup> These dispersions have found widespread applications including: catalysis<sup>4</sup>, food manufacture, pharmaceutical and cosmetic products, decontamination technologies.<sup>11,12</sup> A number of future uses such as in drug delivery,<sup>13-16</sup> synthesis of multi-functional Janus particles<sup>4,17</sup> and gene therapy<sup>5</sup> have been touted. One key feature underlying these applications is the ability of Pickering emulsions to disperse sizeable quantities of a species into an otherwise non-dispersing medium.

Typically, Pickering emulsions feature microscopic particles such as those of poly-styrene, silica and carbon black<sup>7</sup> and contain droplets with diameters of hundreds of microns. Their noted ruggedness is due in part to the penchant of solid particulates to adsorb particularly strongly to the interface between the fluids.<sup>3,9,10</sup> Indeed, long term stability is achievable in these systems even with sub-monolayer coverage of an interface by particulates.

More recently, attention has turned to Pickering emulsions with



**Fig. 1** Reaction vials showing the formation of emulsions. (a) A water-toluene column with curved meniscus and red ink. Clear ink partition to the aqueous phase is visible; (b) red ink, introduced into the vial, following the formation of Pickering emulsions partitions across both solvents. (c) & (d) Show a similar effect with a lipophilic toluene soluble dye that disperses into the aqueous phase following emulsification.

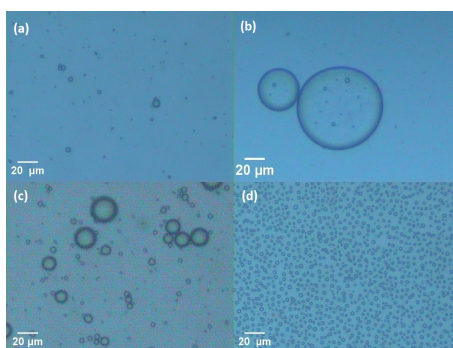
finer droplets stabilised by particles with dimensions less than 20 nm.<sup>2,18-23</sup> These dispersions are more challenging to obtain as they involve weaker stabilizers and require careful tuning of the surface structure of the surfactant particulates. Preparation of such colloids have hitherto relied on multi-step methods involving synthesis of nanocrystals, purification and surface-structure tuning to yield dispersions.<sup>2,18-23</sup> We have, for many years, been interested in deposition of nanocrystals at the interface of two immiscible liquids, starting from molecular precursors.<sup>24</sup> Developing the chemistry of this scheme to yield Pickering emulsions appeared worthwhile. Herein, we describe a simple, single step, one-pot scheme featuring discrete molecular precursors that yield ultra-stable Pickering emulsions featuring Au and Ag nanocrystals.

An hour long ultrasound agitation of toluene dispersion of either Ag(PPh<sub>3</sub>)<sub>3</sub>Cl or Au(PPh<sub>3</sub>)<sub>3</sub>Cl stood on top of an aqueous layer with Tetrakis(hydroxymethyl)phosphoniumchloride (THPC) and NaOH yields two distinct liquid columns with a completely flat meniscus (see figure 1b). This flattening is indicative of forma-

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† Electronic Supplementary Information (ESI) available: Ag(PPh<sub>3</sub>)<sub>3</sub>Cl synthesis, Pickering emulsion preparation method, droplet size analysis with time, HR-TEM images with diffraction patterns and NMR data included. See DOI: 10.1039/b000000x/

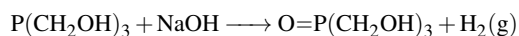


**Fig. 2** Micrographs of oil-in-water droplets. (a) aqueous phase of a freshly prepared emulsion with  $\text{Ag}(\text{PPh}_3)_3\text{Cl}$ ; (b) after 3 months. (c) & (d) correspond to similar emulsions with  $\text{Au}(\text{PPh}_3)\text{Cl}$ , freshly made and aged 1 month respectively.

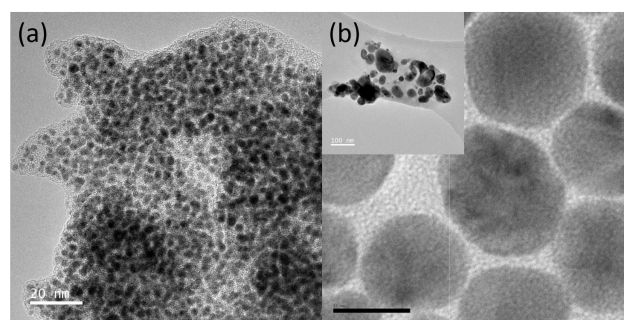
tion of emulsions in these layers. The emulsions in the reaction vessels are able to disperse tangible quantities of oil-based- or aqueous- dyes in the orthogonal medium (Fig. 1). We ascertained by elimination of reagents that THPC, NaOH and metal precursors are necessary for the formation of such emulsions (flattened interface + dye dispersion).

High magnification optical images of the lower water rich layer, examined after three hours, revealed copious quantities of spherical droplets with diameters of around 1–3  $\mu\text{m}$  in the case of the reaction involving  $\text{Ag}(\text{PPh}_3)_3\text{Cl}$  (Fig. 2 a). The droplets in the layer were stable for extended periods of time (over a year on the bench in a stoppered glass vial). With time, fewer, but larger droplets (up to  $\sim 86 \mu\text{m}$ ), along with a fraction of smaller droplets were seen (Fig. 2 b). Droplet diameters could be restored to those in Fig. 2a by briefly shaking the vial. The emulsion retained such behaviour for up to a year following original agitation. Throughout this period, the ability to disperse substances that were otherwise insoluble in the medium was retained. The upper toluene rich layer was also observed under the microscope at several points, where droplets of diameters around 5  $\mu\text{m}$  were seen. However, rapid evaporation of toluene under imaging conditions (thin layers sandwiched between glass slides) made photography impossible. In the case of reactions with  $\text{Au}(\text{PPh}_3)\text{Cl}$ , fresh preparations yielded droplets (in water layer) with diameters between 1–5  $\mu\text{m}$ , some possessing diameters of 25  $\mu\text{m}$  (size distribution curve(s) in ESI). Surprisingly, ageing for a period of a month strongly focuses the diameter distribution to between 1–4.5  $\mu\text{m}$  (Fig. 2 c & d).

Under the reaction conditions employed, THPC is expected to hydrolyse<sup>25</sup> to yield active species capable of reducing Ag and Au precursors. In water:



HCHO,  $\text{H}_2$  and tri(hydroxymethyl)phosphine (THPO) are all capable of being active reducing agents.<sup>26</sup> Ultrasound agitation creates fluid droplets that diffuse into the opposite layer. This process is dynamic, with the droplets coalescing and reforming.



**Fig. 3** HRTEM images of nanoparticles synthesised in-situ of Pickering emulsion preparation. Image (a) shows Au NPs, while (b) shows Ag NPs. Inset is an image of Ag particulates obtained from emulsions, three months after initial agitation.

Effectively, a dynamic biphasic interface with greatly enhanced area of contact is formed. Here,  $\text{Ag}(\text{PPh}_3)_3\text{Cl}$  or  $\text{Au}(\text{PPh}_3)\text{Cl}$  in toluene are reduced by one of the reducing species to form seeds adsorbed to the surface of water droplets forced into the organic layer by ultrasound irradiation. In aqueous phase, metal precursors in the toluene droplets dispersed by agitation, are reduced by THPO (and other reducing agents) present in the water layer. The germination is expected to be followed by a period of particle growth facilitated by formaldehyde reduction<sup>26,27</sup> leading to nanocrystals stabilised by a mixture of ligands including the liberated  $\text{PPh}_3$  groups and THPO. Precious metal particulates dispersible in water<sup>25</sup> or the fluid interface<sup>24,27–31</sup> have previously been obtained under comparable conditions (sans ultrasound irradiation). Also, ultrasound agitation has been used to speed up interfacial aggregation of graphene flakes<sup>32,33</sup> to produce membrane like deposits at the interfacial area after cessation of agitation.

High resolution transmission electron microscopic images on dried dispersions of the contents of the vessel as well as aliquots drawn from with layer confirmed the presence nanocrystals with identical structural characteristics. In the case of Au, spherical crystallites with diameters between 2–4 nm are seen (Fig. 3 a). The tight control over size dispersion evident in this preparation is surprising in the context of generally poorer control seen in other schemes featuring THPC in the absence of sonication<sup>30</sup>. Perhaps, the increased area of contact between the liquids brought about by ultrasound aids quick capping of the surface by THPO and  $\text{PPh}_3$ , leading to better control over diameter. In the case of Ag, larger particles with diameters between 10–14 nm and narrow size distribution are seen (Fig. 3 b). With time, the nanoparticles are observed to grow larger with marked worsening of the size distribution. Ag particulates grow to sizes between 2–100 nm after 3 months (inset image in Fig. 3b), adopting both elongated and spheroidal forms. This is due to low temperature ripening<sup>34–36</sup> proceeding in this medium containing un-reacted reagents (starting materials). We note that such ageing related particle growth, appears not to affect the stability of the colloidal dispersions. The emulsions retain their property for several months in stoppered vessels. Taken together with the observation that the droplet size can be restored by brief shaking, the rela-

relationship between the emulsion droplet dimensions and those of the nanocrystals adorning the surface of such drops is perhaps not strictly tenacious.

Over the course of the reaction two ligands, THPO and  $\text{PPh}_3$ , with known affinity to the surface of Ag and other metal surfaces come into play. Previously, we have shown that Ag deposits obtained at the water-toluene interface in the form of a thin film deposits are adorned with two or more types of phosphinyl ligands on the surface of the particulates<sup>37</sup>. Others have reported similar surface ligands on Au particulates<sup>27</sup>. Here, proton NMR spectra on the dispersion of the Ag revealed a multiplet centered at 7.69 ppm corresponding to  $\text{PPh}_3$  and similar peaks at 1.31 ppm and 0.97 ppm due to THPO (see ESI). Hence, akin to particulates obtained at the water-toluene interface, the surface of the Pickering emulsion stabilising nanocrystals features both ligands. Two-dimensional NMR experiments were performed to probe the interactions between the surface species. NOSEY experiments yielded spectra with no off-diagonal peaks. This suggests that the two types of ligands form contiguous blocks with minimal cross-coupling. Previous studies have taken the absence of cross-coupling peaks as evidence of two-faced Janus particles<sup>38,39</sup>. In the past, off-diagonal peaks have indeed been observed on thiol terminated surface ligands<sup>39</sup>. In order to test the robustness of 2D NMR evidence, we reduced the Ag precursor in a mixture of water and methanol to obtain particulates with similar size and dispersion. However, in this sol, off-diagonal peaks were still absent under conditions favouring the inter-ligand interaction. Hence, this absence of evidence for interactions, while indicative might need further detailed studies to support firm conclusions.

The particulates forming Pickering emulsions are adsorbed to the interface and effectively reduce contact area between the fluids. The Gibbs energy of adsorption ( $\Delta G$ ) is dependent on particle radius ( $r$ ), the tension between the two fluids ( $\gamma_{wo}$ ) and the three phase contact angle ( $\theta$ ), given by:

$$\Delta G = -\pi r^2 \gamma_{wo} (1 - \cos\theta)^2$$

Young equation further relates  $\theta$  to the tension between particle-oil ( $\gamma_{so}$ ) and particle-water ( $\gamma_{sw}$ ) [ $\gamma_{so} - \gamma_{sw} = \gamma_{wo} \cos\theta$ ]. When  $\theta$  is  $90^\circ$ ,  $\Delta G$  reaches a maximum. Using reported values of  $\gamma_{wo}$  ( $36 \text{ mNm}^{-1}$ ),<sup>40</sup> we obtain  $\Delta G$  maximums of  $250 k_B T$  and  $4000 k_B T$  for Au and Ag particulates (3 & 12 nm). Reports have indicated  $\Delta G$ s of  $5 k_B T$  for 2.5 nm CdSe and  $60 k_B T$  for similarly sized Au nanocrystals, depending on surface structure (and hence  $\gamma_{sw}$ ,  $\gamma_{so}$ )<sup>22</sup>. For comparison,  $\Delta G$ s for molecular surfactants are around  $10 k_B T$ .<sup>41–44</sup> We surmise  $\Delta G$ s nearer the maximum<sup>45</sup> underpin the remarkable temporal stability exhibited by the Pickering emulsions herein.

In summary we detail here a novel preparation of stable Pickering emulsions of toluene and water, via an in-situ synthesis of Au and Ag nanocrystals with reactants coming from both present phases and as such forming at the interfaces of these phases. It has been demonstrated that Pickering emulsions are formed in both the oil and water majority phases, and that in the case of Pickering emulsions stabilised by Au nanoparticles the formed particles are morphologically monodisperse. The droplet sizes are

seen to vary over time and this change is dependent on the solid surfactants present.

## Conflicts of interest

There are no conflicts to declare.

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**Graphical Abstract:**View Article Online  
DOI: 10.1039/D0CC00967A

A simple one-pot scheme yielding Pickering emulsions with long terms stability reliant on noble metal nanoparticles surfactant is presented. The dimensions and temporal stability of the emulsion is explored. Spectroscopic and microscopic tools are used to characterize the solid surfactants.

