



## Rapid Communication

## Synthesis and Assembly of Gold and Iron Oxide Particles Within an Emulsion Droplet; Facile Production of Core@Shell Particles

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## ABSTRACT

Here we report a method for synthesising and assembling nanomaterials at the liquid-liquid interface of an emulsion droplet, resulting in a simple strategy for producing hollow Au shells, or Fe<sub>3</sub>O<sub>4</sub>@Au core@shell particles. Mercaptododecanoic acid stabilised Au nanoparticles were added to the aqueous continuous phase, in order to stabilise hexane emulsion droplets formed within a microfluidic chip. The diameters of Au Pickering emulsions could be controlled by varying the flow rates, this produce hollow particles. The addition of a second nanoparticle, Fe<sub>3</sub>O<sub>4</sub> (average diameter of 12 nm), into the organic phase produced core@shell particles. The diameter of the resultant material was determined by the concentration of the Fe<sub>3</sub>O<sub>4</sub>. This report is the first to demonstrate Pickering emulsions within a microfluidics chip for the production of Fe<sub>3</sub>O<sub>4</sub>@Au particles, and it is believed that this could be a versatile platform for the large scale production of core@shell particles.

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Synthesis and fabrication methods for nanoparticles have evolved to the extent that particle size, shape, and composition can be controlled. As such they have been integrated into many aspects of modern life [1]. Gold nanoparticles, Au-NPs, of various morphologies are commonly found as they have numerous applications in catalysis [2], biosensing [3] and therapeutics [4]. Anisotropic particles, in particular gold nanosheets and core@shell particles have gained particular attention [5]. They possess enhanced optical properties for the treatment of tumours [6], enhanced Raman detection [7] and optical sensors [8]. As a result several chemical synthesis strategies have been developed for single and two phase systems [9]. However, most syntheses strategies that lead to high anisotropy require organic solvents, high temperatures, hard reducing agents, polymer and molecular capping agents, although alternative “green” chemistries are emerging [4,6,10].

Conversely, electrochemical techniques allow a degree of control over the growth and assembly of the material through the applied potential or template, allowing nanomaterials to be formed at the solid-liquid and liquid-liquid (liq-liq) interface [11,12]. The interface between two immiscible liquids offers a defect free, reproducible substrate to grow metals. This allows the material to be easily recovered, as the majority of the formed particles remain at the interface upon creation [13]. The interface between two liquids can also be used to assemble nanoparticles with their spacing and composition at the interface as shown in Fig. 1, controlled via capping ligands [8]. The assembly of nanomaterials at the liq-liq interface is spontaneous due to the

favourable stabilisation of the interfacial free energy and was first discovered by Ramsden [14] and Pickering [15]. The preferred location at the interface is determined by the Young's equation and by tailoring the surface chemistry of the particles. The contact angle of the particle at the interface can be controlled and can be used to create oil-in-water or water-in-oil emulsions, known generally as Pickering Emulsions. Pickering emulsion synthesis strategies have assembled a range of both polymer and inorganic materials at the interface of the droplets [16–19], and when materials are present in both phases even core@shell particles can be synthesised [20] as shown in Fig. 1 iii.

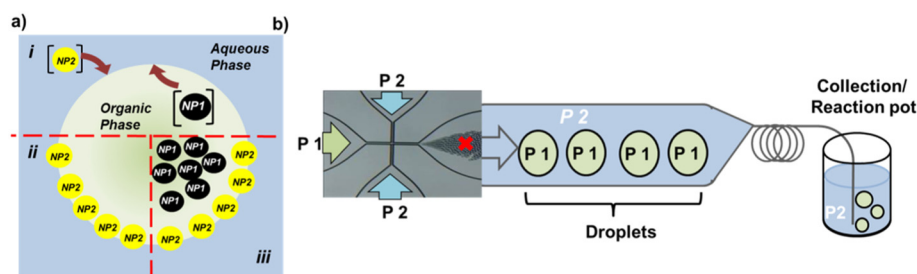
In this paper we present a strategy for producing Fe<sub>3</sub>O<sub>4</sub>@Au particles using Pickering emulsions. The combination of a magnetic core and a biocompatible, chemically inert, and easily functionalized shell, offer biomedical, separation or analytical applications. Au shells have been used as localised hyperthermia treatments of cancer [6], and Iron oxide superparamagnetic materials have been used as contrast agents for MRI imaging [21]. We present the first demonstration of Pickering emulsions within a microfluidics chip for the production of Fe<sub>3</sub>O<sub>4</sub>@Au particles, where the core diameter can be controlled by the concentration of NP1 in the organic phase as shown in Fig. 1 ii. The technique has the advantages of not requiring long reaction times, surfactants or templates to produce the asymmetric materials.

## 1. Chemicals and reagents

The following chemicals are from Sigma Aldrich, U.K. and unless stated the chemicals were used without purification. Sodium Dodecyl Sulfate (SDS) (436143), Iron (II) chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O)

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**Fig. 1.** a) Schematic of liquid-liquid interface with nanoparticles NP1 and NP2 presynthesised and dispersed in the organic of aqueous phase respectively. ii. Particle at a Pickering emulsion interface. iii. Core-shell Pickering emulsion. b). Schematic of the fluidic assembly and droplet collection. P1, P2 represents the organic and aqueous phase respectively. The droplets flowed through a tube 5 cm long into a collection vial.

(220299), Iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) (236489), ammonium hydroxide ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) (338818), Oleic acid (364525), perchloric acid (244252), Gold (III) chloride trihydrate ( $\geq 49\%$ ) (G4022-1G), Tetraoctylammonium bromide (98%) (294136), 12-mercaptododecanoic acid (12-MDA) (675067), sodium borohydride (98%) (452882). The following chemicals are from VWR chemicals, U.K. and unless stated the chemicals were used without purification. Hexane (24,580.324), ethanol absolute (20,821.330), toluene (28,676.322), were used. Deionized (DI) water was collected from Millipore water purification system having 18  $\Omega$  cm conductance) was used throughout.

Microfluidics instruments were supplied by Dolomite, A 14  $\mu\text{m}$  etch depth Dolomite hydrophilic x-junction “small droplet chip” (Part No. 3200136), Dolomite Mitos P-Pump basic (Part No. 3200175) were controlled via the Dolomite Mitos Flow Control Centre Version 2.2.15

Synthesis of hydrophobic nanomagnetic particles (250 mL) scale.  $\text{FeCl}_{12} \cdot 4\text{H}_2\text{O}$  (12 g) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (24.5 g) were dissolved in DI-water (62.5 mL) in a 250 mL three neck bottle. The flask was placed in an ice bath.  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (50 mL) was added rapidly with vigorous stirring. The flask was left in the ice bath for 45 min. The solution was rapidly heated to 85  $^\circ\text{C}$  for 1 h. Oleic acid (7.5 mL) was then added and the solution was further heated for another 1 h. The flask was cooled to room temperature and the slurry was transferred to a 150 mL beaker. Slurry was washed 3 times with ethanol (50 mL) and each time the black magnetite was collected using a block magnet. The slurry was then washed 3 times with DI-water (50 mL) before being washed 3 times with 20% perchloric acid (50 mL) to dissolve  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$ . The slurry was again washed 3 times with DI-water (50 mL), before being washed three times with ethanol (50 mL). Hexane (87.5 mL) was added to the resultant particles so to disperse well, this was called ferrofluid. The particle concentration was determined by weighing the mass of material that remained after the evaporation of a known volume of solvent.

Synthesis of gold nanoparticles coated with 12-mercaptododecanoic acid in toluene. Gold nanoparticles were prepared by the previously reported technique [22], briefly  $\text{HAuCl}_4$  (0.05 M, 4 mL) was mixed with 11 mL of 0.05 M tetraoctylammonium bromide in toluene (0.05 M, 11 mL) in a vial. The mixture was left stirring for a minimum of 2 h, the organic phase was then transferred to another vial and 12-mercaptododecanoic acid (1200  $\mu\text{L}$ ) was added to it followed by freshly prepared  $\text{NaBH}_4$  (0.4 M, 25 mL) with vigorous stirring. Colour change from orange to deep brown indicates completion of the reaction. The mixture was left stirring for a minimum of 3 h. The organic phase was separated from the mixture and transferred to a clean vial. The organic phase (500  $\mu\text{L}$ ) of the Au-NP solution was transferred to an Eppendorf tube allowing the solvent to be evaporated to dryness. Ethanol (1500  $\mu\text{L}$ ) was then added to the precipitate, followed by 2 drops of NaOH (5 M). The Eppendorf tube was vortexed to disperse the pellet and then kept in the freezer for 16 h following a centrifuged process at 12000 rpm for 5 min. The supernatant was removed and washed twice with ethanol (1000  $\mu\text{L}$ ) followed by DI-water (100  $\mu\text{L}$ ). At this

point the particles had dispersed into the aqueous solution and it appeared brown.

Creation of emulsion droplets, hexane, (P1) and aqueous solution (P2) were connected to the droplet chip as guided by the manufacturer instructions. P2 was the continuous phase and the droplets size of P1 was controlled by varying the flow rates of P1:P2. The droplet size was observed through a Celestron LCD digital microscope Model ~44,340. Moreover, the droplet size was determined by analysing an image taken on the microscope and was measured by a point marked X as shown in Fig. 1b. The droplet was collected for 2 h and left for evaporation for 2–3 h.

Collection of particles, the collected sample was centrifuged (12,000 rpm, 5 mins) then the supernatant was discarded and replaced with acetonitrile (500  $\mu\text{L}$ ). The washing process was repeated with DI-water. The sample was then re-dispersed in DI-water (500  $\mu\text{L}$ ). When the sample contained iron oxide nanoparticles, the solution is purified by placing on a magrack (GE, healthcare, UK) for 2 min. The supernatant was discarded and replaced with DI-water (100  $\mu\text{L}$ ) then it was placed on a sonication bath for 1 min. The washing process was repeated three times with DI-water and twice with acetonitrile. The sample was then re-dispersed in either water or acetone (100  $\mu\text{L}$ ).

Scanning electron microscopy (SEM) samples were prepared by dropping the suspension onto conductive copper pad. The SEM used for imaging was a table top SEM Hitachi TM3030, an FEG-SEM JEOL 7800F, a Leo (Zeiss) 1530-VP FEG-SEM.

Transmission electron microscopy (TEM) specimens were prepared by ultrasonating the suspensions followed by pipetting onto standard holey carbon support TEM grids. A Jeol 2000FX TEM equipped with an Oxford Instruments (INCA350) energy dispersive X-ray spectroscopy (EDS) system was used to characterise the samples. The TEM was operated with 200 kV accelerating voltage in conventional bright field mode. Selected area electron diffraction (SAED) patterns were recorded to identify the crystallinity of the particles.

The magnetic properties of the beads were measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, San Diego, CA, USA) at room temperature as described previously [23].

Samples were prepared for analysis by Powder X ray Diffraction (PXRD) from suspensions. The suspensions were dropped onto silicon substrates and the liquid allowed to evaporate before being placed into Perspex sample holders. The sample holders were loaded onto a Bruker D8 Advance Powder X ray Diffractometer set up in reflection geometry with  $\text{Cu K}\alpha_1$  radiation (1.54056  $\text{\AA}$ ), selected from a Ge 111 monochromator and a LYNXEYE™ 1D detector. Data were collected over the  $2\theta$  range 30–80  $^\circ$   $2\theta$  with a step size of 0.007  $^\circ$  and a count time of 2 s per step.

We have previously shown the emulsion templated self-assembly of iron oxide nanoparticles using oil-in-water emulsions. By changing the nanoparticle concentration, NP1, shown in Fig. 1a, the resulting micro-particles diameter can be controlled, creating a high through put

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