## **Supplementary Information**

### Visualization of equilibrium position of colloidal particles at fluid-water interfaces by deposition of nanoparticles

Manigandan Sabapathy, Viswas Kollabattula, Madivala G. Basavaraj and Ethayaraja Mani\*

Polymer Engineering and Colloid Science Laboratory, Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai -600 036, India

#### 1. Effect of gold reduction on fluid-water interfacial tension

Since the three phase contact angle of a particle at an interface is influenced by the fluid-fluid interfacial tension, we first establish that the presence of metal salt and the reducing agent does not affect the air-water and oil-water interfacial tension. The interfacial tension of reaction mixture-air and reaction mixture-decane interface are measured as a function of reaction time. From Fig. S1, we see that the interfacial tensions is observed to be independent of the reaction time up to 2 hr both for citrate and NaBH<sub>4</sub> based reductions. The measured interfacial tensions are in close agreement with the pure decane-water and air-water interfaces.



**Figure S1.** Surface tension measured at different interfaces as a function of reaction time with sodium citrate and sodium borohydride as reducing agents. These measurements were done at room temperature, i.e. 27 C.

#### 2. Effect of gold reduction on contact angle measured at flat substrates

We think that our method gives the original contact angle because we initially localize the particles at the interface, where the particle is pinned at the fluid-water interface. We assumed that any chemical modification done on the particle surface exposed to water do not alter the contact angle because of this pinning effect. We have done several experiments to show that once the particle is pinned at the interface, the contact angle does not change due to the deposition of gold or other nanoparticle depositions. We discuss below the details of experiments and results to justify our argument.

#### 2.1 Sessile drop analysis

In the first set of experiments (details of the experiments are given below), contact angles of pure water and water with reaction mixture (gold salt and reducing agent) on polystyrene (PS) and silica flat substrates are measured. Contact angle of water on a gold pre-deposited flat substrate is also measured to compare with the other data. We intend to show that the contact angle of water on PS and gold-pre deposited substrates would be different because the surfacewater surface energies are different in these cases. However, we would like to see if gold nanoparticles were to be deposited in-situ as a function of time, whether the contact angle remains that of pure water-PS or approaches that of water-gold pre-coated substrate. This experiment will give us evidence to verify whether contact angle would change or not because of in-situ deposition of gold. From Fig. S2A, we note that the contact angles of water on PS and water with reaction mixture are nearly same within the experimental uncertainty, while that of water on gold pre-coated substrate is rather different as expected. The measurements are done upto 10 minutes and beyond this time, evaporation of water from the drop gives rise to uncertainty in the measurement of contact angle. We have also performed these experiments on silica substrate (see Fig. S2) and arrived at same conclusion. We observed a small decrease in the contact angle values with time in all cases because of evaporation of water.

We also found that for all the drops, the diameter of contact line (width of the drop) is constant for the entire duration of the experiment, as shown in Fig. S2B. The constancy of contact line diameter and the decrease in the contact angle values due to evaporation show that the sessile drop is pinned irrespective of the substrates used in these experiments. These results suggest that once the drop is pinned, the deposition of gold do not change the contact angle. As mentioned above a slight decrease in contact angle is observed in all cases due to evaporation of water. Hence the proposed methodology for the visualization of interfacial position of particle does not affect the apparent contact angle of particles at interfaces. Had we pre-coated gold on PS or silica particles before dispersing at the interface, they would have exhibited different contact angle values.



**Figure S2:** Kinetic study of sessile drop on various substrate showing variation of (A) contact angle with time and (B) drop diameter with time. The data shown in are average of three different experiments under identical conditions. The error bars are smaller than the size of the data markers.

#### 2.2. Experimental details

#### 2.2.1. Sessile drop:

In order to measure the contact angle of different fluids on planar substrates, we fabricated planar substrate analogues of colloidal particles used in this study. We use three different substrates namely APTS functionalized glass substrate and silicon wafer coated with polystyrene, gold coated glass substrate (control). The APTS functionalized glass substrate is obtained by the approach used for particles as described in the experimental section of the manuscript. To obtain polystyrene coated substrate, the approach by Stancik et.al (*Langmuir*, **2004**, *20*, 4805–4808) is used. Initially, the amidine functionalized polystyrene (2.2  $\mu$ m) particles are dissolved in chloroform and the molecular solution thus obtained is deposited on silicon wafer by spin coating. A thin film of polystyrene on the substrate is thus obtained. To prepare a gold coated substrate, a thin film of gold is deposited on a glass substrate by using thermal metal evaporator (Model: Q150T, Quorum Technologies, UK). The thickness of the gold film is about 40 nm as measured using spectroscopic Ellipsometer (Woollam Spectroscopic Ellipsometer, USA).

A drop of deionized water of volume approximately 4  $\mu$ l is placed on different substrates and the contact angle is measured using goniometer (GBX instruments, France) as a function of time. Using a high resolution camera the side view of droplet is recorded every 30 sec at 25 fps for 10 min. The contact angle is obtained by averaging measured contact angle from frames of three different experiments at identical time interval. Similar procedure is followed for the analysis of sessile drop of reaction mixture comprising aqueous sodium borohydride and gold aurochloric acid solution. In this case, the contact angle measurements are initiated immediately after the preparation of the reaction mixture. All experiments are conducted at a relative humidity of  $70\pm1$  % and a temperature of 28.5±0.5 °C.

#### 2.2.2. Sputter coating conditions:

Prior to analysis in SEM, a part of the glass slide coated with particles was cut to a dimension 10 mm by 10 mm, and sputter coated. Sputter coating is done for 30 s in all our experiments. To find the grain size of sputter coated gold as a function of coating time, we use a flat Si wafer as a substrate in a control experiment. Using spectroscopic Ellipsometer, the mean grain size was measured (see Figure R1). We find that 30 s of coating corresponds to 1.2 nm grain size of gold.

#### 3. Effect of reaction time

In all our experiments on the measurement of contact angle of particles at fluid-water interface, the chemical reduction of gold is carried out for 2 hr. We have repeated the experiments with 10 and 60 minutes of reaction to optimize the reaction time. The measured contact angle of the PS particles at air-water for reaction time of 10 min and 60 min are  $39.5 \pm 1.4^{\circ}$  and  $37.6 \pm 1^{\circ}$ , respectively. The reported mean contact angle in the manuscript for a reaction time of 2 hr was  $39 \pm 2^{\circ}$ . Therefore, there is no significant variation in the apparent contact angle due to gold deposition for these reaction times, although the quality of gold film strongly depends on reaction time. Film quality in turn affects the accuracy of measurement of contact angle. Fig. S3 shows the image of the amidine functionalized PS of 2.2 µm particles coated with gold nanoparticles with 10 min (A) and 60 min (B) reaction time. The particles in Fig. S3A were

imaged without conventional sputter coating in back scattering mode and it shows a clear demarking of the contact line. The white spots inside the contact line is due to charging effects.

The gold nanoparticles formed during chemical deposition is in the range of 10 - 20 nm for 60 min of reaction time. Since the sputter coated gold grain size is one order of magnitude smaller than deposited gold nanoparticles, sputter coating does not cover the contact line. However, we note that when reaction was carried out for 10 min only, the gold nanoparticle size were much smaller and in this case sputter coating interfered the demarcation of the contact line. This is the reason why we did not sputter coat the samples obtained in 10 min reaction experiments.

# **4.** Measurement of contact angle by deposition of pre-synthesized nanoparticles (other than gold nanoparticles)

The proposed method is based on the in-situ generation of gold nanoparticles for the visualization of equilibrium position of colloidal particles at fluid-water interfaces and calculation of contact angle thereof. We note that the method is not specific to gold nanoparticles. With additional experiments, we show here that the use of nanoparticle adsorption for visualization of contact line of charged particles at interfaces is very generic. To this end, we exploit the phenomena of electrostatic attraction between nanoparticles dispersed in the sub-phase (water) and colloidal particles trapped at the interface.



**Figure S3.** Visualization of equilibrium position of positively charged 2.2  $\mu$ m PS particles at air-water at different reaction time A) 10 min, B) 60 min. Scale bar correspond to 1  $\mu$ m.

For this study, we use a dilute (1 % by weight) aqueous dispersion of either negatively charged Ludox HS-30 (Sigma Aldrich) or positively charged Ludox CL-30 (Sigma Aldrich) nanoparticles of 15 nm diameter, as sub-phase. The zeta potential of silica nano particles for both HS-30 and CL-30 are found to be around -60 mV and +60 mV from dynamic light scattering. First, we consider the measurement of contact angle of positively charged polystyrene (2.2 µm) particles. As soon as the PS particles are spread at air-water interface, the nanoparticles deposit on the surface of the PS particles exposed to aqueous phase due to electrostatic attraction. Fig. S4A shows a dark circular region where there is no nanoparticle deposition, and the contact line is distinct. Moreover, the contact angle of particles ( $36 \pm 0.8^{\circ}$ ) obtained is in agreement with the gold deposition method ( $39 \pm 2^{\circ}$ ). We have also confirmed that this method works equally well for the visualization of equilibrium position of negatively

charged PS particles using positively charged nanoparticles dispersed in the sub-phase (see Fig. S4B). Thus, our method adds more generality to the existing techniques available for the measurement of contact angle.



**Figure S4.** Visualization of equilibrium position of particles using silica nano particles (Ludox, HS-30 and CL-30) after 2 hr of aging time (A) 2.2  $\mu$ m positively charged amidine functionalized polystyrene particles at air-water interface (B) 3  $\mu$ m negatively charged sulfate latex at decane-water interface. Scale bar corresponds to 1  $\mu$ m.

#### 5. Structural features of surfactant treated PS particles

Fig. S5 reveals the structural morphology of surfactant treated particles at three different surfactant concentrations of 0 mM, 0.8 mM and 2 mM. The zeta potential of the particles measured at these concentrations are +82 mV, 0 mV (close to neutral) and -28 mV respectively. The structure of monolayer of modified particles is viewed by scanning the entire regions of petri dish (4.5 cm diameter) containing particles at reaction mixture-air interface using inverted microscope. From Fig. S5 A and C, it is clear that the electrostatic repulsive interaction between the particles due to positive or negative charge leads to two dimensional hexagonally close-packed monolayer of particles. However, at 0.8 mM, the hydrophobic interaction between the particles due to absence of any surface charge on the particle surface and screening of electrostatic by SDS molecules, led to aggregation of particles at the interface.



**Figure S5.** Optical microscopic images showing effect of surfactant concentration on structural morphology of surfactant modified PS particles for SDS concentrations of A) 0 mM, B) 0.8 mM and C) 2 mM. The scale bar corresponds to 20  $\mu$ m.

#### 6. Absence of gold patch on the fluid (oil or air) side

Fig. S6 shows the top morphology of PS particles deposited on glass substrate at reaction mixture-decane interface. The images confirm the absence of gold deposition on the top surface, i.e., the part exposed to oil phase. Hence, carbon tape is used to peel the particles from the glass substrate to view the bottom morphology of particles. The images corresponding to the bottom morphology of PS particles is discussed in the main article (Fig. 3A).



**Figure S6:** HRSEM images showing top morphology of PS particles transferred from the reaction mixture-oil interface to glass substrate at different magnifications.