**Supplementary Material : Aging mechanism in model Pickering emulsion**

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I. NANOPARTICLES PREPARATION

The chemicals used for the NPs synthesis are TetraEthylOrthoSilicate (TEOS), l-Arginine, chloride acid 0.1M and ethanol. They were supplied by Aldrich and used as received. High-purity deionized water (18.2 M.cm) was produced using Millipore Milli-Q Gradient system. The synthesis follows the same protocol as in our previous work [1]. It is performed in a 2000 ml reactor thermostated with hot water circulation at 60˚C and agitated by a blade mixer. The vapors are cooled in a water condenser. 1000 ml of a 6 mM l-Arginine solution is first introduced in the reactor. Once the solution reaches the desired temperature, 80 mL of TEOS is added in the reactor and form an organic phase on top of the aqueous solution. The stirring rate is fixed such that the two phases are well mixed and form an emulsion during the synthesis (1500 rpm). The reaction is kept at constant stirring speed and temperature during at least 24h and then allowed to cool down to ambient temperature. The surface modification of the particles is performed after determination of their size and concentration (i.e. their total exposed surface). A 200 mL volume of suspension is placed in a vial and agitated by a magnetic stirrer (750 rpm). A volume of 0.5 to 4 mL of trimethylethoxysilane (TMES) is added, corresponding to 2.3 to 18.2 TMES molecules/nm² of particle surface and the grafting reaction is performed during 4 to 24 h. Once the reaction is complete, the particles are washed 3 to 5 times in a Millipore Amicon stirred cell (30 kDa membrane) to remove the arginine and reaction by-products. The particles are washed and redispersed in water or ethanol depending on their hydrophobicity: particles grafted with more than 9 TMES molecules/nm² aggregate in water but redisperse readily when washed in absolute ethanol. The size and aggregation state of the NPs is assessed with SAXS and DLS after dialysis.

II. NANOPARTICLES TITRATION

The particles hydrophobicity is characterized via the titration of the residual silanol functions on their surface. Approximately 0.2 g of particles are dried by solvent evaporation in an oven at 90˚C during 24h and then dispersed in 16 mL of a 20 g.L⁻¹ NaCl solution. The titration is performed with a Hanna automatic titrator, after degassing the solution by nitrogen bubbling during 30 min. After each addition of the 0.1M HCl titrating solution, the sample is allowed to equilibrate for at least 2 min before the pH is measured. The titration is stopped when the pH reaches 2. The volume necessary to lower the pH of the solution from 6.5 to 2.5 is recorded. A blank experiment is performed on a nanoparticle-free NaCl solution and subtracted from this value. Since the total area of the particles is known from SAXS measurements, this titration enables the determination of the total number of silanol functions in the sample; hence the surface density of silanol functions.

III. SURFACE MODIFICATION OF NPS

The surface modification of the NPs is assessed through titration after dialysis. Figure 1 shows the quantity of silanol function per unit surface of NPs as a function of the total volume of TMES introduced during the surface modification reaction. It is observed that the more TMES introduced, the less residual silanol groups are present on the surface. Bare silica NPs have 4.5 silanol/nm². This value is reduced to about 2 silanol/nm² when 8 TMES molecules per nm² are introduced in the reaction media. Although the surface modification reaction has a reduced yield between 25-30%, it appears possible to tune the residual silanol groups density efficiently down to about 1 silanol/nm² when 18 TMES molecules per nm² are used. We clearly noticed a change of NPs hydrophilicity since with more than 8 TMES molecules/nm² the NPs do no longer disperse properly in water but in ethanol. These modified surface NPs are then measured by SAXS and DLS.
IV. NPS AGGREGATION

The figure S2 shows the DLS size as a function of TMES molecules/nm$^2$ and SAXS curves corresponding to the bare and surface modified NPs with $\sim$3 silanol/nm$^2$ (4.56 TMES molecules/nm$^2$). On the DLS size measurements, it is observed that up to a total TMES concentration of 4.6 TMES molecules/nm$^2$, the surface modified NPs are still well dispersed in water. The SAXS curves give two useful information. First, the intensity oscillations at large angle are still present after the surface treatment. There is no noticeable shift of these oscillations which shows that the size of the NPs is the same. We also observe the presence of an interaction peak at small angle for both samples. This indicates that a repulsive interaction exists between the NPs even after the surface treatment at 4.6 TMES/nm$^2$.

It is thus possible to maintain the NPs stability while modifying their hydrophobicity. When more than about 8 TMES/nm$^2$ is used in the surface modification reaction, DLS measurements become impossible as the NPs are no longer stable in water. In these cases, it is still possible to partially disperse the NPs using ethanol as a solvent. DLS measurements of the NPs redispersed in ethanol show that the NPs are not fully aggregated. The measured size is slightly different from the one obtained in water indicating that the NPs are probably in the form of small aggregates (50nm instead of 20nm for dispersed NPs).

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**Figure 1**: Titration of the residual silanol on NPs surface as a function of contacted silane molecules.

**Figure 2**: Characterization of the NPs used for the emulsion preparation. Left. DLS measurements of functionalized NPs. Inset TEM (or SEM) picture of bare silica nanoparticles. Right. SAXS measurements of bare and grafted NPs.
V. MICROFLUIDICS DROPLET GENERATOR AND MILLIFLUIDICS EMULSION CLEANER

Microchannels were microfabricated using standard multilayer soft technology [2][3][4]. The polydimethylsiloxane (PDMS) elastomer (Sylgard 184, Dow Corning) was poured and further cured on a SU-8 mold (Microchem). Holes were punched for the inlets and the PDMS replicates were sealed to glass slides following oxygen plasma treatment.

VI. SMALL ANGLE X-RAY SCATTERING

Small Angle X-ray Scattering (SAXS) is a powerful technique to probe the size, shape, polydispersity and concentration of nanoparticles in situ [5]. The scattered intensity $I(q)$ is measured as a function of the scattering wave vector $q = (4\sin(\theta/2))/\lambda$ where $\lambda$ is the wavelength of the incident X-ray beam (=1.54 Å). The measurements are performed on a laboratory SAXS apparatus described by Zemb et al [5]. Since this publication, the following modifications have been performed. The X-ray source is a copper rotating anode operated at 3 kW using a micro focused source. We use a multilayer Xenocs mirror to obtain a monochromatic parallel X-ray beam. The beam is collimated using three slits under vacuum. The sample is placed at 230 cm after the mirror and at 122 cm from the detector plane. A beam stopper is placed under vacuum before the detector. The detector is a Mar300, an automatic imageplate based system from Marresearch. The sample measurements are performed using a specially designed sample cell that allows variable beam path length. The sample thickness is first set to 1 mm and a scattering picture is obtained on the detector after an accumulation time of 3600s. Then a second X-ray scattering image is obtained for the empty sample cell on the detector for the same counting time. The two pictures are radially averaged and normalized with standard procedures to give the scattered intensity of the sample (in cm$^{-1}$).

VII. ANALYSIS OF SAXS MEASUREMENTS

Due to the different size scales involved, with the present SAXS measurement, it is possible to obtain the NPs droplets surface coverage using general scattering properties. First the X-ray beam is attenuated through the sample. This beam attenuation depends on the sample thickness and composition. We have :

$$T = e^{-\sum f_i \mu_i e}$$  \hspace{1cm} (1)

where $T$ is the sample transmission, $f_i$ and $\mu_i$ are respectively the mass fraction and the linear absorption coefficient of the sample component (water, oil, NPs). It is reasonable to assume that the mass fraction of NPs after the droplets rinsing is negligible compared to oil and water as the initial mass fraction is less than 0.3%. Even if a complete coverage of the settled droplets is envisaged, the maximum possible mass fraction will not be in excess of 0.5% due to the large size difference between the droplets (40 μm) and the NPs (7.1 nm). Assuming that the NPs mass fraction is negligible compared to the water and oil fractions, it is possible to obtain the oil mass fraction $f_o$ from the transmission measurements :

$$f_o = \frac{- \ln(T) - e \mu_w}{(\mu_o - \mu_w)e}$$  \hspace{1cm} (2)

The total area of oil is not directly deducible from the mass fraction as some oil droplets may coalesce or evolve through Oswald ripening for example. Thus the initial droplets size can change. The low angle Porod regime however can be used to get an experimental evaluation of the oil droplets area. The Porod regime is given by :

$$I(q)q^4 = \frac{2\pi \Delta \rho^2 S}{V}$$  \hspace{1cm} (3)

where $\Delta \rho$ is the scattering length density contrast between oil and water, $S$ is the area of the oil/water interface and $V$ is the scattering volume. From this equation, it is possible to obtain the total area of the oil droplets. The surface coverage is then obtained by assessing the excess scattering due to the NPs. To obtain this value, we will compute :

$$Q = \int I(q)q^2 dq$$  \hspace{1cm} (4)

The value of $Q$ computed using the experimental scattered intensity is proportional to the sample composition :

$$Q_{tot} = 2\pi^2[\phi_o \phi_w (\rho_o - \rho_w)^2 + \phi_o \phi_s (\rho_o - \rho_s)^2 + \phi_w \phi_s (\rho_w - \rho_s)^2]$$  \hspace{1cm} (5)
with $\phi_o$, $\phi_w$ and $\phi_s$ the volume fractions of oil, water and NPs. $\rho_o$, $\rho_w$ and $\rho_s$ are the scattering length densities of oil, water and NPs. If only the extrapolated low angle Porod regime is used to compute $Q$, then we obtain:

$$Q_P = 2\pi^2 \phi_o \phi_w (\rho_o - \rho_w)^2$$  \hfill (6)

Making the difference between $Q_{tot}$ and $Q_P$, we obtain:

$$Q_{tot} - Q_P = 2\pi^2 \phi_s [\phi_o (\rho_o - \rho_s)^2 + \phi_w (\rho_w - \rho_s)^2]$$  \hfill (7)

knowing the volume fraction of oil from the measured transmission, it is possible to obtain the volume fraction of NPs. As the size of the NPs is precisely known and because no free NPs are present in the sample, it is possible to deduce from the value of the volume fraction the surface coverage of the oil droplets.


