Response to questions on IFPRI Project Brief: "Wetting of heterogeneous particles"

1) What range of particle properties can you synthesize and study?

As described in the proposal, we can produce aggregates of primary particles, aka supraparticles, in various size ranges, from sub-100 micron to millimeter scale, using an evaporation-driven approach. The wettability of the primary particles and the porosity of the supraparticles define the wettability of the aggregates. As described in the proposal, we can both evaporate oil droplets containing hydrophobic primary particles into an aqueous phase or aqueous droplets containing hydrophilic primary particles into an oil phase. The process thus allows us to use primary particles with a broad spectrum of wettability, from very hydrophilic to very hydrophobic and investigate the wetting of their aggregates.

In terms of initial materials for the primary particles, we propose to use commercial polystyrene particles, e.g. sulfonate-polystyrene (charged, stable in aqueous conditions, hydrophobic), and silica particles that we synthesize in house using a Stöber process and of which we can change the wettability by controlled grafting of self-assembled monolayers for instance silanization with dichlorodimethylsilane [1]. In this case, we can go from very hydrophilic for the case of a native silica surface to very hydrophobic (contact angles up to 150^{o} [1]).

The strength of the proposed evaporation method is that it can be essentially extended to any kind of primary particles, so it would be possible to directly use primary particles of industrial relevance and mix/combine together different types of primary particles, provided that they can be encapsulated in the initial droplets.

2) How will you characterize your particles?

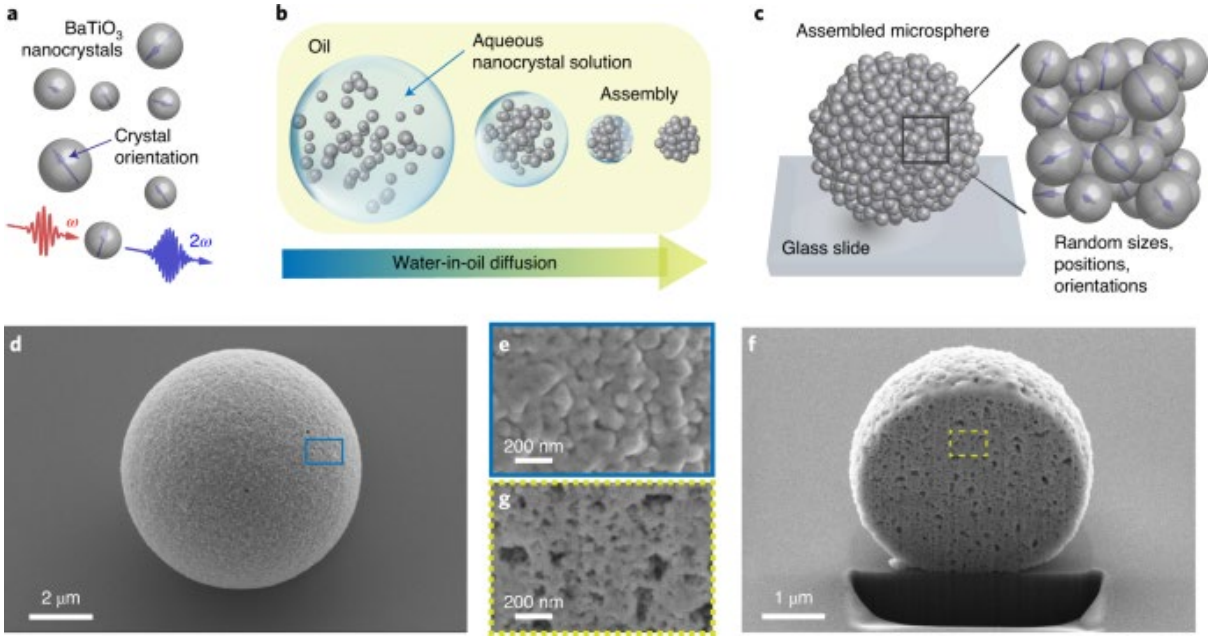
As described in WP1, the proposed synthesis protocols employ the assembly of primary nanoparticles/microparticles into supraparticle aggregates.

The following properties of the primary particles will be characterized:

- Size/size distribution by dynamic light scattering
- Zeta potential/surface charge by electrophoretic mobility measurements (Malvern Zetasizer)
- Single particle wettability/contact angle by gel trapping technique [2] and, if required, by freeze-fracture shadow-casting cryo-electron microscopy (FreSCa cryo-SEM), a method developed in my group that affords the highest resolution to measure single-particle contact angles down to the nanoscale [3].

The following properties of the supraparticles will be characterized before carrying out the kinetic wetting measurements described in WP2:

- Size/size distribution by optical microscopy and scanning electron microscopy (SEM)
- Surface microstructure by SEM
- Internal structure/porosity and effect of sintering by focused ion beam (FIB)-SEM. See the image below for an example of the characterization on barium titanate ($BaTiO_3$) suprapraticles produced following the same process of droplet evaporation as planned in the proposal [4].
- If necessary, the mechanical properties of the supraparticles can be characterized by indentation measurements using the same force sensor employed to characterize wetting. We have already applied this procedure to microcapsules prepared following a similar droplet-based evaporation process [5].



a, Schematic of the $BaTiO_3$ nanocrystals used in the assembly procedure. Their SHG efficiency depends on the size and orientation of the crystal, indicated by the arrows. **b**, Schematic of the emulsion-templated assembly procedure. **c**, Schematic of an assembled microsphere highlighting the randomness in the sizes, positions and orientations of the nanocrystals. **d**, SEM image of a $BaTiO_3$ microsphere assembled on a silicon substrate for better image quality. **e**, Close-up of the surface of the microsphere highlighting the disordered arrangement of the crystalline nanodomains. **f**, SEM image of the cross-section of a $BaTiO_3$ microsphere obtained by focused ion beam (FIB) milling. **g**, Close-up of the disordered, nanoporous inner structure of the microsphere. Figure taken from [4]

The evaporation process and corresponding supraparticle formation can be easily monitored under an optical microscope.

The description of the kinetics of wetting, imbibition and transfer to the aqueous phase are described in WP2 using our combined force sensor/digital holographic microscopy setup. All necessary instrumentation is available in my laboratories or in shared facilities at ETH Zurich.

3) There's also interest in understanding wetting of multicomponent particle assemblies. This isn't explicitly mentioned in the brief, but it's implied in the term "complex surface chemistry". This is relevant in reconstitution of formulated powders and ties this project neatly to the "fisheye" project we are also considering. We understand that this is a significant complication, but it would be helpful to address this in your proposal.

As mentioned in response to point 1) and as already described in the proposal, the proposed methodology is versatile enough to enable mixing different types of primary particles, with different wettability or of different materials. In this case, there is no particular foreseen complication connected to the realization of multicomponent particle assemblies that may approach formulated powders.

In particular, the main research hypothesis is that precisely by having multicomponent assemblies with a sufficient fraction of hydrophilic primary particles one can greatly promote water imbibition and hence transfer to the aqueous phase. This would be an important result of practical relevance, because it would imply that the overall wetting behavior of a formulated powder could be controlled by a small amount of hydrophilic additives.

REFERENCES

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