One-step Pickering emulsions: interplay between surface chemistry and emulsification procedure

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Pickering emulsions represent an attractive alternative to conventional surfactant-stabilized emulsions, as they form highly stable disperse systems without the environmental and health concerns associated with surfactants [1]. Still, optimizing their formulation and scaling up the emulsification process require careful tuning of numerous parameters: nature of the oil phase, phase volume ratio, pH of the aqueous phase, emulsification technique, and nature and surface modification of emulsifier particles. This complexity is also a valuable asset to tailor the physicochemical properties of the resulting system. In particular, the wide range of emulsifier particles, such as oxide semiconductors [2], carbonaceous particles [3] and naturally-derived nanoparticles [4], opens the door to the application of Pickering emulsions in various fields (such as medicine, cosmetics, food formulation, sensing) owing to the diverse chemistry of the different particles. Moreover, the responsiveness of selected particle emulsifiers to stimuli (i.e. change of pH or light irradiation) can be exploited to trigger the inversion or destabilization of the emulsion, leading to the release of active ingredients previously loaded in the dispersed phase [5].

Our research group previously focused on the development of ZnO-stabilized Pickering emulsions with edible oil, obtained by *in situ* functionalization [2]: these systems displayed excellent stability over time and against temperature variations, mechanical stress and increased ionic strength, while also proving suitable for the triggered release of active ingredients using stimuli such as UV lamp irradiation, acids addition or CO_2 bubbling[5]. Here we report on extending this one-step emulsion preparation procedure to other emulsifier materials and on the scaling up of the process. A systematic investigation was performed on the quantity and type of powder (TiO_2, Al_2O_3 and carbonaceous materials), phase volume ratio (from 1:9 to 1:9 oil:water ratio), emulsification technique (sonication, rotor stator homogenization), and final pH (from 5 to 9). Emulsions were characterized by their droplet size, internal phase volume, emulsion stability index and encapsulation efficiency. Due to the high number of variables involved, a chemometric tool, Design of Experiment, was employed to ensure a time-efficient tuning of the emulsification conditions. The type of adopted emulsification strategy enabled to tune the droplet size from few micrometers in diameters (sonication) to tens of micrometers (rotor stator), leading in any case to emulsions stable for weeks. Compared to ultrasound-based emulsification, rotor stator enabled the straightforward tuning of the emulsion type from O/W to W/O emulsions, while the latter could not be directly prepared via sonication due to the high viscosity of the oil phase. We also noted that alkaline pH values improved O/W emulsion stability, possibly as a results of the interplay between the oxide surface charge and adsorption of fatty acid moieties. The role of pH modification and of light irradiation on emulsion stability were investigated to achieve stimuli-responsive disperse systems. The emulsion inversion mechanism was investigated through an in-depth characterization of the emulsifier materials, before and after their removal from the emulsion, focusing on structural, morphological, and surface properties.

References

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