One-step, ultrastable Pickering emulsions stabilized by ZnO: tuning emulsion stability by *in situ* functionalization

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Abstract:

Hypothesis: Oxide-stabilized emulsions generally require a surface functionalization step to tune the oxide wettability, often involving hazardous hydrophobizing agents. Here, we propose the *in situ* functionalization of ZnO in vegetable oils without the addition of any modifier, resulting in the one-step formation of ultra-stable Pickering emulsions.

Experiments: The role of ZnO surface features was studied by modifying the particles' wettability through surface functionalization and by comparing different oil phases. The emulsion stability was assessed through aging tests, multiple hot-and-cold cycles, centrifugation, and addition of multiple electrolytes.

Findings: While the wetting features of the functionalized oxide play a crucial role when the oil phase is methyl octanoate, emulsions based on vegetable oils form also using hydrophilic ZnO. During the emulsification, an *in situ* functionalization of bare ZnO particles takes place due to the fatty acids present in vegetable oil. These *in situ*-generated systems lead to stable emulsions showing <2 μm-diameter oil droplets. The resulting emulsions display excellent stability over time (over seven months) and against temperature variations, mechanical stress and increased ionic strength. Finally, we demonstrate that this approach can be extended to a variety of vegetable oils and oxides with different morphologies.

Keywords:

Pickering emulsion, one step emulsification, surfactant free, zinc oxide, ultra stable emulsion

1. Introduction

Over the last decades, Pickering emulsions have attracted increasing attention due to their advantages compared to conventional surfactant-stabilized emulsions [1–4]. In particular, Pickering emulsions are characterized by long-term stability to coalescence, good mechanical properties, low toxicity and recyclable stabilizers [5,6]. In this context, Pickering emulsions represent promising platforms for applications in numerous fields, such as medicine, pharmaceutics, cosmetics, food industry, and cultural heritage protection [5,7–10]. The most commonly adopted particles for the stabilization of Pickering emulsions include inorganic nanoparticles (such as silica [11–13], iron oxide [14,15], titanium dioxide [16–18], alumina [19] and clay [20]), polymer nanoparticles (*e.g.*, polymethyl methacrylate [21] and polystyrene [22]), and naturally-derived nanoparticles [8] like proteins [23], cellulose [24] and starch [16,25,26].

Zinc oxide, a known food supplement and cosmetic additive, could represent a promising, yet scantly investigated, emulsifier for numerous applications. In the last year, few works reported ZnO-stabilized Pickering emulsions for different purposes. Tian *et al.* [27] adopted ZnO Pickering emulsions with acrylated epoxidised soybean oil to create an antimicrobial polymer foam by templated polymerization. Bordes *et al.* [28] prepared oil-in-water Pickering emulsions with ZnO adopting alkylbenzoate as oil phase for the preparation of sunscreens. Wu *et al.* [29] adopted a ZnO-stabilized Pickering emulsion to functionalize cellulose nanofibrils films. None of these works, however, investigated the role of the surface properties of ZnO in the stabilization mechanism of the Pickering emulsions.

It is widely accepted that, for a more efficient interfacial packing of the particles, which is key for Pickering emulsions' formation [26], the solid particles should have a certain degree of amphiphilicity (*i.e.*, the ability to be partially wetted by both the water and oil phases), thus exhibiting a contact angle at the water-oil interface around 90° [16]. However, most oxides are intrinsically hydrophilic and they hardly localize at the oil-water interface [30]. Therefore, inorganic particles are usually pre-treated with amphiphilic molecules, such as alkylsilanes [13,17,18], in order to balance surface wettability and improve the emulsifying performance [16,26]. However, the particles' surface functionalization usually brings increased processing cost and time and holds environmental concerns. As an alternative to *ex situ* functionalization, the *in situ* surface activation of oxide particles by trace amounts of amphiphilic modifiers, such as anionic and cationic surfactants, has been proposed [31,32]. In this context, the preparation of highly stable and surfactant-free Pickering emulsions stabilized by pristine oxides without the addition of any modifiers still represents a challenge.

In this work, we present an ultra-stable and environmentally-friendly Pickering emulsion system prepared using food-grade vegetable oil and stabilized by the sole addition of pristine ZnO particles. The mechanism of emulsion stabilization was studied by changing the oil phase and by comparing ZnO particles with different degrees of alkylsilane functionalization. The droplet size distribution was investigated as a function of time and under thermal, mechanical and chemical stress. The versatility of this approach was also proved changing the type of vegetable oil, the oxide content and morphology.

2. Experimental section

The adopted reagents were purchased from Merck, unless specified otherwise, and were used without further purification. Edible vegetable oils (peanut, olive and corn oils) from a local retailer were used for emulsion formation. Milli-Q water was adopted for the preparation of all emulsions and solutions.

2.1 ZnO synthesis

Different types of zinc oxide powder were used as Pickering stabilizer: both commercial powders (Sigma Aldrich ZnO nanopowders and Sigma Aldrich ZnO ReagentPlus powder, named respectively *commercial-1* and *commercial-2* in the following) and lab-synthesized particles were adopted. The latter were either synthesized by an ultrasound-assisted procedure (named *ZnO sono-synthesis*) and by precipitation method (labeled as *ZnO precipitation*), according to procedures previously reported by some of us [33]. Moreover, a commercial TiO_2 powder (Kronos 1077) was also tested as stabilizer.

Briefly, in the sonochemical synthesis, a $ZnCl_2$ solution (100 mL, 0.2 M) and a KOH solution (100 mL, 0.5 M) were mixed in a 250 mL beaker. The mixture was irradiated by ultrasound by a Thermo- Fischer Q700 sonicator operating at 20 kHz and equipped with a 13 mm-titanium alloy tip. Sonication was performed in continuous mode and adiabatic conditions at 50% amplitude for 30 min. The resulting precipitate was separated by centrifugation and washed several times with water until neutral pH. The solid was dried overnight and calcined at 400°C under oxygen flux (9 NL/h) with a 4 h heating ramp and 1 h at stationary temperature.

In the precipitation method, a $Zn(NO_3)_2 \cdot 6H_2O$ solution (100 mL, 0.2 M) and a KOH solution (100 mL, 0.5 M) were mixed by mechanical stirring (250 rpm) at 65°C for 30 min. The resulting precipitate was collected by centrifugation, washed, dried and calcined using the same procedure adopted in the sonochemical synthesis.

The physicochemical characteristics of the used powders are summarized in Table S1.

2.2 ZnO functionalization

The wetting properties of the synthesized ZnO powder were tuned by surface functionalization with triethoxy(octyl)silane, according to a previously reported procedure [34]. In a 100 mL round bottom flask, isopropanol (40 mL) and a suitable amount of triethoxy(octyl)silane were mixed together: different contents of alkylsilane were investigated (0, 1.6, 2.0, 2.5 or 5.0% in weight with respect to the ZnO amount). Then, 400 mg of ZnO was added to the solution and rapidly dispersed: the flask was stirred at 200 rpm and heated to 50°C over the course of 30 minutes. The solvent was then removed by rotary evaporator (operating at 80 mbar) and the dry powder was collected and ground in a mortar.

2.3 Pickering emulsion preparation

Pickering emulsion preparation was performed in 50 mL flat-bottomed glass vials with 25 mm diameter. First, 30 mg of ZnO powder (either pristine or functionalized with triethoxy(octyl)silane) was dispersed in 8 mL of water by sonication using a Thermo- Fischer Q700 sonicator operating at 20 kHz and equipped with a 3 mm-titanium alloy microtip. Sonication was performed in pulsed mode (3 s on and 3 s off) at 50% amplitude for 45 s. Afterwards, 2 mL of oil phase (either methyl octanoate, peanut oil, corn oil or olive oil) was added to the ZnO dispersion and the mixture, immersed in a water bath at ambient temperature, was sonicated for overall 90 s by immersing the microtip for 15 mm. The power released to the system by the sonicator was determined by calorimetric method [35] to be 8.88 W. The resulting emulsion was stored in the dark in a closed vial.

For the sake of comparison, a surfactant-stabilized emulsion was prepared as reference: 510 mg (5% in weight) of TWEEN 20 (Polysorbate 20, Sigma Aldrich) was dissolved in 8 mL of water. Then, 2 mL of oil was added to the surfactant solution and emulsified by sonication with the same procedure adopted for Pickering emulsion preparation.

2.3 Characterization methods

The wetting features of the pristine and functionalized oxide powders were studied by static contact angle measurements using a Krüss Easydrop instrument. MilliQ water and diiodomethane were adopted as polar and apolar probe liquids, respectively, depositing 5 droplets of 8 μL, on oxide films prepared by drop casting.

The specific surface area of ZnO powders was determined with the Brunauer-Emmett-Teller (BET) method by N_2 adsorption isotherms in subcritical conditions, measured on a Beckman-Coulter SA3100 instrument.

ZnO particle size and morphology were investigated by Scanning Electron Microscopy (SEM) using a FEI TECNAI G2 F20 equipped with a field emission gun source, working at 200 kV.

Fourier-transform infrared (FTIR) spectra were acquired on a PerkinElmer Spectrum 100 spectrophotometer operating in attenuated total reflection (ATR) mode equipped with a single-bounce diamond crystal with a 45° incidence angle. Spectra were recorded between 4000 and 400 cm^{-1}.

Oil-in-water (O/W) and water-in-oil (W/O) emulsions were recognized by staining the water phase with Rhodamine B dye.

Confocal microscopy images were collected by a Nikon A1 confocal laser scanning microscope (CLSM), working in oil immersion, with numerical aperture 1.4 and equipped with a 60x objective. Before analysis, emulsions were stained with Rhodamine B. Images were acquired with an excitation wavelength of 570 nm and emission wavelength at 620 nm. The droplet size distribution was obtained by processing the images of at least 300 individual droplets by ImageJ software.

2.4 Stability tests

The emulsion stability was evaluated via different tests. Ageing tests were performed storing the emulsion at room temperature in the dark for up to seven months. The influence of temperature variations was evaluated via hot and cold cycles alternating 24 h at 60 °C in a ventilated oven to 24 h in a fridge at 4 °C and repeating the cycle for three times. The resistance to mechanical stress was tested by centrifugation for 20 min at 9300 g. The emulsion stability in the presence of electrolytes (Table S2) was evaluated by preparing a Pickering emulsion with a simulated tap water solution, prepared according to a standard protocol [36,37], as water phase.

3. Results and Discussion

The role of the wetting features of ZnO powders on the emulsion stability was investigated by functionalizing sono-synthesized ZnO with different amounts of trietoxy(octyl)silane (0-5%w). Figure 1 reports the water contact angles and FTIR spectra of bare and functionalized ZnO.
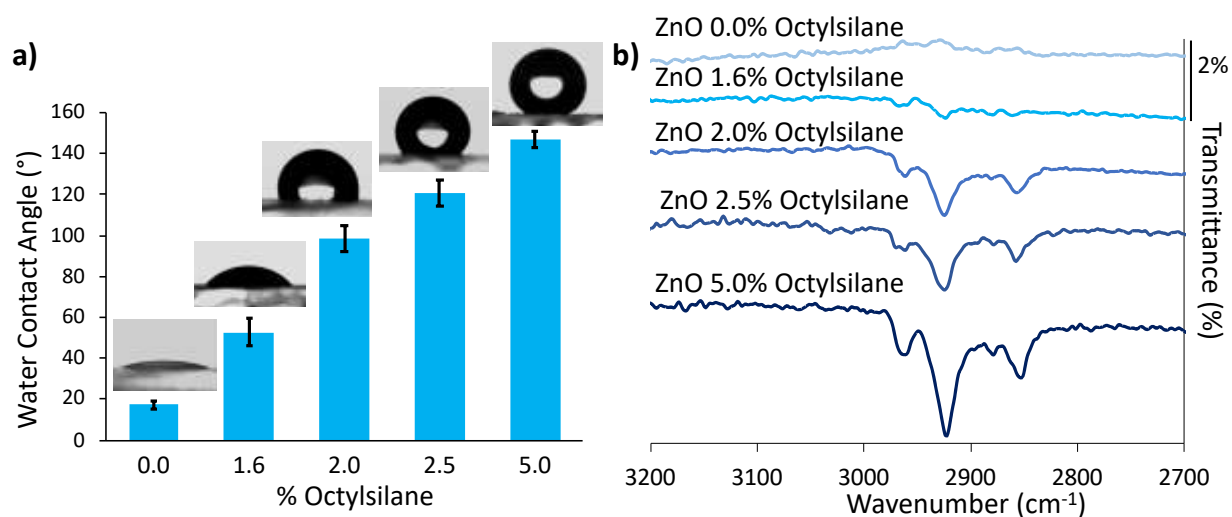
Figure 1 – (a) Static contact angles of water on deposited powders and (b) FTIR spectra of ZnO, both pristine and functionalized with different amounts of octylsilane.

Figure 1b reports the FTIR spectra of ZnO samples functionalized with different amounts of octylsilane [38]. The IR bands at 2800-2900 cm^{-1}, attributed to the stretching vibrations of CH$_x$ groups [39], confirm the successful functionalization of the oxide surface, giving rise to increasing amounts of alkyl chains as a function of the nominal octylsilane content.

Water contact angle values (Figure 1a) are in good agreement with FTIR findings. While bare ZnO is characterized by high hydrophilicity (water contact angle < 20°) and by a complete CH$_2$I$_2$ spreading (Figure S1), upon functionalization both contact angles increase as a consequence of the lower surface free energy of the functionalized surface exposing octyl residues [39]. Hydrophobic contact angles are observed starting from a functionalization degree of 2.0%.

The functionalized oxides were tested as stabilizers for emulsions with different oil phases. In particular, a pure solvent and a natural oil were compared: a long chain ester (methyl octanoate) and a vegetable oil (peanut oil). With each solvent, Pickering emulsions with either bare or functionalized ZnO powders were prepared (Figure 2). Pickering emulsions prepared with methyl octanoate as oil phase show a clear dependence of emulsion stability on the particle wetting features[40,41]. The bare oxide gave rise to a poorly stable O/W emulsion that rapidly undergo creaming, in agreement with the very high particle affinity for the water phase. By increasing the alkylsilane content on ZnO powders, more stable O/W emulsions were obtained, in accordance with the particles' increasing hydrophobicity that promotes the particle adsorption at the oil-water interface. On the other hand, Pickering emulsions prepared with peanut oil (PO) and ZnO powders with different functionalization degrees are all very similar: the prepared Pickering emulsions are characterized by oil-in-water dispersion, comparable phase volume fraction, and stability of several months.
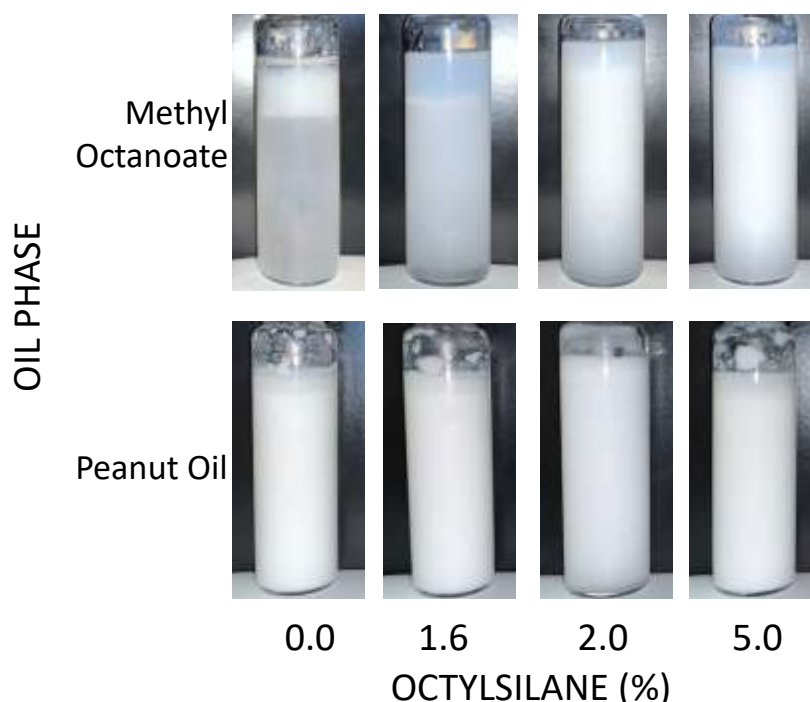
Figure 2 – Fresh Pickering emulsions prepared with either methyl octanoate or peanut oil as oil phase, and ZnO with different functionalization degrees.

The lack of influence of the oxide wetting features on Pickering emulsions prepared with peanut oil, when compared to those prepared with methyl octanoate, could be related to the different chemical composition of the two oil phases. In particular, the presence of free fatty acids in the vegetable oil [42] can give rise to an *in situ* functionalization of the ZnO particles during the emulsification process. Carboxylic acids, such as fatty acids, are known to interact with oxide surfaces via carboxylate–metal bonds, which are however generally unstable in aqueous media [43,44]. Binks and coworkers reported that the addition of carboxylic acids modifiers to toluene and water emulsions stabilized by $CaCO_3$ can lead to multiple phase inversions, especially at increasing alkyl chain length [45]. The same group also reported that fatty acid addition can also lead to switching $CaCO_3$ Pickering emulsions from O/W to W/O [46]. Here, we propose that fatty acids naturally present in the oil phase can act as alkylsilanes at the ZnO surface, increasing the affinity between the oil phase and bare and low-degree functionalized ZnO powders.

To confirm this hypothesis, a Pickering emulsion with bare ZnO powders was prepared using as oil phase methyl octanoate with the addition of lauric acid as a model for fatty acids. The amount of lauric acid (1600 ppm) was selected to mimic the fatty acid content of peanut oil, as determined by acid-base titration. Figure 3a compares the resulting emulsion with two reference emulsions prepared with methyl octanoate as oil phase: a Pickering emulsion stabilized by bare ZnO powder

(without lauric acid), and an ordinary emulsion prepared with only lauric acid as stabilized (without ZnO particles).
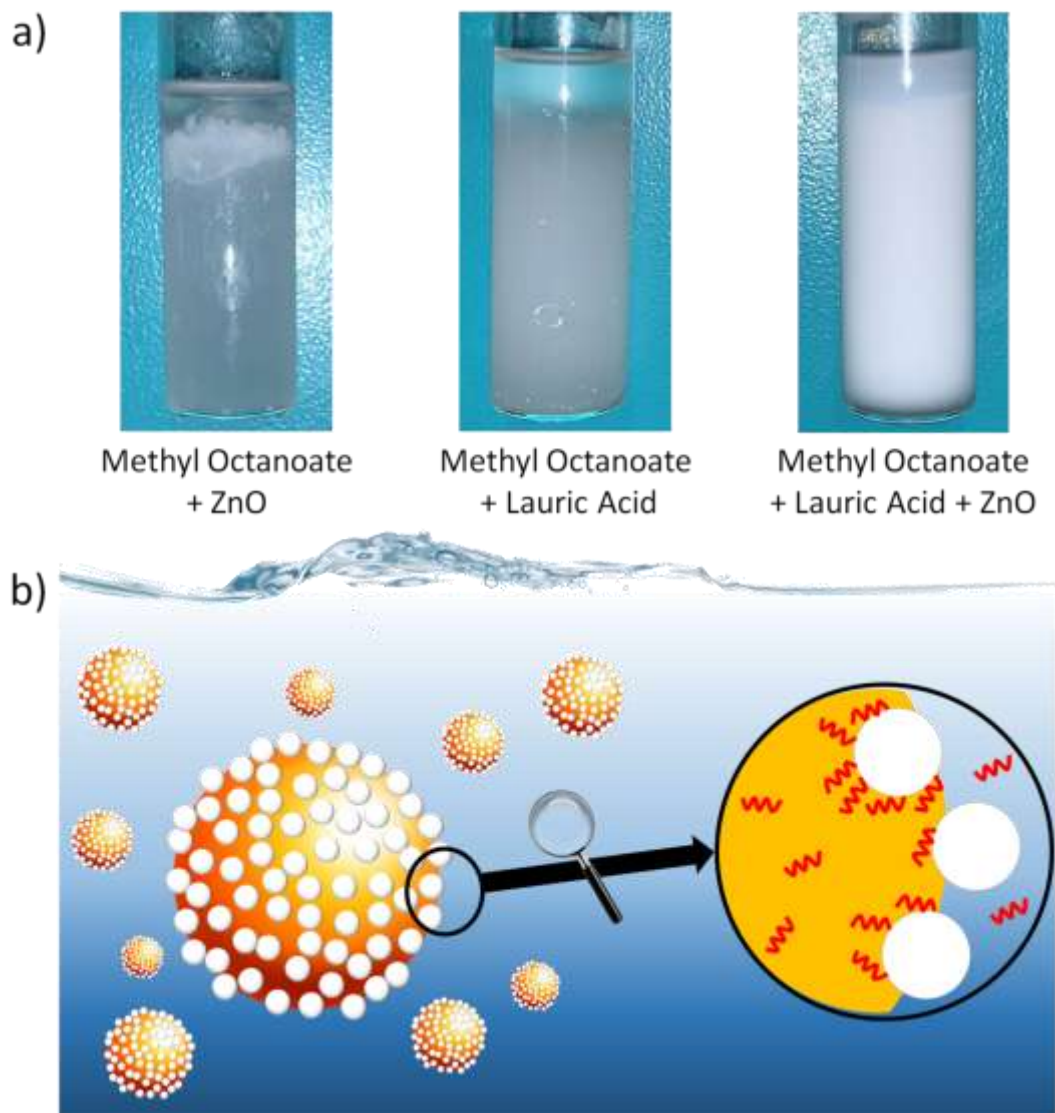

Figure 3 – a) Emulsions prepared with methyl octanoate as oil phase and ZnO bare, lauric acid or both as stabilizers; b) Proposed mechanism of the *in situ* functionalization; yellow spheres represent the oil phase, white ones are ZnO particles and acid residues are represented in red.

Without lauric acid, ZnO addition is not sufficient to result in any stable emulsion. When only lauric acid is adopted as emulsifier, in the absence of bare ZnO powders, a poorly stable O/W emulsion can be obtained. Long chain carboxylic acids have been reported to present a low stabilizing effect due to their low hydrophilic-hydrophobic balance value [47,48]. The addition of lauric acid to the ZnO-oil-water system results in a milky O/W Pickering emulsion with phase volume fraction similar to the O/W emulsions with peanut oil stabilized by ZnO. This supports the

occurrence of an *in situ* functionalization of the ZnO particles by fatty acids present in vegetable oil (Figure 3b), which modify the wetting features of the oxide increasing its affinity for the oil phase. The surface features of ZnO powder retrieved after the emulsification process were investigated by FTIR spectroscopy. Figure 4 reports the FTIR spectrum of ZnO powders after being recovered from an O/W ZnO Pickering emulsion with peanut oil by prolonged centrifugation. FTIR spectra of peanut oil and bare ZnO are also reported as reference.
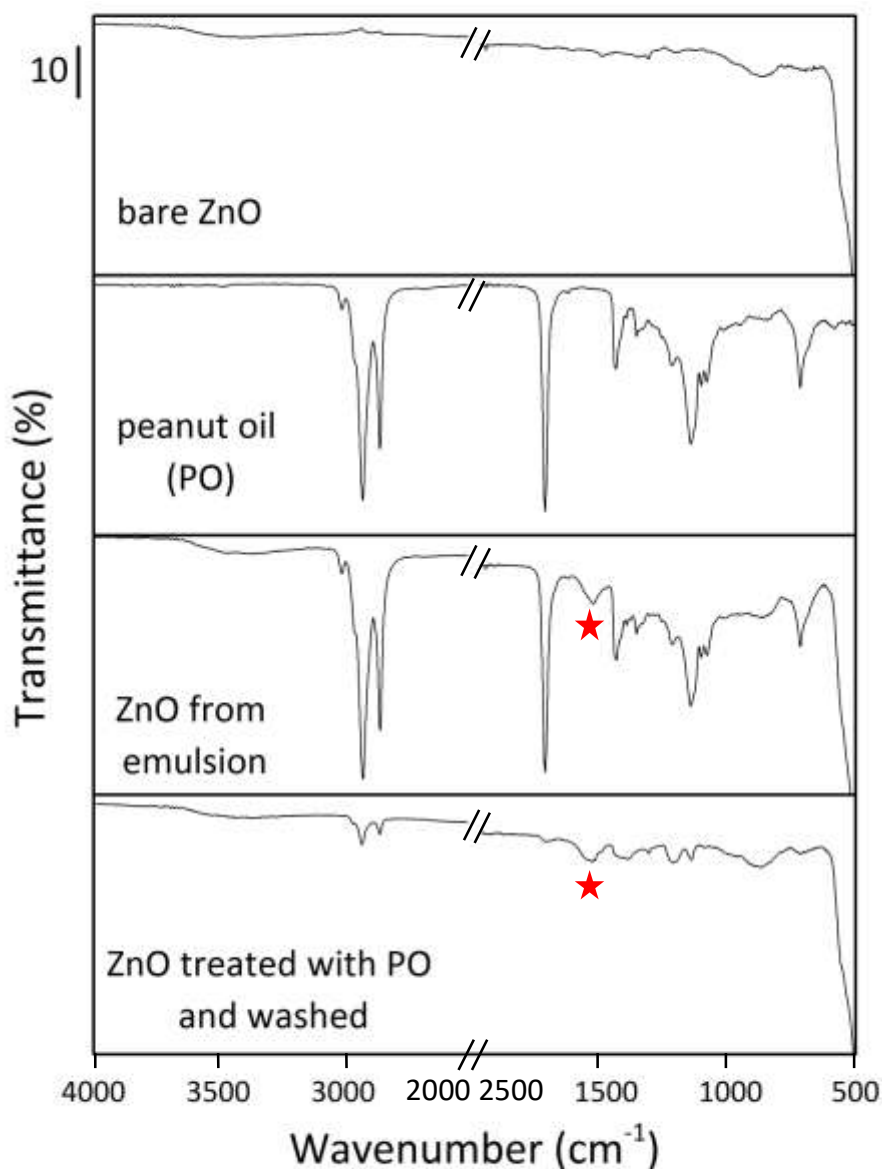

Figure 4 – FTIR spectra of bare ZnO, peanut oil, ZnO recovered from a Pickering emulsion with peanut oil, and ZnO powder after dispersion in peanut oil and washing with toluene and water. The red star highlights a band attributed to carboxylate asymmetric stretch.

Besides the bands characteristic of peanut oil and bare ZnO, the spectrum of ZnO recovered from the emulsion shows an additional feature at *ca.* 1550 cm^{-1} (highlighted with a red star in Figure 4).

This band can be attributed to the carboxylate asymmetric stretch $[\nu_{as}(O–C–O)]$ at the ZnO surface [49,50], which is shifted with respect to the asymmetric stretch $[\nu_{as}(C=O)]$ band of the free acid (1744 cm^{-1}). This attribution is also supported by FTIR spectra of ZnO powder treated with lauric acid (Figure S2), which shows the disappearance of the free carboxyl band at 1695 cm^{-1} and the presence of an additional band around 1540 cm^{-1} not appreciable in the lauric acid spectrum. Figure 4 also reports the FTIR spectrum of ZnO powder after being dispersed in peanut oil and washed with toluene and water. The peak related to the carboxylate-ZnO bond is still present after washing and remains more intense compared to other peanut oil-related peaks, supporting a strong interaction between the oxide surface and fatty acids.

The droplet size distributions of Pickering emulsions with peanut oil were investigated by confocal microscopy after dye-staining with a hydrophilic dye (Rhodamine B). Figure 5 reports confocal microscopy images and the relative droplet size distributions of emulsions stabilized by ZnO prepared with different degrees of surface functionalization. A surfactant-stabilized emulsion is also reported for the sake of comparison. While the surfactant-stabilized emulsion showed the classical red background and black droplets characteristic of O/W emulsions, all Pickering emulsions show a maximum concentration of dye molecules around the droplets' profiles, which can be explained considering a dye adsorption at the oxide particle surfaces. This is confirmed by reflection images (Figure S3a), showing that the oxide particles mainly localize at the surface of oil droplets (as clearly appreciable for larger droplets). Each emulsion was observed after one day from the emulsification (fresh) and after one week (aged). All the ZnO Pickering emulsions present very small, monodisperse droplets with an average size of 1.0 μm, irrespectively of the amount of functionalizing agent. Moreover, the size distribution of the Pickering emulsions shows no significant differences with the passing of time. It is noteworthy that the surfactant-stabilized reference emulsion, while displaying a similar droplet size distribution immediately after emulsification, shows a much broader droplet size distribution after 1 week of ageing, supporting a lower stability with respect to Pickering emulsions.
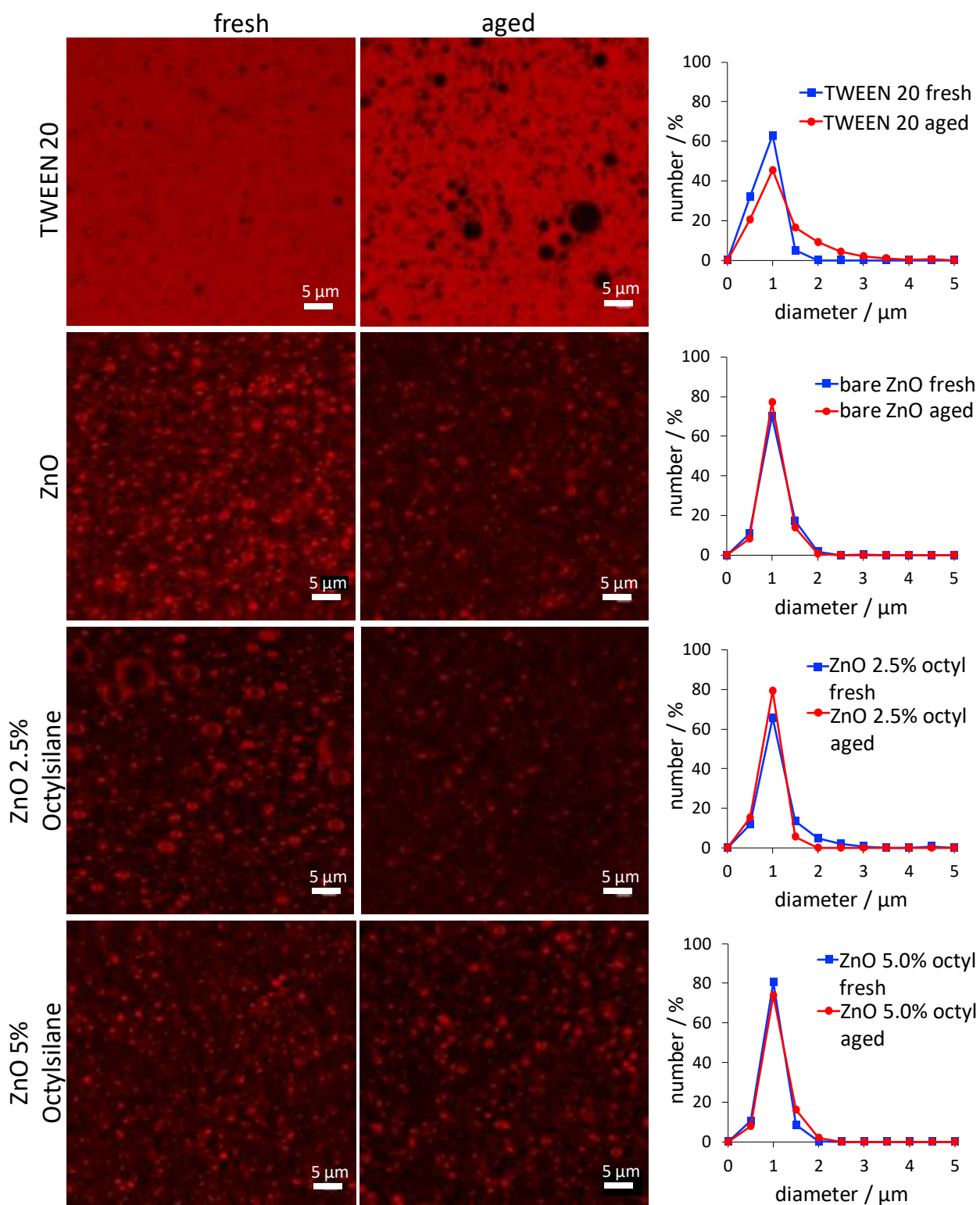
Figure 5 – Confocal microscopy images of dye-stained emulsions prepared with different emulsifiers after one day (fresh) and after one week (aged). On the right, the relative droplet size distributions.

The stability of Pickering emulsion prepared with peanut oil was tested in more demanding conditions. For the sake of brevity, only tests on emulsions stabilized with bare ZnO powder are

here reported. Besides visual inspection to evaluation possible creaming effects, the droplet size distribution was measured to evaluate the emulsion stability over longer ageing time (seven months), against temperature variations, mechanical stress and increased ionic strength, as detailed in Section 2.4. Figure 6 reports droplet size distributions, determined from confocal microscopy images, of ZnO Pickering emulsions before and after the stability tests. Results support an ultra-stability of the presently investigated Pickering emulsions. No additional loss of oil phase and fully comparable droplet size distributions were observed after prolonged ageing, thermal stress and in tests with increased ionic strength. Mechanical stress by prolonged centrifugation leads to the sedimentation of a fraction of powder at the bottom of the test tube and to minor creaming effects, while the O/W emulsion still remains clearly appreciable; the average droplet size decreases possibly as a result of the lower ZnO amount and loss of larger droplets.

The enhanced stability of ZnO-stabilized emulsions can be related to the strong steric hindrance caused by the functionalized ZnO particles at the surface, which prevents coalescence of droplets, as supported by the higher stability of the present Pickering emulsions compared to surfactant-stabilized analogues. The emulsion stability can also be favored by the high viscosity of the oil phase (Table S3), and by the small droplet size promoted by sonication.
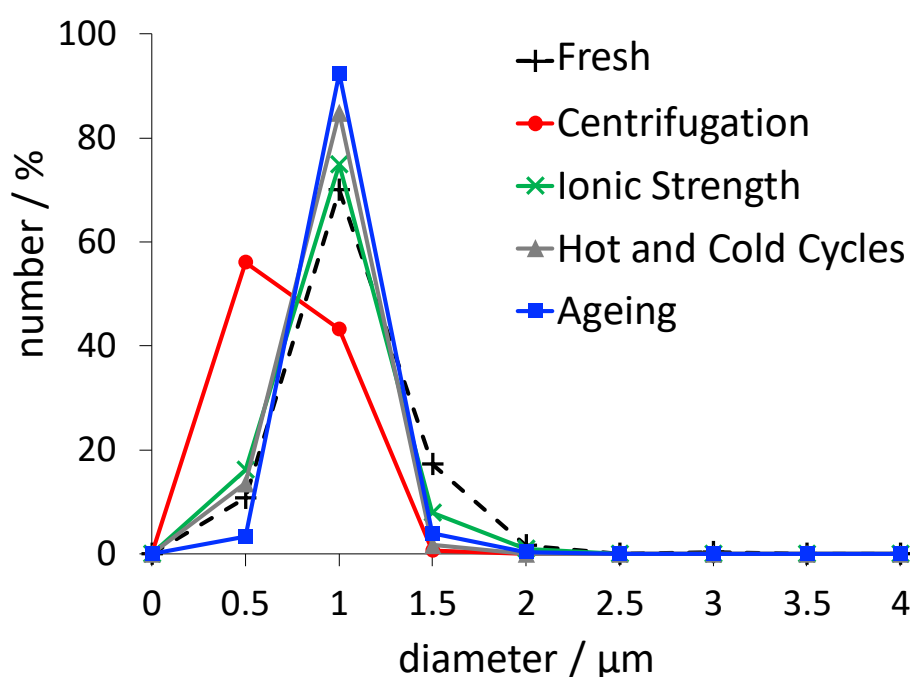
Figure 6 – Droplet size distributions of dye-stained O/W Pickering emulsions prepared with bare ZnO and peanut oil after stability tests: ageing in environmental conditions for 7 months, hot and cold cycles, centrifugation and enhanced ionic strength.

The applicability of the *in situ* functionalization approach is not limited to the present system. Vegetable oils (corn and olive oils) with different composition (Table S3) were also tested.
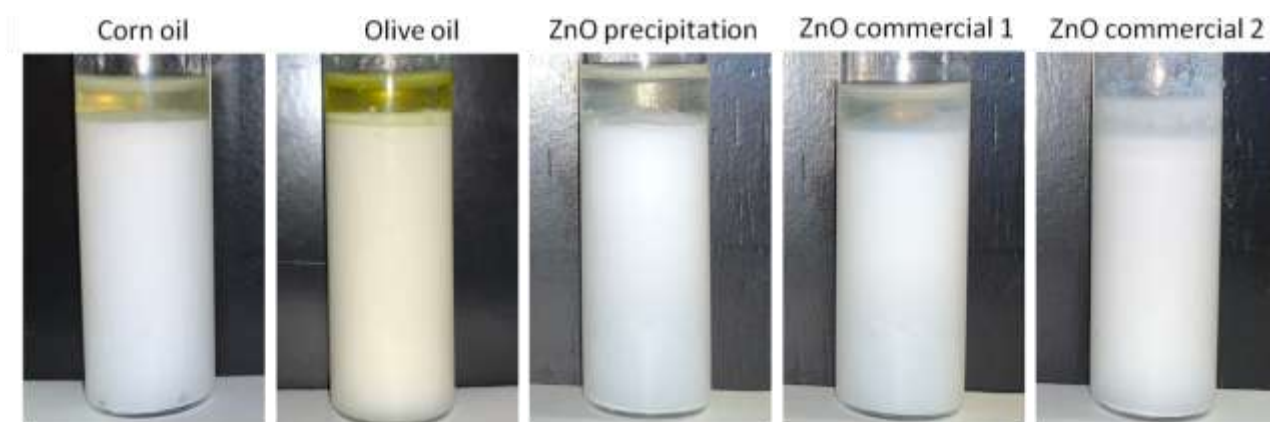

Figure 7 – Pickering emulsions prepared with different vegetable oils and different oxide powders.

Oil-in-water Pickering emulsions with comparable phase volume and stability were prepared using the different oils (Figure 7), showing the possibility to extend the present approach to fatty acids of different chemical nature and to oil phases with diverse viscosity.

Furthermore, several ZnO contents as well as powders with comparable phase composition but different morphologies were tested as stabilizers, while keeping all other parameters invariant. The ZnO content was varied in the range 0.1-1.0% (corresponding to a total oxide available surface area from 0.19 to 1.9 m^2) giving rise, in all cases, to stable and homogeneous O/W Pickering emulsions, despite the change in fatty acid molecules available per particle. Besides ZnO prepared by sonochemical synthesis, a sample prepared by precipitation and two types of commercial ZnO powders were tested. The main physicochemical properties of the bare oxides are listed in Table S1 and representative SEM images are reported in Figure 8. Samples strongly differ for their morphological structure and available surface area, ranging from 19 to 5 m^2g^{-1}. Moreover, the average particle size and aspect ratio varies from powder to powder: sonochemical synthesis gave rise to round primary particles smaller than 100 nm, whereas larger particles and higher aspect ratios are observed for commercial oxides, which show nanorod [33] and platelet-like morphologies (commercial-1 and commercial-2, respectively). Precipitation synthesis gave rise to micrometric flower-like particles, which, after sonication treatment, generate nano-whisker morphologies. As shown by Figure 7 and Figure S4, all types of ZnO powders give rise to stable emulsions with comparable phase volume fraction and average droplet size, confirming the robustness of the present approach. Oxide samples characterized by larger particles show a lower stability to hot and cold cycles, as appreciable from droplet size distribution of thermally stressed emulsions. The

present results support a better stabilizing ability of submicrometric size and of elongated morphologies of emulsifier particles for Pickering emulsions, in agreement with previous reports [51]. Finally, preliminary tests were carried out to extend the present approach to other oxides: replacing ZnO with a TiO$_2$ powder with specific surface area and particle size similar to those of the commercial ZnO (Table S1), resulted in stable emulsions (Figure S5).
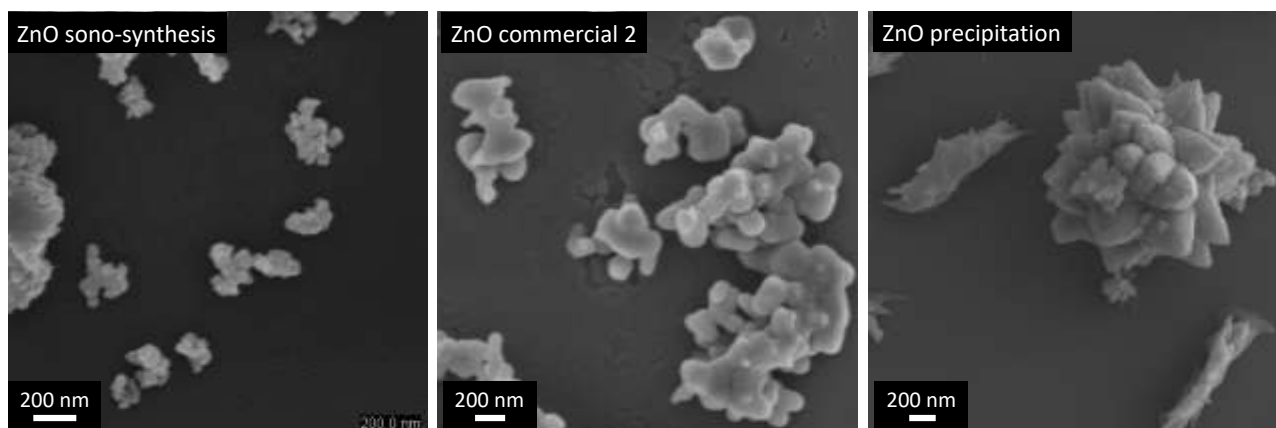
Figure 8 – SEM images of different types of ZnO powders after sonication treatment.

4. Conclusions

Despite numerous applications of ZnO that stem from its antimicrobial, semiconducting, photoactive and UV-shielding properties [52,53], its role as stabilizer in Pickering emulsion has been scarcely investigated. Here, Pickering emulsions were prepared using an edible oil phase by a one-step method requiring the sole addition of hydrophilic ZnO powder as emulsifier. By comparing the behavior of ZnO powder with tailored wetting features in pure solvent and vegetable oil, an *in situ* functionalization of the ZnO particles could be proposed. Fatty acids in vegetable oil create strong interactions with the hydrophilic oxide surface, thus promoting the particle affinity for the oil phase and, in turn, improving their emulsion stabilizing properties. The spontaneously occurring surface functionalization of ZnO particles in vegetable oil could be mimicked by the adsorption of long-chain carboxylic acids purposely added to a pure solvent. While this second avenue, *i.e.* the addition of carboxyl acid modifiers, has been previously reported [45,46,48,54], the use of impurities already present in natural vegetable oils for the stabilization of oil-in-water emulsions is here presented for the first time to the best of the authors' knowledge.

The robustness of the present emulsification approach was demonstrated using vegetable oils with different composition and physicochemical features, and by changing the ZnO amount and morphological features. No destabilization or switching of the emulsion was observed even by varying the available oxide surface area of one order of magnitude. Emulsions produced by the addition of carboxylic acid modifiers to apolar solvents (toluene, hexane) have been instead

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reported to be highly sensitive to the modifier concentration relative to the oxide surface area, leading to destabilization or switching when bilayer or hemimicelle adsorption was achieved instead of monolayer adsorption [45,48].

Besides the simplicity of the approach, which requires no additional reagents with ensuing costs and time involved due to pre-dissolution/mixing steps [54], the prepared Pickering emulsions displayed excellent stability. A long-term stability of emulsions stabilized by SiO_2 particles and carboxylic acid modifiers has been previously reported (up to 4 months for W/O emulsions in environmental conditions[48]) and attributed to a combination of the SiO_2 particles' electrostatic charge and steric hindrance. Here, we demonstrate a far higher stability both in terms of ageing in environmental conditions (more than 7 months) and against perturbing stimuli, such as temperature, mechanical stress and increased ionic strength. The latter suggests a key role of steric hindrance in the stabilization mechanism, as electrostatic repulsion should be negatively impacted by the electrolyte content.

The here demonstrated spontaneous surface functionalization of ZnO using natural, edible oils represents a cost-effective and environmentally-friendly approach to emulsion stabilization, which could be applied in a broad range of fields, from body-care applications to biofuels.

Acknowledgements

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Graphical Abstract: