Preparation of Multicore Colloidosomes:
Nanoparticle-Assembled Capsules with Adjustable Size, Internal Structure, and Functionalities for Oil Encapsulation

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Abstract

Colloidosomes, also known as Pickering emulsion capsules, have attracted attention for encapsulation of hydrophilic and hydrophobic actives. However, current preparation methods are limited to single core structures and require the use of modified/engineered nanoparticles for forming the shell. Here, we report a fast, simple, and versatile method for producing multi-oil core silica colloidosomes via salt-driven assembly of purely hydrophilic commercial nanoparticles.
dispersed within an Oil-In-Water-In-Oil (O/W/O) double emulsion template. The internal structure and overall diameter of the capsules can be adjusted by altering the primary and secondary emulsification conditions. With this approach, 7 to 35 µm diameter multicore colloidosomes containing 0.9 to 4.2 µm large oil cores were produced. The capsules can easily be functionalized depending on the type of nanoparticles used in the preparation process. Here, metal oxide nanoparticles, such as Fe₃O₄, TiO₂ and ZnO, were successfully incorporated within the structure, conferring specific functional properties (i.e. magnetism, photocatalysis) to the final microcapsules. These capsules can also be ruptured using ultrasound, enabling easy access to the internal core environments. Therefore, we believe this work offers a promising approach for producing multicore colloidosomes with adjustable structure and functionalities for the encapsulation of hydrophobic actives.

1. Introduction

Microencapsulation has attracted research interest for protecting and delivering active ingredients in food and beverage,¹,² cosmetic and personal care,³,⁴ agrochemical⁵,⁶ and pharmaceutical⁷,⁸ applications. The method consists of the entrainment of a solid, liquid, or gaseous compound, called the active material, within another structure referred to as the shell, to ensure its protection, control its release or improve its taste, odor, or handling.⁹ Multiple encapsulation techniques have been reported using thermal, electrostatic, or chemical methods to produce core/shell capsules.⁹,¹⁰ Among them, colloidosomes appear as a promising system. Such capsules, originally reported by Velev and co-workers¹¹ and named by Dinsmore et al.¹², are composed of a gel or liquid core surrounded by a nanoparticle-assembled shell.¹³,¹⁴ These superstructures offer high control on permeability,¹⁵,¹⁶ functionalities¹⁷,¹⁸ and release mechanisms,¹⁹ depending on the preparation method and choice of shell colloidal particles.
Colloidosomes are conventionally produced via a two-step approach. First, a particle stabilized emulsion, called a Pickering emulsion, is formed via adsorption of colloidal particles at an oil/water interface. Such particles must exhibit an affinity for both the aqueous and organic phases, which often requires adjustment of particle wettability by the adsorption of additives (e.g. surfactants, polymers) or chemical functionalization. Particles are then locked at the interface, producing a robust microcapsule for utilization. Depending on the preparation method, colloidosomes can be used for encapsulation of hydrophilic or hydrophobic actives. Active materials such as yeast, bacteria, enzymes or therapeutic molecules have been successfully encapsulated within water-core colloidosomes. Oil-core colloidosomes were prepared to address the usual volatility or stability concerns inherent with hydrophobic actives (e.g. Flavors, fragrance, antioxidants, vitamins, pesticides, etc.).

Such oil-core systems were produced from a Pickering-emulsion template, with particles locked together in a robust shell through thermal annealing, layer-by-layer polyelectrolyte deposition, ionotrop gelation, cross-linking, interfacial polymerization or growing of an additional inorganic or metallic shell. However, such approaches exhibit certain limitations. Firstly, the need for an intermediate Pickering emulsion step, requires the design/modification of nanoparticles to obtain suitable Pickering emulsifiers, raising the cost and complexity of the method. Secondly, the locking step may be time-consuming and costly due to modification of experimental conditions (e.g. pH, Temperature) or further addition of toxic chemicals to the system (i.e. Cross-linkers, polymers, polyelectrolytes), which may impact the stability of encapsulated actives. Finally, only single core systems have been reported, limiting such structures to single-step release mechanisms. Producing multicore colloidosomes could enable encapsulation of multiple hydrophobic cargoes, enabling a multi-stage release of actives.
Contrary to polymeric multicore microcapsules, which have been reported at multiple times, multicore colloidosomes have seldomly been explored. To the best of the author’s knowledge, such structures have only been reported by Lee and Weitz, with the preparation of non-spherical multi-compartment colloidosomes obtained from assembly of hydrophobic particles within a Water-in-Oil-in-Water (W/O/W) emulsion template \cite{45}. However, this approach was limited to a water-core structure and required the use of a solvent evaporation approach for producing the capsules. This article investigates the production of multifunctional multi-oil core silica colloidosomes at room temperature via salt-driven assembly of commercial nanoparticles in an Oil-in-Water-in-Oil (O/W/O) emulsion template.

2. Results and discussion

The silica nanoparticles used in these experiments are strongly hydrophilic, inhibiting their adsorption at the oil/water interface for formation of Pickering emulsions. However, these particles can easily be destabilized, and aggregate upon addition of sufficient electrolyte. When these particles were dispersed in ultrapure water, the pH increased slightly to values between 9 and 10. In this pH range, the silica nanoparticles readily disperse and bear a strong negative surface potential measured between -40 and -50 mV. Addition of calcium chloride screens the surface charges resulting in nanoparticle agglomeration. This aggregation approach has recently been reported in reverse emulsions for room-temperature production of magnetic silica microparticles (Fe$_3$O$_4$/SiO$_2$)\cite{46} and magnetic photocatalysts (TiO$_2$/Fe$_3$O$_4$/SiO$_2$)\cite{47}. Here, formation of an O/W/O emulsions serves to structurally template the assembly of capsules, with multiple oil cores embedded within their structure.
The major advantage of the present approach for capsule formation is that it circumvents the necessity for creation of a Pickering emulsion. This can be challenging to achieve, as the colloidal particles must have an inherent affinity for the oil-water interface. Such particles are often surface functionalized (ie. Janus particles) or incorporated with additives to facilitate interfacial adsorption (ie. Polymers or charged surfactants), making the system more complex and expensive. The current method allows for formation of capsules by aggregating purely hydrophilic commercial nanoparticles that are dispersed in the aqueous medium surrounding the surfactant stabilized oil droplets. Therefore, the nanoparticles can be used directly, without adjusting their wettability. The complete preparation method is displayed in **Scheme 1**.

**Scheme 1.** General procedure for preparing multi-oil core silica microcapsules using commercial nanoparticles dispersed in an Oil-in-Water-in-Oil emulsion template.

2.1. Preparation of multicore capsules with tunable core size and overall diameter

In our preparation method, the capsule structure is directly controlled by utilization of primary and secondary emulsions, with the former templating the inner cores and the latter templating the overall capsule size. Therefore, size and stability of these emulsions is crucial in the design of our
capsules. Preliminary experiments were carried out to investigate the impact of mixing conditions and surfactant concentration on emulsion preparation (Figures S1 to S4). Results showed that primary (O/W) emulsions prepared with 5 wt% Tween 80 were stable for more than 24 h and the diameter of the dispersed droplets could easily be adjusted between 0.9 and 4.2 µm, depending on the mixing conditions. Double (O/W/O) emulsions, prepared from those primary emulsions, were stable for 30 min, enabling their use as a microcapsule template.

The impact of primary emulsification parameters on the capsule internal structure was first assessed by producing capsules from double emulsions prepared at different primary emulsification conditions (Ultra-Turrax (UT) operating at 5,000, 10,000 or 15,000 RPM), and fixed secondary emulsification conditions (Vortex mixer (V) operating at 2,000 RPM). Microscopy images confirmed the production of spherical capsules with an average overall diameter of approximately 18 µm, regardless of mixing parameters (Figure 1). STEM and optical microscopy images confirmed the presence of multiple cores within the capsules and showed a significant decrease in internal core diameter with increased mixing speeds (3.3 to 0.8 µm). The size of these cores correlates with the diameter of oil droplets in the primary emulsions (Figure S1), confirming that the primary emulsification conditions dictate the capsule internal structure.

By increasing the energy input, primary emulsions with smaller oil droplets are formed and these template smaller oil cores within the final capsule structure. Triplicated samples confirmed the repeatability of the procedure, with deviation in overall capsule and inner core diameters being less than 15%. Low magnification optical microscopy images and size distribution histograms of those samples are provided in the Supporting Information (Figures S5 to S7). It is worth mentioning that the apparent discrepancy between the reported size values and the SEM images shown in this article, originates from the small number of capsules effectively present in the SEM
images. Size distribution histograms, provided in supporting information, show a Poisson distribution, with capsule diameter ranging from 5 to 50-60 µm. This polydispersity in diameter directly originates from the bulk emulsification approach used for the preparation of the capsule templates.

The surface defects, observed by SEM (Figure 1), are likely to be due to the presence of oil cores adjacent to the double emulsion boundaries prior to capsule formation. In this condition, only a thin layer of aqueous phase is located between the internal oil core and the external oil phase limiting the amount of silica available for colloidal destabilization. This results in two possible situations. A thin silica layer may form upon colloidal destabilization. This thin shell may then break during the mixing process due to high shear stresses, exposing the surface pores. Alternatively, a silica depletion may occur in the thin aqueous layer. As the silica agglomerate grows within the aqueous phase the silica nanoparticles are attracted to the growing fractal structure. Because the silica aggregate occupies less volume than the corresponding aqueous phase there will be insufficient silica within the aqueous layer to form a complete shell, leaving behind surface pores. The oil is then removed from the cavities via coalescence with the external oil phase or during the cleaning stage.

Additional SEM images suggest that the size and frequency of such defects can be significantly reduced by decreasing the diameter of the internal oil cores. This helps to ensure that the cores are more likely to locate completely within the capsule confines. An alternative way to minimize this phenomenon would be to reduce the overall amount of oil within the capsules, enabling enhanced diffusion of oil droplets within double emulsions prior to colloidal destabilization.
Figure 1. Microscopy images of multi-oil-core silica microcapsules prepared with different primary emulsification mixing speeds (shown at the top of the figure). Scale bars are equal to 10 µm. Average size values were obtained from the analysis of optical microscopy images (N=250).
The impact of secondary emulsification parameters on overall capsule structure was investigated, by producing capsules from double emulsions prepared at different primary (UT operating at 5,000, 10,000 or 15,000 RPM) and secondary (Manual mixing, V or UT operating at diverse speeds) emulsification conditions. A decrease in the overall capsule diameter was observed for samples prepared using the higher energy input technique (UT), and this was found to occur irrespective of primary emulsification conditions (Figure 2A-C). By increasing the energy input during the secondary emulsification step, smaller double emulsions are produced resulting in smaller capsules. Using this approach, multicore silica capsules with an overall diameter between 7 and 35 µm can be produced. It is interesting to note that the average diameter of the capsules significantly decreases after modification of the mixing technique but appears to level off for increased mixing speed. This finding suggests an inefficiency in the mixing process, where the excess energy brought to the mixture is mostly converted into viscous losses rather than used for decreasing the diameter of the double emulsion template.

Measurement of internal core diameters showed a significant impact of extreme secondary emulsification conditions on the capsule internal structure. This was evidenced by the decrease in core diameter measured for capsules prepared at high secondary emulsification speed (i.e. 10,000 or 15,000 RPM (UT)) (Figure 2D). At this secondary mixing speed, oil droplets are further dispersed within the double emulsion, resulting in a reduction of average core diameter from 2.8 to 0.8 µm. Therefore, a reduced secondary mixing speed (i.e. 3,000 or 5,000 RPM (UT)) should be exploited to produce small capsules with large oil cores. Optical microscopy images of all samples are provided in the Supporting Information (Figure S8).
These results show that capsules produced using this method display a high degree of tunability, enabling tailoring of their internal structure and overall size by simply adjusting the mixing conditions.

Figure 2. Impact of secondary emulsification mixing speed on (A-C) overall capsule diameter and (D) inner core diameter. Capsules obtained using primary emulsions prepared with an Ultra-Turrax operating at (A) 5,000, (B) 10,000 and (C) 15,000 RPM. Insets are optical microscopy images of capsules produced at the indicated mixing conditions. Scale bars are equal to 20 µm.
2.2. Facile shell functionalization

Metal oxide doped multicore colloidosomes were prepared via dispersion of Fe$_3$O$_4$, TiO$_2$ or ZnO nanoparticles within the aqueous phase prior to capsule formation. EDS elemental mapping analysis confirmed the successful incorporation of nanoparticles within the capsule structure (Figure 3A-C and Figure S9). Optical microscopy images and size distribution histograms showed that this incorporation did not alter the size or structure of the final capsules, resulting in 17 to 20 µm large capsules with 1 µm cores (Figure S10).

The incorporation of various nanoparticles within the capsule structure confers additional physicochemical properties. For instance, exposing Fe$_3$O$_4$-doped microcapsules to an external magnetic field resulted in their recovery from solution in fewer than 30 seconds (Figure 3D). Photocatalytic properties of TiO$_2$ and ZnO doped capsules were investigated by exploring the degradation of an aqueous solution of synthetic dye (Rhodamine B) upon UV-light irradiation. Results display enhanced dye removal for capsules integrating these metal oxides (Figure 3E). In the absence of capsules, minimal degradation of Rhodamine B under UV-light irradiation was observed, confirming the dye stability and importance of the photocatalytic materials. In the presence of multicore silica colloidosomes without metal oxide dopants, a 16% decrease in dye absorbance was observed after 1 hour of UV irradiation. Beyond 10 minutes, any additional irradiation did not result in further decreases in absorption, suggesting that the mechanism may be due to adsorption from solution rather than photodegradation. The capsules bear a negative surface charge at neutral pH, and since Rhodamine B features a cationic quaternary ammonium group, this mechanism is feasible. The observed plateau is likely due to saturation of the capsule surfaces with Rhodamine B, preventing further removal from solution.
In the presence of TiO$_2$ doped capsules, a 72% decrease in the absorption maxima were observed after 1 h of UV irradiation. The corresponding result for ZnO doped capsules was 36%. The steady decrease over time suggests that removal of Rhodamine B from solution is not only based on an adsorption mechanism, as observed with SiO$_2$ microcapsules, but also on a photodegradation mechanism. Absorbance spectra in these cases exhibit both a decrease in the maximum absorbance as well as a hypsochromic shift (towards lower wavelengths). These changes are characteristic of the degradation of the aromatic ring and de-ethylation of Rhodamine B [48-50]. This phenomenon is based on a well-known UV light-induced photoexcitation process. Under UV-light irradiation, electrons are transferred from a valence band to a conduction band within the TiO$_2$ and ZnO nanoparticles incorporated within the capsules. The electron and hole pair generated react with O$_2$ and H$_2$O to subsequently form super-oxide species (O$_2^-$) and hydroxyl radicals (OH$^-$), which are then involved in the oxidation of the dye. The difference in degradation efficiency between the two systems is likely to arise from the lower amount of metal oxide dopant within the ZnO doped capsules compared to those with TiO$_2$. Adjusting the loading of nanoparticles within the capsules as well as capsule diameter or light source conditions, would likely alter the degradation dynamics. It is also worth mentioning that the dye removal results presented here correspond to a combination of adsorption and photodegradation effects of the assembled capsules. A preliminary equilibration of the samples in the dark prior to UV-light irradiation could be implemented to discriminate between the individual mechanisms on the overall dye removal efficiency. Additional EDS mapping analysis, optical microscopy images, size distribution histograms and absorbance spectra are provided in the Supporting Information (Figures S9 to S11).

This approach enables facile, fast, and diverse capsule production and functionalization, without the need for nanoparticle surface modification or post-production capsule coating. This work has
demonstrated the incorporation of Fe₃O₄, TiO₂ and ZnO nanoparticles, although other materials (e.g. metal oxides, charged polymeric particles, carbon nanodots) could be included within the capsule structure, provided they can be homogeneously dispersed in the aqueous phase and destabilized upon addition of salt.
**Figure 3.** Characterization of metal oxide doped multicore silica microcapsules. (A-C) STEM and EDS elemental mapping of capsules (15,000 (UT)-2,000 (V)) doped with (A) Fe$_3$O$_4$, (B) TiO$_2$ and (C) ZnO nanoparticles. Scale bars represent 2 µm. (D) Response of Fe$_3$O$_4$ doped capsules to external magnetic fields. Scale bar is equal to 200 µm. (E) Degradation of a Rhodamine B solution (50 mL, 10 mg.L$^{-1}$) under UV-light irradiation in the presence of TiO$_2$ and ZnO doped capsules (100 mg).
2.3. Rupture of capsules with ultrasound

Ultrasound was applied to multicore silica microcapsules to assess their structural integrity (Figure 4A), with microscopy performed before and after treatment providing key structural information (Figure 4B-E). The presence of oil cores within the capsules was easily confirmed by the difference in contrast between the embedded oil droplets and silica shell. After applying ultrasound, non-miscible droplets and shell fragments were observed in solution confirming capsule rupture and release of the hydrophobic contents (i.e. sunflower oil). Images obtained after increased ultrasound duration suggest a direct correlation between the capsule internal structure and its mechanical strength. Capsules with large cores were observed to break into non-spherical fragments upon ultrasonication, resulting in complete rupture of the capsules after 3 min of treatment (Figure 4B and 4D). Fragments observed following rupture did not show any apparent contrast within their structure, suggesting complete release of sunflower oil. Conversely, capsules with smaller cores remained spherical upon ultrasonication (Figure 4C and 4E). Increasing the ultrasound duration appeared to result in superficial erosion, with spherical capsules measured by optical microscopy to be 17, 38 and 50% smaller after 1, 2, and 3 min of ultrasound. The contrast observed within the final capsules suggests the presence of residual oil cores, still available for further release steps. This ability to adjust the capsule mechanical strength by simple modification of the internal structure makes the production method promising for producing versatile capsules for use in triggered release applications. However, further work is required to quantify this aspect. For this, techniques such as Micromanipulation and Atomic Force Microscopy (AFM) could be considered.

Observation of broken capsules via SEM confirmed the multicore structure with average inner core diameters of 2.8 ± 0.5 and 0.9 ± 0.2 µm for 5,000(UT)-2,000(V) and 15,000(UT)-2,000(V).
capsules. Those values are in concurrence with the results obtained from optical microscopy and STEM images (Figure 1). Low magnification optical microscopy images of samples after ultrasound and additional SEM images of capsules after 1 min of ultrasound are provided in the Supporting information (Figures S12 and S13).

Figure 4. Rupture of dopant-free silica microcapsules using ultrasound. (A) Schematic of the sonication and rupturing process. Optical microscopy images of (B) 5,000 (UT) - 2,000 (V) and (C) 15,000 (UT) – 2,000 (V) capsules after 0 min, 1 min, 2 min or 3 min of ultrasound. Scanning electron microscopy images of (D) 5,000 (UT) - 2,000 (V) and (E) 15,000 (UT) – 2,000 (V) capsules after 1 min of ultrasound. Scale bars are equal to 20 µm for optical microscopy images and 10 µm for SEM images.
2.4. Encapsulation of a hydrophobic compound

Encapsulation of a hydrophobic dye (i.e. Nile red) was used as a simple tool to confirm the presence of oil cores within the capsule structure. A pink solid was visually observed following capsule cleaning, suggesting encapsulation of dye within the structure. Confocal microscopy images of Nile red loaded capsules taken 48 h after preparation exhibited bright pink spots (Figure 5). This observation confirms the presence of oil within the capsule, as well as the multicore structure, corroborating the results from STEM, SEM, and optical microscopy. These results suggest the ability of the system to entrain hydrophobic actives. However, further work is required to explore the encapsulation of diverse hydrophobic actives (e.g. vitamins, antioxidants, etc), and assess how the change of the capsule internal structure can impact the release of such encapsulated materials.
Figure 5. Confocal microscopy images of (A) 5,000 (UT)-2,000 (V) and (B) 15,000 (UT)–2,000 (V) capsules loaded with Nile red. Insets are the corresponding bright field images. Scale bars are equal to 20 µm.
3. Conclusion

This paper reports a novel method for producing multi-oil core silica colloidosomes via salt-driven assembly of nanoparticles in an Oil-in-Water-in-Oil emulsion template. In this approach, capsules are produced without requiring a Pickering emulsion intermediate step, enabling direct use of nanoparticles without any surface functionalization or surfactant adsorption. This approach offers multiple advantages. Firstly, the capsules are easy to produce with minimal lab equipment. Secondly, the entire process can be undertaken at room temperature without harmful or toxic reagents, making the synthesis and final product environmentally friendly. Finally, the emulsion templating route provides a high degree of versatility for controlling the physicochemical properties of the final material. We demonstrate incorporation of Fe$_3$O$_4$, TiO$_2$ and ZnO nanoparticles within the structure for specialized functionalities: magnetic removal and photocatalysis. This preparation method also offers a degree of control on the overall size of the capsules as well as the inner core dimensions by adjusting mixing conditions and system composition. These capsules can easily be ruptured by ultrasound, enabling direct access to the inner cores. We believe this work showcases an effective procedure for producing a novel multifunctional colloidal material that can be tailored for a variety of industrial applications using cheap, commercially available nanoparticles as building blocks.
4. Experimental section

Materials

All chemicals were obtained from Sigma-Aldrich or Fisher scientific, except where otherwise specified, and were used without further purification: Sunflower oil (Sainsburys), Absolute ethanol, Ludox HS-40 (SiO$_2$, 40 wt% in H$_2$O, 15-25 nm diameter), Tween 80, Span 80, Calcium chloride dihydrate (CaCl$_2$, 2H$_2$O), Nile Red (Dry powder, 99%), Rhodamine B (Dry powder, 95%), Iron (II, III) oxide (Fe$_3$O$_4$, dry powder, 50 – 100 nm diameter), Titanium dioxide (TiO$_2$, dry powder, 21 nm diameter, 99.5%) and Zinc oxide (ZnO, 20 wt% in H$_2$O, < 100 nm diameter). It is worth mentioning that a multi-component oil such as sunflower oil was preferred to mono-components oils such as Linseed oil or mineral oils for practical and economic reasons. Sunflower is cheap, safe, and readily available, enabling its use as a proof of principle oil phase. Furthermore, control experiment under UV-light irradiation confirmed that sunflower oil does not generate UV-active by-products, which enable its use in capsules considered for photocatalytic experiments. It is also worth mentioning that the Ludox HS40 was used 6-12 months after opening and exhibited a higher viscosity compared to freshly opened bottles. We believe this was likely due to progressive hydrolysis of the silica nanoparticle surface over time. Supplementary experiments confirmed that the same trends, as reported in this paper, are observed with fresh Ludox HS40 bottles. Adjusting the surfactant concentration serves to compensate for the difference in viscosity (Figures S15 to S17).

Preparation of simple ($O_1/W$) and double ($O_1/W/O_2$) emulsions

The aqueous phase (W) was prepared by addition of silica nanoparticles (35 wt%) and Tween 80 (1, 5 or 10 wt%) to deionized water. The internal oil phase ($O_1$) was composed of sunflower oil
and the external oil phase (O$_2$) was composed of sunflower oil and Span 80 (1 wt%). Primary emulsions were prepared by mixing the internal oil phase (2 g) with the aqueous phase (8 g) for 60 s using an Ultra Turrax mixer (T 25 digital, IKA) set at 3,000, 5,000, 10,000 or 15,000 RPM. Secondary emulsions were prepared by mixing the primary emulsion (1 g) and the external oil phase (9 g) for 60 s using a Vortex mixer (TopMix FB15024, Fischer Scientific) set at 2,000 RPM. The stability of the different emulsions was assessed at regular time intervals using visual observation and optical microscopy.

**Preparation of multi-oil core silica capsules**

Oil core microcapsules were prepared from O$_1$/W/O$_2$ double emulsions using the method presented in **Scheme 1**. The aqueous phase (W) was prepared by addition of silica nanoparticles (35 wt%) and Tween 80 (5 wt%) to deionized water. For metal oxide doping experiments, Fe$_3$O$_4$ (5 wt%), TiO$_2$ (5 wt%) or ZnO (1.5 wt%) nanoparticles were also added to the aqueous phase before homogenization of the mixture for 5 min (30 s on – 10 s off) using an ultrasonic homogenizer (Sonic Dismembrator FB-120, Fisher Scientific) operating at an frequency of 20 kHz and an amplitude of 100%. The internal oil phase (O$_1$) was composed of sunflower oil and the external oil phase (O$_2$) was composed of sunflower oil and Span 80 (1 wt%). Primary emulsions were prepared by mixing the internal oil phase (2 g) with the aqueous phase (8 g) for 60 s using an Ultra Turrax mixer set at 5,000, 10,000 or 15,000 RPM. Secondary emulsions were prepared by mixing the primary emulsion (1 g) and the external oil phase (9 g) for 60 s using a using either a Vortex (V) or an Ultra Turrax (UT) mixer. Capsules were then formed after dropwise addition of a calcium chloride solution (1 mL, 1 mol.L$^{-1}$) into the O$_1$/W/O$_2$ double emulsion, whilst maintaining 2,000 RPM stirring with a Vortex mixer (V). The capsules were then recovered from solution via centrifugation (3,000 RPM, 5 min), and cleaned twice by sequential redispersal in deionized water.
followed by centrifugation (2,000 RPM, 5 min). The cleaned capsules were finally redispersed in deionized water.

**Structural characterization of emulsions and capsules**

The internal structure, overall diameter and chemical composition of the capsules were assessed using optical and electron microscopy. Optical microscopy images of the aqueous dispersion of capsules were obtained using a Leica DME microscope equipped with 10× and 63× objective lenses. Scanning Electron Microscopy (SEM) images were taken using a Tescan Mira3 FEG-SEM microscope (acceleration voltage of 5 kV). Scanning transmission electron microscopy (STEM) images were obtained using a Talos F200X G2 from Thermo Scientific equipped with a Ceta 16 M camera at an acceleration voltage of 200 kV. The same setup was used to examine the incorporation of metal oxides into the structure via Energy Dispersive X-ray spectroscopy (EDS). SEM/STEM samples reported in this article were prepared via deposition and drying of an aqueous dispersion of the capsules on a SEM stub or a TEM membrane. The droplet and capsule diameters were obtained using ImageJ software (imagej.net), analyzing 250 randomly chosen droplets or capsules. Image analysis was mostly carried out on optical microscopy images, due to the low cost, high speed, and ease of this technique compared to electron microscopy techniques. All the reported values correspond to the mean plus or minus one standard deviation. This interval of confidence was preferred to the conventional two standard deviations due to the non-symmetrical distribution of the samples, which appears to follow a Poisson distribution.

**Shell rupture and access to internal cores**

Rupture of capsules was instigated via ultrasonication of an aqueous dispersion (5 mL) for up to 3 min using an ultrasonic homogenizer operating at a frequency of 20 kHz and an amplitude of
Samples were then centrifuged (5,000 RPM – 5 min) and cleaned twice with absolute ethanol before being redispersed in 5 mL of deionized water and observed with optical and electron microscopy.

**Magnetic properties of Fe₃O₄ doped capsules**

The magnetic response of Fe₃O₄ doped silica microcapsules was assessed via exposure to an external magnetic field. For this, an aqueous solution (12 mL) containing Fe₃O₄ doped silica capsules (20 mg.L⁻¹) was exposed to a magnetic field generated by a Rare-earth neodymium magnet (NiCuNi, 19x28.2 mm, 1.2 T, E-magnets UK). Pictures were taken every 15 seconds to analyze the separation process.

**Photocatalytic properties of TiO₂ and ZnO doped capsules**

The photocatalytic properties of TiO₂ and ZnO doped silica microcapsules were assessed via degradation of an aqueous solution of Rhodamine B under UV-light irradiation. Sample preparation involved 100 mg of capsules being added to a Rhodamine B solution (50 mL, 10 mg.L⁻¹). The solutions were then exposed to UV-light (36 W, Light excitation: 365 nm) without preliminary equilibration in dark. 5 mL of solution was collected after 0, 10, 20, 30, 40, 50 and 60 minutes and centrifuged at 5,000 RPM for 5 min. Absorbance of the supernatant was measured using a UV-visible spectrophotometer (Cary 60, Agilent technologies). The absorption maximum was observed to shift from 555 to 528 nm, and therefore was not interpreted at a fixed wavelength but at the position of the maximum. The compacted capsules were then redispersed by manual agitation with the supernatant, and the mixture was reinjected into the original solution. This procedure was repeated at subsequent time intervals. Rhodamine B solutions with and without
SiO$_2$ microcapsules were used as references. Each experimental series was duplicated to ensure reproducibility of results.

*Preparation and characterization of Nile red loaded capsules*

Capsules containing Nile red (150 mg.L$^{-1}$) were prepared. Initially, primary emulsions were prepared using an Ultra-Turrax mixer operating at 5,000 or 15,000 RPM and secondary emulsions were prepared using a Vortex mixer operating at 2,000 RPM. The formed capsules were imaged using a Leica SP5 confocal microscope equipped with a 63x oil objective (Excitation wavelength: 514 nm, Detector range: 530-730 nm).

**ASSOCIATED CONTENT**

**Supporting information available:**

Additional visual observation and optical images of simple and double emulsions; Optical and electron microscopy images of capsules before and after sonication; EDS analysis of metal oxide doped microcapsules; Absorbance spectra of Rhodamine B degradation; Supplementary experiments on the preparation of multicore microcapsules using new Ludox HS40 bottles.

This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org)

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