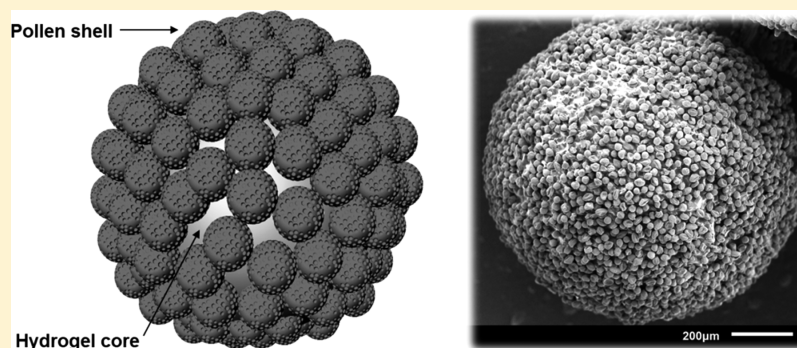# Multifunctional Hierarchically-Assembled Hydrogel Particles with Pollen Grains via Pickering Suspension Polymerization

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S *Supporting Information*

ABSTRACT: Hierarchical assembly of heterogeneous particles is of great importance to interface and colloid science. In this work, a facile but powerful approach for the large-scale production of multifunctional hydrogel particles armored with biological colloidal species is developed by combining Pickering stabilization and photopolymerization. Biocompatible hollow pollen grains extracted from naturally occurring pollen species with an average diameter of ∼32 μm serve as universal solid emulsifiers dispersed in an oil phase and are self-assembled at the interface between an oil phase and a photo-cross-linkable hydrogel to make water-in-oil (W/O) emulsion droplets. While droplets are solidified into hydrogel particles by UV-induced free-radical polymerization, self-assembled hollow pollen grains are transformed to a robust shell on hydrogel particles with supracolloidal structures. The physically adsorbed hollow pollen grains on the hydrogel core can be released by a hydration-induced swelling of hollow pollen grains, leading to a transient floating behavior of core−shell particles. The size of the resultant core−shell particles is easily controlled by tailoring the process parameters such as a liquid volume or a loading mass of hollow pollen grains. The incorporation of magnetic or upconverting luminescent nanoparticles into a hydrogel core successfully expands the functionality of core−shell particles that can provide new design opportunities for floating drug delivery or ecofriendly proppants.

INTRODUCTION

Hydrogel particles, which consist of cross-linked hydrophilic polymer chains, have attracted enormous interest in material science owing to their biocompatibility and mechanical softness.[1] In particular, stimuli-responsive physical and chemical properties make hydrogel particles suitable for various applications such as foods,[2] drug delivery,[3] coatings,[4,5] and membranes.[6] Poly(ethylene glycol) diacrylate (PEGDA), one of the representative photo-cross-linkable hydrogels, based on free-radical polymerization, has been extensively explored for realizing such functional particles.[7] The facile but delicate processability of PEGDA through lithographic processes facilitates the emergence of a wide variety of hydrogel particles with complex structures and composition.[8] For example, spatially and chemically encoded PEGDA barcodes can be produced in large quantities (≥10^4 particles per hour) by single-step, multiple-flow lithography, which successfully expands the application field of hydrogel particles to multiplexed biosensing and anticounterfeiting.[9−11]

One of the promising research directions for extending the usability of hydrogel particles is the development of core−shell structures through conformal coating of heterogeneous materials on hydrogel particles.[12] The proper choice of shell materials can be advantageous to hydrogel particles in several aspects: (1) protection of hydrogel particles from sensitive environments, (2) modification of surface properties related to wetting and dispersion, (3) extension of structural design capability, and (4) providing additional functions to hydrogel particles. The proposed techniques for forming conformal shells on presynthesized particles are roughly categorized by layer-by-layer deposition,[13] selective withdrawal,[14] centrifuga-
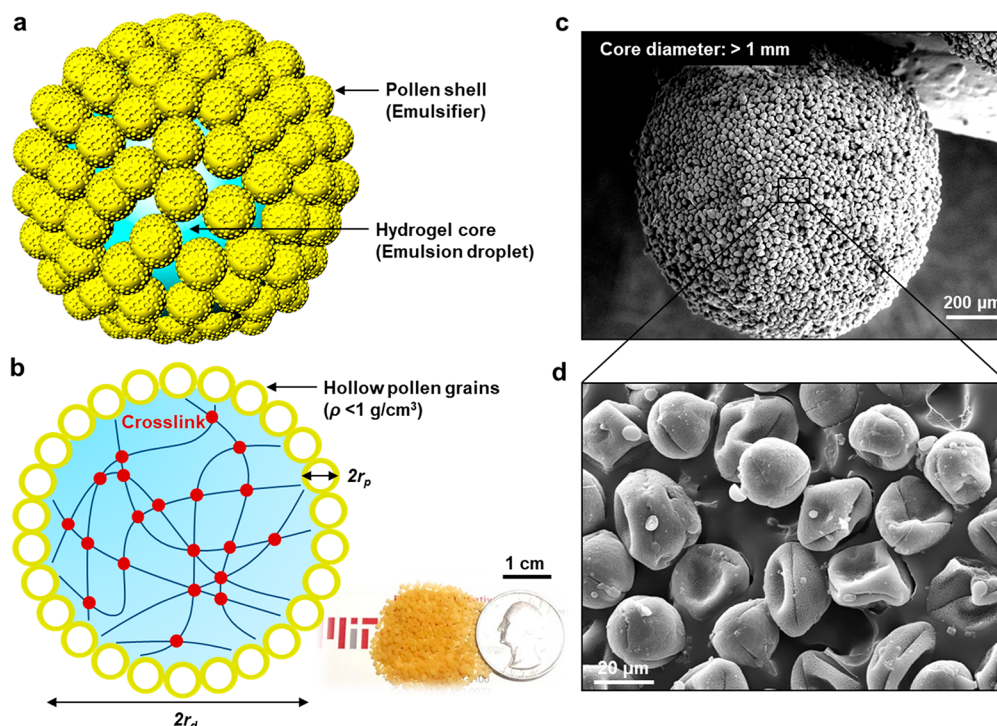
Figure 1. Overview of the core–shell emulsions and particles. (a) Schematic illustration of a core–shell structured hydrogel particle with hollow pollen grains via Pickering suspension polymerization. (b) Cross-sectional view of part a (the rightmost inset: digital image of multiple core–shell particles produced by Pickering suspension polymerization in a single batch). (c) SEM image of a core–shell particle stabilized by hollow pollen grains obtained from Castor beans. (d) Magnified SEM image of part c.

tion,[15] sol–gel coating,[16] and hydrodynamic coating.[17] Although these techniques successfully demonstrate their ability to make functional shells on particles with uniform size distribution, the postsynthetic approaches still suffer from the aggregation of particles during the process, restriction in coating chemistry, and the difficulty of mass-production.

In this regard, batch suspension polymerization can provide an efficient way to produce core–shell particles in quantity by integrating the sequential processes of particle synthesis and shell coating into a single-step.[18] Recent achievements in the fusion of suspension polymerization and Pickering emulsions, which use solid particles in place of surfactant molecules to stabilize emulsion, are particularly promising since this approach can yield unique core–shell particles with supracolloidal structures that cannot be generated by conventional coating methods.[19−21] Replacement of a dispersed phase in Pickering emulsion from oil or water to cross-linkable monomers, generally polystyrene (PS) and poly(methyl methacrylate) (PMMA), enables solidification of particle-stabilized droplets into core–shell particles. Various types of colloidal particles with sizes ranging from a few nanometers to several microns can be used as solid emulsifiers,[22] potentially transforming into functional shells of composite particles after cross-linking of monomers. The resultant core–shell particles can be enlarged to a granule size because Pickering emulsion is extremely stable to coalescence even when the emulsion droplet size reaches the millimeter scale, unlike traditional emulsion systems using surfactants.[23] Despite high degrees of freedom in the structure and function of core–shell particles derived by Pickering suspension polymerization, the combinational library of core and shell materials for functional particles reported to date is very limited.

Here, we introduce a biocompatible and multifunctional composite particle consisting of a hydrogel core and a shell of naturally occurring pollen grains via Pickering suspension polymerization. The partial hydrophobic nature of sporopollenin, which is the outermost shell of pollen grains and is one of the most chemically inert biopolymers,[24] provides a chance to utilize hollow pollen grains as universal emulsifiers. To solidify the resultant emulsion droplet stabilized by hollow pollen grains, a photo-cross-linkable PEGDA monomer with low-viscosity (∼60 cP at 25 °C) serves as a hydrophilic dispersed phase in the emulsion system. The size of the core–shell particles is precisely controlled from a few hundred microns to over a millimeter by tailoring the process parameters (i.e., volume of liquids, size, and loading mass of emulsifiers). The surface coverage of hollow pollen grains on the PEGDA core reaches over 90% at optimized conditions. Interestingly, the hydrophobic nature of hollow pollen grains with low density (ρ < 0.98 g/cm^3) assigns a transient floating ability to core–shell particles until a sufficient number of hollow pollen grains are released from the PEGDA core by hydration-induced swelling. The use of hydrogel nanocomposites, prepared by incorporating magnetic and upconverting nanocrystals (UCNs) into a PEGDA monomer, successfully realizes the multifunctionality of core–shell particles that may be applicable to floating drug delivery, in vivo digestive tracking, or traceable proppant.[25−27]

■ EXPERIMENTAL SECTION

Materials. All chemicals were analytical grade: defatted pollen grains obtained from castor beans (*Ricinus communis*), sunflowers (*Helianthus annuus*), and olives (*Olea europaea*) (Greer Laboratories), poly(ethylene glycol) diacrylate (PEGDA) (Sigma-Aldrich, average M_n of 250, 400, 575, and 700), 2-hydroxy-2-methylpropiophenone (Sigma-Aldrich, 97%), poly(ethylene glycol) (PEG) (Acme Hardesty,

average M_n of 200), hexadecane (Sigma-Aldrich, 99%), Fe$_2$O$_3$ nanopowders (Sigma-Aldrich, <50 nm), GdCl$_3$·6H$_2$O (Sigma-Aldrich, 99.9%), YCl$_3$·6H$_2$O (Sigma-Aldrich, 99.9%), YbCl$_3$·6H$_2$O (Sigma-Aldrich, 99.9%), TmCl$_3$·6H$_2$O (Sigma-Aldrich, 99.9%), NH$_4$F (Sigma-Aldrich, 99.9%), and oleic acid (Sigma-Aldrich, technical grade, 90%).

Preparation of Two Immiscible Solutions. A dispersed phase solution was prepared by the vortex-mixing of a PEGDA monomer with the photoinitiator 2-hydroxy-2-methylpropiophenone with a volume ratio of 95:5. In a case of porosity-tuned core−shell particles, PEG200 (30 v/v %) was added to a dispersed phase solution as a porogen. A continuous phase containing solid emulsifiers was prepared by adding hollow pollen grains (0.15 g), extracted from naturally occurring pollens by alkaline lysis as described in the literature,[28] into hexadecane (5 mL). Alkaline lysis can be briefly described as follows: defatted pollen grains (5 g) were suspended in aqueous KOH solution (6%, 100 mL) and heated at 80 °C for 12 h with stirring. The alkaline solution was refreshed every 6 h. Then, hollow pollen grains were recollected, washed, and dried.

Pickering Suspension Polymerization. A prepared suspension of hollow pollen grains in hexadecane was poured onto a PEGDA prepolymer (1 mL) in a small beaker (50 mL). Mild magnetic stirring with a spin-speed of 500 rpm was applied for 3 min to stabilize the emulsion droplets with hollow pollen grains. The UV light (365 nm) was then applied to a stirred solution, rapidly solidifying a PEGDA monomer in emulsion droplets. The UV exposure was maintained for 10 min to ensure sufficient cross-linking of the PEGDA monomer. The resultant solid particles armored with hollow pollen grains were washed with ethanol several times and were gently filtered under vacuum.

Multifunctional Core−Shell Particles. The multifunctional core−shell particles were synthesized by Pickering suspension polymerization using a composite PEGDA monomer with nanofillers (lanthanide doped NaYF$_4$ and Fe$_2$O$_3$). The lanthanide doped UCNs with different doping ratios and a homogeneous mixture of UCNs and a PEGDA monomer were prepared by following procedures well-described in literatures.[10,11] For this study, the small amounts of UCNs (0.025 g) and Fe$_2$O$_3$ nanopowders (0.05 g) were simultaneously added into a PEGDA monomer (1 mL) to realize magnetic-responsive and upconverting luminescent properties.

■ RESULTS AND DISCUSSION

Strategy to Fabricate Core−Shell Particles. Figure 1a presents a schematic diagram of a hydrogel particle armored with hollow pollen grains as an expected outcome of Pickering suspension polymerization. The process begins with the preparation of two separate solutions which will become the dispersed and continuous phases in an emulsion system. The dispersed phase used in our experiment consists of a homogeneous mixture of a hydrophilic PEGDA monomer (95 v/v %) and a photoinitiator (5 v/v %), which is responsive to UV light, whereas hexadecane is selected as the continuous phase for making a colloidal suspension with hydrophobic hollow pollen grains (Figure S1). In general, Pickering suspension polymerization proceeds with two sequential steps in a single batch: (1) self-assembly of solid particles at the surface of an emulsion droplet and (2) free-radical polymerization of a liquid core by applying external sources such as UV light, heat, or salt (Figure S2). The driving force for particles to adhere to the surface of an emulsion droplet can be understood by the reduction in the overall interfacial free energy[29]

$$\Delta E = \pi r_p^2 \gamma (1 - |\cos \theta|)^2 \tag{1}$$

where r_p is the particle radius, γ is the interfacial tension between the two immiscible phases, and θ is the three-phase

contact angle. This equation shows that a partially hydrophobic ($\theta \sim 90°$) particle is energetically favorable to stabilize the emulsion droplet. A pollen grain, whose structure consists of a cytoplasmic core and an amphiphilic double-walled (called as exine and intine) protective shell, is a rational candidate for Pickering stabilization in this respect. The inside genetic material can be easily removed by alkaline lysis,[28,30] which yields robust hollow pollen grains with sizes ranging from 2.4 to 250 μm, depending on the type of pollen grain.[31] A remaining shell of the resulting hollow pollen grains consists of exine and intine layers. In particular, the outermost exine layer is mainly composed of a tough biopolymer called sporopollenin consisting of highly cross-linked organic substances such as long chain fatty acids, phenylpropanoids, and phenolics (Figure S3).[32] The partial hydrophobicity of sporopollenin makes hollow pollen grains partially wettable by both immiscible liquids, resulting in the emulsion droplets' ability to be stable for coalescence without surface functionalization.[33] Figure 1b schematically illustrates a cross-sectional view of an expected core−shell particle with a supracolloidal structure. Overall, the radius of the emulsion droplet (r_d) achieved by Pickering stabilization is proportional to the radius of hollow pollen grains (r_p), if other process conditions are not changed.[34] The self-assembled hollow pollen grains can be partially buried at the surface of the solid hydrogel core by the cross-linking of the PEGDA monomer under UV light exposure (<1 min). The interfacial location of the hollow pollen grains can be precisely controlled by tailoring the interfacial tension between the two immiscible liquids.[35] A digital image in Figure 1b shows the experimentally realized hydrogel particles stabilized by hollow pollen grains obtained from a single batch experiment. The experimental details are described in the Materials and Methods section. In general, the hydrophilicity of PEGDA depends on the molecular weight, because the mass ratio of the hydrophobic acrylate groups in the PEGDA chain decreases as the molecular weight increases.[36] We note that the emulsion droplet cannot be stabilized by hollow pollen grains when a PEGDA monomer with low molecular weight (M_n = 250) is used as a dispersed phase due to relatively small interfacial tension with hexadecane (Figure S4). When the M_n of a PEGDA monomer increases over 400, the reproducible manufacturing of core−shell particles is possible. Figure 1c shows a microscopic image of densely coated hollow pollen grains of castor beans, whose average r_p is ∼16 μm with small deviation (<5%), on the cross-linked PEGDA core. The particle size was analyzed by postprocessing the images taken through an optical microscope with the software ImageJ. The reason for choosing pollen grains of castor bean as the main emulsifier is that it is a relatively small spherical particle with a smooth surface.

The resultant core−shell particle has a spherical shape with a large core diameter over 1 mm, which is difficult to achieve through surfactant-based emulsion systems.[23] The surface coverage of the particle shell on the core is significantly enhanced compared to those in previous studies that used biopolymers because of well-matched solvent affinity and uniform size distribution of spherical hollow pollen grains.[33] Figure 1d shows a magnified surface of core−shell particles with supracolloidal structures. The hollow pollen grains are physically adsorbed at the surface of the core and are partially embedded in the hydrogel through rapid cross-linking of the PEGDA monomer within a few seconds. The stuck hollow pollen grains shrink in size during the filtering and drying
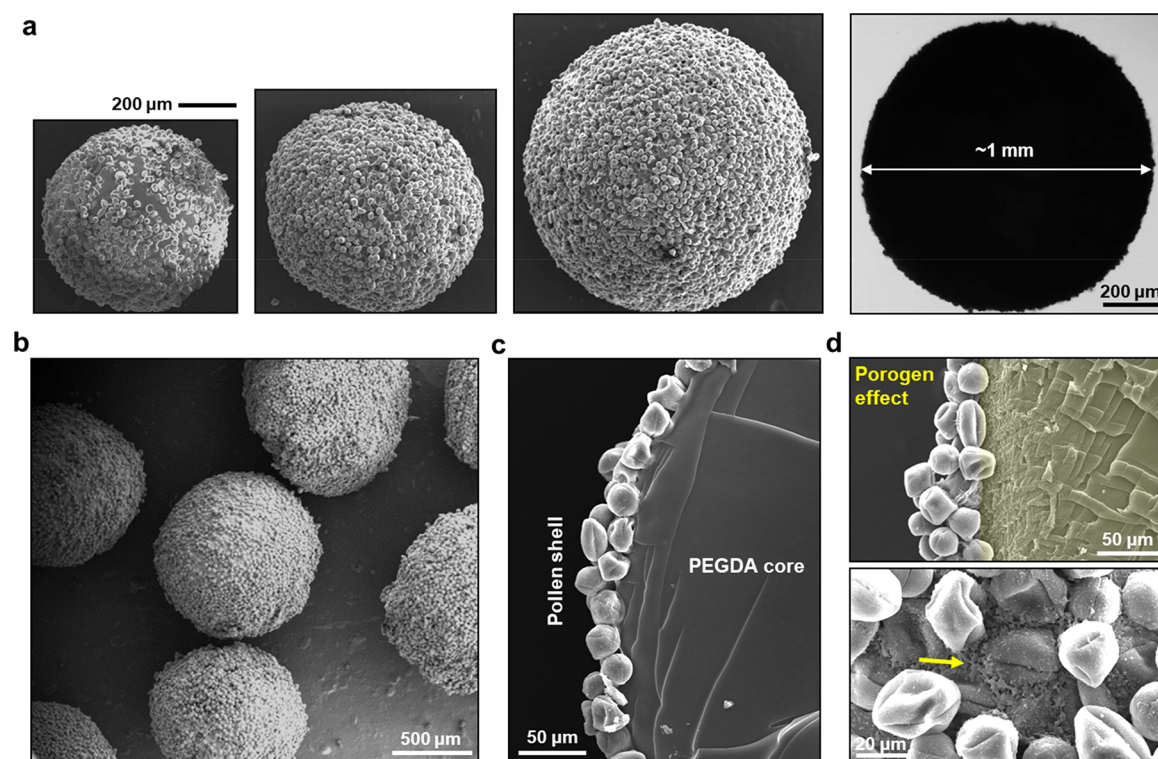
Figure 2. Control of size and morphology of core−shell particles. (a) SEM and optical images of core−shell particles with different diameters ranging from ∼600 to ∼1 mm obtained by controlling the loading mass of hollow pollen grains from 0.05 to 0.25 g. (b) SEM image of multiple core−shell particles, whose average diameter is ∼1 mm with small deviation (<8%) in major axis, produced in a single batch. (c) Cross-section SEM image of a core−shell particle with a smoothly fractured surface in a PEGDA core. (d) SEM images of a core−shell particle with hierarchical porosity along the direction to a center of a core, as a result of adding porogen (30 v/v % PEG200) into a PEGDA monomer (a yellow arrow indicates the outermost nanoporous surface).

processes due to their hollow structure,[37] suggesting that they can later be released from the PEGDA core by rehydration-induced volume expansion when exposed to humid environments.

Control of Size and Morphology. Figure 2a demonstrates precise control over the size of the hydrogel core armored with hollow pollen grains obtained by the tailoring of the process parameters. Our experimental system is classified as an inverse Pickering mode, generating water-in-oil (W/O) emulsions.[38] On the basis of the following assumptions: (1) the emulsion droplets are completely covered by the hollow pollen grains, (2) no excess hollow pollen grains in PEGDA and/or hexadecane, (3) a two-dimensional (2D) square lateral packing of the hollow pollen grains, and (4) monodisperse hollow pollen grains and emulsion droplets, the size of the PEGDA core stabilized by hollow pollen grains can be estimated by the following equation[39]

$$ r_d = C\pi \left(\frac{w_h}{w_p} \right) \left(\frac{\rho_p}{\rho_h} \right) r_p \tag{2} $$

where C is the surface coverage of hollow pollen grains on the PEGDA core, w_h is the weight of the PEGDA monomer, w_p is the weight of hollow pollen grains, ρ_h is the density of the PEGDA monomer, and ρ_p is the density of hollow pollen grains. This equation suggests that the size of core−shell particles becomes larger as the loaded mass of hollow pollen grains into the continuous phase decreases when other parameters are fixed. To isolate the effect of the dispersed phase on the size of core−shell particles in this study, we set

the volume ($v_h = w_h/\rho_h$) of the PEGDA monomer as 1 mL and w_p was changed from 0.05 to 0.25 g with an interval of 0.5 g. Consequently, the r_d is entirely determined by the w_p (Figure S5). The minimum r_d stabilized by hollow pollen grains with r_p ∼ 16 μm is about 200 μm when the w_p is over 0.25 g, which is in agreement with a calculated value of ∼187 μm according to eq 2. A larger core−shell particle, even over the millimeter scale, is achieved by reducing the w_p below 0.15 g. The densely packed hollow pollen grains on the PEGDA core make the core−shell particle optically opaque due to increased absorption and random scattering of the incident light (see the rightmost image in Figure 2a), whereas typical hydrogel particles are transparent. Figure 2b shows a microscopic image of multiple core−shell particles produced by optimized Pickering stabilization with the w_p of 0.15 g in a single batch. The average r_d of the resultant hydrogel particles is ∼510 μm with a small deviation (<8%). Figure 2c presents a microscopic image of a fractured cross-section of a core−shell particle. The inner PEGDA core is cross-linked by free-radical polymerization, and the physically captured hollow pollen grains form a continuous layer on the outermost surface of the core. The structural morphology and physical bulk properties (e.g., density, Young's modulus) of hydrogel particles can be further controlled by adding un-cross-linkable porogens, generally PEG or ethanol,[40] into the PEGDA monomer. Figure 2d demonstrates that hierarchically porous core−shell particles are successfully produced by the use of a mixture consisting of PEGDA ($M_n = 700$) (70 v/v %) and PEG ($M_n = 200$) (30 v/v %) as a dispersed phase. Submicron nanopores
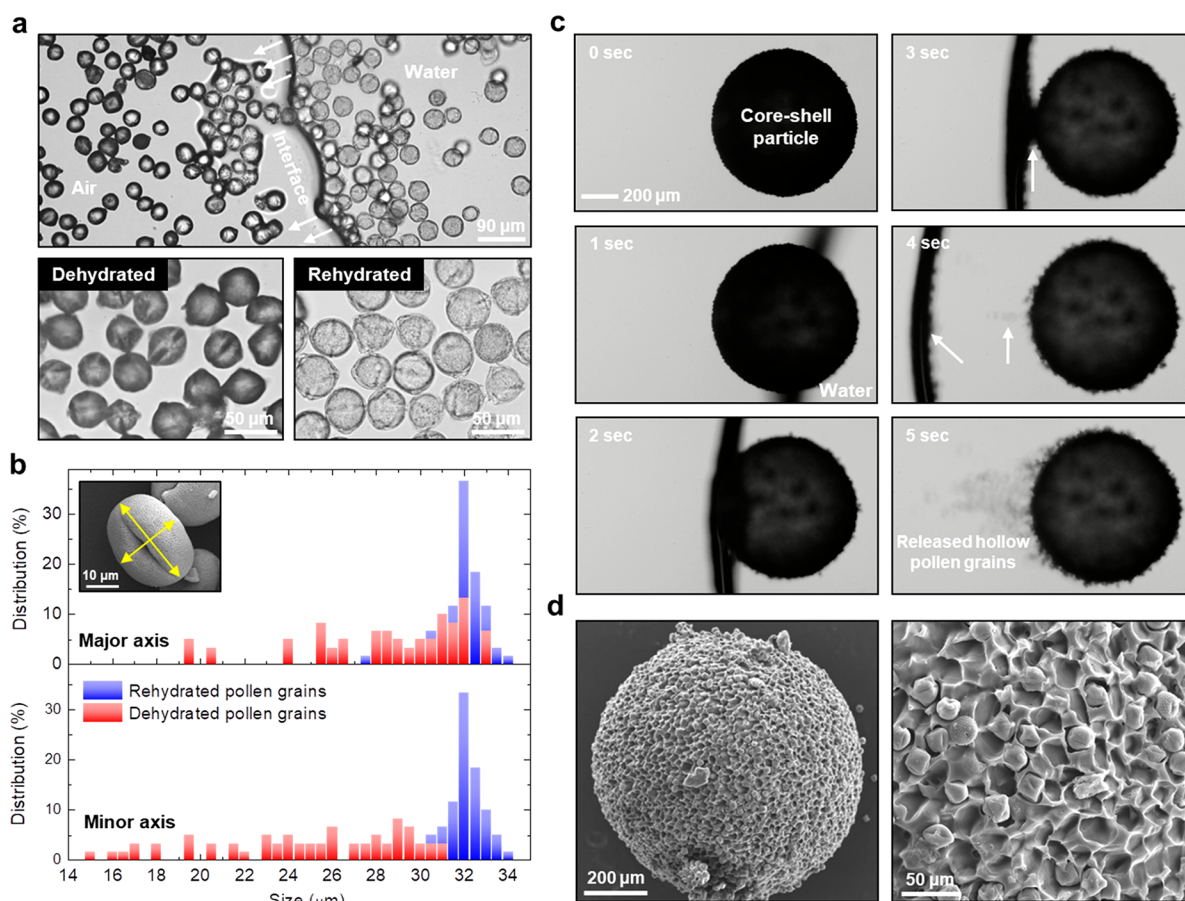
Figure 3. Rehydration-induced release of hollow pollen grains from a PEGDA core. (a) Optical images of dehydrated and rehydrated pollen grains obtained from castor beans. (b) Size distribution of dehydrated and rehydrated pollen grains: major and minor axes (inset is SEM image of single dehydrated pollen grain). (c) Snapshot images from a movie showing dynamic release of hollow pollen grains from a PEGDA core by inducing water influx from right to left. White arrows point to released pollen grains. (d) SEM images of a partially "naked" hydrogel particle produced after release of hollow pollen grains during rehydration.
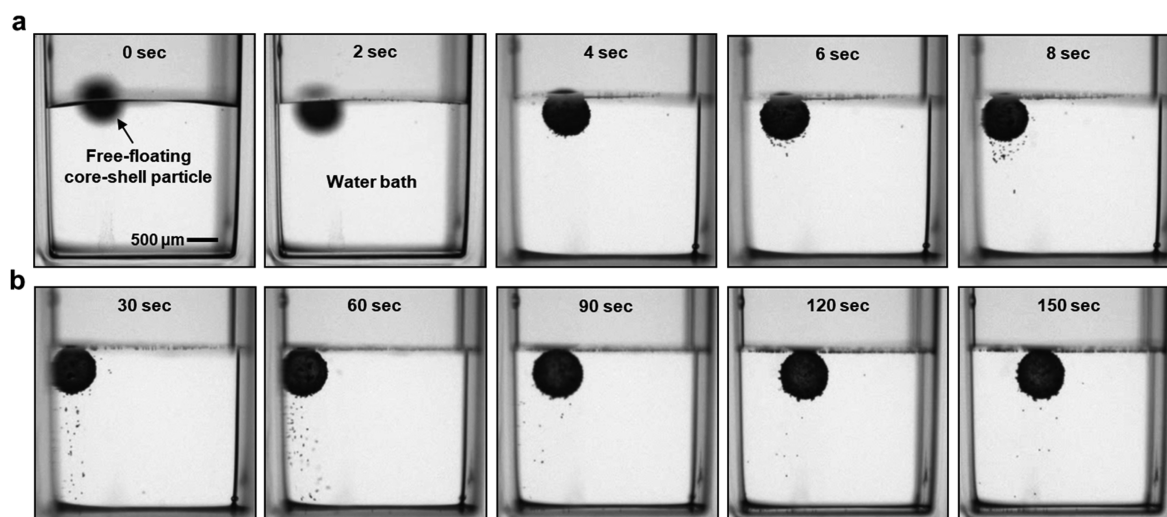

Figure 4. Transient floating behavior of core−shell particles. (a) Successive images showing the transition in a floating behavior of a core−shell particle undergoing a release of hollow pollen grains at an initial stage with a time lag of 2 s. (b) Successive images with a longer time lag of 30 s showing steady release of hollow pollen grains.

with their sizes ranging from ∼300 nm to ∼1 μm are uniformly distributed at the surface of the PEGDA core.

Hydration-Induced Release of Pollen Grains. Figure 3 represents a unique releasing behavior of arrested hollow

pollen grains from the PEGDA core. The pollen grains have strong hydraulic conductivity, originating from the high density of negative charges on sporopollenin, for the pollination of flowers.[41] The shrunken pollen grains by dehydration can be
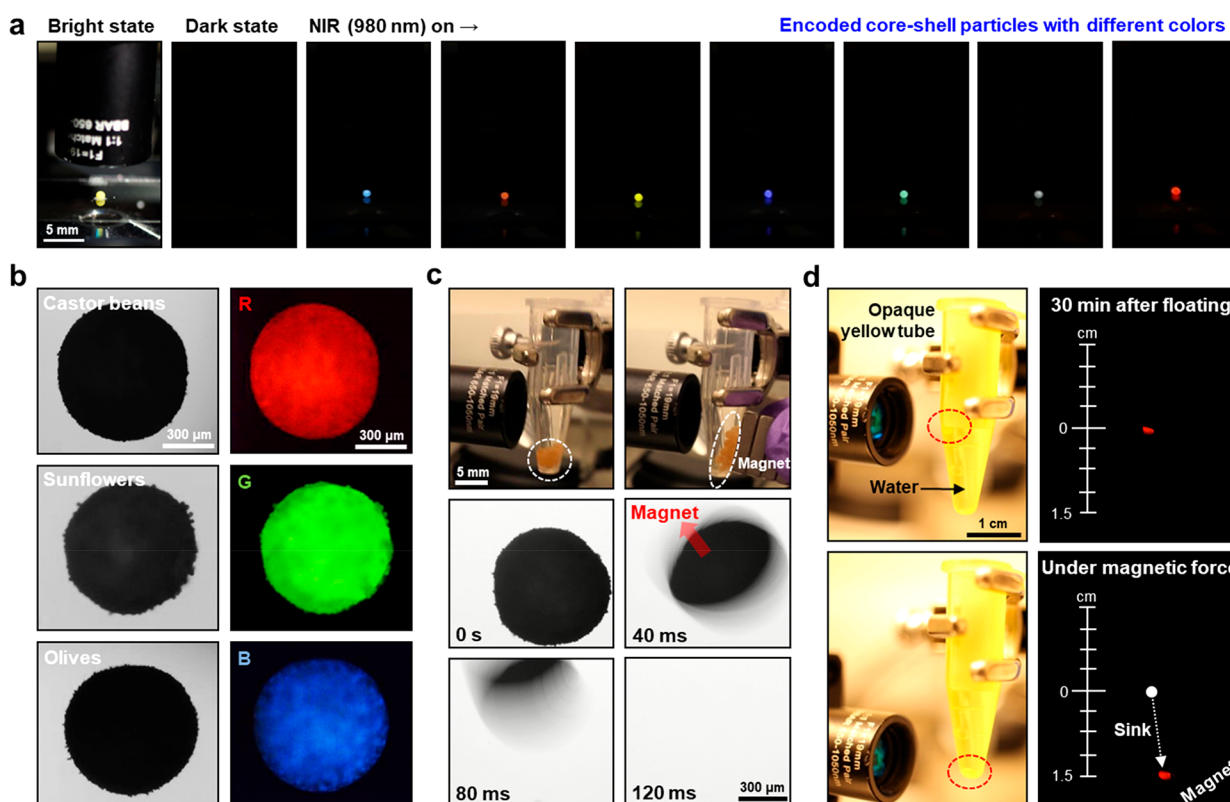
Figure 5. Multifunctional core−shell particles produced by single-step Pickering suspension polymerization. (a) Digital images of luminescent core−shell particles with various colors under excitation of an invisible NIR laser (λ = 980 nm), achieved by incorporation of rare-earth doped upconverting nanocrystals (UCNs) into a PEGDA monomer. (b) Color-coded (R, G, B) core−shell particles stabilized by different hollow pollen grains obtained from sunflowers, castor beans, and olives. (c) Magnetic core−shell particles prepared by incorporation of Fe_2O_3 nanoparticles (<50 nm) into a PEGDA monomer. (d) Tracing test with codoped multifunctional core−shell particle in opaque or dark conditions.

inflated by an influx of water passing through nanoapertures on the surface of hollow pollen grains. Figure 3a shows snapshots from movies capturing the dynamic inflation behavior of pollen grains under water flow (Movie S1). The full inflation of dehydrated pollen grains is quickly completed within 1 s from the start of rehydration. The remaining hydrophilic intine layer allows water to easily penetrate into the hollow pollen grains when contacted with water, which can lead to rapid inflation during rehydration. The average size of the pollen grains increases from ~24 to ~32 μm, and the overall shape becomes more spherical after inflation (Figure 3b). This kind of physical expansion allows the hollow pollen grains to escape from the PEGDA core under a humid environment. Figure 3c shows a profuse release of hollow pollen grains from the PEGDA core by the influx of water. Approximately ~80% of captured hollow pollen grains separate from the PEGDA core, and the resultant core−shell particles become slightly semitransparent because of the lowered density of the captured hollow pollen grains (Movie S2). Figure 3d shows microscopic surface images of the core−shell particles after the partial release of hollow pollen grains. The released hollow pollen grains leave a trace of the basalt-like rough surface, while a few hollow pollen grains (<20%) still remain deeply stuck in the PEGDA core. The remaining hollow pollen grains are fully released from the PEGDA core within 30 min after exposure to the water environment; this accompanies the volume expansion of the PEGDA core by ~10% (Figure S6).

Transient Floating Behavior. Figure 4 shows the floating behavior of core−shell particles facilitated by densely coated

hollow pollen grains. Most hydrogel systems, synthesized through cross-linking of hydrophilic polymer chains, show good wettability with water and polar solvents. The realization of hydrophobic hydrogels with a floating ability on the surface of aqueous media is interesting and is one of the challenging issues that restricts their use in some application fields.[42] With this in mind, the core−shell hydrogel particles developed here show a unique floating behavior based on a constantly changing wetting property, arising from the hydration-induced release of hollow pollen grains (Movie S3). Figure 4a shows the collected frames of a recorded movie visualizing dynamic transition of a floating behavior at an early stage with a time interval of 2 s. More than half of the core−shell particle is exposed to air when the particle is initially dropped on a water bath. Partial sinking of the core−shell particle occurs within 2 s because a number of hollow pollen grains are immediately released by collision with the surface of water. Within 10 s, a large volume (>95%) of the core−shell particle becomes immersed in water, accompanying the profuse release of hollow pollen grains settling to the bottom (Figure S7). The release rate of hollow pollen grains is estimated to be around 8 hollow pollen grains per sec. Figure 4b shows the collected frames with a larger time interval of 30 s after the initial stage. The number of hollow pollen grains released from the PEGDA core per unit time gradually decreases after around 60 s, and after 120 s, only 1 or 2 hollow pollen grains per sec are released. Most interestingly, the partially naked core−shell particle is still attached at the interface between air and water. This pinning of the PEGDA particle at the air−water interface

results from a complex wetting behavior of the re-entrant structured surface containing concave features and the residual hollow pollen grains on the PEGDA particle after the hydration-induced release of hollow pollen grains.[43,44] This immersed floating status persists up to several hours if physical shock is avoided.

Multifunctional Core–Shell Particles. Figure 5 demonstrates the expansion of the developed process to realize multifunctional core–shell particles with supracolloidal structures in a single batch. The PEGDA monomer can serve as a universal matrix for dispersing various types of functional nanofillers (Figure S8).[7–11] Figure 5a shows upconverting luminescent core–shell particles, successfully emitting various colors under the excitation of a NIR source (λ = 980 nm) by incorporating the lanthanide doped upconverting nanocrystals UCNs ($NaYF_4$:Yb/Er/Tm/Gd with different doping ratios) into the PEGDA monomer (Table S1). Under ambient light, all core–shell particles are identically lemon yellow in color due to the existence of uniform pollen shells on the hydrogel core and are no longer invisible when the light is turned off. When the core–shell particles are illuminated by a NIR source, they emit seven different visible colors (sky blue, orange, yellow, blue, green, gray, red) depending on the loaded UCN and can be visually distinguished without the aid of a microscope or other decoders.[10,11] Figure 5b shows optical microscopy images of core–shell particles stabilized by hollow pollen grains extracted from three different pollen species (castor beans, sunflowers, and olives) that brightly emit red, green, and blue colors, respectively, under the NIR excitation. The average sizes of the pollen grains obtained from olives and sunflowers are ~24 and ~38 μm, respectively. The three types of pollen grains that we tested have similar sizes although their surface morphology is slightly different. Numerous combinations of the type of pollen grain (uncountable) and a type of UCN (currently 9 emission colors) can be generated through this approach. Figure 5c shows magnetically responsive core–shell particles achieved by incorporation of Fe_2O_3 nanoparticles (<50 nm) into the PEGDA monomer. The resultant core–shell particles respond rapidly to magnetic force within ~40 ms, indicating that they can be manipulated for targeted delivery and be recollected after use. The functional nanofillers embedded in the PEGDA core remain in the cross-linked gel core after the hollow pollen grains are released. If the functional nanofillers are soluble, some may be released slowly during the gradual swelling of the PEGDA core in a water environment. Particles can be released much more rapidly after fracture of the PEGDA core due to the accumulated stress (Figure S6). Figure 5d proves the multifunctional abilities of core–shell particles that consist of UCNs and Fe_2O_3 nanoparticles together. Practically, the floated core–shell particle in an opaque vessel or a dark state is difficult to distinguish with the naked eye (see the left top image in Figure 5d). In contrast to this, a floating position of core–shell particles can be exactly identified by the visible upconverting emission of UCNs and can be manipulated by applying an external magnetic source, potentially applicable to floating delivery systems, micromachines, or future proppant technology.[25–27,42]

CONCLUSIONS

We report a facile method for the fabrication of core–shell structured hydrogel particles with hollow pollen grains exhibiting unique design capabilities in structure and function.

This study has several strengths: (1) This is the first combination of a biocompatible hydrogel and a hollow pollen grain extracted from naturally occurring pollens for supracolloidal particles. (2) This study newly discovers a transient floating behavior of core–shell particles arising from the hydration-induced release of pollen grains. (3) This study demonstrates the extendibility of the developed strategy to multifunctional core–shell particles. The exploration of other functional hydrogels and biological origins represents another promising direction for future work.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b02957.

> Recipes for preparing UCNs with different emission colors, wetting behavior of hollow pollen grains on hydrophilic and hydrophobic prepolymers, schematic illustrations of experimental details, SEM image of fractured hollow pollen grains, hypothesis of relationship between molecular weight of a PEGDA monomer and interface location of hollow pollen grains resulting in a Pickering emulsion, schematic illustration of relationship between the loading mass of hollow pollen grains and the size of core-shell particles, swelling-induced fracture of naked hydrogel particles, change in immersion depth of a free-floating core–shell particle and water level with time, and SEM images of pollen grains (PDF)

> Dynamic inflation behavior of pollen grains under water flow (AVI)

> Captured hollow pollen grains separate from the PEGDA core and the resultant core–shell particles slightly change to semitransparent appearance because of the lowered density of captured hollow pollen grains (AVI)

> Unique floating behavior based on a constantly changing wetting property, arising from the hydration-induced release of hollow pollen grains (AVI)

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Doshi, N.; Zahr, A. S.; Bhaskar, S.; Lahann, J.; Mitragotri, S. Red Blood Cell-Mimicking Synthetic Biomaterial Particles. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 21495−21499.

(2) Yeung, T. W.; Arroyo-Maya, I. J.; McClements, D. J.; Sela, D. A. Microencapsulation of Probiotics in Hydrogel Particles: Enhancing Lactococcus Lactis Subsp. Cremoris LM0230 Viability Using Calcium Alginate Beads. *Food Funct.* **2016**, *7*, 1797−1804.

(3) Oh, J. K.; Drumright, R.; Siegwart, D. J.; Matyjaszewski, K. The Development of Microgels/Nanogels for Drug Delivery Applications. *Prog. Polym. Sci.* **2008**, *33*, 448−477.

(4) Morin, E. A.; Tang, S.; Rogers, K. L.; He, W. Facile Use of Cationic Hydrogel Particles for Surface Modification of Planar Substrates Toward Multifunctional Neural Permissive Surfaces: an In Vitro Investigation. *ACS Appl. Mater. Interfaces* **2016**, *8*, 5737−5745.

(5) Weissman, J. M.; Sunkara, H. B.; Tse, A. S.; Asher, S. A. Thermally Switchable Periodicities and Diffraction from Mesoscopically Ordered Materials. *Science* **1996**, *274*, 959−960.

(6) Cho, S.-H.; Hong, J. H.; Noh, Y.-W.; Lee, E.; Lee, C.-S.; Lim, Y. T. Raspberry-Like Poly(γ-glutamic acid) Hydrogel Particles for pH-Dependent Cell Membrane Passage and Controlled Cytosolic Delivery of Antitumor Drugs. *Int. J. Nanomed.* **2016**, *11*, 5621−5632.

(7) Le Goff, G. C.; Srinivas, R. L.; Hill, W. A.; Doyle, P. S. Hydrogel Microparticles for Biosensing. *Eur. Polym. J.* **2015**, *72*, 386−414.

(8) Dendukuri, D.; Doyle, P. S. The Synthesis and Assembly of Polymeric Microparticles Using Microfluidics. *Adv. Mater.* **2009**, *21*, 4071.

(9) Pregibon, D. C.; Toner, M.; Doyle, P. S. Multifunctional Encoded Particles for High-Throughput Biomolecule Analysis. *Science* **2007**, *315*, 1393−1396.

(10) Lee, J.; Bisso, P. W.; Srinivas, R. L.; Kim, J. J.; Swiston, A.; Doyle, P. S. Universal Process-Inert Encoding Architecture for Polymer Microparticles. *Nat. Mater.* **2014**, *13*, 524−529.

(11) Kim, J. J.; Bong, K. W.; Reategui, E.; Irimia, D.; Doyle, P. S. Porous Microwells for Geometry-Selective, Large-Scale Microparticle Arrays. *Nat. Mater.* **2017**, *16*, 139−146.

(12) Pan, H. M.; Seuss, M.; Neubauer, M. P.; Trau, D. W.; Fery, A. Tuning the Mechanical Properties of Hydrogel Core-Shell Particles by Inwards Interweaving Self-Assembly. *ACS Appl. Mater. Interfaces* **2016**, *8*, 1493−1500.

(13) Kozlovskaya, V.; Kharlampieva, E.; Erel, I.; Sukhishvili, S. A. Multilayer-Derived, Ultrathin, Stimuli-Responsive Hydrogels. *Soft Matter* **2009**, *5*, 4077−4087.

(14) Cohen, I.; Li, H.; Hougland, J. L.; Mrksich, M.; Nagel, S. R. Using Selective Withdrawal to Coat Microparticles. *Science* **2001**, *292*, 265−267.

(15) Sefton, M. V.; May, M. H.; Lahooti, S.; Babensee, J. E. Making Microencapsulation Work: Conformal Coating, Immobilization Gels and In Vivo Performance. *J. Controlled Release* **2000**, *65*, 173−186.

(16) Goodwin, W. B.; Gomez, I. J.; Fang, Y.; Meredith, J. C.; Sandhage, K. H. Conversion of Pollen Particles into Three-Dimensional Ceramic Replicas Tailored for Multimodal Adhesion. *Chem. Mater.* **2013**, *25*, 4529−4536.

(17) Tsai, S. S. H.; Wexler, J. S.; Wan, J.; Stone, H. A. Conformal Coating of Particles in Microchannels by Magnetic Forcing. *Appl. Phys. Lett.* **2011**, *99*, 153509.

(18) Li, G. L.; Möhwald, H.; Shchukin, D. G. Precipitation Polymerization for Fabrication of Complex Core-Shell Hybrid Particles and Hollow Structures. *Chem. Soc. Rev.* **2013**, *42*, 3628−3646.

(19) Schmid, A.; Tonnar, J.; Armes, S. P. A New Highly Efficient Route to Polymer-Silica Colloidal Nanocoposite Particles. *Adv. Mater.* **2008**, *20*, 3331−3336.

(20) Kim, S.-H.; Lee, S. Y.; Yang, S.-M. Janus Microspheres for a Highly Flexible and Impregnable Water-Repelling Interface. *Angew. Chem., Int. Ed.* **2010**, *49*, 2535−2538.

(21) Sacanna, S.; Philipse, A. P. A Generic Single-Step Synthesis of Monodisperse Core/Shell Colloids Based on Spontaneous Pickering Emulsification. *Adv. Mater.* **2007**, *19*, 3824−3826.

(22) Lam, S.; Velikov, K. P.; Velev, O. D. Pickering Stabilization of Foams and Emulsions with Particles of Biological Origin. *Curr. Opin. Colloid Interface Sci.* **2014**, *19*, 490−500.

(23) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions Stabilised Solely by Colloidal Particles. *Adv. Colloid Interface Sci.* **2003**, *100−102*, 503−546.

(24) Mackenzie, G.; Boa, A. N.; Diego-Taboada, A.; Atkin, S. L.; Sathyapalan, T. Sporopollenin, the Least Known yet Toughest Natural Biopolymer. *Front. Mater.* **2015**, *2*, 235−259.

(25) Singh, B. N.; Kim, K. H. Floating Drug Delivery Systems: an Approach to Oral Controlled Drug Delivery via Gastric Retention. *J. Controlled Release* **2000**, *63*, 235−259.

(26) Ma, X.; Sun, X.; Hargrove, D.; Chen, J.; Song, D.; Dong, Q.; Lu, X.; Fan, T.-H.; Fu, Y.; Lei, Y. A Biocompatible and Biodegradable Protein Hydrogel with Green and Red Autofluorescence: Preparation, Characterization and In Vivo Biodegradation Tracking and Modeling. *Sci. Rep.* **2016**, *6*, 19370.

(27) Liang, F.; Sayed, M.; Al-Muntasheri, G. A.; Chang, F. F.; Li, L. A Comprehensive Review on Proppant Technologies. *Petroleum* **2016**, *2*, 26−39.

(28) Binks, B. P.; Boa, A. N.; Kibble, M. A.; Mackenzie, G.; Rocher, A. Sporopollenin Capsules at Fluid Interfaces: Particle-Stabilised Emulsions and Liquid Marbles. *Soft Matter* **2011**, *7*, 4017−4024.

(29) Binks, B. P.; Clint, J. H. Solid Wettability from Surface Energy Components: Relevance to Pickering Emulsions. *Langmuir* **2002**, *18*, 1270−1273.

(30) Mundargi, R. C.; Potroz, M. G.; Park, J. H.; Seo, J.; Tan, E.-L.; Lee, J. H.; Cho, N.-J. Eco-Friendly Streamlined Process for Sporopollenin Exine Capsule Extraction. *Sci. Rep.* **2016**, *6*, 19960.

(31) Diego-Taboada, A.; Beckett, S. T.; Atkin, S. L.; Mackenzie, G. Hollow Pollen Shells to Enhance Drug Delivery. *Pharmaceutics* **2014**, *6*, 80−96.

(32) Fadiran, O. O.; Meredith, J. C. Surface Treated Pollen Performance as a Renewable Reinforcing Filler for Poly(vinyl Acetate). *J. Mater. Chem. A* **2014**, *2*, 17031−17040.

(33) Binks, B. P.; Lumsdon, S. O. Pickering Emulsions Stabilized by Monodisperse Latex Particles: Effects of Particle Size. *Langmuir* **2001**, *17*, 4540−4547.

(34) Binks, B. P.; Clint, J. H.; Mackenzie, G.; Simcock, C.; Whitby, C. P. Naturally Occurring Spore Particles at Planar Fluid Interfaces and In Emulsions. *Langmuir* **2005**, *21*, 8161−8167.

(35) Ballard, N.; Bon, S. A. F. Hybrid Biological Spores Wrapped in a Mesh Composed of Interpenetrating Polymer Nanoparticles as "Patchy" Pickering Stabilizers. *Polym. Chem.* **2011**, *2*, 823−827.

(36) Zhang, H.; Wang, L.; Song, L.; Niu, G.; Cao, H.; Wang, G.; Yang, H.; Zhu, S. Controllable Properties and Microstructure of Hydrogels Based on Crosslinked Poly(ethylene Glycol) Diacrylates with Different Molecular Weights. *J. Appl. Polym. Sci.* **2011**, *121*, 531−540.

(37) Katifori, E.; Alben, S.; Cerda, E.; Nelson, D. R.; Dumais, J. Foldable Structures and the Natural Design of Pollen Grains. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 7635−7639.

(38) Voorn, D. J.; Ming, W.; van Herk, A. M. Polymer-Clay Nanocomposite Latex Particles by Inverse Pickering Emulsion Polymerization Stabilized with Hydrophobic Montmorillonite Platelets. *Macromolecules* **2006**, *39*, 2137−2143.

(39) Chen, T.; Colver, P. J.; Bon, S. A. F. Organic-Inorganic Hybrid Hollow Spheres Prepared from TiO_2-Stabilized Pickering Emulsion Polymerization. *Adv. Mater.* **2007**, *19*, 2286−2289.

(40) Choi, N. W.; Kim, J.; Chapin, S. C.; Duong, T.; Donohue, E.; Pandey, P.; Broom, W.; Hill, W. A.; Doyle, P. S. Multiplexed Detection of mRNA Using Porosity-Tuned Hydrogel Microparticles. *Anal. Chem.* **2012**, *84*, 9370−9378.

(41) Bohne, G.; Woehlecke, H.; Ehwald, R. Water Relations of Pine Exine. *Ann. Bot.* **2005**, *96*, 201−208.

(42) Oliveira, N. M.; Zhang, Y. S.; Ju, J.; Chen, A.-Z.; Chen, Y.; Sonkusale, S. R.; Dokmeci, M. R.; Reis, R. L.; Mano, J. F.; Khademhosseini, A. Hydrophobic Hydrogels: Toward Construction of Floating (Bio)Microdevices. *Chem. Mater.* **2016**, *28*, 3641−3648.

(43) Paunov, V. N.; Al-Shehri, H.; Horozov, T. S. Attachment of Composite Porous Supra-Particles to Air-Water and Oil-Water Interfaces: Theory and Experiment. *Phys. Chem. Chem. Phys.* **2016**, *18*, 26495−26508.

(44) Al-Shehri, H.; Horozov, T. S.; Paunov, V. N. Preparation and Attachement of Liquid-Infused Porous Supra-Particles to Liquid Interfaces. *Soft Matter* **2016**, *12*, 8375−8387.