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Long-Term Retention of Small, Volatile Molecular Species within Metallic Microcapsules

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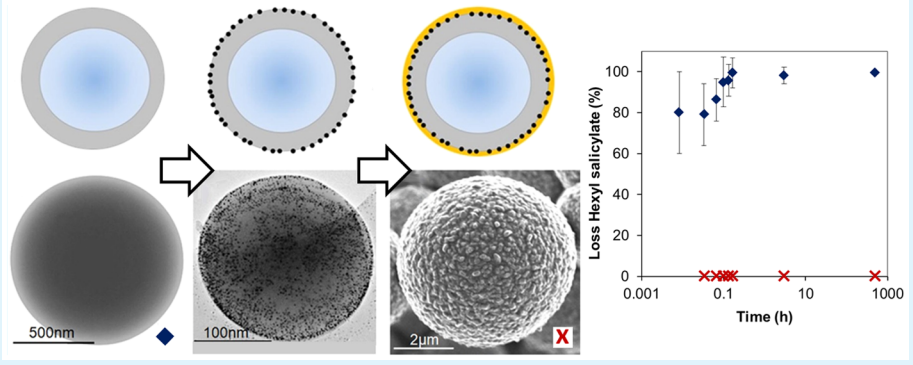
Supporting Information



ABSTRACT: Encapsulation and full retention of small molecular weight active ingredients is a challenging task that remains unsolved by current technologies used in industry and academia. In particular, certain everyday product formulations provide difficult environments in which preventing active leakage through capsule walls is not feasible. For example, a continuous phase that can fully dissolve an encapsulated active will typically force full release over a fraction of the intended lifetime of a product. This is due to the inherent porosity of polymeric membranes typically used as capsule wall material in current technologies. In this study, we demonstrate a method for preventing undesired loss of encapsulated actives under these extreme conditions using a simple threestep process. Our developed methodology, which forms an impermeable metal film around polymer microcapsules, prevents loss of small, volatile oils within an ethanol continuous phase for at least 21 days while polymeric capsules lose their entire content in less than 30 min under the same conditions. Polymer shell−oil core microcapsules are produced using a well-known cosolvent extraction method to precipitate a polymeric shell around the oil core. Subsequently, metallic catalytic nanoparticles are physically adsorbed onto the microcapsule polymeric shells. Finally, this nanoparticle coating is used to catalyze the growth of a secondary metallic film. Specifically, this work shows that it is possible to coat polymeric microcapsules containing a model oil system or a typical fragrance oil with a continuous metal shell. It also shows that the coverage of nanoparticles on the capsule surface can be controlled, which is paramount for obtaining a continuous impermeable metal film. In addition, control over the metal shell thickness is demonstrated without altering the capability of the metal film to retain the encapsulated oils.

KEYWORDS: *encapsulation, electroless deposition, impermeable metal shell*

1. INTRODUCTION

The efficient encapsulation of active chemicals with an associated controlled (and targeted) delivery is increasingly important to a range of industries.[1−6] The targeted delivery of actives using microcapsules provides potential benefits for many applications, for example, in pharmaceutical or agrochemical formulations by lowering the required dose in the final product. This has obvious cost benefits and, importantly, lower doses can reduce or eliminate detrimental side effects. While microencapsulation techniques are increasingly used for specific actives such as fragrances in personal care products, insecticides in agrochemicals, neutraceuticals in foods, and drugs in pharmaceuticals, there remain significant limitations for both the types of actives that can be encapsulated and the characteristics of the release profile that can be achieved.

Numerous methodologies for encapsulating and delivering specific actives (cancer drugs, pesticides, etc.) have been reported in the academic literature.[2,7−13] The proposed methodologies have yielded increasingly functional microcapsules but often the complexity of the synthesis processes involved is a significant barrier to the implementation of these advanced delivery technologies in every day products. A particular area requiring improvement concerns the encapsu-

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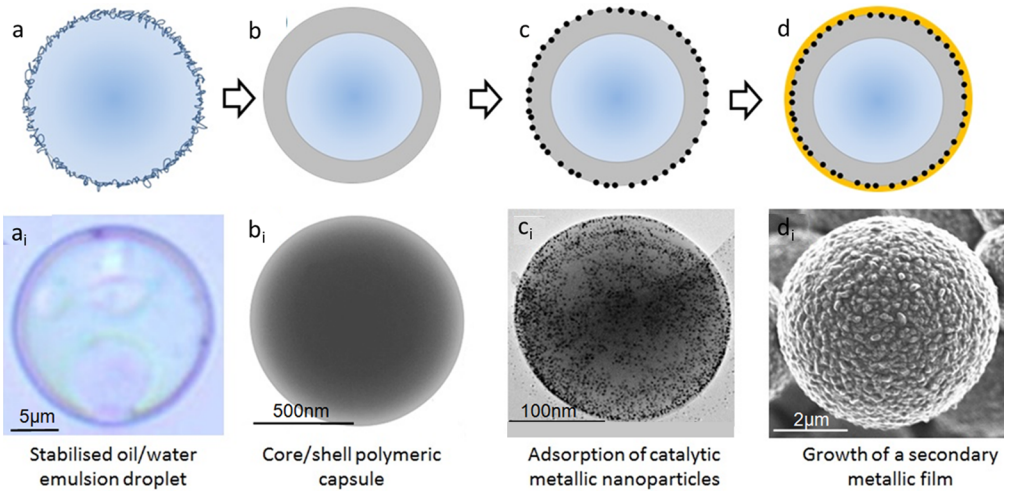

Figure 1. (a–d) Schematic diagrams and corresponding optical and (a_i–d_i) electron microscopy images of the different phases from emulsion droplet to metal coated capsule: (a) emulsion droplet, (b) capsule, (c) capsule with adsorbed NPs, (d) metal (Au) coated capsule, (a_i) emulsion droplet (optical microscopy), (b_i) capsule (TEM), (c_i) capsule with adsorbed NPs (TEM), and (d_i) metal-coated capsule (SEM). The micrographs correspond to different samples and are chosen to illustrate the evolution of the systems over the different steps.

lation and delivery of small molecules to which most typical microcapsule membranes (i.e., polymeric/particulate/lipid-based membranes) are highly permeable. In particular, small volatile compounds present a significantly difficult challenge when designing methods for controllably delivering such actives within formulated products. This is of specific relevance to the incorporation of fragrance oils and other small actives in personal care products, cosmetics, and home care products, for example. It is also important in a wide range of other areas (pharmaceuticals, foods) where the delivery of small actives (e.g., drugs, vitamins) is important. Arguably, the key challenge to using microencapsulation as an efficient delivery route for such small, volatile actives is the ability to retain them within the carrier capsule without leaching or potentially damaged by interaction with the environment. In this work, we propose a method that tackles this challenge in an environment (i.e., the continuous phase in which the capsules are dispersed) that can also dissolve the encapsulated active.

Several methods exist for significantly reducing the release rate of small, volatile actives from microcapsules, and those have been applied on the basis of standard laws of diffusion through membranes. Fickian laws of diffusion are typically used to describe the diffusion rate of an active ingredient permeating across a membrane as a function of time.[14] In the case of diffusion of an encapsulated active through a shell into an immiscible continuous phase, the following equation can be used as a general basis for understanding the microcapsule characteristics that control the release rate.

$$\frac{d_c}{d_t} = AHD(C_{\text{int}} - C_{\text{ext}})/x \quad (1)$$

where A is the surface area, H is the partition coefficient, D is the diffusion coefficient, C is the active concentration, and x is the shell thickness.

Here, the partition coefficient, H, defines the solubility of the core in the shell and, as such, is fixed for a particular core material. The diffusion coefficient, D, describes the diffusion of the core phase through the shell material. According to eq 1, the diffusion rate, d_c/d_t, can be significantly reduced by minimizing the relative solubility of the dispersed phase within the continuous phase.[12] Reducing the concentration difference between the capsule core and the continuous phase can also lead to drastically slower diffusion rates, but this does, of course, obviate the value of encapsulation. Thicker capsule shells will also have a beneficial effect but typically at the cost of reducing the volume of the capsule core, leading to smaller encapsulation efficiencies.[12]

Such measures are often considered/applied but typically do not lead to complete retention of active species. In particular, when the active ingredients have high vapor pressures, the diffusion rates tend to be dictated by the volatility of the species and are typically very high.[15] The successful long-term encapsulation of volatile molecules requires different materials than currently used (organic shells) to create impermeable barriers that can arrest the diffusion of actives from the capsule core. For example, polymeric materials produce diffusion coefficients in the order of 10^{-8} $cm^2.s^{-1}$ for highly volatile small molecules.[16] These relatively high diffusion coefficients render most currently implemented encapsulation methods inappropriate to achieve full retention of such actives, particularly in an environment that is capable of dissolving them. For example, microcapsules for which the release of a specific active is tested (e.g., a dye with suitable solubility characteristics) typically demonstrate a full release of the encapsulated species within days, more often within hours.[12,17,18] Recently, Zieringer et al. have demonstrated significantly low release rate of a dye molecule (>300 $g{\cdot}mol^{-1}$) and a divalent electrolyte in water across a fluoropolymer (PFPE) shell.[19] In this case, the poor wetting of the polymer shell by the solvent facilitates a very low permeability (for release tested over a period of 4 weeks). However, when the wetting is slightly improved by placing the capsules in an organic solvent, a sustained release of a dye initially dissolved in the toluene core was observed.

In this study, we hypothesize that the long-term retention of highly volatile small molecules can be possible in any environment when using amorphous/crystalline metals or inorganic crystals with very low diffusion coefficients (e.g., 10^{-15} cm^2 s^{-1} for hydrogen atoms diffusing across a metal film) as the shell material.[20,21] Films of these materials are considered impermeable due to their crystalline nature.[22] While atomic

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species can permeate through a crystalline metal surface,[23] a hydrocarbon chain larger than the interstitial spacing within the crystal is unlikely to be able to move through the lattice. Thus, metal films in the order of tens of nanometres in thickness should render the movement of small volatile molecules across the membranes negligible over the relevant time scales (i.e., those of product manufacturing, storage and use). Enabling the encapsulation of such small compounds could have very significant impact across many industries where active retention during product storage and triggered release during use (through mechanical action in this case) would be beneficial.

Here, we report a simple method to encapsulate low molecular weight volatile oils, as a proof of concept for the use of metallic microcapsule shells. Importantly, the microcapsules produced are capable of retaining a small aromatic hydrocarbon with negligible leakage upon changing the continuous phase from water to ethanol (which provides an environment where the encapsulated oil is fully soluble). The method we describe here uses an oil-in-water emulsion as the precursor for a polymeric microcapsule. Extraction of a cosolvent from the oil dispersed phase induces precipitation of a polymer (initially dissolved in the oil phase), which forms a shell of the resulting microcapsules.[24,25] This method typically allows for the production of systems with good control over shell thickness. Such microcapsules are not suitable for long-term retention of small, volatile actives. The prepared polymer microcapsules dispersed in water are the basis for the next steps in our procedure, which creates impermeable microcapsule shells through the electroless deposition of a metal film. The second step in the procedure consists of metallic nanoparticle adsorption onto the microcapsule polymeric shells. In a third step, this nanoparticle coating is used to catalyze/nucleate the growth of a secondary metallic film reduced in situ from the continuous phase.[26] Here, the catalytic nanoparticles on the surface of the polymer microcapsules reduce the energy barrier for the metal salt reduction and thereby serve to localize the reduction of the metal salt on the microcapsule surface, which also drastically limits precipitation of solid metal in the continuous phase.

Figure 1 shows a schematic diagram of the complete production process (a–d) and corresponding optical and electron micrographs of examples of microcapsules produced in each stage (a_i–d_i).

While there are methods available in the existing literature, to apply a metal coating to colloidal objects (mostly solid particles),[27−32] the simple three-step method proposed here allows for a full metal coating to efficiently encapsulate small volatile actives in their liquid form. Two other recent articles also report the use liquid core objects to deposit a metal coating.[33,34] In the first example, Patchan et al. sequentially adsorb multiple layers of polyelectrolyte, followed by tin and palladium ions before the target surface is suitable for metal deposition.[33] The method we propose here requires fewer synthetic steps to deposit the metal coating, which offers significant advantages with respect to the viability of an eventual manufacturing process. In the second example, Nocera et al. describe a method that requires the doping of a polymer membrane (surrounding an oil core) with metal ions and subsequent reduction of further ions in the continuous phase.[34] Although the primary aim of these experiments was to create core–shell structures with specific optical properties (the authors do not investigate the permeability of the metal films), this study creates a precedent to the methodology we describe here. However, the method described in Nocera et al. requires specific conditions, including a 2 h reaction time to deposit a layer of polydopamine for subsequent adsorption of the metal ions. In our case, the preparation of the surface for electroless deposition of the metal only requires adsorption of the nanoparticles, a step that can be completed within 10 min. Additionally, PVP-stabilized nanoparticles can be adsorbed to a broad range of surfaces and interfaces (including polymeric and charged surfaces) as a result of the polarity of the polymer stabilizer.[35]

In this study, we demonstrate that by metal coating polymer microcapsules, the release of a volatile oil from the core is effectively prevented, as compared to the core release observed with bare polymeric capsules. We also demonstrate an ability to control the nanoparticle surface density on the polymer, which plays a critical role in ensuring that the metal coating is continuous and impermeable. Finally, we also show control over the metal shell thickness by varying the reaction temperature for the metal growth step without affecting the release characteristics of the resulting microcapsules.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(methyl methacrylate) (PMMA) (120 kDa), cetyltrimethylammonium bromide (CTAB) 98%, toluene 99%, dichloromethane (DCM) >99%, poly(vinyl pyrollidone) (PVP) (40 kDa), chloroplatinic acid (H_2PtCl_6) 99%, chloroauric acid ($HAuCl_4$) 99.99%, 35% hydrogen peroxide, hexyl salicylate, 99%, and sodium borohydride were obtained from Sigma-Aldrich. All solutions were prepared using ultrapure Milli-Q water (resistivity of 18.2 MΩ·cm).

2.2. Methods. *2.2.1. Synthesis of Polymeric Capsules with Oil Core.* PMMA (5–10g) was dissolved in DCM (76–81g). The oil to be encapsulated (14g) was added and mixed until a single phase formed. This was used as the emulsion dispersed phase. CTAB (0.28g) was dissolved into 100 mL Milli-Q water to form the emulsion continuous phase. The dispersed phase (7 mL) and continuous phase (7 mL) were added to a glass vial and emulsified (using IKA T25 Ultra-Turrax) at 15 000 rpm for 2 min. The emulsion was then stirred magnetically at 400 rpm while a further 86 mL of continuous phase was poured in slowly. The diluted emulsion was then stirred at 400 rpm for 24 h at room temperature to allow capsule formation to occur—this stage allows for extraction of DCM into the continuous phase and subsequent evaporation, which forces precipitation of the polymer onto the emulsion droplet surface. The resulting capsules underwent three washing steps via centrifugation (Heraeus Megafuge R16) at 4000 rpm for 5 min, during which the supernatant was removed and replaced with fresh Milli-Q water. Finally, the capsules were redispersed in 50 mL Milli-Q water. Colloidal stability of the prepared capsules was verified over the time scale of the procedure through light scattering measurements.

2.2.2. Preparation of Platinum Nanoparticles. $H_2PtCl_6{\cdot}6H_2O$ (0.23 g) was added to an aqueous solution of PVP (100 mL, 1.56 μM) and stirred to dissolve. An aqueous solution of $NaBH_4$ (0.4 mL, 0.5 mM) was added to the platinum salt–PVP solution with vigorous stirring for 2 min. The mixture immediately turned dark brown, suggesting formation of solid platinum (as illustrated in eq 2), and was left to stand overnight for the formation of PVP-Pt nanoparticles to complete.[26]

$$NaBH_4 + H_2PtCl_6 + 3H_2O \rightarrow Pt + H_3BO_3 + 5HCl + NaCl + 2H_2 \quad (2)$$

The resulting suspensions were characterized through TEM and light scattering measurements, confirming the formation of Pt nanoparticles 2–4 nm in diameter.

2.2.3. Adsorption of PVP-Stabilized Pt Nanoparticles. PMMA capsules (1.0 mL, 2 wt %) were added to the PVP-Pt nanoparticle suspension (5 mL), and mixed for 10 min at 30 rpm. Immediately

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after, the capsules were washed by centrifugation at 4000 rpm for 5 min, three times. The capsules were subsequently redispersed in 30 mL Milli-Q water. Colloidal stability of the resulting Pt-loaded microcapsules was verified through light scattering measurements.

2.2.4. Au Film Growth. $HAuCl_4$ (1 mL, 40 mM), hydrogen peroxide (1 mL, 60 mM) and poly(vinyl pyrollidone) (1 mL, 0.05 mM; used in this procedure as a polymeric stabilizer to provide colloidal stability to the resulting microcapsules) formed the electroless plating solution, which was heated to 60 °C. Pt-loaded polymer capsules (3 mL, 0.6 wt %) pre-heated to 60 °C were added dropwise to the plating solution and stirred vigorously for 5 min, during which the gold ions were reduced to solid gold, as shown in eq 3. The capsules were subsequently washed by centrifugation at 4000 rpm for 5 min, three times.

$$2HAuCl_4 + 3H_2O_2 \xrightarrow{Pt} 2Au + 3O_2 + 8HCl \quad (3)$$

The resulting metallic-shell microcapsules were subsequently characterized through a range of methods described below.

2.3. Characterization. *2.3.1. Microscopy.* The morphology of the microcapsules was studied using an Olympus BX51 optical microscope, a LEO 1530 Gemini field emission gun scanning electron microscopy (FEGSEM), and an FEI Tecnai TF20 field emission transmission gun electron microscopy (FEGTEM) fitted with a HAADF detector and Gatan Orius SC600A CCD camera. Prior to TEM analysis, samples were dispersed on a TEM grid (holey carbon film, 400 Cu Mesh from Agar Scientific). Chemical compositions of the metal-coated microcapsules were analyzed using an Oxford Instruments INCA 350 energy dispersive X-ray spectroscopy (EDX) with 80 mm X-Max SDD detector, within the FEGTEM and FEGSEM instruments. To analyze metal shell thickness, cross sections of the capsules were taken using microtomy, prior to being studied by FEGTEM and analyzed using ImageJ image processing software.

2.3.2. Release Rate of Hexyl Salicylate Using Gas Chromatography (GC). In all our release experiments, we compared the metal-coated capsules against standard polymer-shell capsules. An equal portion of polymer capsules was removed from the sample undergoing the coating procedure. The polymer capsules were subjected to the same washing steps as the metal coated capsules to ensure equivalent losses of encapsulated oil (although minimal over the time scale of the experiment) from the capsule cores through the various stages of the process. Release rates in different solvent conditions were measured using gas chromatography as follows.

In a typical experiment, a known volume of metal-coated capsules was centrifuged to remove the supernatant. A corresponding sample of polymer-shell capsules was also centrifuged to remove the supernatant.

Each sample was dispersed in 2 mL of Milli-Q water and heated to 40 °C. Then, 8 mL of absolute ethanol at 40 °C was added to each sample and the capsules were redispersed and placed in a water bath at 40 °C. This procedure was chosen for compliance with industry standard tests. One milliliter (1 mL) of each agitated suspension was taken at known time intervals over a period of 21 days. The extracted capsule samples were centrifuged at 7000 rpm for 1 min and the supernatant analyzed via GC.

Samples were run on a PerkinElmer Clarus 580GC using the following method and column. GC column: Elite-1 capillary column; length, 30 m; internal diameter, 0.25 mm. The column temperature was programmed from 50 to 300 °C at 20 °C/min at a flow rate of 2 mL/min.

All data were compared against a calibration curve of the encapsulated oil determined in the same continuous phase of 4:1 ethanol−water mixture.

2.3.3. Measuring Nanoparticle Density on Capsule Surfaces Using TEM. TEM was employed to measure the surface adsorption density of PVP-Pt NPs on the capsule surface. Only capsules smaller than ∼500 nm diameter were sufficiently transparent to gather enough contrast between the NPs and the capsules to provide enough information for particle counting. Assumptions were made that no effects of curvature during the nanoparticle adsorption process were to be expected and that capsules of all sizes were coated with Pt nanoparticles to the same degree. The variation of intensity across the spherical capsules meant that automated counting software such as image J proved to be inadequate. Instead, once suitable small capsules were found, images were analyzed manually. The sample area distance from the center of the sphere was noted in each case. Each measurement was corrected for both surface curvature and the transparent nature of the capsules (as nanoparticles on both sides of the capsules were detectable, while only one hemisphere is being accounted for).

3. RESULTS AND DISCUSSION

3.1. Synthesis of Gold-Coated PMMA Capsules Containing a Toluene Core. For proof of principle that a polymer capsule can be coated with a metal film, a model system is used, where toluene is the core material and poly(methyl methacrylate) (PMMA) is the precipitated microcapsule polymer shell. Toluene is a small, volatile oil, which provides a good model for typical fragrance oils. In these experiments, PMMA shell microcapsules were formed from an initial oil-in-water emulsion template via the following steps. The emulsion-dispersed phase contained PMMA dissolved in DCM, a volatile good solvent for the polymer, and toluene, both a poor solvent for the polymer and the model encapsulate. Upon dilution of the emulsion in water, the DCM is extracted from the dispersed droplets, which induces precipitation of the polymer. Under the correct wetting conditions, as DCM is fully extracted (and evaporated), the polymer precipitates at the droplet surface, thus forming a complete shell around the oil core.[25,36,37]

The key variables affecting the capsule morphology and properties are the composition of the emulsion dispersed phase, the type and concentration of stabilizer used, and the method of emulsification. The stabilizer choice is a key determinant in the resulting capsule morphology.[25,36] By varying the "core" phase composition, it is possible to control the resulting polymer shell thickness in relation to the core.[38] For example, using the dispersed phase composition of PMMA 10 wt %, DCM 76 wt % and core oil 14 wt %, we obtain capsules with a 32% shell volume and, correspondingly, a 68% core volume. The size of the final capsules is dependent on the emulsification step, for which a number of routine methods exist for controlling droplet size and size distribution.[39]

Figure 2a shows a scanning electron micrograph of a typical sample of PMMA shell−toluene core microcapsules formed by ultraturrax homogenization.

Platinum nanoparticles are a known catalyst for electroless gold salt reduction and can be tailored to efficiently adsorb onto polymer substrates.[26] In our case, CTAB is used as the stabilizer during the synthesis of the polymer microcapsules and results in a net positive charge to the capsule surfaces (typical measured zeta potential of the polymer capsules is ∼ +60 mV). Such surfaces are thus suitable substrates for adsorption of both negatively charged and uncharged polymer-stabilized nanoparticles. In the example shown in Figure 2b, platinum nanoparticles stabilized with PVP are adsorbed onto the surface of PMMA microcapsules, under similar conditions to those reported by Nakao et al.[40] In brief, the nanoparticles were adsorbed by introducing a known quantity of PVP-stabilized Pt nanoparticles to the microcapsule suspension followed by a 10 min mixing step. This was found to be a sufficient time for the nanoparticles to efficiently adsorb to the capsule surface, as demonstrated in Figure 2b. However, careful consideration must be given to the ratio of PVP to platinum salt when preparing the nanoparticle suspension, as excess PVP in the

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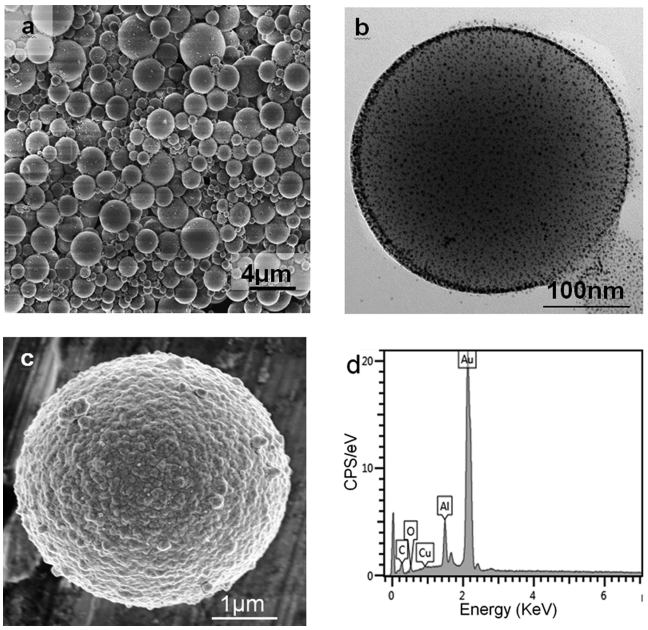

Figure 2. Example of toluene core microcapsules obtained for each step of the process leading to metal coated polymer capsule. (a) Scanning electron micrograph of PMMA microcapsules. (b) Transmission electron micrograph of PVP-stabilized Pt nanoparticle adsorbed onto PMMA microcapsules (note that the TEM observations are specifically focused on the smallest capsules to visualize the Pt nanoparticles throughout the whole shell). (c) Scanning electron micrograph of gold-coated PMMA microcapsules. (d) EDX analysis of metal-coated polymer microcapsules obtained during SEM observation.

system will compete with the PVP-stabilized Pt nanoparticles for surface adsorption sites on the capsule surfaces. This is the subject of further more systematic studies and will be reported separately.

A thin film of solid gold can be grown directly onto the adsorbed platinum nanoparticle layer using electroless plating. This method utilizes the platinum as a catalyst and nucleation site for gold growth in the presence of a reducing agent for the metal ions. By introducing the capsules to the electroless plating solution described in section 2.2.4 at 60 °C, and allowing the reaction to occur under mixing for 5 min, a continuous gold film can be deposited on the PVP-Pt-loaded polymer capsules. It is worth noting here that the presence of the nanoparticles localizes the deposition of solid gold onto the surface of the capsules, which limits further precipitation in the continuous phase. Once all the catalytic platinum sites are covered, the gold film can continue to grow, as gold nanoparticles also act as a catalyst for the decomposition of hydrogen peroxide, although this is a slower process.[41] The reaction is much faster at higher temperatures and so the platinum catalytic sites are used up rapidly, followed by autocatalytic gold growth at a faster rate than under ambient conditions.

The scanning electron micrograph and EDX graph in Figure 2c,d give evidence of the successful growth of the gold film on the capsule surface using this method.

3.2. Controlling the Density of Nanoparticles Adsorbed to the Capsule Surface. Surface adsorption homogeneity, surface density, and energy of adsorption of the catalytic PVP-Pt NP layer onto the microcapsule polymeric shells are important variables which can affect the quality of subsequent secondary metallic film growth via electroless deposition. This part of the work concentrates on the possibility of obtaining films of PVP-Pt nanoparticles of different surface densities, which is likely to affect the quality (i.e., the permeability) and thickness of the metal films.

By changing the concentration of PVP-Pt nanoparticles in the dispersion, it is possible to control the 2D density of the nanoparticles adsorbed onto the surface of the polymer capsules, as shown in Figures 3 and 4. When comparing the

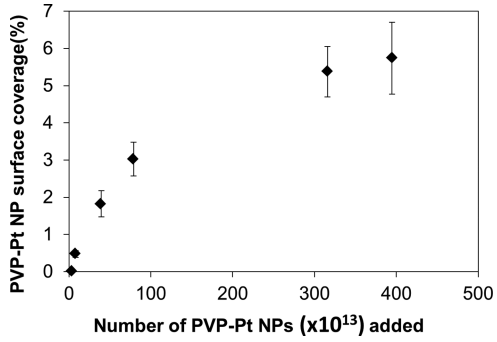

Figure 4. TEM data showing how the concentration of PVP-Pt NPs in the continuous phase affects the resulting adsorption density of the NPs on the polymeric microcapsule surface (conversion of number NPs per μm^2 to percentage surface coverage used mean diameter of NPs).

insets in Figure 3a and d, it is clear that the metal film growth is limited to the surface of the primary nanoparticles. Therefore, it is possible to conclude here that if the 2D density of the

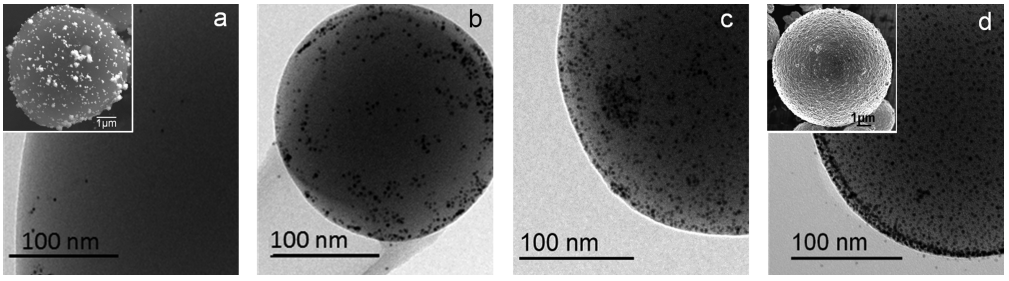

Figure 3. Transmission electron micrographs showing NP adsorption densities on the polymeric microcapsule surfaces as a function of the number of PVP-Pt nanoparticles added to 2 wt % polymer capsules. (a) 1.55×10^{15}, (b) 3.10×10^{15}, (c) 1.26×10^{16}, (d) 1.59×10^{16}. (a and d, insets) Corresponding gold-coated capsules (note that both these images were obtained using different electron beam intensity in order to adjust the required contrast between the polymer and gold areas; the location of the gold on the surface was verified via EDX).

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primary nanoparticle catalyst on the polymer capsule surface is sufficiently low (as shown in Figure 3a), the secondary metal film cannot grow on the full capsule surface. The maximum nanoparticle surface coverage achieved was measured at ~5% of the total surface area of the capsules (Figure 3d). This level of surface coverage is equivalent to a 2D hexagonal close packed PVP-Pt NP core−core separation of ~12 nm. However, it is worth noting here that the measurement only takes into account the platinum core of the nanoparticles and not the surrounding stabilizing PVP shell, as only the high-density Pt is resolved in the TEM. Indeed, close inspection of the nanoparticles on the capsule surface shows that the nanoparticles are not in close contact, which is consistent with other observations of sterically stabilized nanoparticle adsorption on surfaces.[42] Taking account of the stabilizing PVP layer, the observed 5% surface coverage (of the Pt cores) most likely corresponds to the maximum surface coverage. As seen in Figure 4, at higher nanoparticle concentrations, the surface coverage plateaus at this ~5% coverage. Such a low surface coverage is in agreement with surface adsorption of nanoparticles, where the spacing between the adsorbed particles can be influenced by the presence of a large polymer stabilizer or charged species on the surface of the nanoparticles.[43]

3.3. Encapsulation of a Fragrance Oil within an Impermeable Metallic Shell. The potential of metallic shell capsules for "permanently" encapsulating low molecular weight, volatile oils within a continuous phase that can dissolve the encapsulated actives is demonstrated in this section. Polymer capsules are porous and are known to allow diffusion of the core into the external environment,[8] particularly if there is a high solubility of the core in the continuous phase. Here, the potential of the developed metal shell capsules for retaining a volatile fragrance oil within their core is compared to that of the precursor polymer-shell capsules. The procedure for monitoring the release of the fragrance oil from both sets of capsules is described in section 2.3.2.

Although toluene proved to be a suitable system to test the nanoparticle adsorption and subsequent secondary metal film growth, its relatively high solubility in water (~0.52 g·L^{-1} at 25 °C) prevented its use for release testing. Thus, the fragrance oil used here is hexyl salicylate, an oil routinely used as a component of formulated products. It has poor water solubility (~9×10^{-4} g·L^{-1} at 25 °C) which is advantageous as compared to the use of toluene. This ensures maximum core retention through the precursor polymer capsules preparation and washing procedure before porosity testing (at 40 °C) in 4:1 ethanol/water mixtures. In this case, polymer capsules produced from an oil emulsion template initially containing 10 wt % PMMA were coated with Pt nanoparticles and a film of solid gold, as described in sections 2.2.3 and 2.2.4.

Characterization of the release of hexyl salicylate was performed with gas chromatography for both sets of capsules. Figure 5 shows that the bare polymer capsules release their entire contents into the ethanol−water mix within 20 min.

When a gold film is grown on the surface of the precursor polymer capsules (at a reaction temperature of 60 °C), only a small fraction of the initially encapsulated oil is released, (typically smaller than the error associated with the measurement) over the 21 day test period.[22] By mechanically fracturing the metal-coated capsules (as demonstrated in the inset of Figure 5) and testing the sample again for core release, we measured a release of 49% of the initial hexyl salicylate oil present in the precursor polymeric capsules, thus confirming

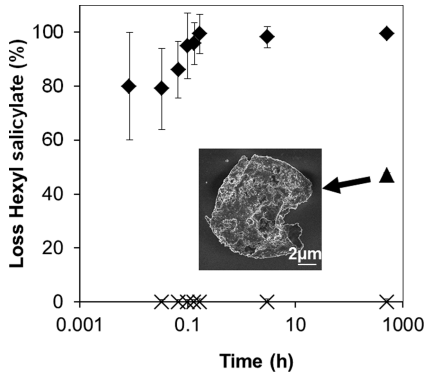

Figure 5. (♦) Hexyl salicylate release profile from PMMA capsules and (×) gold coated PMMA capsules, placed in 4:1 ethanol−water at 40 °C. (▲) Release of encapsulated oil observed from mechanically fractured gold coated capsules (after residing in ethanol−water mixture for 7 days). (Inset) SEM image of a mechanically fractured gold coated PMMA capsule with hexyl salicylate core.

the presence of encapsulated oil within the metal shell microcapsules. The fact that not all of the oil was recovered from the mechanically fractured capsules is likely due to loss of material during the fracturing procedure and because not all capsule shells were successfully broken.

3.4. Controlling Metal Shell Quality. This part of the work investigates the effect of the electroless plating reaction temperature over the shell thickness of the metal film produced and its resulting permeability. By reducing the reaction temperature for the metal growth, it is expected that we will obtain thinner metal films as a consequence of a slower reaction rate.[44] Growth of thinner metal films are a potential cost advantage with regards to a manufacturing process provided the capsule impermeability can be retained.

Figure 6 shows that as the temperature decreases, the measured shell thickness (via transmission electron microscopy

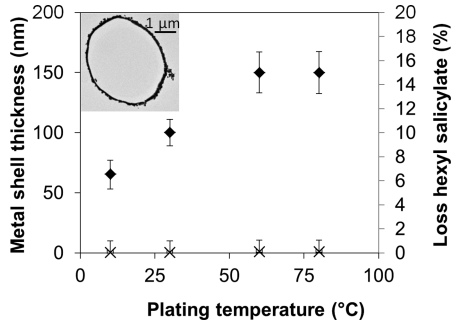

Figure 6. (♦) Thickness of metal shell as a function of plating temperature, measured from microtome images using TEM, and (×) release of core as a function of plating temperature (4:1 ethanol−water mixture for 7 days at 40 °C). (Inset) TEM image showing a microtomed capsule from which shell thicknesses are measured. A high-magnification image of part of this cross section is shown in the Supporting Information.

of microtomed samples and subsequent image processing) decreases significantly from 150 to 60 nm. However, above 60 °C, the film thickness appears to reach a plateau. This phenomenon is potentially linked to the gold salt supply being fully depleted due to the faster rate of reaction at higher temperatures leading to metal formation in the bulk solution.

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Release studies conducted for the four samples of capsules obtained by varying the film growth temperature show no significant release (a maximum of 0.1 wt %, which is within experimental error) of the encapsulated oil into the water/ethanol bulk phase. The full retention of the core oil implies that a complete impermeable shell is formed in all cases independently of its thickness. It is expected that further optimization of the metal film growth conditions could lead to sub-10 nm impermeable films.

4. CONCLUSIONS

In this work, we have successfully demonstrated that a polymeric microcapsule containing a small, volatile oil, can be coated with an impermeable metal shell preventing significant release of the core material over days. The nanoparticle density on the polymeric capsule surface can be controlled, which can be used to vary the final metal film thickness and structure. By reducing the electroless plating reaction temperature we can achieve thinner, continuous films that retain their impermeability. This control provides advantages with respect to cost efficiency and operating conditions, both of which have positive implications for manufacturing. The use of expensive metal components in this demonstrated example can be justified when using these systems in high-margin products such as perfumes, but further work will investigate different catalysts and metal coatings such as silver, copper, and nickel, which will open up the potential of this platform technology for the delivery of a large range of other active ingredients.

■ ASSOCIATED CONTENT

Supporting Information

High-magnification TE micrograph showing part of a cross section of a typical hexyl salicylate core−PMMA shell−gold capsule at a plating temperature of 30 °C (full cross section shown in the inset of Figure 6). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03116.

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Notes

The authors declare no competing financial interest.

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