

Synthesis of Spherical Polymer and Titania Photonic Crystallites

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The fabrication of small structured spherical particles that are essentially small photonic crystals is described. The particles are 1–50 μm in diameter and are porous with nearly close-packed monodisperse pores whose size is comparable to the wavelength of light. The solid matrix of the particles is titania, which provides a large refractive index contrast between the particle matrix and pores. The particles are made by encapsulating polymer colloidal particles in emulsion droplets of hexanes in which a titanium alkoxide precursor is dissolved. Subsequent osmotic removal of the hexanes from the droplets and condensation of the alkoxide precursor leads to spherical aggregates of polymer spheres with titania filling the spaces between the polymer spheres. The polymer particles are then burned out leaving behind the desired porous titania particles. The size and structure of the pores and high refractive index of the titania matrix are expected to produce particles that are very efficient scatterers of light, making them useful as pigments.

Introduction

There are now several well-established methods for making bulk photonic materials from ordered arrays of colloidal particles. The general approach involves first preparing a suitable colloidal crystalline template to produce periodic voids of a specific size and then infiltrating the interstices with either a precursor solution or nanoparticulate suspension of a high-dielectric-constant material such as titanium dioxide (titania). After the template for the periodic voids is removed, the precursor (or particles) can be crystallized and densified to produce a photonic crystal.¹ Various materials have been used to make the monodisperse spherical voids; these include emulsions of identical oil droplets,^{2,3} polymer colloids,^{4–6} and silica spheres.^{7,8} The precursor can be either introduced in situ^{2,3,6} or via infiltration after crystallization of the template.^{4,5}

The resulting ordered, macroporous materials, often called *inverse opals* or *inverse crystals*, have unique and useful optical properties. In principle, if the refractive

index contrast is sufficiently high and the pores are well ordered, an inverse opal can completely inhibit the propagation of light over a finite frequency band. Light incident on such a *photonic band gap* material will be completely reflected, regardless of the angle of incidence. This effect might be exploited to create new types of waveguides and optical devices. Unfortunately, it is extremely difficult to fabricate a material with a band gap in the visible part of the spectrum. It is important to note, however, that even in cases where a complete band gap does not exist, light will be perfectly reflected for waves incident along any direction that couples the light into a stop band within the crystal.⁹ In most cases, this condition leads to the complete reflection of light over a wide range of incident angles, even if a complete photonic band gap is not present. Moreover, for light incident along those directions that do not couple into a stop band, light generally will still be strongly reflected, owing to the large dielectric mismatch between the photonic crystal and air (or other medium). We believe this feature of photonic crystals can be exploited to create small structured particles, approximately 2–50 μm in size, that exhibit much stronger scattering of light than is possible with other comparably sized particles.

The basic idea we pursue in this paper is the fabrication of small, spherical *supraparticles* that are, in effect, little photonic crystals. Instead of focusing on bulk material, the goal here is to fabricate structured, composite particles with diameters in the 1–50 μm range, which could serve as very efficient scatterers of light. Such supraparticles might be used as pigments in paints or as light diffusers

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for various light sources, including light bulbs or display screens. As such, they may be more versatile in practical applications than bulk photonic crystals. Ultimately, they also provide a testing ground for how the optical properties of finite-sized photonic crystals are different from those of bulk photonic crystals. This may provide new opportunities for designing and controlling their optical attributes.

Our method, shown in Figure 1, employs elements of the templating techniques used to prepare bulk photonic materials. However, instead of large colloidal crystals, we prepare dense colloidal aggregates and use these as templates. We refer to these aggregates, which are typically spherical, as *supraparticles* or *direct supraparticles*; we refer to the photonic particles comprising monodisperse spherical holes in a spherical titania matrix as *inverse supraparticles*. Here we focus on the assembly of these structures; the optical properties will be discussed in a subsequent article. The process we describe allows us to produce large amounts of sub-100 μm inverse supraparticles with high refractive index contrast and variable void sizes.

Background

Dense aggregates of colloidal spheres were first reported by Velev et al.¹⁰ They emulsified octanol in an aqueous suspension of latex spheres, which were treated with a surfactant to render them more hydrophobic. This caused the spheres to accumulate at the interface between the octanol and water. After removal of the octanol, spherical aggregates of disordered spheres, on the order of 10–50 μm in diameter, were produced. Later, they produced aggregates of colloidal spheres using a water-in-oil (fluorinated) emulsion.¹¹ The aggregates, which were formed when the water was removed, were well ordered but much larger in size, typically several millimeters across, and of varying shape. We note that direct rather than inverse crystals were made using this method.

Iskander et al.¹² showed that porous, spherical ceramic particles could be fabricated by nebulizing an aqueous suspension of polystyrene (PS) spheres mixed with silica nanoparticles. The nebulized droplets were passed through a furnace to consolidate the latex particles and trap the silica colloid in the interstices. The polystyrene was ultimately burned off, leaving behind spherical voids. The resulting silica particles had an average size of 300 nm with void sizes of about 50 nm. Although the PS spheres were not well ordered, this work did show that large spherical particles could be made with internal spherical voids.

We show below that ordered supraparticles can be formed if the particles can be prevented from collecting at the interface of the droplets. Particle adsorption is driven by surface tension, and it occurs in any system in which the droplet surface energy is higher than the particle–liquid surface energies. A simple geometric argument^{13,14} shows that the energy required to move a particle from the oil–water interface into the oil phase is given by

$$E = \pi r^2 \gamma_{\text{ow}} (1 + \cos \theta)^2 \quad (1)$$

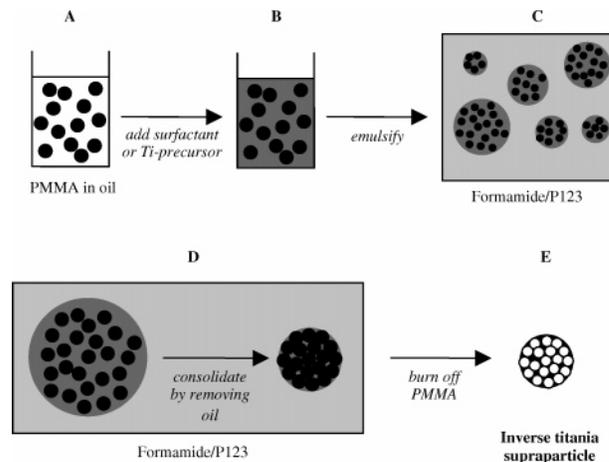


Figure 1. Schematic of the fabrication process for PMMA supraparticles (A–D) and inverse titania supraparticles (A–E).

where r is the radius of the particle, γ_{ow} the oil–water surface energy, and θ the contact angle, as defined by Young's equation

$$\cos \theta = (\gamma_{\text{po}} - \gamma_{\text{pw}}) / \gamma_{\text{ow}} \quad (2)$$

with γ_{po} being the particle–oil surface energy and γ_{pw} the particle–water surface energy. For micrometer-sized particles, the binding energy is typically many times the thermal energy, kT , except when the contact angle approaches 180° .

Methods and Materials¹⁵

Overview. Figure 1 shows how we make inverse supraparticles. First, small spherical assemblies of colloidal spheres are formed within emulsion droplets containing an alkoxide precursor for titania; next, the liquid is removed from inside the emulsion droplets while the alkoxide precursor condenses, forming titania around the colloidal spheres; finally, the colloidal spheres are removed from the assemblies, leaving behind the desired photonic particles consisting of a solid spherical (titania) matrix. Each particle contains a more-or-less close-packed array of monodisperse spherical holes.

Alternatively, the alkoxide precursor can be left out of the emulsion droplets to make spherical particle aggregates. Such direct supraparticles are less useful from the point of having extraordinary optical properties. Nevertheless, they may be of interest for certain applications and, in particular, are useful for studying the ordering of the colloidal spheres inside the emulsion droplets.

There are several constraints that must be considered in fabricating the supraparticles. First, to accommodate the alkoxide titania precursor within the emulsion droplets, it is necessary to exclude any water from the emulsion since water causes the titanium–alkoxide precursors to gel. Even if water is present only in the continuous phase, it still causes the titania precursor in the droplet phase near the droplet interface to condense. For this reason, we use formamide for the continuous phase. An additional and critically important factor in choosing formamide is its ability to accommodate common surfactants that can prevent coalescence of oil droplets.¹⁶ We know of no other nonaqueous polar solvents that can be used as the continuous phase.

Second, the colloidal particles must also repel each other with sufficient force that the particles do not irreversibly aggregate.

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This leaves the colloidal particles free to rearrange and form a close-packed structure. We use poly(methyl methacrylate) spheres sterically stabilized by grafted poly(dimethylsiloxane) (PDMS) chains. The particles are stable in short-chain hydrocarbons and can form ordered packings.¹⁷

Third, as discussed above, the colloidal particles that are placed inside the emulsion droplets must be completely wetted by the oil inside the droplets. Incomplete wetting leads to the accumulation of particles at the interface between the droplets and the continuous phase. We use mixtures of surfactants, both water- and oil-soluble, to control the surface energies and wetting properties.

Unless otherwise noted, all chemicals were used as received without further purification.

Synthesis of Polymer Colloid. PMMA particles with grafted 55 000 g/mol PDMS chains were prepared by dispersion polymerization as described in previous work.¹⁷ After synthesis, the particles were washed and redispersed in hexanes (98.5%, mixture of isomers, Fisher Scientific). The particles used in the experiments described below were 600 nm in diameter with less than 5% polydispersity.

Preparation of PMMA Supraparticles. A schematic of the supraparticle (and inverse titania supraparticle) fabrication process is shown in Figure 1. The PMMA/hexane suspension (Figure 1A) was emulsified in formamide (99%, spectrophoto-metric grade, Aldrich) using the triblock copolymer (ethylene glycol)₂₀–(propylene glycol)₇₀–(ethylene glycol)₂₀ (denoted by the manufacturer as P123, molecular weight = 5800 g/mol, Aldrich) to stabilize the hexane droplets.¹⁶ To change the wetting behavior of PMMA in hexane, an extra surfactant, one of a series called Span-80/83/85, was added to the hexane (Span-80 is sorbitan monooleate, Span-83 sorbitan sesquioleate, Span-85 sorbitan trioleate, Aldrich) (Figure 1B). The PMMA/Span/hexane suspension was emulsified into the P123/formamide solution, either by hand shaking or with the help of a vortex mixer (Figure 1C). For typical preparations, we used 10% v/v PMMA particles in the hexane phase and 1% w/w P123 in formamide.

The hexane was then removed in order to allow the PMMA spheres to consolidate and form supraparticles. This was done either by allowing the hexane to evaporate slowly through the continuous formamide phase into air or, more rapidly, by mixing small droplets of a second oil such as decane (99%+, Aldrich) into the formamide/hexane–PMMA emulsion. The decane droplets adsorb nearly all the hexane within a few seconds, causing the PMMA spheres to pack together (Figure 1D).

Preparation of Inverse Titania Supraparticles. The preparation of inverse supraparticles is similar to that of the (direct) supraparticles, except that a titanium dioxide precursor, typically a titanium (IV) butoxide (Aldrich), is added to the PMMA/hexane suspension prior to emulsification. We also tested several other alkoxides, ranging from titanium methoxide to nonylaloxide, with varying degrees of success (see Results section). The PMMA/alkoxide/hexane suspension was emulsified into a P123/formamide solution as described above. Since absorbed water can trigger premature precipitation of the titanium alkoxide, we prepared fresh P123/formamide solutions in a dry-nitrogen glovebox prior to each synthesis. After the suspension was emulsified, decane was added in the manner described above to absorb the hexane and consolidate the particles. The titanium alkoxide, which is insoluble in formamide, becomes trapped in the voids of the PMMA aggregate when the hexane is removed. To gel the precursor, we added an excess of water. The suspension was then subjected to a heat treatment at temperatures between 350 and 700 °C to burn out the PMMA spheres and crystallize the titania (anatase). After the heat treatment, the inverse titania supraparticles were removed from the oven and redispersed by mild ultrasound (Bath Sonicor, Fisher) in water or alcohol.

Characterization of Supraparticle Formation. We followed the process of supraparticle formation in situ with transmitted light, Nomarski differential interference contrast microscopy. A 100× oil-immersion lens with numerical aperture 1.4 was used. Images were taken with a high-resolution CCD camera attached to the microscope (Nikon Eclipse TE300, Japan).

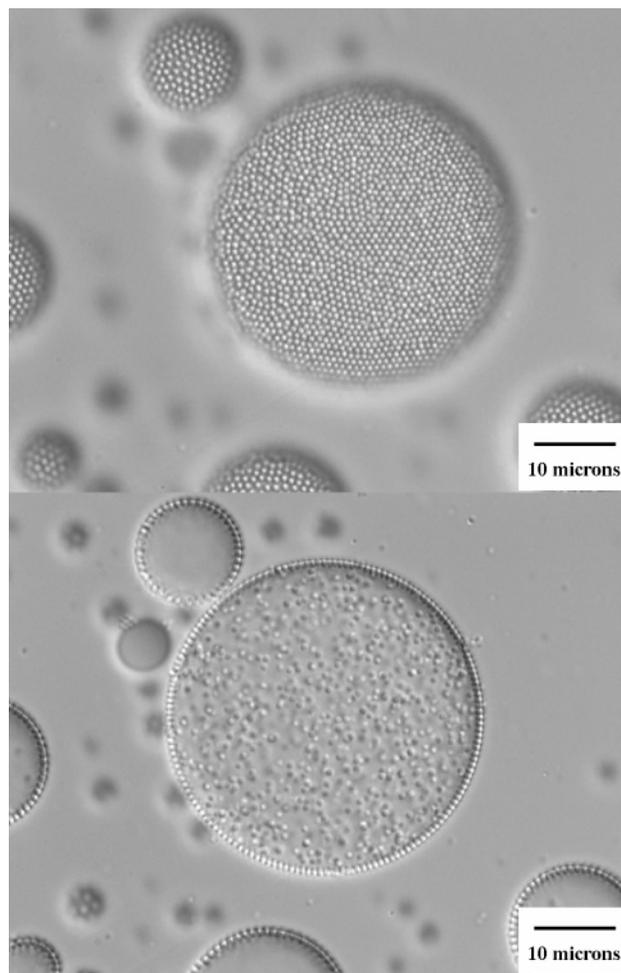


Figure 2. Optical micrographs of 10% v/v PMMA particles in hexane, after emulsifying in P123/formamide. (top) Focal plane near top of droplets. (bottom) Focal plane near equatorial plane of droplets. The PMMA particles prefer to stick to the hexane/formamide interface.

Dried suspensions of supraparticles from various stages of the process were imaged by scanning electron microscopy (SEM, JEOL 6300F field emission microscope).

Interfacial Measurements. To investigate the wetting properties of the particles, we measured the oil/formamide interfacial tension and the contact angle of the PMMA/oil/formamide system. Interfacial tensions were measured with a ring tensiometer and a platinum–iridium ring (Model 20F, Fisher Scientific). Contact angles were measured for hexane droplets on flat PMMA substrates with a contact angle goniometer (Model A-100, Ramé–Hart, Inc). To prepare the substrates, we dried an aliquot of PMMA suspension on a glass slide then heated it to 175 °C for several hours so that the particles sintered together and formed a film. The coated glass slide was placed at the bottom of a square plastic container filled with either hexane or Span-80/hexane solution. A drop of formamide was placed on top of the substrate, and an average contact angle was determined by measuring advancing and receding contact angles.

Results and Discussion

PMMA Supraparticles. For emulsions of hexane droplets in P123/formamide, we found that the PMMA particles preferred to stick to the hexane/formamide interface. Figure 2 shows two optical micrographs taken with narrow depth of focus, one of which shows the top of the emulsion droplets and the other the equatorial plane (the bottom part of the droplet looks very similar to the top). In the smaller droplets, PMMA particles are located only at the interface, whereas in the larger droplets

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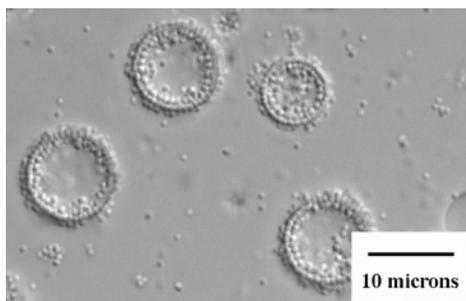


Figure 3. PMMA particles form shells as the hexane is removed from the droplets. The focal plane of these optical micrographs is the equatorial plane of the hexane/PMMA droplets; formamide (containing 1% w/w P123) is the continuous phase.

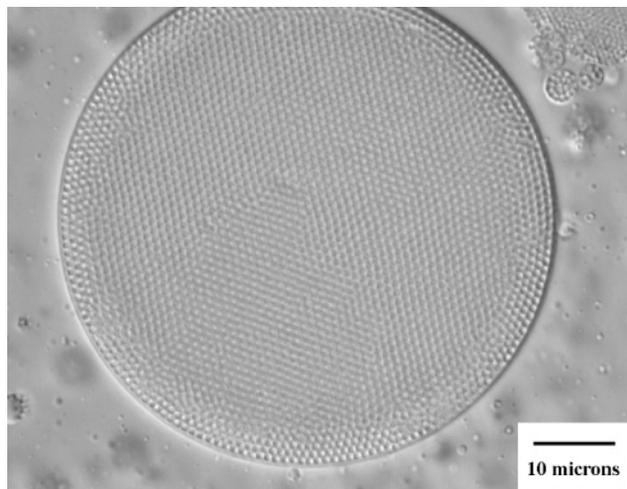


Figure 4. Optical micrograph showing the equatorial cross section of an emulsion droplet (15% v/v PMMA in hexane with 1% v/v Span-80, emulsified in formamide containing 1% w/w P123) after most of the hexane has evaporated. Particles at the interior form close-packed, ordered arrays.

particles are found in the interior as well as at the interface. This observation suggests that the particles must saturate the droplet interface before they can start to fill the interior. Emulsions in which the hexane contained 20% v/v PMMA particles behaved similarly.

When hexane was removed from emulsion droplets such as those in Figure 2, the resulting supraparticles were frequently misshapen, hollow, or fractured shells (see Figure 3). Formation of hollow spheres suggests that the layer of particles that accumulates at the interface prevents the shrinkage of the droplet as hexane is removed. We tried adding different surfactants (in particular, other Pluronic) to the formamide at various concentrations, but no combination of formamide-soluble surfactants prevented the particles from sticking to the interface. Changing the dispersed phase from hexane to other alkanes also did not alleviate the problem.

However, when we used a combination of a formamide-soluble surfactant such as P123 and a hexane-soluble surfactant such as Span-80, we found that far fewer particles stuck to the interface. Furthermore, when we removed the hexane from droplets containing Span-80, the particles consolidated into dense aggregates. Figure 4 shows an equatorial cross section of such a supraparticle during the later stages of hexane evaporation. Although near the interface the particles form rings (ostensibly shells in three dimensions), the inner particles self-assemble into close-packed, ordered arrangements. In addition, no hollow or misshapen supraparticles were formed in this sample.

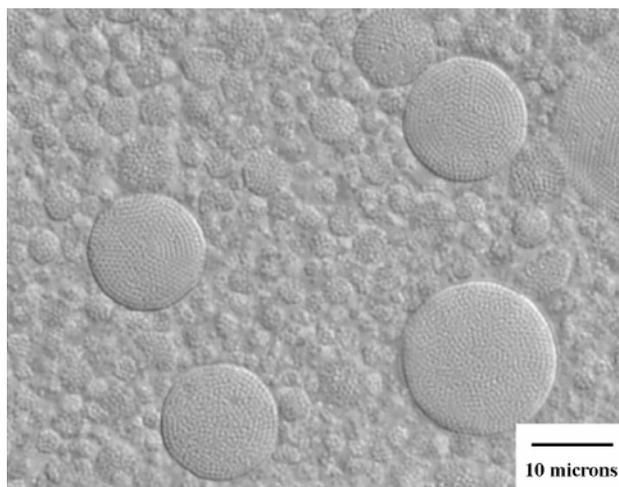


Figure 5. Optical micrograph of supraparticles made from samples containing Span-80. The moderately sized (roughly 10 μm in diameter) supraparticles show complex, polycrystalline morphology, presumably due to surface effects during consolidation. Some of these supraparticles are no longer perfectly spherical, but have developed facets.

Increasing the volume fraction of PMMA in Span-80/hexane increased the fraction of supraparticles with well-ordered interiors. However, below 10% v/v PMMA, few supraparticles were ordered. Varying the concentration of Span-80 from 1 to 5% v/v (in the hexane phase) did not change the consolidation behavior, but at 10% the particles could not pack densely and at 25% the particles flocculated. In all the formulations, it was necessary to add the P123 to the formamide; when Span-80 was the only surfactant, the system formed an unstable inverse (formamide-in-hexane) emulsion upon mixing.

Although the consolidation rate was not well controlled, we found that very rapid consolidation, achieved by adding large quantities of emulsified decane, produced supraparticles with poorly ordered PMMA particles.

Interfacial Measurements. We expect that the two surfactants, P123 and Span-80, adsorb not only on the formamide-hexane interface but also on the particle-liquid interfaces. Thus, all three surface energies in the system can vary with the addition of surfactant. Fortunately, as eq 1 shows, the effects of the addition of surfactant on the adsorption behavior of the particles can be described in terms of two macroscopic parameters: the hexane-formamide surface energy (analogous to the oil-water surface energy, γ_{ow}) and the three-phase contact angle, θ . We measured both of these parameters for the two solvents, both with and without surfactant.

We found the surface tension of a pure hexane-formamide interface without any surfactant to be 21.0 ± 1.0 mN/m. When either 1% w/w P123 was added to the formamide or 1% v/v Span 80 was added to the hexane, the surface tension dropped to less than 0.5 mN/m (in both cases, the absolute surface tension value was smaller than the measurement error). When both surfactants were added, it was not possible to measure the surface tension since a macroemulsion tended to form whenever the two liquids were disturbed.

The addition of Span-80 to the hexane also increased the contact angle substantially. We measured a contact angle of $149^\circ \pm 5^\circ$ for the PMMA/hexane/formamide bulk system and a contact angle of $169^\circ \pm 3^\circ$ when 5% v/v Span-80 was added to the hexane. In other words, the Span-80 allowed the hexane to better wet the PMMA substrate. Since the energy of binding a particle to a droplet

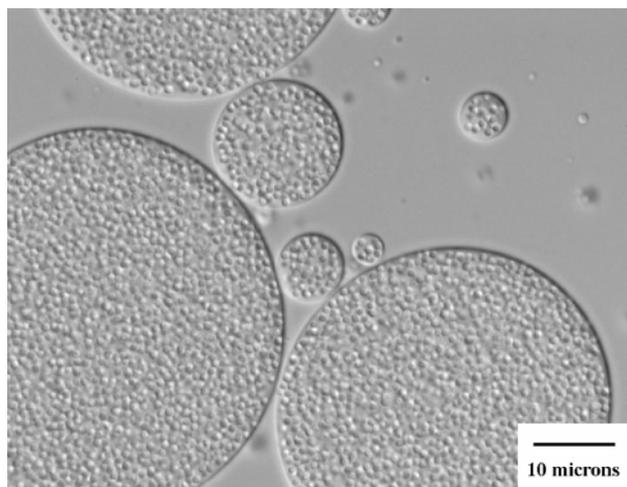


Figure 6. Optical micrograph of PMMA/hexane emulsified in P123/formamide where the emulsion droplets contain titanium *n*-butoxide. The focal plane is near the equatorial plane of the droplets. Long-chain titanium alkoxides prevent the PMMA particles from sticking to the interface of the droplets, allowing them to pack densely upon consolidation.

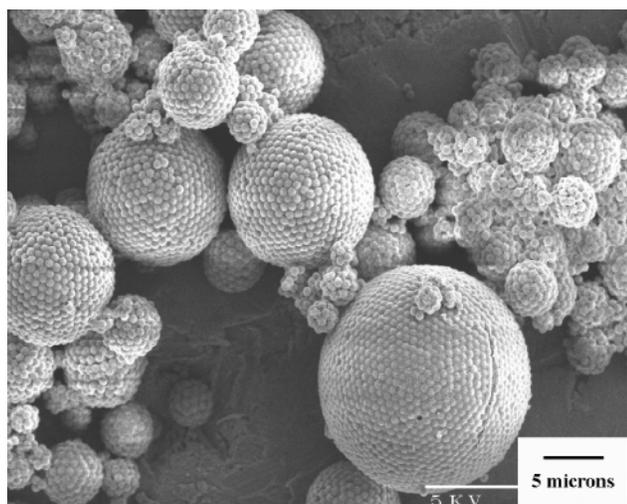


Figure 7. Scanning electron micrograph of PMMA supraparticles containing gelled titanium alkoxide precursor prior to heat treatment.

interface goes as $(1 + \cos \theta)^2$, the observed change in contact angle reduces the binding potential by a factor of 60. If we assume a hexane–formamide interfacial tension of 0.1 mN/m, consistent with our measurements, then according to eq 1, the interface binds a 600 nm diameter particle by a potential of about $100kT$. When Span-80 is present, the potential drops to $1-2kT$. This explains why particles are less likely to be found at the interface in the Span-80 system.

Even when the particles do not stick to the droplet surface, the spherical formamide–hexane interface can influence the packing during consolidation. For a large supraparticle, one with a diameter many times the particle diameter, we would expect this influence to be weak far from the interface. As seen in Figure 4, particles near the center of large supraparticles do tend to form face-centered cubic (FCC) crystallites. Smaller supraparticles, however, show more-complex structures, presumably because surface effects dominate the packing (Figure 5). Similar types of surface reconstruction have been observed at the atomic scale in spherical nanocrystals.^{18,19}

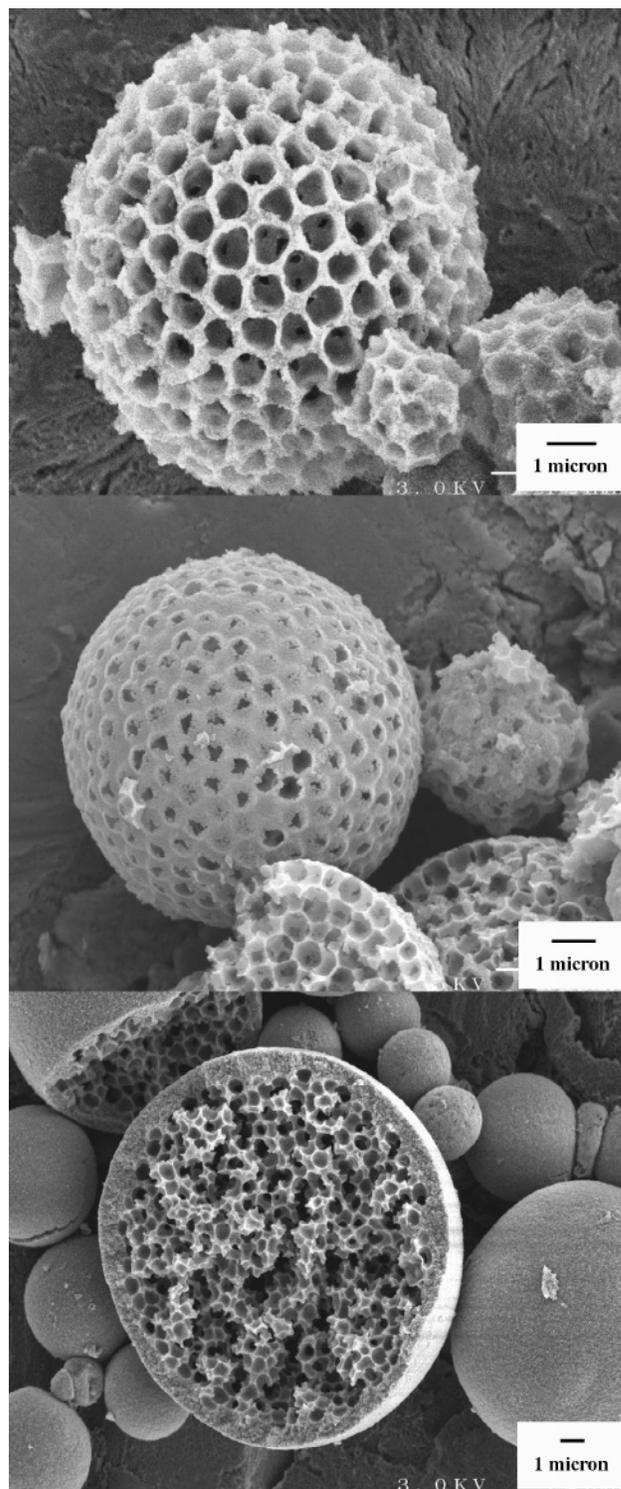


Figure 8. Scanning electron micrographs of inverse titania supraparticles prepared by burning out the PMMA from direct supraparticles containing alkoxide. These images are from three different batches, with varying amounts of titanium alkoxide relative to PMMA. (top) Inverse titania supraparticle with open void structure formed at low alkoxide/PMMA ratio. The second layer of pores can be seen through the first. (middle) A slight excess of alkoxide leads to a thin shell of titania on the outside of the supraparticles. Fractured particles show that the interior is still porous. (bottom) A large excess of alkoxide leads to a thick shell. Again, the supraparticles retain their internal porous structure.

Preparation of Inverse Titania Supraparticles. Although the fabrication process for inverse titania supraparticles is similar to that of PMMA (direct) su-

praparticles, the reactivity of the titanium alkoxide presents some obstacles. No stable emulsions could be prepared with short-chain, reactive alkoxides such as titanium ethoxide, titanium *n*-propoxide, or titanium isopropoxide. These gelled as soon as the PMMA/alkoxide/hexane dispersion was mixed with the P123/formamide solution. Even though we took all necessary precautions to keep the formamide dry, there was apparently enough water to induce hydrolysis and condensation.

On the other hand, longer-chain alkoxides such as titanium *n*-butoxide and titanium 2-ethylhexoxide did not gel until water was added to the dispersion. Interestingly, when these alkoxides were used, the PMMA particles did not stick to the interfaces of the droplets (no Span-80 was added to the alkoxide systems). Figure 6 shows an emulsion where the dispersed phase contains PMMA and titanium *n*-butoxide in hexane. We suspect that either the alkoxides or the alcohols liberated upon partial hydrolysis of the alkoxides act as oil-soluble surfactants, much like Span-80. Unfortunately, the reactivity of the titania precursors prevented us from measuring the interfacial tension or contact angle of the alkoxide systems.

The SEM images in Figure 7 show the sample after consolidation of the PMMA spheres and gelation of the titania precursor. The gelled titania is difficult to see because it remains inside the interstices of the PMMA spheres. We found no hollow supraparticles in this or any of the other samples prepared from long-chain alkoxides. Optical micrographs taken during the evaporation of hexane show that the particles are densely packed near the center of the supraparticles but are not as well ordered as in the direct supraparticles prepared with Span-80.

Burning out the PMMA spheres yields spherical macroporous titania particles. These inverse supraparticles can be redispersed in water or other polar liquids such as ethanol by mild ultrasonication. Figure 8 shows SEM images of three different batches prepared with varying ratios of alkoxide to PMMA. When more alkoxide is used than is needed to fill the interstices of the PMMA supraparticle, the excess forms a solid exterior shell. In all cases, however, the interiors of the inverse supraparticles were completely porous.

Conclusions

The synthetic method presented here affords a quick and straightforward preparation of highly spherical and stable colloidal supraparticles and inverse supraparticles. The yield of this process is high, with nearly all of the

polymer spheres being incorporated into the assemblies. The process also allows us to produce inverse supraparticles with intact pore structures and variable exterior shell thickness. Because the technique is emulsion-based, it can readily be scaled up to produce large quantities of supraparticles.

An important feature of the method described here is the use of two different kinds of surfactants: standard water- or formamide-soluble surfactants, such as P123, and oil-soluble species, such as the Span surfactants or the titanium alkoxides. When both of these are present, the particles do not collect at the droplet interface. The change in the three-phase contact angle induced by the addition of these secondary surfactants brings the binding energy close to the thermal energy, allowing the particles to roam freely throughout the droplet and form dense, ordered supraparticles upon consolidation. In addition, the use of sterically stabilized polymer (PMMA) spheres prevents the formation of aggregates in the hexane emulsion droplets.

In this article, we have focused on TiO₂ because of its high refractive index and strong light-scattering properties. As such, it may be useful in coatings applications where thin, opaque coatings that use a minimum of titania are needed. In principle, inverse supraparticles can be made from any other materials, such as silica, for which a precursor can be found and emulsified as shown here. An important remaining task is to investigate the optical properties of the inverse supraparticles, using theoretical modeling, as well as light scattering measurements. To make meaningful comparison between theory and experiment, we would like to be able to fabricate monodisperse or nearly monodisperse supraparticles, that is, supraparticles where the overall diameter, and not only that of the macropores, is uniform. To this end, a more controlled emulsification method is required.

Finally, we note that the supraparticles have potential applications beyond optical materials. The direct supraparticles may, for example, serve as a model system for examining surface reconstruction in finite-sized crystallites such as atomic nanocrystals. Also, because it is possible to vary the inverse supraparticle size, air hole size, and porosity, these materials should find uses in catalysts, filters, or photovoltaic materials, especially when the process is expanded to materials other than titania.

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