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Wettability Engendered Templated Self-assembly (WETS) for Fabricating Multiphasic Particles

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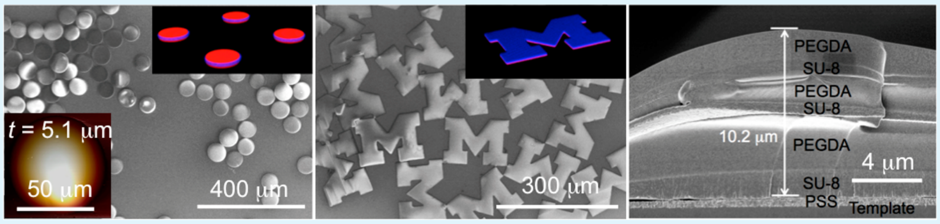
Supporting Information



ABSTRACT: Precise control over the geometry and chemistry of multiphasic particles is of significant importance for a wide range of applications. In this work, we have developed one of the simplest methodologies for fabricating monodisperse, multiphasic micro- and nanoparticles possessing almost any composition, projected shape, modulus, and dimensions as small as 25 nm. The synthesis methodology involves the fabrication of a nonwettable surface patterned with monodisperse, wettable domains of different sizes and shapes. When such patterned templates are dip-coated with polymer solutions or particle dispersions, the liquids, and consequently the polymer or the particles, preferentially self-assemble within the wettable domains. Utilizing this phenomenon, we fabricate multiphasic assemblies with precisely controlled geometry and composition through multiple, layered depositions of polymers and/or particles within the patterned domains. Upon releasing these multiphasic assemblies from the template using a sacrificial layer, we obtain multiphasic particles. The templates can then be readily reused (over 20 times in our experiments) for fabricating a new batch of particles, enabling a rapid, inexpensive, and easily reproducible method for large-scale manufacturing of multiphasic particles.

KEYWORDS: *multiphasic particles, precise patterning, particles fabrication, patterned surfaces, wettability*

INTRODUCTION

Precise control over the geometry and chemistry of multiphasic (monophasic, biphasic or Janus, triphasic, quad-phasic, etc.) micro- and nanoparticles is of significant importance for a wide range of applications including drug delivery,[1−3] vaccines and inhalation biotherapeutics,[4] biological sensors,[5] optical devices,[5] and nanomotors.[6] Further, in the bottom-up approach envisioned for building materials and devices of the future, it is necessary to develop precisely designed particles (building blocks) that can assemble in a preprogrammed manner to yield desired structures and properties.[7−14] However, typically, fabricated particles have a uniform distribution of all materials (isotropic). In order to design particles that self-assemble in a preprogrammed manner, it is essential to control the size, shape, and distribution of dissimilar materials within each particle to form anisotropic particles, such as Janus, triphasic, or quad-phasic particles.[7−11] Although many different routes for synthesizing such multiphasic particles have been explored previously,[15−19] a simple technique for the fabrication of monodisperse, multiphasic particles of any desired composition and size, with precise control over particle geometry, has not been developed thus far. In this work, we have developed a facile technique termed WETS (Wettability Engendered Templated Self-assembly) which provides an unprecedented ability for the large scale manufacturing of monodisperse, multiphasic particles possessing almost any projected shape, composition, modulus, and dimensions as small as 25 nm, using a simple dip-coating process.

When a liquid comes in contact with a smooth homogeneous surface, it can either wet the surface completely, or partially, making a finite equilibrium contact angle (θ_E) with the surface. The equilibrium contact angle is determined by the balance between the solid−vapor (γ_{SV} or the surface energy), solid−liquid (γ_{SL}), and liquid−vapor (γ_{LV} or the surface tension) interfacial tensions acting at the three-phase contact line and is given by Young's relation $\cos \theta_E = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$.[20] The contact angles for a liquid as it advances or recedes from a smooth surface are called the advancing (θ_A) and receding (θ_R)

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contact angles, respectively. When a substrate with a receding contact angle, $\theta_R = 0$, is pulled through a liquid, the substrate is coated with a uniform liquid film of finite thickness, controlled by the dip-coating velocity.[21−23] In contrast, when a partially wetting surface ($\theta_R > 0$) is dip-coated, the liquid film is unstable and dewets off the surface, leaving the surface completely dry for dip-coating velocities below a critical value[21−24] (see Supporting Information (SI) section 1). Similarly, when a nonwettable (or low surface energy) surface patterned with wettable domains is dip-coated, the liquid wets and coats only the wettable (or high surface energy) domains and leaves the nonwettable surface completely dry.[24−28] This wettability engendered self-assembly of the liquid within the patterned wettable domains is due to unbalanced forces acting on the solid−liquid−air three phase contact line (see SI section 1).

There have been several reports[24,26−28] on using surfaces with patterned wettability to engender the self-assembly of water ($\gamma_{LV} \sim 72$ mN/m) and water-based polymer solutions or dispersions. However, typically, it has been more difficult to self-assemble low surface tension organic liquids (such as alcohols, dimethylformamide, tetrahydrofuran, toluene, etc.) or polymer solutions within patterned high surface energy domains.[25] This is because organic solvents and polymer solutions possess low surface tension values ($\gamma_{LV} \sim 15−30$ mN/m), and as a consequence they tend to wet and spread on both the high and low surface energy patterned domains, forming a film over the entire surface.

■ RESULTS AND DISCUSSION

In this work, we employed smooth, low surface energy, silanized titanium dioxide (TiO_2) surfaces (see Experimental Methods) that possess finite receding contact angles (θ_R) for both water and different low surface tension liquids (including fluorinated liquids) and patterned them with high surface energy domains ($\theta_R = 0$) of different shapes and sizes. Such surfaces serve as templates to engender the self-assembly of both aqueous and organic polymer solutions and dispersions (see SI section 2). We fabricated the patterned templates by irradiating the TiO_2 surfaces with deep UV light (254 nm) through a quartz photomask possessing any desired pattern (see Figure 1a). Upon deep UV irradiation, the surface energy of TiO_2 surfaces in the unmasked regions increases significantly due to the photocatalytic cleavage of the TiO_2−silane bond.[28−30] This simple fabrication process gave us a nonwettable surface patterned with wettable domains defined by the mask geometry. When such templates are dip-coated with a polymer solution (or dispersion), the solution preferentially wets and self-assembles within the patterned wettable domains. Upon evaporation of the solvent, the polymer (or particles from a dispersion) deposits within the patterned high surface energy domains, conforming to their shape and size (see Figures 1 and 2).

We observe similar assembly of liquids within the patterned high surface energy domains for spin- or spray-coating. Further, this wettability-engendered templated self-assembly of polymers or particles works effectively with a wide variety of polymer solutions and dispersions (see SI section 2). Thus, the WETS technique can serve as a facile, bottom-up approach to pattern a wide variety of polymers and particles with precise control over geometry. In addition, utilizing the WETS technique, we sequentially deposited multiple polymers and inorganic particles, one on top of another within the wettable domains, to fabricate multiphasic assemblies. Upon releasing the multiphasic assemblies from the template by dissolving away a predeposited sacrificial layer, we obtained multiphasic particles with precisely controlled geometry and chemistry.

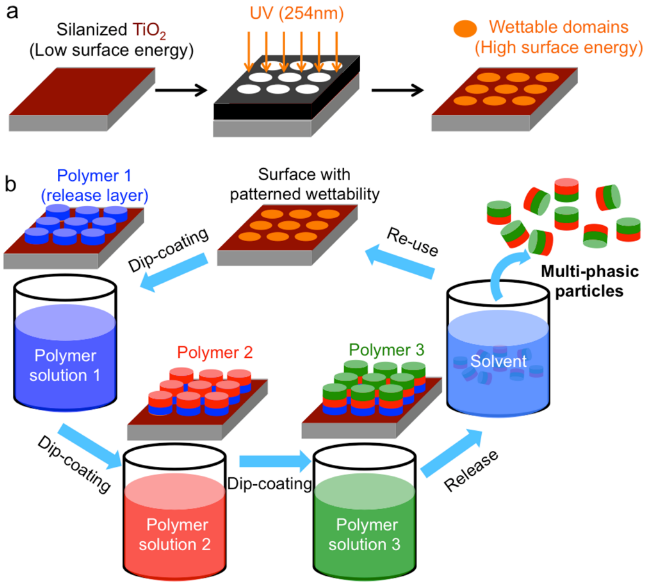

Figure 1. WETS technique for fabricating multiphasic particles. (a) A schematic illustrating the fabrication of TiO_2 templates with patterned wettability. (b) A schematic illustrating the WETS technique for fabricating multiphasic particles.

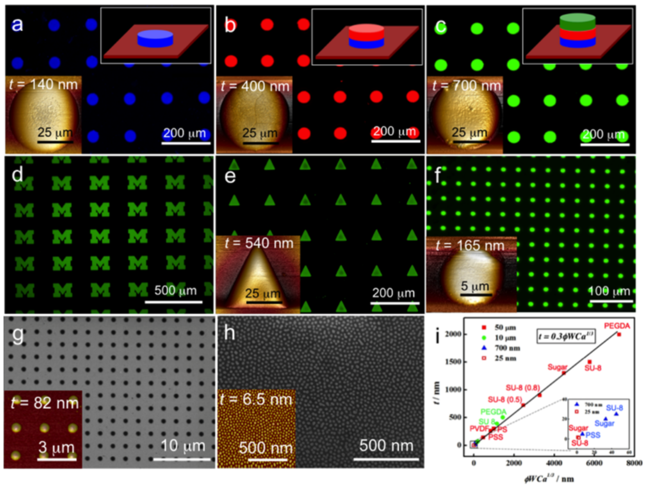

Figure 2. WETS enabled multiphasic assemblies. Fluorescent micrographs showing wettability engendered assembly of (a) poly(sodium 4-styrenesulfonate) (PSS; dyed blue), (b) poly(vinylidene fluoride) (PVDF; dyed red) on top of PSS, and (c, d, e, and f) polystyrene (PS; dyed green) on top of PVDF and PSS. The top insets in a−c show schematics of the polymer layers within the high surface energy (or wettable) domains. The bottom insets in a−c, e, and f show the corresponding AFM height images and the thickness (t) of the polymer assembly. (g and h) SEM images of the multiphasic assemblies, TiO_2−PSS−SU-8−PS and TiO_2−Sugar−SU-8−PS within the 700 and 25 nm high surface energy domains, respectively. The bottom insets show the corresponding AFM height images and the thickness (t) of the multiphasic assembly. The thickness "t" corresponds to thickness measured at the center of the particle. (i) A plot comparing the predicted (solid black line) and measured (individual data points) thicknesses for a variety of polymers. The thickness t for the polymer depositions within patterned domains is an average value across 30 domains.

After release of the particles from the template, the templates can be readily reused (over 20 times in our experiments) for fabricating a new batch of multiphasic particles (see Figure 1), enabling a rapid, inexpensive, waste-free (significant when fabricating particles that encapsulate expensive biomolecules and drugs),[1] and easily reproducible method for manufacturing multiphasic particles.

In order to demonstrate the fabrication of multiphasic polymer particles using the WETS technique, we first deposited poly(sodium 4-styrenesulfonate) (PSS; using PSS in water solution) within the wettable domains (see Figure 2a), followed by poly(vinylidene fluoride) (PVDF; using PVDF in dimethylformamide solution) on top of PSS (see Figure 2b) and finally polystyrene (PS; using PS in toluene solution) on top of PVDF and PSS (see Figure 2c). Note that the preferential assembly of polymer solutions on top of the preceding polymer patterns is driven by the difference in receding contact angles between the polymer patterns and the nonwettable background (see SI section S2). After depositing each polymer layer, we annealed the surfaces slightly above the glass transition temperature of the polymers to ensure good adhesion between the layers. We confirmed this sequential deposition of polymers, one on top of another, using fluorescence microscopy and atomic force microscopy height measurements (see Figure 2a–c, corresponding insets, and SI section 3). Additional layers can be stacked within the wettable domains from other polymer solutions, as long as the solvents do not affect the already deposited polymer layers. The projected shape and size of the multiphasic assemblies (PSS–PVDF–PS) can be precisely controlled by utilizing a patterned surface possessing the desired geometry as a template (see Figure 2d–f).

Further, the methodology works across a wide range of domain sizes. Figure 2g shows the assembly of PS, on top of SU-8 (MicroChem Corp, Epoxy series), on top of PSS (see AFM measurements in SI section 4), within 700 nm domains. Fascinatingly, the WETS technique even extends to the sub-50-nm-length scale (see AFM measurements in SI section 4). Figure 2h shows the assembly of PS, on top of SU-8, on top of sugar within patterned 25 nm wettable domains. The templates with 25 nm wettable domains were developed utilizing block copolymer nanolithography (BCNL). BCNL was necessary to fabricate these monodisperse (~25 nm diameter) domains because the inherent diffraction limit of light precludes the use of common photolithographic techniques. BCNL is a scalable alternate approach that utilizes molecular self-assembly processes to generate regular nanoscopic patterns, ~5–50 nm, in size.[31,32]

The thickness (t) of the liquid or polymer solution film deposited within the wettable domains of a patterned surface is dependent on the width of the wettable domain (W) and the capillary number ($\mathrm{Ca} = \mu V/\gamma_{\mathrm{LV}}$) for dip-coating. Here, μ is the viscosity of the polymer solution, and V is the dip-coating velocity. The thickness of the polymer solution deposited within the wettable domain is given by $t = kW\mathrm{Ca}^{1/3}$ where k is a proportionality constant.[24] After the solvent has evaporated, the thickness of the polymer layer deposited within the wettable domain can be approximated as $t = k\phi W\mathrm{Ca}^{1/3}$, where ϕ is the volume fraction for the polymer in the solution. The thicknesses predicted using this approach matched well with our experimental thickness measurements (as shown in Figure 2i) for different polymer solutions deposited within wettable domains, possessing a range of different sizes (25 nm to 50 μm). Using this understanding, it is possible to directly control the specific thickness of each individual layer within the multiphasic particles to within a few nanometers of any desired value. The variation in thickness of the biphasic (PSS–SU-8–PS) and triphasic (PSS–SU-8–PS) polymer assemblies deposited within 700 nm wettable domains is ±1 nm and ±2 nm, respectively (SI section 4). The thickness (t) values reported for the particles here correspond to the thicknesses measured at the center of the particle. The thickness profile for the polymer solutions deposited within the wettable domains is convex due to the liquid droplet morphology. However, upon evaporation of the solvent, the thickness profile of the polymers deposited within the patterned domains can be either convex or flat or concave (coffee-ring effect) -shaped depending on the solvent evaporation rate and contact-line pinning.[33] The assembled multiphasic particles can be released upon dissolving the sacrificial polymer layer (PSS) in water (see Figure 3). In this manner, the WETS technique allows for the fabrication of a wide variety of monodisperse (see SI sections 4 and 5), multiphasic particles with precise control over the size, projected shape, composition, thickness, and placement of the different polymer phases within the particle.

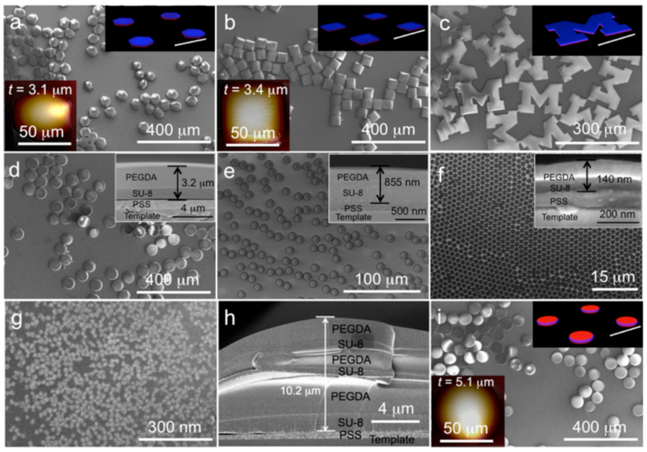

Figure 3. Multiphasic particles fabricated using the WETS technique. (a–f) SEM images of the released biphasic amphiphilic particles comprising SU-8 (dyed red) and PEGDA (dyed blue) polymers of hexagon (a), square (b), complex shapes (c), and circular shapes of diameters 50 μm (d), 10 μm (e), and 1.5 μm (f). (g) SU-8–PS biphasic polymeric nanoparticles, 25 nm in diameter. (h) A cross-sectional SEM image for a hexa-phasic particle composed of alternating layers of SU-8 and PEGDA, on top of the PSS sacrificial layer. The thickness of each layer can be independently controlled. (i) SU-8–PEGDA–SU-8 triphasic particles. The top insets in a–c show corresponding 3-D stacked fluorescence confocal microscopy images of the particles before release. SU-8 is dyed red, and PEGDA is dyed blue. Scale bars for the top insets in a–c represent 100 μm. The top insets in d–f show the corresponding SEM cross-section images of the multiphasic particles before release. The bottom insets in a and b show the corresponding AFM height images and thickness (t) of the released particles.

We also fabricated multiphasic particles by utilizing cross-linkable oligomers. The cross-linkable oligomers offer the freedom to deposit multiple layers using the same polymer solution without any detrimental effects on the already deposited layers. Here, we chose one of the cross-linkable oligomers to be hydrophobic (SU-8) and the other to be hydrophilic (poly(ethylene glycol)diacrylate, PEGDA) in order

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to impart amphiphilicity to the cross-linked multiphasic particles. To fabricate these amphiphilic particles, first PSS patterned templates (see Figure 2a) were dip-coated with SU-8 and cross-linked with UV irradiation (365 nm). Next, the templates were dip-coated with a mixture of PEGDA and its cross-linker (Darocur 1173) and also cross-linked with UV irradiation (365 nm). This process resulted in biphasic amphiphilic assemblies deposited on top of PSS within the patterned domains (see SI section 6). The amphiphilic particles were subsequently released from the templates by dissolving the PSS sacrificial layer in water. By changing the volume fraction of the cross-linker, it was easy to control the modulus of each individual phase within the amphiphilic particles.[34] Precise control over the modulus[34,35] and projected shape[1,2,4,34−36] of the fabricated particles can be critical in developing drug carriers with enhanced circulation times and enabling their accumulation within specific target sites. Figure 3a−c show PEGDA−SU-8 amphiphilic particles of different shapes, fabricated using the WETS technique.

Figure 3d−g show different circular biphasic (PEGDA−SU-8) particles, of different dimensions, fabricated in this work. Cross-sectional SEM images of the multiphasic assemblies in different sizes clearly highlight the distinct phases comprising the multiphasic particles (see Figure 3d−f and SI section 6). We also fabricated biphasic, polymer nanoparticles with diameters as small as 25 nm (see Figure 3g) by releasing the multiphasic polymer assemblies shown in Figure 2h (and SI section 4). While there have been a few previous reports,[37,38] in general it has been extremely difficult to fabricate organic nanoparticles of desired chemistry possessing all dimensions below 50 nm.[16,34] Thus, although various inorganic nanoparticles, possessing different shapes and with all dimensions below 30 nm are commercially available, even single-phase organic nanoparticles possessing similar dimensions are not. To the best of our knowledge, the WETS technique is the only methodology that allows for the fabrication of monodisperse, multiphasic particles of essentially any projected shape, composition, and dimensions as small as 25 nm. Particles within the size range of 10−100 nm, when used as drug carriers, exhibit high circulation time in blood and provide high tumor accumulation.[1,2,35]

In addition, we fabricated hybrid, organic−inorganic, biphasic particles with SU-8 and SiO$_2$ nanoparticles (see SI section 7). Furthermore, we stacked up to six polymer layers, comprising alternate layers of hydrophobic and hydrophilic phases, within the wettable domains (see Figure 3h and SI section 8). Cross-sectional SEM images of the multiphasic assembly clearly show the deposition of alternating SU-8 and PEGDA layers on top of PSS. Note that we can independently tailor the thickness of each layer within the hexa-phasic particles. The assembled triphasic and hexa-phasic particles were released from the template (see Figure 3i and SI section 8) by dissolving the sacrificial polymer (PSS) layer in water. Such multiphasic particles, if formulated with alternating layers of a biodegradable polymer and a pharmacologically active agent, with precisely controlled thicknesses, may be ideal for the controlled and sustained delivery of drug molecules at the optimal rate and dose regimen, over several days.[3]

The multiple phases within the particles may be independently loaded with different cargos to provide the particles with multifunctional capabilities. Such particles can be beneficial in developing multifunctional therapeutic systems,[1,2,34,35] as they can encapsulate multiple drugs simultaneously. It is also possible for the different drugs to possess different, independently controlled release kinetics, depending on the degradation/swelling behavior of their respective encapsulant phases in the target environment. In addition, some of the particle phases can be loaded with functional nanoparticles or molecules to aid in the imaging and transportation of the particles within a biological system using an external field.[39] For example, as shown in Figure 4a−c, we have developed triphasic particles integrated with three different functionalities. Here, the first phase is SU-8 loaded with magnetite nanoparticles; the second phase is SU-8 loaded with a fluorescent red dye, and the third phase is a hydrogel (cross-linked PEGDA). Such triphasic particles can function as drug carriers (hydrogel phase) that are easy to track (fluorescent imaging) and manipulate using a magnetic field to evade biological hurdles and guide toward the target site. Movies S1 and S2 show the transport of the trifunctional particles on a water surface using an external magnetic field. Figure 4c shows the trajectory of the motion of the particles upon application of the field in different directions.

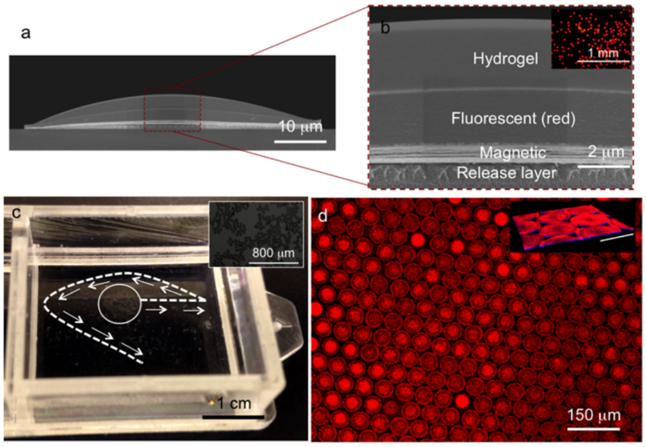

Figure 4. Multifunctional particles fabricated using the WETS technique. (a) A cross-sectional SEM image of a trifunctional particle comprising magnetic, fluorescent, and hydrogel phases. (b) Higher magnification image of the area indicated by the dashed red square shown in a. Inset in b shows a fluorescent microscope image of the trifunctional particles, released from the WETS template. (c) A cluster of trifunctional particles on a water surface. The cluster was transported along the trajectory indicated by the white dashed line using an external magnetic field (see Movies S1 and S2). The inset is a higher magnification optical micrograph of the particle cluster indicated by the white circle in c. (d) Two-dimensional self-assembly of biphasic amphiphilic particles (shown in Figure 3d) at an oil (top)−water (bottom) interface. The top insets show corresponding 3-D stacked fluorescence confocal microscopy image of the assembly. Scale bar in the inset represent 50 μm.

We have also studied the two-dimensional self-assembly of the fabricated biphasic amphiphilic particles at an oil−water interface. First, we added the amphiphilic particles to an oil−water mixture and agitated the system vigorously through sonication. Then, the amphiphilic particles were allowed to settle at the oil−water interface. Further, we have used a vibrating stage to induce in-plane movement of the particles. The frequency and amplitude of the vibrations were adjusted to bring the particles close to one another, and to break misaligned particle aggregates. The biphasic amphiphilic particles assembled into close packed structures with the hydrophobic phase (SU-8) preferentially oriented toward the oil layer and the hydrophilic phase (PEGDA) toward the water layer (see Figure 4d). The assembled structures grew in size with time (see SI section 9). This assembly of particles is driven by the minimization of interfacial free energy at the oil−water interface.[40] Figure 4d and SI section 9 show that the self-assembled close packed structures obtained were defined by the geometry (circle, square, and hexagon shapes) of the amphiphilic building blocks. These results illustrate the utility of the WETS technique for developing a variety of amphiphilic building blocks that are expected to be of importance for fundamental studies on particle self-assembly, as well as the bottom-up approaches envisioned to build materials and devices of the future.

■ CONCLUSION

In conclusion, we have demonstrated that the WETS technique can be used to fabricate a wide variety of monodisperse, multiphasic particles in complex shapes and sizes as small as 25 nm, while maintaining control over the thickness, composition, and modulus of each particle phase. We have also fabricated a range of multiphasic, amphiphilic particles that are anisotropic in both geometry and chemistry. We have further demonstrated the utility of the WETS technique in developing multifunctional nanoparticles and cargo carriers that are of significant importance in developing drug carriers with controlled release kinetics, increased circulation half-life, and enhanced targeting efficacy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods, additional data and discussion, and movies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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