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Light-Responsive, Shape-Switchable Block Copolymer Particles

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KEYWORDS. block copolymer particles, light-responsive particles, shape-changing particles, light-active surfactants, hydrogel display

ABSTRACT

A robust strategy is developed for preparing light-responsive block copolymer (BCP) particles in which shape and color can be actively controlled with high spatial and temporal resolution. The key to achieving light-responsive shape transitions of BCP particles is the design and synthesis of surfactants containing light-active groups (*i.e.,* nitrobenzyl esters and coumarin esters) that modulate the amphiphilicity and interfacial activity of the surfactants in response to light of a specific wavelength. These light-induced changes in surfactant structure modify the surface and wetting properties of BCP particles, affording both shape and morphological transitions of the particles, for example from spheres with an onion-like inner morphology to prolate or oblate ellipsoids with axially stacked nanostructures. In particular, wavelength-selective shape transformation of the BCP particles can be achieved with a mixture of two light-active surfactants that respond to different wavelengths of light (*i.e.*, 254 and 420 nm). Through the use of light-emitting, photo-responsive surfactants, light-induced changes in both color and shape are further demonstrated. Finally, to demonstrate the potential of the light-triggered shape control of BCP particles in patterning features with microscale resolution, the shape-switchable BCP particles are successfully integrated into a patterned, free-standing hydrogel film, which can be used as a portable, high-resolution display.

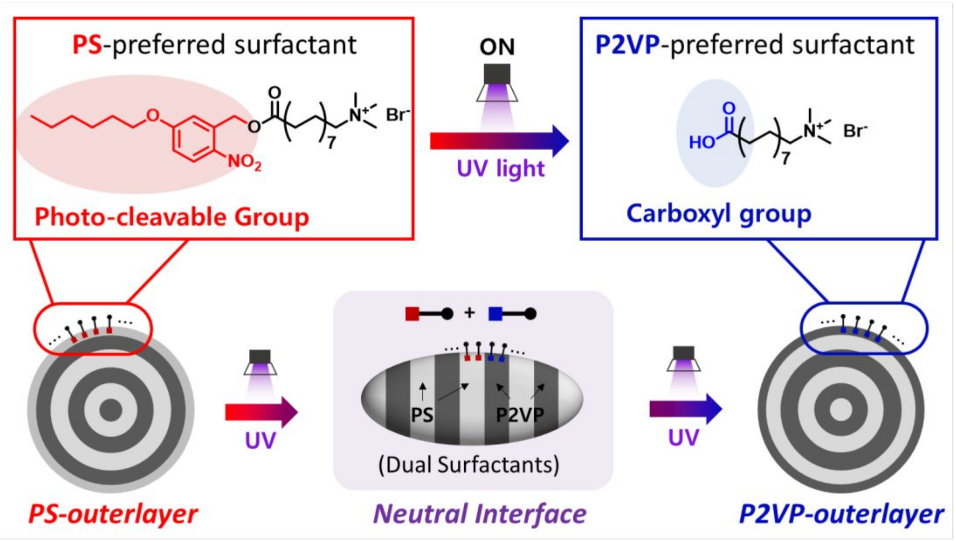
INTRODUCTION

Shape-changing particles have gained a considerable amount of attention in the production of smart materials for a wide range of applications. For example, the rheological behavior,[1-4] optical properties,[5] and capillary interactions[6] can be controlled through changes of particle shape in response to specific external stimuli to afford smart solutions for industrial paints and coatings, as well as bio-inspired materials for artificial camouflage and drug delivery systems.[7-9] In particular, the development of light-responsive shape-changing particles has been a long-thought dream for generating active, programmable smart systems. Distinct from particles that respond to other physicochemical stimuli (*i.e.*, pH, temperature, redox, and biomolecules), the shapes and properties of the light-responsive, shape-switching particles can be tuned actively with high spatial and temporal resolution.[10-13] Also, the shape and property of the particles can be tuned without time delay when the light is switched on and off.[14-15] Moreover, the capability to precisely modulate the wavelength and intensity of light provides a powerful strategy for tuning particle shape in a programmed manner.[16-18] In the pursuit of light-responsive systems, extensive progress has been made to develop photo-responsive polymers and solution assemblies by the use of polymers having photo-cleavable groups or photochromic units that undergo reversible isomerization upon light irradiation.[19-26] However, examples of shape-tunable polymer particles that respond to light are very limited, especially in the size range of 100 nm to a few micrometers,[27-29] which is ideal for the practical applications described above.

One promising approach is to design photo-responsive polymers and surfactant molecules, which can manipulate the shape of polymer particles. Recently, to prepare shape-transforming, nanostructured polymer particles, self-assembly of block copolymers (BCPs) confined in soft and mobile emulsion droplets has been utilized.[30-44] This method enables the large-scale production of uniform particles in the size range of 100 nm to several micrometers,[45-46] which fulfills the important requirements for a variety of practical applications. The use of the stimuli-responsive BCPs and/or surfactants in these particle systems can allow fine-tuning of particle shape and nanostructures in response to external stimuli.[47-51] For example, elongation of polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) BCP particles was achieved by triggering a solubility change of pH-responsive P2VP.[47-48] Recently, our group reported that the use of responsive polymer surfactants can facilitate temperature- and pH-driven shape transformations of BCP particles.[49-50] Therefore, we expected that judiciously designed, light-responsive surfactants, which adjust the interfacial properties of the BCP particles in response to light irradiation, would afford polymer particles exhibiting light-responsive, shape-switchable properties.

In this work, we develop shape- and color-switchable BCP particles in response to a light signal. The structural changes of the photochromic unit, which can be reversibly isomerized between two or more states, are often insufficient to exert a significant effect on interfacial activity. Therefore, our strategy starts from the design of photo-cleavable surfactants, which undergo a significant change in amphiphilicity and interfacial activity under light irradiation. The use of these surfactants significantly changes the interfacial interactions between the BCPs and surrounding environment in response to the light irradiation, affording shape transformations of the particles from spheres to striped footballs (prolate particles) or convex lenses (oblate particles). Wavelength-selective shape transformation of BCP particles is realized using a mixture of light-active surfactants, which respond to light of two different wavelengths (*i.e.*, 254 nm and 420 nm). To demonstrate the potential of such light-responsive BCP particles, the particles are incorporated into a hydrogel film to produce a portable display with microscale resolution. The shape and color tuning of the BCP particles at the desired locations in the film is achieved by irradiation through a photomask.

RESULTS AND DISCUSSION



Scheme 1. Schematic illustration of the photo-induced shape transformation of PS-*b*-P2VP particles enabled by light-active 5-hexyloxy-2-nitrobenzyl-16-N,N,N-trimethylhexadecan-1-ammonium bromide (N-CTAB) surfactants.

PS_{102k}-*b*-$P2VP_{97k}$ (number-average molecular weight ($M_{n,PS}$) = 102 kg mol^{-1}, $M_{n,P2VP}$ = 97 kg mol^{-1}, dispersity ($Đ$) = 1.15) particles were prepared by emulsifying polymer solution (1 wt% in chloroform) into aqueous solution containing light-active surfactant, 5-hexyloxy-2-nitrobenzyl-16-N,N,N-trimethylhexadecan-1-ammonium bromide (N-CTAB). The chloroform was evaporated, resulting in the production of the solid BCP particles. Then, the particles dispersed in water were treated by different times of light irradiation with solvent vapor.

Several aspects of the light-active N-CTAB surfactant design were carefully considered to achieve particle shape transformation in response to light irradiation. First, N-CTAB is composed of light-cleavable nitrobenzyl ester linkages, which upon irradiation at 254 nm cleave to yield a carboxylic acid-terminated surfactant (*i.e.*, HOOC-CTAB).[52] The ability of the pyridine groups in P2VP to hydrogen bond with carboxylic acids is exploited to provide preferential interaction between the cleaved surfactants and the P2VP domains of the BCP particles.[48] Therefore, it was hypothesized that the preferential interaction between the BCPs and surfactants (*i.e.*, PS with N-CTAB (before light irradiation) and P2VP with HOOC-CTAB (after irradiation)) could be tailored by light irradiation to transform the interfacial properties, and therefore, the shape of PS_{102k}-*b*-$P2VP_{97k}$ BCP particles using these surfactants (**Scheme 1**).

The N-CTAB surfactant was synthesized from 5-hydroxy-2-nitrobenzaldehyde as described in the supporting information, and the photolysis studied at the small molecule level prior to use for particle shape transformations. Photolysis of N-CTAB surfactant was monitored by ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Under light irradiation, N-CTAB surfactants were cleaved, with the overall conversion of N-CTAB to HOOC-CTAB reaching 92 % in 2 h (200 $\mu W/cm^2$). As shown in **Figure S2a**, the intensities of the benzylic proton resonances on the nitrobenzene ring of N-CTAB at 8.19 and 7.04 ppm decreased, while new peaks appeared at 8.06 and 7.47 ppm, corresponding to the nitrosoacetophenone photoproduct. ATR-FTIR spectra (**Figure S3**) show the appearance of a broad absorption peak at 3500-2500 cm^{-1}, which corresponds to O-H stretching of carboxylic acid, after light irradiation. Temporal control of the cleavage reaction progress was demonstrated by switching the light on and off (**Figure S4**).

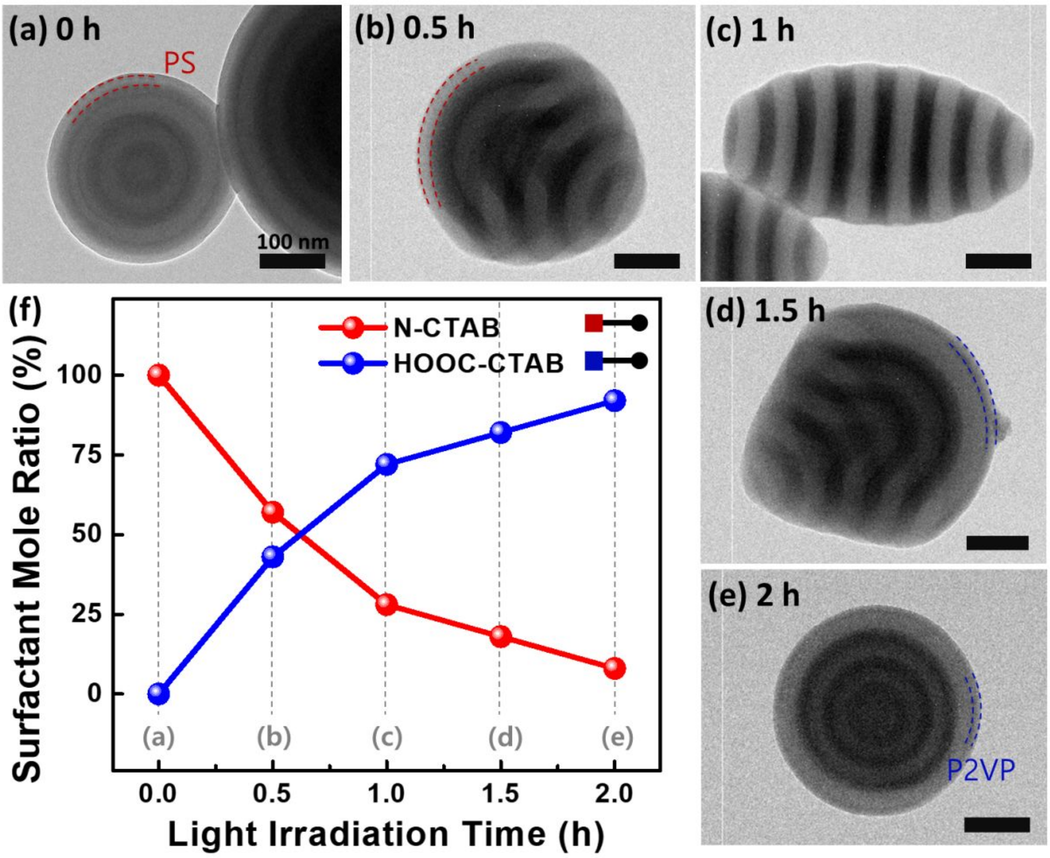


Figure 1. Shape-switching BCP particles induced by light-active surfactants. (a-e) TEM images of PS_{102k}-*b*-$P2VP_{97k}$ particles prepared with N-CTAB surfactants. The onion-shaped particles were treated with light irradiation at 254 nm for (a) 0 h, (b) 0.5 h, (c) 1.0 h, (d) 1.5 h, and (e) 2.0 h.; (f) The time-dependent mole percent of surfactants (N-CTAB and HOOC-CTAB) during photo-cleavage of N-CTAB.

Having characterized the photocleavage of these surfactants at the small molecule level, we then implemented them to stabilize particles and facilitate light-triggered transformations. First, onion-shaped PS_{102k}-*b*-$P2VP_{97k}$ BCP particles were prepared with N-CTAB surfactants (**Figure 1a**). To provide enough mobility of polymer chains during the shape transformation, we performed solvent vapor annealing with chloroform, which is a good solvent for both PS and P2VP blocks (**Figure S5**).[53] The BCP particles in water were subject to the chloroform-saturated atmosphere with different times of UV light irradiation (0.5, 1, 1.5, and 2 h). Then, the absorbed chloroform was completely released for 36 h. Transmission electron microscopy (TEM) images in **Figure 1** show the shape transformation of PS_{102k}-*b*-$P2VP_{97k}$

BCP particles depending on the light irradiation times. Before irradiation, onion-like spherical BCP particles with PS at the outermost layer were obtained (**Figure 1a**). Subsequent light irradiation led to a remarkable transition of the overall shape as well as the inner morphology of the BCP particles. After irradiation for 0.5 h, the BCP particles showed a mixture of axially and radially stacked lamellar morphologies, forming tulip bulb shapes (**Figure 1b**). In this case, PS and P2VP lamellae were exposed alternately at the surface with high curvature, while only PS was surface-exposed on the interface with low curvature. Prolonged irradiation resulted in the generation of striped prolate particles after 1 h (**Figure 1c**). As the time of the light exposure increased to 2 h, inverse tulip bulb-like particles (**Figure 1d**) and spherical particles with P2VP outer layers (**Figure 1e**) were produced.

To understand the role of the light-active N-CTAB surfactants on the shape transition of BCP particles, the ratio of N-CTAB to HOOC-CTAB surfactants was monitored as a function of irradiation time. The ratio of N-CTAB to HOOC-CTAB was calculated from the ^{1}H NMR spectra, by comparing the integration of the nitrobenzene resonances at 8.19 and 7.04 ppm to those of the nitrosoacetophenone photoproduct at 8.06 and 7.47 ppm; the results are summarized in **Figure 1f**. The use of solely N-CTAB surfactants resulted in spherical particles with preferential localization of the PS domain at the surface, driven by the favorable hydrophobic interactions between N-CTAB and PS.[48, 54] After irradiation for 1 h, the conversion of N-CTAB to HOOC-CTAB resulted in prolate particles. Importantly, the ratio of N-CTAB and HOOC-CTAB determined particle shape and morphology. For example, after light exposure for 1 h, 72 mol % of the N-CTAB had converted to HOOC-CTAB. This condition produced neutral interfaces such that both PS and P2VP blocks localized at the particle surface, leading to the perpendicular orientation of the BCPs relative to the surface and generating ellipsoid-shaped particles with axially stacked lamellar morphologies.[34, 38] Lower and higher percentages of carboxylic acid-terminated surfactants (*i.e.*, 57 mol% after 0.5 h and 82 mol%

after 1.5 h irradiation) afforded the presentation of primarily PS and primarily P2VP, respectively, at the particle surface. Therefore, both radially and axially stacked lamellae were formed within a particle (*i.e.*, one block on the low curvature, and stripe distribution on the high curvature), producing tulip bulb-like particles.[55] Finally, as the ratio of HOOC-CTAB increased to 0.92 after irradiation for 2 h, inverse onion-like spherical particles with P2VP-outermost layers were produced driven by hydrogen bonding interactions between HOOC-CTAB and P2VP (**Figure 1e**).[48] We note that most of the nitrosoacetophenone photoproduct of N-CTAB migrate to the surrounding aqueous media and are removed by repeated washing steps, therefore these molecules do not affect the morphology of the BCP particles.

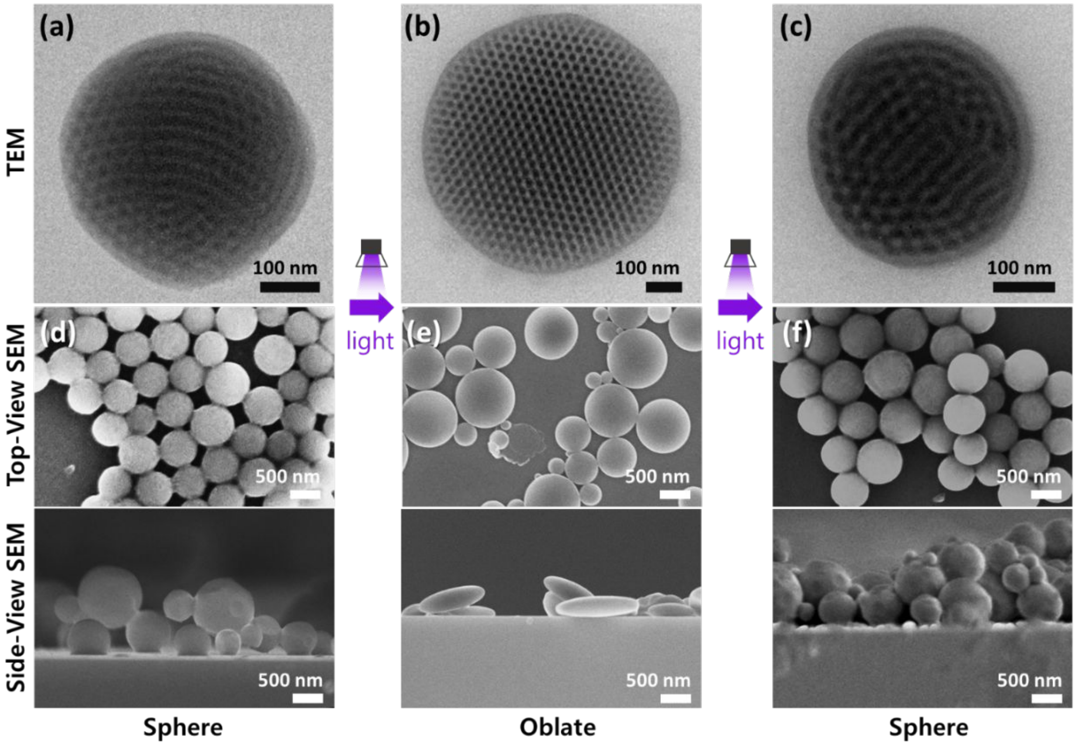


Figure 2. Light-responsive, shape transformation of cylinder-forming BCP particles. (a-c) TEM and (d-f) SEM (top-view and side-view) images of PS_{15k}-*b*-$P4VP_{7k}$ particles prepared with N-CTAB surfactants. The spherical particles (a, d) were treated with irradiation at 254 nm for (b, e) 0.5 h, and (c, f) 2 h.

To investigate the general applicability of the light-active surfactants for producing particles with various shapes with different BCPs, N-CTAB was applied to encapsulate cylinder-forming polystyrene-*b*-poly(4-vinylpyridine) (PS_{15k}-*b*-$P4VP_{7k}$) ($M_{n,PS}$ = 15 kg mol^{-1}, $M_{n,P4VP}$ = 7 kg mol^{-1}, $Đ$ = 1.15). **Figure 2** shows the scanning electron microscopy (SEM) and TEM images of PS_{15k}-*b*-$P4VP_{7k}$ BCP particles before exposure and after light irradiation for different amounts of time. First, spherical BCP particles with coiled cylinders were produced (**Figure 2a**), where the preferable hydrophobic interaction between PS and N-CTAB generated particles with PS as the outermost layer.[36, 56] Subsequently, when the BCP particles were subjected to light irradiation, the overall particle shape transformed to oblate with hexagonally packed cylindrical morphology (**Figure 2b**). Again, conversion of the N-CTAB surfactant to HOOC-CTAB afforded neutral wetting conditions at the particle surface, however, a different molar ratio of N-CTAB to HOOC-CTAB was required due to the different relative surface area of each domain at the surface of the particles with cylindrical morphology relative to those with lamellar morphology.[45, 57] For example, for cylinder-forming BCPs, 40 % conversion of N-CTAB to HOOC-CTAB (after 0.5 h) was sufficient to generate neutral surfaces allowing the presentation of both PS and P4VP blocks at the surface. The neutral surfaces created upon irradiation yielded perpendicularly oriented cylinders, resulting in the formation of oblate particles.[36, 56] Similar to the previous results, prolonged light exposure (> 2 h) changed the particle shape back to the spherical BCP particles, but with P4VP outermost layers (**Figure 2c**).

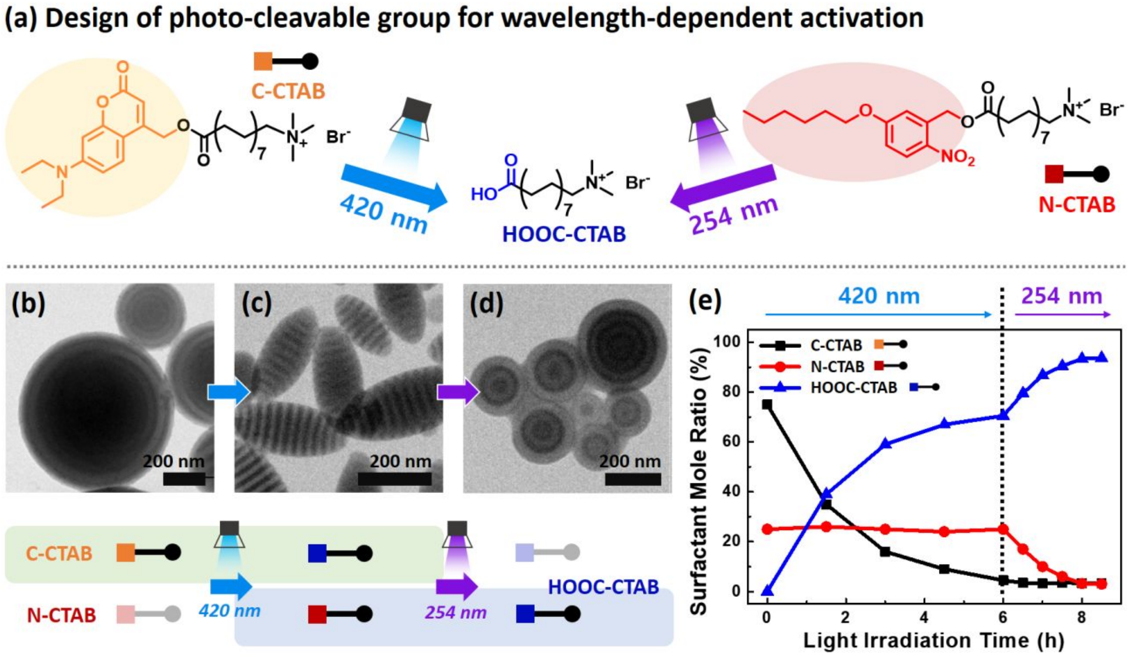


Figure 3. Wavelength-dependent, orthogonal activation of shape-switching properties. (a) Chemical structures of two light-active surfactants (C-CTAB and N-CTAB) having different activation wavelengths (420 nm for C-CTAB and 254 nm for N-CTAB); (b-d) TEM images of PS_{102k}-*b*-$P2VP_{97k}$ particles prepared with a mixture of C-CTAB and N-CTAB surfactants (b) before light exposure, (c) irradiated at 420 nm for 6 h, and (d) irradiated for an additional 2 h at 254 nm. (e) Time-dependent mole fraction of each surfactant (C-CTAB, N-CTAB, and HOOC-CTAB) during light irradiation.

A distinct advantage of the light-activated, shape-transforming BCP particles is the ability to selectively engineer and trigger multiple transformations depending on the light wavelength and intensity. To demonstrate the potential of the wavelength-dependent shape-switching behavior of BCP particles, we developed a model system to prepare BCP particles with a mixture of two light-active surfactants having different activation wavelengths. For this purpose, we designed another light-responsive surfactant, 7-(diethylamino)-4-(N,N,N-trimethylhexadecan-1-ammonium bromide)coumarin (C-CTAB), composed of a coumarin ester group, which can be activated and deprotected at 420 nm (**Figure 3a**).[58-59] Similar to the N-CTAB surfactants, cleavage of C-CTAB leads to the generation of carboxylic acid groups, forming HOOC-CTAB (**Figures S2-4**). Accordingly, the use of C-CTAB surfactants in the preparation of PS_{102k}-*b*-$P2VP_{97k}$ particles produced similar light-induced shape transformations of the particles from spheres to striped prolate particles, however, using lower-energy 420 nm light to trigger this transformation (**Figure S6**).

We then monitored the orthogonal, wavelength-triggered shape change of PS_{102k}-*b*-$P2VP_{97k}$ BCP particles stabilized by a mixture of N-CTAB and C-CTAB surfactants at a molar ratio of 1:3. As expected, the BCP particles were initially spherical with PS outermost layers due to the preferential hydrophobic interactions of PS with alkyl chains of both N-CTAB and C-CTAB (**Figures 3b**).[48, 54, 60] The BCP particles were then sequentially irradiated at 420 nm, followed by 254 nm to investigate the resulting shape and morphological changes (**Figures 3b-d**). Irradiation at 420 nm led to a transformation of particle shape from spheres with onion-like morphology to prolate ellipsoids with stacked lamellar morphology. During irradiation at 420 nm, C-CTAB molecules were selectively converted to HOOC-CTAB, resulting in a ratio of HOOC-CTAB/C-CTAB = 0.73/0.02 while the fraction of N-CTAB (0.25) remained unchanged after 6 h. Photolysis of C-CTAB was clearly proved by ^{1}H NMR spectra (**Figure S2b**), where the intensities of the proton resonances on 7-(diethylamino)-4-(hydroxymethyl)coumarin of C-CTAB (*i.e.*, 4.79 and 3.38 ppm) decreased according to the light irradiation. We note that the N-CTAB surfactants were stable under 420 nm light irradiation (**Figure 3e**). The second irradiation step at 254 nm decreased the ratio of N-CTAB, resulting in the overall ratio of HOOC-CTAB/N-CTAB/C-CTAB to be 0.95/0.03/0.02. In this case, inverse onion-like spherical particles with P2VP-outermost layers were obtained. Therefore, the shape transition of BCP particles from onion-like spheres to striped prolate particles was achieved by irradiation at 420 nm light, followed by another shape transition from prolate particles to spheres at 254 nm, highlighting the excellent wavelength-selectivity of the shape transformations of these particles.

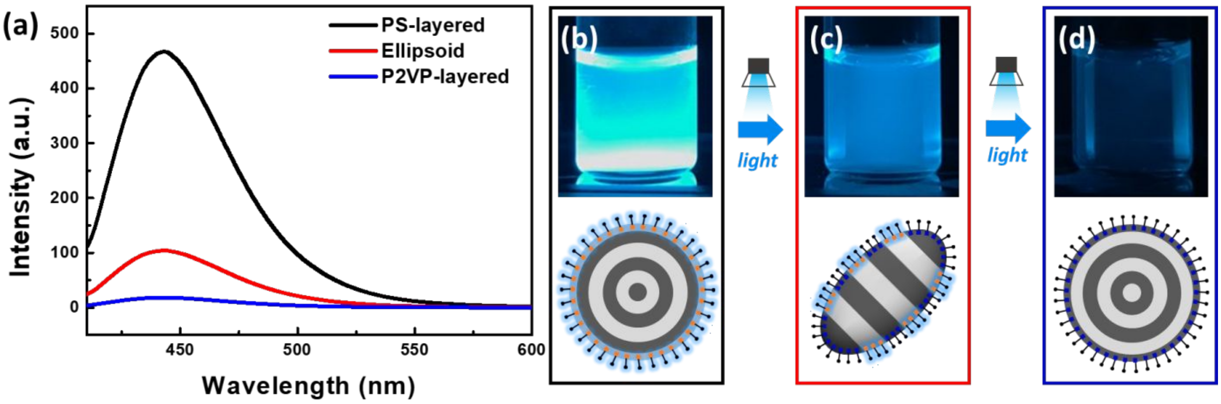


Figure 4. Light-triggered, shape-dependent optical properties of BCP particles. (a) PL spectra and (b-d) photographs showing the fluorescence of PS_{102k}-*b*-$P2VP_{97k}$ particles prepared with C-CTAB surfactants before and after irradiation at 420 nm for (b) 0 h (black line, onion-like particles with PS outermost layers), (c) 3 h (red line, prolate particles), and (d) 6 h (blue line, reverse onion-like particles with P2VP outermost layers).

Direct, colorimetric visualization of particle shape change is highly beneficial for the clinical and biological applications, such as drug delivery.[7, 49] In our system, the light-cleavable coumarin ester group of C-CTAB is strongly emissive, imparting tunable optical properties to the BCP particles and allowing monitoring of the light-triggered shape transformation by color change. In order to demonstrate the correlation of particle shape to the optical signal, we examined the emission properties of the BCP particles during the irradiation-induced particle shape transformation. **Figure 4a** shows the photoluminescence (PL) spectra of the BCP particles prepared with C-CTAB surfactants before light exposure and the following irradiation at 420 nm for 3 and 6 h. Note that the PL spectra were acquired after removal of excess surfactants by repeated centrifugation. The spherical particles stabilized with C-CTAB showed a strong blue emission peak at 440 nm from the coumarin chromophore of the C-CTAB surfactants, as depicted in **Figure 4b**. After irradiation for 3 h, the particle deformed to a striped prolate, while the fluorescence decreased by 74 %, resulting in the dark blue BCP particle suspension shown in **Figure 4c**. After prolonged irradiation (6 h), the suspension of spherical

BCP particles with reverse onion morphology (*i.e.*, with a P2VP outermost layer) became nearly colorless and the fluorescence intensity decreased by 92% (**Figure 4d**). This result corresponds closely with the conversion ratio of C-CTAB to HOOC-CTAB (91%) after 6 h of irradiation.

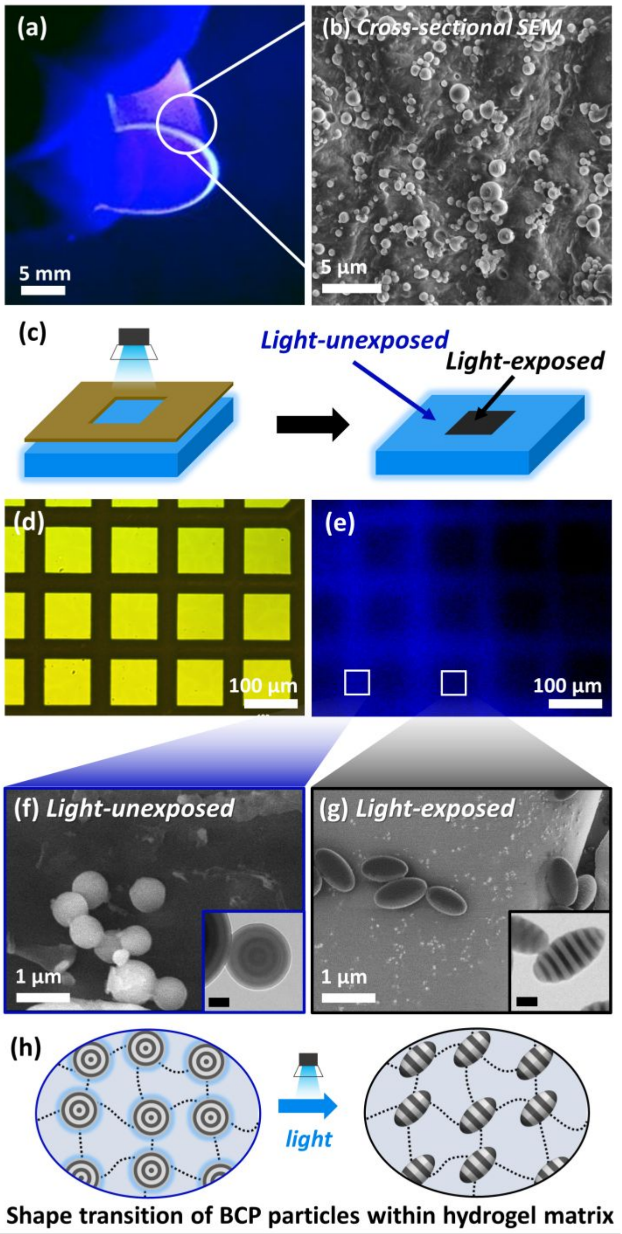


Figure 5. Fabricating portable, high-resolution displays by incorporating light-responsive BCP particles into patterned hydrogel matrices. (a) Photograph of a particle-containing hydrogel film exhibiting blue fluorescence; (b) cross-sectional SEM images of a freeze-dried hydrogel film; (c) schematic illustration of the preparation of patterned hydrogel film by UV light irradiation through a patterned photomask; (d) optical micrograph of the patterned

photomask; (e) fluorescence images of the hydrogels after irradiation for 3 h at 420 nm through the photomask; (f, g) high-magnification SEM and TEM images of the freeze-dried hydrogel on the (f) light-unexposed region (boxed blue region in e) and (g) light-exposed region (boxed black region in e); and (h) schematic illustration of the hydrogel film containing shape-switching, fluorescent BCP particles.

Finally, to demonstrate the potential of the light-triggered shape control of BCP particles in patterning features with microscale resolution, we fabricated hydrogel films containing the BCP particles, irradiated it through a photomask, and examined the local shape and fluorescence characteristics in the exposed and unexposed regions. We chose a hydrogel as the host matrix because the elastic and moldable properties of hydrogels allow for successful embedding and immobilization of the polymer particles; further, the swelling of hydrogels in aqueous media provides sufficient mobility of the surfactants to facilitate the particle shape transition.[61-63] Also, the hydrogel film is free-standing and flexible, thus can be engineered for desired applications. The BCP particle-containing hydrogel film was prepared by UV-initiated polymerization of the aqueous suspension of poly(ethylene glycol) diacrylate, sodium acrylate, and BCP particles. After polymerization, the un-reacted components and excess surfactants were removed by repeated washing of the hydrogel with deionized (DI) water (See the experimental section and the Supporting Information for details). **Figure 5a** shows the photograph of the hydrogel film containing PS_{102k}-b-$P2VP_{97k}$ particles stabilized by C-CTAB. Due to the homogenous embedding of BCP particles within the matrix, a blue emission was observed over the entire hydrogel film. This was also demonstrated by the cross-sectional SEM image of the freeze-dried hydrogel film shown in **Figure 5b**. Given the good dispersion of the BCP particles within the hydrogel matrix, each particle can act as a photographic pixel, such that changes in the particle shape and fluorescence response can be displayed as a fluorescence map with microscale resolution. To explore the local transitions of particle shape and optical properties, a square lattice photomask with 100 μm features was placed on top of the pre-cured hydrogel film, which was irradiated at 420 nm through the mask (**Figures 5c to e**). The photo-responsive shape transformation of the BCP particles was realized successfully within the hydrogel film (**Figures 5f-h** and **S7-8**). As shown in the cross-sectional SEM images of the freeze-dried hydrogels (**Figure 5f** and **Figure S7a**), spherical particles were observed in the light-unexposed region. In contrast, prolate ellipsoids were observed in the light-exposed region (**Figure 5g** and **Figure S7b**). Consistent with the results in **Figure 4** showing reduced fluorescence upon conversion of C-CTAB to HOOC-CTAB, the fluorescence intensity decreased only in the light-exposed area, as seen by the dark square patterns shown in **Figure 5e**.

CONCLUSIONS

In this work, we developed a robust and effective method to prepare particles that exhibit light-triggered changes in shape and color. The photo-responsive surfactants N-CTAB and C-CTAB were designed such that irradiation changed their molecular structure, resulting in modulation of their amphiphilicity and interfacial activity and corresponding changes to the shape of the PS-*b*-P2VP or PS-*b*-P4VP BCP particles. The light-responsive shape transformation of the BCP particles from spheres to prolate or oblate ellipsoids was achieved with high temporal resolution and wavelength selectivity. In addition, the use of light-emitting, photo-responsive surfactants allowed direct, colorimetric visualization of the shape change of these BCP particles. And, we demonstrated the potential of the shape- and color-changing BCP particles by integrating them into the free-standing patterned hydrogel film, which can be used as a portable display with micrometer-scale resolution. Nevertheless, the non-reversible character of the photo-cleavable surfactants can limit the use of these particles in some practical applications, which require the particles with reversible shape and color transformation. Therefore, the design of photo-active surfactants containing the photochromic units that can be reversibly isomerized between different states upon light irradiation (*i.e.*, spiropyran derivatives)[26, 64] is an important future direction to realize the light-active BCP particles with different switching modes.

EXPERIMENTAL SECTION

Synthesis of N-CTAB and C-CTAB. Detailed synthetic procedures are provided in the Supporting Information. 5-hexyloxy-2-nitrobenzyl-16-bromo-hexadecanoate or 7-(diethylamino)-4-(bromo-hexadecanoate)coumarin (3.0 g, 5.3 mmol) was added into a sealed tube with trimethylamine (5.4 g, 53.0 mmol) and ethyl acetate (15 mL). The reaction mixture was held under argon for 7 d at 60 °C. The products were purified by recrystallization from water to obtain N-CTAB as a light yellow powder (2.2 g, yield 67.4%) or C-CTAB as a white powder (2.3 g, yield 67.9%).

Preparation and shape transformation of PS-b-P2VP BCP particles. A chloroform solution (50 μL) containing PS-*b*-P2VP (0.5 mg) was emulsified in DI water (1 mL) containing 0.1 wt% of light-responsive surfactant (N-CTAB or C-CTAB) using a homogenizer. Then, the chloroform was slowly evaporated for 36 h to obtain solid particles. The shape transformation of the BCP particles is performed by the following procedure: a vial containing the particle suspension (1 mL) in water was placed inside a larger vial containing chloroform (2 mL) to produce a chloroform-saturated atmosphere, and irradiated under 254 or 420 nm for different times (0.5-6 h). Then, the absorbed chloroform was completely removed for 36 h. The particles were washed by repeated centrifugation (13000 rpm) to remove remaining surfactants.

Fabrication of BCP particle-containing hydrogel films. An aqueous solution (5 mL) of poly(ethylene glycol) diacrylate ($M_n \approx 1000$ g mol^{-1}, 0.9 g), sodium acrylate (0.1 g), 2-hydroxy-2-methylpropiophenone (10.0 mg), and BCP particles prepared by C-CTAB (5.0 mg) was injected into the gap between two glass slides spaced by Kapton spacers (1 mm), and irradiated by UV light (254 nm, 200 μW/cm^2) for 10 min to initiate polymerization and gelation.[61] To remove unreacted residues, the resulting hydrogel was rinsed with DI water. An additional patterned hydrogel film was prepared by placing a square lattice photomask on top of the BCP particle-containing pre-cured hydrogel films, followed by irradiation at 420 nm for 3 h. Solvent vapor annealing was then performed using chloroform for 12 h.

ASSOCIATE CONTENT

Supporting Information: Experimental details and additional characterization data (NMR, FT-IR, TEM, and SEM). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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