

Tunable Superhydrophobic and Optical Properties of Colloidal Films Coated with Block Copolymer Micelles/Micelle Multilayers**

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Many naturally occurring surfaces such as lotus leaves and butterfly wings exhibit the remarkable self-cleaning effect. The hydrophobicity of these surfaces arises from their hierarchical surface roughness at two different length scales (specifically, at ca. 3–10 μm and about 100 nm length scales).^[1–11] Artificial superhydrophobic surfaces have attracted considerable attention owing to their potential applications for fabricating glass covers for solar cells, eye glasses, and waterproof clothes. Much research effort at preparing these synthetic surfaces has focused on film structures exhibiting roughness at two different length scales. For example, superhydrophobic surfaces showing water-droplet contact angles greater than 150° have been prepared from porous multilayer films,^[11] binary colloidal assemblies,^[12] raspberry-like colloidal films,^[13] sodium silicate multilayer-coated colloidal films,^[14] 2D nanopillar arrays,^[15] and electrochemically deposited gold films.^[16] Recently, there have been several attempts to prepare smart and intelligent superhydrophobic films exhibiting responsive

optical properties.^[17,18] For example, it has been reported that Si nanowire films containing photochromic spiropyran molecules exhibit light-responsive water contact angles because the spiropyran dye is hydrophobic under visible light, whereas UV irradiation converts the dye into its hydrophilic form.^[17] Furthermore, Sato and co-workers have reported that the structural color of inverse opal films (arising from light diffraction) modified with fluoroalkylsilanes can be modulated from blue to red by changing the size of the colloidal particles; remarkably, the films can also be simultaneously tuned to exhibit superhydrophobicity with a high water contact angle of about 155°.^[18]

Charged block copolymer micelles (BCMs) composed of hydrophilic and hydrophobic segments, such as polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) and polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP), have been known to incorporate hydrophobic materials (e.g., gold nanoparticles,^[19,20] quantum dots (QDs),^[21] magnetic nanoparticles,^[22] fluorescent dyes,^[23,24] or spiropyran dyes)^[25] into the hydrophobic cores of the micelles in water. Recently, it has been reported that charged BCMs containing hydrophobic organic dyes can be self-assembled with BCMs exhibiting a complementary charge onto flat^[25] and colloidal substrates^[26] using layer-by-layer (LbL) deposition. Specifically, in the case of multilayer films assembled using protonated PS-*b*-P4VP and anionic PS-*b*-PAA, because of aggregation between the adsorbed micelles, the size of the micelles is strongly dependent on the charge density of the hydrophilic corona chains, the molecular weight (M_w), and the number of bilayers of BCMs. Accordingly, if the BCM multilayer films are coated onto micrometer-sized colloidal particles on the nanometer scale, upon the further adsorption of fluoroalkylsilane, superhydrophobic surfaces with hierarchical dual-scale roughness can be prepared. Furthermore, the superhydrophobicity of these surfaces can be finely tuned by the adsorption conditions (such as the solution pH, M_w , and the number of bilayers of BCMs). These superhydrophobic films can exhibit interesting optical properties upon the incorporation of hydrophobic QDs and dyes within the PS cores of the two different types of BCMs. We have also determined that these BCM-encapsulated QDs show much improved fluorescence efficiency as compared to QDs dispersed in water by exchanging the stabilizer. To the best of our knowledge, there have not been any systematic studies of superhydrophobic surfaces with optical functional-

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ity prepared by LbL deposition using BCMs incorporating hydrophobic nanoobjects within the BCM cores.

This approach may be widely applicable to technologies requiring optical imaging and self-cleaning in air. Furthermore, considering the broad range of applications of both LbL multilayers^[27–33] and block copolymer thin films,^[34–38] the approach developed here may lead to new possibilities for the fabrication of thin films endowed with multiple functionalities. Therefore, our motivation has been to employ BCM-coated colloidal particles as building blocks to achieve hierarchical surface roughness for the fabrication of tunable superhydrophobic films. At the same time, we have also attempted to use the BCMs as nanocontainers to prepare films endowed with unique optical properties originating from the inclusion of QDs or fluorescent dyes within the BCMs.

In this study, we report the preparation of BCM-multilayer-coated colloidal silica particle films with both superhydrophobic and optically tunable properties. The BCM multilayers have been assembled on colloidal silica surfaces via electrostatic and hydrogen-bonding interactions between complementary BCMs, cationic PS-*b*-P4VP and anionic PS-*b*-PAA. The nanostructured surface morphology of BCM multilayers on colloidal silica particles has been controlled by varying either the charge density of hydrophilic BCM coronas (i.e., P4VP or PAA) or the M_w of the hydrophobic core (PS) and hydrophilic corona blocks. This provides a handle to control the degree of superhydrophobicity of the film. We also show that BCM multilayer films incorporating hydrophobic CdSe@ZnS (i.e., CdSe cores with ZnS shells) nanoparticles and dyes within the PS cores of PS-*b*-P4VP and PS-*b*-PAA exhibit remarkable optical properties such as color rendering. We strongly believe that this approach will enable the fabrication of smart superhydrophobic films with desired and tailored properties. The use of BCMs as nanocontainers in the films enables the inclusion of various functional materials with useful optical, electrical, and magnetic properties.

Electrophoresis experiments have been performed to monitor the multilayer growth of BCMs on colloidal particles since alternating ζ -potentials have been shown to be an excellent indicator of the stable growth of multilayer films.^[39] In this case, the ζ -potential of hairy BCMs (i.e., PS_{10.6k}-*b*-P4VP_{42.4k} at pH 4 and PS_{2k}-*b*-PAA_{8k} at pH 6, the subscripts denote the M_w of the segments) with relatively long hydrophilic chains, as well as crew-cut BCMs (i.e., PS_{49.5k}-*b*-P4VP_{16.5k} at pH 4 and PS_{16k}-*b*-PAA_{4k} at pH 6) with short hydrophilic chains, periodically and uniformly oscillates from ca. +23–29 mV (for PS-*b*-P4VP at pH 4) to ca. –33 to –35 mV (for PS-*b*-PAA at pH 6), indicating the stable growth of multilayers upon the sequential and alternate adsorption of PS-*b*-P4VP and PS-*b*-PAA BCMs onto silica colloids with a diameter of about 600 ± 10 nm (Supporting Information, Fig. S1). Based on the stable growth of BCM multilayers on colloids, we have investigated the surface morphology of silica colloids decorated with both hairy and crew-cut BCMs, as shown in the scanning electron microscopy (SEM) images of Figure 1. In the case of hairy BCM multilayers assembled at pH 4/6, each BCM bi-

layer (from 1 to 3 bilayers) has been uniformly coated onto the silica colloids, yielding a smooth surface morphology for the resulting structures. The diameter of the silica colloids increases from 600 nm for bare silica colloids to 733 ± 13 nm after the deposition of 3 BCM bilayers. In previous work, we have shown that {PS_{10.6k}-*b*-P4VP_{42.4k}/PS_{2k}-*b*-PAA_{8k}} multilayers assembled on a flat substrate at pH 4/6 yield a highly protuberant surface structure;^[25] the smooth surface morphology obtained on the surface of the colloids is partially caused by the high degree of interdigitation between the relatively thick corona shells of PS_{10.6k}-*b*-P4VP_{42.4k} and PS_{2k}-*b*-PAA_{8k} BCMs during the separation of the colloidal particles using a centrifuge (see Experimental). It is quite likely that the exertion of a strong centrifugal force (centrifugation speed of about 8000 rpm) squashes the porous polymeric structure. In contrast, when crew-cut BCMs are used as the multilayers adsorbed onto silica colloids at the same combination of pH values, the BCMs do not sufficiently cover the surface of the colloids and vacancies still remain between neighboring micelles even upon the deposition of 3 BCM bilayers. As a result, BCM-coated colloids with 3 bilayers have a diameter of about 670 ± 30 nm, which is much smaller than the corresponding value for 3-bilayered hairy-BCM-coated colloids (ca. 733 nm). This observation evidently implies that hydrophilic corona blocks (P4VP or PAA) with low molecular weights do not penetrate the shells of adjacent micelles to a large extent owing to their relatively short chain lengths and the long-range electrostatic repulsion between PAA corona blocks possessing the same charge (for PS_{16k}-*b*-PAA_{4k} at pH 6, ca. 93 % of the PAA is ionized). As mentioned before, in order to prepare artificial superhydrophobic surfaces with dual-scale surface roughness based on 600 nm silica colloids and nanometer-sized BCMs, the surface roughness imparted by the adsorbed BCMs should be uniform on the colloidal particle surfaces. To optimize the hierarchical surface morphology of the films, the deposition conditions with crew-cut BCMs have been readjusted to a pH combination of 4/4 (ca. 18 % of the PAA is ionized at pH 4) such that electrostatic repulsions between PS_{16k}-*b*-PAA_{4k} micelles possessing the same charge are decreased, giving rise to a rough surface structure with adequate surface coverage. The validity of this approach has also been corroborated by the increase in the ζ -potential of colloids with an outermost layer of PS_{16k}-*b*-PAA_{4k} upon decreasing the solution pH from 6 to 4 (Supporting Information, Fig. S2). In this case, very rough surface shell films ranging from about 40 (for 1 bilayer) to 100 nm (for 2 and 3 bilayers) have been uniformly coated onto the colloidal particles. Furthermore, these roughened colloids are well dispersed up to 3 bilayer depositions, as shown in Figure 1c, as the number of bilayers of PS_{49.5k}-*b*-P4VP_{16.5k}/PS_{16k}-*b*-PAA_{4k} at pH 4/4 is increased from 1 to 3. The deposition of 3 bilayers of crew-cut BCMs also causes the colloids to increase in size to about 940 ± 23 nm. Although the uniform growth of BCM multilayers on colloidal silica by adjusting the pH conditions to 4/4 suggests the occurrence of some interactions between the corona blocks, we note that the BCM

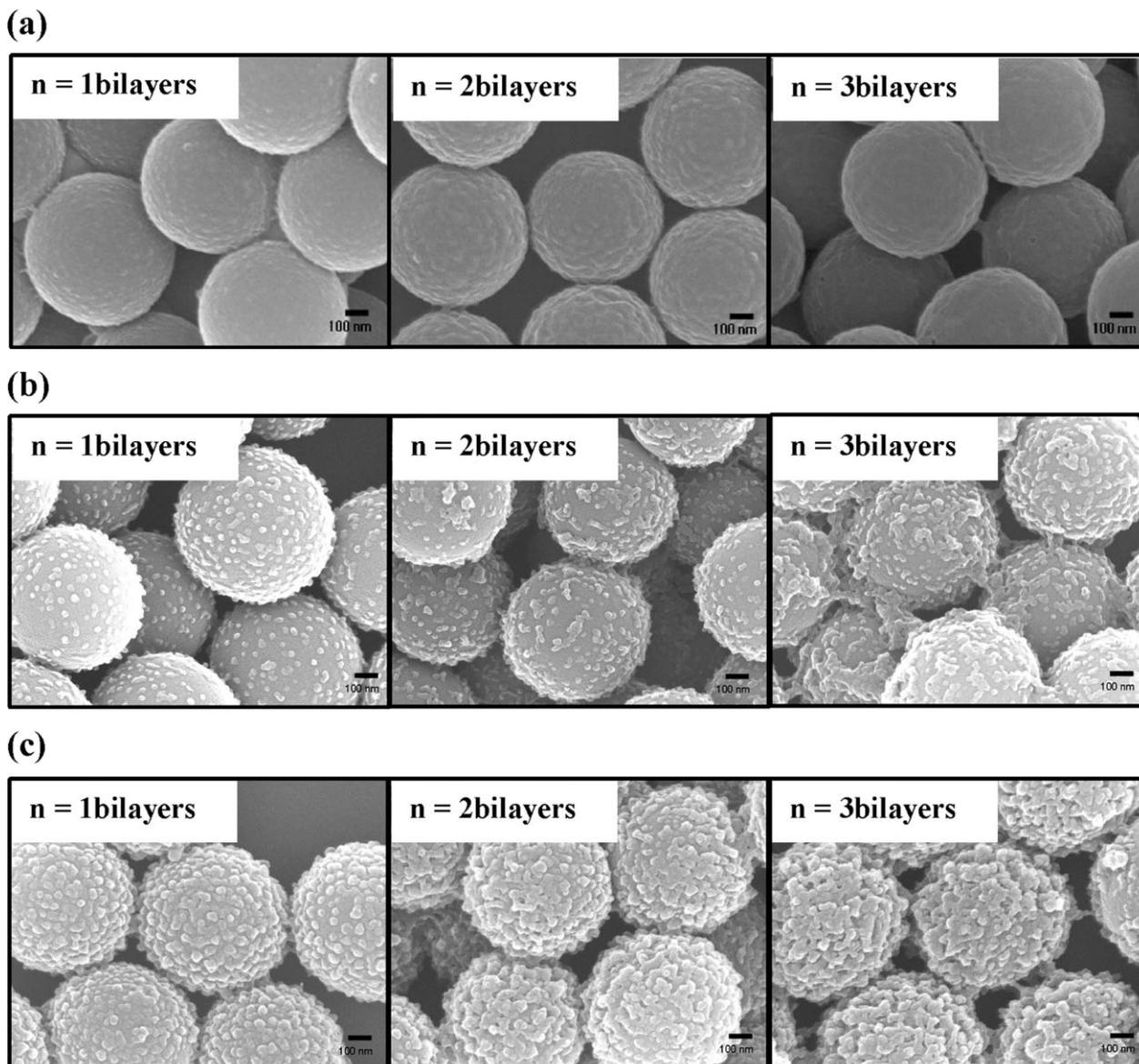


Figure 1. SEM images of silica colloids coated with a) hairy $\{PS_{10.6k}\text{-}b\text{-}P4VP_{42.4k}/PS_{2k}\text{-}b\text{-}PAA_{8k}\}_{n=1-3}$ micelles deposited at pH 4/6, b) crew-cut $\{PS_{49.5k}\text{-}b\text{-}P4VP_{16.5k}/PS_{16k}\text{-}b\text{-}PAA_{4k}\}_{n=1-3}$ micelles at pH 4/6, and c) crew-cut $\{PS_{49.5k}\text{-}b\text{-}P4VP_{16.5k}/PS_{16k}\text{-}b\text{-}PAA_{4k}\}_{n=1-3}$ micelles at pH 4/4.

multilayers do not form hollow shells upon the removal of the colloid templates due to the relatively low degree of interdigitation in this system, which is very different from the behavior observed for hairy micelle multilayers. Indeed, hollow shells are reproducibly formed with even a single bilayer of hairy BCMS assembled at pH 4/4 upon the removal of the sacrificial colloids (Supporting Information, Fig. S3).

Based on the roughened surface morphology of silica colloids controlled by the M_w and charge density of the BCM blocks, we have attempted to prepare colloidal films with superhydrophobic properties. For this purpose, BCM-coated colloidal films have been prepared on Si wafers by the convective assembly of colloidal suspensions at a fixed colloid concentration (0.5 wt%) and dispensing amount (1 mL). Subse-

quently, these films have been dipped in a solution containing fluoroalkylsilane polymers for 20 min at 70°C to further increase the hydrophobicity of the surface (Supporting Information).^[40] The bare and hairy BCM (i.e., $PS_{10.6k}\text{-}b\text{-}P4VP_{42.4k}/PS_{2k}\text{-}b\text{-}PAA_{8k}$)-coated silica colloidal films without any evident nanostructured roughness display similar water contact angles of about 122° (the difference between the advancing and receding angle, $\Delta\theta_{ad-re}$ is about 18°), as shown in Figure 2a. On the other hand, silica colloids coated with 3-bilayered crew-cut BCMS at pH 4/6 show a relatively high water contact angle of 148° ($\Delta\theta_{ad-re} \sim 8^\circ$) despite the inadequate surface coverage (Fig. 2b). This observation implies that even crew-cut BCMS deposited at pH 4/6, which exhibit a non-uniform surface morphology on the colloid particle surface, can

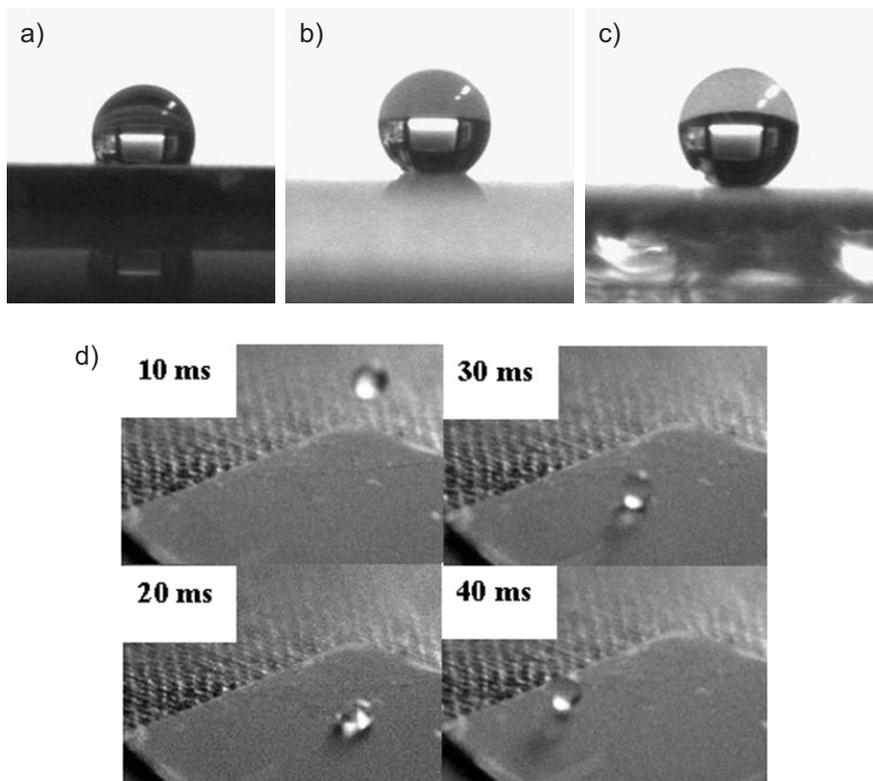


Figure 2. Water droplets on colloidal silica films coated with a) $\{\text{PS}_{10.6\text{k}}\text{-}b\text{-P4VP}_{42.4\text{k}}/\text{PS}_{2\text{k}}\text{-}b\text{-PAA}_{8\text{k}}\}_{n=1-3}$ (hairy BCMs) at pH 4/6, b) $\{\text{PS}_{49.5\text{k}}\text{-}b\text{-P4VP}_{16.5\text{k}}/\text{PS}_{16\text{k}}\text{-}b\text{-PAA}_{4\text{k}}\}_{n=1-3}$ (crew-cut BCMs) at pH 4/6, and c) $\{\text{PS}_{49.5\text{k}}\text{-}b\text{-P4VP}_{16.5\text{k}}/\text{PS}_{16\text{k}}\text{-}b\text{-PAA}_{4\text{k}}\}_{n=1-3}$ (crew-cut BCMs) at pH 4/4. The measured water contact angles are a) 122° , b) 148° , and c) 171° . d) Snapshots of a water droplet bouncing off a colloidal silica film coated with $\{\text{PS}_{49.5\text{k}}\text{-}b\text{-P4VP}_{16.5\text{k}}/\text{PS}_{16\text{k}}\text{-}b\text{-PAA}_{4\text{k}}\}_3$ at pH 4/4 over a period of 40 ms. Note that for samples in (a) to (d), the outermost surface of the films have been coated with a fluoroalkylsilane polymer.

still have a significant effect on the superhydrophobicity of colloid films. Furthermore, colloids with a uniform and well-defined nanostructured surface roughness at pH 4/4 exhibit significantly improved superhydrophobic properties with a water contact angle above 170° (Fig. 2c). Moreover, the hierarchical surface of the colloidal film prepared with BCMs at pH values of 4/4 is best characterized as being in Cassie's state,^[1] which implies that $\Delta\theta_{\text{ad-re}}$ is smaller than 6° . A water droplet deposited on the film bounces like a rubber ball, as shown in Figure 2d. It has been reported that Cassie's state with a characteristic low hysteresis of the contact angle arises from the increased air trapped at the interface between the film surface and the water droplet.^[11] In other words, as shown in Figure 1c, the superhydrophobic properties exhibited by colloidal films with crew-cut BCMs adsorbed at pH 4/4 arise from the increased amount of trapped air because of the hierarchical dual-scale roughness. The increased surface area made available by the micrometer-sized colloids (about 933 nm in diameter), as well as the nanostructured surface roughness realized with BCMs, leads to ideal conditions for superhydrophobicity.

In order to demonstrate optical functionality in the superhydrophobic films, hydrophobic CdSe@ZnS QDs (ca. 5 nm in

diameter with a PL emission peak at 560 nm, corresponding to a green–yellow color; and 5.4 nm in diameter with a PL emission peak at 600 nm, red in color) as well as a hydrophobic organic dye (Coumarin 30 with a PL emission peak at 480 nm, bluish green in color) have been incorporated into the hydrophobic PS cores of both crew-cut $\text{PS}_{49.5\text{k}}\text{-}b\text{-P4VP}_{16.5\text{k}}$ and $\text{PS}_{16\text{k}}\text{-}b\text{-PAA}_{4\text{k}}$ micelles, as shown on Figure 3. The transmission electron microscopy (TEM) image shown in Figure 3a indicates that the hydrophobic CdSe@ZnS QDs are uniformly entrapped within the PS cores of $\text{PS}_{49.5\text{k}}\text{-}b\text{-P4VP}_{16.5\text{k}}$ micelles by the self-diffusion of the QDs owing to the more energetically favorable interactions between the PS blocks and the QDs. The micelle size has been measured to be ca. 40 ± 10 nm. Based on this self-diffusion process, we have prepared four different sets of 3-bilayered BCM colloidal suspensions (Fig. 3b and c) and convectively assembled films from these suspensions containing CdSe@ZnS QDs and/or an organic dye, as shown in the fluorescent images of Figure 3d. Interestingly, in the case of $\{\text{PS}_{49.5\text{k}}\text{-}b\text{-P4VP}_{16.5\text{k}}$ loaded with CdSe@ZnS (5 nm)/ $\text{PS}_{16\text{k}}\text{-}b\text{-PAA}_{4\text{k}}$ loaded with Coumarin 30) or $\{\text{PS}_{49.5\text{k}}\text{-}b\text{-P4VP}_{16.5\text{k}}$ loaded with CdSe@ZnS

(5.4 nm)/ $\text{PS}_{16\text{k}}\text{-}b\text{-PAA}_{4\text{k}}$ loaded with Coumarin 30) multilayer-coated colloids, the fluorescent colors of the obtained structures show mixed colors between the green–yellow color of CdSe@ZnS (5 nm) and blue–green color of Coumarin 30 or between the red color of 5.4 nm CdSe@ZnS and the blue–green color of Coumarin 30, respectively, because there is no significant fluorescence resonance energy transfer (FRET) between CdSe@ZnS QDs and Coumarin 30, as confirmed by the photoluminescence spectrum of Coumarin 30 and the UV-vis spectrum of CdSe@ZnS QDs (Supporting Information, Fig. S4). It has recently been reported by Sohn and co-workers that FRET in mixed micellar films of two kinds of PS-*b*-P4VP micelles containing different dye molecules is effectively suppressed by the corona gap between the micellar cores, which exceeds the Förster radius (about 4.1 nm) for effective energy transfer.^[24] It should be noted that in our approach the respective corona blocks (i.e., P4VP and PAA) of $\text{PS}_{49.5\text{k}}\text{-}b\text{-P4VP}_{16.5\text{k}}$ and $\text{PS}_{16\text{k}}\text{-}b\text{-PAA}_{4\text{k}}$ crew-cut micelles are not crosslinked for the formation of LbL multilayers via electrostatic interactions between oppositely charged BCMs. Although it has been reported by Taton and co-workers that the crosslinking of PAA corona blocks in PS-*b*-PAA BCMs containing hydrophobic QDs can enable

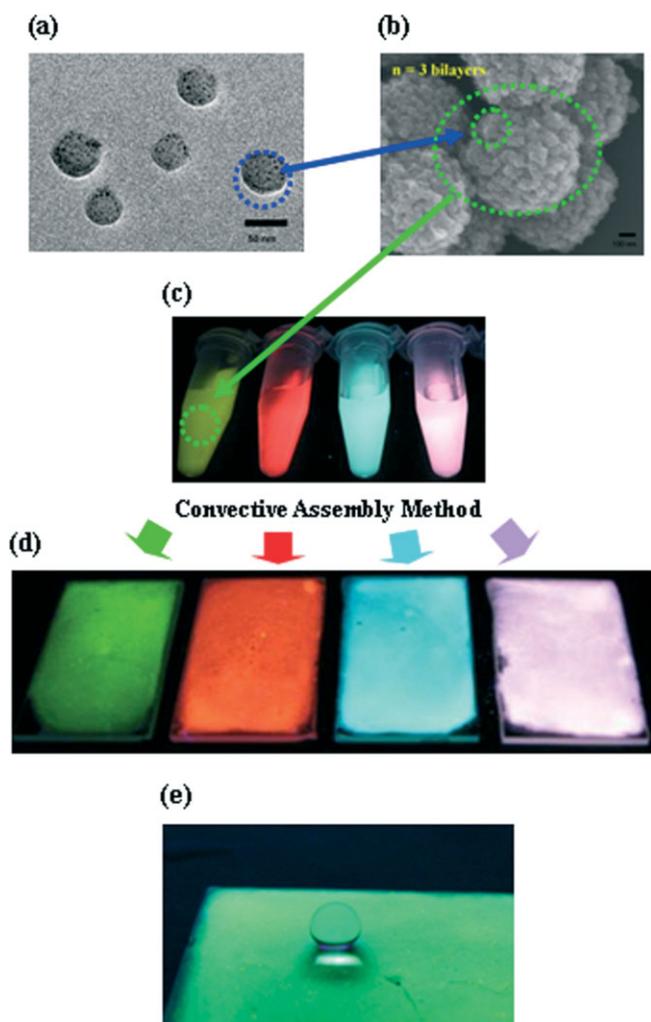


Figure 3. a) TEM image of PS_{49.5k}-*b*-P4VP_{16.5k} crew-cut micelles with the PS cores loaded with hydrophobic CdSe@ZnS (5 nm) QDs. b) SEM image of silica colloids coated with {PS_{49.5k}-*b*-P4VP_{16.5k} loaded with CdSe@ZnS (5 nm)/PS_{16k}-*b*-PAA_{4k}}₃. c) Colloidal suspensions and d) films coated with {PS_{49.5k}-*b*-P4VP_{16.5k} loaded with CdSe@ZnS (5 nm)/PS_{16k}-*b*-PAA_{4k}}₃, {PS_{49.5k}-*b*-P4VP_{16.5k} with CdSe@ZnS (5.4 nm)/PS_{16k}-*b*-PAA_{4k}}₃, {PS_{49.5k}-*b*-P4VP_{16.5k} with CdSe@ZnS (5 nm)/PS_{16k}-*b*-PAA_{4k} with Coumarin 30}₃, and {PS_{49.5k}-*b*-P4VP_{16.5k} with CdSe@ZnS (5.4 nm)/PS_{16k}-*b*-PAA_{4k} with Coumarin 30}₃ multilayers (from left to right). e) The shape of a water droplet in contact with a colloidal silica film coated with {PS_{49.5k}-*b*-P4VP_{16.5k} loaded with CdSe@ZnS (5 nm)/PS_{16k}-*b*-PAA_{4k}}₃ at pH 4/4. The measured water contact angle is greater than 170°.

the formation of stable hybrid micelles, it is non-trivial to use such a BCM as a charged component for LbL multilayer deposition due to the loss of the charged sites upon crosslinking.^[19–22]

These results clearly imply that various hydrophobic nanoparticles can be incorporated into the LbL multilayer films within the BCMs without any need for exchanging the stabilizers to enable dispersion in water. Furthermore, it should be emphasized at this point that the fluorescence efficiency of BCM-encapsulated CdSe@ZnS is much higher than that of water-dispersed CdSe@ZnS QDs prepared by exchanging the

stabilizer (Supporting Information, Fig. S5). In general, it has been reported that the fluorescence efficiency of water-dispersed QDs, obtained by exchanging the trioctylphosphine oxide (TOPO) ligands on the QDs, decreases more than 30–40% relative to the efficiency of TOPO-capped QDs in organic solvents.^[41,42]

In this work, we have demonstrated that the hydrophobization of BCM-multilayer-coated colloidal films yields superhydrophobic surfaces with water contact angles above 170° arising from the hierarchical surface roughness of these films. The films show nanoscale as well as microscale roughness and also exhibit optical properties such as the rendering of different colors, as shown in Figure 3d and e. We emphasize that the present approach incorporating silica colloids that are about 600 nm in size and nanometer-sized BCMs is not limited to the system mentioned here, but should be broadly generalizable to other areas for incorporating additional functionalities such as metal or magnetic nanoparticles and nanowires.

In conclusion, we have demonstrated that multifunctional films with tunable superhydrophobicity and multicolor rendering can be realized via the LbL deposition of positively charged PS-*b*-P4VP and negatively charged PS-*b*-PAA micelles (BCM) onto colloidal particles. It has been shown that the surface hydrophobicity, as measured by the water contact angle, can be readily controlled from 122 to 171° by controlling the nanoscale roughness of the colloidal particles, which in turn is controlled by the *M_w* of the block segments and the charge density of the hydrophilic corona blocks. Furthermore, the incorporation of hydrophobic fluorophores such as CdSe@ZnS QDs and an organic dye into the PS cores of BCMs leads to the combination of multicolor emission with superhydrophobicity. Considering the broad applications of both LbL multilayers and block copolymer thin films, our approach is likely to open up new possibilities for thin films possessing multiple functionalities.

Experimental

Materials: PS_{10.6k}-*b*-P4VP_{42.4k} and PS_{49.5k}-*b*-P4VP_{16.5k} block copolymers were synthesized by anionic polymerization. PS_{2k}-*b*-PAA_{8k} and PS_{16k}-*b*-PAA_{4k} block copolymers were purchased from Polymer Source Inc. The deposition solutions containing cationic PS-*b*-P4VP and anionic PS-*b*-PAA micelles for LbL deposition were prepared as previously reported [25]. In this case, the pH of the PS-*b*-P4VP solution was fixed at pH 4, whereas the solution pH of PS-*b*-PAA was adjusted to either 4 or 6. The TOPO-stabilized CdSe@ZnS QDs with diameters of 5.0 and 5.4 nm were synthesized as reported previously in the literature (Supporting Information, Fig. S6) [41,42]. Coumarin 30, a water-insoluble fluorescent dye, was purchased from Sigma Aldrich. Silica colloids with a diameter of about 600 nm were purchased from Microparticles GmbH. 1H,1H,2H,2H-perfluorodecyltrichlorosilane was purchased from Johnson Matthey.

Preparation of BCM Multilayer Films: The concentration of the BCM solutions used in all the experiments was fixed at 1 mg mL⁻¹ and no extraneous ionic salts were added. The PS-*b*-P4VP/PS-*b*-PAA multilayer-coated silica colloids were prepared as follows: 100 μL of a concentrated dispersion (6.4 wt%) of negatively charged 600 nm silica colloids was diluted to 0.5 mL with deionized water. Subsequently, 0.5 mL of PS-*b*-P4VP (1 mg mL⁻¹ at pH 4) was added. After deposi-

tion for 10 min, the excess PS-*b*-P4VP BCs were removed by three centrifugation (8000 rpm, 5 min)/wash cycles. PS-*b*-PAA (1 mg mL⁻¹ at pH 4 or 6) was then deposited onto the PS-*b*-P4VP-coated silica colloids under the same conditions. The above process was repeated until 3 bilayers of PS-*b*-P4VP/PS-*b*-PAA were deposited on the colloidal silica.

Encapsulation of CdSe(ZnS) QDs and a Fluorescent Dye: 1.5 mL of TOPO-stabilized CdSe@ZnS QDs with a concentration of 0.16 mg mL⁻¹ (in tetrahydrofuran (THF)) and 0.08 mg of water-insoluble Coumarin 30, a fluorescent dye, were mixed in PS_{49.5k}-*b*-P4VP_{16.5k} (50 mg mL⁻¹ in 2 mL *N,N*-dimethylformamide (DMF)) and PS_{16k}-*b*-PAA_{4k} (25 mg mL⁻¹ in 2 mL DMF) solutions, respectively. Subsequently, 96 mL of deionized water was added slowly with vigorous stirring.

Preparation of Superhydrophobic Films: The hydrophobization of the convectively assembled PS-*b*-P4VP/PS-*b*-PAA multilayer-coated silica colloidal films was performed by dipping the films in a solution of *n*-hexane containing 1H,1H,2H,2H-perfluorotrichlorosilane (6 mg mL⁻¹) for 20 min, followed by mild baking at 70 °C for 30 min under vacuum.

ζ-Potential Measurements: The ζ-potentials of PS-*b*-P4VP and PS-*b*-PAA micelles were measured using an electrophoretic light scattering spectrophotometer (ELS-8000). The periodic changes in the ζ-potentials were measured upon the alternate deposition of cationic PS-*b*-P4VP and anionic PS-*b*-PAA micelles onto colloidal silica particles.

Surface Morphology: The surface morphology of BCM-multilayer-coated silica colloids was investigated by field-emission SEM (XL30FEG, Philips).

Contact Angle Measurements: Water contact angles of the BCM-multilayer-coated colloidal silica films were measured using a DSA100 drop-shape-analysis system (Kruss GmbH).

TEM: A Philips Electron Optics CM-20 instrument was used for TEM investigations of PS_{49.5k}-*b*-P4VP_{16.5k} micelles loaded with CdSe@ZnS QDs and hollow-shell films composed of PS-*b*-P4VP/PS-*b*-PAA multilayers. The samples for TEM were prepared by depositing aqueous solutions onto carbon-coated copper grids. The mixtures were allowed to air-dry for 1 day.

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