Layer-by-Layer Assembled Janus Microcapsules

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Considerable interest has been focused on the surface modification of colloidal particles to precisely tune their optical, mechanical, and physical properties.[1,2] Particle surface modification methods include the deposition of various types of molecules from the liquid[3] or vapor phase,[4] surface-initiated polymerization schemes,[5] and the adsorption of inorganic materials.[4,6] In general, these methods provide a means to control the functionality or surface charge of the entire colloid surface in a uniform manner. Recently, however, the preparation of asymmetrically functionalized particles (also known as Janus particles) has received much attention due to potential applications in fields such as photonics, optical biosensors, drug delivery, and electronics.[7−10] Asymmetry provides an additional functionality that can be utilized to build complex structures (e.g., polygons) that would not be accessible with uniformly functionalized colloids.[8] A number of different approaches to prepare asymmetrically functionalized particles have been reported. These methods include the vapor deposition of metals onto a surface-supported monolayer of colloids,[11] the partial modification of particles using a long-chain alkylsilane,[12] the deposition of thin polymer layers onto colloids using the Langmuir−Blodgett technique,[13] microcontact printing of molecules,[14,15] a gel trapping method,[16] laser photochemical deposition,[17] and the use of the gas−liquid interface as an asymmetrization tool.[18] Shchukin et al. have also utilized laminar flow of polyelectrolyte solutions in microfluidic channels to asymmetrically modify microparticles.[19]

The layer-by-layer assembly of polymers using secondary bonding interactions such as electrostatic attraction and hydrogen bonding offers opportunities in engineering the surface properties of particles in the size range from tens of nanometers to tens of microns.[3,20,21] In previous work, we demonstrated that solution cross-linked hydrogen-bonded multilayer coatings comprised of a weak polyelectrolyte (poly(acrylic acid)) (PAA) and a neutral polymer (polyacrylamide) (PAAm) can be produced successfully on colloidal particles.[22] These multilayer coatings on microparticles exhibited excellent resistance toward cell adhesion[22] and also were used as templates for in situ nanoparticle synthesis.[23] In this communication, we demonstrate that it is possible to prepare asymmetrically functionalized microparticles based on the hydrogen-bonded multilayer coatings and subsequent polymer-on-polymer stamping (POPS).[24] It is also shown that chemical reactions can take place selectively on one side of the particle coatings that have been functionalized with positively charged polymers. By extracting the core polystyrene particles from the interior of the Janus microparticles, asymmetrically functionalized hollow microcapsules are obtained. While several examples of the formation of Janus particles have been reported, to our knowledge, this work is the first example where hollow Janus microcapsules are created.

Scheme 1 shows the procedure involved in creating asymmetrically functionalized Janus microparticles and hollow Janus microcapsules. 5.6 μm amine-functionalized polystyrene particles (PS) were coated with 4.5 bilayers of hydrogen-bonded multilayers at pH 3.0 as described in our previous papers.[22,23] The hydrogen-bonded multilayer coatings are comprised of poly(acrylic acid) (PAA; M_w 90 000) and polyacrylamide (PAAm; M_w 800 000). It should be noted that the outermost layer of the coatings was always PAA in order to facilitate transfer of the positively charged polymer, poly(allylamine hydrochloride) (PAH; M_w 70 000), via electrostatic interaction during POPS. The hydrogen-bonded multilayers were cross-linked using water-soluble carbodiimide chemistry.[22,23,25] The multilayer-coated microparticles were deposited onto glass slides that had been coated with $(PAH8.5/PAA3.5)_{10.5}$.[26] This particular multilayer system firmly secured the deposited multilayer-coated microparticles to glass surfaces during the subsequent POPS step while allowing the particles to be redispersed from the glass surface into solution upon sonication after POPS. A poly(dimethylsiloxane) (PDMS) stamp that was inked with positively charged PAH was brought into contact with the deposited microparticles. To visualize the asymmetric nature of the Janus particles, fluorescein-labeled PAH (FITC-PAH; M_w 70 000) was also used to ink the PDMS stamps (Supporting Information). After transferring a thin layer of PAH onto the top halves of the multilayer-coated particles, the particles were redispersed in deionized water by sonication and observed under fluorescence microscope. Koo et al.[15] and Cayre et al.[14,27] also utilized microcontact printing to create asymmetrically functionalized particles from bare polystyrene latex particles.

FITC-PAH was successfully stamped selectively onto the top halves of the multilayer-coated particles as can be seen in Figure 1. The PAH layer was readily transferred from the PDMS stamp to the multilayer-coated microparticles via electrostatic interaction between PAH and the outermost PAA layer.[24] The faint fluorescence on the left edge of the dark hemisphere is due to reflection from the other half through the bulk of the microsphere. A similar phenomenon was also observed by others.[27] Because of the electrostatic interaction between the oppositely charged sides of redispersed particles, the colloidal stability of these Janus particles was low in deionized water.

The surface of the asymmetrically functionalized particles can be further modified by utilizing the available functional groups present on either half of the particles (e.g., the amine groups in the stamped PAH layer). Figure 2 is a schematic representation of possible additional modifications that can be performed on the

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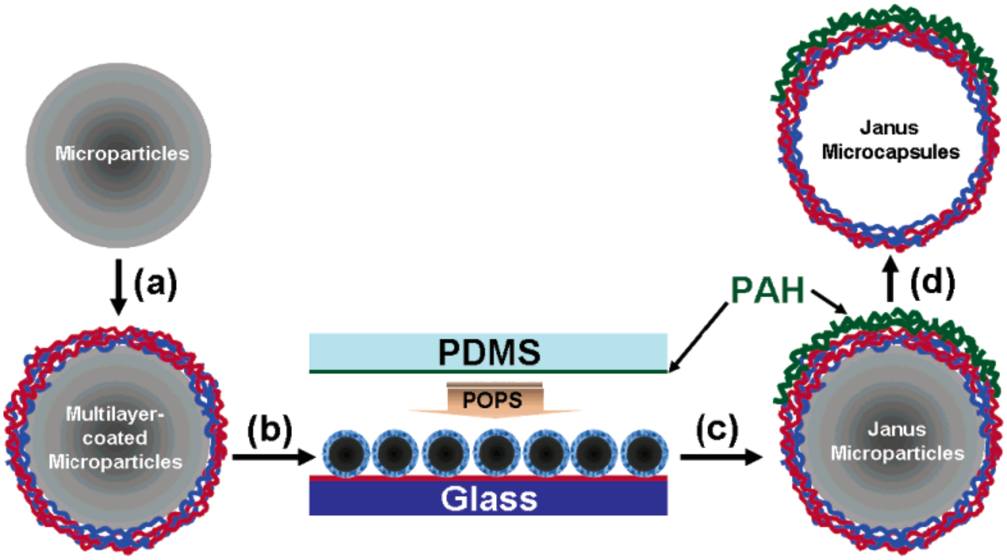
Scheme 1. Formation of Asymmetrically Functionalized Microcapsules[a]



[a] (a) Layer-by-layer assembly of $(PAA3.0/PAAm3.0)_{4.5}$ and subsequent EDC cross-linking, (b) adsorption of multilayer coated microparticles atop $(PAH8.5/PAA3.5)_{10.5}$-coated glass slides and subsequent transfer of PAH from PDMS stamp, (c) redispersion of asymmetrically functionalized microparticles using sonication, and (d) core dissolution using THF (see Supporting Information for details).

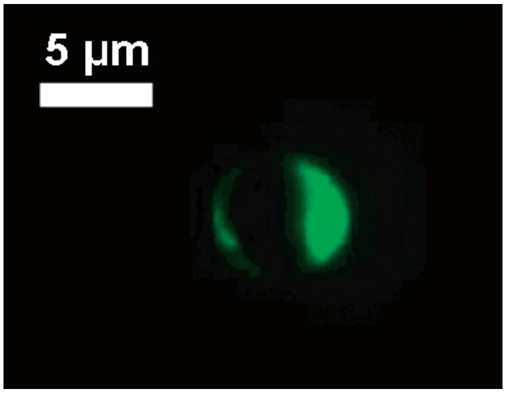


Figure 1. Fluorescence microscopy image of a 5.8 μm multilayer coated amine-PS particles stamped with FITC-PAH.

asymmetrically functionalized particles. Negatively charged homopolymers or diblock copolymers can be selectively adsorbed onto the positively functionalized hemisphere of the Janus particles. Also, polymer chains with reactive end groups can be covalently linked via chemical reaction. Attached chains can offer specific functionalities such as hydrophobicity, polarity, and additional functional groups. By using core particles with different sizes and attached chains with different lengths, these asymmetric particles can assemble into complex suprastructures.[12,28]

The PAH side of the Janus particles was modified by adsorbing a negatively charged polyelectrolyte, sodium poly(styrenesulfonate; M_w 70 000) (PSS), or a poly(ethylene oxide)-*b*-poly(methacrylic acid) (PEO−PMAA; M_w 7800−2000) diblock copolymer onto the positively charged FITC-PAH side of the Janus particles via electrostatic interaction. When the adsorption of PSS or PEO−PMAA was carried out, the asymmetrical nature of the Janus particles was still retained (determined by fluorescence microscopy) while the colloidal stability of these particles improved noticeably (not shown). We believe that the adsorbed PSS and PEO−PMAA chains stabilized the colloidal system via electrostatic repulsion and steric stabilization, respectively.

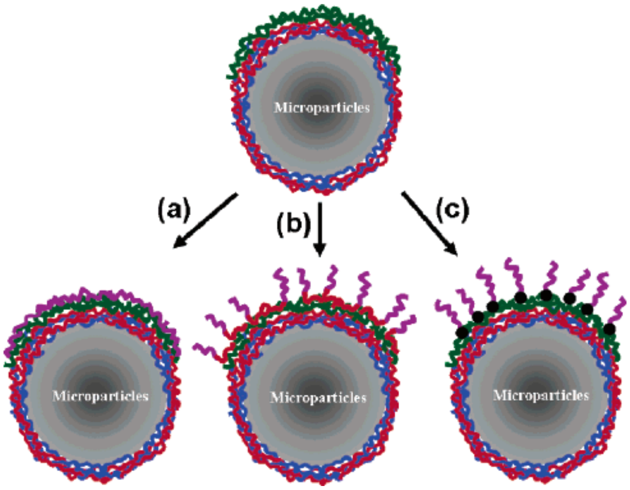


Figure 2. Schematic representation of additional modification of Janus particles by (a) the adsorption of a polyanion (e.g., PSS), (b) the adsorption of a diblock copolymer (e.g., PEO−PMAA), and (c) the formation of covalent links by grafting chains with reactive ends.

The amine groups of the PAH side of the Janus particle can be used to form covalent links as illustrated in Figure 2 (method c). Prior to the POPS step, the $(PAA3.0/PAAm3.0)_{4.5}$ hydrogen-bonded multilayer coatings were labeled with Alexa Fluor555 hydrazide, tris(triethylammonium). This labeling was accomplished by reacting free carboxylic acid groups in the multilayer coatings with hydrazide groups of the Alexa Fluor molecules to form covalent bonds.[22] After PAH was transferred onto one side of the particles via POPS, the amine groups of stamped PAH were reacted with *N*-hydroxysuccinimide (NHS) groups of FITC-labeled poly(ethylene glycol)-*N*-hydroxysuccinimide (NHS-PEG-FITC; M_w 3400). Figure 3a shows that the hydrogen-bonded multilayers that coat the entire particle surface exhibit red fluorescence under a red filter due to the presence of labeled Alexa Fluor molecules. When the same particles were observed under a green filter, particles show green fluorescence only on one side,

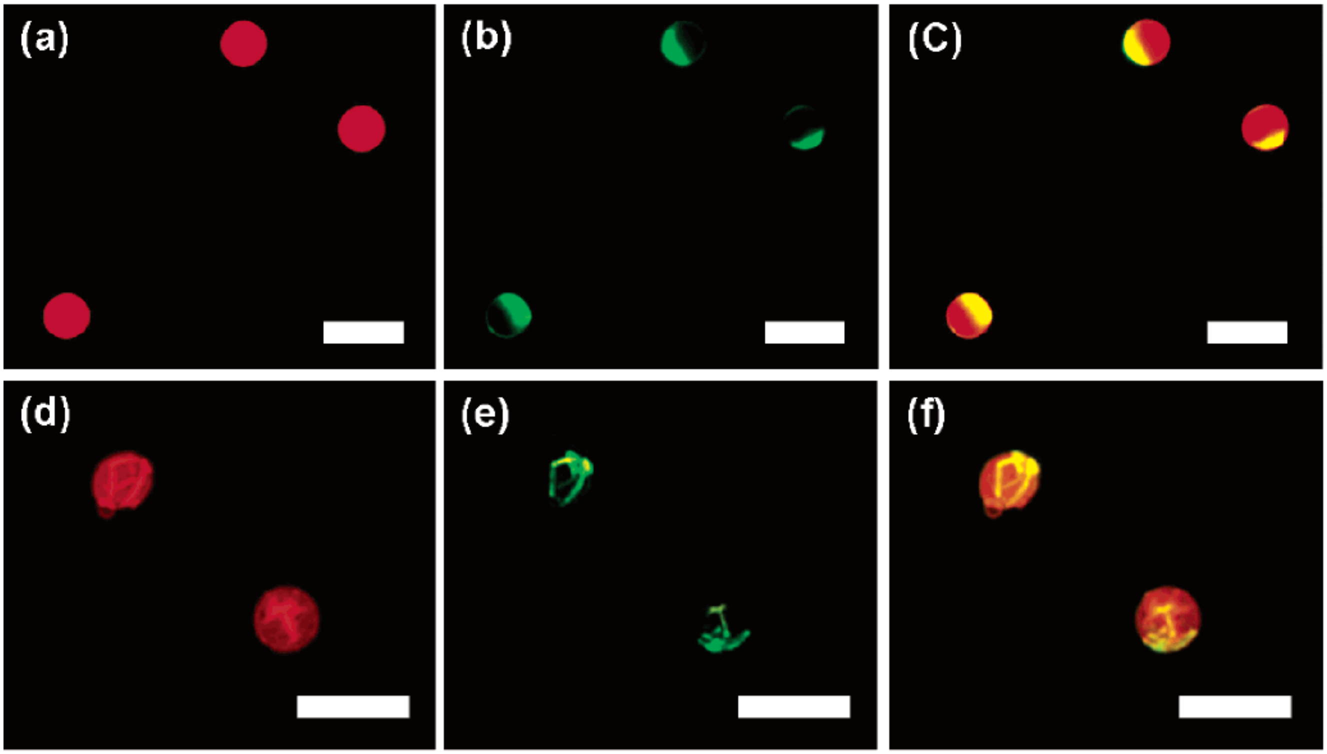


Figure 3. Fluorescence microscopy images of $(PAA3.0/PAAm3.0)_{4.5}$ multilayer-coated PS microparticles asymmetrically functionalized with PAH-NHS-PEG: (a) Alexa Fluor fluorescence, (b) FITC fluorescence, and (c) overlay. Fluorescence microscopy images of corresponding hollow Janus microcapsules after treatment with THF: (d) Alexa Fluor fluorescence, (e) FITC fluorescence, and (f) overlay. Scale bars = 10 μm.

demonstrating that NHS chain ends reacted only with the amine groups of the stamped PAH layer. Figure 3c shows the overlay image of Figure 3a,b. As can be seen in this figure, each particle exhibits a bright yellow color on one side which is the combination of green and red fluorescence. Particle suspensions also showed enhanced colloidal stability in water after the FITC-labeled PEG chains were grafted to the PAH layer.

Asymmetrically functionalized hollow microcapsules (Janus microcapsules) were obtained by extracting the core microparticles by treating the Janus particles in THF.[16] Although the microcapsules collapsed to some extent after the extraction process, it is evident in Figure 3 that while an entire capsule exhibits red fluorescence (Figure 3d) only small portion of a capsule surface exhibits green fluorescence (Figure 3e). By overlaying these two figures, hollow Janus microcapsules that have two distinct functionalities can be seen (Figure 3f).

In conclusion, we have demonstrated that asymmetrically functionalized microparticles as well as hollow microcapsules can be produced by first coating the particles with cross-linked hydrogen-bonded multilayers followed by polymer-on-polymer stamping. The asymmetric outermost layer was further functionalized by attaching other polymers on one hemisphere of the particles. Also, it is possible to modify the hydrogen-bonded multilayers by utilizing the free carboxylic acid groups (e.g., in situ synthesis of nanoparticles[23]) that are present in the coatings. Although the number of Janus particles/microcapsules that can be prepared via the POPS technique is limited, with the choice of different multilayer systems and the attachment of different functional moieties we believe that our method can be utilized to prepare Janus particles for a variety of applications. In the future, we intend to explore the use of other methods such as photochemistry[17,29] to increase the yield of Janus particles.

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Supporting Information Available: Experimental details for the preparation of Janus microparticles/microcapsules. This material is available free of charge via the Internet at http://pubs.acs.org.

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