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Genesis of Anisotropic Colloidal Particles via Protrusion of Polystyrene from Polyelectrolyte Multilayer Encapsulation

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Received March 5, 2009; E-mail: dayang.wang@mpikg.mpg.de

Anisotropic particles gain increasing attention to mimic molecular assembly behaviors.[1−3] By properly choosing the materials for a better crystalline facet matching, one can directly synthesize anisotropic Janus inorganic nanoparticles, but their surfaces are typically coated with the same ligands due to a one-pot synthesis procedure.[4,5] Template-assisted fabrication can yield truly Janus particles composed of chemically different constituent particles with different surface chemistry, but the production yield is relatively low as compared with that of direct synthesis procedures.[6−9] Direct synthesis of anisotropic polymer particles has been of experimental and theoretical interest in macromolecular science for decades.[10,11] Anisotropic particles of polystyrene (PS) with a snowman-like or egg-like shape have been obtained by swelling cross-linked PS particles by styrene, followed by polymerization.[11] This is due to the fact that, upon being in contact with styrene, the cross-linked PS network first swells to absorb styrene and then shrinks to repel styrene, what is known as overswelling, as the cross-linked polymer network is far from equilibrium.[11] Herein we present a rather simple and flexible alternative to directly produce anisotropic polymer particles with a snowman-like shape and the surface being well-separated into two distinct functional domains.

Based on well-established electrostatic assembly,[12] cationic poly(allylamine hydrochloride) (PAH) and anionic sodium poly(styrene sulfonate) (PSS) were alternately deposited to form polyelectrolyte multilayer (PEM) shells on negatively charged PS particles (Figure S1a). The $(PAH/PSS)_5$ coating renders the particle surfaces negatively charged while the $(PAH/PSS)_5PAH$ coating renders the particle surfaces positively charged. When PEM-coated PS particles were dispersed in pure tetrahydrofuran (THF), the PS cores completely dissolved, thus leading to PEM capsules (Inset in Figure S1a). In contrast, when a small amount of THF was added to aqueous suspensions of PEM-coated PS particles (e.g., the THF-to-water volume ratio was 0.5:1), PS cores could not dissolve completely and no PEM capsules were observed. Instead, small protrusions were visible as soon as THF was added (less than several seconds), transforming the spherical shape of the particles into a snowman-like shape (Figure 1a and movie S1). Scanning electron microscopy (SEM) imaging testified to the size increase of the protrusions with incubation time in the THF/water mixture (Figure 1). We calculated the volumes of the protrusions based on the geometry transformed from the SEM images and found that while protrusions swelled with the incubation time in a THF/water mixture, the parent particles first swelled and then shrunk (Figure S2). Transmission electron microscopy (TEM) imaging indicated the hollow character of the PEM-coated parent particles (Figure S3); a number of voids were visible within the PS protrusions.

Labeling one PAH layer with fluorescein isothiocyanate (FITC) allowed the PEM shells to be distinguished from the PS cores by means of confocal laser scanning microscopy (CLSM). Figure 2 shows that the fluorescent PEM shells are exclusively located on the parent particles; no fluorescence is visible on the protrusions. Accordingly we deduce that the protrusions are made of PS and few PEM shells are coated on their surfaces. The protrusion can be terminated by adding a huge excess of water, and this structural anisotropy can be maintained for months after removal of THF. Increasing the THF-to-water volume ratio above 8:1 caused complete dissolution of PS cores, thus leading to hollow PEM capsules (Figure S1b). Due to the existence of water—nonsolvent for PS—in the surrounding, the dissolved PS chains precipitated into secondary particles with a broad size distribution and a number of dents on the surfaces (Figure S1b).

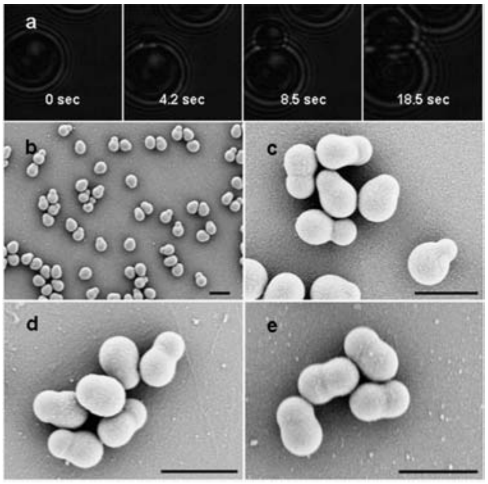

Figure 1. (a) A time series of optical photographs recorded soon after dropping 1.5 mL of THF into 1 mL of aqueous dispersion of $(PAH/PSS)_5$-coated 4.4 μm PS particles, showing that as soon as THF is added, the PS particles swelled and a small protrusion appeared and enlarged with the incubation time. Low magnification (b) and high magnification SEM images (c) of the anisotropic particles obtained by incubation of $(PAH/PSS)_5$-coated 1.1 μm PS particles in a THF/water mixture for 1 min, followed by redispersion in water with the means of centrifugation. The THF-to-water volume ratio is 0.5:1. High magnification of the SEM images of the anisotropic particles obtained at 2 h (d) and 1 d (e) of incubation in the THF/water mixture. The scale bar is 2 μm.

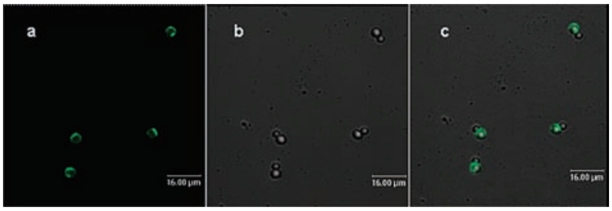

Figure 2. Fluorescence (a) and transmission (b) CLSM images of the anisotropic particles obtained by incubation of $(PAH/PSS)_3$/FITC-PAH/PSS/PAH/PSS-coated 4.4 μm PS particles in a THF/water mixture for 2 min, followed by redispersion in water with the means of centrifugation. (c) Overlay of the fluorescence and transmission CLSM images. The THF-to-water volume ratio is 1.5:1.

10.1021/ja901705f CCC: $40.75

Based on the aforementioned observation, the mechanism of turning isotropic PEM-coated PS microspheres to anisotropic particles is proposed (Scheme S1). Upon THF addition into aqueous dispersions of PEM-coated PS particles, the PS cores start to dissolve. Due to the hydrophilic PEM coating and the presence of excess water in the surrounding media, the THF dissolution of the hydrophobic PS cores can cause a high osmotic pressure, thus driving the PEM-coated PS particles as a whole to swell (Figures 1 and S2). This osmotic pressure should be sufficiently large to open holes on the closed PEM shells, which was clearly evidenced by the existence of a number of broken hollow capsules when a high amount of THF was added to decompose PEM-coated PS particles (Figure S1b). But the hydrophobic PS chains cannot diffuse into the water-rich surrounding media through the holes. On the other hand, the PS particles used are negatively charged due to the sulfate groups on the surfaces derived from persulfate initiators used during the particle synthesis via emulsion polymerization. As such the outmost shells of PS particles should be rich in sulfate-terminated PS chains. Upon dissolution of the PS cores by THF, these sulfate-terminated PS chains should first dissolve and easily diffuse through the PEM shells, and their sulfate termini can stabilize the protrusion front of the PS chain flow from the THF-swollen PS cores in contact with the polar surrounding through the openings of the PEM shells (Scheme 1). Opening holes on the PEM shells is expected to be thermodynamically random. While one hole is kinetically occasionally created, as suggested in literature,[13] it will become the preferential channel for the PS chains to be released out, thus leading to a snowman-like rather than raspberry-like protrusion (Figure 1). In the current work the optimal PEM thickness to create only one hole ranges from 5 to 10 bilayers. After the THF swollen in them dissolves back into the surrounding media, the PS protrusions are solidified, leading to the anisotropic particles. The presence of sulfate groups on the PS protrusions was demonstrated by the fact that the zeta-potential of the resulting anisotropic particles (−30.8 mV) was rather similar to that of original $(PAH/PSS)_5$-coated PS particles (−30.6 mV); otherwise a zeta-potential reduction might be observed. Obviously, a longer incubation time and/or a larger THF-to-water volume ratio can lead to a larger PS protrusion from the PEM shell as more PS chains can diffuse into the protrusions (Figures 1 and S2). Since the amount of PS should remain constant, the PS protrusion led to the hollow structures of the parent PEM-coated PS particle parts of the anisotropic particles obtained (Figure S3). The hollow parent particles remained spherical due to the osmotic pressure arising from free PS chains inside (Figure 1); precipitating the PS chains caused the collapse of the parent particles (Figure S4).

Figure 3a shows that, upon incubation in the mixture of THF/water, $(PAH/PSS)_5PAH$ coated PS particles become anisotropic, suggesting that the PS protrusion is independent of the charge nature of the outmost layer of the PEM shells. The anisotropic particles derived from $(PAH/PSS)_5PAH$-coated PS particles should have two well spatially separated positively and negatively charged regions; the surfaces of the newly formed PS protrusions were negatively charged, and the $(PAH/PSS)_5PAH$ coating of the parent particles remained positively charged. To demonstrate that, the resulting anisotropic particles were incubated in aqueous suspensions of negatively charged gold nanoparticles (NPs). Figure 3b shows that the gold NPs selectively are adsorbed on the $(PAH/PSS)_5PAH$ shells of the parent particles; no gold NP is found on the protrusions. Furthermore, the selective adsorption of gold NPs, and especially subsequent modification of them, on the parent particles can largely enhance the chemical anisotropy on the surfaces.

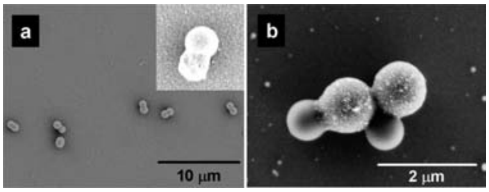

Figure 3. (a) SEM image of the anisotropic particles obtained by incubation of $(PAH/PSS)_5PAH$-coated 1.1 μm PS particles in a THF/water mixture for 1 min, followed by redispersion in water with the means of centrifugation. The THF-to-water volume ratio is 0.5:1. The high magnification SEM image is shown in the inset. (b) SEM image after gold NPs are selectively adsorbed on the parent PEM-coated particles.

In conclusion we have succeeded in the growth of both structurally and chemically anisotropic polymer particles by protrusion of the PS cores from the PEM shells when PEM-coated PS particles are incubated in water/THF mixtures. Our approach is rather simple and rapid (within minutes) and easy to scale up as compared with the methods reported in literature. It is little dependent on the core size and the PEM coating composition, leading to the freedom to choose materials to create anisotropic particles and to diversify the chemical anisotropy on their surfaces. Besides our approach may also be generalized to use different core and surface coating materials instead of PS and PEM, thus providing a new concept of growing both structurally and chemically anisotropic particles and shedding light on the study of controlled self-assembly of colloidal particles.[1−3]

Acknowledgment. This work is financially supported by the Max Planck Society and in part by a DFG grant (WA1704/4-1). The authors are indebted to H. Möhwald for valuable discussions and support.

Supporting Information Available: Experimental details, SEM and TEM images of the resulting snowman particles, plots of the volumes of the PS protrusions and the parent PEM-coated PS particles versus the incubation time in the THF/water mixture, and movie S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA901705F