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Fabrication of Stable Hollow Capsules by Covalent Layer-by-Layer Self-Assembly

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Introduction

Core−shell particles and the free-standing hollow capsules, a special kind of core−shell particle, in which the core consists of air or solvent, are of great interest due to their potential applications and fundamental importance.[1] In recent years the layer-by-layer (LbL) self-assembly technique was introduced for their synthesis. This strategy possesses several advantages: finely tuned polymer layer thickness, easily assembled multicomposite coatings and no limit to the size, shape and composition of the templates. Up to now, a variety of core−shell particles[2] and hollow capsules[3] have been synthesized using this strategy.

Although LbL strategies based on hydrogen bond,[4] charge-transfer interaction,[5] coordination bond,[6] and covalent bond[7] have also been developed, up to now almost all papers employed the electrostatic self-assembly (ESA) method, except several cases with minor modification.[8] It was limited to aqueous system and the shell is not stable enough due to the ionic cross-linking nature of the self-assembled layer, which attracted attention recently.[9] One way to improve the shell stability is to chang the cross-linking nature from ionic to covalent under external stimuli as shown by Caruso et al.[10]

Herein we report the use of covalent layer-by-layer self-assembly (CSA) in the synthesis of core−shell particles and hollow capsules. Since CSA can be carried out in organic solutions, the extension of this technique to three-dimensional system will extend the use of LbL strategy from aqueous system to nonaqueous system. More importantly, a highly stable shell can be obtained directly because of the covalent nature of the resulting films.

Experimental Section

Materials. *N*-Methyl-2-nitro-diphenylamine-4-diazoresin (NDR) was prepared according to ref 11. *m*-Methylphenol−formaldehyde resin (MPR) was purchased from Beijing Nanyuan Chemical Factory. The negatively charged, sulfonate-stabilized polystyrene latex with an average diameter of 260 nm was prepared according to ref 12. Other chemicals are analytical grade and were used as received.

Preparation of Core—Shell Particles and Hollow Capsules. The preparation of core−shell particles is almost identical with the ESA process. First the PS latex was centrifuged for 10 min at 10000*g* to replace the aqueous solution with methanol. Then 1 mL of a 1 mg/mL NDR solution in methanol was added. The positively charged NDR would adsorb onto the PS particles under gentle stirring. After 10 min, the PS latex was centrifuged, and the supernatant solution was replaced with methanol 3 times. Then 1 mL of a 1 mg/mL MPR solution in methanol was added and allowed to stand for 10 min for the deposition of MPR. After being cleaned for 3 times, NDR was added again for the deposition of another layer of NDR. The process was repeated until the desired number of bilayer reached. To avoid the decomposition of NDR, the whole process was carried out in the dark.

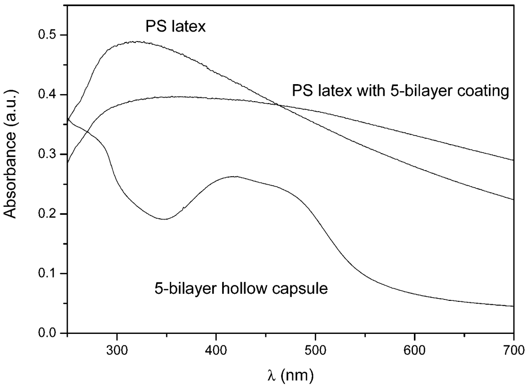
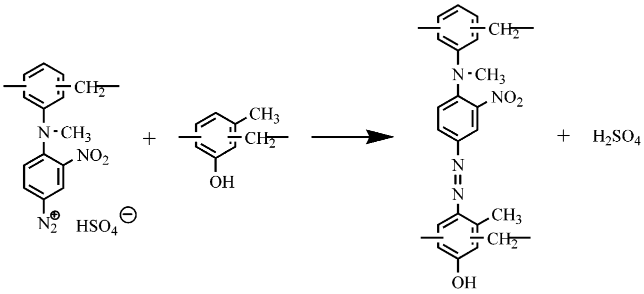


Figure 1. UV−vis spectra of PS latex, PS latex with 5-bilayer NDR-MPR coating, and 5-bilayer NDR-MPR hollow capsules.

Scheme 1. In Situ Coupling Reaction between NDR and MPR



To prepare the hollow capsules, the solvent, methanol, was replaced with THF, and we allowed for at least 2 h for the dissolution of the PS core. The process was repeated to ensure the complete removal of the PS core.

Characterization. UV−vis absorption spectra were measured on a Shimadzu UV 1601 PC spectrophotometer. FTIR spectra were recorded on a Bruke Equinox 55 FT-IR/FAR 106 spectrophotometer. TEM measurements were carried out on a JEM-100CX microscopy (Japan Electronic Co.). Samples were prepared by dropping a suspension onto Formvar-coated copper grids. AFM images were recorded on a Nanoscope IIIa AFM (Digital Instruments) in tapping mode. Samples were prepared by spin-coating onto new cleaved mica.

Results and Discussion

The covalent self-assembly of NDR and MPR is based on the in situ coupling reaction as shown in Scheme 1. The synthesis of core−shell particles and hollow capsules using covalent self-assembly is almost identical with that using electrostatic self-assembly. Comparing with the UV−vis spectrum of the bare PS latex, absorption of the particles in the visible range increases significantly after being coated with five bilayers of NDR and MPR (Figure 1), which is in acoordance with the color change from white to yellow observed by the eyes. After the removal of the PS core, the solution became

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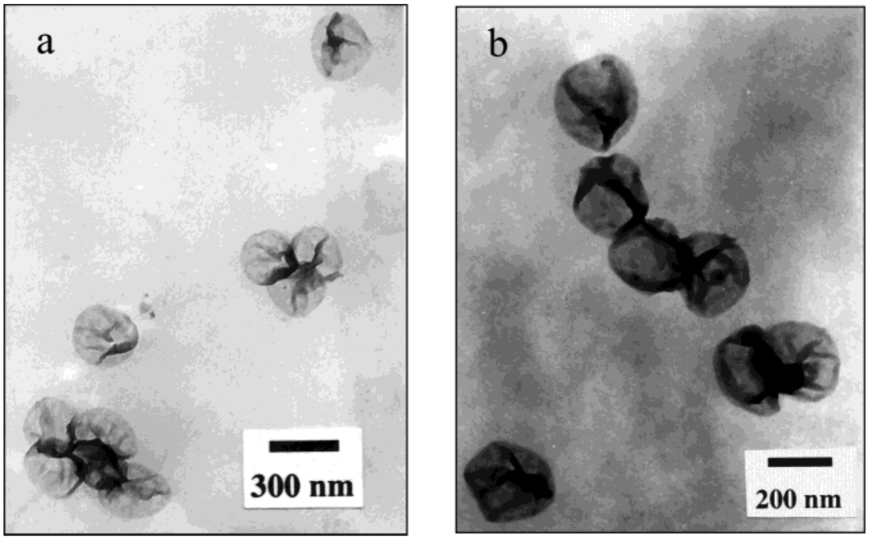

Figure 2. TEM micrograph of $(NDR/MPR)_5NDR$ hollow capsules before (left) and (right) after being exposed to DMF for 40 h.

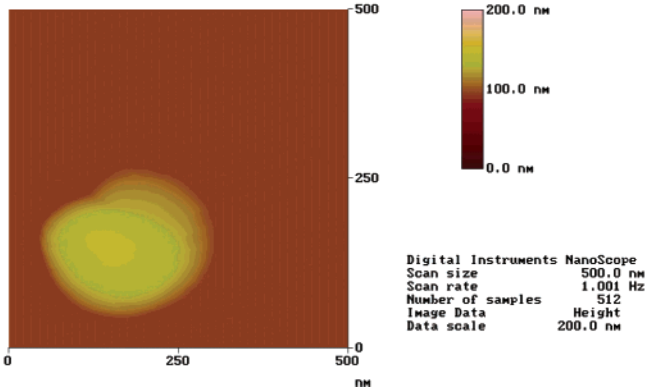

Figure 3. Tapping mode AFM micrograph of $(NDR/MPR)_5NDR$ hollow capsule.

almost transparent. The broad band from about 350 to about 530 nm is attributed to the absorption of the azo dye. In addition, the hollow capsule does not show the characteristic peak of diazonium group, which should appear at about 375 nm, indicating the diazionium group was consumed and converted to azo group.

Figure 2a shows the TEM image of air-dried $(NDR/MPR)_5NDR$ capsules. They are nearly round, continuous films; i.e., no rupture occurred during preparation. Similar to their polyelectrolyte analogue, they all exhibit creases and folds clearly, which result from the evaporation of solution in the capsules. The average diameter is about 260 nm, which is in accord with the average size of the template. A typical AFM image of the capsule is shown in Figure 3. From this image, a lower area with a height of about 30 nm and a higher area with a height of about 62 nm were observed. The high area may result from the folding of the capsule wall. From the height of the lower area, which corresponds to twice the wall thickness, the wall thickness is estimated to be about 15 nm.[3b,10] The data are in accordance with the result obtained on a planar substrate.[8a]

Studies on planar supports have shown that the ESA films cannot withstand the etching of polar organic solvent or saline solution with high ionic strength.[13] To enhance the stability of these films, one tries to chang the cross-linking nature from ionic to covalent using external stimuli, such as light[13] and heat.[14] In contrast, covalent bonds form in situ during the fabrication process in the case of CSA. The resulting films possess a covalent cross-linking structure. So without any need for any postpossessing, they are stable enough to withstand solvent etching.[7] The stability of the NDR/MPR capsule toward solvent etching was studied by exposing them to DMF for 40 h. As shown in Figure 2b, no change in the capsule morphology is observed. The result clearly indicates that the capsule is stable enough to withstand DMF etching.

Conclusion

We demonstrate that CSA can be used for the fabrication of core−shell colloids and hollow capsules. To the best of our knowledge, this is the first example to extend CSA from 2-dimensional to 3-dimensional systems. Besides the advantages of the ESA technique, the capsules fabricated using the CSA technique possesses high stability, which is very important for certain application of the capsules. The use of organic solution and the covalent nature of the capsule wall make CSA a useful complement to the ESA technique.

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