Hollow Capsules Constructed of Poly(thiophene-3-acetic acid) and Hyperbranched Azobenzene-containing Polymeric Diazonium Salt

Haoyu Zhang, Xinyang Li, and Xiaogong Wang*

Department of Chemical Engineering, Laboratory for Advanced Materials, Tsinghua University, Beijing 100084, P. R. China

(Received November 10, 2008; CL-081058; E-mail: wxg-dce@mail.tsinghua.edu.cn)

In this work, hyperbranched azobenzene-containing polymeric diazonium salt (HB-DAS) and poly(thiophene-3-acetic acid) (PTAA) were used as building components to fabricate hollow capsules. The capsules were prepared through layer-by-layer self-assembly of the components on PS latex spheres followed by removal of the PS cores with THF dissolution. The TEM, SEM, and AFM observations confirmed that uniform hollow capsules with an average wall-thickness of 5.9 nm were obtained.

Layer-by-layer (LBL) electrostatic adsorption has attracted great attention since it was introduced by Decher in 1991.[1] In recent years, this technique has been extended to prepare various self-assembled multilayer hollow structures by using removable substrates as templates. Hollow capsules have been prepared by this method using polystyrene (PS) latex particles as the substrates.[2,3] The hollow capsules can be expected to be used for many applications such as microreaction cages,[4] biosensors,[5] and photorelease systems.[6]

Fabrication of self-assembled multilayer films containing functional polyelectrolytes is a promising area for the application of the LBL methodology. The self-assembled films containing azo chromophores can show some interesting photoresponsive properties, such as optical second-harmonic generation (SHG) without electric-field poling,[7,8] photoswitching,[9] optical thickness modulation,[10] and surface hydrophilicity variation.[11] However, to our knowledge, construction of hollow capsules from azobenzene-containing polymeric diazonium salt has not been reported in the literature. In this communication, we report the LBL self-assembly fabrication of hollow capsules by using hyperbranched azobenzene-containing polymeric diazonium salt (HB-DAS) and poly(thiophene-3-acetic acid) (PTAA). The hollow capsules constructed of these two polyelectrolytes can combine photoresponsive and electroactive properties of the components. One possible interesting property, which will be explored in the future, is stimuli-response of the hollow capsules to both light and electric field. The chemical structures of HB-DAS and PTAA are shown in Figure 1.

The hyperbranched azobenzene-containing polymeric diazonium salt (HB-DAS) was synthesized through a route developed in our previous work.[12] The number-average molecular weight and the polydispersity index of the hyperbranched polymer were estimated to be 7000 and 1.5 by gel permeation chromatography (GPC).[12] The dipping solution of HB-DAS was obtained by diluting a DMF solution with deionized water to a concentration of 1 mg/mL. PTAA was obtained through the hydrolysis of poly(thiophene-3-acetic acid ethyl ester) which was polymerized through an oxidative coupling method in chloroform by using anhydrous iron(III) chloride as an oxidant.[13] The number-averaged molecular weight (M_n) of PTAA was 6000 obtained by GPC. The solution of PTAA in water (1 mg/mL) was prepared to have pH of 5.5. The PS colloidal spheres were synthesized by emulsion polymerization.[14] The average diameter of the latex particles (0.43 wt %) was 484 nm with a polydispersity of 0.03.

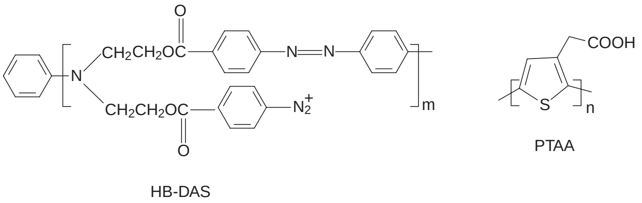

Figure 1. Chemical structures of HB-DAS and PTAA.

For electrostatic LBL self-assembly on the colloids, the PS latex was filtered and dialyzed against water for 24 h. The PS latex (2 mL) was centrifuged (12000 rpm) and the supernatant fluid was removed. The colloidal particles were dispersed in deionized water (1 mL) and then the HB-DAS dipping solution (1 mL) was added. After 20 min, the dispersion was centrifuged and the colloidal particles were washed with deionized water three times to thoroughly remove the remaining HB-DAS. The PTAA adsorption process was the same. After several adsorption/washing/redispersion cycles, required numbers of multilayers were assembled on the PS particle surfaces. The hollow capsules were prepared by treating the polyelectrolyte-coated spheres with THF for 3 h to dissolve the PS cores.

In order to study the electrostatic adsorption ability, the LBL self-assembly of the same polyelectrolyte pairs was first tested by using quartz and silicon slides as substrates. The concentrations of HB-DAS and PTAA solutions were both 0.5 mg/mL. Figure 2a shows a series of UV–vis spectra of the HB-DAS/PTAA multilayer films varied with the number of bilayers. The multilayer film exhibits a broad absorption band at around 424 nm from both HB-DAS and PTAA. The dependence of

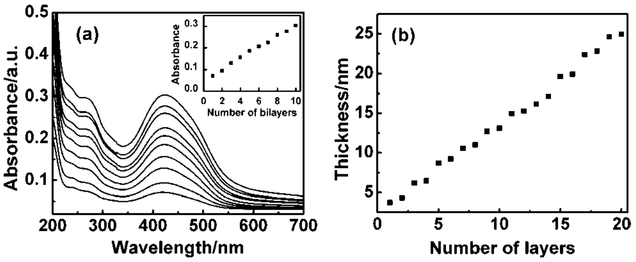

Figure 2. (a) UV–vis absorption spectra of HB-DAS/PTAA multilayers with different number of the bilayers, 1 to 10 form bottom to top, (inset: the absorbance at 424 nm of the film versus the number of bilayers); (b) the thickness of the film versus the number of layers.

the absorbance at 424 nm on the number of bilayers is shown in the inset of Figure 2a. The increase of absorbance has a linear dependence upon the number of the deposition cycles. Figure 2b gives the ellipsometric thickness of the self-assembled films as a function of the layer numbers. It shows a linearly increasing relationship between the thickness and the number of deposition cycles. The average bilayer thickness obtained from the figure is 2.3 nm.

The LBL deposition process on PS latex was monitored by measuring the zeta potentials. In order to avoid the possible decomposition of the diazonium groups at room temperature, the process of the polyelectrolyte adsorption, separation by centrifugation, and washing with water was carried out at 0 °C. The zeta potential of the particles with the PTAA as the outermost layer was about −35 mV. The adsorption of HB-DAS increased the value of zeta potentials to about −27 mV. The presence of HB-DAS on the outermost layer was incapable of causing a complete inversion of the charges on the PS particle surfaces, as reported for a similar case of diazoresins deposition.[15] The regular and alternate changes of zeta potentials were observed during the self-assembly cycles of HB-DAS and PTAA. This result confirms the sequential adsorption of HB-DAS and PTAA on the PS latex particles.

The inset in Figure 3a shows the TEM image of the PS spheres covered by three bilayers of HB-DAS/PTAA. The HB-DAS/PTAA-coated particles show increased surface roughness compared with the original PS particles. After exposing the HB-DAS/PTAA-coated spheres to THF for 3 h, the PS templates could be completely removed. The hollow capsules were obtained after the dissolved PS chains penetrated smoothly through the HB-DAS/PTAA multilayers. Figure 3a shows a typical TEM image of the hollow capsules composed of three HB-DAS/PTAA bilayers. The hollow capsules can be clearly identified through the creases and folds of the collapsed hollow structures on the copper grid. Figure 3b shows an AFM image of a capsule made up of three HB-DAS/PTAA bilayers. The largest dimension of the collapsed capsules is about 900 nm, which is much larger than the diameter of the PS particles due to spreading on the silicon wafer. The average height of the collapsed capsules on the silicon slide is 11.8 nm, which corresponds to the twofold thickness of the capsule wall. The thickness of 5.9 nm for the capsule wall is slight thinner than that for its counterpart obtained by self-assembly on the plane substrate (6.9 nm).

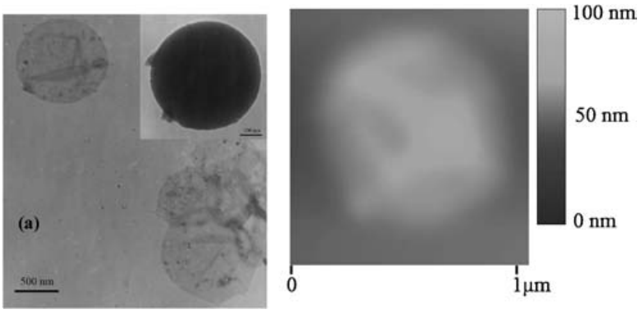

Figure 3. (a) TEM images of the hollow capsules and a PS particle coated with three HB-DAS/PTAA bilayers (inset). (b) AFM image of a hollow capsule on a silicon wafer.

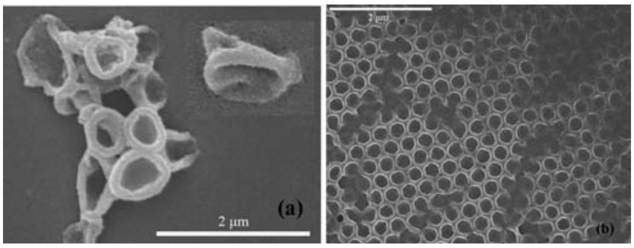

Figure 4. The SEM photographs of capsules on silicon wafers: (a) capsules made of three HB-DAS/PTAA bilayers and a magnified image (inset); (b) 2D array of the hollow capsules.

Figure 4a gives a SEM image of the aggregated hollow capsules and the inset shows a single collapsed capsule with the folds. The irregular torus morphology reflects the topographic contrast of the folding edges and creases. The above method can also be used to prepare the hollow capsule array. To show the possibility, the HB-DAS/PTAA-coated PS spheres were assembled into two-dimension (2D) colloidal arrays on silicon wafers through the vertical deposition method.[16] The silicon wafers were vertically dipped in a dilute colloidal dispersion and kept in 45 °C for 48 h to obtain the two-dimension array. After that, the PS sphere templates were removed by dipping the slides in THF for 3 h. Figure 4b shows a typical SEM image of the capsule arrays. The collapsed capsules appear as the white ring-like structures indicated by the topographic contrast of the edges.

This study demonstrates that by using PS latex particles as templates, hollow capsules composed of layered HB-DAS/PTAA membranes can be obtained. The TEM, SEM, and AFM observations confirm that the structures formed by this process are hollow capsules with an average wall-thickness of 5.9 nm.

The financial support from the NSFC under Project 50533040 is gratefully acknowledged.

References

1 G. Decher, *Science* **1997**, *277*, 1232.
2 F. Caruso, R. A. Caruso, H. Mohwald, *Science* **1998**, *282*, 1111.
3 F. Caruso, H. Mohwald, *J. Am. Chem. Soc.* **1999**, *121*, 6039.
4 L. Dähne, S. Leporatti, E. Donath, H. Möhward, *J. Am. Chem. Soc.* **2001**, *123*, 5431.
5 A. Yu, F. Caruso, *Anal. Chem.* **2003**, *75*, 3031.
6 B. Radt, T. A. Smith, F. Caruso, *Adv. Mater.* **2004**, *16*, 2184.
7 X. Wang, S. Balasubramanian, L. Li, X. Jiang, D. J. Sandman, M. F. Rubner, J. Kumar, S. K. Tripathy, *Macromol. Rapid Commun.* **1997**, *18*, 451.
8 S. Balasubramanian, X. Wang, H. C. Wang, K. Yang, J. Kumar, S. K. Tripathy, L. Li, *Chem. Mater.* **1998**, *10*, 1554.
9 A. Toutianoush, B. Tieke, *Macromol. Rapid Commun.* **1998**, *19*, 591.
10 S. Dante, R. Advincula, C. W. Frank, P. Stroeve, *Langmuir* **1999**, *15*, 193.
11 L. Wu, X. Tuo, H. Cheng, Z. Chen, X. Wang, *Macromolecules* **2001**, *34*, 8005.
12 P. Che, Y. He, Y. Zhang, X. Wang, *Chem. Lett.* **2004**, *33*, 22.
13 B. S. Kim, L. Chen, J. Gong, Y. Osada, *Macromolecules* **1999**, *32*, 3964.
14 K. Furusawa, W. Norde, J. Lyklema, *Kolloid Z. Z. Polym.* **1972**, *250*, 908.
15 I. Pastoriza-Santos, B. Scholer, F. Caruso, *Adv. Funct. Mater.* **2001**, *11*, 122.
16 L. M. Goldenberg, J. Wagner, J. Stumpe, B. R. Paulke, E. Gornitz, *Langmuir* **2002**, *18*, 3319.