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Polymer micelles as building blocks for layer-by-layer assembly of multilayers under a high-gravity field

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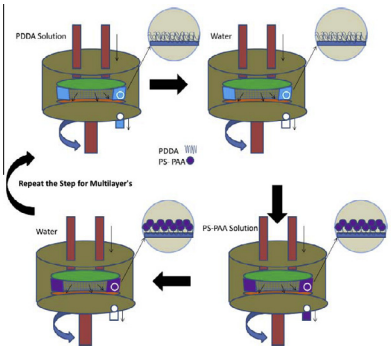
HIGHLIGHTS

- A high-gravity method for LbL assembly of multilayers using polymer micelles.
- Shortened deposition time via the high-gravity technique assisted LbL assembly.
- High-gravity technique assisted LbL assembly of PDDA/PS-PAA micelle multilayers.

GRAPHICAL ABSTRACT



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ABSTRACT

Construction of layer-by-layer (LbL) self-assembled multilayers is fundamental to various research fields. But most conventional processes for LbL are time consuming, which restricts its further applications. There has been a general demand for shortening the construction time without affecting the multilayer structures. High-gravity (HG) technique is a well-established chemical engineering process which can strongly intensify mass and heat transfer. In this study, we introduced the HG technique into construction of multilayers through LbL self-assembly concerned with polymer micelles as building blocks. By using a model system of poly(diallyldimethyl ammonium chloride) (PDDA)/polystyrene-poly(acrylic acid) (PS-PAA) polymer micelle multilayers, the LbL process was examined under both conventional dipping conditions and a HG field. Ultraviolet–visible spectra and atomic force microscopy results showed that the time for LbL under a HG field has been shortened 6 times compared with dipping assembly while the resultant multilayers achieved comparable quality as those prepared under conventional dipping LbL.

1. Introduction

Since its rediscovery in 1991 by Decher [1,2], layer-by-layer (LbL) self-assembly has been proven as a powerful method of constructing tailored thin films with wide applications, such as hollow capsule [3], protein [4] and enzyme immobilization [5], sensors [6], light-emitting diodes [7], photoelectrochemically active electrode [8], separation membranes [9], surface patterning [10], surface imprinted multilayers [11], microporous films [12], erasable films [13], freestanding films [14], superhydrophobic coatings [15] and biocompatible coatings [16], nanocomposites [17], reinforcing materials [18], and various other functionally advanced materials [19–22]. LbL self-assembly has realized assemblies numerous substances containing polyelectrolytes [23], dendrimers [24], dyes [25], nanoparticles [26], carbon nanotubes [27], clay nanoplates [26], proteins [4,23], DNA [1], polypeptides [28], enzymes [5],

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polysaccharides [29], viruses [30], and polymer micelles [31]. Among the various building blocks, polymer micelles have attracted tremendous interest. Polymer micelles are known to possess core–shell structures [32] which enable incorporation of hydrophobic materials [31] into cores of micelles showing high capacity as drug carriers. Also the core–shell structures of micelles are stimulus-responsive to pH, temperature, chemicals, and light [33], which enables sustained release of hydrophobic materials. Due to these unique properties, polymer micelles have been extensively utilized in applications as carriers for hydrophobic dyes and drug delivery [33].

A limit of the LbL assembly using polymer micelles as building blocks which restricts its further industrial applications is that conventional LbL dipping method is time-consuming [2,19]. With the progress of the LbL assembly, several ways have been developed to shorten the LbL assembly time for construction of multilayers, such as spin-spray, electrically driven, roll-to-roll, dewetting, dynamic and agitated-dipping [19–22,34]. Beyond these above mentioned methods, a high-gravity (HG)-assisted LbL (HG-LbL) has been introduced for fabricating polyelectrolyte multilayers [35–39]. The HG technology is a well-established effective industrial method in chemical engineering to enhance mass and heat transfer between different phases in multiphase systems [40]. In the HG environment, fluids could be accelerated by a high rotating rate, which generates a large centrifugal force, spreading or splitting the liquid into tiny droplets. The resulting micro-mixing would largely enhance the mass transfer between the fluid elements [40]. We have begun to explore the feasibility of LbL self-assembly under HG fields.

However, the possibility of applying the HG technique for fabrication of multilayers through LbL self-assembly concerned with polymer micelles as building blocks still remains to be proven. Therefore, we endeavor to use poly(diallyldimethyl ammonium chloride) (PDDA)/polystyrene-poly(acrylic acid) (PS-PAA) polymer micelle multilayers as a model system to explore this possibility. We used PS-PAA polymer micelles as building blocks by alternating pumping solutions of PDDA and PS-PAA polymer micelles into the HG equipment. The results showed that the HG environment could highly hastening the LbL process compared with conventional dipping assembly, proving the possibility of the HG technique for fabrication of multilayers using polymer micelles as building blocks. Moreover, we wondered if polymer micelle-incorporated molecules could be released from the prepared multilayers. For this purpose, pyrene loaded PS-PAA polymer micelles were also used as building blocks for multilayer construction. The resultant multilayers achieved comparable pyrene releasing quality as that prepared under conventional dipping conditions. Considering the great potential of polymer micelles for applications in biology and pharmacy [33], we believe that the HG-LbL technique for construction of multilayers using polymer micelles as building blocks would promote the LbL self-assembly in both fundamental and industrial applications.

2. Materials and methods

2.1. Materials and instrument

The following chemicals were used as supplied: poly(styrene-b-acrylic acid) Mn: PS(42,000)-PAA(4500), Mw/Mn: 1.18 (PS-PAA) from Alfa Aesar (Britain); poly(diallyldimethyl ammonium chloride) solution (PDDA, 20 wt.% in H_2O, M.W. 200,000–350,000) and pyrene from Aldrich; H_2SO_4 (98%), H_2O_2 (30%), N,N-dimethylformamide (DMF), acetone and ethanol from Sinopharm Chemical Reagent Beijing Co. (Beijing, China).

The high gravity (HG) equipment is customized and has been described elsewhere [35–39] (Fig. 1). Generally speaking, the essential component is a rotating packed bed. The rotator is installed inside the fixed casing. The inner and outer diameters of the rotator are 20 and 50 mm, respectively. The internal axial width of the rotator is 10 mm, and the external width is 17 mm. Four slots (14 mm × 12 mm × 1 mm) are set in four directions inside of the rotator. The distributor consists of two pipes (5 mm × 1 mm) with a diameter of 1 mm. The solutions of the PDDA and PS-PAA were pumped into the cavity by a peristaltic pump (BT100-2J) from Baoding Longer Precision Pump Co., Ltd. The rotator rotated at 2400 rpm during the experiments.

UV–Vis spectra were obtained on a Hitachi U-3900H spectrophotometer (Tokyo, Japan). AFM images were obtained with atomic force microscopy (AFM, Dimension 3100) from Veeco (NY, USA) using a tapping mode in air at ambient temperature. The thicknesses of the films with selected number of layers were also determined by AFM following previously described method [41]. Generally speaking, the substrates deposited with multilayer films were scratched using a blade to remove part of the deposited films. A 50 μm × 50 μm area of the sample including the scratched part was scanned. The film thickness was estimated by measuring the average difference between the scratched and unscratched areas at randomly chosen spots.

Release of pyrene was induced by immersing pyrene loaded multilayer films into NaCl solutions. The release process was monitored by fluorescence emission spectra (recorded with a Hitachi F-7000 FL Spectrophotometer). Amounts of the pyrene remaining in the multilayer films were calculated by normalizing fluorescence intensity to initial fluorescence intensity of the pyrene at immersing time of 0.

2.2. Preparation of substrate

To clean quartz substrate, fresh Piranha solution (30% H_2O_2/98% H_2SO_4, V/V = 1/3) was used. The solution was extremely corrosive with heat and bubbles. The appropriate safety precautions should be applied which includes acid resistant gloves and also cleaning handled in fume cupboard. When the solution was cool to room temperature the substrate was rinsed with deionized water and dried with nitrogen gas.

2.3. Preparation of (pyrene loaded) polymer micelles

The block polymer (PS-PAA) was dissolved in DMF solution. Water was added slowly in the solution under stirring by using peristaltic pump. The solution was allowed to stirring for a night then allowed for dialyzes against water for 72 h with water changed every 8 h. The prepared polymer micelle solution was used to incorporation of water insoluble dye-pyrene. 2 ml of 0.5 mg/ml solution of pyrene in acetone was added into 250 ml of the polymer micelle solution. The solution was ready for use after 30 min sonication.

2.4. Fabrication of multilayers under conventional dipping conditions

The cleaned quartz substrate was dipped in the solution of PDDA (1 mg/ml) for 30 min. Subsequently, the substrate was rinsed with water and dried with nitrogen gas, and then placed into the solution of PS-PAA polymer micelles. The quartz substrate was again rinsed with deionized water and dried with nitrogen gas. The dipping time is 10 min in the PDDA solution and also 10 min in the PS-PAA polymer micelle solution. Repeat the steps in cyclic way to develop layer-by-layer (LbL) self-assembled multilayer films.

2.5. Fabrication of multilayers in HG fields

The preparation process of the multilayers was shown in Fig. 1. The cleaned quartz substrates were dipped in the solution of PDDA,