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Formation of multilayer through layer-by-layer assembly of starch-based polyanion with divalent metal ion

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ABSTRACT

The layer-by-layer (LbL) assembly between metal ion and starch-based anion driven by electrostatic interaction was investigated. Multilayer films were obtained from starch-based derivative containing carboxyl groups (SC) with copper or lead ions. It was found that the concentration of metal ion in aqueous solution decreased with increasing the layers. X-ray photoelectron spectroscopy exhibited the content of Cu(II) was higher when the surface was copper-ion-layer than that composed of SC. The surface of the film was smooth and no obvious fault plane was observed on its cross-section, which also indicated that the LbL assembly between starch-based polyanion and metal ion was carried out. Sodium alginate was adopted as another polyanion to conduct the LbL assembly. Part of metal ion was replaced with rhodamine B to fabricate composite multilayer. During such an assembly, the concentration of copper ion in aqueous solution decreased with increasing the layers as well. These phenomena suggested that the LbL assembly between polysaccharide-based polyanion and metal ion was feasible.

1. Introduction

Polyelectrolytes are easily to be processed into devices for electrochemical, biotechnological and other applications. Moreover, the structure and properties of the polyelectrolytes-based devices are able to be tailored for meeting various demands (Jessica, Spencer, & Luis, 2017). The electrostatic interaction between two oppositely charged polyelectrolytes lead to forming polyelectrolyte complex (PEC). PEC is usually obtained at ambient temperature and using water as a solvent. Such a mild preparation condition is attractive and useful to create materials with interesting and versatile functions (Faul & Antonietti, 2003; Hartig, Carlesso, Davidson, & Prokop, 2007; Stana et al., 2017). Specially, layer-by-layer (LbL) assembly is carried out when PECs are produced in an alternative form. LbL assembly offers an effective approach to design and fabricate functional multilayer materials (Hammond, 2011).

Evidently, charged water-soluble polymers are suitable candidates for preparing multilayer materials through LbL assembly. Among the water-soluble polyelectrolytes, charged polysaccharides are attractive (Silva, García, Reis, García, & Mano, 2017). Starch is a water-soluble, renewable and biodegradable polysaccharide (Araújo & Cunha, 2004; Lu, Xiao, & Xu, 2009). Although it is a neutral one, it is easily to be transferred into an anionic starch-based polyelectrolyte via chemical modification (Grote, Lazik, & Heinze, 2003; Renil & Ronald, 2013). Sodium alginate (SA) is another natural anionic polyelectrolyte. It is readily to combine with multivalent metallic ions (Drury & Mooney, 2003). In viewing of their biodegradability and biocompatibility, both the starch-based polyanion and sodium alginate can be considered as good candidates for constructing functional multilayer materials via LbL assembly.

Generally, the other component to perform LbL assembly with an anionic polyelectrolyte is a cationic polyelectrolyte, such as chitosan (Assaad, Wang, Zhu, & Mateescu, 2011). Noting that the multivalent metal ion can form complex with anionic polysaccharide, such as the complexation between calcium ion and sodium alginate (Drury & Mooney, 2003), we suppose that the multivalent metal ion can be utilized as the component to conduct LbL assembly with a polysaccharide-based polyanion. It is reported that the divalent metal ions including zinc and copper ions have been used for LbL assembly via the coordinative interactions between the ions and the ligand groups on the side chain of polystyrene (Krieger & Tieke, 2017). Recently, we have taken advantage of the LbL assembly among water-soluble chitosan, SA and copper ion to form flame retardant coating on polyester fabric (Liu & Xiao, 2018).

The LbL assembly method has been applied to prepare various starch-based materials. For examples, it is employed to fabricate starch-based nanocapsules for controlled delivery of protein (Zhang et al., 2017) or surface protection of cotton (Carosio, Fontaine, Alongi, &

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Bourbigot, 2015). The components for constructing the starch-based carrier or coating include cationic starch, anionic starch and poly (phosphoric acid), but nothing to do with the metal ions. To our knowledge, no starch-based functional multilayer material prepared from LbL assembly of starch-based polyanion and multivalent metal ion has been reported so far. In this article, the LbL assembly between starch-based polyanion and the model multivalent metal ion such as copper or lead ion was investigated. Meanwhile, the LbL assembly between sodium alginate and copper ion as well as among sodium alginate, copper ion and rhodamine B were taken as controls. The obtained experimental results show that our hypothesis is practicable. Such a strategy provides an efficient approach for fabricating polysaccharides-based multilayer functional materials.

2. Experimental

2.1. Materials

Starch-based derivative that contained carboxyl groups (SC, 11.3% COOH) was prepared through the esterification between starch and maleic anhydride (Xiao & Ye, 2005). PVA-based macromonomer (PVAM, 8.78% C═C) was obtained from the esterification between poly(vinyl alcohol) and maleic anhydride (Huang & Xiao, 2013). Sodium alginate (SA, its weight molecular weight is ca. 33,000) was dried before use. Potassium persulphate (KPS) was purified by recrystallizing from distilled water. Acrylic acid (AA) was purified by soaking with activated carbon. Rhodamine B (RB), xylenol orange (XO), 95% ethanol, thiourea, sodium hydroxide (NaOH), hydrochloric acid (HCl), copper sulfate, lead nitrate, sodium dihydrogen phosphate and disodium hydrogen phosphate were all analytical grade reagents, purchased domestically and used as received.

2.2. Fabrication of multilayer films

In order to fabricate the targeted starch-based multilayer material, the substrate for LbL assembly should be a starch-based one too. To prepare such a substrate, a mixture of 5 g SC and 0.5 g PVAM was dissolved in 25 mL distilled water. Then the aqueous solution was homogenously mixed with 1 mL AA and 0.5 g KPS at ambient temperature and sprayed on a petri dish. After being kept in a water-bath of 75 °C for 5 h, the mixture became a gel. The obtained SC-based gel was dried in a vacuum oven at 40 °C.

The dried SC-based gel was re-swollen by immersing it in aqueous solution of copper sulfate at 25 °C for 6 h. It was rinsed with distilled water for three times to remove the copper ions remained on the surface of the substrate. Then the multilayer films were fabricated through alternative LbL method (Kosbar et al., 2006). Typically, the pretreated SC-based gel was adopted as the substrate and immersed in 10 mL aqueous solution of 10% SC or 2% SA for 15 min, rinsed with distilled water for three times, immersed in 80 mL 200 mg/L Cu(II) aqueous solution or 40 mL 50 mg/L Pb(II) aqueous solution for 15 min, and rinsed with distilled water for three times. In order to precisely monitor the LbL assembly through UV spectroscopy, the concentration of copper and lead ions is adopted as mentioned. This alternate LbL process was performed at ambient temperature and repeated as many times as expected. The obtained multilayer films were dried in a vacuum oven at 40 °C for 24 h.

2.3. Characterizations of multilayer films

The concentration of metal ion in aqueous solution during LbL assembly was monitored with UV–vis spectroscopy. Five milliliters Cu(II) solution or 1 mL Pb(II) was sampled, mixed homogeneously with chelator (1 mL xylenol orange for lead ion, 1.55 mL EDTA for copper ion) and buffer solution of pH5.8 (2 mL for lead ion, 3 mL for copper ion). The concentration of Pb^{2+} or Cu^{2+} was analyzed with a UV-2600 UV–vis spectrophotometer at 575 and 730 nm respectively. The concentration of metal ion was calculated according to the linear absorbency (A) and concentration (C) relationship (Cu^{2+}: $A = 0.00131C + 0.03596$, $R^2 = 0.9996$; Pb^{2+}: $A = 0.01757C + 0.03398$, $R^2 = 0.9995$). An average of triplicate measurements was taken.

The water-erosion behavior of the multilayer film was analyzed by using the sample obtained from SA and Cu(II) as a model. Firstly, the multilayer film was prepared as aforementioned with two modifications. One change is to employ a fresh SC-based gel as the substrate instead of the pretreated one. Another is to keep the gel in the solution of SA or $CuSO_4$ for 1 min to avoid adsorption. Subsequently, the samples including the SA-Cu(II) 20-layer and a control, which was obtained by immersing a fresh gel in the same solution of $CuSO_4$ at ambient temperature for 20 min, were placed in distilled water. The concentration of Cu^{2+} released from the samples at various time intervals was analyzed with UV–vis spectroscopy. Its concentration was calculated according to the linear absorbency (A) and concentration (C) relationship ($A = 0.00138C + 0.05594$, $R^2 = 0.9999$). The release percentage of Cu(II) was calculated as RP (%) = $Wr/Wb \times 100$, where Wr and Wb were the released amount of copper ion and the amount of Cu (II) bound onto the SC-based gel respectively. Wb was around 0.34 mg/g, which depended on the mass weight of the sample. An average of triplicate measurements was taken.

X-ray photoelectron spectrometer (XPS) spectra of 4-layers films with the surface of copper ion and SC respectively were collected on a Thermo ESCACAB 250 XI with Al Kα X-ray source (148.6ev, operated at 150 W). The Au-coated morphology of the cross-section of the starch-based multilayer film was examined with a Hitachi S-8000 F scanning electron microscope (SEM, 3000 V). Thermogravimetric analysis (TGA) of the SC-based gel, SA-Cu(II) and SC-Cu(II) multilayer films were performed with a TA V2.4 F thermoanalyzer, which was conducted over the temperature range from 25 to 600 °C with a programmed temperature increment of 20 °C/min under argon atmosphere. The SC-based gel, SC, $CuSO_4$, and 10-layers SC-Cu(II) were powdered. The SC-based gel and SC were mixed with $CuSO_4$ in the ratio of 1:1 (wt/wt) respectively. Then, Fourier transform infrared (FTIR) spectra of the SC-based gel, the mixture of SC-based gel and $CuSO_4$, the mixture of SC and $CuSO_4$, and 10-layers SC-Cu(II) were recorded using a Nexus 470 FTIR spectrometer in ATR mode.

3. Results and discussion

As mentioned in the introduction part, no report about LbL assembly between anionic starch and metal ion has been found so far. Therefore, the goal of this article is to examine whether the LbL assembly between metal ion and starch-based anion is able to be carried out by the aid of electrostatic interaction. Accordingly, the substrate and the metal ion are two basic issues we need to deal with at first. A gel derived from SC is a good candidate for fabricating starch-based multilayer material via LbL assembly as it is charged. However, the mechanical strength of a totally starch-based gel may be not good enough for alternate LbL process. Owing to its good mechanical property, PVAM is adopted to be incorporated into the gel via covalently cross-linking (Xiao, You, Fan, & Zhang, 2016). Therefore, SC and PVAM (SC:PVAM = 10:1, wt/wt) are adopted as macromonomers to prepare a starch-based gel. Such a gel contains carboxylic groups, which enable it to attract metal ions. For sake of avoiding the effect of adsorption, the gel is saturated with copper ions in advance. As a result, the pretreated SC-based gel meets the requirements of a substrate for our intension.

Another key factor for our target is to choose suitable model metal ions. The potential application of the starch-based multilayer material depends on the kind and the amount of the metal ion. It is reported that a certain quantity of zinc and copper ions is benign for people's health, but the excess metal ions will lead to problem (Qin & Yang, 2015). If the LbL assembly between the starch-based substrate and metal ion is available, the expected functional multilayer material can be generated