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Peach gum polysaccharide polyelectrolyte: Preparation, properties and application in layer-by-layer self-assembly

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ABSTRACT

The hydrolyzed peach gum polysaccharide (HPGP) prepared at acidic condition is investigated as an anionic polyelectrolyte for the first time. A hydrolysis mechanism is proposed by monitoring the hydrolysis efficiency and morphological change of crude peach gum, and the intrinsic viscosity of resulted HPGP as a function of hydrolysis time. Fourier transform infrared (FTIR) spectroscopy and ζ-potential measurements reveal that HPGP with multiple carboxylic groups is negatively charged in water in the pH range 3–11. The HPGP exhibits remarkable pH and ionic strength responsiveness, as proven by dynamic light scattering (DLS) and atomic force microscopy (AFM) measurements. Moreover, the layer-by-layer (LbL) self-assembly experiments further confirmed that the HPGP can be utilized as an anionic polyelectrolyte. Considering the facile availability, favorable compatibility and intriguing functionality of HPGP, this study opens up enormous opportunities for the large-scale utilization of peach gum resource.

1. Introduction

Exploring new properties associated with advanced applications of renewable carbohydrate resources is of critical importance. Polyelectrolytes, including natural polyelectrolytes and synthetic polyelectrolytes, are macromolecules bearing ionizable groups along their backbone (Popa-Nita, Rochas, David, & Domard, 2009). During the past decades, polyelectrolytes have attracted rapidly growing interest based on their intriguing physicochemical properties and tremendous potential applications. In particular, natural polyelectrolytes are being intensively studied due to their low cost, easy availability, excellent biodegradability, and low toxicity (Dinu, Mihai, & Dragan, 2010; Wang, Qian, & Roman, 2011). For example, a variety of polysaccharide polyelectrolytes, such as sodium carboxymethyl cellulose (Radeva, Kamburova, & Petkanchin, 2006), xanthan gum (Kocherbitov, Ulvenlund, Briggner, Kober, & Arnebrant, 2010), sodium alginate (Li et al., 2013), hyaluronic acid (Vasiliu, Popa, & Rinaudo, 2005; Zhang et al., 2005) and carrageenan (Hugerth, Caram-Leiham, & Sundelöf, 1997), have been utilized for a wide range of applications such as drug delivery, biosensor, coating and light-emitting diodes.

As a kind of gum exudate, peach gum (PG) is produced from the fruit and trunk of peach tree as a consequence of physiological process or mechanical injury (*Prunus persica*, family *Rosaceae*) (Simas-Tosin et al., 2009). PG is an acid polysaccharide, which generally consists of galactose (42%), arabinose (36–37%), uronic acid (7–20%), xylose (7%) and mannose (2%) (Simas et al., 2008; Simas-Tosin et al., 2009). However, crude PG (CPG) is insoluble in aqueous solution because of its extremely high molecular weight (Simas-Tosin et al., 2010; Yao, Cao, Pan, & Wu, 2013b). The poor water-solubility seriously limits its wide applications. In order to overcome this drawback, an effective approach is to treat the CPG with alkaline, enzyme or hydrogen peroxide to afford water-soluble hydrolyzed PG polysaccharide (HPGP) (Kardošová, Rosík, & Kubala, 1978; Qian, Cui, Wang, Wang, & Zhou, 2011; Yao et al., 2013b). In view of its unique composition, the HPGP is expected to be utilized as a polyelectrolyte for expanding the application fields of PG. The HPGP macromolecule contains multiple negatively charged carboxylic groups that can adsorb positively charged polyelectrolyte or molecule through strong electrostatic interactions (Rosík, Kardošová, & Kubala, 1971). On the other hand, the HPGP can be easily prepared from CPG, which is abundant in many areas of the world. For instance, more than 10 billion tons of CPG is yielded in China annually (Xie & Ren, 2008). Although PG has been studied for various applications such as food industry, printing, medicine, cosmetic, fluorescent material and adsorbent material (Xie, Zhou, & Qian, 2006; Yao, Cao, & Wu, 2013a; Zhou, He, & Huang, 2013;

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Zhou, Huang, He, Zhang, & Li, 2014), the investigation of PG as polysaccharide polyelectrolyte has rarely been reported to date.

In this contribution, the HPGP is systematically investigated as a natural polyelectrolyte for the first time. The HPGP was prepared by the hydrolysis of insoluble CPG in water at pH 3. The hydrolysis process was investigated in detail by monitoring the hydrolysis efficiency and morphological change of CPG, and the intrinsic viscosity of resulted HPGP with increasing hydrolysis time. In addition, the influences of pH and ionic strength on the hydrodynamic size (D_h) and morphology of the HPGP were investigated. Furthermore, the employment of HPGP as an anionic polyelectrolyte for layer-by-layer (LbL) self-assembly was studied. The LbL self-assembly method, which is based on the alternate adsorption of oppositely charged species, is a versatile approach for the fabrication of multilayer films (Landoulsi, Roy, Dupont-Gillain, & Demoustier-Champagne, 2009; Lefaux, Zimberlin, Dobrynin, & Mather, 2004). Recently, the utilization of natural polyelectrolyte for preparing multilayer films based on the LbL self-assembly technique has attracted considerable attention (Liu et al., 2012). Compared with synthetic polyelectrolyte, the natural polyelectrolyte exhibits favorable biocompatibility and biodegradability, posing great promise for biomedical applications. In this work, the LbL self-assembly results demonstrate that the HPGP is a typical anionic polyelectrolyte. From the application perspective, this work provides new opportunity for expanding the application fields of natural PG.

2. Materials and methods

2.1. Materials

Gum exudates of peach (*P. persica*) tree trunk were collected at Xishan Park (Guilin, China). Poly(diallyldimethylammonium chloride) solution (PDAC) (M_w = 100–200 kDa; 20 wt%), 3-aminopropyltriethoxysilane (APS) and toluene were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China) and used as received. Silica sphere (around 200 nm) was purchased from Alfa Aesar. All other chemicals were analytical grade and used as received without further purification. Milli-Q water (18.2 MΩ) was used throughout the experiments, which was purified with a Millipore system.

2.2. Preparation of hydrolyzed peach gum polysaccharide (HPGP)

The preparation of HPGP was carried out according to the literature (Wang, Xie, Zhong, & Du, 2008) with some modification. Typically, dried crude PG exudates (6 g) were soaked and stirred overnight in water (400 mL) to give a dispersion containing swelling gum. The swelling gum was homogenized through an iron wire sieve (200 mesh) to yield a gum suspension. The pH of gum suspension was adjusted to 3 by adding 1 M HCl. Then the suspension was stirred at 95 °C. The reaction mixture was periodically collected and purified. After hydrolysis reaction, the final mixture was filtrated, dialyzed (molecular weight cut-off: 1800 Da) and freeze-dried to give HPGP. Hydrolysis efficiency = (the mass of water-soluble HPGP/the mass of CPG used) × 100%.

2.3. Intrinsic viscosity ([η]) measurements

The intrinsic viscosity ([η]) of HPGP in water with different hydrolysis time was determined by using an Ubbelohde capillary viscometer in a constant temperature bath at 25 °C. HPGP solutions with concentration in the range of 0.02–0.2 g/dL were prepared. The [η] was calculated according to the Huggins equation (Huggins, 1942) by extrapolation of concentration to zero ($c \to 0$) as follows.

$$\frac{\eta_{sp}}{c} = [\eta] + k[\eta]^2 c \quad (1)$$

where η_{sp}/c is the reduced specific viscosity, and k is the constant for a given polymer in given conditions.

2.4. Synthesis of amino-functionalized silica (SiO_2–NH_2)

In order to perform the LbL self-assembly experiments, positively charged SiO_2–NH_2 particle was chosen as a representative substrate. For the synthesis of SiO_2–NH_2 particle, typically, SiO_2 sphere (50 mg), toluene (20 mL) and APS (0.5 mL) were placed in a 50 mL flask, which was equipped with a condenser and sealed with rubber plugs. The mixture was stirred at 95 °C for 24 h at argon gas atmosphere. The product was separated by centrifugation and washed thoroughly with excess ethanol several times. The final product was dried at 50 °C under vacuum overnight to give SiO_2–NH_2.

2.5. Layer-by-layer (LbL) self-assembly by using HPGP as an anionic polyelectrolyte

We used as-prepared SiO_2–NH_2 as substrate, and PDAC and HPGP as polycation and polyanion, respectively, to investigate the LbL self-assembly behavior. All the LbL self-assembly experiments were carried out in a saltwater solution (0.1 M NaCl) at pH 6 and 11 for PDAC and HPGP, respectively (adjusted by 1.0 M HCl or 1.0 M NaOH) (Gelissen, Schmid, Plamper, Pergushov, & Richtering, 2014). Solutions of HPGP (1 mg/mL) and PDAC (1 mg/mL) were used. Typically, the SiO_2–NH_2 (20 mg) was alternatively stirred for 1 h with negatively charged HPGP solution and positively charged PDAC solution, respectively. After each stirring step, the excess polyelectrolyte was removed by centrifugation and washed with water. The alternative self-assembly of PDAC and HPGP was repeated to increase the number of bilayer. Five bilayers were coated on the surface of SiO_2–NH_2, The ultimate sample (designated as SiO_2–(HPGP/PDAC)5) was obtained by drying overnight in a vacuum at 60 °C.

2.6. Characterization

Atom force microscope (AFM) was measured by a NT MDT (Ntegra Prima) SPM, operating at the tapping mode, with samples prepared by spin-coating solution onto freshly cleaved mica substrate at 1000 rpm/min. Fourier transform infrared (FTIR) spectra were measured on a Thermo Nexus 470 FTIR spectrometer (KBr disk). Optical microscope image was obtained using an optical microscope (LEICADM RXP) with imaging software. The ζ-potential value and dynamic light scattering (DLS) measurements of the HPGP in aqueous solution (0.1 mg/mL) were made using Zetasizer Nano ZS90 analyzer (Malvern instruments Ltd., UK). Thermogravimetric analysis (TGA) was carried on a TGA Q500 analyzer with a heating rate of 20 °C/min in nitrogen flow. Transmission electron microscope (TEM) measurements were performed on a JEM-2100F TEM operated at an accelerating voltage of 200 kV.

3. Results and discussion

3.1. Preparation and characterization of HPGP polyelectrolyte

In order to track the hydrolysis process, hydrolyzed samples with different hydrolysis time were taken out from the reaction system. After standing for 1 h, suspension solid (below the dashed line) can be clearly observed for the sample with hydrolysis time less

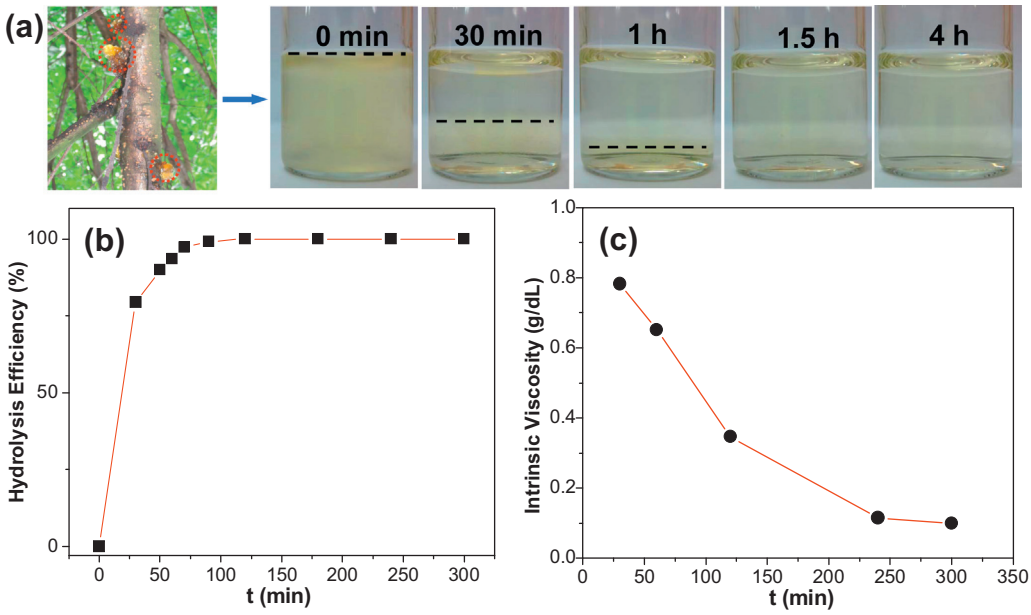

Fig. 1. (a) Photographs of crude peach gum (CPG) and hydrolyzed mixture with different hydrolysis time. (b) Hydrolysis efficiency of CPG as a function of time. (c) Intrinsic viscosity of HPGP with diverse hydrolysis time.

than 1.5 h (Fig. 1a). With increasing hydrolysis time, the suspension solid gradually disappeared and highly transparent solution could be obtained. This is because the insoluble CPG was gradually hydrolyzed into water-soluble HPGP.

In addition, the hydrolysis efficiency of CPG at diverse hydrolysis time was determined. As depicted in Fig. 1b, the hydrolysis efficiency of CPG at 30 min and 1 h is 79% and 93%, respectively. The hydrolysis efficiency can reach 100% within 1.5 h. These results are in good agreement with the above observation (Fig. 1a). Therefore, the hydrolysis process from insoluble CPG particles to water-soluble HPGP is achieved within 1.5 h. On the other hand, the intrinsic viscosity ([η]) of HPGP, which is associated with the molecular weight of HPGP macromolecule (Huggins, 1942), was determined by using an Ubbelohde capillary viscometer. As illustrated in Fig. 1c, the [η] values gradually decreased with the increase of hydrolysis time, revealing that the molecular weight of HPGP decreases with increasing hydrolysis time. The [η] values (0.1–0.8 g/dL) of HPGP in our case are similar to other reported natural polysaccharides (Goycoolea, Morris, Richardson, & Bell, 1995; Oliveira, Silva, de Paula, Feitosa, & Paula, 2001). Therefore, it is possible to attain HPGP with suitable molecular weight by controlling the hydrolysis time.

In order to gain more insight into the hydrolysis process, the morphological change of hydrolyzed mixture with diverse hydrolysis time was observed by optical microscope (OM) and atom force microscope (AFM). As presented in Fig. 2a, the original CPG particles are roughly in spherical shape with size in the range of 10–100 μm. At 1 h, it is difficult to detect particles by OM. This is due to the fact that the large CPG particles are hydrolyzed into small particles and water-soluble HPGP macromolecules. As confirmed by the AFM image in Fig. 2b, small CPG particles with size of around 500 nm and thickness of 100 nm can be detected. In addition, network-like HPGP aggregates are also clearly seen. Further hydrolysis reaction affords water-soluble HPGP sample without suspension solid (Fig. 1a). Compared with Fig. 2b, only island-like HPGP aggregates with relatively good dispersibility and thickness of 1–1.5 nm are observed from the sample with hydrolysis time of 4 h (Fig. 2c). Although the accurate mechanism for the hydrolysis of CPG is not completely known, we could speculate the possible hydrolysis mechanism according to the observed phenomena and obtained results. First, the hydrolysis reaction occurred at the surface of CPG particles to afford water-soluble HPGP with high molecular weight and highly branched structure (Fig. 3). By increasing hydrolysis time, the CPG particles become smaller and smaller and finally disappear. At the same time, the highly branched HPGP macromolecules with very high molecular weight were gradually hydrolyzed into HPGP macromolecules with relatively low molecular weight and branched density as depicted in Fig. 3.

The structure information of the resulted HPGP was further characterized by Fourier transform infrared (FTIR) spectra and ζ-potential measurements. Fig. 4a shows the FTIR spectra of the HPGP with hydrolysis time of 1 h and 4 h. As can be seen, the band

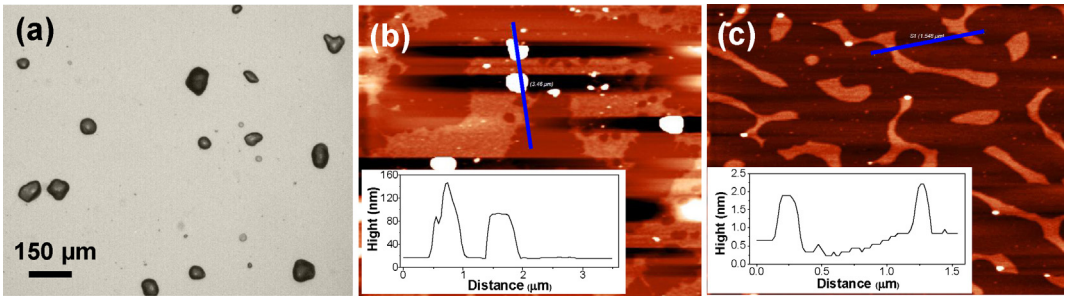

Fig. 2. (a) OM image of suspension solid of crude peach gum (CPG). AFM images of hydrolyzed mixture with hydrolysis time of 1 h (b) and 4 h (c).

Fig. 3. Hydrolysis process scheme for the preparation of hydrolyzed peach gum polysaccharide (HPGP) from CPG.

at 3415 cm^{-1} associated with O—H stretching vibration, the two peaks at 2935 and 2883 cm^{-1} associated with C—H stretching vibration, the peak at 1615 cm^{-1} corresponding to —COO^- stretching vibration which is derived from the uronic acid component, and the peak at 1036 cm^{-1} corresponding to C—O stretching vibration can be clearly observed. All these FTIR data are well in accordance with the composition of PG (Rosík et al., 1971; Xie et al., 2006). It is worth noting that both of the two samples exhibit similar FTIR result, demonstrating that the HPGPs with different hydrolysis time possess similar chemical composition. Therefore, we chose the HPGP sample with hydrolysis time of 4 h as representative for the following studies. To further confirm the presence of negatively charged carboxylic groups, the ζ-potential values of HPGP in aqueous solution at different pH values were determined. As presented in Fig. 4b, the ζ-potential values dramatically decreased from −15.8 mV to −38.8 mV with the increase of pH from 3 to 11, apparently as a result of ionization of the carboxylic acid.

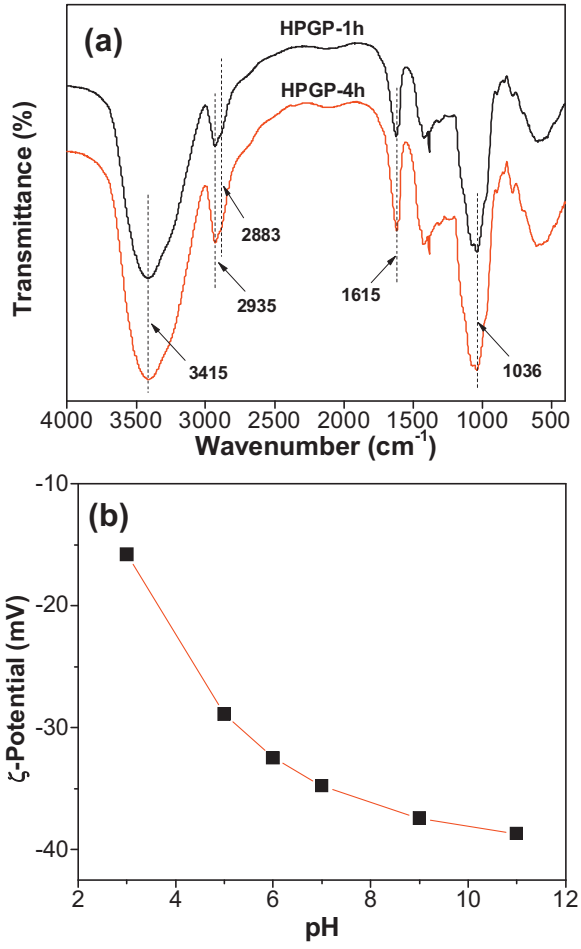

Fig. 4. (a) FTIR spectra of HPGP with hydrolysis time of 1 h and 4 h. (b) ζ-potential value of HPGP as a function of pH (0.1 mg/mL).

Accordingly, the HPGP holds great promise for using as a natural anionic polyelectrolyte.

3.2. Effect of pH

Since HPGP macromolecule possesses numerous carboxylic groups along its molecular chain, its degree of ionization should depend on pH. At the same time, a change in ionization is expected to induce structural changes. Dynamic light scattering (DLS) measurements for the HPGP macromolecules at diverse pH values were carried out in aqueous solution. Fig. 5a shows the hydrodynamic size (D_h) of the HPGP macromolecules at different pH values. All measurements were performed at very low concentration (0.1 mg/mL) to avoid intermolecular aggregation. An obvious pH dependence of the D_h is observed. the D_h value increases by 49 nm from pH 3 to pH 11, which is explained by the stretching of the HPGP chains with increasing pH (high ionization) (Wang et al., 2011). Under acidic conditions (pH <5), the HPGP is almost uncharged (in —COOH form) with collapsed conformation, whereas the ionization of carboxylic groups is greatly enhanced at high pH. This induces high electrostatic repulsion between HPGP macromolecules, which is observed as increase in D_h value. In order to check the morphological changes of the HPGP, AFM measurements were performed at pH 3, pH 7 and pH 11 in the absence of salt. As one can see (Fig. 5b), continuous three-dimensional network structure that indicates the presence of intermolecular association of the HPGP is observed for the sample prepared at pH 3. With the increase of pH values, the network structure gradually transformed into island-like structure (pH 7) and spherical structure (pH 11) (Fig. 5c and d). This result is presumably due to the fact that the HPGP chains are fully ionized and extended with relatively weak intermolecular association at high pH value (Chun, Cho, & Choi, 2004).

3.3. Effect of ionic strength

Generally, electrostatic repulsion plays an important role in polyelectrolyte. The addition of salt ions should be able to weaken the stretching of polyelectrolyte chains because of the screening of electrostatic interaction (Irigoyen et al., 2012). In this study, we performed the DLS and ζ-potential value measurements at a wide range of salt concentrations at pH 7. At pH 7, the ζ-potential value of HPGP is −34.7 mV (Fig. 4b). Generally, ζ-potential values beyond ±20 mV are considered characteristics of a stable solution because the charge density is high enough to stretch the HPGP chains. Fig. 6a shows the changes of D_h at pH 7 with increasing NaCl concentration. As expected, an obvious decrease of D_h (12 nm) is detected at very low concentration of NaCl (<0.1 M). However, further increase of the NaCl concentration from 0.1 M to 0.8 M leads to an increase of 31 nm in D_h. At this stage, the electrostatic repulsion is fully screened and specific interactions between the anionic HPGP chains and the Na^+ ions prevail (Irigoyen et al., 2012). The Na^+ ions are anchored onto the HPGP chains at high concentration of NaCl, leading to repulsive interactions of the chains and the stretching of the HPGP again. In addition, Fig. 6a also shows that the increase of ionic strength leads to a gradual decrease of ζ-potential absolute values. These results are in agreement with McConaughy, Stroud, Boudreaux, Hester, and McCormick (2008), who reported that the increase of ionic strength leads to lower ζ-potential absolute values for galacturonate solutions. The morphological variation of HPGP aggregates with increasing NaCl concentration was observed by AFM (Fig. 6b–d). Relatively continuous network structure is obviously seen at very low concentration of NaCl (0.05 M) due to the presence of intermolecular associations induced by the collapse of HPGP molecular chains. Similar to the AFM images at high pH values (Fig. 5), continued addition of NaCl

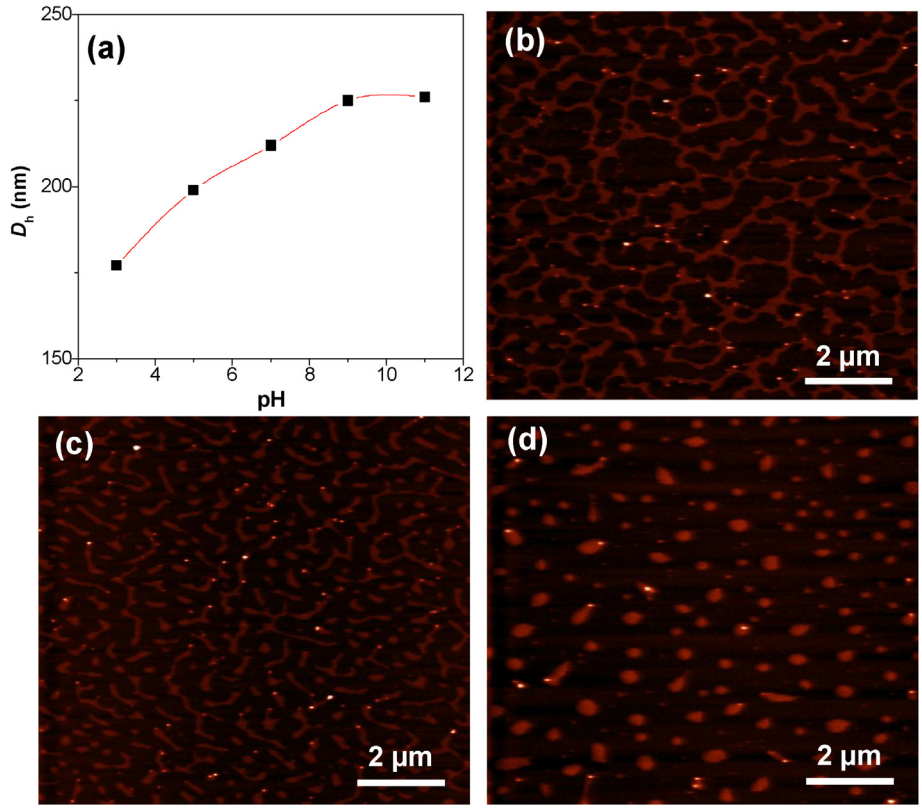

Fig. 5. (a) Hydrodynamic size (D_h) of HPGP (0.1 mg/mL) at diverse pH values in the absence of salt. Representative AFM images of HPGP at (b) pH 3, (c) pH 7, and (d) pH 11.

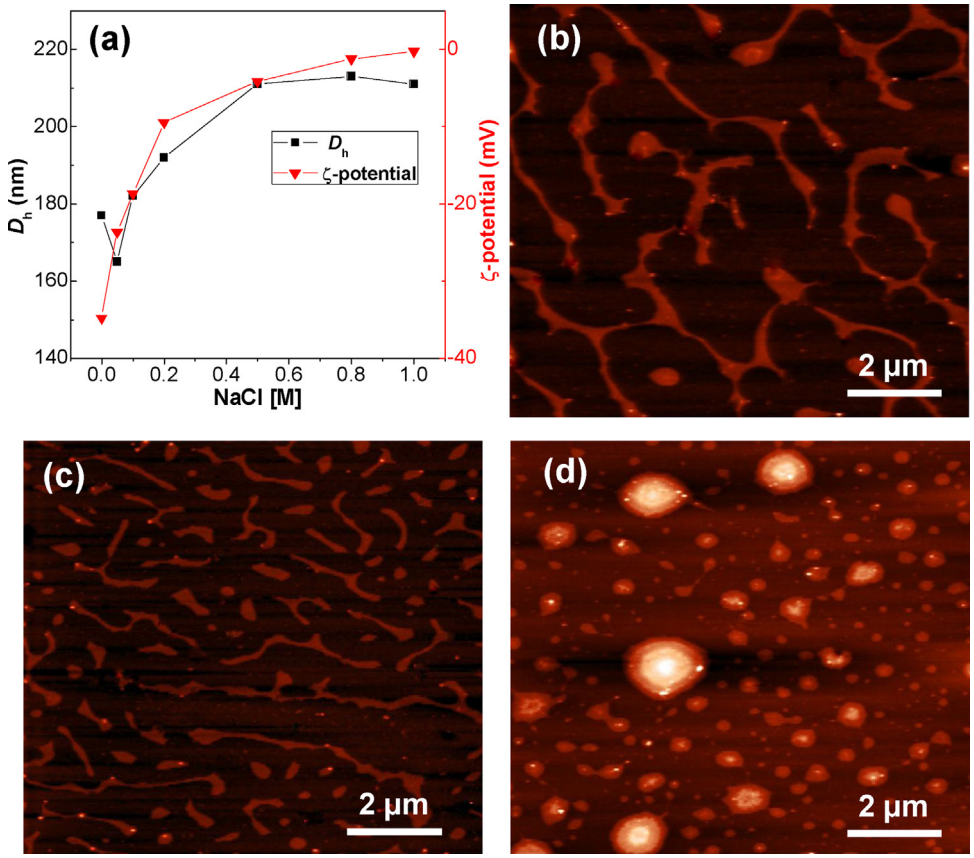

Fig. 6. (a) Hydrodynamic size (D_h) and ζ-potential value of HPGP (0.1 mg/mL) at pH 7 as a function of NaCl concentration. Representative AFM images of HPGP with the NaCl concentration of (b) 0.05 M, (c) 0.1 M, and (d) 0.8 M.

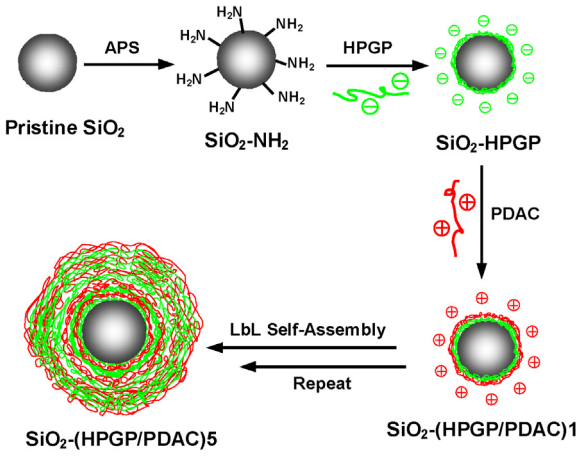

Fig. 7. Schematic illustration of layer-by-layer (LbL) self-assembly process on the surface of SiO_2 particles by using HPGP as an anionic polyelectrolyte.

leads to formation of individual HPGP aggregate with enhanced dispersion because of the presence of strong repulsive interactions.

3.4. LbL self-assembly on the surface of SiO_2 particles

In order to make sure that the HPGP can be used as an anionic polyelectrolyte, LbL self-assembly experiments were conducted by using SiO_2 particles as substrate as depicted in Fig. 7. The pristine SiO_2 was modified by 3-aminopropyltri-ethoxysilane (APS) to afford amino-functionalized silica (SiO_2–NH_2). The resulted SiO_2–NH_2 was characterized by thermogravimetric analysis (TGA) and FTIR. The pristine SiO_2 shows good thermal stability and only a 1.9 wt% weight loss below 800 °C is detected (Fig. 8a). This weight loss is possibly due to the presence of adsorbed water. In contrast, the SiO_2–NH_2 exhibits a weight loss of 6.6 wt% between 150 and 800 °C, indicating that amino groups have been attached on the surface of SiO_2. Additional evidence is the two peaks at 2850 and 2915 cm^{-1} derived from C—H stretching vibration, can be clearly observed in the FTIR spectrum of SiO_2–NH_2.

The LbL self-assembly process can consecutively deposit the oppositely charged HPGP and poly(diallyldimethylammonium chloride) (PDAC) on the surface of the SiO_2–NH_2. The main driving force in the alternate adsorption should be electrostatic interaction between negatively charged HPGP and positively charged PDAC. To confirm the stepwise deposition of two polyelectrolytes, the changes in the surface ζ-potential of SiO_2–NH_2 during the assembly process were determined. Fig. 8c exhibits the change of ζ-potential of the HPGP/PDAC coated SiO_2–NH_2 particles as a function of the number of deposited polyelectrolyte bilayer. The ζ-potential value for the original SiO_2–NH_2 particles was +28.6 mV. When adsorbed with one layer of HPGP polyanion, the ζ-potential value changed to −28.3 mV. Then with the adsorption of a layer of PDAC polycation to form a HPGP/PDAC bilayer, the ζ-potential became +41.2 mV. With alternative adsorption of oppositely charged polyelectrolytes, the ζ-potential values varied periodically between positive and negative. The results thus demonstrated that the HPGP/PDAC realized LbL self-assembly on the surface of SiO_2–NH_2 particles.

Owing to the attachment of five bilayers of HPGP/PDAC, the band at 3422 cm^{-1} corresponding to O—H stretching vibration and the peaks at 2915 and 2850 cm^{-1} associated with C—H stretching vibration are enhanced in the FTIR spectrum of SiO_2–(HPGP/PDAC)5 as compared with that of the SiO_2–NH_2 (Fig. 8b). In addition, the intensities of peaks at 796 and 470 cm^{-1} corresponding to Si—O vibration are significantly decreased after LbL self-assembly due to the silica core was covered with HPGP/PDAC shell. Direct evidence is given in the transmission electron microscope (TEM) of SiO_2–(HPGP/PDAC)5. As can be seen in Fig. 8d, the polymer phase

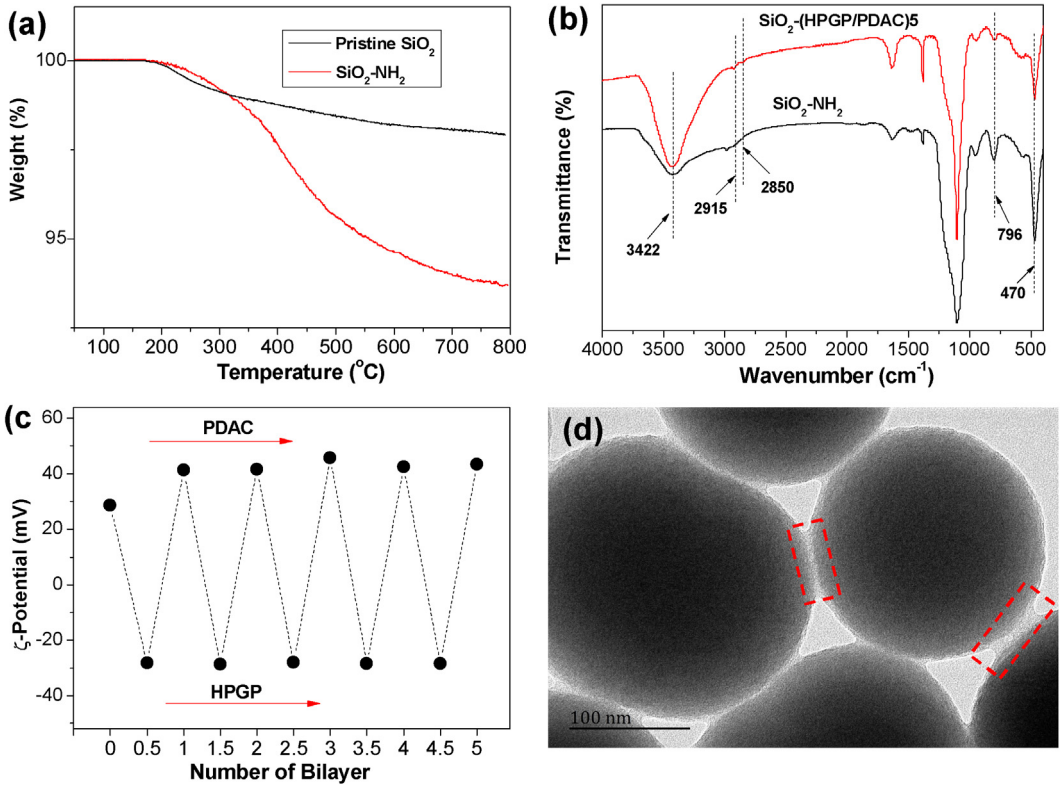

Fig. 8. (a) TGA curves of pristine SiO_2 and SiO_2–NH_2. (b) FTIR spectra of SiO_2–NH_2 and SiO_2–(HPGP/PDAC)5. (c) ζ-potential value as a function of number of bilayer for SiO_2–NH_2 particles alternatively coated with HPGP and PDAC as the outer layer. (d) Representative TEM image of SiO_2–(HPGP/PDAC)5.

can be clearly observed on the surface of SiO_2 particles. On the basis of the LbL self-assembly results, it is concluded that the HPGP can be utilized as a natural anionic polyelectrolyte.

4. Conclusion

In conclusion, we have demonstrated that HPGP polyelectrolyte with numerous carboxylic groups and negative charges in aqueous solution can be readily prepared by hydrolysis of CPG at 95 °C and pH 3. Large-sized CPG particles are gradually hydrolyzed into HPGP macromolecules with increasing hydrolysis time, as proven by the hydrolysis efficiency, intrinsic viscosity, OM and AFM measurements. The HPGP polyelectrolyte shows apparent pH and ionic strength responsiveness, as confirmed by the changes of hydrodynamic size and morphology. Layer-by-layer self-assembly results further demonstrated that the HPGP is a typical natural anionic polyelectrolyte. This study highlights the potential application of peach gum biomass as a natural polyelectrolyte. Given the intriguing properties of HPGP polyelectrolyte arising from its unique composition, we expect that the natural peach gum holds great promise for even richer applications.

Acknowledgments

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