Materials Research Express

PAPER

Synthesis and characterization of starch ether/alginate hydrogels with reversible and tunable thermoresponsive properties

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Keywords: hydrogel, thermoresponsive, alginate, starch ether

Abstract

A thermoresponsive hydrogel that was composed of 2-hydroxy-3-isopropoxypyrryl starch (HIPS) and alginate was synthesized via cross-linking with hybrid crosslinkers including ethylene glycol diglycidyl ether (EDGE) and calcium chloride (CaCl₂). Attenuated total reflection infrared spectroscopy (ATR-IR), thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were used to confirm that cross-linking occurred. The porous architecture of the HIPS/SA composite hydrogels was investigated using scanning electron microscopy (SEM). Composite hydrogels had a tunable volume phase transition temperature (VPTT) that was in the range from 29.4 to 40.2 °C and resulted from changes in the compositions (HIPS concentration from 5.5 to 7.5 wt%). It was also found that the presence of NaCl (0 to 20 g l⁻¹) or organic solvents (alcohols, 0 to 50 g l⁻¹) in aqueous medium changed the VPTT of the composite hydrogels; also, the VPTT decreased as the concentration of NaCl or organic solvents increased. Additionally, alcohols that have long carbon chains (isopropanol > ethanol > methanol) exhibited a more significant effect on the VPTT of hydrogel. The hydrogel could shed and absorb most of the water in a very short time and demonstrate a stable reversible swelling-deswelling property after 5 swelling-deswelling cycles.

1. Introduction

Utilization of natural polysaccharide polymers for the design of hydrogels has long been a research hotspot in the past several years (Bibi et al. 2019, Graham et al. 2019). Of the numerous macromolecules that have been used for the synthesis of hydrogels, polysaccharide-based hydrogels exhibit a number of advantages over synthetic polymers. On one hand, polysaccharide-based hydrogels have a three-dimensional network structure that is like that of traditional synthetic polymer hydrogels; this makes the hydrogels insoluble in water and able to maintain a stable structure in water (Wei et al. 2017). On the other hand, because of the biocompatibility and biodegradability of polysaccharides (Hubbe et al. 2019b), polysaccharide-based hydrogels possess excellent properties and show potential application value in several fields (Stabenfeldt et al. 2006, Vulic et al. 2015, Hubbe et al. 2019a). Because of the superiority of polysaccharide-based hydrogels, particularly, hydrogel prepared from sodium alginate displays outstanding characteristics such as gelling capacity, low toxicity, high availability and low cost (Giri et al. 2012, Hernandez-Gonzalez et al. 2020), and it can be tailor-made to fit different demands of various practical fields.

Sodium alginate (SA) is a kind of naturally-occurring polysaccharide that is mainly extracted from brown seaweed (Smidsrod and Skjakbraek 1990) and is an anionic copolymer composed of 1,4-linked-α-L-guluronic acid and β-D-mannuronic acid (Wan et al. 2018). It tends to ionically cross-link in the presence of divalent cations such as calcium ions (Tan and Ting 2014), and thus, it has been generally used for preparing hydrogel. To leverage the excellent biocompatibility, high availability, nontoxicity, and biodegradability of SA, SA-based hydrogel has been investigated in depth and applied in multiple fields, such as tissue engineering (Reakasame
and Bocaccini 2018), wound healing (Aderibigbe and Buyana 2018), drug delivery (Motealleh et al 2019), cell culture (Lee et al 2010), and adsorbents (Ren et al 2016). Recently, the functional properties of SA-based hydrogel have been improved, and the addition of stimuli-sensitive moieties in alginate can lead to ‘smart’ materials that have stimuli-responsive hydrogel characteristics (Kass et al 2019, Swamy et al 2013, Soledad Lencina et al 2015).

Thermoresponsive hydrogels are a class of smart hydrogels that are able to change their physicochemical properties (for example, volume) with respect to changes in temperature (Kim and Matsunaga 2017, Zhao et al 2019). Specifically, thermoresponsive hydrogels can switch from being in a hydrophilic, water swollen state to being in a hydrophobic, shrunken state when they are heated to a temperature above the volume phase transition temperature (VPTT) (Chang et al 2015). Such hydrogels that exhibit reversible volume transition behavior have received widespread attention because changing the temperature is convenient and cost-effective in potential applications (Jeong et al 2002). Therefore, endowing SA hydrogels with a thermoresponsive property can make it possible to make full use of the potential of SA hydrogels. Scientific studies have focused on hydrogel formation via the grafting of copolymers, which have an alginate backbone and synthetic thermoresponsive polymer side chains. The most typical thermoresponsive grafted copolymer hydrogels that have been prepared involve grafting poly(N-isopropylacrylamide) (PNIPAM) onto an alginate (ALG) backbone (Ciocoiu et al 2018). ALG-g-PNIPAM hydrogels have a VPTT of 32°C–35°C, depending on the grafting characteristics (Leal et al 2013). In other words, synthetic thermoresponsive polymer moieties control the VPTT of these hydrogels. However, these thermoresponsive hydrogels have their own limitations: (i) It is difficult to tune the VPTT of these hydrogels because the methods used to change the thermoresponsive nature of a synthetic polymer are complex. (ii) The disadvantages of biomedical potential applications of PNIPAM are that they are nonbiodegradable, synthetic polymers and are mostly cross-linked with toxic chemical components (Haq et al 2017). When these factors are taken into consideration, it is of great interest to substitute polysaccharides in synthetic polymers to prepare thermoresponsive alginate/polysaccharide composite hydrogel. Additionally, it is not surprising that polysaccharide-based thermoresponsive hydrogels will attract more extensive use in many biomedical applications if convenient methods can be used to adjust their VPTT.

Starch is a natural polymer that is low-cost, plentiful, easily modified, and environmentally friendly (Xie et al 2013). Starch ether is a typical kind of modified starch that can acquire a thermoresponsive property if the hydrophilic and hydrophobic balance is modified (Liu et al 2018). In our previous work (Ju et al 2012, Ju et al 2014), a series of novel thermoresponsive starch erts with a network structure were synthesized, and they seem to be ideal candidates for preparing thermoresponsive hydrogels. We propose that composite hydrogels consisting of starch ether and SA can possess a thermoresponsive property and macroporosity.

In the present work, starch ether and sodium alginate were used with a hybrid cross-linking agent to prepare a thermoresponsive polysaccharide composite hydrogel. The thermoresponsive property of the composite hydrogel was investigated in terms of the swelling ratio (SR). The obtained HIPS/SA hydrogels were measured using attenuated total reflection infrared spectroscopy (ATR-IR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG). Swelling and deswelling kinetics were investigated. The VPTT was tuned as a result of changes in the HIPS concentration to systematically investigate the NaCl concentration and organic solvent.

2. Experimental

2.1. Materials

Waxy maize starch was purchased from the National Starch and Chemical Company. Sodium alginate (SA, analytical reagent, weight-average molecular weight: 40.9 kDa) was obtained from Aladdin. Ethylene glycol diglycidyl ether (EDGE) (mixture) and isopropyl glycidyl ether (IPGE) (>96%) were purchased from Tokyo Chemical Industry Co., Ltd Calcium chloride (CaCl2, analytical reagent) sodium chloride (NaCl, analytical reagent), and sodium hydroxide (NaOH, analytical reagent) were supplied by Damao Chemical Reagent Factory. Methanol (analytical reagent), ethanol (analytical reagent), and isopropanol (analytical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd 2-Hydroxy-3-isopropoxypropyl starch (HIPS) was synthesized according to a method reported in previous work (molar substitution of HIPS: 1.67) (Ju et al 2013). Other chemical reagents were used as received without further treatment.

2.2. Methods

2.2.1. Synthesis of thermoresponsive HIPS/SA composite hydrogel

2 g of HIPS solution (5.5, 6.5, or 7.5 wt%) and SA solution (2 g of 4.5 wt%) were mixed in a 25 ml beaker. NaOH (300 μl of 40 wt%) was then added to the mixture with slow stirring using a glass bar. The bubbles were removed via ultrasonication for 30 min in an ice-water bath. EDGE (300 μl) and CaCl2 (900 μl of 1 wt%) were both added...
to the mixture, and then bubbles were removed via sonication for 30 min in an ice-water bath. Finally, the mixture was gelled at 55 °C in a water bath for 3 h (Scheme 1). The hydrogel was washed several times with hot and cold water until the water became limpid, and then the hydrogel was immersed in deionized water for 48 h with repeated changes of water to completely remove the unreacted monomers and impurities. A dry hydrogel was produced using the freeze-drying method (Dai et al. 2019). The concentrations of HIPS solution were 5.5 wt%, 6.5 wt%, and 7.5 wt%, and the HIPS/SA composite hydrogels were named as hydrogel-5.5%, hydrogel-6.5%, and hydrogel-7.5%, respectively.

2.2.2. Characterization

Microstructures of SA, waxy maize starch, HIPS, and HIPS/SA hydrogel were determined using an attenuated total reflection infrared spectroscope (ATR-IR, Nicolet iS50) over the range of 400–4000 cm⁻¹. Analysis of the morphologies was obtained using a scanning electron microscope (SEM, Hitachi SU8010) with an accelerating voltage of 5 kV. The SEM images of HIPS/SA hydrogel were imported into ImageJ software, and the pore sizes could be measured after setting the scale. Then, the average and standard deviation values of pore size were obtained through mathematic calculation. Thermal analyses (TGA and DTG) of the HIPS/SA hydrogels were carried out using a thermogravimetric analyzer (TGA, NETZSCH STA 449F3) under a nitrogen atmosphere from 40 to 500 °C at a heating rate of 10 K min⁻¹. All of the samples were freeze-dried prior to characterization.

2.2.3. Equilibrium swelling ratio (ESR) and VPTT

The SR of the HIPS/SA hydrogel was determined using the gravimetric method. Dry hydrogel (0.15 g) was placed in deionized water from 0 to 50 °C at a heating rate of 2.5 °C h⁻¹ to reach swelling equilibrium. Filter paper was used to remove surface water before the sample was weighed. The point at which a significant change in the slope of the equilibrium swelling ratio (ESR) curve appears is regarded as the VPTT (Suljovrujic et al. 2019). The ESR of hydrogel is defined as follows:

\[
ESR = \frac{(W_T - W_d)}{W_d}
\]

where, \(W_T\) (g) is the weight of the hydrogel at T °C, and \(W_d\) (g) is the weight of the dry hydrogel.

Dry hydrogel (0.15 g) was immersed in 40 ml of NaCl solutions of different concentrations (0, 5 g l⁻¹, 10 g l⁻¹, 15 g l⁻¹, and 20 g l⁻¹) to assess the effects of NaCl concentrations on VPTT. Dry hydrogel (0.15 g) was placed in 40 ml of organic solvent (methanol, ethanol, and isopropanol) solutions of different concentrations (0, 10% v/v, 30% v/v, and 50% v/v) to assess the effects of organic solvent concentrations on VPTT.

2.2.4. Deswelling, reswelling, and oscillatory kinetics

For thermoresponsive deswelling tests, HIPS/SA hydrogel was placed in a 20 °C water bath for 24 h to reach equilibrium, and then the hydrogel was removed and placed in 50 °C deionized water. The hydrogel was weighed every 0.5 min until the weight of the hydrogel showed no remarkable change. For reswelling tests, the deswelling hydrogel was transferred into a 20 °C water bath and weighed every 0.5 min until the weight of the hydrogel displayed no remarkable change. Oscillatory kinetics were assessed at 20 and 50 °C. First, the hydrogel was immersed in 20 °C deionized water for 24 h to reach equilibrium. Then, it was moved to a 50 °C water bath.

Scheme 1. Synthesis of HIPS/SA hydrogel
for 2 min followed by swelling in 20 °C deionized water for 2 min. Filter paper was used to wipe off surface water before the sample was weighed.

The values of the SR of the hydrogel at different times can be defined using the following equation:

\[ SR = \frac{(W_t - W_d)}{W_d} \]

where \( W_t \) (g) is the weight of the hydrogel at time \( t \) (min) and \( W_d \) (g) is the weight of the dry hydrogel.

3. Results and discussion

3.1. Characterization of the HIPS/SA composite hydrogel

Figure 1 presents the ATR-IR spectra of the starch, HIPS, SA, and HIPS/SA composite hydrogel in the wavelength range of 400–4000 cm\(^{-1}\). The prominent band at 1018 cm\(^{-1}\) was originated from the asymmetrical stretching of C–O–C (corresponding to the ether peak of HIPS and the cross-linking of HIPS and SA). The occurrence of band at 1370 cm\(^{-1}\) was the rocking vibration of CH\(_2\) at the C\(_6\) position of the anhydroglucose unit of HIPS and SA. There was a remarkable band at 2926 cm\(^{-1}\), which arose from the bending vibration of C–H (corresponding to the C–H peak of HIPS and SA). The high band at 3361 cm\(^{-1}\) was attributed to the stretching vibration of O–H (corresponding to the O–H of the anhydroglucose unit of HIPS and SA) (Huang et al. 2014, Li et al. 2019). In addition, the stretching vibration of C=O, which is around 1615 cm\(^{-1}\) (corresponding to the –COOH of SA) can be observed in the spectra of SA and HIPS/SA hydrogel (Kuang et al. 2011). All of these observations in ATR-IR indicate the successful synthesis of the HIPS/SA hydrogel. Additionally, the swelling test of hydrogel was performed to confirm the effective crosslinking according to previously reported work (Zhang et al. 2018). Both HIPS and SA can well dissolve in water. The appearance and weight of HIPS/SA hydrogel were almost no change after emerging it in water for one week, indicating the crosslinking networks were formed.

SEM analysis was used to study changes in the surface morphology and the porous structure of HIPS/SA hydrogel with respect to changes in composition or temperature. Specimens were dried via freeze-drying because this method can preserve the structure and volume of hydrogels even if the water is removed. As shown in figure 2, the porosity and pore size of the composite hydrogel presented a increasing trend with respect to an increase in the HIPS-content. Specifically, the average pore sizes of the dried HIPS/SA hydrogel (hydrogel-5.5% (figure 2(a)), hydrogel-6.5% (figure 2(b)) and hydrogel-7.5% (figure 2(c))) were measured (ImageJ software) as 82.45 ± 28.45 μm, 71.86 ± 21.80 μm and 42.90 ± 17.21 μm, respectively. The starch ether possessed a network structure that contributed to the formation of larger pore sizes in the hydrogel. For example, the microstructure of hydrogel-6.5% showed significant differences at temperatures below and above the VPTT (figures 2(b) and (d)). At 20 °C, hydrogel-6.5% showed a three-dimensional network and macroporous structure; in contrast, at 50 °C, the pores of hydrogel-6.5% shrunk sharply, and only micropores were present in the SEM image. The above results suggest that the porosity of the composite hydrogels can be controlled by the HIPS content as well as by temperature.

TGA was used to investigate the state and intermolecular interaction of the composite hydrogels. As seen in figure 3(a), the three different hydrogels showed nearly the same TGA curves. The weight loss below 100 °C was a
result of evaporation of residual water from the hydrogels. This was followed by a slight decrease over the temperature range from 100 to 280 °C, which is attributable to the decomposition of EDGE (Cortes-Trivino et al 2018). Typically, the characteristic weight loss between 280 and 400 °C corresponds to degradation of anhydroglucose rings in the backbone of HIPS and SA (Hu et al 2018). Furthermore, there is only one sharp drop between 280 and 400 °C in the three DTG curves of the hydrogels (figure 3(b)). Different from the single peak,
the physical mixture of HIPS and SA would display two evident endothermic peaks, according to the previous literature (Zheng et al 2016, Geng 2018). Thus, the above results indicates the successful chemical cross-linking in the synthesis process.

3.2. Thermoresponsive properties of HIPS/SA hydrogel
In the HIPS/SA composite hydrogels, HIPS composition plays an important role in controlling the thermoresponsive property. Thus, in this work, three kinds of composite hydrogels with different amounts of HIPS were prepared: hydrogel-5.5%, hydrogel-6.5%, and hydrogel-7.5%. The ESR values of these samples were measured from 0 to 50 °C to determine the thermoresponsive property. As seen in figure 4, the ESR indicated a significant volume loss for all of the hydrogels around VPTT; obviously, the size of the hydrogel shrunk sharply, as indicated by the photographs inset in figure 4. When the temperature was increased to the VPTT, hydrogen bonding between water and HIPS was weaker, and the hydrophobic interaction between the hydrophobic chains of HIPS became dominant, causing the hydrophobic chains in HIPS to collapse (Burek et al 2017). Thus, the water was expelled from the hydrogel structure, and the pores shrunk. Additionally, with an increase in the HIPS concentration from 5.5 to 7.5 wt%, the VPTT decreased from 40.2 to 29.4 °C. Hydrogel with higher HIPS concentration presented more significant hydrophobic character when it was heated. This resulted when hydrophobic chains formed and easily collapsed the structure. Therefore, it is concluded that the hydrogel was dehydrated at lower temperature (Vancoillie et al 2014). It is noteworthy that the VPTT can be tuned by changing the HIPS concentration. Interestingly, it is also observed in figure 4 that at the same temperature, the hydrogel that has a higher HIPS concentration exhibited lower SR. This was because the higher HIPS concentration resulted in more hydrophobic chains inside the hydrogel, and hence, less water was retained in the hydrogel. However, the swelling-deswelling behavior of the hydrogel was insensitive to a temperature stimulus when the concentration of HIPS was lower than 5.5%, and the VPTT of the hydrogel showed no remarkable change when the HIPS concentration was higher than 7.5%.

3.3. Effects of NaCl concentrations on VPTT of HIPS/SA hydrogel
In this study, we found that the presence of inorganic salts in an aqueous medium has a remarkable influence on the thermoresponsive properties of HIPS/SA hydrogel. NaCl is a common inorganic salt and essential electrolyte in the body, and thus, effects of NaCl concentration on the VPTT of HIPS/SA hydrogel were investigated. Variations in the SR values of hydrogel-5.5%, hydrogel-6.5%, and hydrogel-7.5% with different NaCl concentrations (no salt, 5, 10, 15, and 20 g l⁻¹) during heating were recorded (figures 5(a)–(c)). In figure 5(d), with an increase in the NaCl concentration from 0 to 20 g l⁻¹, the VPTT decreased from 40.2 to 25.2 °C for hydrogel-5.5%, 34.9 to 19.9 °C for hydrogel-6.5%, and 29.4 to 15.0 °C for hydrogel-7.5%. Two different mechanisms can be introduced to explain these phenomena: (i) According to the dehydration mechanism, the hydrogen bonds between HIPS hydrophobic chains and water molecules break with the addition of NaCl because of the strong hydration interaction between NaCl and water. Also, because of Donnan osmotic pressure between the interior hydrogel and external solution, the hydrogels are more susceptible to dehydration (Hong and Bae 2002, Seo et al 2012, Yan et al 2016). (ii) According to the surface tension mechanism, an increase in the NaCl concentration causes the enhanced surface tension between polymer chains and water molecules. This

Figure 4. SR changes for HIPS/SA hydrogel with different HIPS concentrations.
results in free energy between the hydrophobic group/water interface and the dehydration of hydrogel (Kohler et al 2006, Zavgorodnya et al 2014, Hiruta et al 2015).

3.4. Effects of organic solvent concentrations on VPTT of HIPS/SA hydrogel
We evaluated the effects of adding three kinds of alcohol (methanol, ethanol, and isopropanol) on the VPTT of HIPS/SA hydrogel. Similar to NaCl, adding methanol, ethanol, and isopropanol resulted in a decrease of the hydrogel SR. As seen in figure 6, the VPTT of different hydrogels decreased with an increase in the concentration of organic solvents. For instance, with an increase in the concentration of the organic solvents from 10 to 50% v/v, the VPTT of hydrogel-6.5% decreased from 34.1 to 31.3 °C (methanol), 33.9 to 30.8 °C (ethanol), and 33.5 to 30.2 °C (isopropanol). Moreover, the effectiveness of these solvents at reducing the VPTT follows the order: isopropanol > ethanol > methanol; that is, alcohol molecules that have longer carbon length caused a larger decrease in the VPTT. For example, the VPTT of hydrogel-6.5% respectively decreased by 3.6, 4.1, and 4.7 °C when the concentrations of methanol, ethanol, and isopropanol increased from 0 to 50% v/v. The effect of alcohol concentration on SR and VPTT can be explained by the following facts: (i) Polarity of these solvents follows the order water > methanol > ethanol > isopropanol, and this resulted in a decrease of SR (Ju et al 2013, Bonetti et al 2020). (ii) Alcohol molecules in aqueous solution induce a collapsed state of polymer chains, and the hydrophilic portion of the HIPS/SA hydrogel was shielded by alcohol molecules. This hinders the formation of hydrogen bonds with water molecules and causes a lower VPTT (Dhara and Chatterji 2000, Lucht et al 2017). (iii) With an increase in the concentration of alcohol, the formation of alcohol/water complexes required more water to participate in the hydration structure of the hydrogel, and thus, the VPTT was reduced with an increase in the alcohol content (Dhara et al 2000).

3.5. Deswelling, reswelling, and oscillatory kinetics
Swelling kinetics are a key indicator for estimating whether a hydrogel is appropriate for use in the field of biomedicine. As seen in figure 7(a), the hydrogel lost most of its water in about 1.5 min at 50 °C and reached...
deswelling equilibrium in 2 min. This means that the hydrogel showed fast response rates and lost most of its water in a very short time. It is worth noting that hydrogel-5.5% lost most of its water in 1.5 min but that the other two samples lost most of their water in 1 min. The VPTT of hydrogel-5.5% was 40.2 °C, which was higher than that of hydrogel-6.5% (34.9 °C) and hydrogel-7.5% (29.4 °C). Also, the VPTT of hydrogel-5.5% was close to 50 °C, and thus, hydrogel-5.5% required more time to reach equilibrium. Furthermore, hydrogel-5.5% ended up with a relatively high SR at equilibrium. Because of the relatively poor hydrophobicity of hydrogel-5.5%, more residual water was in the pores after heating.

Reswelling behavior curves are shown in figure 7(b). Hydrogels reached reswelling equilibrium in approximately 3 min. Interestingly, after 3 min of reswelling, the SR values reached 52.6 g g⁻¹ for hydrogel-5.5%, 44.7 g g⁻¹ for hydrogel-6.5%, and 40.6 g g⁻¹ for hydrogel-7.5%. However, before deswelling, the SR values were 53.8 g g⁻¹ for hydrogel-5.5%, 45.5 g g⁻¹ for hydrogel-6.5%, and 42.5 g g⁻¹ for hydrogel-7.5%. The SR values did not reach the original levels and showed decreases to some extent. This was because interchain association after heating required extra energy to break the interchain hydrogen bonds in the cooling process. This consequently led to lower SR values.

Figure 7(c) shows swelling-deswelling cycles of different hydrogel samples. A smaller decrease in the SR of HIPS/SA hydrogels was observed in 5 heating-cooling cycles, and this indicates that the HIPS/SA hydrogels had a stable and reversible thermoresponsive property.

4. Conclusions

A series of thermoresponsive HIPS/SA composite hydrogels with different HIPS contents were successfully synthesized via cross-linking using hybrid crosslinkers. The results show that the HIPS/SA hydrogel processed a desirable, reversible, and tunable thermoresponsive property. Adjusting the HIPS concentration, NaCl concentration, and organic solvent concentration enables the VPTT of the HIPS/SA hydrogel to be easily...
changed. Specifically, the VPTT values decreased from 40.2 to 29.4 °C when the HIPS concentration was increased from 5.5 to 7.5 wt%. The addition of additives (NaCl and alcohol) significantly reduced the SR of the hydrogels. When the NaCl concentration was increased from 0 to 20 g l\(^{-1}\), the VPTT decreased from 40.2 to 25.2 °C for hydrogel-5.5%, 34.9 to 19.9 °C for hydrogel-6.5%, and 29.4 to 15.0 °C for hydrogel-7.5%. The addition of alcohol also decreased the VPTT of the hydrogels, and the effectiveness of the different organic solvents at reducing the VPTT was observed to follow the order: isopropanol > ethanol > methanol. Moreover, the hydrogel that had lower HIPS concentration exhibited higher SR, and all of the hydrogels were able to expel most of their water in a very short time. The HIPS/SA hydrogel demonstrated an excellent reversible thermoresponsive property, and there was only a slight reduction in the SR after 5 swelling-deswelling cycles. The HIPS/SA composite hydrogel that was fabricated in this study has huge potential value in practical applications.

Acknowledgments

This research was supported by the National Key R&D Program of China (2017YFD0701700), National Natural Science Foundation of China (Nos., 31901775, 31472312, 31672673 and 21878036), Key R&D Program of Guangdong Province (2019B020215001), and Liaoning S&T Project (2017203002).

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