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Formation, influencing factors, and applications of internal channels in starch: A review

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ABSTRACT

Starch, a natural polymer, has a complex internal structure. Some starches, such as corn and wheat starches, have well-developed surface pores and internal channels. These channel structures are considered crucial in connecting surface stomata and internal cavities and have adequate space for loading guest molecules. After processing or modification, the starch-containing channel structures can be used for food and drug encapsulation and delivery. This article reviews the formation and determination of starch internal channels, and the influence of different factors (such as starch species and processing conditions) on the channel structure. It also discusses relevant starch preparation methods (physical, chemical, enzymatic, and synergistic), and the encapsulation effect of starch containing internal channels on different substances. In addition, the role of internal channels in regulating the starch digestion rate and other aspects is also discussed here. This review highlights the significant multifunctional applications of starch with a channel structure.

1. Introduction

Starch, a renewable carbohydrate in nature, serves as energy storage in plant tissues (roots, stems, seeds, and fruits) (Doutch & Gilbert, 2013). Native starch is a polymer of dehydrated glucose, a combination of amylose and amylopectin, together with some lipids and proteins. Different types of starch vary in composition (especially amylose-amylopectin ratio), granule size (sub-microns to 100 μm) and shape (oval, spherical, or angular) depending on botanical origin and maturity (Li, et al., 2020a; Perez & Bertoft, 2010). Because of its low cost and easy accessibility, starch is extensively used in food, papermaking, medicine, textile materials, and other fields (Veelaert, Polling & De Wit, 1995). In addition, increasing evidence has confirmed that the internal structure of starch granules affects their function and properties.

Under a microscope, starch can be visualized as a semicrystalline polymer with a multilevel and multiscale organization (Ge, et al., 2022). Generally, the alternating crystalline and amorphous layers inside the starch granules result in different types of crystallization: A-type, B-type, C-type (A + B-type), and V-type (amylose–lipid V-type inclusion complexes) (Zobel, 1988). Other levels of starch structure include single/double helix, polymorphism (crystal), growth ring, and whole granule (Perez & Bertoft, 2010). Different locations have slightly different structures and provide heterogeneous regions within the starch granule (Qi & Tester, 2019). During special processing and storage of starch, these structures undergo different changes. Therefore, studies investigating the starch microstructure are conducive to the mastery of the macro properties of starch.

Starch’s internal structure, which is not completely solid, includes pores present on the surface of granules, internal cavities at the granule hilum, and the channels connecting them (Fig. 1). In starch having the channel structure, internal channels of different lengths (serpentine) extend to the central cavity through the aforementioned pores (Baldwin, Adler, Davies & Melia, 1994; Chemists, 1993; Huber & BeMiller, 2000). Using the helium stereo-turbidimetric method and mercury porosity measurement, Karathanos and Saravacos determined the overall porosity and pore size distribution of waxy corn starch granules. They obtained pore sizes ranging from 0.005 to 0.400 μm (Karathanos & Saravacos, 1993). Although the number of starch channels is random,

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Widya et al. (2010) studied six methods for determining the average number of channels per granule in a population of starch granules (Widya, Gunawan & BeMiller, 2010). They believed that the granular actin measurement was the preferred method. Moreover, the presence of a channel structure enriches the functional applications of starch and broadens its applicable fields. For instance, starch rich in the channel structure can be used as the functional component carrier, encapsulation agent, desiccant, and adsorbent (J. Chen et al., 2020).

To completely understand the starch channel structure and its applications, recent literature related to this topic is reviewed here, where the formation of starch channels and their components are discussed. The differences in channels of starches from different plant sources and the effects of different processing methods on the channels are elucidated. The applications related to starch internal channels and their processing methods are also explored.

2. Internal channels of starch

2.1. Formation of channels

The origin of surface pores and channels has yet to be confirmed. Based on previous research, their formation is attributable to two factors: self-development and external effects. Initially, Han and Hamaker (2002) reported that the channels of normal corn, wave-corn, and A-type wheat starch granules contain proteins. Fannon et al. (2004) observed that channels contain the same components (e.g. some proteins and phospholipids) as the amyloid plasma membrane. They therefore hypothesized that channels are formed with the development of a granule around radially oriented microtubules in the amyloplast. Subsequent studies have demonstrated that the starch channels contained the same protein components (actin, tubulin, and adenosine transporter) as the microtubules of corn endosperm amyloplasts and corn starch granules. In addition, visual evidence suggests the presence of filamentous structures adjacent to the starch outer membrane in the corn endosperm amyloplast. The aforementioned evidence supports the hypothesis that channels in corn starch granules are remnants of amylosomal microtubules (Benmoussa, et al., 2010).

Regarding external factors, the starch surface of sorghum and millet had pores, whereas the surface of large starch grains of barley, wheat, and rye had randomly distributed equatorial grooves (He, et al., 2012; Naguleswaran, Li, Vasanthan & Bressler, 2011). Their study demonstrated that the pores on some starch surfaces are native and randomly formed, rather than being products of sample processing. Drought, acidity, and salinity in the soil all affect starch microstructure formation, with drought being the main environmental factor (Li, et al., 2015; He, et al., 2012). Compared with the surface of normal wheat, more pits and pores appeared on the starch surface under drought stress, and morphological changes were also reported in other microstructures (Li, et al., 2015). These pores on the starch surface serve as the openings of snake-like channels toward inside. Thus, channels of different depths, diameters, and numbers are formed (Chemists, 1993; Huber & BeMiller, 2000). Channels of varying depth permeate the granule texture, with some reaching the central cavity, and dehydration has been demonstrated to have a role in the development of these cavities (Huber & BeMiller, 2000). These pores and channels are sufficiently large to allow the passage of common chemicals and even enzymes, enabling the diffusion of external substances into the starch. The enzyme action also affects the size, length, and number of channels to some extent (Dhital, Shelat, Shrestha & Gidley, 2013). In short, starch channels produced under natural conditions may serve as the medium of communication between the external world and the inside of starch.

2.2. Material composition in channels

The composition and number of channels vary between different starch species and between different granules of the same starch. The starch channel structure is believed to influence the action of hydrolases, which in turn affect the starch digestion process and gelatinization properties. On the other hand, the starch channel structure also affects the diffusion of dyes and the reactivity of chemical reagents (Huber & BeMiller, 1997, 2001). Many studies have attempted to determine the substance composition of starch channels (e.g. protein and lipid).

2.2.1. Proteins in channels

Proteins in starch, collectively called starch granular-associated proteins (SGAPs), bind to the surface and internal matrix of the starch granules (Tester, Karkalas & Qi, 2004). Studies have shown that protein globules in maize, wheat, and potato starch are composed of grain-bound starch synthase (Chemists, 1993). 3-(4-Carboxybenzoyl) quinoline-2-carboxaldehyde (CBQCA, a protein-specific probe) was used for protein labeling. Confocal laser scanning microscopy (CLSM) revealed that the starch channels of wheat, maize, waxy corn, and sorghum contained certain proteins. The movement of fluorescent proteins was detected when the starch granules were intact, which thus proved that the channels were open to the external environment (Han, Benmoussa, Gray, BeMiller & Hamaker, 2005). Moreover, proteins are present not only in the channels but also inside the starch and on its surface. Similarly, CBQCA-labeled wheat A-type granules exhibited a radial channel protein network structure, while the fluorescence signal of protease-treated starch granules was significantly stronger than that of

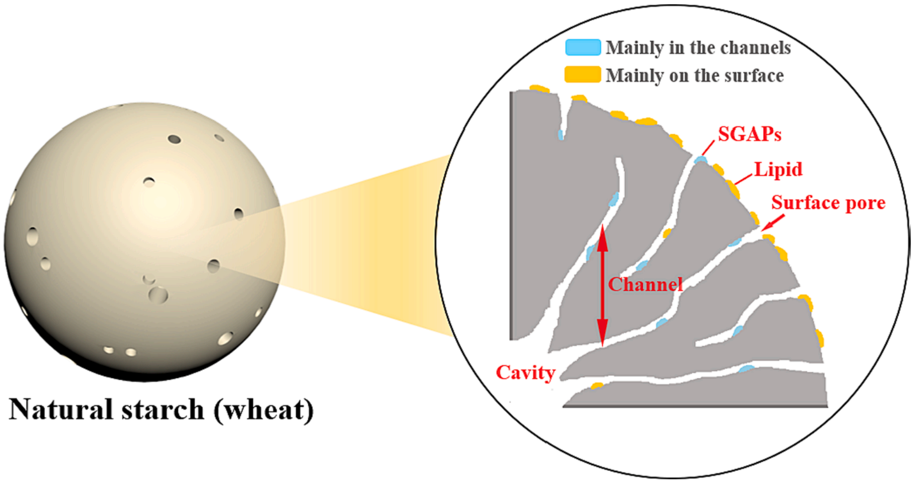

Fig. 1. Natural starch granules containing channels.

untreated starch granules, as observed after staining with methanolic merbromin solution (fluorescent dye). This suggests that the channels of A- and B-type starch granules, treated with proteases, contribute to the transfer of chemical reagents into the granule matrix (Kim & Huber, 2008). Further, Bae et al. (2020) indicate that the presence of SGAPs enhances the rigidity of starch granules and increases the stability of expanded starch granules, while removing SGAPs via protease treatments improves their resistance to retrogradation in native starches.

2.2.2. Lipids in channels

Lipids in starch include starch internal lipids and starch granule-associated surface and channel lipids (SGALs) (Ma, et al., 2022). Starches in cereals such as wheat, barley, corn, and rice typically contain 0.25–0.6 % (w/w) protein and 0.6–1 % lipids, which are primarily phospholipids (Debet & Gidley, 2006). Using the reflection CLSM (R-CLSM) method, Gray (2003) discovered that channels in corn and sorghum endosperm starch granules are lined with proteins (including F-actin) and phospholipids. Subsequently, through lipid fractionation of cornstarch granules and MALDI-TOF mass spectroscopy analysis, phospholipids within the starch channels were identified as lysophosphatidylcholine (Lee & BeMiller, 2008). Glaring et al. (2006) analyzed phospholipid distribution in granules by using phosphate-bound fluorescent dyes and CLSM. The content and distribution of different starch lipids in granules vary, and differences are also observed between different granules of the same starch. In triticale starch, phospholipids are mainly distributed on the granule surface and partially within the granules and channels. In corn starch granules, phospholipids are mainly distributed in the starch channels (Naguleswaran, Li, Vasanthan & Bressler, 2011). The lipids in the channel also affect some properties of starch. Ma et al. (2022) stained corn starch with Pro-Q Diamond and revealed the distribution of phospholipids on surfaces, channels and substrates. In addition, they found that the presence of SGALs enhanced the elastic gel network structure of cross-linked corn starch, while the removal of SGALs increased the anti-thixotropy of crosslinked starches, facilitating the reorientation of crosslinked amylopectin/amylose molecules during shearing.

Proteins and phospholipids in starch channels or their complexes may have crucial roles in maintaining the starch internal structure and channel stability. Moreover, protein and phospholipid content in the channels can hinder the diffusion of chemical reagents and enzymes inside the starch granules. This affects the surface characteristics and physical and chemical properties of the starch (Karathanos & Saravacos, 1993).

2.3. Effects of different starch sources on internal channels

Natural starches are present in the grain or seed endosperm and are surrounded by the protein matrix and cell walls, which serve as a physical barrier, somewhat preventing the enzyme from contacting and hydrolyzing the starch. At the same time, starch cannot come in contact with an adequate amount of water, and therefore, gelatinization and expansion of starch are not easy. The microstructure of the starch internal channels is in a relatively stable state. This paper lists different starch sources (Fig. 2) and some processing conditions and their effects on starch channels and other microstructures (Table 1).

The structure of natural starch is regulated by the plant genome and influenced by external growth conditions. Grain starch (mainly A-type), tuber starch (mainly B-type) and leguminous starch (mainly C-type) exhibit different crystal types under X-ray diffractometry (XRD), and their internal channels and other structural features are also significantly different. First, not all types of starch contain internal channels. Dhital et al. (2013) have reviewed and discussed starch pores and channels, and they indicate that most A-type grain starches contain pores (the beginning of channels) on the granules that lead to internal serpentine channels, while the relative lack of pores and channels in B-type polymorphic starches (such as potatoes and high amylose) is still not understood. It can generally be observed that B/C-type starches have no surface pores or channels compared to A-type starches, which is consistent with the findings of Li et al.(2020b). Further, different starch channels vary in size, number, and depth. Some starches have natural pores (diameter: 1–3 μm) on their surfaces (Madene, Jacquot, Scher & Desobry, 2006). Other studies have reported that the peak pore diameter of corn and rice starch is 100–200 nm (Sujka & Jamroz, 2010). According to the study of Dhital et al. (2017), grain starches can naturally form pores having a diameter of 0.1–0.3 μm on the surface (the beginning of the channel), whereas the inner channel diameter is 0.07–0.1 μm. In addition, the size and number of starch pores can be modulated by controlling the amylase type and level. The hydrolysis effect of the same amylase on different types of starch is also different. Compared with tuber starches, starches derived from grain after enzymatic hydrolysis have larger and deeper pores, presenting deep holes with some degradation of its internal part. (Benavent-Gil & Rosell, 2017b).

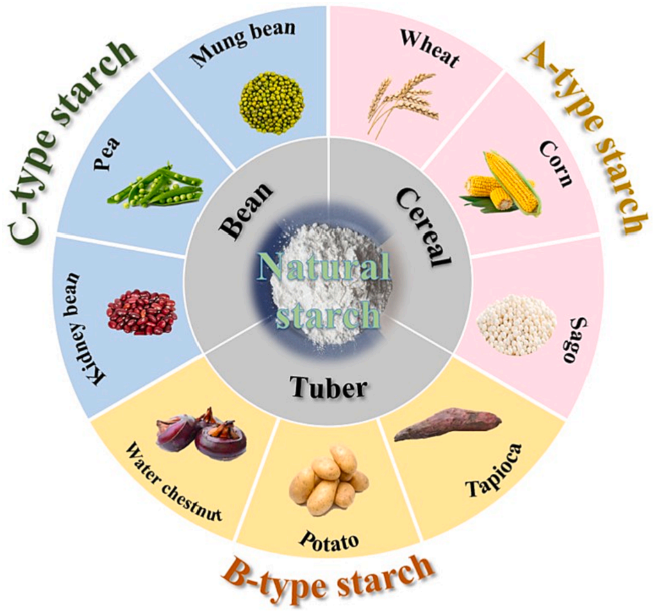

Fig. 2. Starches and their crystal types from different plant sources.

The channel structure of corn starch is considered more developed, because both common and waxy corn starches exhibit clearer pores and a rough granule surface under scanning electron microscopy (SEM), compared with other starches (e.g. mung bean, wheat, tapioca, pea, potato, and sago) (Li, et al., 2020c). Under natural conditions, the rough starch surface facilitates hydrolase attachment, and the large pores allow the passage of enzymes and the formation of new channels through corrosion (Dhital, Shrestha, & Gidley, 2010a). Furthermore, the scattering peak area (Apeak) measured through small-angle X-ray scattering (SAXS) followed the order of wheat > waxy corn > mung bean > corn > pea > tapioca > sago > potato (Li, et al., 2020). The Apeak value positively correlates with the degree of order in the lamellar region, indicating that the degree of order in the wheat and corn starch layers is relatively low, which is related to the existence of internal channels. According to the XRD results, potato starch exhibited the highest crystallinity, which was consistent with previous SEM observations that potato starch granules had smoother surfaces and fewer pores (the channel's beginning) (Karathanos & Saravacos, 1993).

Common corn starch also has lower crystallinity and Apeak values but larger granule sizes and granule surface areas than water chestnut starch (Qiao et al., 2019). Under normal conditions, with an increase in the granule surface area, the enzyme attachment sites on the starch surface increase, thereby facilitating new pore and channel formation (Mahasukhonthachat, Sopade & Gidley, 2010). In the digestion process, starches with more developed channel structures also seem to break

Table 1
Effect of different processing conditions on the starch channel structure.

Main processing conditions	Processing object	Main results	References
Screw extruder (200 rpm, 160 ℃, and 18 % of water content)	Lentil starch	↑ Number of starch channels	(Rathod & Annapure, 2016)
Ultrasonic temperature control treatment (5 ℃, 15 ℃, and 25 ℃)	Corn starch, potato starch, and pea starch	The internal structure of corn starch was dominated by rearrangement, and that of potato and pea starches by disruption	(Ouyang, et al., 2021)
Freezing–thawing cycles (1, 3, 7, and 10 times)	Glutinous rice starch	↑ Number of starch channels ↑ Starch channel diameter	(Tao, et al., 2015)
Microwave treatment of starch slurry (8 W/g, 3 min)	Indica rice starch	↓ Number of starch channels	(N. N. Li, et al., 2020)
Hot air (RH 0.9——4.3 %); or humidified hot air (RH 5.9–30.9 %), 100 ℃–150 ℃	Brown rice starch	The texture of brown rice stiffens and starch–lipid complexes were formed	(Rattanamechaiskul, et al., 2013)
Superheated steam or hot air (120 ℃, 1.0 m/s, 2.5 min)	Lightly milled rice starch	V-type starch - lipid complex is formed, which enhances the stability of starch	(Wu, et al., 2016)
Bile or bile salts were added to form starch–bile salt complexes	tarch–iodine complex (buckwheat starch)	Bile inhibited the formation of starch–iodine complexes and inhibited trypsin-induced starch digestion	(Takahama & Hirota, 2011)
Transglutaminase was added to form starch–zein microgranules	Corn starch	The core shell structure of zein formed protected the internal structure of starch	(C. Wang, et al., 2022)

Notes: ↑, promotion; ↓, inhibition

down into glucose more efficiently. In *in vitro* simulated digestion experiments, Li et al. (2020) and Qiao et al. (2019) treated various natural starches using α-glucosidase/trypsin and starch glucosidase, where glucose concentration in the digestion solution was measured using the glucose oxidase/peroxidase reagent. After the 120-min digestion period, maize (C120 79 %), tapioca (C120 90 %), pea (C120 73 %), wheat (C120 96 %), and waxy corn (C120 82.1 %) starches exhibited a considerably higher rate and extent of digestion (Li, et al., 2020). After 12 h of digestion, corn starch (82. 11 %) was digested more than water chestnut starch (71.96 %) (Qiao, et al., 2019). Kidney bean starch has higher amylose content and C-crystallinity, more stable internal structure, and exhibits lower digestibility than potato or cereal starch (Zhou, et al., 2021).

2.4. *Influences of different processing methods on internal channels*

Physical extrusion is a method of processing starch by heating, stirring, puffing, and subjecting to other unit operations, the changes that occur in the starch structure during extrusion are regulated by food raw materials and extrusion conditions. (Huang, Liu, Ma, Mai & Li, 2022). Because of a decrease in pressure and the rapid evaporation of water, starch has variable pore size and quantity during bulking. Researchers have found that the porosity of starch could be improved by increasing the feed moisture (14–22 %), while high temperatures cause starch gelatinization and structural weakening, which in turn affected the number of internal channels of starch (Rathod & Annapure, 2016).

A study investigated the consequence of ultrasonic temperature on the structure and digestion behavior of corn starch (CS, A-type), potato starch (PtS, B-type), and pea starch (PS, C-type) (Ouyang, et al., 2021). Rearrangement dominates the internal structure (helix and crystal) of A-type corn starch at a low ultrasonic temperature, whereas destruction dominates the structure (helix and crystal) of B-type potato starch and C-type pea starch. Changes in low-level structures affect higher structures such as starch channels. Indica rice starch (IRS) was isolated from indica rice. Compared with the conventional cooked starch, the microwave-treated starch exhibited stronger molecular reorganization during digestion, which was reflected in the enhancement of the nanoscale order after 20 min of *in vitro* digestion and the higher density of the ordered regions after 120 min of the same treatment. The strong molecular reorganization partly enhances the stability of starch internal channels (Li, et al., 2020).

Freeze–thaw cycle (FTC) treatment promoted the formation of internal starch channels, primarily because the phase transition between water molecules and ice crystals during the FTC generated mechanical forces that enlarged the internal channels of starch granules without hydrolyzing the starch glycosidic bonds (Tao, et al., 2015). In addition, ice expansion during FTC destroyed the structure of brown rice bran, cracked the surface of starch granules, and increased the corrosion and contact of starch channels under external conditions (enzymes), thus making gelatinization and digestion of starch easier. Nonthermal plasma (cold plasma, CP) has been increasingly used to design and customize starch macromolecules, and CP indirectly affects the degree of starch crystallization by attacking the amorphous region of starch. In addition, CP can induce starch surface corrosion and channel decomposition, causing changes in the starch functional properties for related applications (Zhu, et al., 2023).

Although high-temperature steam treatment or hot air treatment aggravates starch gelatinization, makes the starch surface rough, and improves the enzyme digestion efficiency, at the same time, it also promotes the formation of the V-type starch–lipid complex. The complex protects internal structures such as starch channels, thereby making it difficult for enzymes to act on starch. For example, hot air treatment causes a stiffening of brown rice texture, formation of starch–lipid complexes, and a decrease in the rate of amylase-induced digestion (Rattanamechaiskul, et al., 2013). Similarly, high-temperature fluidization of jasmine brown rice starch increased the content of starch–lipid complex and decreased the postprandial glycemic index (GI) value (Jaisut, Prachayawarakorn, Varanyanond, Tungtrakul & Soponronnarit, 2009). For lightly milled rice (which retains most of the bran layer), short-time superheated steam treatment destroys the long-range and short-range structures of starch, causing an increase in starch digestibility, but the change is relatively small. This may be related to the V-type starch–lipid complex, which can partially counteract the changes of starch fractions induced by partial gelatinization (Wu, et al., 2016).

In addition to the starch–lipid complex promoted by high temperature, some researchers studied the effect of binding of bile salts to starch (Takahama & Hirota, 2011). Compared with the normal group, the bile/bile salt–buckwheat starch complex exerted a more significant inhibitory effect on pancreatase-induced starch digestion. The binding of bile salt and amylopectin mainly improved the stability of the starch microstructure in the channel. Forming a shell seems to provide a better protection. Wang et al. (2022) achieved a starch/zein core–shell structure by coating starch granules with a heat-treated zein solution, and enhanced this cross-linking with transglutaminase. The zein shell acted as a physical barrier, reduced the contact between starch and the external environment, and protected the internal structure of starch granules from being hydrolyzed by digestive enzymes to a certain extent.

3. Applications

By taking advantage of the internal channels naturally present in starch grains or those can be obtained through processing, porous starch can be prepared, which is a crucial multifunctionsal auxiliary material. Moreover, starch and its modified products can be applied in nutrition-enhanced foods, packaging materials, medical materials, drug molecular transport and excipients, environmental protection, and other aspects (Sathyan & Nisha, 2022). As a biomaterial obtained from various sources, starches containing internal channels have the following advantages (He, et al., 2022; Wang, Yuan & Yue, 2015).

1. Starches (such as corn starch) containing surface pores (channel beginning), channels, and cavities (channel end) form additional contact space, increase the contact sites of the contained substances, and to a certain extent, increase the amount of drugs and nutrients that can be encapsulated.
2. Natural or modified starch (obtained through green processing) offer nutritional and safety advantages as a delivery agent.
3. Starch as an embedded wall material promotes a relatively higher sensitivity to enzymatic hydrolysis.
4. The delivery material physically attached to the channel can achieve continuous and complete release.
5. Starches high in slow digestion starch (SDS) and resistant starch (RS) have an additional prebiotic effect, thereby promoting the growth of gut microbiota and subsequently inducing health benefits *in vivo*.
6. Starches with small granules, white color, and light taste can provide attractive sensory characteristics for food applications.

3.1. Preparation of porous starch as an auxiliary material

Compared with natural starch, porous starch enriches the pore and channel content without changing the grain structure (Zhang, et al., 2012). Porous starch has been described as sponge-like or honeycomb-like structures, the pore size varies from a few nanometers to a few microns, and the micropore and mesopore have good commutability (Wang, Blazek, Gilbert & Copeland, 2012). Porous starch can be obtained through physical, chemical, enzymatic, and synergistic (appropriate combinations of the first three methods) methods (Latip, Samsudin, Utra & Alias, 2021). Table 2 summarizes the different porous

Table 2
Preparation of porous starch by different methods and their effects.

Methods	Starch source	Process conditions	Main results	References
Ultrasonic method	Potato starch	100 W, 22 kHz, 30 min	A starch nanoparticle with controllable particle size was prepared	(Qiu, et al., 2019)
Microwave method	Bambara groundnut starch	700 W, 2450 MHz, 60 s	Gelatinization and thermal properties of porous starch were improved	(Oyeyinka, et al.,2019)
Ultrasonic + microwave method	Corn starch, potato starch	U: 500 W, 20 kHz, 60 min; M: 60 W, 2450 MHz, 90 s	The starch helix structure was destroyed and the surface pits increased	(L. Wang, et al., 2022)
Ethanol exchange method	Corn starch	Solvent exchange of ethanol and water, freeze drying	The higher the ethanol concentration, the larger the pores formed by the porous starch	(Oliyaei, et al., 2019)
Hydrochloric acid method	Starch from Merck	HCl (37 wt%) was added to form a porous structure	This structure had a good adsorption effect on the dye	(Pourjavadi, et al., 2016)
Alcohol alkali method	Waxy corn starch	Absolute ethyl alcohol, sodium hydroxide solution (3 M)	The P-GCWS obtained had good freeze–thaw stability and oil absorption ability	(Y. Chen, et al., 2020)
Methods	Starch source	Process conditions	Main results	References
Enzymatic method (single enzyme)	Popcorn starch, corn starch	AM (69.38 U/g), pH 6.0, 50 ℃, 50 rpm, 12h	PCS had larger pores and the ability to absorb water and oil	(Zhiwei, 2020)
Enzymatic method (single enzyme)	Rice starch	AMG or AM (100 U/g), pH 5.5, 60 ℃, 180 rpm, 24h	Starch pores after AM treatment were narrower but deeper than those after AMG	(Keeratiburana, et al., 2020)
Enzymatic method (two enzymes)	Corn starch	AM/AMG = 100:30 U/g, pH 5.5, 50 ℃, 80 rpm, 12h	A high porosity starch with a stable granule structure was obtained	(Piloni, et al., 2022)
Enzymatic method (two enzymes)	Potato starch, corn starch, wheat starch, sweet potato starch	GT (1500 U/g), pH 5, 45 °C, 3h; BE (300 U/g), pH 5.5, 50 ℃, 4h	GT/BE produced more macropores (>50 nm) and had a larger adsorption capacity	(L. Guo, et al., 2020)
Enzymatic method (three enzymes)	Wheat starch, corn starch	AM (100 U/g), pH 6.9; BE (100 U/g), pH 6.5, 45 °C, 10*h*; AMG (1500 U/g), pH 5.5, 48 °C, 12h	The porous starch formed had good adsorption capacity for oils, dyes, and heavy metals	(L. Guo, et al., 2021)
Methods	Starch source	Process conditions	Main results	References
Ultrasonic + enzymatic method	Wheat starch	240W, 35 kHz, 40 min; 0.4% AM (10000 U/g), pH 6.0, 45 ℃, 24h	The hydration rate and adsorption capacity of treated starch were improved	(Majzoobi, et al.,2015)
Microwave + enzymatic method	Corn starch	300 W, 2 min; AM/AMG (0.4%/1.6% starch mass), pH 4, 56 °C, 160 rpm, 12h	The porous starch prepared by the composite treatment had greater specific surface area and oil–water absorption	(Jiang, et al.,2023)
Electric field + enzymatic method	Rice starch	MEF (0–20 V, 0–400 Hz、0–2h, RT); AM, pH 8, 20–120 min	When the voltage was increased from 2 V to 15 V, the average number of pores in the hydrolyzed starch increased	(D. Li, et al., 2021)
Ethyl alcohol + enzymatic method	Corn starch	70% ethanol; AM (200 U/mg)/AMG (260 U/mL) = 1:4, pH 5 45 ℃, 500 rpm	The porous starch formed had high crystallinity and oil–water adsorption capacity	(X. Zhou, et al., 2021)
Methods	Starch source	Process conditions	Main results	References
Critical melting + freeze–thawing method	Corn starch	CM: −20 ℃, 12h; FT: 25 ℃, 2 h, repeated for 0, 5, 10, and 20 cycles	CMFT significantly improved the thermal stability of the prepared porous starch	(C. Zhang, et al., 2022)
Glycerin + unidirectional freeze-drying method	Potato starch, corn starch	15% Gly, 85 ℃, 600 rpm, 20 min; UFDM, 48h	Porous starch blocks prepared from glycerol-oxidized starch had good mechanical strength and moisture absorption ability	(Mi, et al., 2012)

Notes: +, joint treatment; Single enzyme, a single enzyme was processed; Two or three enzymes, two or three different enzymes are involved in processing. Abbreviations: U, ultrasonic; M, microwave; P-GCWS, porous waxy corn starch; PCS, popcorn starch; AM, α-amylase; AMG, amyloglucosidase; GT, glycosyltransferase; BE, branching enzyme. MEF, moderate electric field; CM, critical melting; FT, freeze–thawing; CMFT, combined treatment of critical melting and freeze–thawing; Gly, glycerin; UFDM, unidirectional freeze-drying.

starch preparation methods applied in the last decade and the differences in the properties of the resulting products.

The physical methods commonly used for processing porous starch include ultrasonic, microwave and extrusion, the electric field technology has gradually been applied to machining in recent years (BeMiller & Huber, 2015). A single physical processing method has the advantages of simple operation, high efficiency, economy, and so on. The mechanism of partial porous starch preparation is presented in Fig. 3. For example, the ultrasound-induced cavitation effect could cause local high pressure of granules and bubble rupture, thereby leading to the formation of more pores and cracks on the solid surface (Qiu, Cai, Wang & Yan, 2019). However, the cavitation effect loosens the internal space of starch granules and destroys the structure, resulting in an increase in the damaged starch content (Wang, Wang, Zhou, Wu & Ouyang, 2022). Pore formation in the porous starch is not uniform, which is unsuitable for industrial application (Wang, et al., 2022). Porous starches can also be prepared through solvent exchange or acid-base treatment. Among them, the combination of ethanol/water is the most commonly used system for the solvent exchange method. This method is advantageous because it uses ethanol as an exchange solvent, which is green, safe, and

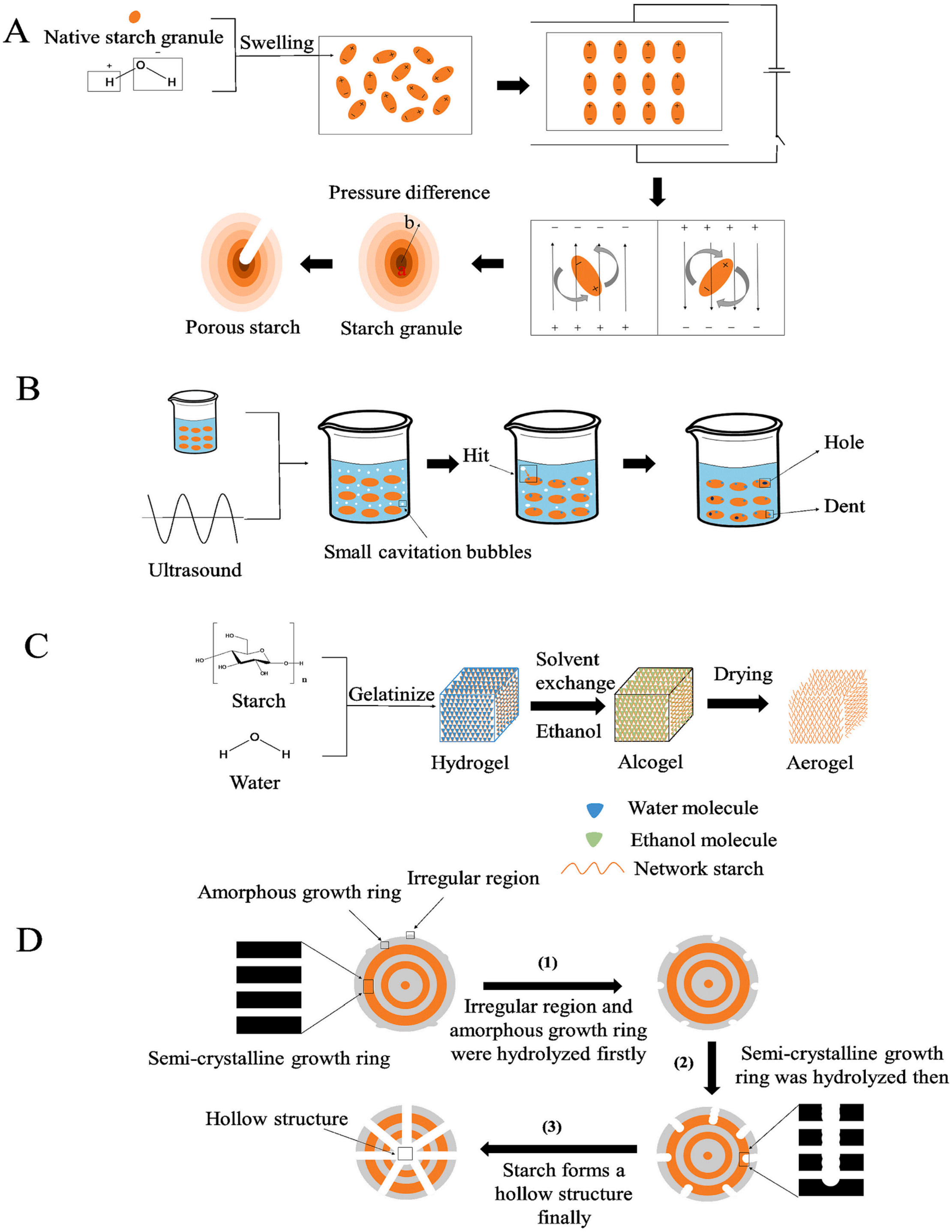

Fig. 3. Mechanism diagrams for porous starch preparation by using the microwave method (A), ultrasonic method (B), solvent exchange (C), and enzymatic hydrolysis (D). a and b represent high- and low-pressure areas in starch granules, respectively (J. Chen et al., 2020).

pores can be easily formed (Oliyaei, Moosavi-Nasab, Tamaddon & Fazaeli, 2019). Hydrochloric acid can corrode the starch structure, and therefore, it can only be added indirectly to assist in porous starch preparation. The porous structure of the starch composite gel can be formed using calcium carbonate granules as a solid pore agent with the addition of hydrochloric acid for calcium carbonate removal (Pourjavadi, Nazari, Kabiri, Hosseini & Bennett, 2016). Furthermore, the porous starch was modified by chemical reactions (esterification, crosslinking, and oxidation) to improve its weak mechanical strength and low thermal resistance, which can further expand its applicable fields (Cao, Lu, Wang, Zheng & Quek, 2023). However, for environmental reasons, safer and greener chemical processing methods still need to be explored for preparing porous starch.

In starch, enzymatic hydrolysis mainly acts on intermolecular glycosidic bonds, and most starches typically contain 20–30 % amylose (mainly connected by α1-4 glycosidic bonds) and 70–80 % amylopectic starch (mainly connected by α-1,4 and α-1, 6-glycosidic bonds) (Kainuma, 1984). Therefore, complex enzymatic hydrolysis is often used for processing porous starch, and enzymes that can be used for hydrolysis include α-amylase (AM), β-amylase, starch glucosidase, cyclodextrin glycosyltransferase (CGTase), branching enzyme (BE), etc. (Uthumporn, Zaidul & Karim, 2010). The influence of enzymeson the preparation of porous starch is complex, and at the same time, the properties of porous starch can be regulated by using different types of enzymes and different enzyme concentrations. (Benavent-Gil & Rosell, 2017a). In most cases, to better meet the needs of the product,complex enzymes must be used for starch processing. However, the optimal processing parameters and high cost of using multiple enzymes for industrial production of porous starch still need to be further explored and solved.

In terms of yield, cost, and feasibility of industrial production, the single processing method of porous starch is associated with limitations. Therefore, researchers have continued to study synergetic treatment methods. Among them, the enzymatic method is a crucial synergy object because of its specificity and high efficiency (Dura, Blaszczak & Rosell, 2014). Moreover, many synergetic methods with enzymes (wet heat, extrusion, and freeze–thaw treatment) and other composite methods are available for porous starch preparation and modification. For example, Zhang et al. (2022) prepared porous starch using the green method of critical melting (CM) and freeze–thaw (FT) treatment. The pore-forming properties of starch granules rather than enzymes depend on the freezing rate, where the rapid freezing rate mainly produced pores in starch granules. By using glycerin as a plasticizer, some researchers prepared porous starch monoliths through freeze-drying (Mi, et al., 2012).

3.2. *Loading and delivery of functional components*

The loading and delivery of functional components currently remains the main application direction of channel-rich starch, which includes various encapsulation systems such as native starch, porous starch, starch microgels, molecular aggregates, starch granule aggregates, and other encapsulation systems (Guo, Qiao, Zhao, Zhang & Xie, 2021). Over the past decade, several papers have been published on different types of starch encapsulation systems and their delivery. Some of them have been discussed here to represent the delivery of different types of substances, mainly involving the binding of the delivered molecules to the internal channels of starch.

As mentioned above, natural starches, such as corn and wheat starch granules, have surface pores and internal channels that can be directly used for loading and delivering some active ingredients (such as proteins, vitamins, natural pigments, flavor substances, and microorganisms) (Qi & Tester, 2019). Being a naturally degradable material, starch, to some extent, maintains the stability and biological activity of its guest molecules, improves nutrient and drug utilization by the human body, and enhances the texture and rheological properties of protein gels (Ge, et al., 2022; Qi & Tester, 2019). Janaswamy et al. (2014) demonstrated that starch channels can bind and successfully transport ibuprofen, benzocaine, sulfampyridine, curcumin, thyme, and ascorbic acid and that the addition of these substances affected the digestive properties of starch itself. Under simulated gastrointestinal conditions, the encapsulation by natural water chestnut starch protected the coated camel milk probiotics (*Pediococcus acidolactici*) from heat treatment and allowed it to maintain good biological activity, thereby achieving targeted delivery to the gut (Ahmad, Gani, Hamed & Maqsood, 2019). In addition, natural biopolymers having the ability to absorb odors, such as aromatic compounds, can also bind and interact with starch structures, and the amount of aromatic substances retained in starch depends on the type of starch and aromatic substances (Jorgensen, et al., 2012). However, the delivery by natural starch as a carrier has some limitations, which mainly depend on the molecular size, shape, and solubility of the delivered substance.

The natural starch channels contain free fatty acids, lysophospholipids (especially cereal starches), and some SGAPs (Gray, 2003; Tester, et al., 2004). Processing natural starch into porous starch is a common and effective method for facilitating the delivery of materials in starch and increasing the amount of single delivery. Through the modification of the process, some natural starches (e.g. potato starch and high-amylose corn starch) with underdeveloped channel structures can also be used as raw materials for a carrier (Keeratiburana, et al., 2020). Compared with natural starches, the porous starch formed through various methods (physical method, chemical method, enzymatic method, and collaborative method) mostly exhibits larger pores and stronger adsorption capacity. It has a broader range of acceptance for the size and shape of the delivered substance. Moreover, porous starches also have other advantages and generally have a wider range of applications than natural starches (Latip, et al., 2021).

For some lipid macromolecules, porous starch can more appropriately meet the encapsulation and storage conditions. Belingheri et al. (2015) encapsulated high oleic acid sunflower oil (HOSO) using porous starch and performed accelerated oxidation (light and heat treatment). Compared with bulk oil, porous starch exhibited lower conjugated diene levels in the loaded HOSO, demonstrating that encapsulation effectively reduced the effect of light on oil oxidation. Porous starch could effectively prevent the oxidation, decomposition or precipitation of some environmentally sensitive compounds (affected by light, oxygen, temperature, *etc*.), such as vitamins, carotene, minerals, anthocyanins, docosahexaenoic acid, and eicosapentaenoic acid (Benavent-Gil & Rosell, 2017b). In addition, porous starch is useful for loading liquid flavors, thereby effectively extending their shelf life (Belingheri, Ferrillo & Vittadini, 2015). Porous starch prepared using the enzyme method is effective in improving the rate of inclusion of some probiotics such as *Lactobacillus plantarum* (Li, Ho, Turner & Dhital, 2016). The application of porous starch also improved the acid and heat resistance of *L. plantarum*. This further ensured that the viable bacteria count remained above the minimum dose required for food processing and *in vivo* digestion.

Undoubtedly, natural starches and porous starches have numerous applications in food and drug delivery. However, starch itself has several major shortcomings such as insolubility in cold water, excessive viscosity after heating, weak mechanical properties, and decomposition (Ranjbar, Namazi & Pooresmaeil, 2022). Moreover, compared with modified porous starches, porous starches are brittle in texture and poor in mechanical strength and wear resistance, and have lower expansibility and viscosity (Han, et al., 2022). These factors limit the application of porous starches in various fields. Therefore, starch modification has recently been the research focus and has been used in many aspects of substance encapsulation and delivery. Acevedo-Guevara et al. (2018) prepared acetylated banana starch that could envelope more curcumin molecules, while succinacylated potato starch exhibited high encapsulation rates and good stability in natural pigment (betaine) encapsulation (Vargas-Campos, et al., 2018). Modification enhanced some properties of porous starch. For example, octenyl succinic anhydride-modified porous starch was used in a β-carotene-loaded milk base transfer system, and it exhibited good emulsification and stability (Li, et al., 2020). Bae et al. (2021) used proteases to remove SGAPs from granule surfaces and channels at 37 ℃. This method increased starch dilatability and viscosity and enhanced starch intercessions against λ-carrageenan during the embedding process. Other researchers have also observed that chemical modification could enhance the hydrophobicity of porous starch (Wang, et al., 2020).

3.3. Regulation of the starch digestion rate by internal channels

In general, when ingested, foodborne starch is rapidly digested into glucose into the bloodstream. This then enhances the hyperglycemic response and subsequently triggers insulin release and glucose uptake by cells, leading to hypoglycemia (Birt, et al., 2013). The high and low blood sugar cycle may lead to diabetes, colon cancer, and obesity, which is detrimental to human health (Cheng, et al., 2022). Therefore, regulation of the starch digestion rate will be not only beneficial for preventing the occurrence of related chronic diseases but also conducive for developing starch products with different digestion rates.

During starch digestion, the enzyme digestion rate is controlled by the limited enzyme diffusion in the grain structure. Shrestha et al. (2012) demonstrated that the external size of internal channels and pores determine the effective surface area of enzyme attack. Dhital et al., (2010b) suggested that differences in the digestion of corn and potato starches were due to differences in surface pores and channels. These findings demonstrate that starch internal channels are key factors affecting digestion. In natural starch, the channels in the granules vary with the parent plant's genetic composition. However, the number and size of these channels can be regulated through various processing methods, thereby regulating the starch digestion rate (Widya, et al., 2010). As described in 2.4, different processing methods have varying effects on starch digestion. For example, certain extrusion conditions could increase the channel opening size on the starch surface and improve the starch digestion rate. Microwave treatment could enhance the molecular recombination inside starch, maintaining the internal structure stability and reducing the starch digestion degree (Li, et al., 2020; Rathod & Annapure, 2016). In the early stage of hot steam treatment, high temperature can cause partial gelatinization of starch and improvement of surface roughness, which result in more enzymes adhering to the surface or entering the internal channel, and causing the rapid hydrolysis of starch. However, in the late stage of high temperature treatment, the starch–lipid complex is formed, and the starch digestion rate is reduced (Jaisut, et al., 2009; Rattanamechaiskul, et al., 2013). The aforementioned research results also demonstrated significant differences in different conditions of the same processing method.

Similarly, the formation of starch complexes or physical protective shells through the encapsulation of substances can affect the starch digestion rate (Janaswamy, 2014). Foreign substances that form a physical barrier on the starch surface or a blockage in the internal channels, which reduces the hydrolysis of starch from the inside by enzymes to a certain extent. When benzocaine and ibuprofen bind to starch channels, the digestion rate of starch is reduced by 24 % and 6 %, respectively, indicating that the addition of both benzocaine and ibuprofen regulated the digestibility of starch (Janaswamy, 2014). Moreover, the other added dietary compounds such as proteins, lipids, polyphenols, and non-starch polysaccharides could interact with starch, preserving its ordered structure and limiting enzyme binding (Chi, et al., 2022). The *in vitro* digestion rate of porous starch depends on the processing of the porous structure. Benavent-Gil & Rosell (2017c) reported that the size of channel openings (surface pores) was significantly related to the degree of digestion *in vitro*, and the content of digestible starch increased with an increase in the enzyme treatment intensity. Moreover, amyloglucosidase treatment alone improved starch digestion and the glycemic index (GI), whereas AM, CGTase, and BE reduced them (Benavent-Gil & Rosell, 2017c). Therefore, when customizing starch-based products with different digestion rates in the future, the characteristics of the internal channels are worth considering.

3.4. Other applications based on starch channels

In addition to the food industry, starch or porous starch, which is rich in surface pores and internal channels, can be used as a green, simple, and low-cost environmentally friendly materials because of its strong adsorption capacity. Porous starch exhibits good adsorption uniformity. It can absorb different types of heavy metal ions (such as Zr^{4+}, Al^{3+}, Fe^{3+}, La^{3+}, Pb^{2+}, and Cu^{2+}) and dyes (Pourjavadi, et al., 2016; Xu, et al., 2017). Starch subjected to crosslinking and modification can also be used as a green desiccant for purifying ethanol and as a hemostatic material (Mi, et al., 2012; Qian, et al., 2020). Recent research on starch-based adsorption materials mainly focuses on simpler starch preparation methods and starch with stronger adsorption effects. However, because of the complex factors in the processing environment, the toughness and strength of starch-based materials must be improved. Improving the stability of starch-based materials in application remains a hot topic for the future.

4. Conclusions and future perspectives

Being a natural polymer, starch has an internal channel structure connecting surface pores and internal cavities. Channel formation is related to internal starch microtubules and external conditions, which can be characterized by determining the proteins and lipids in the channel structure. Moreover, the presence of channels in starch can be reflected through CLSM, SEM, XRD, SAXS, and *in vitro* digestion experiments. Significant differences are observed in the channels of starch from different plant sources. In general, maize and wheat starch channels are considered as more developed. Different processing methods also affect the channel structure. Processing of porous starch is a critical application of starch channels. Porous starch is a type of multifunctional auxiliary material that can be prepared through physical, chemical, enzymatic, and collaborative methods. Starch with a developed channel structure (porous starch) is mainly used in the loading and delivery of active ingredients, such as nutrients and medicines. It can also be used in other fields such as environmental protection. Furthermore, the starch digestion rate can be regulated through internal channels, which is helpful for the treatment of chronic diseases such as diabetes and obesity. Therefore, starch-based products with different digestion rates must be developed. However, further studies investigating the formation mechanism and influencing factors of the starch channel structure are required to better guide the application of the channel structure. In addition, more green and feasible composite processing methods need to be explored, and animal experiments are warranted to further verify the effect of the product. The research exploring these problems will be conducive to the application of starch as a natural degradable material in more fields.

CRediT authorship contribution statement

Junzhe Zhu: Methodology, Software, Investigation, Writing – original draft, Writing – review & editing. **Lingyu Han:** Conceptualization, Methodology, Writing – review & editing. **Meini Wang:** Methodology, Software, Investigation, Writing – original draft, Writing – review & editing. **Jixin Yang:** Conceptualization, Methodology, Writing – review & editing. **Yapeng Fang:** Software, Validation, Writing – review & editing. **Qiuyue Zheng:** Software, Validation, Writing – review & editing. **Xiaobo Zhang:** Software, Validation, Writing – review & editing. **Jijuan Cao:** Conceptualization, Methodology, Writing – review & editing. **Bing Hu:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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