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## Ultramicropore-Confined Solvation and Interphase Regulation Unlock High-Performance Hard Carbon Anodes for Sodium-Ion Batteries

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### HIGHLIGHTS

- An iodine-mediated oxidative cross-linking strategy enables the synthesis of spherical hard carbon with uniformly distributed ultramicropores (<0.9 nm) and carbonyl-rich surfaces from starch precursors.
- Ultramicropore-confined solvation favors anion-enriched electrolyte structures, while carbonyl groups promote NaF-rich inorganic interphases, enabling synergistic interfacial regulation.
- The optimized hard carbon delivers high initial Coulombic efficiency (88.4%), large plateau contribution (64.1%), excellent rate capability (288.9 mAh g<sup>-1</sup> at 5C), and stable cycling (95.6% retention after 200 cycles)

**ABSTRACT** Hard carbon (HC) anodes are promising for sodium-ion batteries, yet achieving high initial Coulombic efficiency (ICE), large plateau contribution, and fast charge-transfer kinetics remains challenging due to insufficient control of micro-nanostructure and interphase chemistry. Here, we present a precursor-level molecular engineering strategy that simultaneously regulates sodium desolvation and interphase chemistry in HC. An iodine-mediated oxidative cross-linking process converts starch into spherical HC with uniformly distributed ultramicropores and carbonyl-rich surfaces. These nanoconfined pores are proposed to act as molecular sieves, preferentially excluding bulky solvent molecules while allowing PF<sub>6</sub><sup>-</sup>-coordinated Na<sup>+</sup> access, thereby favoring anion-enriched electrolyte structures under confinement. Surface carbonyls exhibit strong PF<sub>6</sub><sup>-</sup> affinity, which may promote fluorine-rich inorganic interphases on pore surfaces. The synergistic effects of anion-selective adsorption and confined desolvation are suggested to favor thin and robust NaF-rich interphases at external surfaces and within nanoconfined pore regions, contributing to reversible interfacial reactions and rapid Na<sup>+</sup> storage kinetics. Consequently, the HC delivers an ICE of 88.4%, a reversible capacity of 352.9 mAh g<sup>-1</sup> at 0.1C, excellent rate capability (288.9 mAh g<sup>-1</sup> at 5C), and 95.6% capacity retention over 200 cycles. This work offers a molecular-level design paradigm integrating efficiency, capacity, and kinetics in HC anodes.

**KEYWORDS** Sodium-ion batteries; Hard carbon; Ultramicropores; Nanoconfined desolvation; NaF-rich interphases

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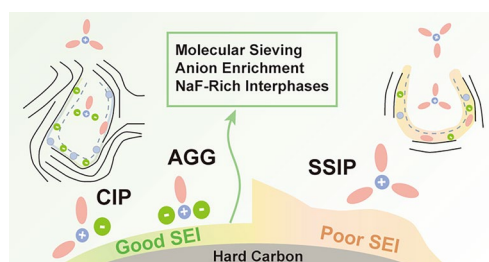
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## 1 Introduction

Sodium-ion batteries (SIBs) are emerging as promising complements to lithium-ion technologies for large-scale energy storage and electric mobility, driven by the natural abundance and low cost of sodium [1–4]. However, the larger ionic radius of  $\text{Na}^+$  (1.02 vs. 0.76 Å for  $\text{Li}^+$ ) leads to sluggish diffusion kinetics and pronounced volume variation during sodiation/desodiation [5, 6], which limiting the feasibility of conventional graphite and silicon–carbon anode materials in SIB systems. Hard carbon (HC) has therefore become the most viable anode material, owing to its disordered structure, enlarged interlayer spacing ( $> 0.37$  nm), and nanoporous architecture, enabling relatively high capacity, low operating potential, and stable cycling. Nevertheless, However, sodium storage in HC involves multiple concurrent mechanisms, including surface adsorption, interlayer insertion, and pore filling, which complicate micro–nano-structural regulation and interfacial chemistry and often hinder the simultaneous achievement of high initial Coulombic efficiency (ICE), large plateau capacity, and fast charge-transfer kinetics [7, 8].

The electrochemical performance of HC is critically governed by its internal pore architecture and surface chemistry, both of which affect  $\text{Na}^+$  solvation, desolvation and interphase formation [9, 10]. Closed-pore size directly controls the thermodynamics of pore-confined sodium species that enlarged pores promote metallic Na clustering and shift storage towards deposition-like behavior [11], whereas ultramicropores ( $< 1$  nm) stabilize Na clusters at higher potentials and favor plateau-region storage [12]. These pores also act as selective nanoreactors, enabling desolvation while restricting solvent ingress and thereby biasing solid electrolyte interphase (SEI) formation toward thin, inorganic-rich layers that lower interfacial resistance [13–16]. Surface functional groups further steer interphase chemistry. Some quinone-type  $\text{C}=\text{O}$  motifs strongly bind  $\text{Na}^+$  and catalyze excessive solvent decomposition, leading to thick and resistive SEI layers, whereas carbonyl  $\text{C}=\text{O}$  functionalities enable reversible  $\text{Na}^+$  adsorption and promote anion-derived inorganic SEI formation that facilitates fast ion transport [17, 18]. Collectively, these insights highlight that the synergistic regulation of ultramicropore confinement and surface-active functionalities is not merely beneficial but essential for unlocking high-efficiency, high-rate HC anodes.

From a materials-design perspective, the precursor chemistry, including molecular-chain configuration and functional-group distribution, critically governs the pore architecture and surface chemistry of HC. Considerable efforts have therefore focused on regulating the thermochemical evolution of carbon precursors through molecular engineering [19–21]. For example, acid-assisted pre-oxidation has been explored to regulate oxygen-functional-group evolution during carbonization [20]. Carbonyl-rich components exhibit high steric hindrance and strong conjugation with aromatic domains, which suppress oxygen adsorption and limit further oxidation reactivity. By contrast, pre-oxidatively introduced  $\text{C}(\text{O})-\text{O}$  species can stabilize adjacent  $\text{C}-\text{C}$  bonds, thereby suppressing macromolecular depolymerization and inhibiting thermal rearrangement of carbon layers, ultimately promoting disordered frameworks with uniformly distributed closed micropores. Similarly, hydrogen-bond-mediated assembly enables molecular-level immobilization of glucose during dehydration and aromatization, yielding HC spheres with tunable crystallinity and enhanced electrochemical accessibility [21]. These studies collectively underscore the decisive role of precursor-level molecular interactions and functional-group chemistry in governing pore evolution and sodium-storage behavior in biomass-derived HCs.

Among various biomass precursors, starch is particularly attractive because of its high carbon content, natural abundance, and intrinsic spherical morphology, which favor dense particle packing and structural uniformity. However, direct pyrolysis of starch suffers from extensive glycosidic-bond cleavage, generating levoglucosan (LG) intermediates and volatile small molecules that induce severe structural collapse and carbon loss, often resulting in low carbon yield, excessive surface defects, and limited closed-pore formation [22, 23]. Although strategies such as esterification-induced cross-linking have been explored to stabilize the starch framework and preserve spherical morphology during pyrolysis [24, 25], many existing approaches still rely on complex processing, prolonged treatment, or limited structural controllability. Cost-effective and intrinsically controllable routes for simultaneously regulating pore evolution and surface chemistry therefore remain scarce.

Here we introduce a molecular-level cross-linking strategy that reconceptualizes starch-derived HC as a platform for the coordinated regulation of nanoconfined pore architecture

and surface chemistry. By directing aromatization through iodine-mediated oxidative cross-linking, this approach stabilizes the spherical framework of starch-derived HC while promoting the formation of uniformly distributed ultramicropores ( $<0.9$  nm) and carbonyl-rich active sites. The resulting HC is proposed to facilitate nanoconfined desolvation and anion-enriched interfacial environments, which may contribute to improved interfacial charge transfer and sodium-storage reversibility. Consequently, the long-standing trade-off among ICE, plateau capacity, and rate capability can be effectively alleviated. This work establishes a general design principle in which precursor-level molecular engineering modulates solvation and interphase chemistry, offering a conceptual pathway towards high-performance HC anodes for next-generation SIBs.

## 2 Experimental Section

### 2.1 Reagents

Starch, iodine, and N-methyl-2-pyrrolidone (NMP) were purchased from Aladdin Biochemical Technology Co., Ltd. (China). The sodium-ion battery (SIB) electrolyte (1 M  $\text{NaPF}_6$  in EC/DEC = 1:1, vol%) was supplied by DoDochem Technology Co., Ltd. Sodium vanadium phosphate (NVP), polyvinylidene difluoride (PVDF), polytetrafluoroethylene (PTFE), carbon-coated aluminum foil, aluminum foil, Super P, and conductive carbon black (CB) were obtained from Shenzhen Kejing Star Technology Co., Ltd. All chemicals were used as received without further purification.

### 2.2 Material Preparation

Starch (S) and iodine were first mechanically mixed at a mass ratio of 1:1 and pre-oxidized in a tubular furnace at 205 °C for 6 h under an  $\text{Ar}/\text{O}_2$  (8:2, v/v) atmosphere with a heating rate of 2  $\text{min}^{-1}$ , yielding a black powder denoted as IOS. For comparison, S was subjected to the same pre-oxidation treatment without iodine, producing a yellow powder labeled OS. The S, OS, and IOS precursors were then pyrolyzed at 600 °C for 1 h under flowing Ar at 5 °C  $\text{min}^{-1}$  to obtain S-600, OS-600, and IOS-600, respectively. Due to the severe foaming observed during this stage, S-600 and OS-600 were ball-milled into fine

powders before further treatment. Finally, all intermediate products were carbonized at 1200 °C for 2 h under Ar with the same heating rate to yield the corresponding HCs, designated S-1200, OS-1200, and IOS-1200.

Notably, iodine-containing volatile species generated during oxidation, pyrolysis, and carbonization processes can, in principle, be captured and reintroduced into the precursor oxidation step, suggesting a potential closed-loop process design from an engineering perspective.

### 2.3 Material Characterization

Thermogravimetric analysis (TGA550, USA) was performed to investigate the different pyrolysis behaviors of the precursors. Fourier transform infrared spectroscopy and mass spectrometry (TG-FTIR-MS, PerkinElmer TGA8000-FTIR-GCMS-ATD) was employed to analyze the gaseous products generated during the pyrolysis process. Fourier transform infrared spectroscopy (FTIR) spectra were collected to examine the evolution of functional groups (Thermo Fisher Scientific Nicolet iS20). X-ray diffraction (XRD, Rigaku SmartLab SE, Cu K $\alpha$  radiation,  $\lambda = 0.154$  nm) and Raman spectroscopy (Horiba LabRAM HR Evolution, 532 nm laser excitation) were used to characterize the crystalline structure of the HC. X-ray photoelectron spectroscopy (XPS) was conducted to determine the elemental composition and chemical states using a Thermo Scientific ESCALAB Xi+. The microstructural features were examined by scanning electron microscopy (SEM, TESCAN Vega3) and high-resolution transmission electron microscopy (HRTEM, JEOL F200). The total specific surface area (SSA) and pore-size distribution were determined by nitrogen adsorption–desorption measurements using a Quantachrome Autosorb IQ analyzer. Closed pores were further characterized by small-angle X-ray scattering (SAXS, Xenocs Xeuss 2.0).

### 2.4 Electrochemical Measurement

The HC, Super P, and PVDF were mixed in a weight ratio of 90:2:8 in NMP to form a homogeneous slurry, which was subsequently coated onto carbon-coated aluminum foil. The prepared electrodes were dried in a vacuum oven at 80 °C for 12 h. The mass loading of the active material (electrode



diameter: 10 mm) was approximately  $2.0 \text{ mg cm}^{-2}$ . CR2032 coin cells were assembled to evaluate the electrochemical performance of the HC anode. Sodium metal foil was employed as both the counter and reference electrode, while 1 M  $\text{NaPF}_6$  dissolved in EC/DEC (1:1, vol%) was used as the electrolyte. Glass fiber (Whatman GF/F) served as the separator.

Galvanostatic charge/discharge (GCD) measurements were conducted using a LAND battery testing system within a voltage range of 0–2.0 V. Cyclic voltammetry (CV) tests were carried out at scan rates ranging from 0.1 to  $1.0 \text{ mV s}^{-1}$ . The CV curves collected at different scan rates were used to analyze the sodium-ion storage kinetics according to the following relationship:

$$i = av^b \quad (1)$$

$$\log i = b \log v + \log a \quad (2)$$

where  $i$  represents the current response,  $v$  refers to the scan rate, and  $a$  and  $b$  are variable parameters. The  $b$  value is commonly used to evaluate the charge-storage kinetics. A  $b$ -value close to 0.5 suggests a diffusion-controlled process, whereas a value approaching 1.0 indicates a predominantly pseudocapacitive behavior.

In situ electrochemical impedance spectroscopy (EIS) measurements were performed using a Solartron Analytical 1470E eight-channel electrochemical workstation over a frequency range from 0.01 Hz to 100 kHz at a current density of 0.1C. The galvanostatic intermittent titration technique (GITT) was carried out on the LAND battery testing system with a pulse current of 0.05C applied for 1 h, followed by a relaxation period of 2 h. The sodium-ion diffusion coefficient ( $D_{\text{Na}^+}$ ) was calculated according to Fick's second law using the following simplified equation:

$$D_{\text{Na}^+} = \frac{4 \left( \frac{m_b V_m}{M_b S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_\tau} \right)^2}{\pi \tau} \quad (3)$$

where  $\tau$ (s),  $m_b$ (g),  $V_m$ ( $\text{ml mol}^{-1}$ ), and  $M_b$ ( $\text{gmol}^{-1}$ ) are the pulse duration, the mass of the active material, the molar volume of the active material, and the molar mass of the active material, sequentially.

To further evaluate the practical sodium-storage performance, NVP/NPCS full cells were assembled in CR2032 coin cells using IOS-1200 as the anode and NVP as the cathode. The NVP cathode slurry was prepared by mixing 80 wt% NVP, 10 wt% conductive carbon black (CB), and 10 wt% PVDF in NMP solvent. The slurry was coated

onto Al foil and dried in a vacuum oven at  $100^\circ\text{C}$  for 24 h. The mass loading of the NVP cathode was approximately  $1.1\text{--}1.2 \text{ mg cm}^{-2}$ . The activated IOS-1200 anode obtained from half-cells was subsequently paired with the NVP cathode to assemble the full cells using the same electrolyte. The N/P capacity ratio was controlled at approximately 1.2, and the full-cell measurements were conducted within a voltage range of 1.8–3.8 V.

For in situ XRD measurements, HC and PTFE were mixed in a weight ratio of 9:1 and rolled into a dry electrode as the anode. The electrode was assembled into a customized electrochemical cell in an argon-filled glovebox using a beryllium (Be) window as the X-ray transparent window. In situ XRD patterns were recorded on a Bruker D8 Advance diffractometer at room temperature under a constant current density of 0.1C over a diffraction angle range of  $15^\circ\text{--}35^\circ$ .

For in situ Raman measurements, the electrochemical cell was assembled following a similar procedure to that used for in situ XRD, except that a quartz plate was employed as the optical window. Raman spectra were collected on a RENISHAW spectrometer using a 532 nm laser as the excitation source.

Small-angle X-ray scattering (SAXS) measurements were conducted to investigate the pore structure characteristics of the carbon samples. A Porod analysis method proposed by Stevens and Dahn was employed to analyze the SAXS data using the following simplified equation:

$$I(Q) = \frac{A}{q^a} + \frac{B_1 a_1^4}{(1 + a_1^2 Q^2)^2} + D \quad (4)$$

where  $I(Q)$  represents the scattering intensity as a function of the scattering vector  $Q$ .  $A$  is the scaling factor associated with surface scattering in the low- $Q$  region, while  $B_1$  corresponds to the pore-scattering contribution and is proportional to the total pore surface area.  $D$  denotes the constant background term, and  $a_1$  is the characteristic length related to the radius of spherical pores according to  $R = a_1 \sqrt{10}$ .

## 2.5 Theoretical Calculation

Density functional theory (DFT) calculations were performed using the projector augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP) [26]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was employed to describe exchange–correlation interactions

[27]. A plane-wave kinetic energy cutoff of 400 eV was used for structural optimizations [28]. The Brillouin zone was sampled using Monkhorst–Pack  $k$ -point grids [29]. Structural relaxations were carried out until the residual forces on each atom were less than  $0.02 \text{ eV } \text{\AA}^{-1}$  and the total energy convergence threshold was set to  $10^{-5} \text{ eV}$  [28, 30]. Long-range dispersion interactions were accounted for using the zero-damping DFT-D3 method of Grimme [31].

To simulate closed ultramicropores in HC, carbon nanotube (CNT) models with different diameters were constructed as simplified structural descriptors. Although real HCs possess highly disordered structures with curved graphene layers, defects, and heteroatom functionalities, CNT-based models have been widely used to qualitatively evaluate pore confinement effects and Na adsorption behaviors in nanoporous carbons [13, 14, 32]. Therefore, the present calculations mainly aim to reveal the relative influence of pore size on Na adsorption behavior.

### 3 Results and Discussion

#### 3.1 Molecular Engineering Strategy and Structural Evolution Mechanisms

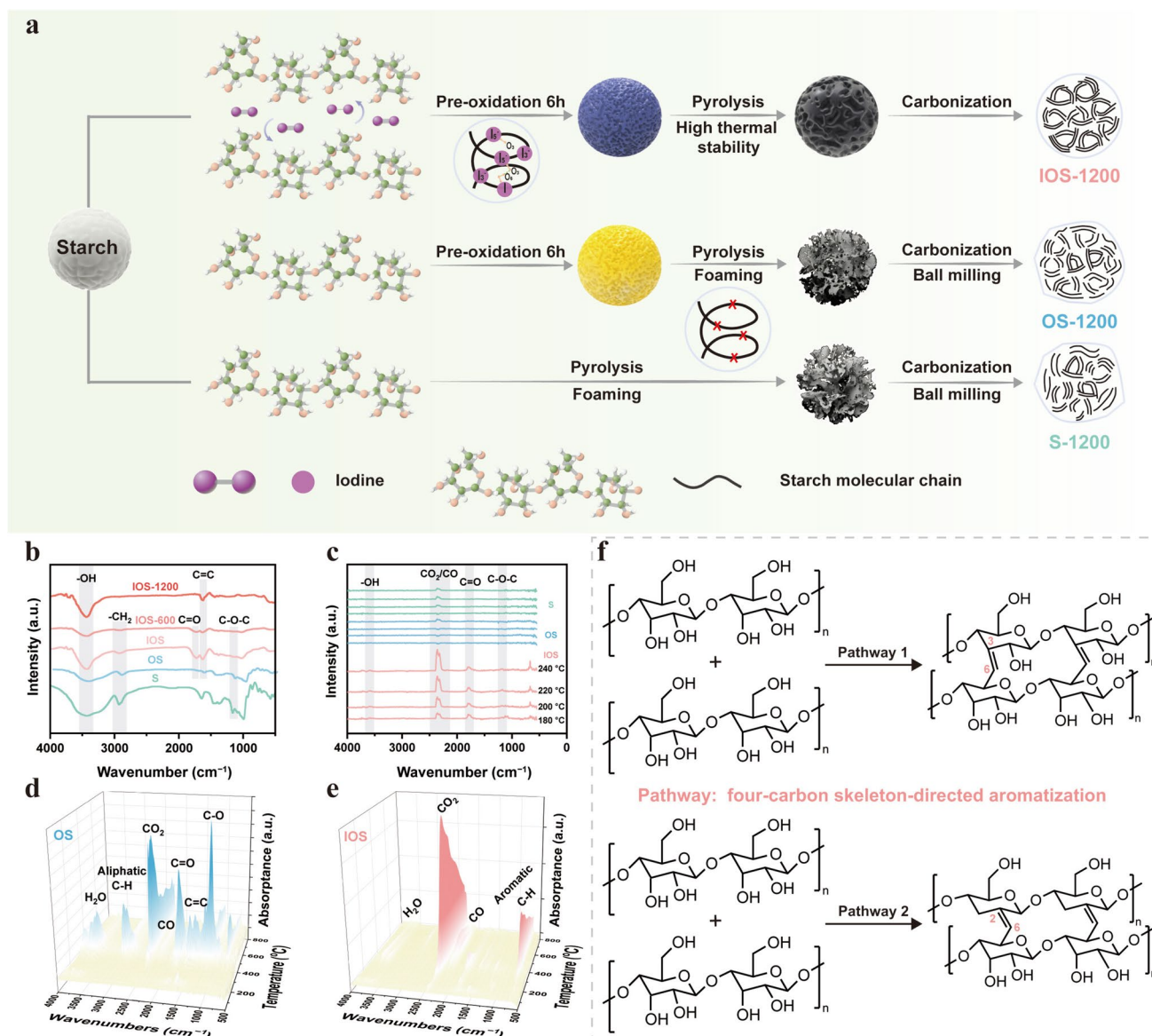
Starch (S) is a widely used industrial product and an attractive precursor for HC synthesis owing to its low cost and environmental benignity. However, its direct pyrolytic conversion is intrinsically problematic, as thermal cleavage of glycosidic bonds generates volatile intermediates that induce severe foaming and structural collapse, as reflected by the disordered products S-600 and S-1200 obtained at different carbonization temperatures (Fig. S1a, d). Although thermal pre-oxidation can partially stabilize the polymeric framework, short oxidation times provide only limited cross-linking, so that pre-oxidized S (OS, 6 h) still undergoes pronounced foaming during subsequent pyrolysis at  $600^\circ\text{C}$  (OS-600), while further carbonization at  $1200^\circ\text{C}$  yields the corresponding HC, denoted as OS-1200 (Fig. S1b, e).

Introducing iodine fundamentally alters this stabilization chemistry. Iodine acts as a redox catalyst that promotes oxidative aromatization and interchain cross-linking at the molecular level, thereby converting the S framework into a thermally robust, conjugated network during a short pre-oxidation step (6 h). This iodine-mediated stabilization prevents the formation and volatilization of levoglucosan, enabling

the pre-oxidized S (IOS) to retain its structural integrity during carbonization, as evidenced by the stable, non-foaming morphology of IOS-600. Subsequent heating to  $1200^\circ\text{C}$  then drives controlled carbonization into HC (IOS-1200; Fig. S1c, f). The overall synthesis strategy, together with the corresponding control samples, is schematically illustrated in Fig. 1a and the critical stabilization temperature of  $205^\circ\text{C}$  was identified by coupled thermogravimetric analysis–differential scanning calorimetry (TG-DSC) (Fig. S2) [23, 33]. Consistently, iodine-mediated pre-oxidation increases the carbon yield to 45.5%, compared with  $< 10\%$  for iodine-free samples, directly reflecting its ability to kinetically suppress chain scission and volatilization while promoting carbon-forming reactions (Fig. S3).

The chemical structural evolution of S during oxidation and subsequent thermal treatment was monitored. FTIR shows that S and OS exhibit a characteristic absorption band at  $1160 \text{ cm}^{-1}$ , attributed to C–O–C stretching vibrations of glycosidic linkages, which becomes nearly absent in IOS, indicating suppression of LG formation. Meanwhile, IOS preferentially undergoes oxidation toward carbonyl functionalities, as evidenced by the emergence of a pronounced C=O stretching band at  $\sim 1730 \text{ cm}^{-1}$ , which is much less evident in OS. Upon subsequent carbonization, IOS-1200 displays a markedly intensified C=C stretching band at  $\sim 1630 \text{ cm}^{-1}$ , confirming enhanced conjugation and aromatization (Fig. 1b). Furthermore, the gaseous products and structural evolution during pyrolysis are characterized using thermogravimetric analysis coupled with TG-FTIR-MS. Figures 1c and S4 show the FTIR spectra of the evolved gases at different temperatures, and Figs. S5 and 1d–e present the corresponding TG-FTIR contour plots. S and OS exhibit distinct bands  $\sim 2900$  to  $3000 \text{ cm}^{-1}$ , assigned to asymmetric C–H stretching, indicating the cleavage of small alkyl fragments or aliphatic side chains during thermal treatment [34, 35]. A strong C=O stretching band at  $\sim 1750 \text{ cm}^{-1}$ , characteristic of aldehydes and ketones, reaches maximum intensity at  $\sim 400^\circ\text{C}$  and diminishes at higher temperatures due to secondary cracking reactions [36–39]. In contrast, IOS exhibits only very weak signals corresponding to small alkyl fragments across  $200$ – $800^\circ\text{C}$ , indicating that the formation of labile aliphatic species is effectively suppressed in the presence of iodine. Concurrently, relatively enhanced C=O and C=C vibrations ( $\sim 1510 \text{ cm}^{-1}$ ) emerge at  $600$ – $800^\circ\text{C}$  (Figs. 1c and S4f), highlighting the superior thermal robustness of its evolving aromatic framework.





**Fig. 1** **a** Schematic diagram of the synthesis procedures of S-1200, OS-1200 and IOS-1200. **b** FTIR spectra of S, OS, IOS-600 and IOS-1200. **c** FTIR spectra of gases produced from S, OS, and IOS at varying temperatures. **d–e** TG-FTIR analysis of gas evolution from S, OS, and IOS. **f** Proposed cross-linking pathways of IOS-1200 [22, 33, 44]

MS-derived evolution profiles were analyzed to resolve the distinct pyrolysis pathways of S, OS, and IOS (Fig. S6). For S, cleavage of inter-unit glycosidic bonds above 280 °C generates LG accompanied by H<sub>2</sub>O release ( $m/z$  18). The volatilized LG subsequently undergoes ring-opening fragmentation and secondary oxidation to yield aldehydes ( $m/z$  29,  $\bullet\text{CHO}^+$ ), acetyl fragments ( $m/z$  43, 43,  $\text{CH}_3\text{CO}^+$ ), CO ( $m/z$  28), and CO<sub>2</sub> ( $m/z$  44), driving severe foaming and poor carbon retention.

In OS, oxygen-containing groups introduced during pre-oxidation partially redirect the pyrolysis chemistry toward a pathway herein referred to as the “hydroxyl–aldehyde–carboxylic acid–anhydride” pathway, as evidenced by intensified MS signals at  $m/z$  29, 43, 44, and 60 ( $\text{CH}_3\text{COOH}^+$ ) [23, 40]. During this process, aldehydes are further converted into carboxylic acids, while adjacent carboxyl groups undergo dehydration condensation to form anhydride-related intermediates [40]. Although anhydride

formation partially suppresses foaming by promoting dehydration and cross-linking reactions, the limited 6 h oxidation duration fails to fully inhibit glycosidic-bond cleavage and LG formation, resulting in competition between the anhydride-forming pathway and LG-driven volatilization, as well as incomplete framework stabilization (Fig. S7).

In contrast, IOS exhibits a fundamentally altered pyrolysis behavior characterized by strongly constrained bond cleavage and suppressed volatilization. Below 300 °C, pronounced attenuation of MS signals at  $m/z$  32 ( $\text{CH}_3\text{OH}^+$ ), 29 ( $\bullet\text{CHO}^+$ ), and 28 ( $\text{CO}^+$ ) indicates effective suppression of glycosidic-bond cleavage, LG formation, and its subsequent fragmentation into volatile oxygenated species. Concurrently, only weak signals associated with carboxylic acids ( $m/z$  45) and acetyl fragments ( $m/z$  43) are detected, demonstrating that the oxygen-functional-group-driven “hydroxyl–aldehyde–carboxylic acid–anhydride” pathway is no longer dominant in IOS. Pronounced  $\text{I}^+$  ( $m/z$  127) and  $\text{I}_2^+$  ( $m/z$  254) signals are observed in the temperature range of approximately 230–420 °C, indicating gradual iodate decomposition and the continuous generation of reactive iodine species during early-stage carbonization (Fig. S6l, m) [41, 42]. At the early stage of carbonization (<400 °C), iodine-mediated pre-oxidation facilitates the stabilization of oxygen within the carbon framework through the formation of embedded carbonyl ( $\text{C}=\text{O}$ ) structures, as reflected by the markedly enhanced  $\text{C}=\text{O}$  stretching band in the FTIR spectra (Fig. 1b).

XPS analysis further corroborates the iodine-mediated regulation of the carbon framework (Figs. S8 and S9). The C 1s spectra can be deconvoluted into  $sp^2$ -hybridized  $\text{C}=\text{C}$ , C–O (ether/hydroxyl),  $\text{C}=\text{O}$ , and  $\text{O}-\text{C}=\text{O}$  species, while the O 1s spectra consist of contributions from carbonyl oxygen (O-I), hydroxyl/ether oxygen (O-II), and carboxyl/ester oxygen (O-III). Notably, IOS-1200 exhibits the highest proportion of carbonyl functionalities (15.25%, Table S1) among all samples, accompanied by a substantial fraction of retained C–O bonds (13.22%). Such a chemical signature suggests that iodine-mediated pre-oxidation favors the formation of chemically constrained and conjugation-stabilized carbon frameworks enriched with carbonyl functionalities. The pronounced  $\pi-\pi^*$  satellite at 289.89 eV in the C 1s spectrum further confirms the formation of an extended conjugated framework (Fig. S9d).

Collectively, the suppressed formation of labile oxygenated fragments revealed by TG–FTIR–MS, together with the  $\text{C}=\text{O}$ -enriched and conjugation-dominated chemical states identified by XPS, indicate a fundamentally altered thermal evolution pathway in IOS. Instead of undergoing the random chain scission and volatilization characteristic of S and OS, the stabilized backbone preferentially undergoes site-specific decarboxylation at the C2 or C3 positions [13, 19, 20]. This process generates C3–C6 (pathway 1) or C2–C6 (pathway 2) four-carbon motifs (Fig. 1f) [22, 23, 44], which serve as key intermediates for the construction of thermally stable conjugated aromatic frameworks. The resulting four-carbon-skeleton-directed aromatization pathway effectively suppresses catastrophic LG-driven volatilization and promotes carbon-framework stabilization during carbonization.

Meanwhile, the evolution of gaseous products plays an important role in regulating the final pore architecture. During carbonization, decomposition of oxygen-containing functional groups releases  $\text{CO}_2$  and CO, whose gradual evolution generates internal nanopores within the constrained carbon framework. In particular, gas-phase FTIR reveals a  $\text{CO}_2$ -dominated evolution behavior for IOS, indicating that decarboxylation reactions are the primary devolatilization pathway during carbonization. The continuous release and escape of  $\text{CO}_2$  promote the formation and interconnection of internal nanopores [43], while the iodine-stabilized  $\text{C}=\text{O}$ -rich framework suppresses excessive carbon-layer rearrangement and structural collapse during devolatilization [20]. Consequently, IOS preferentially develops abundant interconnected ultramicropores with confined pore sizes, which later serve as the primary sodium-storage sites in the plateau region.

### 3.2 Microscopic Structure Analysis

SEM and HRTEM analyses reveal that, unlike S-1200 and OS-1200, which undergo particle fusion and agglomeration at 1200 °C, IOS-1200 retains its original polyhedral/near-spherical morphology with smooth edges (Figs. 2a–c and S10). At the nanoscale, all samples feature short-range ordered carbon domains within long-range disordered matrices and curved graphitic layers forming pores (Fig. 2d–f). However, IOS-1200 exhibits a higher density of closed nanopores together with locally expanded graphitic layers compared with S-1200 and OS-1200, indicating enhanced



structural disorder and enlarged ion-accessible regions, which are favorable for  $\text{Na}^+$  storage and transport.

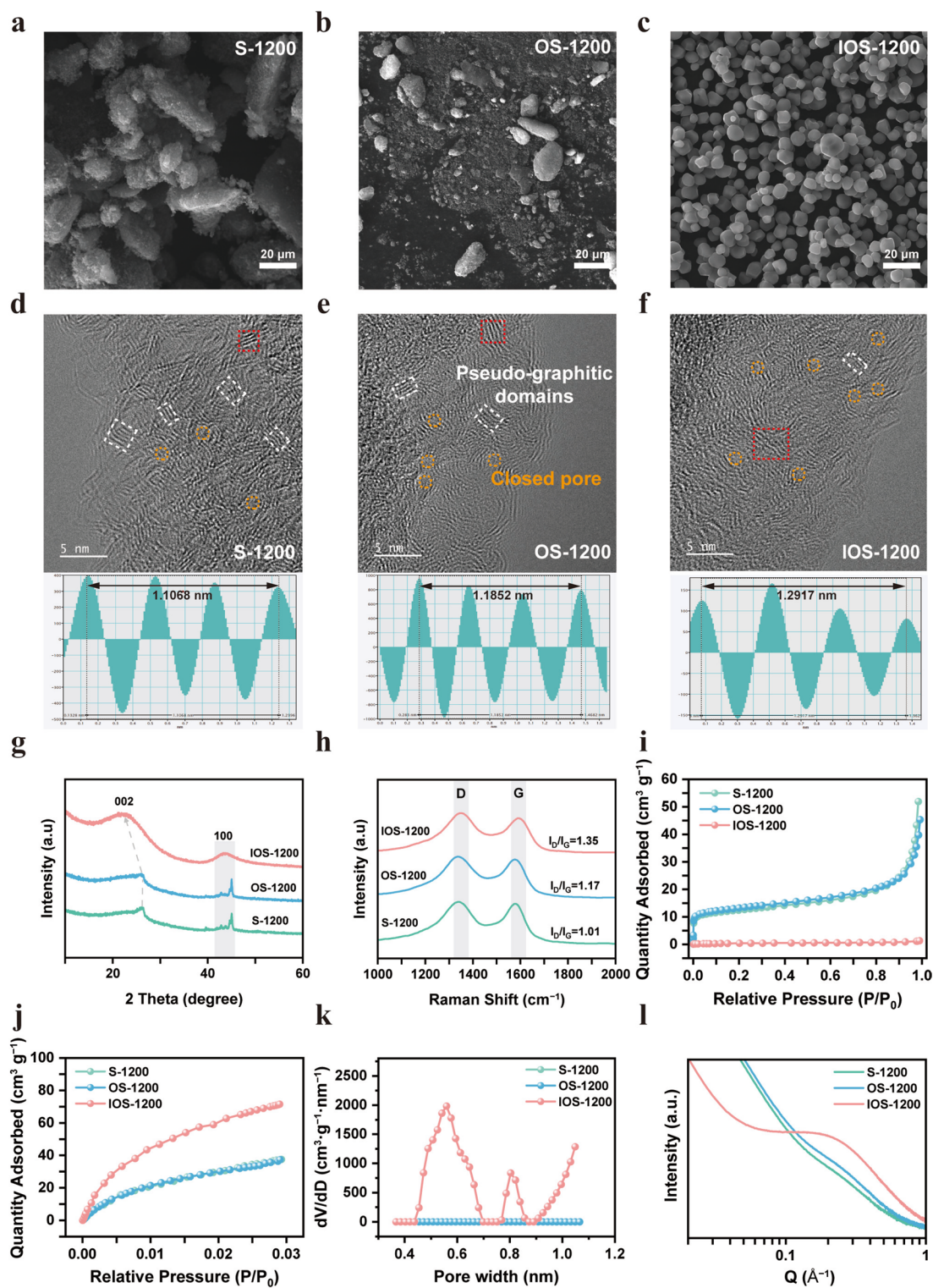
XRD, Raman spectroscopy and gas adsorption collectively reveal a highly disordered yet functionally optimized carbon framework in IOS-1200. Compared with S-1200 and OS-1200, which show typical turbostratic carbon reflections at  $\sim 26^\circ$  and  $\sim 44^\circ$ , IOS-1200 exhibits broadened and downshifted (002) and (100) peaks ( $\sim 22.5^\circ$  and  $\sim 43.5^\circ$ ) in Fig. 2g, indicative of suppressed crystallinity and pronounced turbostratic disorder. The corresponding interlayer spacing expands to 0.405 nm, markedly larger than those of S-1200 (0.342 nm) and OS-1200 (0.344 nm), which is favorable for lowering the  $\text{Na}^+$  migration barrier [14, 45]. The slight deviation between the XRD-derived  $d_{002}$  value and the locally observed HRTEM lattice spacing can be attributed to the distinct measurement principles of the two techniques, where XRD reflects the bulk-averaged interlayer spacing while HRTEM probes localized nanoscale regions with structural heterogeneity. Raman spectra further corroborate this structural evolution (Figs. 2h and S11), with IOS-1200 displaying the highest  $I_D/I_G$  ratio (1.35), reflecting increased defect density and structural disorder.

Despite its highly disordered nature, IOS-1200 exhibits an exceptionally low external surface area ( $1.5 \text{ m}^2 \text{ g}^{-1}$ ), as revealed by Type III  $\text{N}_2$  adsorption–desorption isotherms (Fig. 2i), which is expected to suppress electrolyte penetration and mitigate initial irreversible capacity loss. In contrast,  $\text{CO}_2$  adsorption discloses a substantially higher ultramicropore volume ( $0.144 \text{ cm}^3 \text{ g}^{-1}$ ), dominated by pores of 0.4–0.9 nm centered at 0.5–0.6 nm (Fig. 2j, k). Small-angle X-ray scattering (SAXS) measurements further identify a distinct high- $q$  shoulder exclusively in IOS-1200, indicative of abundant closed ultramicropores (Figs. 2l and S12). This unusual combination of expanded disordered carbon layers, ultralow external surface area and abundant closed ultramicropores arises from iodine-mediated regulation of oxygen-functional-group evolution, gas-release behavior, and carbon-framework stabilization during carbonization, thereby providing a structural basis for nanopore-filling-dominated  $\text{Na}^+$  storage with high reversibility in the low-potential plateau region [12, 46].

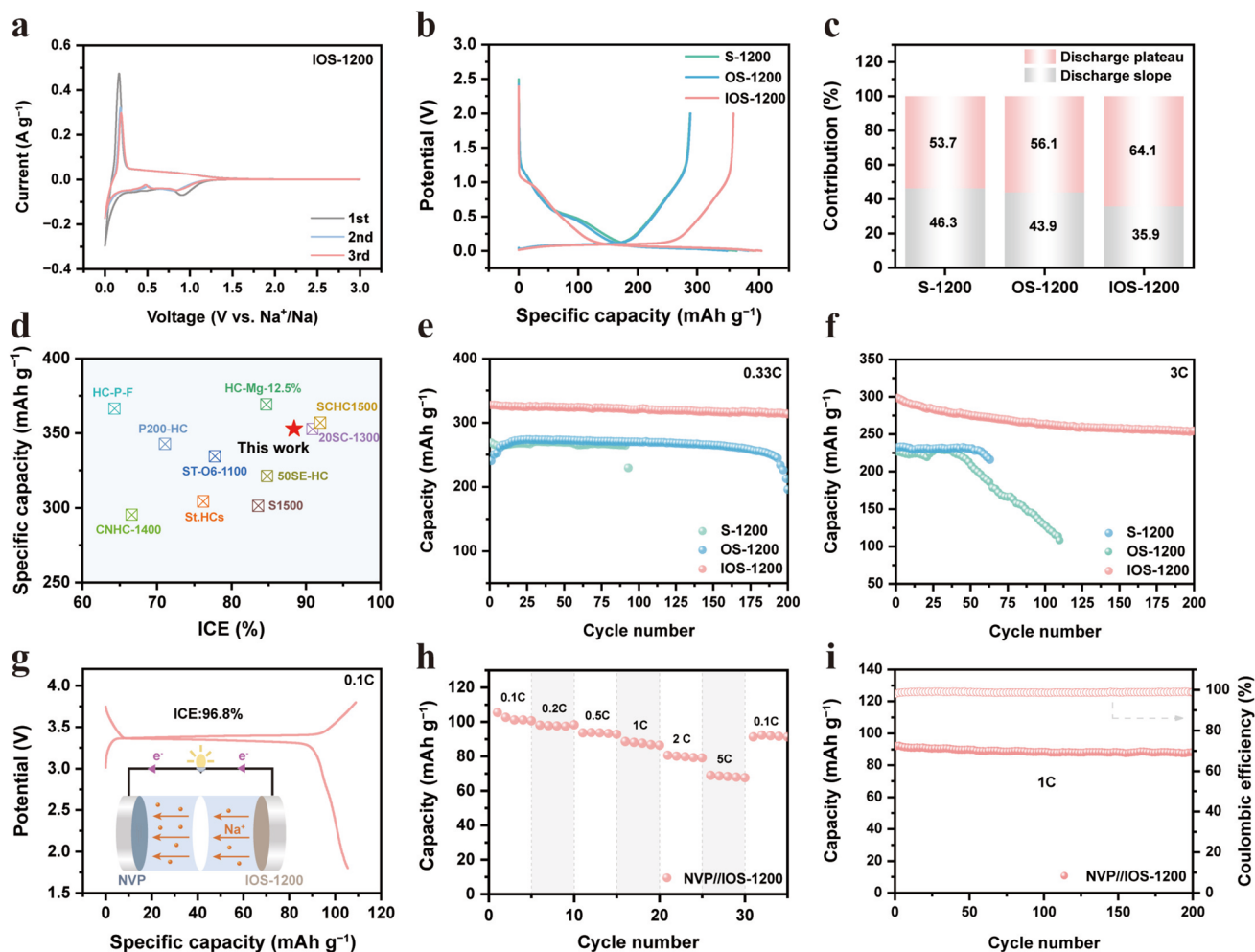
### 3.3 Sodium-Storage Performance Analysis

The electrochemical performance of the HC materials is evaluated in half-cells using sodium metal as the counter electrode. CV reveals markedly suppressed irreversible reactions for IOS-1200, evidenced by a weaker and narrower reduction feature between 0.2 and 1.0 V in the first cycle compared with OS-1200 (Figs. 3a and S13). A pronounced redox peak near 0.1 V is observed for IOS-1200, corresponding to  $\text{Na}^+$  insertion into closed ultramicropores and accounting for its enhanced low-voltage storage contribution. Consistently, GCD profile shows that IOS-1200 delivers a high reversible capacity of  $352.9 \text{ mAh g}^{-1}$  at 0.1C with an ICE of 88.4%, substantially outperforming OS-1200 ( $288.6 \text{ mAh g}^{-1}$ , 74.8%) and S-1200 ( $287.9 \text{ mAh g}^{-1}$ , 73.0%) (Fig. 3b and Table S2). Notably, the plateau capacity contributes 64.1% of the discharge capacity for IOS-1200 (Fig. 3c), consistent with efficient  $\text{Na}^+$  filling within abundant ultramicropores. Moreover, IOS-1200 exhibits outstanding rate capability, delivering  $288.9 \text{ mAh g}^{-1}$  at 5C and fully recovering its initial capacity upon returning to 0.1C (Fig. S14a). This behavior highlights the robust structural stability and fast  $\text{Na}^+$ -transport kinetics enabled by the IOS architecture. In comparison with recently reported starch-derived HC anodes, IOS-1200 demonstrates a well-balanced electrochemical performance in terms of initial capacity, ICE and rate capability (Figs. 3d and S14b), highlighting its competitive advantages for practical SIB applications [23, 40, 47–54]. Long-term cycling tests demonstrate the outstanding durability of IOS-1200, which retains  $313.3 \text{ mAh g}^{-1}$  at 0.33C and  $254.5 \text{ mAh g}^{-1}$  at 3C after 200 cycles, corresponding to capacity retentions of 95.6% and 85.3%, respectively (Fig. 3e, f). These results highlight the synergistic role of preserved particle morphology, expanded interlayer spacing and strong nanoconfinement in enabling highly reversible and kinetically favorable  $\text{Na}^+$  storage.

To assess practical viability, a full cell was assembled using  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) as the cathode and IOS-1200 as the anode. The full cell exhibits highly reversible charge–discharge behavior within 1.8–3.8 V (Fig. 3g) and delivers discharge capacities of 105.5, 100.4, 96.1, 91.4, 84.1, and  $72.6 \text{ mAh g}^{-1}$  at rates from 0.1C to 5C (Fig. 3h). When cycled at 1C, the cell maintains 95.6% of its initial capacity (Fig. 3i), demonstrating excellent rate performance and cycling stability, and underscoring the practical promise of IOS-1200 anode for SIBs.



**Fig. 2** Microscopic structure characterization of S-1200, OS-1200, and IOS-1200. **a–c** SEM images of S-1200, OS-1200 and IOS-1200. **d–f** HRTEM images of S-1200, OS-1200, and IOS-1200 (regions for interlayer spacing measurement are marked by red dashed rectangles). **g** XRD patterns, **h** Raman spectra, **i**  $N_2$  sorption isotherms, **j**  $CO_2$  sorption isotherms, **k** pore-size distributions derived from the  $CO_2$  adsorption data. **l** SAXS patterns



**Fig. 3** Electrochemical characterization of HC anode materials and the corresponding full cell. **a** CV profiles of IOS-1200 at a scan rate of 0.1 mV s<sup>-1</sup>. **b** GCD curve of HC samples at 0.1C. **c** Contributions of the plateau (<0.1 V) and slope (>0.1 V) regions to the discharge specific capacity. **d** Comparative study of the ICE and first-charge specific capacity of IOS-1200 and other reported carbon anodes [23, 40, 47–54]. **e–f** Cycling performance at 0.33C and 3C of HC samples. **g** GCD curve at 0.1C, **h** rate performance and **i** long-cycle test of NVP//IOS-1200 full cell

### 3.4 Charge-Transfer Kinetics and SEI Layer Evolution

To elucidate the sodium-storage kinetics of the materials, CV analyses were conducted on OS-1200 and IOS-1200. The capacitive contributions were quantified using CV curves collected at scan rates from 0.2 to 1.0 mV s<sup>-1</sup> (Figs. 4a–c and S15). According to the relationship  $i = av^b$ , the corresponding  $b$  values were determined from the slope of the fitted  $\log(i)$  versus  $\log(v)$  plots [55]. For IOS-1200, the  $b$  values of peaks 1 and 2 are 0.60 and 1.03, respectively (Fig. 4b), while OS-1200 shows values of 0.75 and 1.06 (Fig. S15b). These results indicate mixed diffusion–capacitive behavior in the low-voltage plateau region

and predominantly capacitive behavior in the high-voltage sloping region. The relative contributions of diffusion-controlled and capacitive processes were further quantified using the equation  $i = k_1 v^{1/2} + k_2 v$ , where  $k_1$  and  $k_2$  correspond to diffusion-controlled and surface-controlled contributions, respectively [56]. As shown in Figs. 4c and S15c, OS-1200 consistently exhibits a higher capacitive contribution than IOS-1200 (67.9–82.6% vs. 56.5–73.5%), which can be attributed to its larger specific surface area that facilitates stronger surface adsorption.

To further probe Na<sup>+</sup> transport, GITT measurements were performed at 0.05C to evaluate the Na<sup>+</sup> diffusion coefficient ( $D_{\text{Na}^+}$ ) during sodiation/desodiation. IOS-1200 exhibits

consistently higher  $D_{\text{Na}^+}$  values than OS-1200 and S-1200 at voltages above 0.1 V (Fig. S16), where  $\text{Na}^+$  storage is dominated by defect adsorption and benefits from the more favorable diffusion kinetics associated with abundant C=O functional groups [18]. However, as the voltage approaches 0.1 V,  $D_{\text{Na}^+}$  shows a pronounced decrease followed by a rapid increase, corresponding to the sequential  $\text{Na}^+$  intercalation and accumulation processes and the subsequent pore-filling stage, respectively [14].

The chemical composition and depth profile of the SEI are subsequently examined by ex situ XPS after 10 cycles (Figs. 4d–f and S17). In the C 1s and O 1s regions, signals assigned to C–O, C=O, and O–C=O species originate predominantly from solvent-derived organic components such as  $\text{ROCO}_2\text{Na}$ , and decay rapidly upon  $\text{Ar}^+$  sputtering, indicating preferential enrichment in the outer SEI. In contrast, the  $\text{CO}_3^{2-}$  signal remains pronounced after etching, implying that inorganic carbonates (e.g.,  $\text{Na}_2\text{CO}_3$ ) constitute the SEI framework. Notably, IOS-1200 shows a much stronger Na–F signal in the F 1s region after sputtering, consistent with extensive  $\text{PF}_6^-$  anion decomposition and the formation of a NaF-rich inner layer (Fig. 4f). OS-1200 and S-1200, however, display weak Na–F signals even after sputtering, indicating limited  $\text{PF}_6^-$  participation and a predominantly organic SEI (Fig. S17e, f). High-resolution TEM characterization of the cycled electrodes after 5 cycles further corroborates these results, revealing a thinner and more uniform SEI on IOS-1200, whereas OS-1200 develops a thicker and less homogeneous film (Fig. 4g, h). The reduced thickness and enhanced continuity on IOS-1200 are consistent with suppressed solvent decomposition and the formation of a mechanically robust inorganic inner layer.

To assess the kinetic consequences of this SEI chemistry, in situ EIS coupled with distribution of relaxation times (DRT) analysis was performed. During the initial sodiation and desodiation process, IOS-1200 exhibits significantly lower impedance than OS-1200 (Fig. S18), reflecting greatly accelerated interfacial kinetics. DRT analysis reveals four characteristic processes:  $\tau_1$  ( $\sim 10^{-5}$ – $10^{-4}$  s) for contact resistance ( $R_s$ ),  $\tau_2$  ( $\sim 10^{-4}$ – $10^{-2}$  s) for ion migration through the SEI ( $R_{\text{SEI}}$ ),  $\tau_3$  ( $\sim 10^{-2}$ –1 s) for charge-transfer resistance ( $R_{\text{ct}}$ ), and  $\tau_4$  ( $> 1$  s) for solid-state  $\text{Na}^+$  diffusion [57, 58]. IOS-1200 maintains substantially lower  $R_{\text{SEI}}$  and  $R_{\text{ct}}$  throughout sodiation from 0.50 to 0.01 V (Figs. 4i and S19), reflecting facilitated ion transport through the inorganic-rich SEI. In contrast, OS-1200 shows only modest changes in

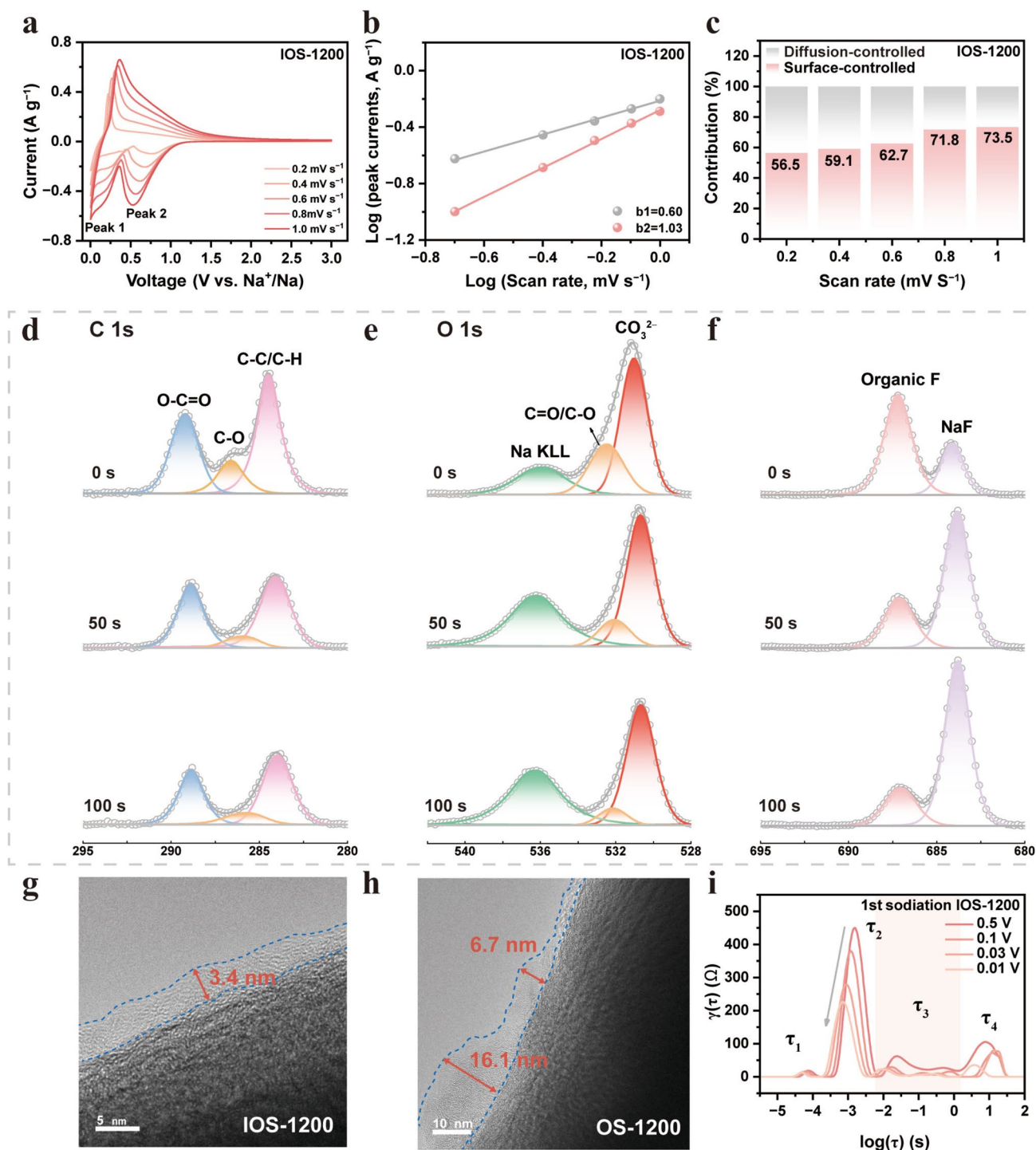
$R_{\text{SEI}}$  and nearly constant  $R_{\text{ct}}$ , consistent with a discontinuous, organic-rich SEI that offers limited kinetic benefit.

The pronounced differences in SEI composition can be attributed to the unique ultramicroporous, C=O-rich interfaces generated by iodine-catalyzed cross-linking in IOS-1200, whose porosity is dominated by pores of 0.4–0.9 nm centered at 0.5–0.6 nm. To elucidate how such ultramicropore confinement regulates interfacial solvation and SEI formation, DFT calculations were carried out using CNT models with diameters of 0.484, 0.559, 0.681, 0.804, and 1.013 nm to simulate pores of different sizes. The adsorption energies of representative electrolyte components ( $\text{Na}^+$ , ethylene carbonate (EC) and  $\text{PF}_6^-$ ) were systematically evaluated (Fig. 5a, b). The calculations show that EC molecules are sterically excluded and cannot be spontaneously adsorbed when the pore diameter is below 0.804 nm, whereas  $\text{Na}^+$  preserves strong intrinsic adsorption across all examined pore sizes. This indicates that sub-0.804-nm pores effectively block solvated species while remaining accessible to the small-radius  $\text{Na}^+$ , so that ultramicropores act as molecular sieves that promote the transition of interfacial solvation from solvent-rich configurations to anion-enriched contact ion pairs (CIPs) and aggregates (AGGs) [16, 59]. In parallel,  $\text{PF}_6^-$  adsorption becomes energetically more favorable than EC once the pore diameter exceeds 0.681 nm, further enhancing anion enrichment within sufficiently wide ultramicropores.

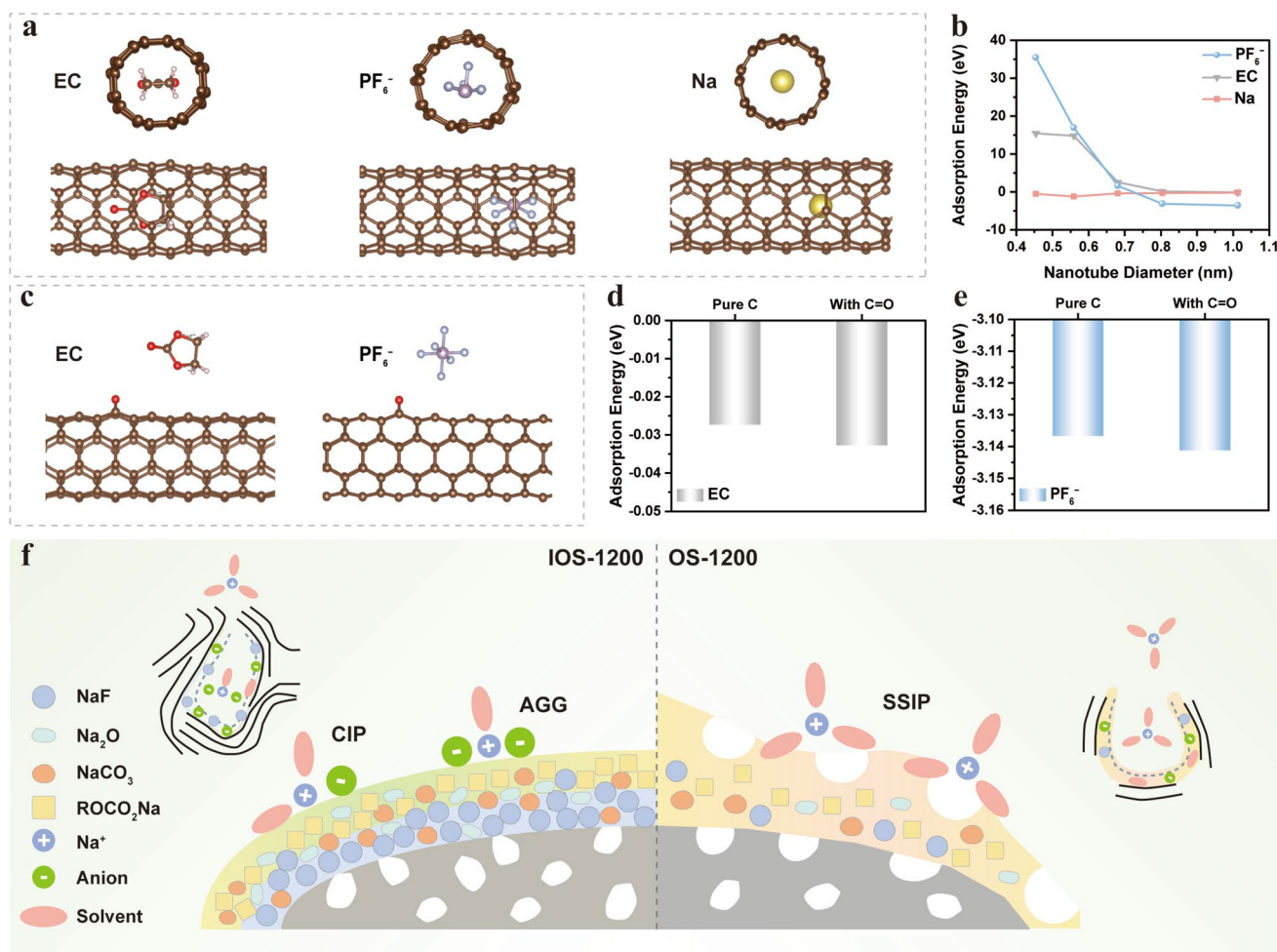
To assess the contribution of surface chemistry, additional DFT calculations were performed on C=O-functionalized CNT models (Figs. 5c–e and S20). The C=O-decorated surfaces exhibit significantly stronger adsorption toward  $\text{PF}_6^-$  than toward EC, indicating that oxygen-containing functionalities further promote anion-enriched interfacial environments and favor anion-derived interfacial reactions.

Taken together, ultramicropore-induced size-selective ion sieving, coupled with strong  $\text{PF}_6^-$  binding at C=O-rich interfaces, is expected to create an anion-enriched interfacial microenvironment that favors  $\text{PF}_6^-$ -derived inorganic interphases on the external surface and potentially within nanoconfined pore regions (Fig. 5f). Such inorganic-rich interphases can substantially lower the interfacial energy barrier, thereby enabling fast  $\text{Na}^+$  transport, high ICE and superior rate capability.





**Fig. 4** Interfacial kinetic and structural characterization. **a** CV curves of IOS-1200 at different scan rates ranging from 0.2 to 1.0 mV s<sup>-1</sup>. **b** Corresponding *b*-values determined from linear fitting of the redox peak currents. **c** Capacitive contribution to the total capacity of IOS-1200 at various scan rates. Depth-profiling XPS spectra of the SEI on the IOS-1200 anode after 10 cycles charged to 3.0 V: **d** C 1s, **e** O 1s, and **f** F 1s. HRTEM images of **g** IOS-1200 and **h** OS-1200 anodes after 5 cycles charged to 3.0 V. **i** DRT curves fitted from EIS spectra for IOS-1200

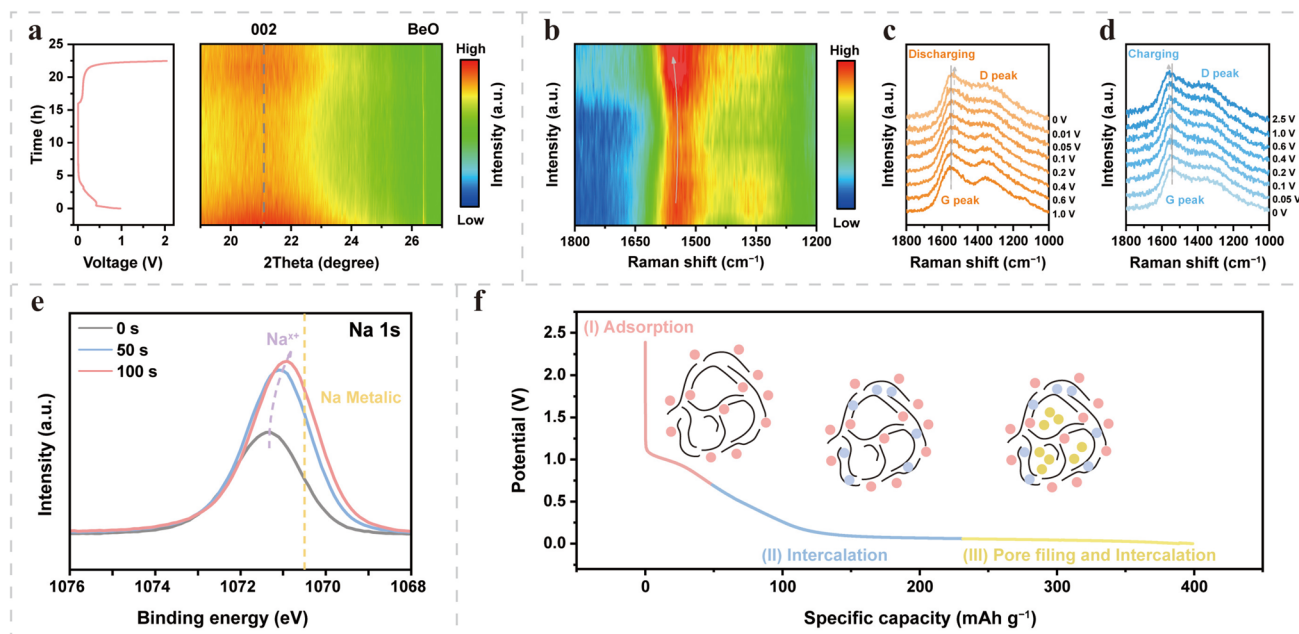


**Fig. 5** Theoretical Calculations and Schematic Illustrations of SEI. **a** Schematic adsorption model of EC, and  $\text{PF}_6^-$  and Na on a CNT. **b** Corresponding calculated adsorption energies across CNTs with different diameters. **c** Schematic adsorption model of EC and  $\text{PF}_6^-$  on a C=O-functionalized carbon surface, along with the corresponding adsorption energies on **d** the pure and **e** functionalized surfaces. **f** Schematic illustration of the distinct SEI structures. The mechanism guided by ultramicropores and C=O functionalities in IOS-1200 (left) produces a uniform SEI with an inorganic-rich inner layer, while OS-1200 (right) forms an uneven, predominantly organic SEI

### 3.5 Sodium-Storage Mechanism Analysis

In situ XRD and Raman spectroscopy were employed to elucidate the structural evolution of IOS-1200 during sodium storage. As shown in Figs. 6a and S21, the nearly unchanged (002) peak during the first cycle indicates robust structural stability, which accounts for the excellent long-term cycling performance of IOS-1200. The in situ Raman spectra (Fig. 6b–d) exhibit the characteristic D and G bands. During the discharge process, the attenuation of the D-band intensity reveals that  $\text{Na}^+$  is preferentially adsorbed at surface and defect sites [60, 61]. As the potential decreases

to 0.6 V, the decrease in intensity and broadening of the D band without a noticeable shift suggest that  $\text{Na}^+$  storage in the sloping-voltage region is dominated by adsorption onto C=O active sites and structural defects [62]. Meanwhile, an evident red shift in the G band emerges at 0.6 V, indicative of  $\text{Na}^+$  insertion into the carbon layers and occupation of  $\pi^*$  antibonding orbitals [59, 63]. In the plateau region from 0.1 to 0 V, the G band further shifts toward lower frequencies due to enhanced electron occupation in the  $\pi^*$  band of the carbon framework, resulting in strong electron–phonon coupling and the formation of Na–C interactions [13, 14]. Concurrently, the near disappearance of the D band suggests



**Fig. 6** Sodium-storage mechanism of IOS-1200. **a** In situ XRD patterns during the initial cycle. **b** In situ Raman spectra collected during the initial cycle, and selective in situ Raman spectra during **c** discharge process and **d** charge process. **e** Ex situ XPS spectra of the Na 1s region in the fully sodiated (0 V) states. **f** Schematic illustration of the sodium-ion storage mechanism

effective passivation of carbon-surface defects through the generation of Na clusters. During the subsequent charging process, both the D-band intensity and G-band position recover to their initial states, confirming the highly reversible  $\text{Na}^+$  storage mechanism in IOS-1200.

Ex situ XPS was conducted on IOS-1200 electrodes in the fully sodiated states to clarify the chemical states of stored sodium (Fig. 6e). The Na 1s peak at  $\sim 1071$  eV, originating from SEI-derived Na–O–C species [64, 65], shifts slightly to lower binding energy with sputtering while metallic Na remains undetected, evidencing the coexistence of  $\text{Na}^+$  and quasi-metallic sodium. To further support this conclusion, fully sodiated electrodes at different potentials were immersed in a 1% phenolphthalein–alcohol solution. As shown in Fig. S22, electrodes discharged below 0.01 V exhibit a distinct red coloration, evidencing Na cluster formation during the pore-filling process under the low-potential plateau. Upon charging, the color fades, demonstrating the high reversibility of Na cluster formation. Consequently, the sodium-storage mechanism of the IOS-1200 anode can be classified into three stages (Fig. 6f). Stage I (2.5–0.6 V):  $\text{Na}^+$  adsorption dominates, involving external surface sites (open pores and edge defects) and internal surface sites associated with

structural defects and C=O functional groups. Stage II (0.6–0.01 V):  $\text{Na}^+$  intercalation into graphitic layers occurs continuously, accompanied by the progressive formation of  $\text{NaC}_x$  species. Stage III (0.01–0 V): the abundant ultramicropores induce a pore-filling process at the low-potential plateau, leading to the formation of quasi-metallic sodium clusters.

## 4 Conclusions

In summary, starch-derived spherical HC (IOS-1200) was synthesized via an iodine-mediated oxidative cross-linking strategy, producing abundant ultramicropores ( $< 0.9$  nm) and C=O functionalities. The ultramicropores function as nanoconfining sieves, regulating the electrolyte solvation structure into anion-enriched CIPs/AGGs and favoring the formation of inorganic-rich interphases within nanoconfined pore regions. Meanwhile, ultramicropores wider than 0.681 nm, together with C=O groups, promote favorable  $\text{PF}_6^-$  adsorption on pore surfaces, further contributing to anion-derived interfacial chemistry. Additionally, C=O groups act as highly reversible  $\text{Na}^+$  adsorption sites, enabling fast charge-transfer kinetics in the sloping-voltage

region. Benefiting from these synergistic desolvation, nanoconfinement, and interfacial-regulation effects, IOS-1200 achieves excellent sodium-storage performance in ester-based electrolytes, including a high ICE (88.4%), high reversible capacity ( $352.9 \text{ mAh g}^{-1}$  at 0.1C), outstanding rate capability ( $288.9 \text{ mAh g}^{-1}$  at 5C), and stable cycling performance (95.6% retention at 0.33C after 200 cycles). These findings provide a promising materials-design strategy for high-performance SIB anodes.

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## Declarations

**Conflict of interest** The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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