

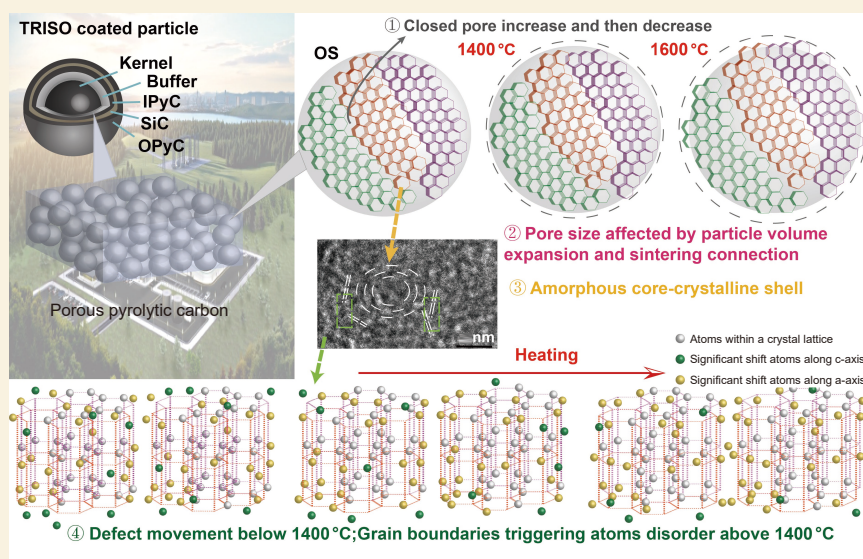


Revealing abnormal micro- and meso-structure evolution mechanism of porous pyrolytic carbon in TRISO coated fuel particles under high-temperature treatment

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Abstract: Porous pyrolytic carbon (PPyC) serves as the buffer layer in TRI-structural ISotropic (TRISO) fuel particles, where it provides storage for fission gases, prevents damage to the outer layers, and absorbs stresses caused by fuel-kernel swelling. However, the changes of the PPyC micro- and meso-structure at high-temperatures remains insufficiently understood. In this study, PPyC fabricated by chemical vapor deposition was heat-treated from 1200 to 1600 °C and characterized across the atomic-to-mesoscopic scales. The results show



that structure of the PPyC changes with temperature with a transition at approximately 1400 °C. Below 1400 °C, a decrease in the Raman peak ratio I_D/I_G , a narrowing of the graphite diffraction peak, and an increase in the amount of sp^2 hybridization collectively indicate progressive ordering associated with defect redistribution. Concurrent decreases in true density and mesopore volume, together with increased closed porosity, are consistent with the partial conversion of open pores into closed pores. Above 1400 °C, the increased I_D/I_G ratio, broadening of the diffraction peak near the position of the rhombohedral graphite (101) reflection planes, and transition regions between crystalline and amorphous material observed by transmission electron microscopy collectively indicate increasing structural disorder. Meanwhile, the initially distinct boundaries of the PPyC particles become blurred and appear to merge into broad, plate-like domains. The subsequent decrease in closed porosity and increase in mesopore surface area are consistent with partial connection of closed pores to the open-pore network. This work shows that the intrinsic coupling between atomic-scale structural change and mesoscale pore connectivity provides a basis for assessing the high-temperature structural stability of PPyC in TRISO fuel particles.

Key words: TRISO coated fuel particles; Porous pyrolytic carbon; High temperature treatment; Transition zone; Pore evolution

1 Introduction

Porous pyrolytic carbon serves as a cornerstone material in fourth-generation nuclear energy systems, specifically constituting the buffer layer within tris-structural isotropic (TRISO) coated fuel particles for high-temperature gas-cooled reactors (HTGRs)^[1–3]. The capacity of buffer layer to accommodate fission-

product-induced swelling and mitigate stress transfer is vital for maintaining fuel integrity under extreme

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conditions. Post-irradiation examinations of TRISO particles have consistently revealed microstructural degradation within the buffer layer, including densification, fracture, and interfacial separation^[4–5]. Furthermore, Griesbach et al.^[6] demonstrated that as-fabricated porous pyrolytic-carbon (PPyC) exhibits pronounced microstructural heterogeneity, characterized by porosity gradients and complex pore networks. This suggests that the initial architecture of PPyC critically governs its subsequent thermomechanical response.

Significant progress has been achieved in understanding the thermal evolution of various carbon materials. Pyrolytic carbon, synthesized by chemical vapor deposition (CVD), is a thermodynamically metastable solid composed of nanoscale turbostratic domains^[7–10]. Upon annealing, structural reorganization occurs, including sp²-to-sp³ conversion^[11], ordering of disordered carbon clusters^[12] and recombination of topological defects such as pentagon-heptagon pairs^[13]. Thermodynamic analyses indicate that graphitization becomes favorable at elevated temperatures, where larger lamellae heal edge defects more efficiently than smaller ones^[14]. Experimental studies on anthracite graphitization reported that (002) carbon layer spacing decreases above 1600 °C and coexistence of amorphous, turbostratic, and graphite phases at 2300 °C^[15], while molecular dynamics simulations predicted layer-driven transitions near 2427–2727 °C^[16–17]. However, existing theories derived from dense carbons fail to explain the high-temperature evolution of PPyC. While this evolution is empirically confirmed, its underlying mechanisms remain poorly understood due to unique low-density and porous architecture of PPyC, which exhibits thermal kinetics fundamentally different from conventional carbon systems.

To elucidate these structural transformations, Raman spectroscopy combined with quantum mechanics is widely employed. This relationship is quantified by the Cançado formula, which links the in-plane crystallite size L_a with the intensity ratio of the defect-induced D band and E_{2g} -symmetric G band^[18]:

$$L_a(\text{nm}) = \frac{560}{E_{\text{laser}}^4} \left(\frac{I_D}{I_G} \right)^{-1} \quad (1)$$

As the number of graphene layers increases, the G band shifts to higher wavenumbers, while the $2D$ (G') band reflects changes in stacking order^[19–21]. In addition, the D_3 peak is generally associated with structural disorder^[22]. Pisana et al.^[23] established the relationship between Fermi-level shifts and G -band stiffening in graphene as follows:

$$\hbar\Delta\omega = \alpha' |\Delta E_F| \quad (2)$$

where $\alpha' = 4.39 \times 10^{-3}$ and ω is wave number. This electronic-structure effect remains comparatively underexplored in defect-saturated PPyC, despite its significant potential to advance our understanding of structural evolution trends.

In this study, PPyC derived from commercial TRISO fuel fabrication processes was utilized, with heat treatment experiments conducted from 1200 to 1600 °C in order to mimic HTGR environments. Multi-dimensional characterization techniques, including high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS), were employed. An abnormal structural transformation induced by the low density of PPyC was identified, which is crucial for elucidating the evolution mechanisms of internal defects at high temperatures. Furthermore, the cross-scale correlations governing the microstructural and mesostructural evolution of PPyC were clarified. These findings hold substantial scientific significance for understanding the structure-performance relationships of PPyC and offer critical implications for nuclear engineering applications.

2 Experiment

2.1 Sample synthesis

All samples were prepared by fluidized bed chemical vapor deposition (CVD). Acetylene was introduced as a precursor under an argon atmosphere and pyrolyzed at 1260 °C onto 3YSZ particle cores (0.5 mm diameter). This process yielded PPyC layer with a thickness of $95 \pm 5 \mu\text{m}$ and density $1.01 \pm 0.01 \text{ g/cm}^3$. These samples were subsequently heat-treated

in a tube furnace at temperatures of 1200, 1300, 1400, 1500 and 1600 °C for 10 h, respectively, followed by cooling to room temperature at a rate of 5 °C/min. The heat-treated samples were designated as BS-Temperature, while the untreated specimen was designated as the original sample (OS), representing the room-temperature (RT) condition.

2.2 Microstructure characterization

Phase and microstructural analyses were conducted using an X-ray diffractometer (XRD, Rigaku D/max-2500/PC) with Cu target and $K\alpha_1$ monochromator. This analysis was operated at a continuous scanning rate of 5°/min, scanning the total surface area of approximately 600 PPyC particles loaded into the cavity of a standard quartz powder sample holder, and the diffraction data were collected from the exposed surface region of the packed particles. Based on the acquired XRD patterns, the diffraction peaks and full width at half-maximum (FWHM) of the (101) and (003) crystal planes for pyrolytic carbon were identified. The corresponding (101) interplanar spacing $d_{(101)}$ and $d_{(003)}$ lamellar spacing $d_{(003)}$ were subsequently calculated using the Bragg diffraction equation^[24]. Besides, theoretical density (ρ_{th}) was calculated by the formulate:

$$\rho_{th} = \frac{Z \cdot M}{N_A \cdot V_{th}} \quad (3)$$

where Z represents the number of carbon atoms in the unit cell ($Z=6$), M referred to the molar mass of carbon and the theoretical unit-cell volume is defined as $V_{th} = \frac{\sqrt{3}}{2} a^2 c$. The lattice parameters a and c were derived from $d_{(101)}$ and $d_{(003)}$, using the relation $\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$, where (hkl) represents the Miller indices. N_A denotes Avogadro's constant. The structure of the pyrolytic carbon was analyzed using a high-resolution laser confocal micro-Raman spectrometer (Renishaw Qontor) with a 532 nm laser. Deconvolution of the spectra relied on energy peaks, identifying an D_3 peak located between the D and G peaks. The Raman detector scanned the surface vertex of the PPyC spheres, collecting data from 15 PPyC samples. A hard X-ray photoelectron spectrometer (ULVAC-PHI PHI GENESIS 900) with a micro-area selection

function was applied to characterize the local band structure and atomic binding energy evolution. These data were also acquired from the sample surface. To further analyze microstructural evolution, focused ion beam (FIB, Zeiss Auriga) sectioning and high-resolution transmission electron microscopy (HRTEM, JEOL F200) operated at 200 kV were employed.

2.3 Mesosstructure and porosity measurement

To investigate the temperature-dependent mesostructural changes of the PPyC, porosity-related characterizations were performed. A scanning electron microscope (SEM, Hitachi S-3000N) was used to observe surface and cross-sectional morphologies. The diameters of 400 deposited spherical carbon particles, randomly selected from three surface-view SEM graphs at 20k× magnification, were statistically analyzed for samples under different heat treatment conditions. Submicron-resolution computed tomography (CT, Carl Zeiss Xradia 610 Versa) was utilized to characterize internal mesostructural evolution with a voxel resolution of approximately 0.800 μm. A nitrogen expansion true density meter (Ultracyc 7000 Micro, Anton) was used to calibrate true density variations, thereby eliminating the influence of open porosity. The density of the kernels under different treatment conditions was also measured to exclude the YSZ kernel effect. A specific surface area and pore size analyzer (BSD INSTRUMENT BSD-660M) was employed to evaluate porosity by the static volumetric method. The specific surface area was determined by the BET multi-point method, the mesopore ratio was measured using the BJH method, and the average pore distribution was described using the NLDFT method.

3 Results and discussion

3.1 Microstructure evolution of PPyC induced by heat treatment

Pyrolytic carbon is thermodynamically metastable, and its atomic structure evolves upon heating. Raman spectroscopy was employed to provide further insight into the structural evolution of PPyC during heat treatment. As shown in Fig. 1a, Raman spectra

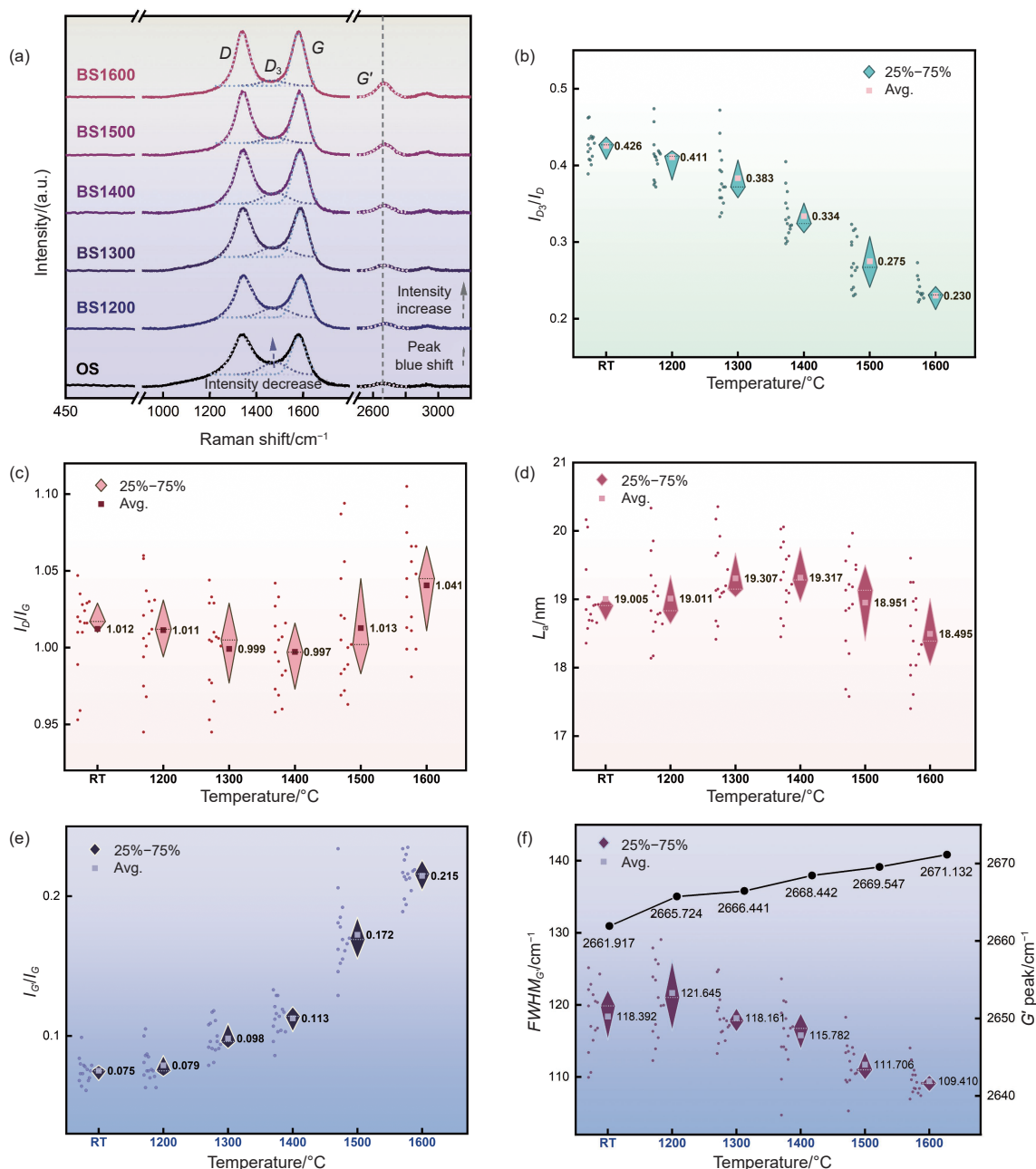


Fig. 1 (a) Raman spectra of OS and heat-treated samples. (b) Intensity ratio of peak D₃ to D. (c) Intensity ratio of peak D intensity to G. (d) Evolution of the in-plane crystallite size L_a . (e) Intensity ratio of peak G' to G. (f) Variation tendency of FWHM and position of G' peak under different heat treatment conditions

exhibit the D, D₃, G, and G' peaks. As reported previously^[22], the D₃ band is commonly assigned to amorphous carbon, while the D band reflects disorder in the graphitic lattice, especially that associated with edge defects. Accordingly, the intensity ratio I_{D_3}/I_D , which can be used to evaluate structural disorder with reduced influence from edge-related defects, shows a marked decrease. This reduction indicates an increased degree of structural ordering induced by high-temperature treatment. However, the evolution of the

intensity ratio of the D peak to the G peak (I_D/I_G) shows a change in trend around 1400 °C, and the rate of evolution appears to slow down after 1300 °C. Correspondingly, the in-plane crystallite size L_a , calculated by Eq. (1), reaches a maximum of approximately 19.317 nm at 1400 °C. These results suggest that graphitization proceeds progressively below 1400 °C, whereas the elimination of edge-related defects becomes less pronounced above 1300 °C, indicating that the structural evolution exhibits a clear temperature

dependence. Besides, there is a surge in structural defects above 1400 °C, a tendency that has not been previously reported.

For a more detailed analysis, the intensity ratio of the G' peak to the G peak ($I_{G'}/I_G$, in Fig. 1e) was employed for the first time to quantify the proportion of intervalley-structured graphite relative to intravalley structure. The G' peak could be fitted with a single peak around 2662 cm^{-1} , and a blue shift is observed after heating, which is consistent with a 2D turbostratic structure^[25]. The temperature-dependent increase reflects enhanced second-order phonon dispersion of K-point inter-valley transitions and an improved degree of structural order. However, compared with the OS, the higher FWHM of the G' peak at 1200 °C suggests that disorder associated with the intervalley double-resonance process remains relatively pronounced. It indicates that interlayer coupling and ordered multilayer stacking are still not well developed at this stage.

XRD carbon peaks and their FWHM values for all samples reveal that the pyrolytic carbon with poor crystallinity is mainly composed of graphite with a $R\bar{3}m$ crystal space group, while the $P6_3/mmc$ space group also exists (Fig. 2a). In Fig. 2c, the lamellar spacing $d_{(003)}$ and its FWHM decrease with increasing temperature, which aligns well with previous studies^[10]. However, a dramatic drop in the FWHM of the (003) peak between 1300 and 1400 °C is clearly observed for the first time. Combined with the rapid surge of the Raman G' peak intensity starting from 1400 °C (Fig. 1e), it can be concluded that the kinetics of lamellar structure formation are accelerated above this temperature.

The intraplanar spacing $d_{(101)}$ rises steadily, which corresponds to the positive a-axis thermal expansion coefficient of bulk graphite calculated through first-principles by Mounet^[26]. However, the FWHM of the (101) peak ($\text{FWHM}_{(101)}$) surges abnormally above 1400 °C.

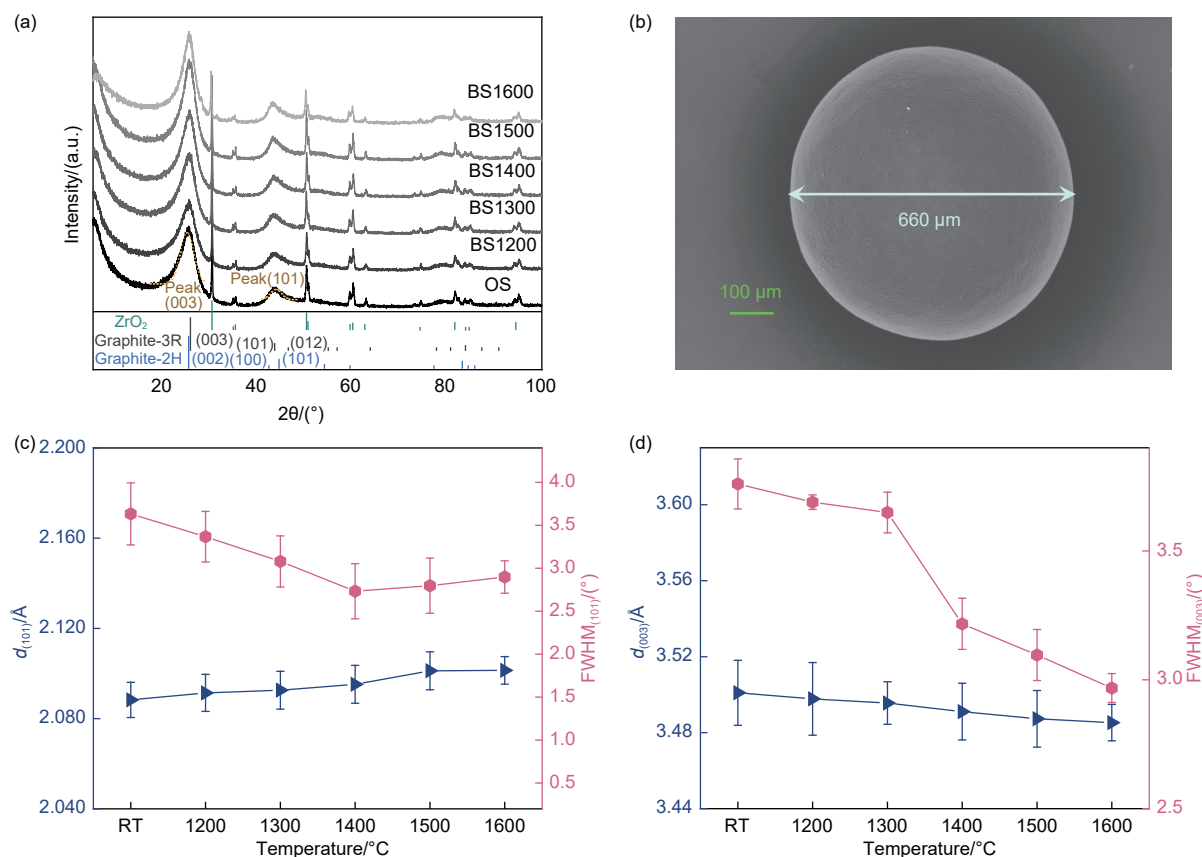


Fig. 2 (a) Evolution of XRD patterns from OS to heating samples, grey dot line represented the peak corresponding to the graphite (003) crystal plane. (b) SEM image of a sample at 100 $\times$ magnification. (c) The variation of (003) lamellar spacing with a 95% confidence interval. (d) The variation of (101) interplanar spacing with a 95% confidence interval

To clarify the underlying reason for the confusing in-plane structural evolution reflected by $\text{FWHM}_{(101)}$, X-ray photoelectron spectroscopy (XPS) measurements were conducted to distinguish the relevant mechanisms. As clearly shown in Fig. 3, the proportion of sp^2 hybridization shows an inflection in its evolution trend around 1400 °C. This result suggests that the progressive ordering of in-plane carbon atoms is accompanied by the formation and stabilization of sp^2 hybridization, and that the trends in Fig. 1c and Fig. 2c are therefore associated with the same ordering process. The oxygen defect also facilitates graphitization behavior, which has been previously reported by Barbera^[27].

However, the reduction in the L_a size and sp^2 fraction, together with the increase in XRD $\text{FWHM}_{(101)}$ above 1400 °C, suggests that the high-temperature evolution can no longer be described as a simple continuation of the low-temperature ordering process. This interpretation is supported by the noticeable decrease in the oxygen content of PPyC after heat treatment at 1500 and 1600 °C (Fig. 3b).

To elucidate the reason for structural disordering above 1400 °C, the Fermi energy and valence band energy were measured (Fig. 4). The elevation in Fermi and valence band binding energies below 1400 °C and their decline above 1400 °C are both related to the presence of defects. However, the oxygen defect content is reduced above 1400 °C, indicating that other

types of structural defects become dominant. The band gap between the Fermi energy and valence band indicates the proportion of ordered structures, which can be elucidated by Eq. (4)^[28]:

$$E = H_0 - 1/2(\gamma_1\Gamma)^2 - [1/4(\gamma_1\Gamma)^2 + (\gamma_0|S|)^2]^{1/2} \quad (4)$$

where H_0 is the energy Hamiltonian operator, γ_1 is the interlayer interaction, γ_0 is the nearest neighbor atomic interaction, $\Gamma = 2\cos\pi k_z c$, $|S|^2 = (1 - 2\cos\pi k_y a)^2$, k is reciprocal lattice vector, a and c are lattice constants. It is well known that γ_1 augments with shrinking interlayer spacing, which contributes to the narrowing of the band gap below 1400 °C. However, above 1400 °C, increased atomic movement enhances structural disorder, leading to a reduction in the nearest-neighbor atomic interaction and γ_0 . This broadening of the band gap again indicates that defects are induced by nearest-neighbor atomic disorders.

To gain deeper insights into the microstructure evolution of PPyC, TEM observations were conducted to verify the atomic migration theory. In this study, Fig. 5f shows that PPyC annealed at 1400 °C contains distinct onion-like carbon (OLC) and a central amorphous region. Highly ordered polycrystals are observed at the junctions of multi-directional OLC (Fig. 5h), and the disorder at these junctions reflects boundary conditions. Transition regions^[29] in the middle and outer amorphous zones surround the OLC internally. These transition regions tend to transform

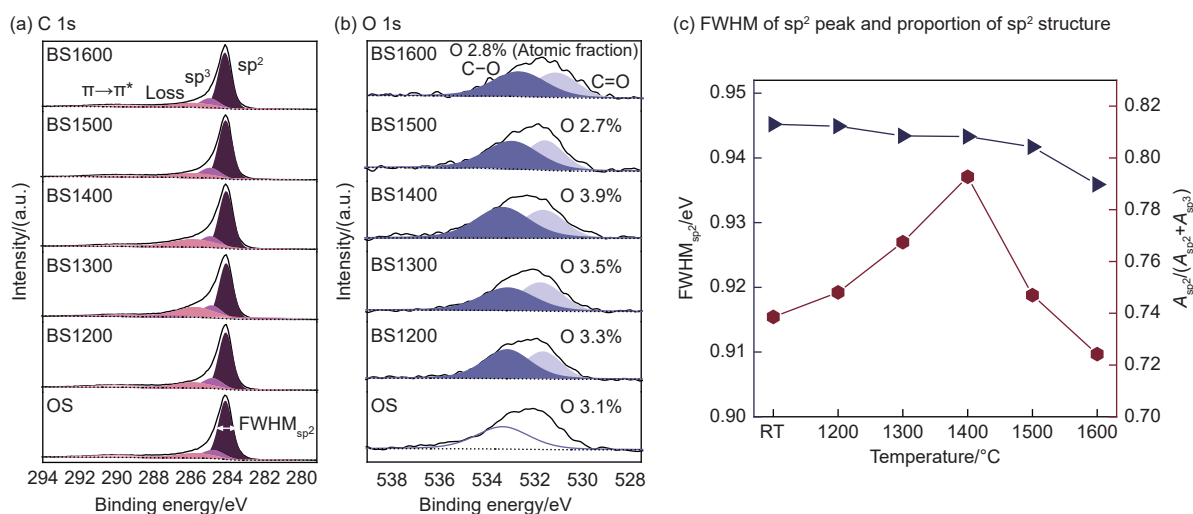


Fig. 3 XPS spectra: (a) C 1s spectrum and (b) O 1s spectrum. (c) Variation of the FWHM of the sp^2 peak (blue curve) and the proportion of the sp^2 peak area relative to the total area of sp^2 and sp^3 structures (red curve) under different heat treatment conditions

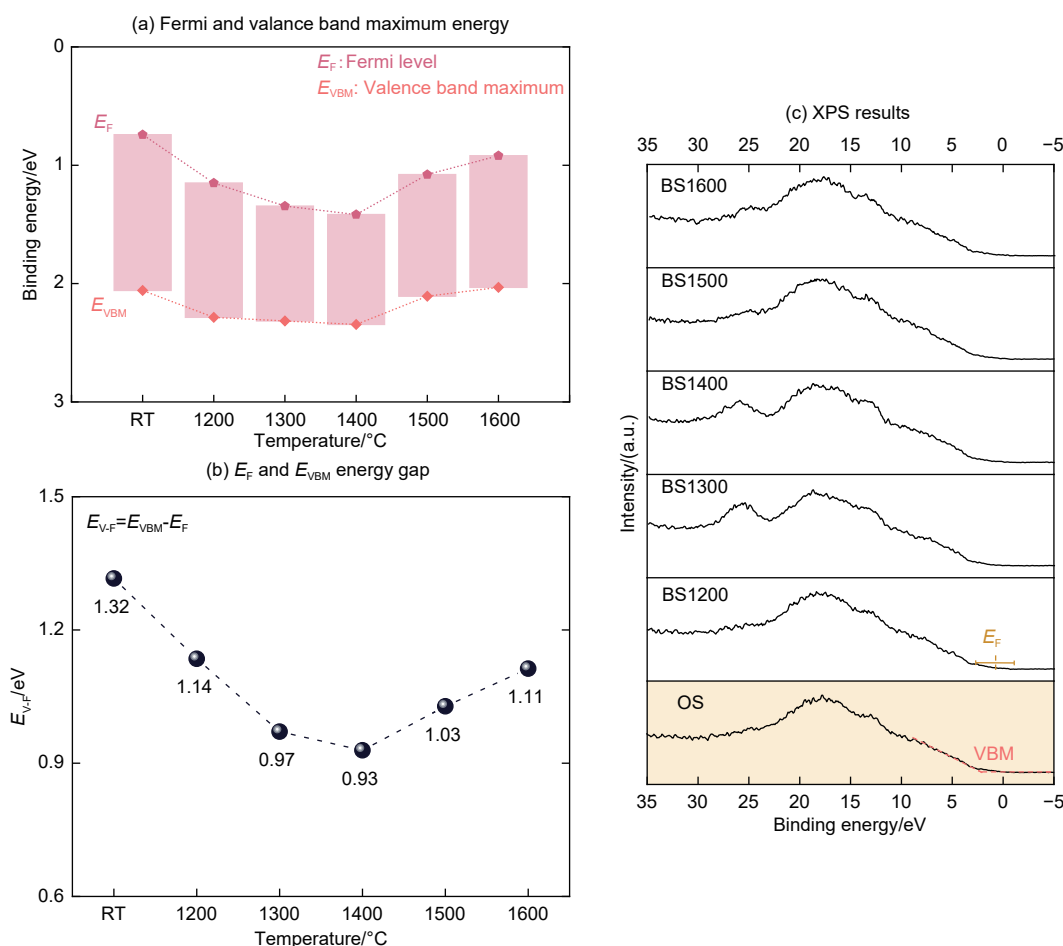


Fig. 4 (a) XPS spectrum of valance band maximum (VBM) and Fermi Energy (E_F). (b) Energy gap of E_F and VBM evolution tendency. (c) XPS results for different treatment condition

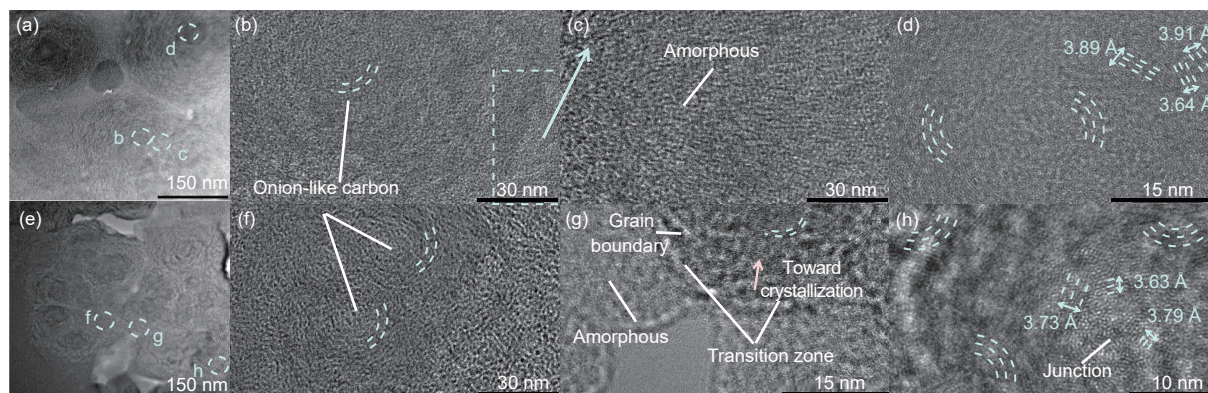


Fig. 5 High-resolution TEM images of samples. (a–d) show structural changes at 1200 °C, (e–h) show structural changes at 1400 °C. The circular regions indicate onion-like carbon (OLC) structures, and the disordered regions adjacent to the OLC correspond to amorphous carbon structures

into crystalline domains, but atomic migration toward ordered spacing generates abundant vacancies.

Vacancy accumulation at grain boundaries induces microcrystallization, which results in a tendency for L_a to diminish above 1400 °C (Fig. 5h). Throughout the structural transformation process, the grain boundary pinning effect becomes more prominent

with the augmentation of microcrystal content. When in-plane structural expansion occurs, more space is available for atomic movement, leading to the formation of structural vacancy defects, such as pentagon-heptagon pairs^[13].

At 1200 °C, the OLC-related region still contains a relatively large amorphous core and only a

small number of layered crystalline structures (Fig. 5d), while its surroundings remain dominated by the amorphous phase. At this stage, the structural evolution is mainly reflected by atomic migration from the amorphous zone toward the transition zone, leading to the formation of an intermediate structure with clearer short-striped graphitic feature but without long-range periodic lattice fringe. This transition-state evolution is consistent with the reduction of defects and the gradual increase in structural ordering below 1400 °C.

The interlayer spacing of the layered structure (Fig. 5(d, h)) matches the *c*-axis interlayer spacing obtained from XRD results. During high-temperature treatment, the layered structures tend to stabilize. In contrast, the structure at 1200 °C contains many short-stripe clusters and fluctuating *c*-axis distances, indicating that the interlayer arrangement is still not well developed, which is consistent with the Raman *G'* band behavior.

Above 1400 °C, intense atomic migration induces atomic distance contraction and stronger interatomic interactions, leading to atomic mismatch and heightened structural disorder. To better describe the internal structural changes, this study proposes that ordered atomic movement tends to form nanocrystals, while disordered atomic rearrangement and defect accumulation contribute to the formation of structurally heterogeneous carbon regions or boundary. To clarify the relationship between in-plane atomic migration and defect migration (including oxygen defects and vacancies), the free energy of atomic movement is used to describe their contributions. The defect creep coefficient^[30] is given by:

$$\dot{\epsilon}_d = A\sigma^n e^{-Q/RT} \quad (5)$$

where *A* is a constant, *n* is the stress exponent, *Q* is the apparent activation energy for creep, and *σ* is the stress. The atomic migration force follows the relationship proposed in^[31–32]:

$$F = \int \left\{ \left[\frac{\rho}{2} \left(r + (1 + \nabla^2)^2 \right) \right] \rho + \frac{\rho^4}{4} \right\} dr \quad (6)$$

where the atomic density $\rho = \sum_{n,m} a_{n,m} e^{ikx} + \rho_0$, *x* is the atomic position, *k* is the movement wave vector, ∇^2 is

Laplace operator, and $E = \frac{k^2 \hbar^2}{2m}$. Based on the analysis of the above equations, it can be inferred that below 1400 °C, the evolution of interplanar spacing is mainly associated with defect reduction, particularly oxygen defect migration, which promotes gradual structural ordering. Above 1400 °C, however, the structure evolution is no longer adequately described as a simple graphitization process. Although elevated temperature enhances atomic mobility, the effective driving force for long-range outward migration of internal vacancies remains limited. In the heterogeneous PPyC matrix, local atomic rearrangement, nanocrystal formation, grain-boundary-related defect accumulation, and edge-defect evolution become the dominant processes. Under these conditions, internal vacancies are more likely to be trapped or redistributed within the interior defective regions than to be efficiently eliminated through outward migration, thereby retaining or even enhancing structural disorder.

3.2 Mesostructure evolution and pore structure changes of PPyC

High-temperature microstructure evolution drives the mesostructure and pore structure changes of PPyC-deposited spherical carbon particles. Fig. 6(a–f) demonstrate good spheroidization of surface carbon particles under heat treatment below 1400 °C, while obvious lamination and sharp-edged structures emerge at higher temperatures. Cross-sectional SEM images in Fig. 7 reveal that the number of sharp-edged structures and larger laminated structures augments with rising temperature. Compared with the cross-sectional image of the OS sample, the structure becomes increasingly tightly bonded.

To clearly identify the diameter distribution of spherical carbon particles in the surface SEM images, Fig. 8 illustrates that higher temperature treatment leads to smaller spherical carbon particles and a more concentrated diameter distribution. As observed in Fig. 7e, some volatilized tiny PPyC spherical carbon particles tend to connect with large laminated carbon structures. A portion of the diameter shrinkage can be attributed to the volatilization of PPyC spherical carbon particles.

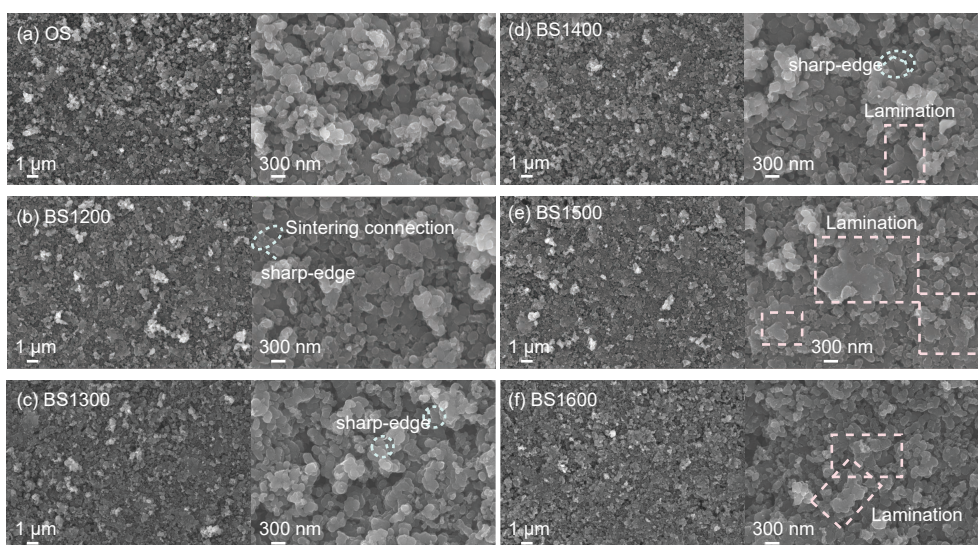


Fig. 6 SEM images of cross-section: (a) OS, PPyc heated 10 h at (b) 1200 °C, (c) 1300 °C, (d) 1400 °C, (e) 1500 °C, (f) 1600 °C. Green circle represents the sintered neck or sharp-edge, and the red square means the lamination structure

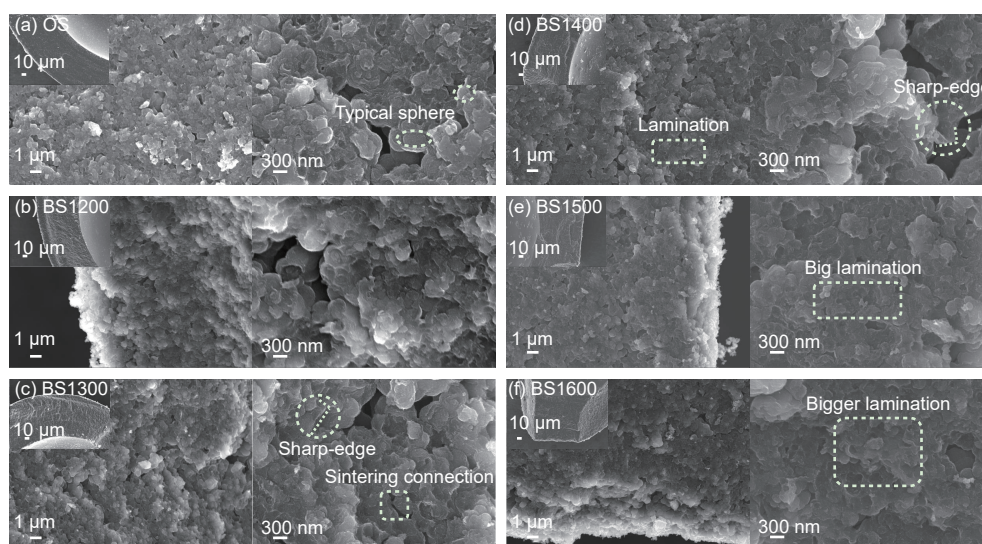


Fig. 7 SEM images of cross-section: (a) OS, PPyc heated 10h at (b) 1200 °C, (c) 1300 °C, (d) 1400 °C, (e) 1500 °C, (f) 1600 °C. Cyan circles indicate sharp edges, and cyan squares denote laminated structures

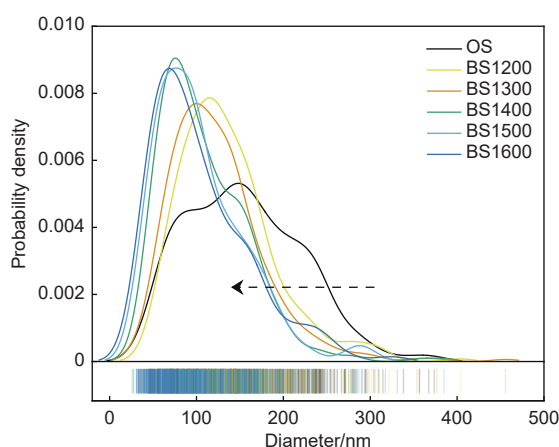


Fig. 8 Evolution of surface particle size distribution of PPyc under different heat treatment conditions

Micro-CT tests were used to reflect the meso-structure. The original sample shows a distinct multilayer structure (Fig. 9a). After heat treatment at 1400 °C, the interlayer pores within the structure are already reduced. As the temperature further increases, these interlayer pores gradually decrease, and the shrinkage becomes more evident at 1600 °C, where the overall interlayer pore space is reduced.

The small diameter of spherical carbon particles facilitates the filling of gaps between different layers. Simultaneously, the small spherical carbon particles and their gap-filling behavior contribute to the shrink-

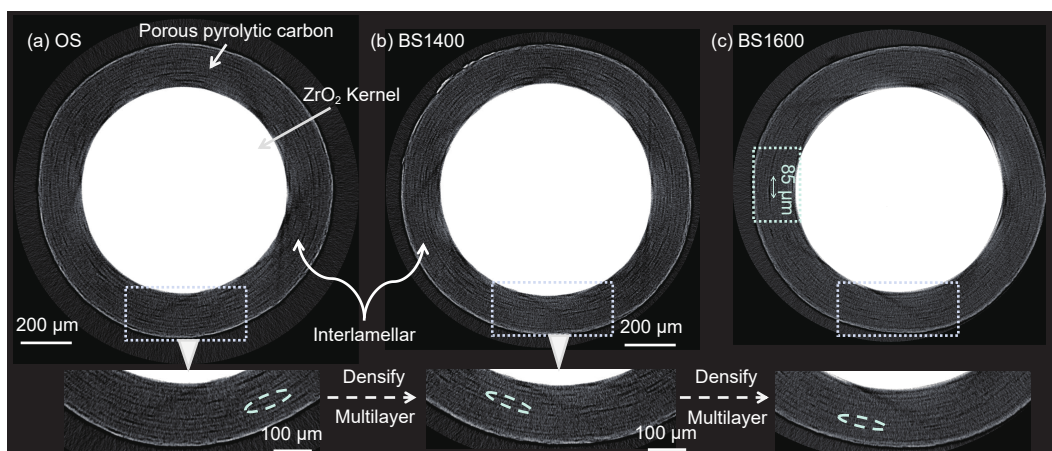


Fig. 9 CT images of (a) original sample (OS) with a pixel size of 0.806 μm , (b) 1400 $^{\circ}\text{C}$ heating sample with a pixel size of 0.782 μm (BS1400) and (c) 1600 $^{\circ}\text{C}$ heating sample with a pixel size of 0.732 μm (BS1600)

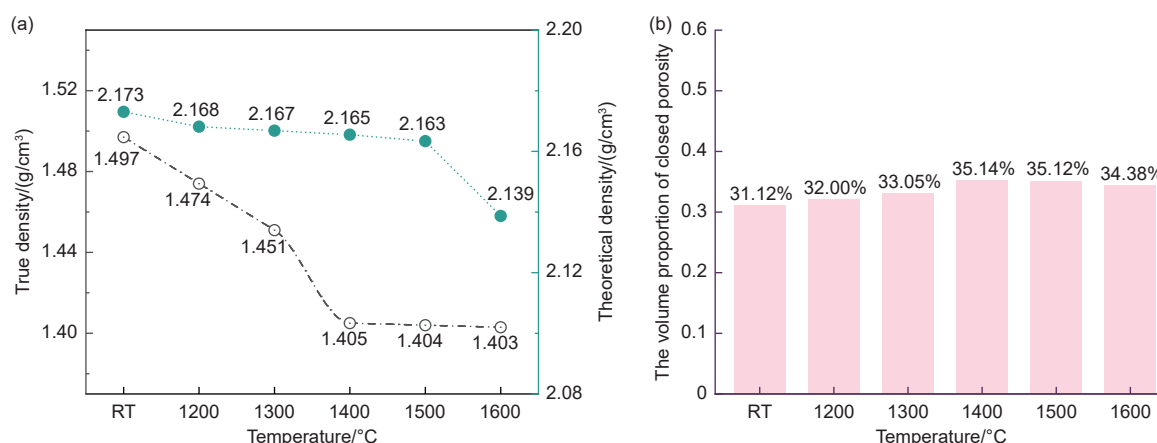


Fig. 10 (a) True density of samples measured using nitrogen expansion true density meter and theoretical density calculated by XRD data. (b) Evolution tendency of the closed porosity proportion

age of layer thickness.

However, the true density and theoretical density of PPyC particles diminish (Fig. 10a). The proportion of closed pores augments before 1400 $^{\circ}\text{C}$ and declines slightly above this temperature (Fig. 10b), which is calculated using the following Eq. (7):

$$P_{\text{closedhole}} = \frac{V_r - V_{\text{th}}}{V_r} \times 100\% = \frac{\rho_{\text{th}} - \rho_r}{\rho_{\text{th}}} \times 100\% \quad (7)$$

where $P_{\text{closedhole}}$ means the volume ratio of closed pores excluding open pores, V_r and ρ_r are the true volume and true density, respectively. The steep slope of ρ_r indicates that the rapid surge in true volume is attributed to the conversion of open pores to closed pores. This process is also confirmed by the growing number of laminated carbon structures and sintered necks observed in SEM results. Furthermore, the deviation between the diminishing density and the shrinking diameter of spherical carbon particles can be attrib-

uted to the sintering process, which alters the shape of the particles (e.g., lamination, sintered necks, or crystalline sharp edges).

The BJH method, suitable for mesopore analysis, was used to calculate 10-50 nm mesopores (open hole), which reaches a minimum within 1300-1400 $^{\circ}\text{C}$ (Fig. 11b). Calculated results by NLDFT (Fig. 11(c-d)) reveal that micropores below 2 nm and large mesopores above 50 nm follow the same trend around 1400 $^{\circ}\text{C}$, with total pore volume first decreasing then increasing. All of them reconfirmed that a part of closed hole converts into open hole again above 1400 $^{\circ}\text{C}$ for the sake of microstructure expansion and evolution.

Matrix shrinkage induces differences in the size and volume of internal open pores. At lower temperatures, the surging true volume reduces the true density,

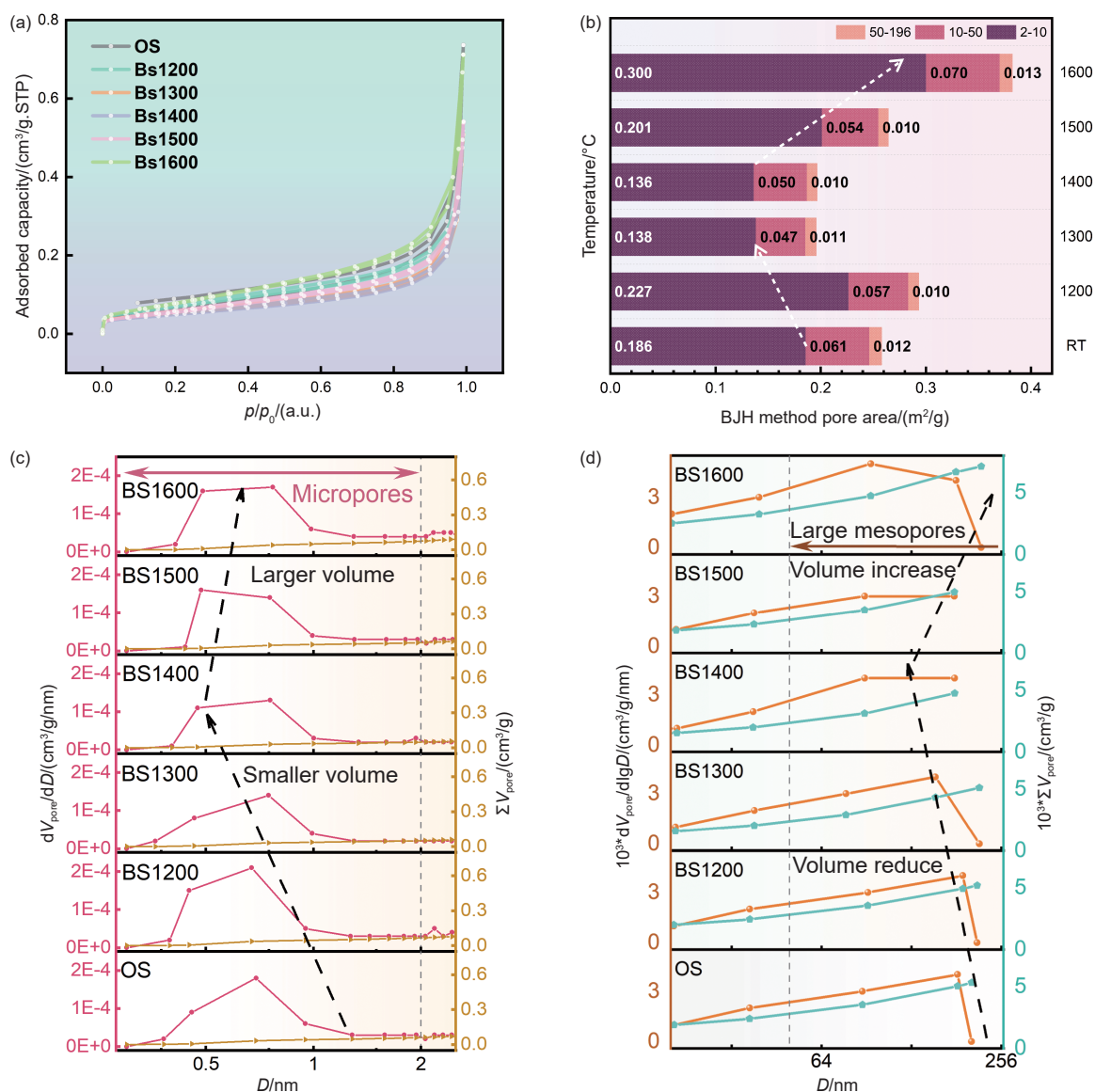


Fig. 11 (a) Nitrogen adsorption curves obtained by the BET method. (b) Analysis mesopores by BJH method. (c) Analysis micropores by NLDFT method. (d) analysis large mesopores by NLDFT method through plotting y-axis as $dV/d\lg D$

and atoms occupy the internal through-pore space, leading to a decline in total pore volume. When the temperature exceeds 1400 °C, enhanced atomic activity within small particles and surface sintering necks of pyrolytic carbon particles indicate particle merging. This process further drives the merging of pores around the particles, resulting in an augmentation of pore volume.

3.3 Coupling between microstructure and pore structure evolution

The evolution of the microstructure and mesostructure is interrelated (Fig. 12). Below 1400 °C, all characterization methods confirm an improvement in

structural order, which is associated with ordered atomic arrangement along both the a -axis and c -axis. This sp^2 -hybridization-induced structural ordering process lowers the Fermi level, narrows the band gap, and mitigates defect-induced electron-phonon scattering, reflected by the Raman D peak. Above 1400 °C, increased atomic mismatch along the a -axis leads to higher structural disorder, accompanied by energy gap expansion, as well as enhanced in-plane phonon scattering.

With rising temperature, the unique crystallization mode of the core-shell structure generates multiple edge crystal orientations, promoting defect accu-

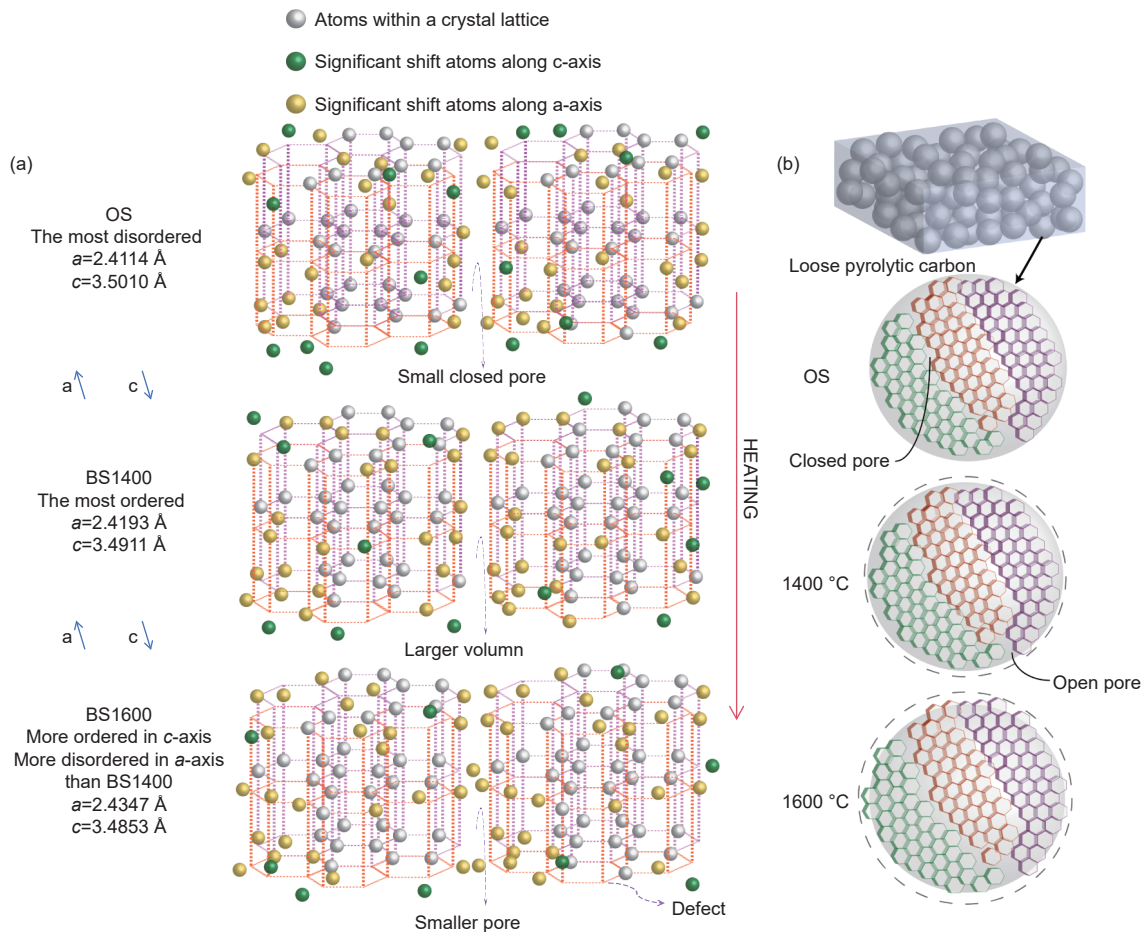


Fig. 12 Schematic of pyrolytic carbon: (a) atom microstructure evolution, (b) mesostructure evolution with heating process

mulation at grain boundaries. Grain boundaries remain difficult to eliminate even at temperatures up to 1600 °C. Thus, structure evolution at low temperatures induces defect aggregation, and intensified atomic mobility at higher temperatures accelerates this trend. However, a large number of defects pinned at grain boundaries hinder smooth atomic movement.

The heating process causes c -axis contraction, a -axis expansion, and an overall augmentation in the volume of PPyC. Below 1400 °C, carbon atoms exhibit high mobility during the sintering process. At the microscale, atomic filling of internal defects and, at the mesoscale, sintering connection of carbon particles lead to a decline in open pores, which are replaced by closed pores (Fig. 12b). Meanwhile, above 1400 °C, the sintering volume ratio does not augment continuously with temperature but remains at a certain level. The expansion of PPyC volume converts closed pores back to open pores, resulting in a dramat-

ic surge in internal pores.

4 Conclusions

In this study, the high-temperature structure evolution mechanism of low-density PPyC in TRISO coated fuel particles by comprehensive characterizations was investigated. It confirms 1400 °C as the critical temperature where oxygen defect migration dominates below it and disorder atomic migration induced vacancies prevail above. An onion-like carbon (OLC) with an amorphous-core/crystalline-shell growth mode and its three transformation stages is discovered, and a correlation model between structural order-disorder transitions and atomic motion is established. A microstructure-mesopore coupling mechanism is proposed to resolve the contradiction between theoretical volume expansion and experimental thickness shrinkage. These findings deepen the understanding of low-density PPyC unique evolution and provide

theoretical support for optimizing TRISO particles and functional carbon materials.

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