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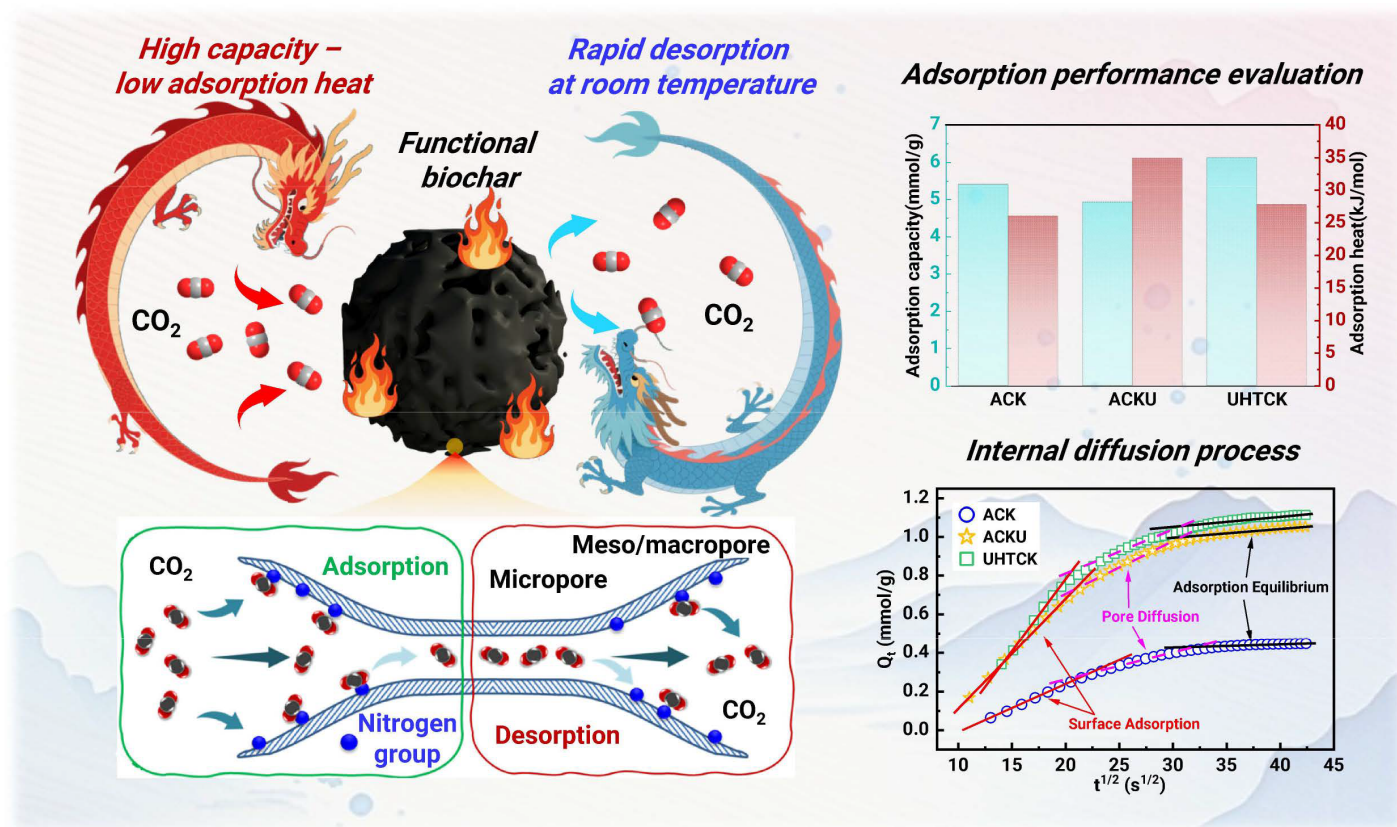
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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- The orderly construction of nanopores is crucial for the performance of the adsorption-compressed CO₂ energy storage system.
- Hierarchical pore functionalization enables high-capacity carbon storage at ambient pressure and flexible adsorption-desorption.
- A framework targeting efficient thermal and mass storage/exchange in adsorbent materials is established for energy storage systems.

Ordered construction of multiscale functional biochar: Mechanistic insights into high-capacity CO₂ adsorption at ambient pressure

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The development of functional biochar with high-capacity and rapid CO₂ adsorption/desorption capabilities is pivotal for compressed CO₂ energy storage systems, effectively mitigating renewable energy intermittency and advancing carbon-neutral power grid infrastructure. A porous biochar with hierarchically structured pores and deliberately incorporated nitrogen functional groups is fabricated through hydrothermal treatment followed by chemical activation in this study. A multimodal approach combining experimental adsorption analyses with molecular dynamics and density functional theory simulations systematically elucidates the structure-activity relationships governing CO₂ adsorption-desorption equilibrium. The UHTCK biochar demonstrates narrowly distributed micropores (centered at 0.7 nm) within an ideal hierarchical architecture, achieving a CO₂ adsorption capacity of 6.01 mmol/g at 0 °C with 92.05% regeneration efficiency after 20 cycles. Edge functionalization enhances surface polarity, facilitating electrostatic-driven weak interactions (e.g., hydrogen bonding) that promote monolayer CO₂ confinement in micropores. Mesopores exhibit wall-proximal CO₂ accumulation, while nitrogen-doped mesopores optimize diffusion kinetics. Mechanistic analysis reveals that high microporosity enables substantial CO₂ storage, while nitrogen-functionalized surfaces and mesopores thermodynamically balance the adsorption and heat to meet the requirements of adsorption-compression CO₂ energy storage systems. Strategic pore-functionality engineering enables ambient-condition rapid CO₂ cycling through regulated gas-solid-thermal interactions. This work provides theoretical insights and design principles for developing atmospheric-pressure CO₂ capture materials, offering transformative potential for next-generation energy storage systems.

INTRODUCTION

The escalating energy crisis and geopolitical tensions have imposed urgent demands for global energy transition, driving a profound transformation in energy consumption patterns from traditional fossil fuel dependence toward clean and efficient energy systems.^{1,2} This paradigm shift necessitates renewable energy-dominant power systems, yet the inherent volatility and intermittency of renewable resources have disrupted the conventional "source-follows-load" unidirectional regulation mode,^{3,4} posing significant stability challenges to the generation-grid-load triad. These challenges underscore the critical need for advanced energy storage systems to decouple generation and consumption while mitigating grid fluctuations. Compressed gas energy storage (CGES) has emerged as a promising solution for large-scale, long-duration storage in carbon-neutral power systems, particularly suited for high renewable penetration scenarios.⁵ While compressed air energy storage (CAES) dominates current commercial projects, its development is constrained by low gas storage density requiring massive infrastructure.^{6,7} Comparatively, compressed CO₂ energy storage exhibits superior cycle efficiency (60–75%) and energy density advantages.^{8,9} The closed-cycle operation mandated by CO₂'s greenhouse properties presents technical challenges in achieving high-density storage under low-pressure conditions. To overcome critical pressure limitations on CO₂ storage capacity, our team previously proposed an innovative adsorbed-compressed CO₂ super/transcritical energy storage system,¹⁰ featuring a core atmospheric adsorption storage mechanism that enables low-pressure high-density CO₂ storage with medium-temperature thermal management. This creates a demand for developing porous adsorbents with tunable pore struc-

tures and high carbon storage density to achieve high-capacity adsorption at ambient pressure and flexible adsorption-desorption performance.

Given its cost-effectiveness and carbon-neutral feedstock,¹¹ combined with tunable pore characteristics¹² and surface functionality¹³ that align with the technical requirements of high adsorption capacity and rapid cycling, biochar is selected as the core carbon storage material for the adsorption-compression CO₂ energy storage system. Recent investigations reveal that ambient-pressure CO₂ adsorption in nanoporous biochar is predominantly governed by ultra-micropores,^{14,15} while deep neural network predictions¹⁶ highlight the crucial mass transfer role of meso/macropores (>2 nm). The hierarchical pore structure combining meso/macropores with micropores facilitates synergistic "diffusion-transport/adsorption-enrichment" of CO₂ molecules. Nitrogen-containing basic functional groups enhance CO₂ selectivity through multifactorial interactions (hydrogen bonding, electrostatic fields, polarization, and acid-base reactions),^{17,18} with computational analyses demonstrating nitrogen's chemical adsorption contribution ranging from 0.9% to 78.2%,¹⁹ depending on its spatial distribution across pore hierarchies.²⁰ The orchestrated design of surface functionalities and carbon matrix enables directional CO₂ migration and equilibrium desorption, establishing multiscale structural control as the cornerstone for low-pressure high-capacity CO₂ adsorption. However, the exothermic nature of CO₂ adsorption introduces thermal management complexities, where adsorption-induced heat accumulation degrades performance. The closed-system integration of adsorption-desorption cycles with heat exchange demands novel thermodynamic-mass transfer balance strategies, making thermal-mass storage coordination a pivotal requirement for biochar development. Pore structure and nitrogen functionalities differentially influence physical (15–50 kJ/mol)^{21,22} and chemical adsorption heats (60–110 kJ/mol),^{23,24} necessitating precise characterization of CO₂ adsorption kinetics/thermodynamics relative to specific pore architectures and nitrogen configurations.

This work employs an integrated approach combining thermochemical processing and chemical activation to innovatively prepare functional biochar featuring ordered configurations of ultra-micropores (<1 nm), meso/macropores, and nitrogen functional groups, establishing the structural foundation for high-capacity CO₂ adsorption at ambient pressure in adsorption-compression energy storage systems. Through systematic investigation of ambient-pressure CO₂ adsorption performance and associated kinetics/thermodynamics, we elucidate synergistic mechanisms between pore hierarchies and nitrogen groups. Multiscale theoretical models developed based on biochar's physicochemical characteristics enable comparative analysis of experimental and computational results, revealing thermo-mass dependence during CO₂ adsorption/desorption. The established low-pressure high-capacity storage mechanism provides theoretical foundations for advancing adsorbed-compressed CO₂ super/transcritical energy storage systems, addressing both technical barriers to renewable integration and environmental imperatives for carbon management.

MATERIAL AND METHODS

Preparation methods for biochar

Based on its ready availability and inherent inorganic framework that naturally facilitates the formation of hierarchical pore structures,²⁵ rice husk was selected as the raw material for functional biochar production. The biomass raw material used in this paper was rice husk from Wuchang City, Heilongjiang Province. The rice husk, which was crushed and sieved with a

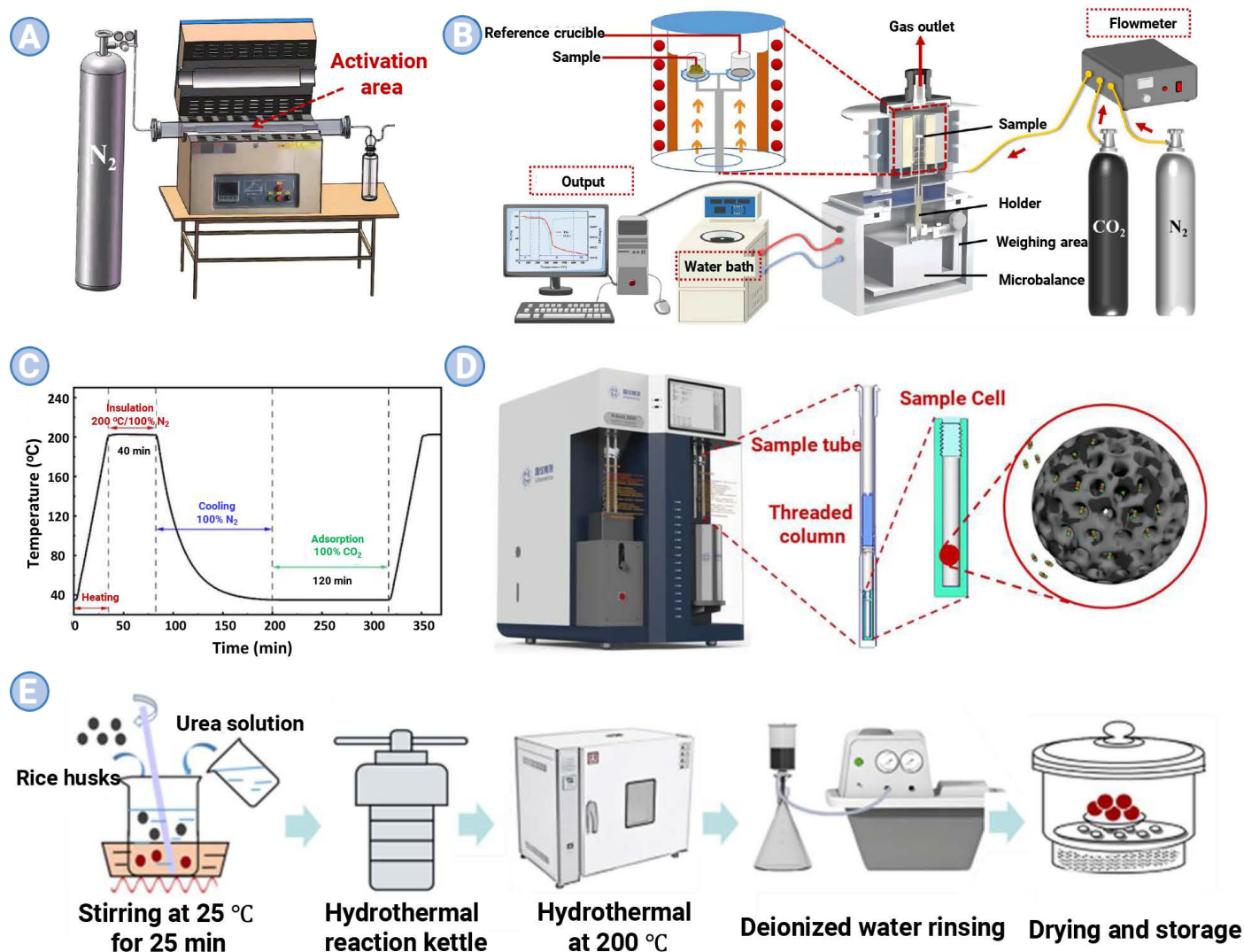


Figure 1. The system and part of the process used for the preparation of functional biochar and adsorption experiments (A) Horizontal tube system (B) HCT-4 thermal analyzer system (C) CO₂ adsorption and desorption cyclic experiment process (D) Gas sorption analyzer (E) UHTC preparation process

100/60 mesh sieve, then washed with a certain concentration of H₂SO₄ (solid-liquid ratio 1:30) for 12 hours until the filtrate is neutral. Acid washing can remove ash blockage within pores and mitigate interference from AAEMs with subsequent selective adsorption processes.²⁶ The collected material was dried in an 85 °C oven to obtain acid-washed rice husks for later use. Table S1 shows the elemental analysis and industrial analysis of rice husk.

The functional biochars were synthesized through chemical activation coupled with thermal treatment processes. Thermal processing was conducted using a muffle furnace pyrolysis system and horizontal tube activation system (Figure 1A), with specific preparation protocols for different samples illustrated in Figure 2A and Table S2. The hydrothermal treatment procedure (Figure 1E) involved: (1) dispersing acid-washed rice husk in 10 wt.% aqueous urea solution under magnetic stirring for 5 min, (2) transferring the mixture into an autoclave and conducting 24-hour hydrothermal treatment at 200 °C to achieve both structural expansion of the biomass precursor and effective incorporation of nitrogen functional groups,²⁷ and (3) washing the cooled product with deionized water to neutral pH to obtain urea hydrothermal treated biochar (UHTC). Pyrolysis was performed by carbonizing predetermined quantities of acid-washed rice husk in the muffle furnace system under N₂ atmosphere (2 L/min flow rate) with controlled heating parameters: 20 °C/min ramp rate to target temperature followed by 30 min isothermal holding, yielding acid-washed biochar (AC). Primary KOH activation comprised three stages: (1) mixing UHTC or AC with 5 wt.% KOH solution at 1:10 solid-liquid ratio for initial silicon dissolution over 2 h, (2) thor-

ough washing to neutral pH, and (3) drying at 85 °C to obtain primarily activated biochar. Secondary KOH activation proceeded via: (1) homogenizing primarily activated biochar with KOH at 1:3 mass ratio in the horizontal tube furnace system (Figure 1A), (2) thermal activation at 750 °C under inert atmosphere for 1 h, and (3) post-treatment through deionized water washing and drying to produce functional biochars (designated ACK-Acid-washed biochar with KOH activation/UHTCK- Urea hydrothermal treated biochar with KOH activation). The rice husk was subjected to two-stage KOH activation, allowing complete dissolution of the inherent SiO₂ network and thereby achieving a well-developed porous structure.²⁵ The ACKU (Acid-washed biochar with KOH and urea activation) variant followed identical procedures to ACK with urea addition during secondary activation.

Evaluation of adsorption and desorption performance experiments

CO₂ adsorption measurements were performed using a high-pressure/high-temperature (HPHT) gas sorption analyzer (H-Sorb X600, Beijing Jin Aipu Technology Co., Ltd., China) as illustrated in Figure 1D. Prior to adsorption analysis, the functional biochar sample was subjected to vacuum degassing at 200 °C for 12 h within the sample chamber to ensure complete surface purification. Subsequently, CO₂ adsorption isotherms were systematically acquired under controlled temperature conditions of 0 °C and 25 °C. The thermodynamic parameter of isosteric heat of adsorption (Q_{st}) was determined through rigorous analysis of temperature-dependent adsorption data employing the Clausius-Clapeyron equation (Equation 1). This dual-tempera-

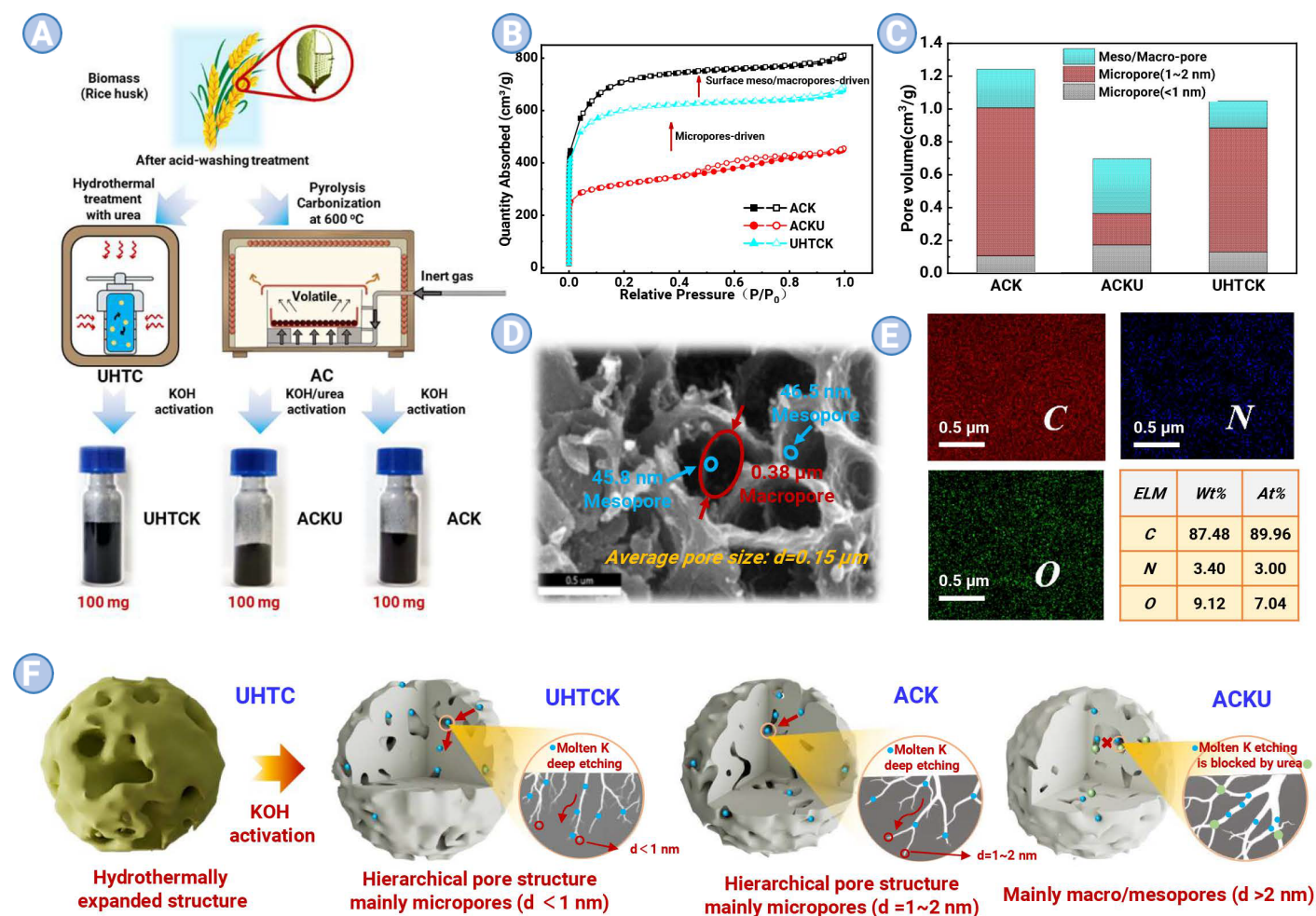


Figure 2. Preparation of functional biochar and characterization of pore structure (A) Preparation methods for functional biochar (B) Nitrogen adsorption isotherms (C) Pore size distribution (D) SEM image of UHTCK (E) EDS results of UHTCK (F) Influence mechanism of the activation methods on pore structure development

ture approach enables precise quantification of adsorption energetics while maintaining measurement integrity under subcritical conditions.

$$\left(\frac{\partial (\ln P_{\text{CO}_2})}{\partial (1/T)} \right)_{q_n} = \frac{Q_{\text{st}}}{R} \quad (1)$$

Where P_{CO_2} denotes CO_2 partial pressure (Pa), Q_{st} represents isosteric heat of adsorption (kJ/mol), and q_n corresponds to specific adsorption capacity at defined equilibrium conditions (mmol/g). Linear regression of $\ln P_{\text{CO}_2}$ versus $1/T$ at different adsorption levels on the adsorption isotherms was performed, and the slope of the regression line enables the determination of the isosteric heat of adsorption for CO_2 on the functional biochar.

The cyclic CO_2 adsorption-desorption experiments were conducted in a synchronized thermal analyzer (HCT-4, Beijing Hengjiu Experimental Equipment Co., Ltd., China) as depicted in Figures 1B. Approximately 5 mg of the sample was loaded into a crucible and initially purged with N_2 (100 mL/min flow rate) for 30 min to establish baseline conditions. Subsequently, the system was subjected to a precisely controlled thermal treatment protocol (Figure 1C) comprising three phases: (1) Heating to 200 °C at 5 °C/min under N_2 atmosphere followed by 40-min isothermal stabilization; (2) Controlled cooling to 30 °C at 10 °C/min; (3) In-situ gas switching to CO_2 for 120-min adsorption. This adsorption-desorption cycle, incorporating regenerative thermal desorption under N_2 atmosphere, was systematically repeated 20 times to evaluate cyclic stability. The resulting multicycle adsorption-desorption hysteresis profiles were quantitatively analyzed to determine the dynamic adsorption capacity and structural integrity of the functional biochar material.

Structural characterization and simulation methods

Physicochemical testing characterization. (1) Specific surface area and pore size distribution test

The specific surface area and pore size distribution of the samples were measured using a specific surface area and pore size analyzer (BELSORP-mini II, MicrotracBEL, Japan). The pore size distribution curve in the range of 0.3 to 1 nm was determined via CO_2 adsorption measurements.

(2) Scanning electron microscope (SEM)

A field emission scanning electron microscope (Merlin Compact, Carl Zeiss, GER) was used to observe apparent morphologies of the samples. Before testing, samples underwent ultrasonic dispersion treatment with ethanol and gold sputtering to minimize aggregation and surface roughness. The testing procedure utilized a 20 kV accelerating voltage for mapping scans. The area with typical microstructure was characterized by a magnification of 100000 times.

(3) X-ray Photoelectron Spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) analysis was conducted using an X-ray photoelectron spectrometer (ESCALAB 250, Thermo Fisher Scientific, USA) equipped with a monochromatic Al K α source ($h\nu=1486.6$ eV). The sample penetration depth was 2 nm. Both the wide spectrum (0 to 1400 eV) and the high-resolution narrow spectrum of all elements were recorded. The binding energy was calibrated using a constant carbon (C1s=284.8 eV) reference.

Simulation Methods and Parameter Settings. (1) Quantum Chemical Calculations

CO_2 adsorption simulations (Figure S4-S6 and Figure 5E) were performed using Gaussian 16. All calculations were carried out using the B3LYP func-

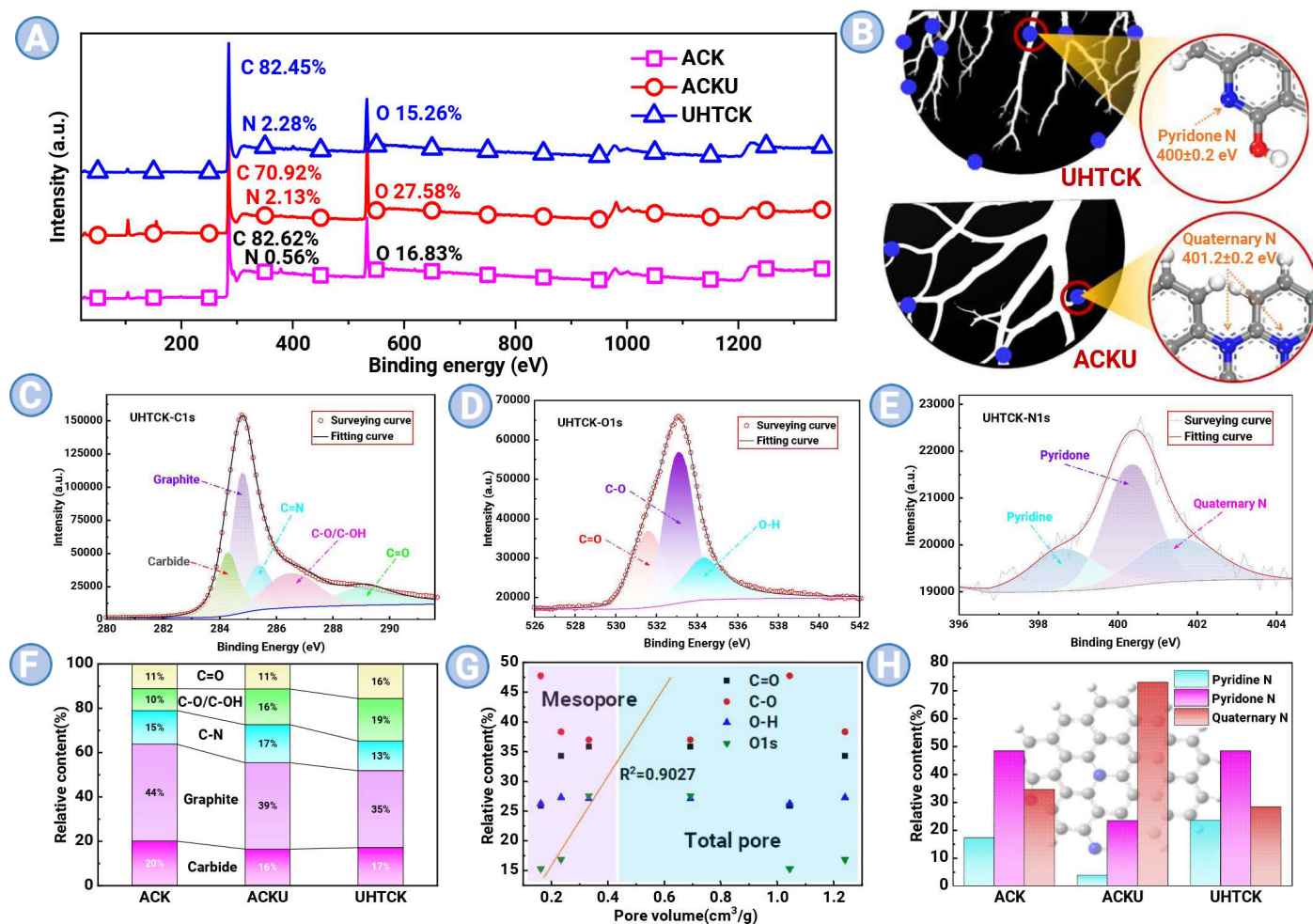


Figure 3. Construction of functional groups in functional biochar and mechanisms (A) XPS energy spectrum (B) Functionalization differences between UHTCK and ACKU (C) XPS C1s peaks (D) XPS O1s peaks (E) XPS N1s peaks (F) Proportion of carbon-containing functional groups (G) Fitting results of the oxygen-containing functional groups and pore volume (H) Proportion of nitrogen-containing functional groups

tional, with DFT-D3 dispersion corrections applied. For geometry optimization and frequency calculations, a smaller basis set was employed, while single-point energy calculations were conducted using a larger basis set.²⁸ Specifically, carbon and hydrogen atoms were treated with the 6-31G(d,p) basis set for geometry optimization, vibrational frequency analysis, zero-point energy, and entropy calculations. Nitrogen and oxygen atoms were treated with the 6-31+G(d,p) basis set. Single-point energy calculations were performed using the 6-311+G(2df,p) basis set. The selected functional and basis set ensure accurate and reliable analysis of interaction mechanisms between functional groups on the biochar surface and adsorbate molecules.^{14,29} Frequency analysis was conducted at 25 °C and 1 atm, with a frequency scaling factor of 0.9857.³⁰ Wavefunction analysis and reduced density gradient (RDG) visualization for noncovalent interactions (NCI) were performed using the Multiwfn program,³¹ and visualizations were generated using VMD.³² The adsorption energy (E) was calculated using the following equation:

$$E_{\text{ads}} = E_{\text{t}} - E$$

Wherein, E_{t} , E_{CO_2} , and E_{FC} correspond to the energies of the functional biochar adsorption model, CO₂ molecule, and functional biochar molecule, respectively.

(2) Molecular Dynamics

Molecular dynamics (MD) simulations (Figure 5D, F & G and Figure S7) were performed using the Forcite module in Materials Studio software. The COMPASS force field was employed to calculate interatomic interactions. The simulations were conducted at 25 °C under the canonical (NVT) ensemble,

maintaining constant number of atoms, volume, and temperature throughout the simulation. A 200 ps production run was executed with a time step of 0.25 fs. Temperature regulation was achieved through the Nose thermostat, while the Verlet algorithm was adopted to solve Newton's equations of motion. The periodic boundary conditions were initialized with the origin coordinates set to 0 Å. This well-established methodology has been successfully applied in previous studies for constructing slit-pore models.²⁷

(3) Monte Carlo Simulations

Monte Carlo (MC) simulations (Figures 6-7) were performed using the Amorphous Cell module in Materials Studio to construct the functional biochar structures. Adsorption phenomena were modeled with the Sorption module, and statistical data were obtained through calculations in the Forcite module. Interactions between the functional biochar and CO₂ molecules were described by the Lennard-Jones (LJ) potential. Interatomic electrostatic interactions were treated through the Ewald summation method, while the Metropolis sampling criterion³³ governed the acceptance/rejection of creation, annihilation, translation, and rotation operations for gas molecules to maintain thermodynamic equilibrium. The fugacity was calculated using the Peng-Robinson equation of state. Atomic charges were determined using the charge equilibration (Q_{eq}) method,³⁴ with electrostatic and van der Waals energies calculated through Ewald summation and atom-based approaches, respectively, employing a cutoff radius of 15.5 Å. These computational settings comprehensively account for various intermolecular forces involved in the adsorption of polar CO₂ molecules by the functional biochar models. The simulation protocol comprised 2×10^6 steps for equilibration followed by an equivalent production phase to ensure statistical reliability of ensemble

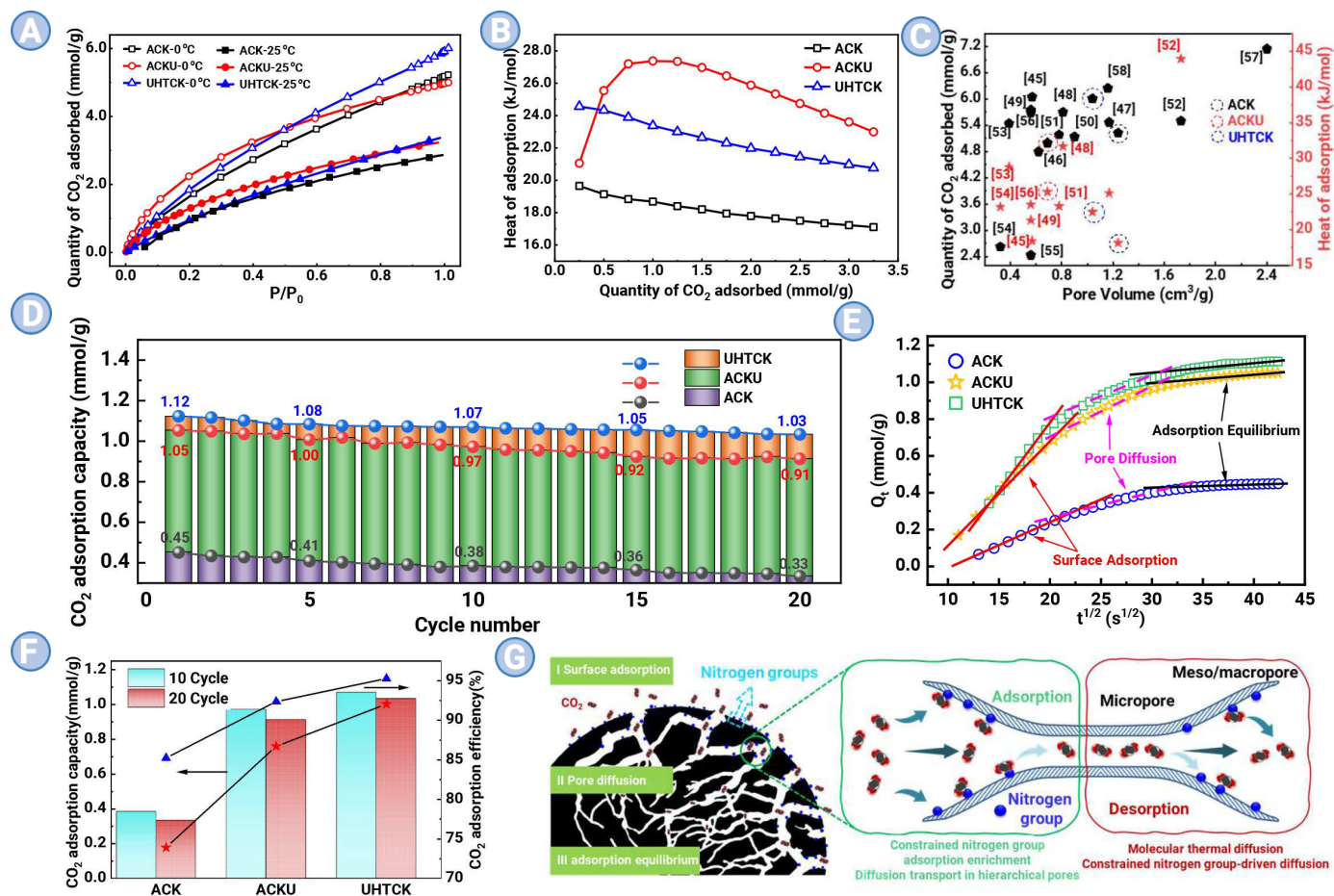


Figure 4. Evaluation of CO₂ adsorption and desorption performance of functional biochar (A) CO₂ adsorption isotherms (B) Relationship between CO₂ adsorption heat and adsorption quantity (C) Comparison of CO₂ adsorption capacity and adsorption heat of functional biochar⁴⁵⁻⁵⁸ (D) CO₂ cyclic adsorption and desorption characteristics (E) W-M diffusion model curves (F) CO₂ adsorption capacity and efficiency after multiple cycles (G) Mechanism of rapid CO₂ adsorption/desorption by functional biochar

averages. Subsequent molecular dynamics simulations (200 ps, NVT ensemble) were performed in the Forcite module under ambient conditions (25 °C, 1 atm) to refine the equilibrated configuration and facilitate subsequent data acquisition.

RESULTS AND DISCUSSION

Multiscale structural characterization of functional biochar architectures

Nitrogen-containing groups promote CO₂ adsorption at low temperatures and exhibit higher CO₂ retention capacity than micropores under high-temperature conditions.^{35,36} Therefore, the introduction of nitrogen groups into meso/macropore systems can enhance CO₂ adsorption/desorption kinetics. A dependent relationship exists between the formation of surface functional groups and pore structure distribution in functional biochar materials. Consequently, the structural compatibility and functional effectiveness between biochar's pore architecture and surface characteristics are crucial.

Hierarchical pore structure characterization. The specific surface areas and pore volumes of functional biochar samples are summarized in Table S3. ACK exhibits a well-developed microporous structure with a specific surface area of 2504.13 m²/g. Although UHTCK shows slightly lower surface area and total pore volume compared to ACK, its micropore volume proportion (84.5%) significantly exceeds that of ACK. Nitrogen adsorption isotherms (Figure 2B) reveal that both ACK and UHTCK follow Type I isotherms according to the IUPAC classification.^{37,38} The rapid N₂ uptake at low relative pressures ($P/P_0 \leq 0.1$) indicates predominant micropore filling, consistent with their abundant microporous structures. At high pressures ($P/P_0 > 0.9$), the isotherms approach saturation with a weak H4-type hysteresis loop, suggesting limited meso/macropores forming hierarchical pore architectures. Notably, the carbonization method demonstrates negligible influence

on the pore-formation characteristics during subsequent KOH activation, as evidenced by the similar pore distribution patterns across samples. In contrast, ACKU displays a distinct Type IV isotherm with a prominent hysteresis loop and a reduced micropore volume (0.3597 cm³/g, 51.9% of total pore volume). Compared to ACK and UHTCK, ACKU shows enhanced mesoporosity but compromised microporosity. This structural alteration arises from urea's interference with KOH penetration into the carbon matrix, which promotes pore-widening effects by accelerating the etching of existing micropores, thereby generating abundant mesopores³⁹ (Figure 2F).

The pore size distributions of the functional biochar samples derived from the N₂ adsorption and CO₂ adsorption tests are presented in Figure 2C. The ultra-micropore data (<1 nm) was determined by CO₂ adsorption, while the pore size distribution above 1 nm was obtained from N₂ adsorption measurements. All three samples exhibit predominant pore sizes below 2 nm, while ACKU displays reduced micropores (1-2 nm) and enhanced mesopore volume (>2 nm). In contrast, both ACK and UHTCK show negligible cumulative mesopore volume increments, demonstrating urea's catalytic role in mesopore formation through selective etching of micropores to generate 2-10 nm mesopores. Notably, the analogous surface areas and pore volumes between ACK and UHTCK are corroborated by their nearly identical pore size distributions. Although UHTCK exhibits a lower total micropore volume than ACK, it possesses enriched ultra-micropores (<1 nm) and hierarchical porosity, including well-developed 1~2 nm micropores and interconnected mesoporous channels, whereas ACK primarily contains 1~2 nm micropores. The mildly alkaline environment provided by urea during UHTCK preparation facilitates the separation of macromolecular chains in acid-washed rice husk,⁴⁰ inducing a swelling effect that promotes the formation of <1 nm ultra-micropores during subsequent KOH activation (Figure 2F). These analyses reveal

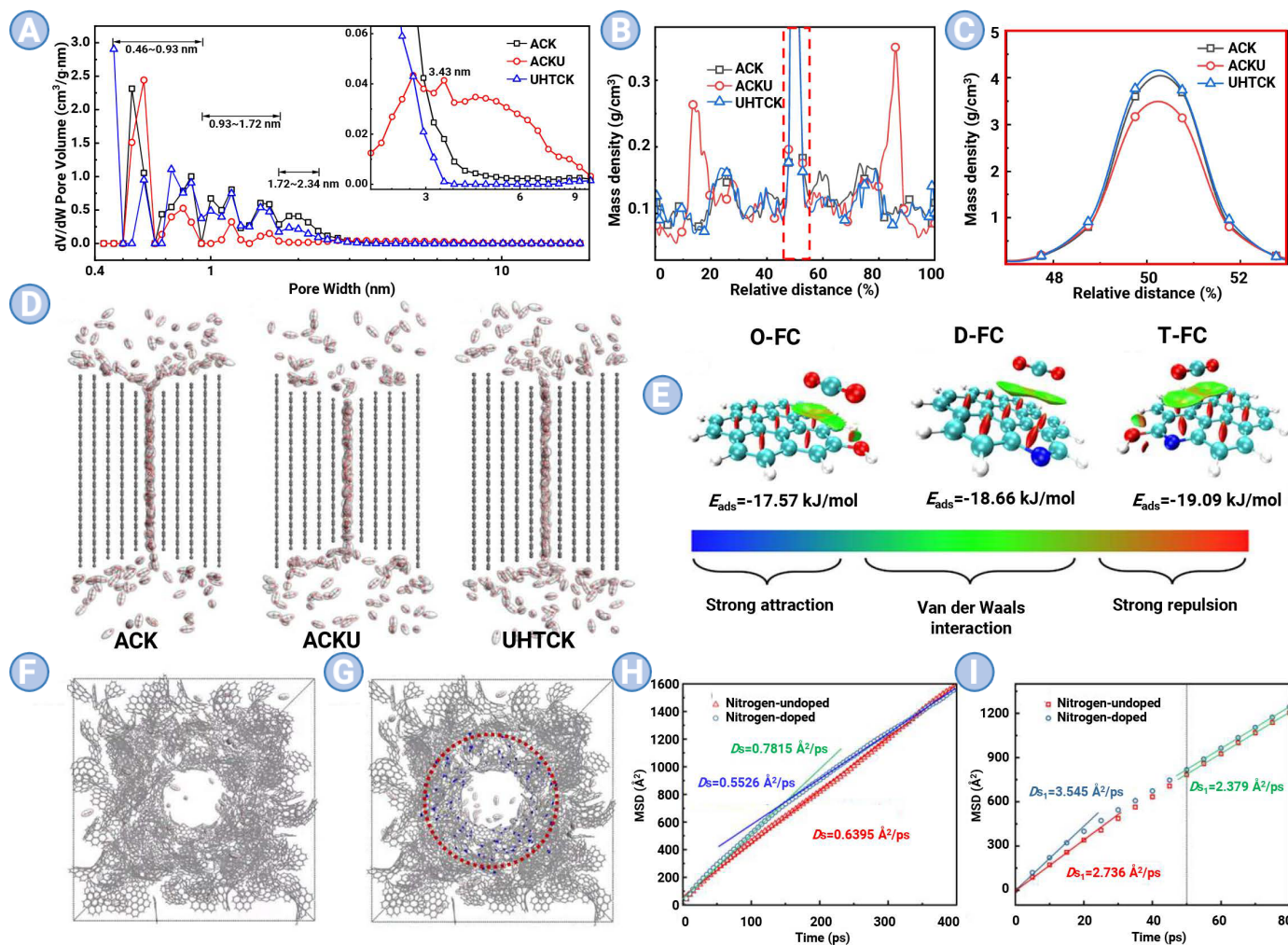


Figure 5. Effects of pore hierarchy and surface functionalization on CO₂ adsorption and desorption (A) Pore size distribution curves (B) CO₂ mass density distribution (C) Enlarged view of CO₂ mass density distribution (D) Adsorption simulation equilibrium snapshots (E) Contour plot of the adsorption configuration of CO₂ on functional biochar and weak interaction isosurfaces (F) 50 ps snapshot of CO₂ desorption in the nitrogen-free model (G) 50 ps snapshot of CO₂ surface desorption in the nitrogen-doped mesoporous surface model (H) Mean square displacement and self-diffusion coefficient of adsorbed CO₂ (I) Mean square displacement and self-diffusion coefficient of desorbed CO₂

that urea-assisted hydrothermal pretreatment followed by KOH activation enables the fabrication of functional biochar samples with ordered and concentrated pore size distributions, achieving an optimized hierarchical pore architecture.

Surface morphological features and element distribution. Integrating the N₂ adsorption data and CO₂ capture performance (Figure 4A) of the three functional biochar samples, UHTCK was selected as the representative sample for SEM-EDS analysis to investigate its surface morphology and elemental distribution (Figures 2D & F). The KOH activation process induces a highly corrugated surface morphology with dense pore networks, dominated by pores around 0.12 μm and partial mesopores. EDS quantification reveals a carbon atomic content of 89.96% and a nitrogen content of 3.00%, demonstrating successful nitrogen group incorporation onto the biochar surface and meso/macropores during urea hydrothermal treatment, which facilitates CO₂ diffusion kinetics. Notably, EDS analysis primarily characterizes elemental distribution on macropore surfaces but lacks resolution for micropore morphology and sub-surface elemental mapping, necessitating complementary XPS analysis (discussed later).

Energy spectrum analysis. Figure 3A presents the X-ray Photoelectron Spectroscopy (XPS) spectra of the functional biochar samples, revealing carbon contents of 82.62% and 82.45% for the ACK and UHTCK samples, respectively. These values are significantly higher than that of the ACKU sample, which is attributed to a greater degree of carbon matrix etching. Both nitrogen-doped functional biochar samples demonstrate elevated nitrogen content, approximately three times higher than that of the non-doped

samples. To further elucidate the distribution of functional groups on the surface of the functional biochar, the XPS spectra were deconvoluted in accordance with the reference provided in Table S4 to derive the relative proportions of specific functional groups.

The deconvoluted C1s spectra of functional biochar samples are presented in Figures 3C & F (using UHTCK as the representative sample, hereafter the same). All three samples exhibit dominant C-C bonding configurations ($\geq 82.6\%$), indicative of high aromatic condensation induced by thermal treatment. The O1s spectral analysis (Figure 3D and Table S5) reveals comparable proportions of oxygenated functional groups across samples, with aromatic C-O bonds constituting the primary oxygen species. Notably, a positive correlation exists between O1s content and mesopore volume (Figure 3G), demonstrating preferential localization of oxygen functionalities within mesopores. Distinct nitrogen speciation emerges between ACKU and UHTCK in N1s analysis (Figures 3E & H). ACKU exhibits predominant quaternary nitrogen (72.91%), attributed to urea-derived nitrogen incorporation during KOH/urea co-activation. The hydroxyl-KOH system facilitates urea decomposition, enabling nitrogen insertion into carbon lattices through reactions between amine groups and oxygenated intermediates. This nitrogen subsequently transforms into graphitic nitrogen under high-temperature conditions while being anchored within micropores via KOH etching (Figure 3B). In contrast, the limited porosity of the precursor biomass in UHTCK confines nitrogen doping primarily to mesopores and macropores during hydrothermal treatment. Subsequent KOH activation triggers evaporation of volatile nitrogen compounds, diminishing nitrogen retention in micropores.

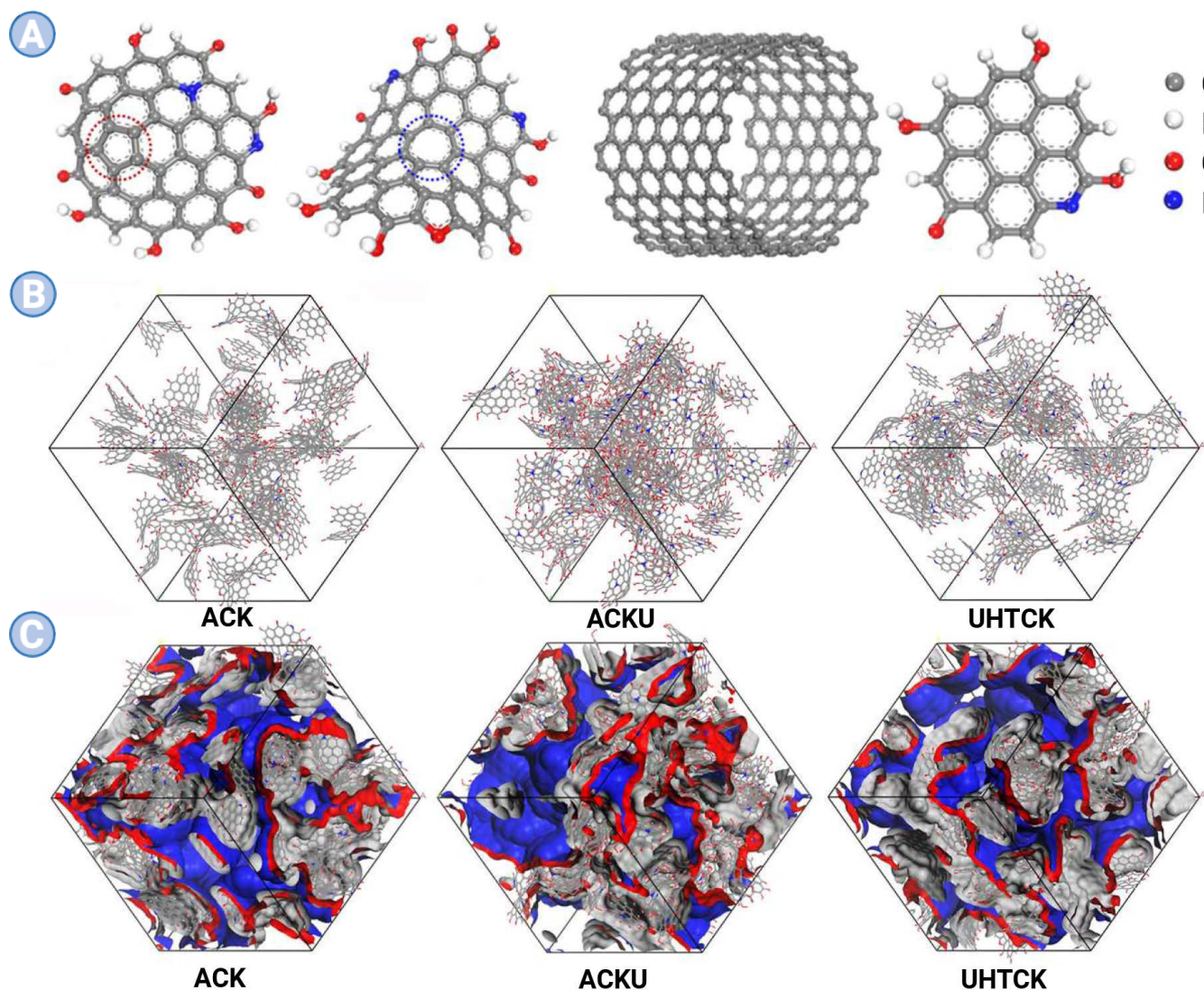


Figure 6. Functional biochar basic units and hierarchical pore-surface functionalization models (A) Basic units (B) Functional biochar models (C) Functional biochar specific surface area and pore volume distribution (blue: solvent surface; red: Connolly surface)

These transformations shift the nitrogen speciation toward pyridone configurations (Figure 3B & H). Coupled with existing TPD evidence demonstrating preferential localization of pyridone nitrogen in larger pores,⁴¹ the pyridinic nitrogen in UHTCK is predominantly distributed within mesopores and macropores. This structural differentiation critically governs CO₂ desorption behavior. UHTCK's surface-bound nitrogen species enhance CO₂ retention through alkaline interactions while enabling rapid desorption kinetics via meso/macropore-mediated diffusion pathways. Specifically, nitrogen-active sites in meso/macropores facilitate CO₂ migration from micropores to surface desorption zones, achieving efficient gas-solid phase separation.

Adsorption and desorption performance of functional biochar

To comprehensively evaluate the CO₂ adsorption performance of the synthesized functional biochar, static CO₂ adsorption tests and adsorption heat calculations were conducted. Figure 4A presents the CO₂ adsorption isotherms for three functional biochar samples. The maximum CO₂ adsorption capacity of UHTCK functional biochar at standard atmospheric pressure (0 °C) is 6.01 mmol/g, attributed to its abundant ultra/micropores and surface nitrogen functional groups. However, at 25 °C, this capacity decreases to 3.4 mmol/g due to the predominance of physical adsorption during the process. Since physical adsorption is an exothermic process, the CO₂ adsorption capacity diminishes with increasing temperature.^{42,43} At low pressure, the CO₂ uptake of ACKU exceeds that of the other two samples, attributed to ultra-

micropore filling and abundant quaternary nitrogen confined within micropores.⁴⁴ However, this adsorption stability at elevated pressures becomes weaker than that of UHTCK. At 0 °C/1 bar, ACK functional biochar exhibits a greater adsorption capacity than ACKU functional biochar; conversely, at 25 °C/1 bar, the relationship reverses. This phenomenon can be attributed to the critical role of ultra-micropores in facilitating physical CO₂ adsorption at lower temperatures, while at higher temperatures, nitrogen functional groups mediate chemical adsorption that moderately influences the CO₂ adsorption capacity of the functional biochar. Consequently, under normal pressure, UHTCK functional biochar, characterized by its ultra/micropore-nitrogen group structure, demonstrates superior adsorption capacity at both temperatures compared to the other two functional biochar samples. The adsorption heat of CO₂ for functional biochar can be determined from the slope of the regression line of the Clausius-Clapeyron equation, as illustrated in Figure 4B. The adsorption heat for all functional biochar samples is less than 40 kJ/mol, indicating that CO₂ adsorption is primarily physical. The trend of adsorption heat for UHTCK with varying adsorption amounts aligns with that of ACK functional biochar but is higher due to the greater abundance of ultra/micropores in UHTCK. Additionally, the pyridone nitrogen adjacent to phenolic hydroxyl sites in the mesopores forms hydrogen bonds with CO₂, releasing a substantial amount of heat. As a result, the adsorption heat in the later stages of adsorption is greater for UHTCK than for ACK functional biochar. The isosteric heat of adsorption for the ACKU functional biochar initially increases

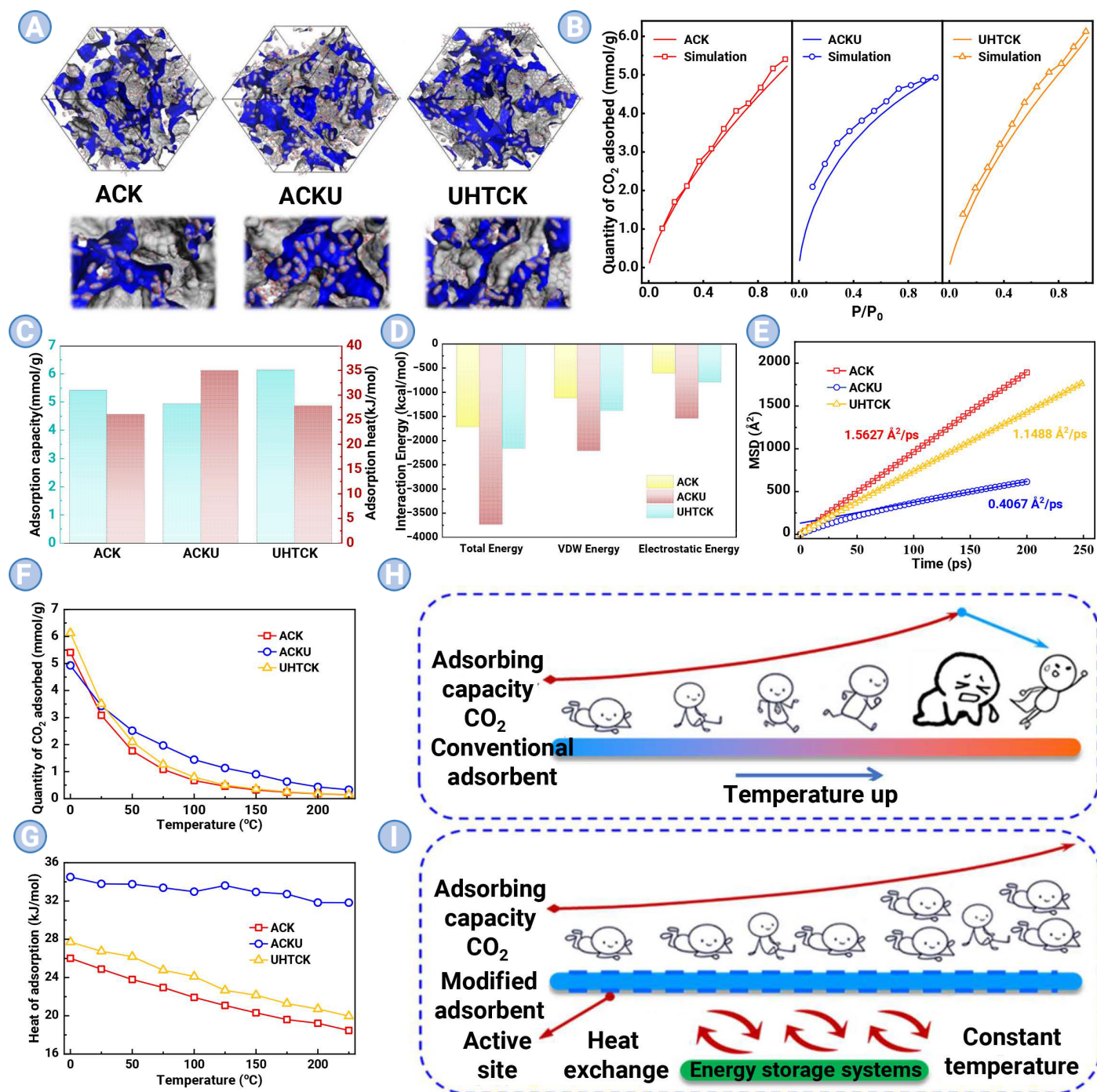


Figure 7. Thermal capacity and CO₂ storage and release characteristics of functional biochar (A) CO₂ adsorption configurations of functional biochar (B) Comparison of experimental and simulated CO₂ adsorption isotherms (C) CO₂ adsorption capacity and average adsorption heat of the functional biochar models (0 °C/1 bar) (D) Interaction energy composition and contributions of CO₂ adsorption in the functional biochar models (0 °C/1 bar) (E) Self-diffusion coefficients of CO₂ (F) CO₂ desorption curve of the functional biochar models (G) CO₂ desorption heat of the functional biochar models (H) Thermal and adsorption variation mechanism (I) Framework for efficient thermal and mass storage/exchange

then decreases with increasing adsorption amount. This trend is attributed to the chemisorption of CO₂ molecules at some highly active surface sites during the low-pressure stage, which releases increasing heat. As adsorption progresses and pressure rises, the occupation of surface pores weakens the van der Waals interactions between CO₂ molecules and the biochar surface, reducing the heat of adsorption. Nevertheless, the adsorption heat remains higher than that of the other two samples. Considering the CO₂ storage space provided by micropores and the contributing effects of nitrogen groups in mesopores through chemical adsorption, UHTCK exhibits superior overall adsorption performance compared to existing research results (Figure 4C),

balancing high adsorption capacity with a structure conducive to easy desorption. Nevertheless, UHTCK demonstrates potential for further enhancement in adsorption capacity.

Cyclic CO₂ adsorption-desorption tests (Figures 4D & F) reveal CO₂ capture capacities of 0.45, 1.05, and 1.12 mmol/g for ACK, ACKU, and UHTCK, respectively, consistent with static equilibrium adsorption results. Progressive structural degradation occurs during cycling, where unstable pore architectures and thermally labile functional groups undergo decomposition, leading to diminished adsorption performance. After 20 cycles, ACK and ACKU exhibit regeneration efficiencies below 90%, whereas UHTCK retains >90%

efficiency, demonstrating superior cyclic stability attributed to weaker CO₂-active site interactions.⁵⁹ The enhanced durability of UHTCK stems from its hydrothermally derived framework: SiO₂ leaching from the biomass matrix during KOH activation selectively etches unstable carbon domains, yielding a robust hierarchical structure with stabilized active sites. Desorption kinetics analysis (Figure S1) further confirms UHTCK's rapid CO₂ uptake via surface basic groups and efficient high-temperature desorption mediated by mesopore-confined nitrogen functionalities. Specifically, alkaline moieties accelerate CO₂ migration from micropores to mesoporous channels, followed by thermal diffusion-driven release. These findings highlight that nitrogen group-mesopore synergy critically governs CO₂ adsorption/desorption kinetics in functional biochar samples.

To elucidate the structure-activity relationships between hierarchical functionalized pores and rapid CO₂ adsorption/desorption in functional biochar samples, comprehensive kinetic analyses were performed using the Langmuir adsorption model, Freundlich thermodynamic model, and modified Dubinin-Radushkevich (D-R) model (Table S6 and Figure S2). The Freundlich and Dubinin-Radushkevich (D-R) models, which demonstrated superior fitting quality, are selected for parameter calculation, with the results summarized in Table S7. At 0 °C, the saturated CO₂ adsorption capacities follow UHTCK > ACKU > ACKU, consistent with the micropore-filling theory of the D-A model, as UHTCK and ACK possess larger micropore volumes and total pore capacities. Although ACKU exhibits lower micropore volume than the other samples, its comparable saturation capacity to ACK originates from mesopore-mediated CO₂ storage via capillary condensation. Collectively, these models confirm that micropores dominate CO₂ adsorption capacity, while mesopores provide supplementary CO₂ storage through capillary condensation effects. The Weber-Morris (W-M) diffusion model was employed to evaluate dynamic adsorption processes (Figure 4E and Table S7). The three-stage nonlinear W-M profiles correspond to sequential mass transfer phases: (1) rapid surface adsorption/diffusion, (2) rate-limiting intra-particle diffusion, and (3) dynamic adsorption-desorption equilibrium. This mechanistic progression aligns with molecular dynamics simulations of CO₂ adsorption (Figure 5D). Notably, UHTCK achieves the fastest surface adsorption rate, effectively minimizing duration in diffusion-limited and equilibrium phases.

The CO₂ adsorption/desorption characteristics of functional biochar arise from the multiscale structural features of their carbon skeletons/morphology, nanoporous channel architectures, and surface-functionalized groups. CO₂ molecules predominantly reside within micropores, while hierarchical architectures comprising meso/macropores facilitate transport pathways, thereby balancing microporous adsorption capacity with mesoporous diffusion kinetics. Nitrogen-containing groups exert directional traction forces to promote CO₂ desorption. Notably, CO₂ diffusion into pore channels initiates only after surface adsorption sites become saturated, with diffusion rates governed solely by pore topology and thermal dynamics. This phenomenon underscores that rational modulation of nanoporous hierarchical frameworks and spatially confined surface functionalities—through enhanced surface-active site density and strategic incorporation of alkaline groups in meso/macropores—optimizes gas-solid interactions. Such engineering enables rapid CO₂ adsorption/desorption kinetics at ambient conditions by synergistically elevating surface adsorption rates while maintaining high storage capacity.

Structure-performance relationship of multi-scale functional biochar in CO₂ adsorption and desorption

To elucidate CO₂ adsorption/diffusion behavior within hierarchical pore channels of functional biochar samples, molecular dynamics (MD) simulations were conducted based on pore size distributions and volumetric data from BET analysis (Table S3 and Figure 5A). A slit-pore model (Figure S3) was constructed with characteristic hierarchical features: mesoporous regions (gray), micropores (pink/red), and graphene-like carbon plates (5×5 nm) containing optimized 0.7 nm micropores for CO₂ storage. Using the Packmol toolkit,⁶⁰ a periodic simulation system (40×50×80 Å³) was established by positioning 100 CO₂ molecules within 10 Å-thick gas layers adjacent to the pore structure. Simulation snapshots (Figure 5D) and relative mass density profiles (Figures 5B & C) demonstrate preferential CO₂ adsorption in 0.7 nm micropores, where overlapping surface potentials induce monolayer confinement. Mesopores exhibit limited CO₂ accumulation near

pore walls. Statistical analyses confirm that hierarchical pore architectures and well-developed micropores critically govern high-capacity CO₂ adsorption. However, this model focuses solely on pore structural effects. Subsequent studies will incorporate surface functional groups and pore-functionality coupling mechanisms to comprehensively decode the intrinsic CO₂ adsorption mechanisms.

The interactions between surface functional groups of functional biochar and CO₂ molecules are investigated via density functional theory (DFT). Five carbon models with distinct N/O functionalities are constructed (Figure S4): pristine functional biochar (FC), pyridinic-N-functionalized (D-FC), pyridonic-N-functionalized (T-FC), hydroxyl-functionalized (O-FC), and quaternary-N-functionalized (Q-FC). Electrostatic potential-guided geometric optimization identifies energy-minimized adsorption configurations (Figure 5E and Figure S5). Two primary CO₂ adsorption configurations are identified: face-on and edge-on adsorption. Geometry optimizations performed between CO₂ and the five functional carbons reveal that edge-on configurations are unstable for both FC and Q-FC, consistently relaxing into face-on adsorption. This indicates that FC and Q-FC do not adopt stable edge-configurations for CO₂; consequently, only face-on adsorption is considered for these models in subsequent analyses. D-FC and T-FC exhibit higher adsorption energies than FC (basal plane: FC = -18.33 kJ/mol, D-FC = -18.66 kJ/mol, T-FC = -19.09 kJ/mol), whereas O-FC and Q-FC show lower basal plane affinity and unstable edge adsorption geometries. To quantify weak interactions, Multiwfn, VMD, and gnuplot are integrated to generate reduced density gradient (RDG) isosurface maps and sign(λ₂) *p* vs. RDG scatter plots (Figure S6). O-FC and T-FC display characteristic spikes near -0.01 a.u. in their RDG profiles, originating from hydroxyl-oxygen/hydrogen interactions at carbon edges. The orange/green isosurfaces correspond to scatter plot spikes at *x* ≈ +0.01 and -0.005, respectively, confirming enhanced hydrogen bonding between hydroxyl groups (electron acceptors) and CO₂ oxygen atoms. This hydroxyl substitution increases hydrogen's electrostatic potential, stabilizing adsorption configurations. Notably, T-FC exhibits a strong hydrogen-bond-related spike (sign(λ₂) *p* = -0.02 a.u.), visualized as blue isosurfaces, indicative of robust donor-acceptor interactions.

The interplay between hierarchical pore structures and confined functional groups in governing CO₂ adsorption/desorption performance is systematically investigated. The hierarchical pore structure of biochar is constructed using an extended magnetic disk model, with the resulting functional carbon building units illustrated in Figure S7A. To simulate CO₂ diffusion within hierarchical pores, a microporous-mesoporous biochar model is developed, employing single-walled carbon nanotubes (SWCNT (15,15)) with 2.1 nm diameter to represent the mesoporous structure. The hierarchical porous biochar and meso/macropore-confined nitrogen-functionalized biochar models (Figure S7B) are simulated in a 70×70×70 Å³ periodic box. The nitrogen-functionalized model in Figure S7B is constructed by determining the total number of nitrogen atoms based on the overall nitrogen content from Figure 3A, while the specific incorporation sites within the unit module are assigned according to the distribution of nitrogen functional groups provided in Figure 3H. Molecular dynamics simulations are conducted at an adsorption temperature of 0 °C and a desorption temperature of 200 °C. The total simulation time was 500 ps with a time step of 1 fs, a cutoff radius of 12.5 Å, and trajectory frames saved every 5000 steps. To obtain an optimized diffusion model, the simulations sequentially employed NVT and NVE ensembles, following which the trajectories are analyzed for diffusivity. Figure 5F-I illustrates CO₂ desorption snapshots, mean square displacements (MSD), and self-diffusion coefficients within these hierarchical models. At elevated temperatures, nitrogen functionalities exhibit stronger affinity toward CO₂ than micropores, generating a directional "tugging" effect. Consequently, nitrogen-doped mesopores demonstrate higher initial diffusion coefficients compared to non-doped counterparts. During the initial adsorption stage, the self-diffusion coefficient of CO₂ in nitrogen-doped mesoporous biochar surpasses that of the non-functionalized model. These findings suggest that hierarchical porosity coupled with confined nitrogen groups synergistically enhances CO₂ surface diffusion, thereby optimizing both adsorption and desorption kinetics.

Analysis of thermal and CO₂ storage and release mechanisms

To investigate the multiscale component coupling effects on CO₂ thermal-mass storage characteristics in functional biochar samples, hierarchical pore-surface functionalization models are developed through synergistic integration of optimized carbon disk architectures and Monte Carlo simulations (Figure 6A). A single-walled carbon nanotube (SWCNT (15, 15)) with a pore diameter of 2 nm is selected to represent the mesoporous structure. Hierarchical pore-surface functionalized models for the three functional carbons (Figures 6B & C) are constructed by randomly packing different numbers of functional carbon base units and SWCNTs into a cubic box, with the pore structure modulated by varying the content of graphene units and carbon nanotubes. The elemental compositions of the ACK, ACKU, and UHTCK models are C₃₂₁₂H₉₅₇N₂₂O₆₂₇, C₃₇₀₅H₉₇₅N₁₁₇O₁₃₂₆, and C₃₃₉₆H₉₆₀N₁₃₂O₆₂₄, respectively, consistent with the experimental XPS data (Figure 3A). The specific surface area and pore volume of the models were characterized using the "Atom Volume & Surfaces" tool, whereby a rigid probe molecule with a radius of 1.84 Å (corresponding to the kinetic diameter of an N₂ molecule) is rolled along the pore surface of the functional carbon models, thereby calculating the specific surface area and pore volume. The specific surface areas and pore volumes calculated via Equations (3) and (4) exhibit excellent agreement with experimental physicochemical characterization data (Table S4), validating the structural fidelity of these computational models. This quantitative consistency confirms the suitability of the proposed multiscale frameworks for mechanistic studies of CO₂ adsorption behavior in functional biochar samples.

$$\text{Surface Area (m}^2\text{/g)} = \frac{\text{Surface Area per cell (}\text{\AA}^2\text{)}}{\text{Density (g/cm}^3\text{)} \times \text{Cell Volume (}\text{\AA}^3\text{)}} \times 10^4 \quad (3)$$

$$\text{Pore Volume (cm}^3\text{/g)} = \frac{\text{Cell Free Volume (}\text{\AA}^3\text{)}}{\text{Density (g/cm}^3\text{)} \times \text{Cell Volume (}\text{\AA}^3\text{)}} \quad (4)$$

The CO₂ adsorption configurations in functional biochar samples (Figure 7A) reveal preferential adsorption within hierarchical pore channels, with predominant localization in micropores (<2 nm). Grand Canonical Monte Carlo (GCMC)-simulated CO₂ adsorption isotherms (Figure 7B) align closely across all three models, validating the predictive accuracy of the constructed frameworks. Quantitative analysis of CO₂ uptake capacities and average adsorption enthalpies at 0 °C/1 bar (Figure 7C and Table S8) shows discrepancies of 3.5%, 1.4%, and 2.5% for the three models, respectively. The enthalpy trend (ACK > ACKU > UHTCK) matches experimental observations. ACKU demonstrates superior low-pressure adsorption performance but diminished capacity at elevated pressures. This behavior originates from micropore-dominated CO₂ storage: unsaturated micropores govern adsorption at low pressures, while saturation effects and limited pore accessibility reduce incremental uptake at higher pressures.

To elucidate the intrinsic mechanisms governing CO₂ adsorption enthalpy, the contributions of van der Waals (vdW) and electrostatic interactions to CO₂ adsorption under ambient conditions are quantitatively analyzed (Figure 7D). All three functional biochar samples exhibit vdW-dominated adsorption mechanisms, supplemented by electrostatic interactions from surface functional groups, including weak hydrogen bonding. The ACKU model demonstrates the highest total interaction energy, with both vdW and electrostatic contributions surpassing those of ACK and UHTCK. This enhanced energy landscape correlates with its elevated adsorption enthalpy and increased desorption energy consumption, reflecting stronger CO₂ retention. In contrast, ACK and UHTCK share analogous pore architectures, resulting in minimal energy distribution differences. Self-diffusion coefficients of adsorbed CO₂ (Figure 7E) further validate these trends: ACKU's strong CO₂ retention corresponds to high adsorption enthalpy and low diffusivity, whereas ACK's limited functionalization yields weak retention and maximal diffusivity. UHTCK exhibits intermediate diffusivity, balancing adsorption capacity with moderate interaction strength and reduced desorption energy consumption—a pattern corroborated by temperature-programmed desorption profiles and enthalpy curves (Figures 7F & G). CO₂ adsorption proceeds via coupled thermal-mass dynamics involving adsorption-induced exothermicity, heat accumulation, and desorption equilibrium (Figure 7H). Strategic integration of hierarchical porosity, surface functionalities, and thermal regulation units enables

simultaneous high-capacity CO₂ capture and efficient thermo-mass storage-regulation concept under ambient conditions (Figure 7I). This mechanistic analysis reveals that hierarchical microporous frameworks with rationally designed surface groups achieve multi-objective optimization: high adsorption capacity, low thermal hysteresis, and rapid adsorption-desorption kinetics through balanced gas-thermo coupling. However, more detailed temperature distribution simulations and experimental validation will require further studies to establish a more robust foundation for refining the synthesis of functional adsorbent materials.

CONCLUSIONS

1. UHTCK exhibits narrowly distributed micropores with optimized hierarchical pore architecture, demonstrating a CO₂ adsorption capacity of 6.01 mmol/g at 0 °C. Its moderate adsorption enthalpy ensures high uptake while minimizing desorption energy consumption, achieving a 92.05% regeneration efficiency after 20 cycles, which highlights exceptional cyclic stability.

2. CO₂ adsorption on functional biochar is governed by multiscale factors, where intra-particle diffusion acts as the rate-limiting step. Synergistic pore-functionality configurations enable rapid CO₂ adsorption by reducing diffusion barriers and equilibrium time. At elevated temperatures, surface alkaline groups facilitate CO₂ desorption from micropores via thermally driven diffusion pathways.

3. Edge functionalization enhances surface polarity, promoting electrostatic-driven weak interactions (e.g., hydrogen bonding). In slit-pore models, CO₂ predominantly occupies 0.7 nm micropores as monolayers, while mesopores retain limited CO₂ accumulation near pore walls. Hierarchical porosity and developed micropores are critical for high-capacity adsorption, whereas nitrogen-doped mesopores optimize diffusion-mediated adsorption/desorption kinetics.

4. High microporosity enables substantial CO₂ storage capacity, while nitrogen-functionalized surfaces and mesopores achieve thermodynamically balanced adsorption-heat coupling required for adsorption-compression CO₂ energy storage systems. This strategic integration achieves dual optimization: ambient-condition rapid adsorption/desorption kinetics and high storage capacity through regulated gas-thermo interactions.

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AUTHOR CONTRIBUTIONS

All authors contributed to the manuscript and approved the final version.

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

Data are available from the corresponding author upon reasonable request.

SUPPLEMENTAL INFORMATION

It can be found online at: <https://doi.org/10.59717/j.xinn-energy.2026.100131>