

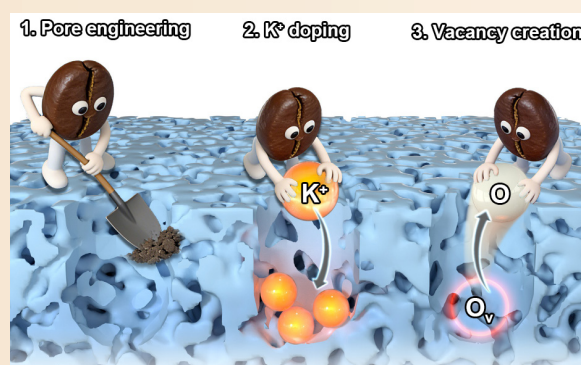
Spent coffee grounds as multifunctional modifiers for triple-synergistic enhancement of Li_4SiO_4 ceramic sorbents in high-temperature CO_2 capture

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ABSTRACT: Practical deployment of Li_4SiO_4 as a high-temperature CO_2 sorbent requires pelletization, which inevitably densifies the microstructure and imposes severe CO_2 diffusion limitations. Conventional sacrificial pore-forming agents address this issue but remain single-purpose, serving solely as structural templates without conferring chemical benefits. Here, we demonstrate that spent coffee grounds (SCGs), an abundant food-industry waste, can serve as a single-source modifier that achieves three colocalized enhancements in Li_4SiO_4 pellets: hierarchical pore engineering, *in situ* K-doping, and oxygen vacancy generation. The thermal decomposition of SCG creates an interconnected hierarchical macroporous network that effectively reduces intraparticle CO_2 diffusion resistance. Meanwhile, the mineral-rich SCG ash provides *in situ* potassium doping, generating a localized eutectic molten carbonate phase that accelerates liquid-phase ion transport. Crucially, the transient reducing atmosphere during biomass combustion introduces oxygen vacancies into the silicate lattice; density functional theory (DFT) calculations reveal that these vacancies serve as highly active CO_2 adsorption sites with a strongly exothermic adsorption energy of -0.914 eV. Benefiting from this triple-synergistic enhancement, the SCG-modified sorbent (LSO-50) achieves a CO_2 adsorption capacity of 0.275 g/g at 650°C under 15 vol% CO_2 , representing a more than fourfold improvement over unmodified pellets. When further combined with Na_2CO_3 codoping to promote additional eutectic formation, the optimized sorbent (LSON-50) reaches 0.330 g/g, retains 0.284 g/g after 50 adsorption–desorption cycles, and exhibits robust mechanical stability ($< 10\%$ attrition loss). By collocating structural, chemical, and defect features within a single biomass-derived modifier, this work establishes a scalable waste-valorization route for high-performance, eco-friendly CO_2 capture.

KEYWORDS: Li_4SiO_4 ceramic sorbent; CO_2 adsorption; spent coffee grounds (SCGs); hierarchical porous structure; potassium doping; oxygen vacancies



1 Introduction

The escalating concentration of atmospheric CO_2 has intensified the urgency for developing efficient carbon capture technologies [1–5]. Among the various solid sorbents available, lithium orthosilicate (Li_4SiO_4) has emerged as a promising candidate for high-temperature CO_2 capture, owing to its high theoretical adsorption capacity of 36.7 wt%, excellent thermal stability, and more favorable thermodynamic properties compared to calcium-based sorbents [6–9]. However, the practical deployment of Li_4SiO_4 in industrial fluidized bed reactors is significantly hindered by intrinsic engineering trade-offs. While fine powders exhibit

superior kinetics in laboratory settings, industrial applications mandate the use of robust pellets to prevent elutriation and minimize pressure drop [10–12]. However, the densification of powders into mechanically stable ceramic pellets during high-temperature sintering inevitably reduces the specific surface area [13–15]. This structural densification increases the intraparticle diffusion resistance of CO_2 , resulting in sluggish adsorption kinetics and reduced conversion efficiency over prolonged cycling.

To alleviate these diffusion limitations, researchers have extensively explored the incorporation of sacrificial pore-forming agents into Li_4SiO_4 precursors to engineer porous structures. For instance, Yang *et al.* [16] employed graphite molding, where the

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burnout of graphite particles creates macroscopic pores to facilitate gas transport. Fu *et al.* [17] achieved a high CO₂ adsorption capacity of 0.3 g/g by utilizing polyvinyl alcohol (PVA), which generated abundant spherical pores. Similarly, Hu *et al.* [18] reported that rice husk templating enhanced the adsorption capacity to 0.210 g/g, nearly double that of unmodified pellets. However, a key limitation of these conventional agents is that they typically yield a monomodal pore size distribution dictated by the uniform size of the additive particles. Such a uniform pore structure often lacks the interconnected hierarchical network essential for minimizing diffusion resistance. Moreover, these agents function merely as sacrificial templates, contributing solely to physical porosity without imparting any chemical benefits to the final sorbent [16,19]. Furthermore, the use of refined synthetic polymers increases production costs and raises environmental concerns regarding their sourcing and processing. In parallel, substantial research efforts have focused on improving the intrinsic adsorption kinetics of Li₄SiO₄ through alkali metal doping [20,21]. Studies have demonstrated that the introduction of potassium or sodium species can significantly accelerate CO₂ uptake by forming eutectic molten salts that promote lithium-ion mobility and facilitate the carbonation reaction [22,23]. However, this enhancement typically requires an additional doping step using alkali metal carbonates, thereby complicating the synthesis procedure and increasing material costs. This raises the question of whether a single additive can simultaneously create hierarchical porosity and provide beneficial chemical modification.

Biomass-derived materials present a promising avenue to reconcile these dual requirements. Among various agricultural and food industry wastes, spent coffee grounds (SCGs) emerge as a particularly attractive candidate [24–26]. Despite being one of the most abundant food industry wastes globally, their potential as multifunctional modifiers for ceramic CO₂ sorbents remains largely unexplored. Unlike conventional synthetic pore formers, SCG possesses three distinctive advantages that align perfectly with the requirements of high-performance Li₄SiO₄ pellets [27–30]. First, the inherent lignocellulosic structure of SCGs features interconnected cell walls and natural pores, which can template biomorphic hierarchical porosity upon thermal decomposition. Second, the mineral-rich ash residue of SCGs, containing approximately 20–40 wt% potassium along with magnesium, calcium, and phosphorus, enables *in situ* alkali metal doping without additional chemical precursors. Third, as a waste stream with negligible economic value, SCG provides a cost-effective and environmentally benign alternative. To the best of our knowledge, the use of SCG as a multifunctional modifier for Li₄SiO₄ ceramic pellet fabrication has not been reported.

Herein, we report a single-step strategy to fabricate robust, chemically activated Li₄SiO₄ pellets using SCG as a single-source, multifunctional modifier. By investigating the effect of SCG content, we elucidate a triple-synergistic mechanism encompassing hierarchical porosity engineering, *in situ* K-doping, and oxygen vacancy formation. While pore engineering, K-doping, and oxygen vacancies have each been individually explored in Li₄SiO₄ studies, the conventional approach of mixing separate additives often leaves the resulting structural and chemical features randomly distributed at the microscopic scale. The fundamental novelty of using SCG lies in the precise colocalization of all three enhancements within the sorbent. As an SCG particle undergoes thermal decomposition to template a macroscopic pore, its inherent K-rich ash is naturally deposited on the inner walls of that pore, and the localized combustion concurrently generates oxygen vacancies at the same interface.

This built-in colocalization delivers a true synergistic enhancement that goes beyond what physical mixing of separate additives can achieve. This work not only provides a high-performance material for CO₂ capture but also proposes a scalable waste-to-material strategy for designing functional ceramics through defect and impurity engineering.

2 Experimental

2.1 Materials

Lithium hydroxide monohydrate (LiOH·H₂O, ≥ 98%), tetraethyl orthosilicate (TEOS, analytical grade), and sodium carbonate (Na₂CO₃, analytical grade) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. SCGs were collected from commercial coffee capsules (Nestlé Nespresso SA, Lausanne, Switzerland). Anhydrous ethanol and deionized water were utilized as the solvent and hydrolysis initiator, respectively. All commercial chemicals were used as received without further treatment.

2.2 Preparation of Li₄SiO₄ sorbents

The overall fabrication procedure of the SCG-modified Li₄SiO₄ pellets is schematically illustrated in Fig. 1. The Li₄SiO₄ precursor powder was synthesized via a sol-gel method. Specifically, LiOH·H₂O and TEOS were dissolved in anhydrous ethanol under continuous magnetic stirring. To compensate for lithium volatilization during high-temperature sintering and to ensure stoichiometric formation of the target Li₄SiO₄ phase, a slight excess of lithium was maintained (Li : Si molar ratio of 4.1 : 1). Deionized water was then rapidly injected into the solution to initiate hydrolysis and induce gelation. The resulting gel was dried at 120 °C for 24 h and subsequently ground. This intermediate powder was then calcined at 200 °C to yield the Li₄SiO₄ precursor.

Prior to use, the raw SCGs were dried at 80 °C for 24 h and sieved through a 200-mesh screen. To prepare the modified Li₄SiO₄ sorbents, the as-prepared precursor powder and the sieved SCGs were homogeneously mixed in an agate mortar at designated mass ratios. Subsequently, 10 wt% Na₂CO₃ was introduced to synergize with the intrinsic K in SCG, forming a lower-melting Na/K eutectic carbonate phase that accelerates CO₂ diffusion [31]. This specific dosage, established as optimal in prior Li₄SiO₄ studies [31,32], balances the need for a continuous eutectic liquid phase (requiring > 5 wt%) against the risk of severe sintering and pore blockage (occurring at > 15 wt%). Crucially, this 10 wt% dosage was kept constant across all SCG loadings to isolate SCG content as the sole variable because the eutectic formation between Na₂CO₃ and *in situ* Li₂CO₃ is largely independent of the SCG-derived K. Following this addition, deionized water was mixed to form a homogeneous paste, which was then uniaxially pressed into pellets using a tungsten carbide die. Finally, the green pellets were sintered at 800 °C for 120 min (heating rate: 5 °C/min), cooled to 500 °C at 3 °C/min and then naturally cooled to room temperature to obtain the target porous sorbents. The as-synthesized samples were designated as LSON-*x* or LSO-*x*, where “N” indicates the intentional incorporation of Na₂CO₃ and the suffix “*x*” denotes the mass fraction of the SCG additive (e.g., 10, 30, 50, or 70 wt%). For instance, LSON-10 refers to the Li₄SiO₄ sorbent co-modified with 10 wt% SCGs and the standard 10 wt% Na₂CO₃ dopant.

2.3 CO₂ sorption/desorption tests

The CO₂ capture performance was evaluated using a

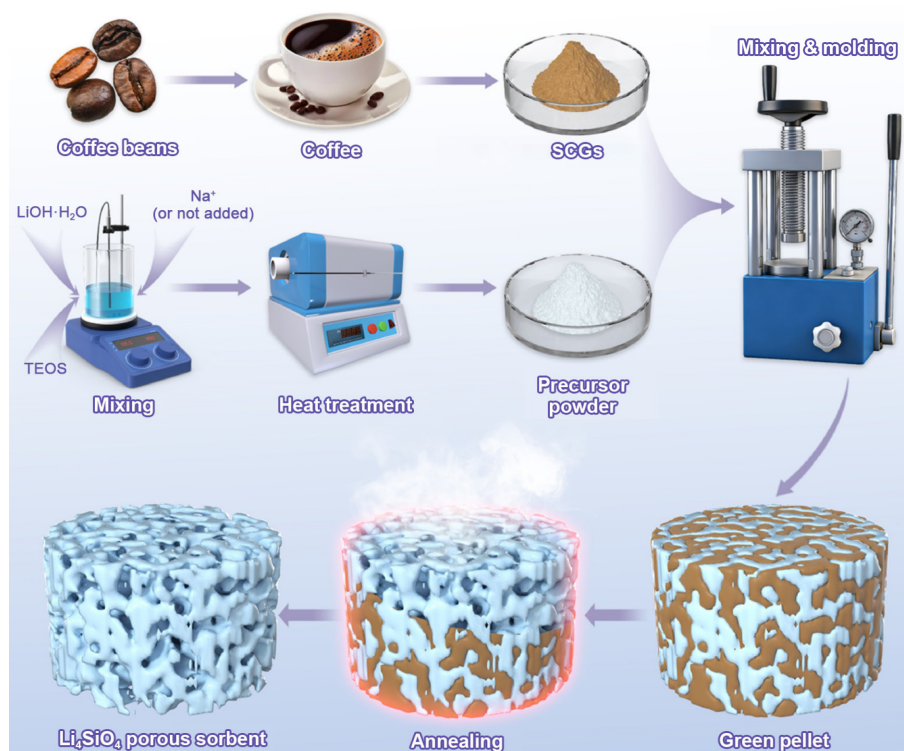


Fig. 1 Schematic illustration of the fabrication process for Li_4SiO_4 porous sorbents.

thermogravimetric analyzer (TG-209F1, Netzsch, Germany). To determine the optimal operating temperature window, dynamic TG analysis was conducted by heating ~ 10 mg of sample from room temperature to 1000°C at $10^\circ\text{C}/\text{min}$ under 15 vol% CO_2 (balanced with N_2). Isothermal adsorption tests were then performed at selected temperatures under 15 vol% CO_2 to assess the maximum capture capacity. This concentration was chosen to approximate the CO_2 content of postcombustion flue gas from coal-fired power plants (typically 12–15 vol%) and has been widely adopted as a benchmark condition in the Li_4SiO_4 sorbent literature [21,22,33,34].

Cyclic stability under practical conditions was evaluated using a dual-zone fixed-bed reactor (OTF-1200X-II, Shenzhen Kejing Zhida Technology Co., Ltd., China) [34]. The sample boat was reciprocated between the adsorption and desorption zones. Each cycle consisted of an adsorption stage at 650°C under 15 vol% CO_2 for 30 min, followed by a desorption stage at 750°C under pure N_2 for 15 min. A constant total gas flow rate of 1 L/min was maintained throughout the testing procedure. This N_2 -purge desorption protocol was adopted to align with standard practices in the Li_4SiO_4 literature, allowing for a direct comparison of cyclic performance with previously reported pellet-form sorbents.

2.4 Characterization techniques

The elemental composition of the SCGs was quantitatively analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES; iCAP PRO, Thermo Fisher Scientific, USA). The crystal structure of the as-prepared samples was identified using an X-ray diffractometer (XRD; D8 Advance, Bruker, Germany) in the 2θ range of 10° – 80° . Microstructural characterization was performed by scanning electron microscopy (SEM; JIB-4700, JEOL, Japan). Attrition resistance was assessed using a CS-2 friability tester following standard test protocols [35]. To evaluate the mechanical stability of the prepared pellets for potential fluidized-bed applications, the single-pellet compressive strength was measured using a digital force gauge/universal testing

machine (AGS-X Series, Shimadzu Europa GmbH, Germany). Electron paramagnetic resonance (EPR) spectroscopy was conducted on a JES-FE3X spectrometer (JEOL, Japan) operating at X-band frequency (9.5 GHz) to detect paramagnetic oxygen vacancy centers in the sintered sorbents. The measurements were performed at room temperature with a modulation frequency of 100 kHz, a magnetic field modulation amplitude of 5 G, and a microwave power of 20 mW. The surface chemical states and oxygen vacancies of the samples were characterized by X-ray photoelectron spectroscopy (XPS; K-ALPHA, Thermo Fisher Scientific, USA).

2.5 DFT calculations

All spin-polarized density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP 6.3.0) [36]. The exchange-correlation energy was described by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [37]. The interactions between valence electrons and ionic cores were treated using the projector augmented-wave (PAW) method and pseudopotentials [38,39]. A plane-wave kinetic energy cutoff of 400 eV was employed. Brillouin zone integration was performed using a $3 \times 3 \times 1$ Monkhorst–Pack k -point grid for surface slab calculations. Structural relaxations were continued until the total energy change and the maximum residual force on each atom converged to below 10^{-6} eV and 0.03 eV/Å, respectively.

Based on prior studies demonstrating that the (010) surface of Li_4SiO_4 possesses the lowest surface formation energy among all low Miller index surfaces [40], this surface was selected for all CO_2 adsorption simulations. A slab model was constructed by cleaving the fully relaxed bulk structure along the (010) direction. Three surface models were constructed to systematically assess the individual and combined effects of K-doping and oxygen vacancy formation, as motivated by the experimental observations: (i) a stoichiometric Li_4SiO_4 (010) surface (model a), (ii) a K-substituted surface in which one Li site is replaced by a K atom (model b:

$\text{Li}_4\text{SiO}_4\text{-K}$), and (iii) a K-substituted surface additionally containing one oxygen vacancy (model c: $\text{Li}_4\text{SiO}_4\text{-K-O}_v$). The CO_2 adsorption energy (E_{ads}) for each model was calculated according to Eq. (1):

$$E_{\text{ads}} = E_{\text{CO}_2 + \text{Li}_4\text{SiO}_4(010)} - E_{\text{CO}_2} - E_{\text{Li}_4\text{SiO}_4(010)} \quad (1)$$

where $E_{\text{CO}_2 + \text{Li}_4\text{SiO}_4(010)}$ is the total energy of the system, E_{CO_2} is the energy of a single CO_2 molecule, and $E_{\text{Li}_4\text{SiO}_4(010)}$ is the energy of a pure sorbent.

3 Results and discussion

3.1 Characterizations of raw materials and sintered sorbents

Figure 2(a) shows the SEM image of the SCGs, revealing a fragmented and irregular morphology with a rough surface texture. The particle size distribution is broad, spanning from submicrometer to tens of micrometers. This broad size distribution is beneficial for creating hierarchical pore structures: the interstitial voids between large particles serve as macropores for gas transport, while the burnout of fine particles generates mesopores that increase the accessible surface area. Moreover, the rough surface, with its inherent cracks and microdefects, may serve as nucleation sites for pore formation during thermal decomposition, potentially yielding a more interconnected pore network than smooth-surfaced synthetic polymers such as PVA.

The phase composition of the SCGs was analyzed by XRD, as

shown in Fig. 2(b). The pattern exhibits broad diffraction peaks, indicating low crystallinity and suggesting that the sample is primarily composed of small crystalline domains dispersed within an amorphous matrix. The pattern reflects contributions from cellulose, hemicellulose, lignin, and residual oils inherent in the structure of the SCGs [41]. Specifically, a weak shoulder at $\sim 16.4^\circ$ is attributed to the overlap of arabinan (a hemicellulose polysaccharide) with the (110) reflection of cellulose. The peak at $\sim 21.48^\circ$ corresponds to overlapping contributions from hemicellulose polysaccharides (e.g., arabinogalactans and glucomannans) and lignin. The broad hump between 30° and 40° further corroborates the amorphous character of the cellulosic component. To complement the structural analysis, EDS elemental mapping of the SCGs is presented in Figs. 2(c)–2(g). In addition to the dominant carbon and oxygen signals from the lignocellulosic framework, the mapping reveals a homogeneous distribution of inorganic species, including potassium and calcium. The uniform distribution of potassium is particularly significant, as it enables homogeneous *in situ* doping during high-temperature sintering. For quantitative analysis, ICP-OES measurements were performed on both raw SCG and its calcined ash (Table 1). The raw SCG contains K, Ca, Mg, and P at the subpercent level (0.310, 0.110, 0.085, and 0.048 wt%, respectively), reflecting their distribution within the organic matrix. After thermal decomposition of the organic framework at 800°C , these mineral elements become substantially concentrated in the residual ash, which is dominated by K (31.45 wt%, corresponding to ~ 38 wt% K_2O), followed by Ca, Mg, and P at 7.33, 4.29, and

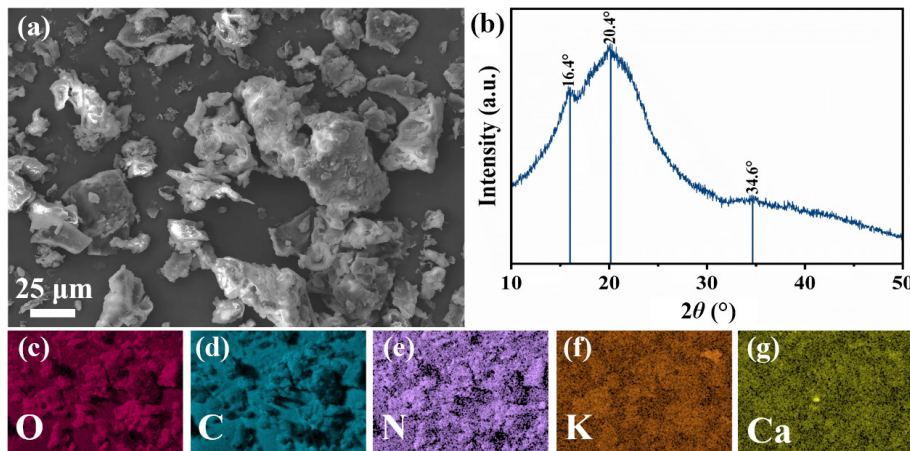


Fig. 2 Characterization of SCGs: (a) SEM image, (b) XRD pattern, and (c)–(g) EDS elemental maps showing the distribution of C, O, N, K, and Ca.

Table 1 Elemental composition of raw SCG and SCG ash obtained after calcination at 800°C , determined by ICP-OES

(Unit: mg/kg)

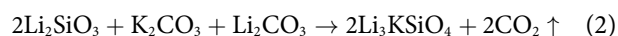
Element	Raw SCG	SCG ash
K	3127	314,521
Ca	1101	73,254
Mg	850	42,911
P	475	28,637
S	1323	22,709
Fe	47	8339
Al	9	7218
Si	n.d.	3786
Mn	23	2168
Na	50	1499

Note: Other trace elements (B, Ba, Cr, Cu, Li, Mo, Nd, Ni, Rb, Sr, Ti, Zn, and Zr) were each detected at concentrations below 1000 mg/kg in ash and below 100 mg/kg in raw SCG. Si was determined only in the calcined ash. Conversion: 1 wt% = 10,000 mg/kg.

2.86 wt% (~10 wt% CaO, ~7 wt% MgO, and ~7 wt% P_2O_5 , respectively). This distribution is in good agreement with previously reported SCG ash analyses [42,43], confirming the representativeness of our SCG source. Although SCG composition is known to vary with source (e.g., coffee species, roasting degree, and brewing method), the dominance of K as the principal mineral constituent is a consistent feature across all reported SCG ash analyses, indicating that the *in situ* K-doping strategy proposed in this work should be reproducible across moderately varied SCG sources. Consequently, K serves as the principal active alkali species for *in situ* doping into the Li_4SiO_4 lattice during sintering. In contrast, owing to the inherently low ash yield of SCG (~1.5 wt%), the absolute amounts of Ca, Mg, and P contributed to the final sorbent matrix are correspondingly low. The as-synthesized precursor powder exhibits a heterogeneous morphology (Fig. 3(a)), consistent with its multiphase composition identified by XRD (Fig. 3(b)). The characteristic peaks are assigned to lithium metasilicate (Li_2SiO_3), residual lithium hydroxide (LiOH), and lithium carbonate (Li_2CO_3), confirming that the sol-gel process facilitated a preliminary reaction among the raw materials. EDS mapping (Figs. 3(c) and 3(d)) further reveals a uniform distribution of Si and O, indicating good compositional homogeneity favorable for the subsequent solid-state reaction.

Since the final sorbents are fabricated by cosintering the precursor powder with SCGs, understanding their thermal behavior is essential for optimizing the sintering protocol. Figures 4(a) and 4(b) illustrate the TG and DTG profiles of the raw SCGs and the Li_4SiO_4 precursor, respectively. As shown in Fig. 4(a), the thermal decomposition of SCGs proceeds in three distinct stages. The initial weight loss below 150 °C corresponds to the evaporation of physically adsorbed water. The second and most significant stage, occurring between 200 and 500 °C, is attributed to the volatilization and oxidative decomposition of organic components, including hemicellulose, cellulose, and lignin. Above 500 °C, the weight curve plateaus, indicating complete removal of the organic skeleton and leaving behind the inorganic ash residue. In contrast, the Li_4SiO_4 precursor (Fig. 4(b))

exhibits a delayed reaction window. Following a minor dehydration step, the major weight loss initiates above 500 °C and extends to approximately 750 °C. This weight loss corresponds to the solid-state reaction among the intermediate phases to form the target Li_4SiO_4 phase. This temporal mismatch, in which the template decomposes before the ceramic phase consolidates, is favorable for pore preservation, as diffusion channels are established prior to framework densification. Based on these results, 800 °C was selected as the optimal sintering temperature for the composite pellets to ensure complete removal of the pore former, full crystallization of the Li_4SiO_4 phase, and preservation of the hierarchical porous structure. To further probe the interaction between SCG and the Li_4SiO_4 precursor during sintering, TG-DTG analysis was also performed on a mixture of the precursor powder and 50 wt% SCG (Fig. 4(c)). In addition to the mass-loss features inherited from each pure component, a distinct new DTG peak emerges at ~568 °C, which is absent in either pure SCG (Fig. 4(a)) or the pure precursor (Fig. 4(b)). This new peak is attributed to the K-mediated formation of Li_3KSiO_4 through a molten K–Li carbonate intermediate, following Reaction (2):



Specifically, the K released from SCG ash forms a Li_2CO_3 – K_2CO_3 eutectic with the precursor at 500 °C [32], generating a reactive molten phase that converts Li_2SiO_3 into Li_3KSiO_4 with concurrent CO_2 release. This eutectic-mediated synthesis route, enabled by the K introduced from SCG, can be further verified by examining the phase composition of the resulting LSON sorbents.

To investigate the effect of SCG content on the phase composition of the sintered sorbents, XRD patterns of samples with different SCG loadings (10, 30, 50, and 70 wt%) were obtained, as shown in Fig. 4(d). All samples contained a fixed amount of 10 wt% Na_2CO_3 as a dopant and were sintered at 800 °C. For clarity, the samples are denoted as LSON-10, LSON-30, LSON-50, and LSON-70, corresponding to their respective SCG contents of 10, 30, 50, and 70 wt%. For LSON-10 and LSON-

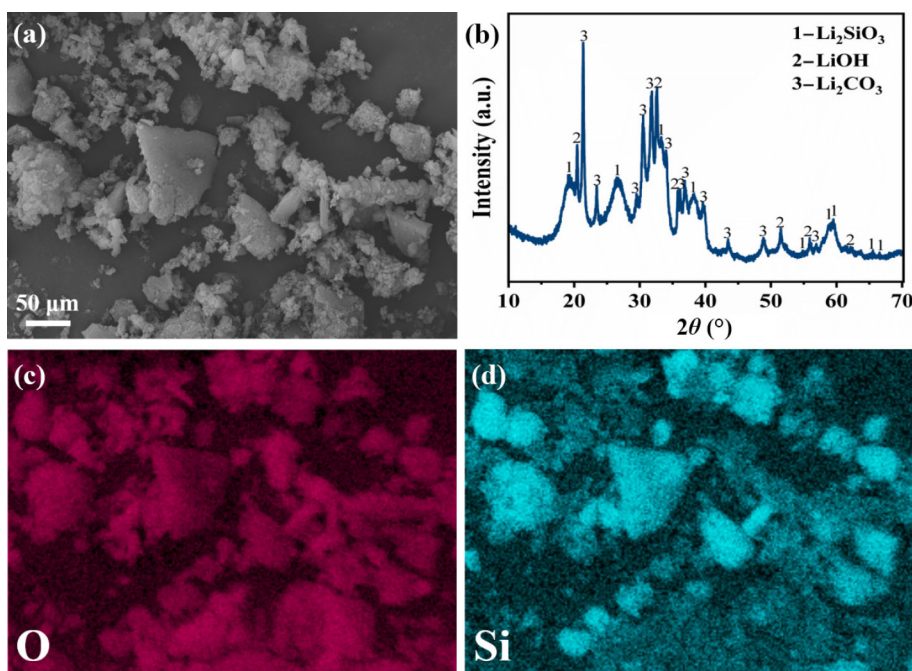


Fig. 3 Characterization of the as-synthesized Li_4SiO_4 precursor powder: (a) SEM image, (b) XRD pattern, and (c, d) EDS elemental maps of Si and O.

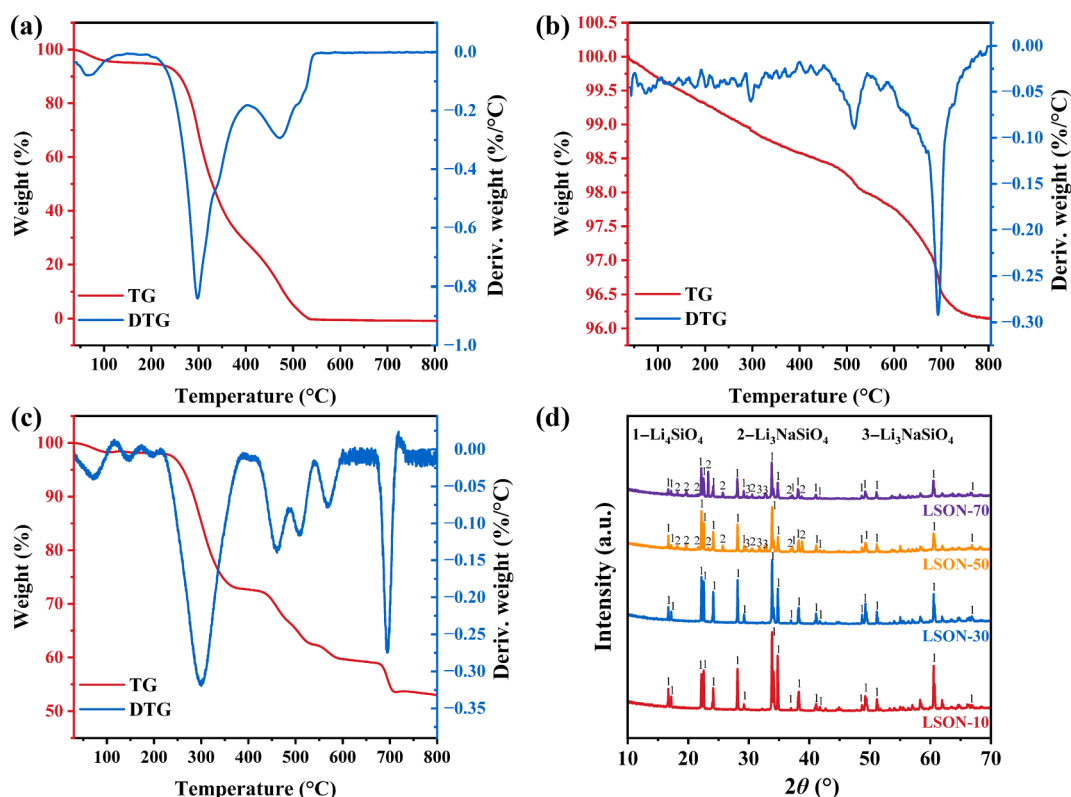


Fig. 4 Thermal analysis and phase identification: TG/DTG profiles of (a) raw SCG, (b) Li_4SiO_4 precursor, and (c) mixture of Li_4SiO_4 precursor and 50 wt% SCG; (d) XRD patterns of LSON sorbents sintered at 800 °C with different SCG loadings.

30, all diffraction peaks match well with the standard Li_4SiO_4 pattern (JCPDS:37-1472), confirming the formation of phase-pure Li_4SiO_4 . This result indicates that moderate SCG additions (≤ 30 wt%) do not interfere with the crystallization of the target phase, and the organic template is completely removed during sintering without leaving any detectable residues or secondary phases. However, when the SCG content increases to 50 and 70 wt%, additional peaks corresponding to $\text{Li}_3\text{NaSiO}_4$ and Li_3KSiO_4 appear in the XRD patterns of LSON-50 and LSON-70. The formation of $\text{Li}_3\text{NaSiO}_4$ is attributed to the incorporation of Na^+ from the Na_2CO_3 dopant into the Li_4SiO_4 lattice, where Na^+ partially substitutes for Li^+ sites. Meanwhile, the emergence of Li_3KSiO_4 is attributed to the potassium inherently present in the SCG mineral ash, as confirmed by EDS mapping. At higher SCG loadings, the increased concentration of K^+ released during the burnout of the organic template promotes the formation of this potassium-containing phase. Notably, both $\text{Li}_3\text{NaSiO}_4$ and Li_3KSiO_4 can form low-melting-point eutectic carbonates with Li_2CO_3 , which is beneficial for improving CO_2 adsorption performance. In addition, no Ca-, Mg-, or P-related diffraction peaks were detected even at the highest SCG loading, consistent with the low absolute amounts of these elements introduced via SCG (Table 1).

The microstructural evolution of the sintered sorbents with different SCG contents was examined by SEM, as shown in Figs. 5(a1)–5(d1). LSON-10 exhibits a relatively dense surface with only a few uniformly dispersed micrometer-sized pores. The pore size corresponds well to the original SCG particle dimensions observed in Fig. 2(a), confirming that the pores originate from SCG burnout rather than CO_2 release during phase transformation. As the SCG content increases to 30, 50, and 70 wt%, the pore density increases significantly, and the pore size also becomes larger. LSON-50 and LSON-70 display highly porous structures with interconnected macropores, which are

expected to provide abundant gas transport channels for CO_2 capture. The elemental distribution of the sintered samples was further analyzed by EDS mapping (Figs. 5(a2)–5(d7)). All sintered LSON samples exhibit a uniform distribution of Si, O, Na, K, Ca, and Mg throughout the matrix. Although no Ca- or Mg-containing crystalline phases are identified by XRD at any SCG loading, both elements are clearly detected by EDS, indicating that Ca and Mg are present either in an amorphous form or as minor lattice dopants at concentrations below the XRD detection limit. Importantly, the homogeneous distribution of all elements demonstrates that sol-gel synthesis combined with the SCG templating approach achieves good compositional homogeneity even at high SCG loadings.

3.2 Pore structure and mechanical properties

To further evaluate the pore structure characteristics of different sorbents, N_2 adsorption-desorption measurements were performed. As shown in Fig. 6(a), all samples exhibit type IV isotherms according to the IUPAC classification, indicating a predominantly mesoporous structure. At low relative pressures (P/P_0), the adsorption quantity increases gradually, corresponding to monolayer-to-multilayer adsorption. When $P/P_0 > 0.45$, a distinct hysteresis loop appears, which is attributed to capillary condensation of N_2 within the mesopores. Comparing the different samples, the saturation adsorption capacity in the plateau region exhibits an overall increasing trend as the SCG content rises from 10 to 70 wt%. LSON-70 demonstrates the highest N_2 uptake, implying the largest total pore volume, whereas LSON-10 exhibits the lowest. The pore size distributions calculated by the Barrett-Joyner-Halenda (BJH) method are presented in Fig. 6(b). All samples display a sharp, high-intensity peak in the 2–5 nm range, indicating that the material system retains a uniform and abundant structure of primary small mesopores regardless of the additive amount. However, significant differences emerge in the

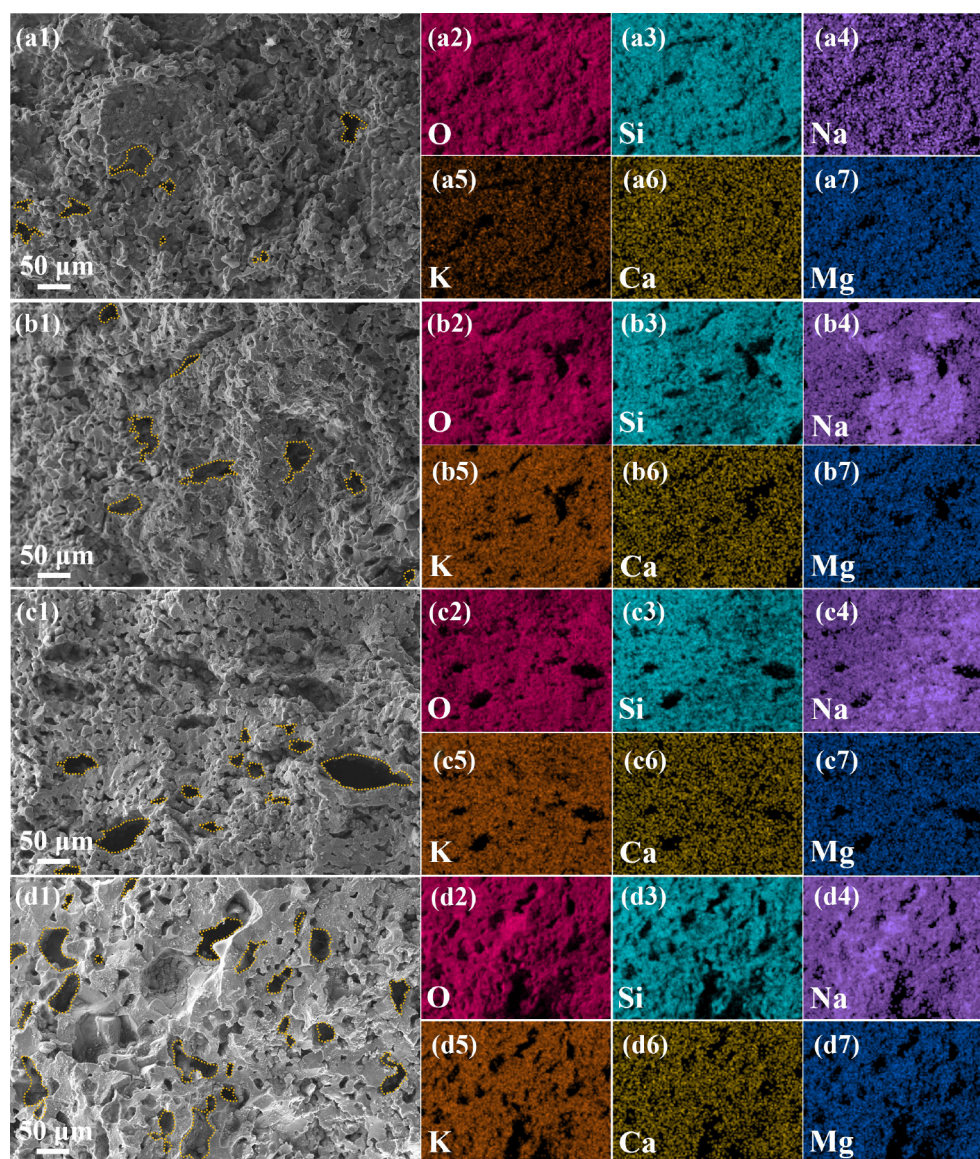


Fig. 5 (a1–d1) SEM images and (a2–d7) EDS elemental maps of sintered LSON-10, LSON-30, LSON-50, and LSON-70 sorbents.

pore diameter range greater than 10 nm. For LSON-10 and LSON-30, the distribution in this region is relatively flat. In distinct contrast, both LSON-50 and LSON-70 exhibit prominent secondary peaks in the larger mesopore region (10–50 nm). This multimodal distribution confirms that increasing the SCG content to ≥ 50 wt% induces a hierarchical pore structure characterized by the coexistence of small primary mesopores and large secondary transport channels. This interconnected hierarchical network is crucial for minimizing diffusion resistance during the CO_2 capture process.

For practical deployment in industrial fluidized bed reactors, sufficient mechanical robustness of the sorbent pellets is essential to prevent elutriation. Figure 6(c) illustrates the cumulative mass loss of the LSON sorbents during mechanical attrition tests (up to 3000 rotations). For all samples, the mass loss increases monotonically, with a slightly higher initial rate attributed to the shedding of loosely bound surface particles. Importantly, the attrition rate increases progressively with SCG loading. After 3000 rotations, the mass loss increases from 6.11% for LSON-10 to 9.82% for LSON-50, all of which demonstrate satisfactory attrition resistance, with mass losses remaining below 10%. In stark contrast, LSON-70 undergoes substantially greater structural

degradation, with its mass loss sharply increasing to 14.06%. This progressive decline in mechanical strength is a direct consequence of the microstructural evolution discussed above. While excessive SCG loading (70 wt%) generates a highly interconnected macroporous network, it fundamentally weakens the solid skeletal framework of the ceramic pellets. These results indicate that to preserve sufficient mechanical endurance for long-term fluidization operations, SCG addition should be restricted to a moderate level. To further characterize the mechanical properties of the LSON sorbents, single-particle compressive strength tests were performed (Fig. 6(d)). The compressive strength decreases monotonically with increasing SCG content, from 14.05 MPa for LSON-10 to 7.81 MPa for LSON-30, 2.16 MPa for LSON-50, and only 0.088 MPa for LSON-70. This trend mirrors the attrition behavior described above (Fig. 6(c)) and confirms that the strength-porosity trade-off governs the mechanical response of the SCG-templated sorbents. LSON-50 retains a compressive strength of 2.16 MPa, exceeding the typical industrial threshold (> 2 MPa) required for fluidized-bed operation. In stark contrast, LSON-70 has a compressive strength two orders of magnitude lower than LSON-50, indicating that it is not suitable for practical applications.

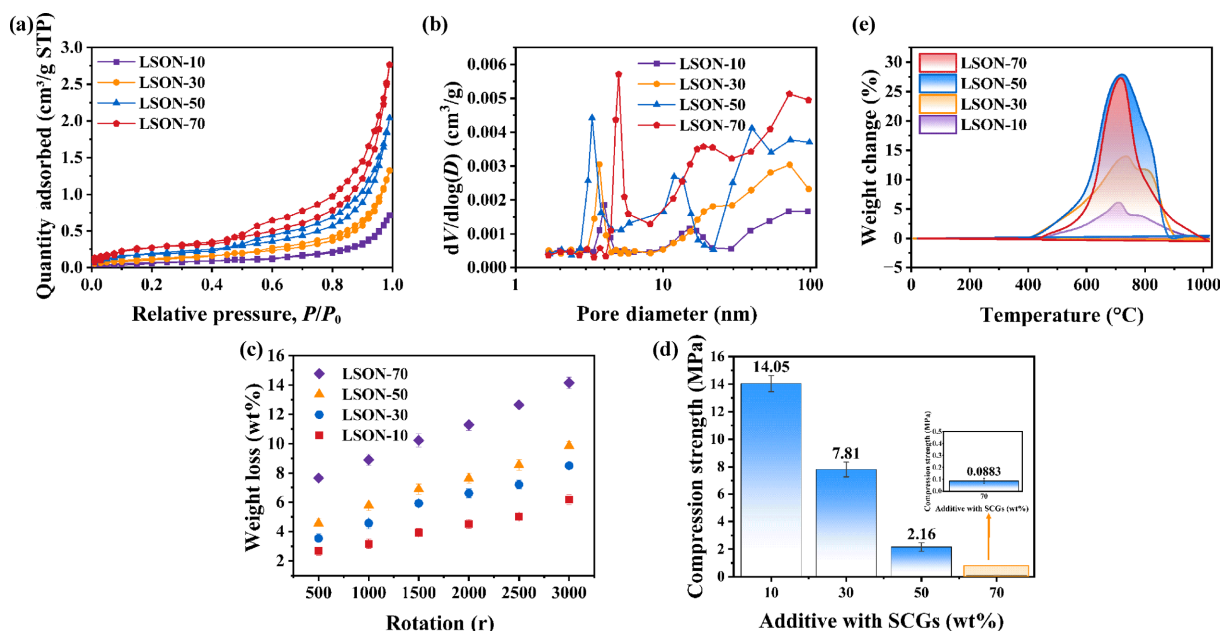


Fig. 6 Pore structure analysis of LSON sorbents: (a) N_2 adsorption-desorption isotherms; (b) BJH pore size distributions; (c) cumulative mass loss of LSON sorbents as a function of rotation number during mechanical attrition tests; (d) single-particle compressive strength of LSON sorbents; (e) dynamic TG weight change curves of LSON sorbents recorded under 15 vol% CO_2 during programmed heating.

3.3 CO_2 adsorption performance and cyclic stability

To evaluate the CO_2 capture performance of the modified sorbents, dynamic TG analyses and isothermal adsorption tests were conducted under 15 vol% CO_2 , simulating typical industrial flue gas conditions. As depicted in the dynamic weight change curves (Fig. 6(e)), the carbonation reaction ($Li_4SiO_4 + CO_2 \rightarrow Li_2CO_3 + Li_2SiO_3$) for all samples generally initiates at approximately 400–450 °C. LSON-10 exhibits a severely restricted adsorption capacity, with a maximum weight gain of only ~6.1%. This poor performance is a direct consequence of its dense microstructure and low pore volume, which severely hinder CO_2 mass transfer. In stark contrast, as the SCG content increases, the dynamic capture performance improves dramatically. LSON-50 demonstrates the best dynamic performance, reaching a remarkable peak weight gain of ~28.0%. This improvement is attributed to the hierarchical pore structure, which facilitates rapid gas transport. However, further increasing the SCG content to 70 wt% results in a slight decrease in peak capacity, suggesting that excessive porosity does not yield further kinetic benefits, potentially due to localized structural instability or inefficient gas channeling. When the temperature exceeds the peak, the weight curves sharply decline for all samples, indicating that the endothermic desorption reaction becomes thermodynamically dominant.

To further elucidate the adsorption kinetics and equilibrium capacities, isothermal adsorption tests were performed at various constant temperatures (550, 600, 650, and 700 °C), as shown in Figs. 7(a)–7(d). The adsorption capacity of all samples is significantly limited at 550 and 600 °C. According to the double-shell model [44–46], the initial reaction generates a dense Li_2CO_3 product shell on the surface of the unreacted Li_4SiO_4 core. At these lower temperatures, the solid Li_2CO_3 shell imposes substantial resistance to the solid-state diffusion of Li^+ and O^{2-} , leading to premature kinetic stagnation. However, as the temperature rises to 650 °C, the adsorption curves exhibit two distinct stages, specifically, an extremely rapid initial mass increase followed by a gradual plateau. The pronounced enhancement in

kinetics and capacity is largely attributed to the *in situ* K and Na doping. At elevated temperatures, the doped alkali metals form a localized eutectic molten carbonate phase that effectively softens the product shell, transforming the sluggish solid-state ion diffusion into significantly faster liquid-phase mass transfer. Nevertheless, when the temperature is elevated to 700 °C, the equilibrium adsorption capacity experiences a noticeable decline. This reduction is governed by chemical thermodynamics; since the carbonation of Li_4SiO_4 is an exothermic reaction, higher temperatures inherently shift the reaction equilibrium toward the desorption side, thereby limiting the maximum achievable CO_2 adsorption capacity.

Among the tested samples, LSON-10 and LSON-30 reach equilibrium capacities of ~11.1 wt% and ~19.5 wt% at 650 °C, respectively, and still exhibit sluggish mass-transfer kinetics. In sharp contrast, LSON-50 (Fig. 7(c)) not only achieves an exceptional maximum weight gain of ~33.0 wt% but also reaches its adsorption plateau in less than 30 min. LSON-70 (Fig. 7(d)) shows similarly rapid kinetics but yields a slightly lower final capacity of ~31.3 wt%. The extraordinary performance of LSON-50 clearly stems from a synergistic dual-enhancement mechanism, wherein the interconnected hierarchical macropores minimize the gas-phase diffusion resistance of CO_2 into the pellet interior, and the *in situ* formed eutectic molten carbonates effectively transform the sluggish solid-state ion diffusion into rapid liquid-phase mass transfer.

Based on the isothermal adsorption results, 650 °C was identified as the optimal operating temperature and thus selected for the subsequent 50-cycle durability test (Fig. 8). All modified sorbents demonstrate favorable cyclic stability throughout the extended testing period. Interestingly, a distinct activation phenomenon is observed during the initial stages, particularly for the highly porous samples. For instance, the adsorption capacity of LSON-50 gradually increases from 0.316 g/g in the first cycle to a peak of 0.330 g/g in the 10th cycle. This initial enhancement is commonly attributed to the progressive redistribution of the eutectic molten salts and the gradual penetration of CO_2 , which steadily activate the deeper, unreacted Li_4SiO_4 cores. Following

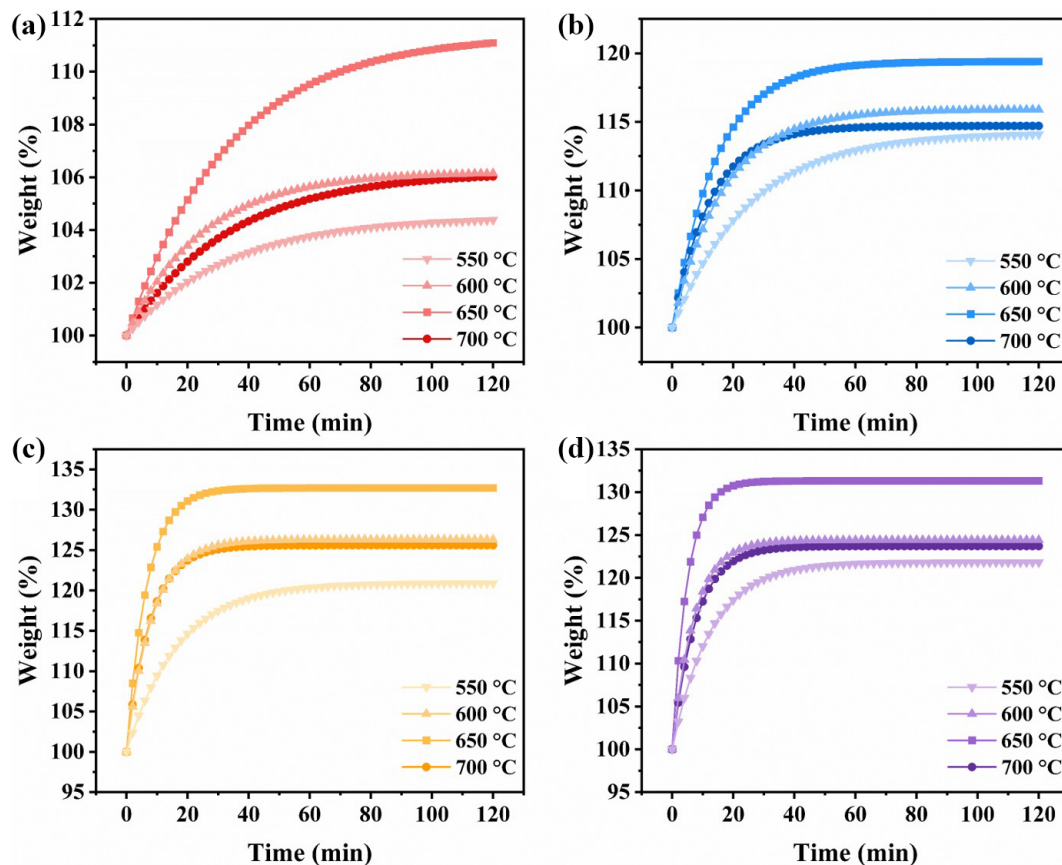


Fig. 7 Isothermal CO_2 adsorption profiles of (a) LSON-10, (b) LSON-30, (c) LSON-50, and (d) LSON-70 at 550, 600, 650, and 700 °C under 15 vol% CO_2 .

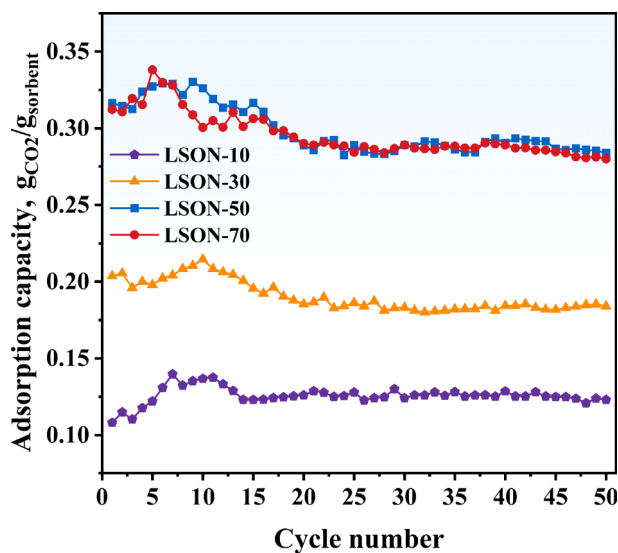


Fig. 8 Cyclic CO_2 adsorption-desorption performance of LSON sorbents over 50 consecutive cycles at 650 °C/750 °C under 15 vol% CO_2/N_2 .

this activation phase, a slight capacity decay is observed in the subsequent cycles, which is primarily attributed to the inevitable thermal sintering of the sorbent and the consequent partial blockage of microscopic diffusion pathways under prolonged high-temperature exposure. Nevertheless, after 50 complete cycles, LSON-50 retains a high capacity of 0.284 g/g, significantly outperforming the denser LSON-10 and LSON-30 sorbents, which yield only 0.123 g/g and 0.184 g/g, respectively. Although LSON-70 exhibits a comparable capacity of 0.280 g/g, its severe mechanical degradation makes LSON-50 a superior and more

reliable choice for long-term operation. This capacity-mechanical trade-off can be quantified against widely adopted industrial benchmarks for fluidized-bed operation (compression strength > 2 MPa, attrition loss < 10 wt%) [33]. LSON-10, LSON-30, and LSON-50 satisfy both criteria, while LSON-70 fails on both counts, with values of 0.088 MPa and 14.06 wt%, respectively. The relationship is highly nonlinear: increasing SCG from 10 to 50 wt% delivers a 2.3-fold capacity gain, from 0.140 to 0.330 g/g, at the cost of an 85% reduction in compression strength, from 14.05 to 2.16 MPa, and a 61% rise in attrition loss, from 6.11 to 9.82 wt%. A further increase to 70 wt%, however, yields no additional capacity, while the compression strength collapses by another 96%, dropping to 0.088 MPa. LSON-50 thus sits at the edge of this engineering window, combining near-saturated CO_2 capacity with mechanical performance just above industrial requirements.

To elucidate the microstructural origins of this excellent cyclic durability, the morphologies and elemental distributions of the sorbents after 50 cycles were examined (Fig. 9). A comparison of the postcyclic SEM images (Figs. 9(a1)–9(d1)) with those of the fresh samples (Fig. 5) reveals a certain degree of grain growth and surface agglomeration. This localized sintering is an inevitable consequence of the repeated melting and solidification of the eutectic carbonate phase at high operational temperatures. However, crucially, the interconnected hierarchical macroporous framework in LSON-50 (Fig. 9(c1)) and LSON-70 (Fig. 9(d1)) remains largely intact. According to the classical double-shell model [44], the continuous formation of the Li_2CO_3 and Li_2SiO_3 product shell is accompanied by a significant molar volume expansion, which typically induces severe pore blockage and performance degradation in conventional dense sorbents. In the present system, the robust macroporous network originally templated by the SCGs serves as a physical buffer zone that

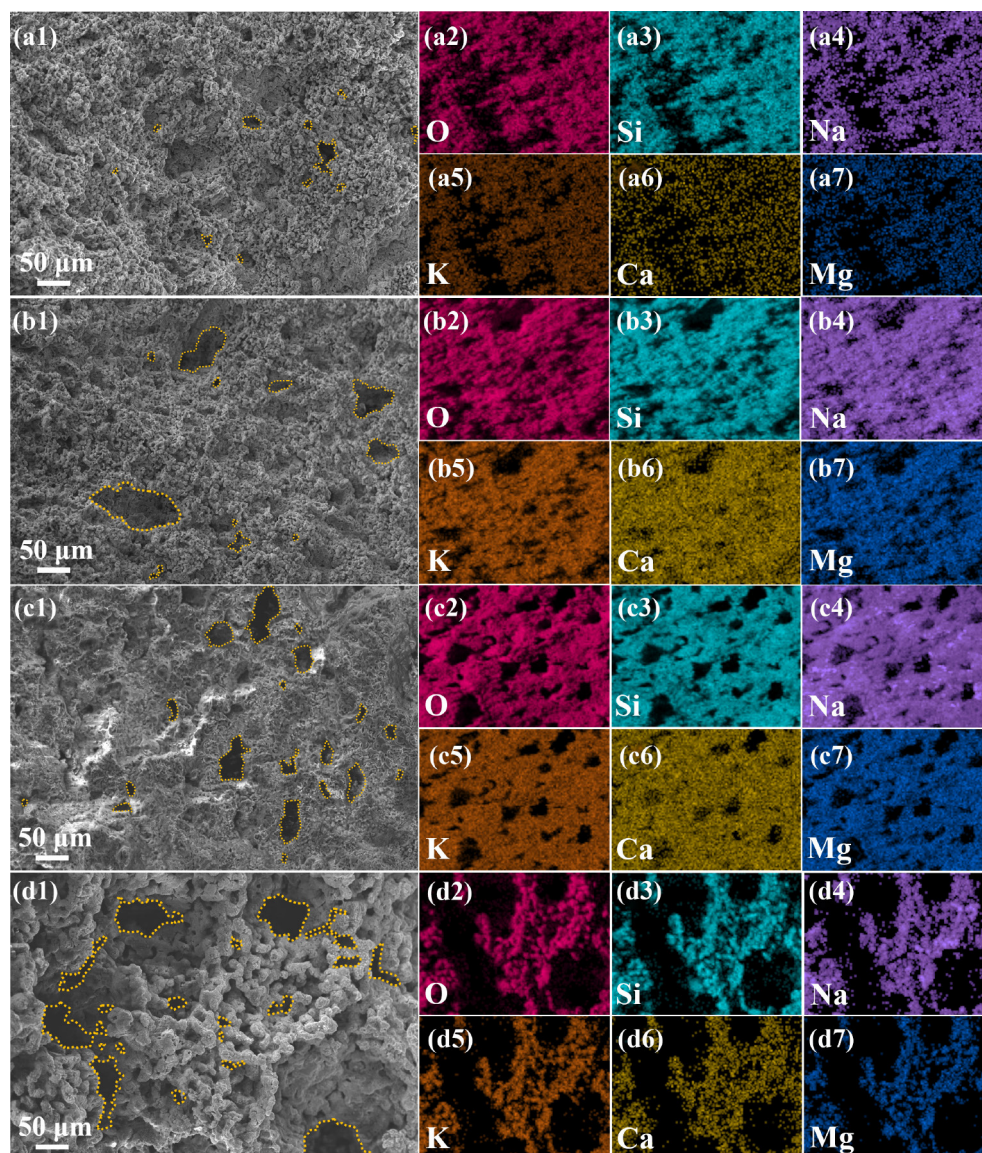


Fig. 9 Postcyclic microstructural characterization: (a1–d1) SEM images and (a2–d7) EDS elemental maps of LSON sorbents after 50 adsorption–desorption cycles.

successfully accommodates this structural swelling. This crucial structural resilience prevents the closure of internal channels, thereby sustaining rapid CO_2 diffusion pathways over prolonged cycling. Furthermore, the corresponding post-cyclic EDS mapping images confirm that the key elements (Si, O, Na, K, Ca, and Mg) remain uniformly dispersed throughout the matrix. The absence of severe elemental segregation ensures the stable and continuous formation of the eutectic molten carbonate phase, ultimately guaranteeing the reliable long-term CO_2 capture performance of the LSON-50 pellets.

3.4 Mechanism of SCG modification

The outstanding CO_2 capture performance of LSON-50 demonstrates the effectiveness of the SCG-based modification strategy. However, because LSON-50 contains both 50 wt% SCG and an external 10 wt% Na_2CO_3 dopant, the individual contributions of each component cannot be individually assessed. To decouple these effects and systematically establish the underlying enhancement mechanisms, two reference samples were prepared: LSO-0 (pure Li_4SiO_4 without any additives) and LSO-50 (Li_4SiO_4 modified with 50 wt% SCG only, without Na_2CO_3 incorporation).

The phase compositions of the three samples, as revealed by XRD (Fig. 10(a)), provide the first layer of mechanistic insight. LSO-0 displays exclusively the characteristic diffraction peaks of phase-pure Li_4SiO_4 , serving as the unmodified baseline. In the LSO-50 pattern, additional peaks corresponding to Li_3KSiO_4 clearly emerge, unambiguously confirming that the potassium inherent in the SCG mineral ash is released during sintering and spontaneously incorporated into the silicate lattice. This finding confirms that *in situ* K-doping can be achieved without the addition of any external chemical precursor. Additionally, the LSON-50 pattern is included in Fig. 10(a) for comparison, and its phase composition has been discussed in Section 3.1.

Isothermal CO_2 adsorption tests at 650 °C (Fig. 10(b)) translate these structural differences into quantifiable performance outcomes. The unmodified LSO-0 pellet captures only ~6.5 wt% CO_2 within 120 min, a result consistent with the dense, low-porosity microstructure that severely restricts gas-phase mass transfer and imposes a substantial solid-state diffusion barrier. In marked contrast, LSO-50 achieves a weight gain of ~27.5 wt%, representing a more than fourfold improvement over LSO-0. This substantial improvement clearly establishes SCG addition as the dominant driver of performance enhancement. To verify whether

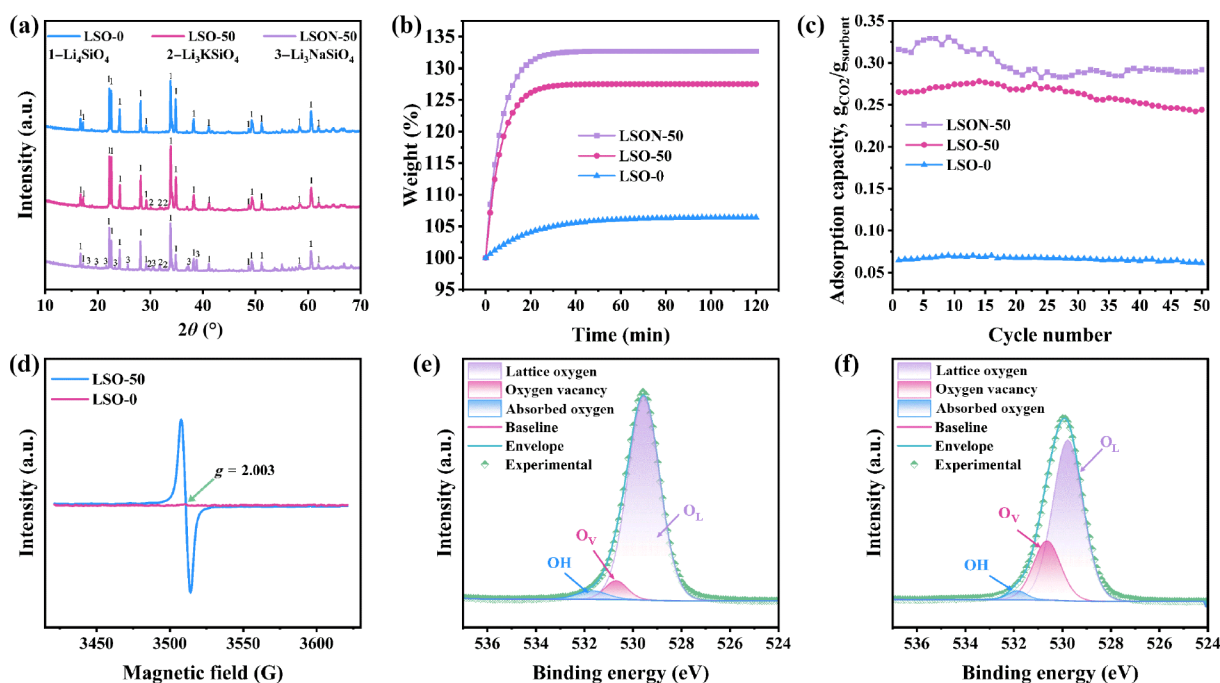


Fig. 10 (a) XRD patterns of LSO-0, LSO-50, and LSON-50; (b) isothermal CO_2 adsorption comparison at 650 °C; (c) cyclic CO_2 adsorption-desorption performance of LSO-0, LSO-50, and LSON-50 over 50 consecutive cycles at 650/750 °C under 15 vol% CO_2/N_2 ; (d) EPR spectra confirming oxygen vacancy formation in LSO-50; (e) LSO-0 and (f) LSO-50, deconvoluted into O_L , O_V , and surface hydroxyl/OH components.

this performance hierarchy persists under realistic long-term operation, extended 50-cycle adsorption-desorption tests were performed on LSO-0, LSO-50, and the Na_2CO_3 codoped LSON-50 (Fig. 10(c)); capacities reported in g/g hereafter to follow the convention of cyclic studies). LSO-0 remains nearly inactive throughout cycling, with a capacity hovering approximately 0.062–0.068 g/g, consistent with its dense, low-porosity microstructure. LSO-50 reaches a peak capacity of 0.275 g/g at cycle 14 and retains 0.244 g/g after 50 cycles (~88% of peak), confirming that the fourfold capacity improvement from SCG modification is preserved over extended cycling. LSON-50 reaches a peak of 0.330 g/g at cycle 10 and retains 0.284 g/g after 50 cycles (~87% of peak). The comparable retention rates between LSO-50 and LSON-50 (~87–88%) further indicate that the supplementary capacity contribution from Na_2CO_3 is preserved throughout cycling without compromising long-term stability. The remaining ~5.5 wt% gap between LSO-50 and LSON-50 observed in the isothermal test, equivalent to an ~0.05 g/g supplementary capacity that is consistently maintained throughout cycling, reflects the supplementary contribution of Na_2CO_3 codoping, which is supported by two literature-established mechanisms. First, the coexistence of Na, K, and Li carbonates enables the formation of a Li_2CO_3 – Na_2CO_3 – K_2CO_3 ternary eutectic that melts at approximately 397 °C [47], substantially below the 500 °C Li–K binary eutectic accessible from SCG-derived K alone [32]. This lower-melting ternary phase exhibits reduced viscosity and faster Li^+ transport, thereby accelerating the diffusion of Li^+ through the product Li_2CO_3 shell during carbonation. Second, Na^+ incorporation generates $\text{Li}_3\text{NaSiO}_4$, an additional CO_2 -reactive secondary phase that participates reversibly in CO_2 sorption [31], in contrast to the less reactive K-containing analogs. The presence of $\text{Li}_3\text{NaSiO}_4$ in LSON-50, confirmed by XRD (Fig. 4(d)), provides direct structural evidence consistent with this mechanism. Together, these two complementary pathways account for the supplementary capacity gain from LSO-50 to LSON-50. Beyond K, SCG also introduces trace amounts of Mg and Ca via its

mineral ash, and the potential role of these elements warrants a brief clarification. Guo *et al.* [22] reported that high doping levels of Mg (15 wt%) or Ca (25 wt%) can enhance the initial CO_2 uptake of Li_4SiO_4 but compromise its cyclic stability. In the present system, however, the absolute Mg and Ca contents are far lower: based on the ICP-OES quantification and the inherently low ash yield of SCG (~1.5 wt%), the Mg and Ca contents in LSON-50 are estimated to be well below 0.1 wt% each in the final sorbent, roughly two orders of magnitude lower than the doping levels at which such effects have been reported. The contribution of Mg and Ca to the performance of LSON-50 is therefore expected to be negligible.

Beyond the pore-forming and K-doping effects of SCG established above, it is important to investigate whether the high-temperature combustion of carbonaceous biomass also introduces activation effects at the atomic scale. During the burnout of SCG, the organic constituents undergo oxidative decomposition, transiently generating a localized carbon-rich, oxygen-deficient atmosphere within the ceramic matrix. Such carbothermic conditions are known to promote the extraction of lattice oxygen from metal oxides, potentially creating point defects in the sintered framework. To verify this hypothesis, EPR spectroscopy was employed to probe the presence of unpaired electrons associated with such defects (Fig. 10(d)). The pristine LSO-0 sample shows a featureless baseline, characteristic of a structurally ordered lattice. In contrast, the SCG-modified LSO-50 sample displays a sharp, intense resonance signal centered at a g -value of approximately 2.003—a spectroscopic fingerprint widely assigned to paramagnetic oxygen vacancy (O_V) centers in oxide ceramics. This finding provides direct experimental evidence that the thermal decomposition of SCG induces oxygen vacancy formation within the Li_4SiO_4 framework, introducing a third, fundamentally distinct enhancement mechanism beyond simple pore templating and alkali doping. To further verify the presence of oxygen vacancies and investigate the surface chemistry, X-ray photoelectron spectroscopy (XPS) of the O 1s region was

performed on LSO-0 and LSO-50 (Figs. 10(e) and 10(f)). Following standard analytical conventions for oxide ceramics, the spectra were deconvoluted into three components: lattice oxygen (O_L) at ~ 529.6 eV, defect oxygen adjacent to O_v at ~ 531.0 eV, and surface-adsorbed oxygen or hydroxyl groups (OH) at ~ 532.0 eV. Although lattice oxygen dominates both samples, the O_v component is markedly more pronounced in LSO-50 than in LSO-0. This distinct spectral broadening toward a higher binding energy indicates a clearly elevated concentration of defect oxygen. Therefore, the XPS observations provide robust surface-chemical evidence that independently corroborates the EPR signal at $g = 2.003$, confirming the SCG-induced formation of oxygen vacancies in the Li_4SiO_4 framework.

To elucidate how these oxygen vacancies contribute to CO_2 capture at the atomic level, DFT calculations were performed on the thermodynamically favorable (010) surface of Li_4SiO_4 . Three surface models were constructed based on the experimental observations: a defect-free surface (model a: Li_4SiO_4), a K-substituted surface in which one Li site is replaced by K (model b: Li_4SiO_4-K), and a K-substituted surface additionally containing one oxygen vacancy (model c: $Li_4SiO_4-K-O_v$), as shown in Figs. 11(a)–11(c). The corresponding CO_2 adsorption configurations are presented in Figs. 11(d)–11(f), with the calculated E_{ads} directly annotated, revealing a clear, progressive trend. On the perfect Li_4SiO_4 surface, the adsorption energy is slightly positive (+0.079 eV), indicating that the interaction between a CO_2 molecule and the stoichiometric lattice is thermodynamically unfavorable, and chemisorption relies entirely on thermal activation rather than intrinsic surface affinity. Upon K substitution (Li_4SiO_4-K), the adsorption energy shifts to a negative value (−0.283 eV), demonstrating that K incorporation not only modifies bulk ion transport but also directly enhances the surface binding affinity for acidic CO_2 molecules, consistent with the well-known Lewis base character of K-enriched surfaces. When an oxygen vacancy is additionally introduced ($Li_4SiO_4-K-O_v$), the adsorption energy drops substantially to −0.914 eV. This highly exothermic adsorption energy indicates that the electrons trapped at the oxygen vacancy site, as evidenced by the EPR signal at $g = 2.003$, provide additional electron density that strengthens the surface affinity for CO_2 adsorption. This behavior is consistent with previous studies on ceramic CO_2

sorbents. For example, DFT calculations on CaO have shown that oxygen vacancies enhance the CO_2 adsorption energy by approximately 1.81-fold relative to the pristine surface [48], and Na^+ -induced oxygen vacancies in CaO-based sorbents have been experimentally demonstrated to significantly improve cyclic CO_2 capture performance [49]. These observations across diverse oxide systems [50,51] support our interpretation that the oxygen vacancies generated in Li_4SiO_4 contribute substantively to its enhanced CO_2 uptake.

We acknowledge that the DFT model employed here is an idealized representation of the complex experimental system. The calculations were performed on the Li_4SiO_4 (010) surface with isolated point defects (K substitution and oxygen vacancies). This is a well-established methodology for assessing atomic-level chemical interactions in alkali-silicate and metal-oxide CO_2 sorbents [40,50,51]. While minor secondary phases (Li_3NaSiO_4 and Li_3KSiO_4) emerge at higher SCG loadings, they share the same orthosilicate structural motif as Li_4SiO_4 . Therefore, they are expected to interact with CO_2 through analogous alkali-substitution and oxygen-vacancy mechanisms rather than through fundamentally different chemistries. The model therefore serves as a per-site mechanistic probe that complements, rather than replaces, the macroscopic measurements.

The experimental and theoretical results converge on a coherent triple-synergistic mechanism (Fig. 12): (i) at the structural level, SCG burnout creates a hierarchical pore network that accelerates CO_2 diffusion and buffers the molar volume expansion during cycling; (ii) at the chemical level, *in situ* K-doping generates eutectic molten carbonates that transform solid-state ion diffusion into rapid liquid-phase transport; (iii) at the defect level, oxygen vacancies introduced by carbothermic reduction substantially strengthen the surface affinity for CO_2 chemisorption. Beyond delivering three individual enhancements, this triple-synergistic mechanism gains its full effectiveness from the colocalization of the three contributions within the same microscopic regions. Because the SCG skeleton, its mineral ash, and the localized reducing atmosphere all originate from the same particle, the resulting macropores, eutectic carbonates, and oxygen vacancies form along the inner walls of the same diffusion channels. Incoming CO_2 molecules therefore encounter active chemical capture sites immediately upon entering the macropores,

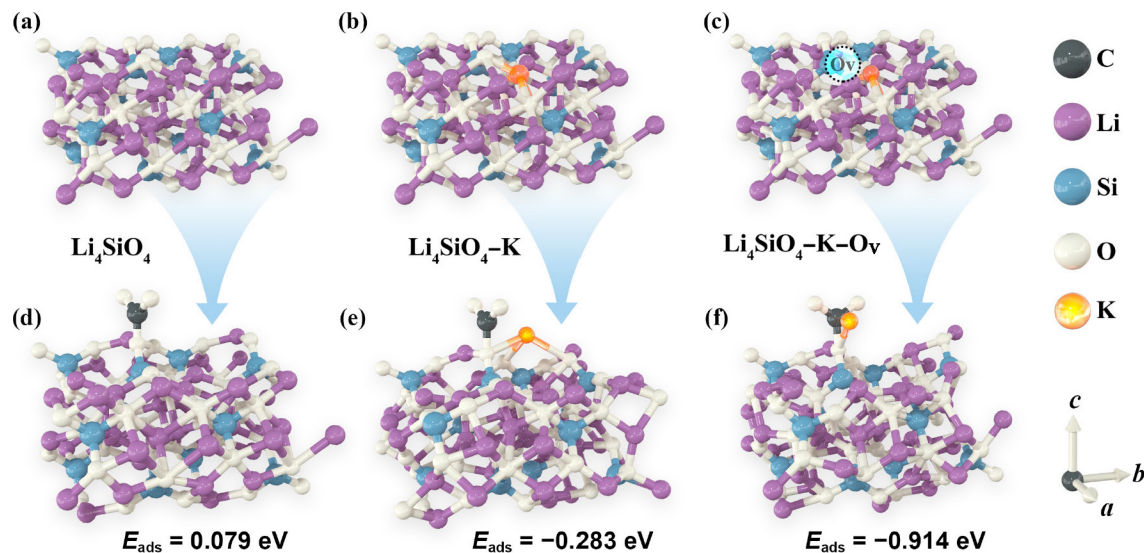


Fig. 11 DFT investigation of CO_2 adsorption: (a–c) optimized surface models of Li_4SiO_4 , Li_4SiO_4-K , and $Li_4SiO_4-K-O_v$; (d–f) corresponding CO_2 adsorption configurations with calculated E_{ads} annotated

1. Pore engineering 2. K^+ doping 3. Vacancy creation

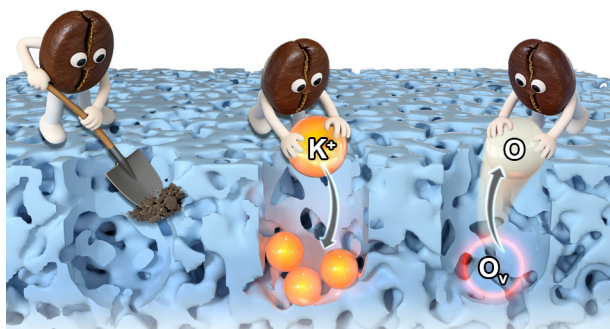


Fig. 12 Schematic illustration of the triple-synergistic mechanism of SCG modification.

providing a synergy that goes beyond the additive combination of three isolated modifications. [Table 2](#) benchmarks the CO_2 capture performance of the sorbents developed in this work against recently reported Li_4SiO_4 analogs modified with biomass or

organic pore-forming agents, with the peak capacity and capacity retained after cycling listed separately for fair comparison. A key distinction is the CO_2 partial pressure: most literature benchmarks were evaluated under pure or near-pure CO_2 , whereas all samples in the present work were assessed under the more demanding condition of 15 vol% CO_2 . Despite this thermodynamic penalty, LSON-50 achieves a peak capacity of 0.330 g/g at 650 °C, rivaling or surpassing sorbents tested under 100 vol% CO_2 , and retains 0.284 g/g after 50 cycles. Under the realistic 15 vol% CO_2 condition, LSON-50 exceeds the peak capacity of LO-P-20MC (0.295 g/g), PE-LTSO (0.270 g/g), and OPM- Li_4SiO_4 (0.243 g/g at 550 °C). Although Li_4SiO_4 -GC reports a slightly higher peak of 0.350 g/g, its capacity decreases to 0.230 g/g after 100 cycles (~34% decay), whereas LSON-50 retains ~87% of its peak after 50 cycles, demonstrating substantially more robust capacity preservation. Moreover, even LSO-50, modified by SCG alone, retains 0.244 g/g after 50 cycles, demonstrating that the SCG-only modification delivers competitive performance against the most recent pelletized Li_4SiO_4 analogs evaluated under realistic flue-gas conditions.

Table 2 Comparative CO_2 capture performance of Li_4SiO_4 sorbents modified with biomass-derived or organic pore-forming agents

Sorbent	Modifier	Form	CO_2 Conc. (vol%)	T_{ads} (°C)	Peak capacity (g/g)	Capacity after cycling (g/g)	Cyclic No.	Ref.
LSON-50	SCGs + Na_2CO_3	Pellet	15	650	0.330	0.284	50	This work
LSO-50	SCGs	Pellet	15	650	0.275	0.244	50	This work
LO-P-20MC	Microcrystalline cellulose	Pellet	15	550	0.295	0.282	70	[33]
Li_4SiO_4 -GC	Spent LIB + iron tailings	Pellet	15	525	0.350	0.230	100	[52]
PE-LTSO	K-Ti + carbon fiber	Pellet	15	650	0.270	Stable	100	[53]
OPM- Li_4SiO_4	Orthoclase + microcrystalline cellulose	Pellet	15	550	0.243	Stable	10	[54]
LA-WS30	Wheat straw	Pellet	100	600	0.150	Stable	5	[55]
FSC	PVA (freeze-drying)	Pellet	100	710	0.305	Stable	40	[56]
Li_4SiO_4 -A-C	Corn straw	Powder	100	670	0.325	0.303	20	[57]

4 Conclusions

In conclusion, this study presents a highly effective waste-value strategy to address the severe gas-diffusion limitations inherent in densified Li_4SiO_4 pellets by employing SCGs as a multifunctional modifier. Systematic evaluation of varying SCG loadings (10, 30, 50, and 70 wt%) revealed that LSON-50 achieves the optimal balance between CO_2 adsorption performance and mechanical stability. The optimized LSON-50 pellets demonstrated a remarkable CO_2 adsorption capacity of 0.330 g/g at 650 °C under 15 vol% CO_2 , demonstrating excellent cyclic stability (retaining 0.284 g/g capacity after 50 cycles) and favorable mechanical endurance (attrition loss < 10%). Comparative studies with LSO-0 and LSO-50 confirmed that SCG addition alone drives the primary performance enhancement (0.275 g/g without external Na doping), while LSON-70 was excluded from practical consideration due to insufficient mechanical stability. This remarkable improvement is ascribed to a unique triple-synergistic mechanism induced by SCG: (i) the creation of a hierarchical macroporous network that accelerates intraparticle mass transfer and buffers product shell expansion; (ii) the *in situ* potassium doping from SCG ash that facilitates rapid liquid-phase ion diffusion via eutectic melts; and (iii) the generation of oxygen vacancies through localized carbothermic reduction, which significantly enhances CO_2 chemisorption. This work offers both a high-performance sorbent for practical CO_2 capture and a scalable strategy for valorizing low-value biomass waste into functional ceramic materials.

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Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article. The author Jianqi Qi is the Editorial Committee member of this journal.

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