



Tuning porosity and capacitance of laser-assisted grown graphene by controlled thermal annealing

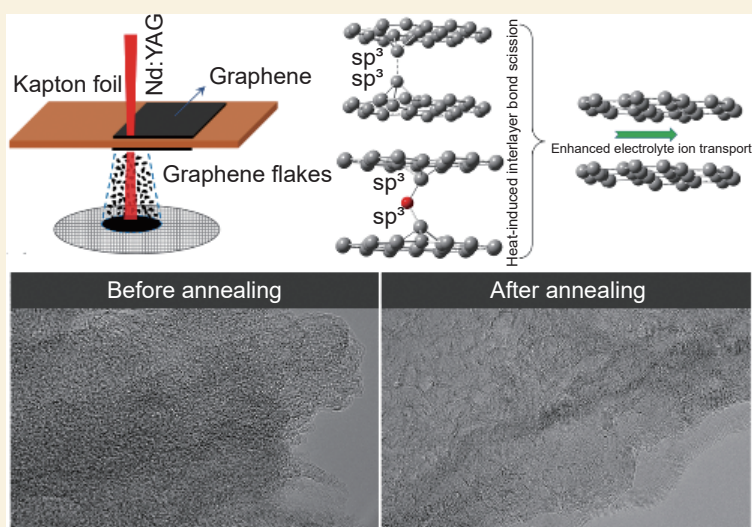
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Abstract: Graphene-like electrodes produced by a laser-assisted method are attractive for electrochemical energy storage. However, their performance is strongly affected by the pore network created during manufacture, which is difficult to control reproducibly. We have examined how a simple thermal post-treatment modifies the porosity and surface chemistry of these electrodes, and how these changes influence their capacitive performance. Parameters such as the annealing temperature, dwell time, and atmosphere (air versus inert) were varied. Mild annealing in air (up to 500 °C) decreased the number of oxygen-containing functionalities and increased the sp^2/sp^3 carbon ratio, while significantly increasing the specific surface area from 110 to 498 m² g⁻¹ and broadening the pore-size distribution. These structural and chemical changes correlate with a large increase in capacitance, approaching an order-of-magnitude compared with the untreated electrodes. The best annealed electrodes produced retained 92% of their capacitance when the current increased by a factor of 25, and had stable long-term cycling with 99% capacitance retention after 10 000 cycles. Because the process is based on laser processing followed by simple thermal annealing, it is compatible with scalable manufacturing and avoids wet-chemical activation routes.

Key words: Laser-assisted graphene; Supercapacitors; Annealing; Pore structure refinement; DFT



1 Introduction

Supercapacitors have gained significant attention due to their high-power density, rapid charge-discharge cycles, long lifespan, higher safety, and lower maintenance cost compared to conventional batteries. The performance of supercapacitors depends heavily on the properties of the electrode materials used, including porosity, conductivity, and structure. Among electrode materials, carbon-based nanomaterials are at the forefront due to carbon's low weight, enhanced electrical conductivity, robustness in harsh environments, and high specific surface area (SSA)^[1]. While carbon-based supercapacitors effectively bridge the

energy/power density gap between batteries and conventional capacitors, their low energy density poses a significant challenge for large-scale applications. In parallel, many state-of-the-art routes for producing advanced carbon electrodes rely on energy-intensive processing, complex multistep syntheses, or environmentally malign reagents, which limit scalability and practical implementation despite high electrochemic-

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al performance. To address these challenges, research over the past decades has largely focused on 2 complementary strategies: (1) enhancing energy density by optimizing carbon's pore structure or/and introducing electrochemically active redox sites; and (2) developing novel, cost-effective, and environmentally friendly synthesis routes for carbon nanostructures.

Regarding approach (1), several strategies have been proposed, including: (i) Chemical activation, which etches carbon frameworks with agents such as KOH, K_2CO_3 , H_3PO_4 , to boost porosity and SSA^[2]. (ii) Template-based synthesis, enabling the formation of carbon precursors with controlled, well-defined pore architectures that survive pyrolysis^[3]. (iii) Heteroatom doping, where elements like N, S, or P are introduced into the carbon scaffold to create redox-active sites and enhance capacitance^[4]. (iv) Decoration with transition-metal compounds, such as oxides or sulfides^[5]. Despite their effectiveness, these methods often depend on expensive reagents, involve harsh chemical treatments, or require complex, multi-step workflows with limited prospects for large-scale implementation. Regarding approach (2), although porous carbon can be produced by established thermal or chemical methods, the transcendence toward green, scalable manufacturing protocols compatible with additive manufacturing has rapidly increased the popularity of laser-assisted techniques^[6–8]. Unlike energy-intensive thermal and chemical methods, which often involve the use or release of harmful substances, laser techniques enable the in-situ growth of graphene-like structures with controlled spatial resolution, simplifying electrode patterning and miniaturization for wearable electronics^[6,9]. Most laser-assisted graphitization studies focus on directly converting polyimide foils (Kapton) into graphene-like structures, an effect known for over 30 years^[10], while the term “laser-induced graphitization” (LIG) has recently popularized this process^[8].

This process is severely limited because the porous LIG film grows directly on the Kapton foil, restricting its versatility. Consequently, transferring LIG to alternative substrates requires post-synthetic meth-

ods, such as mold casting and peeling off the graphene structures, or dry/wet transfer methods^[11–14]. However, these methods neither guarantee preservation of graphene film quality nor extend graphitization beyond Kapton foils. To address these limitations, we have developed a novel laser-mediated explosive synthesis and transfer (LEST) protocol that produces uniform, porous films of few-layer turbostratic graphene on a wide variety of flexible and rigid substrates^[15]. This method accommodates a range of precursors beyond Kapton, including biomass, ensuring consistent film quality and broadening the applicability of LEST graphene across diverse fields. Consequently, the LEST protocol has been used to fabricate graphene-based electrodes for various supercapacitor configurations^[16–17].

Here, we investigate the influence of mild thermal post-processing on the structure and capacitive performance of LEST-graphene electrodes. By varying annealing temperature, duration, and atmosphere (air or inert), we demonstrate a roughly tenfold enhancement in the electric double-layer capacitance of these graphene-based electrodes. Annealing-based post-processing has recently been used by Cheng et al. to enhance the properties of laser-derived graphene films on Kapton^[18]. The authors applied a flash-Joule heating process where high-energy electrical pulses could momentarily heat laser-induced graphene up to 2500 °C to reduce defect density and enhance conductivity fivefold, while preserving the graphene film porosity unchanged. However, our approach is based on a fundamentally different mechanism. Unlike flash-Joule heating, which focuses on ultrafast defect repair at constant porosity, our moderate thermal annealing approach refines pore architecture, increasing electric double layer capacitance, and by extension energy density, by almost an order of magnitude. Conducted at a moderate temperature of ~ 400 °C, the proposed post-processing method is compatible with a range of planar or fibrous substrates, including metals, ceramics, glasses, and heat-resistant polymers such as polyimide and polybenzimidazole. The process does not require inert gases or

hazardous/expensive chemicals, which facilitates its integration into roll-to-roll production of large-area graphene electrodes. More broadly, this simple processing step provides a straightforward route to high-performance laser-induced graphene for applications in energy storage or flexible electronics.

2 Experiment

2.1 Laser-assisted fabrication of binder-free graphene electrodes

The LEST-graphene substrate is carbon fiber paper current collector (Sigracet 29AA, non-woven PT-FE-free) with a thickness of 190 μm . The thickness of LEST-graphene films is of a few tens of μm . The carbon precursor is a commercially available polyimide (DuPont™ Kapton® HN) foil of 75 μm thickness. The laser operates at a laser fluence of 74 J cm^{-2} , a pulse width of 1.5 ms, a spot size of 1.4 mm and a pulse overlap of $\sim 33\%$. Finally, 9 mm disks were punched out to serve as electrodes.

2.2 Annealing post treatment of graphene-based electrodes

The LEST-graphene electrodes underwent thermal post-treatment at various temperatures (300, 400 and 500 $^{\circ}\text{C}$) and exposure durations (0.5, 1.5, 3 and 6 h) under ambient conditions. To assess the effect of atmosphere, electrodes annealed at 500 $^{\circ}\text{C}$ for 3 h were evaluated under both ambient air and inert argon conditions. For ambient treatments, electrodes were placed directly into a preheated oven at the selected temperature. For Ar-treated samples, electrodes were loaded into a quartz tube (1000 mm length, 29 mm inner diameter), purged with high-purity Ar at 100 mL min^{-1} for 1 h, and then heated to the target temperature.

2.3 Physicochemical characterization

Field-emission scanning electron microscopy (FE-SEM) was conducted with a Zeiss SUPRA 35VP instrument operated at 10 kV. High-resolution field emission transmission electron microscopy (HR-TEM) was conducted with a JEOL JEM-2100 instrument, operated at 200 kV. Thermogravimetric analysis was conducted using a heating rate of 10 $^{\circ}\text{C min}^{-1}$.

Raman spectroscopy was performed with the 514 nm laser line, using a Jobin-Yvon T-64000 instrument and a laser power of 1 mW. The $\sim 520 \text{ cm}^{-1}$ band of Si was used for calibration of the wavenumber scale. Nitrogen physisorption isotherms at 77 K were acquired with a Quantachrome Autosorb iQ instrument. Samples in powdered form were heated and outgassed at 150 $^{\circ}\text{C}$ for 2 h. X-ray photoelectron spectroscopy (XPS) measurements were conducted in an ultrahigh vacuum chamber, equipped with a SPECS Phoibos 100-1D-DLD hemispherical electron analyzer and a non-monochromatized dual-anode Mg/Al x-ray source. XP spectra were acquired with the MgK α (1253.6 eV) source, and the samples were pressed onto indium substrates.

2.4 Assembly of supercapacitors and their electrochemical assessment

Swagelok-type cells were assembled with 6 mol L^{-1} KOH electrolyte, employing 2 identically annealed 9 mm-diameter electrodes separated by 2 membrane separators (Dreamweaver Titanium T 0.58/30, GLATFELTER). After assembly, the cells were left idle for 24 h to facilitate wetting of the electrodes. The electrochemical evaluation of supercapacitors included cyclic voltammetry (CV), galvanostatic charging/discharging (GCD) and electrochemical impedance spectroscopy (EIS). CV and EIS were performed using an electrochemical workstation (VersaSTAT 4, AMETEK SI, USA). The frequencies for EIS ranged from 10 mHz to 100 kHz, with a perturbation amplitude of 5 mV. GCD curves were acquired using a CTS Standard system (BaSyTec GmbH).

The areal capacitance was calculated from CV and GCD curves, using the following equations:

$$C_{\text{areal}} = \frac{S}{2\nu A \Delta V} \quad (1)$$

$$C_{\text{areal}} = \frac{I \Delta t}{A \Delta V} \quad (2)$$

where S is the CV integrated area, ν is the scan rate, A is the device area, ΔV is the voltage window, I is the applied current, and Δt is the discharging time. The reported capacitance corresponds to the device capacitance.

The energy $E_d [\mu\text{Wh cm}^{-2}]$ and power density

$P_a[\mu\text{W cm}^{-2}]$ of the devices were calculated using formulas (3) and (4), respectively:

$$E_a = \frac{C\Delta V^2}{2 \times 3.6} \quad (3)$$

$$P_a = \frac{3600 \times E_a}{\Delta t} \quad (4)$$

2.5 Computational methods and details

The B3LYP hybrid density functional method^[19], which combines density functional theory with Hartree–Fock exchange and employs Becke’s three-parameter exchange functional^[20] together with the Lee–Yang–Parr correlation functional^[21], as well as its long-range corrected version using the Coulomb-attenuating method (CAM-B3LYP)^[22], were employed as implemented in the Gaussian 16 program package^[23]. The electronic structures of the atoms involved in the investigated systems (H, C, O) were described using the cc-pVDZ basis sets^[24]. The geometries of the structural models were fully optimized at the CAM-B3LYP/cc-pVDZ level of theory using the Berny optimization algorithm, as implemented in Gaussian 16.

3 Results and discussion

3.1 Annealing-induced changes in structure, composition and morphology of graphene-based electrodes

The graphene-based electrodes were fabricated using the LEST method^[16], a schematic of which is shown in Fig. 1a. In brief, a millisecond Nd:YAG

laser was employed to decompose a carbon-based precursor (polyimide) yielding graphene structures that were simultaneously transferred onto carbon fiber paper current collector (placed beneath the precursor), resulting in its homogeneous coverage with LEST-graphene. After depositing LEST-graphene on one side, the carbon paper was flipped and the LEST process was repeated to coat the opposite side of the current collector. Subsequently, LEST-graphene was annealed at different temperatures, for variable duration, and in different environments (Fig. 1b).

A representative FE-SEM image at low magnification reveals the foam-like, porous texture of the LEST graphene film (Fig. 2a). This morphology is consistent across all samples and results from the rapid release of gaseous byproducts during the polymer’s laser-assisted decomposition. Fig. 2b shows a high-magnification image of the as-prepared graphene films, revealing their relatively low surface roughness. Fig. 2(c–e), illustrate the progressive increase in the roughness of graphene films annealed for 3 h, under ambient conditions at 300, 400 and 500 °C, respectively, suggesting the emergence of meso- and micro-porosity.

Comparison of Fig. 2(e, f) highlights the critical role of the atmosphere during thermal treatment. Although both samples were annealed under identical conditions (500 °C for 3 h), the graphene films treated under inert Ar atmosphere (Fig. 2f) exhibit significantly lower surface roughness than those treated in air

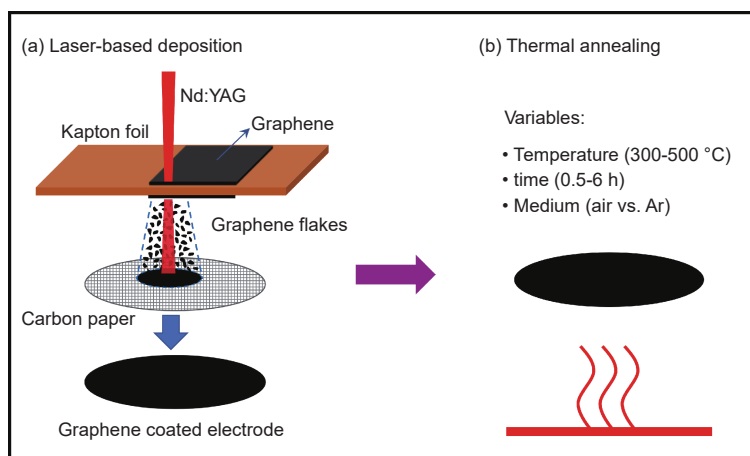


Fig. 1 Schematic of (a) the LEST process for the simultaneous synthesis and transfer of porous graphene structures on carbon paper current collector, and (b) the annealing post-synthetic process

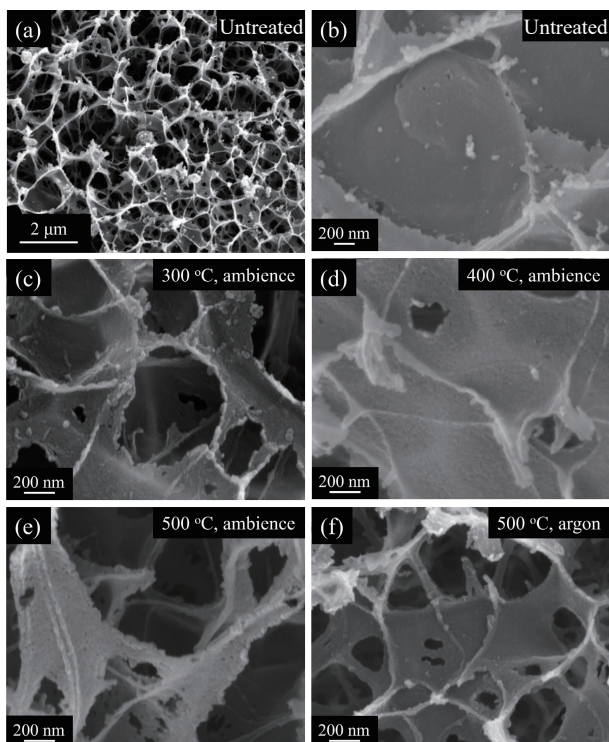


Fig. 2 (a) Low and (b) high magnification FE-SEM images of as-deposited LEST-graphene. High magnification images of LEST-graphene films treated for 3 h under ambient conditions at (c) 300 °C, (d) 400 °C, and (e) 500 °C. (f) Image corresponds to graphene annealed at 500 °C for 3 h under Ar gas atmosphere

(Fig. 2e). This morphological change is consistent with previous studies, which attributes such alterations to the selective oxidative etching of defective carbon, as observed in both graphite^[25] and carbon nanotubes^[26–27]. The oxidative etching of carbon was supported by HR-TEM findings, which indicated the eradication of defect-rich amorphous carbon and the emergence of nanopores after ambient annealing of LEST-graphene at 500 °C (Fig. 3). To further assess the effect of the environment on LEST-graphene during its annealing, thermogravimetric (TG) analysis was conducted. The TG profiles of Fig. S1 suggest that annealing of LEST-graphene in Ar results in a mass loss of 12%, which is due to the breakdown of oxygen-containing functional groups, whereas annealing of LEST-graphene in ambient environment incurs a more significant mass loss of 19%, supporting the etching of carbon due to its reaction with atmospheric oxygen.

Nitrogen physisorption studies were conducted for the as-prepared and all treated samples. The find-

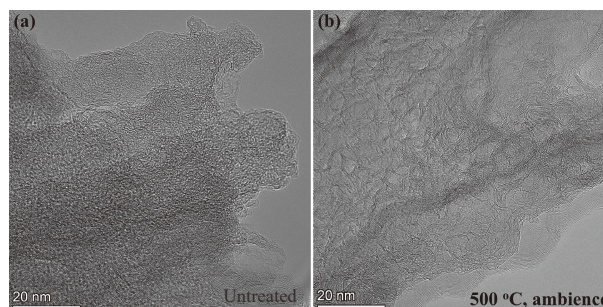


Fig. 3 HR-TEM images of (a) untreated LEST-graphene and (b) LEST-graphene after a 3 h long ambient annealing at 500 °C

ings provide solid evidence on the microporosity enhancement ($< 10 \text{ \AA}$ pore radius) after annealing (Fig. 4). The N_2 adsorption-desorption isotherms for electrodes annealed at 400 °C in air for 0.5–6 h are shown in Fig. 4a, while those for electrodes annealed for 3 h at temperatures from 300 to 500 °C are presented in Fig. 4b. All isotherms correspond to type IV according to the IUPAC classification^[28]. As shown in Fig. S2, the untreated LEST-graphene possesses a specific surface area (SSA) of $110 \text{ m}^2 \text{ g}^{-1}$. Annealing LEST-graphene in ambient air at 400 °C increases the specific surface area to 163, 260, 272 and $274 \text{ m}^2 \text{ g}^{-1}$ after 0.5, 1.5, 3 and 6 h, respectively. Similarly, isochronous 3 h annealing of LEST-graphene in ambient air at 300, 400 and 500 °C increases drastically the SSA values to 151, 272 and $498 \text{ m}^2 \text{ g}^{-1}$, respectively. Annealing LEST-graphene in inert Ar (500 °C, 3 h) also raises the SSA but to a much lesser extent than air annealing, i.e. to $164 \text{ m}^2 \text{ g}^{-1}$. This finding suggests that oxidative etching, which preferentially removes vulnerable sp^3 carbon sites or terminal carbon atoms^[25,27,29], is the dominant mechanism driving pore restructuring in annealed LEST-graphene. Prolonging (Fig. 4c) or intensifying (Fig. 4d) annealing of LEST-graphene changes the pore size distribution notably, shifting the balance toward smaller micropores and broadening the overall pore-width profile. Although as-prepared LEST-graphene exhibits only a minor micropore population with pore radius distribution centered at $\sim 5.5 \text{ \AA}$, ambient annealing broadens this distribution, shifts its peak to $\sim 4.0 \text{ \AA}$ and amplifies the overall micropore volume.

The impact of annealing on the quality and surface chemistry of laser-assisted graphene was studied

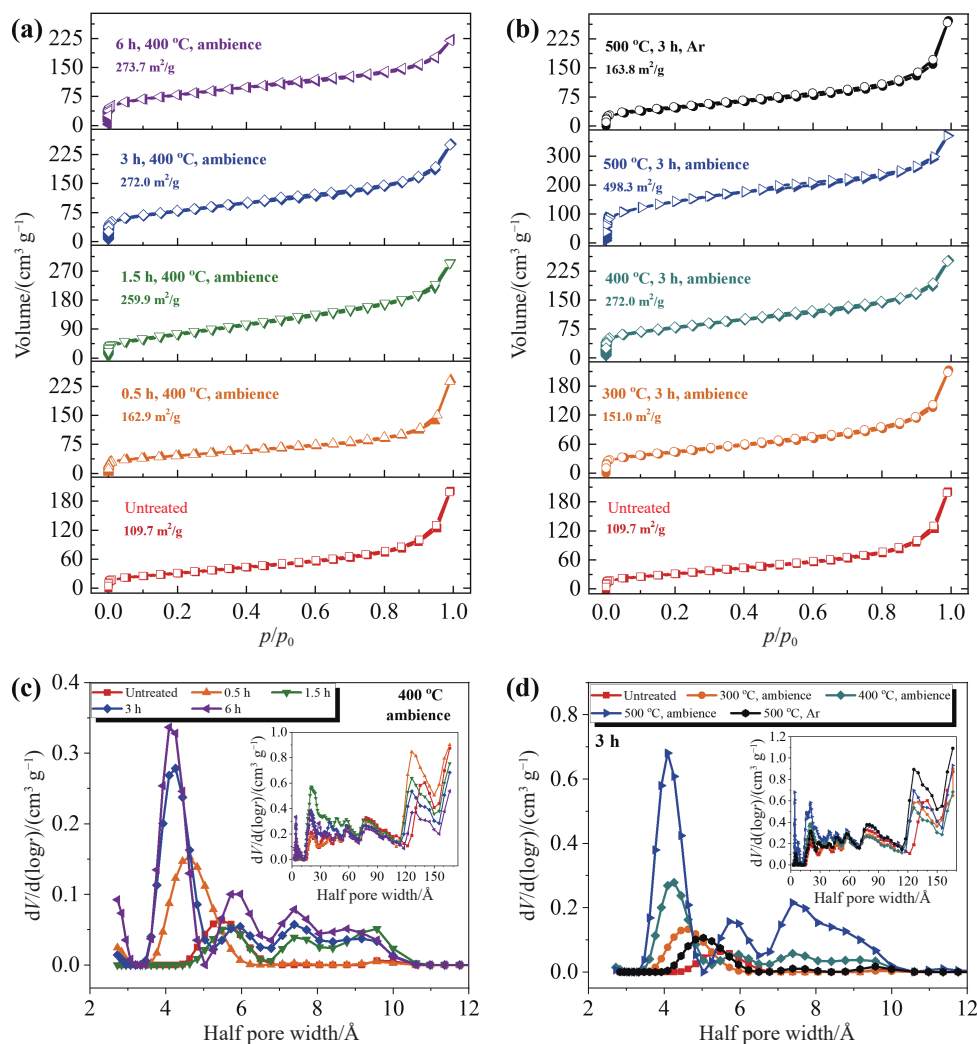


Fig. 4 (a, c) N₂ physisorption isotherms and pore size distribution of LEST-graphene annealed at 400 °C, under ambient conditions, for various durations. (b, d) N₂ physisorption isotherms and pore size distribution of LEST-graphene treated at different temperatures and atmospheres, using a fixed annealing duration of 3 h

using Raman spectroscopy and XPS. The Raman spectra in Fig. 5a, and in particular the intense and symmetric 2D band, confirm that the laser-assisted porous film exhibits a graphene-like structure. As detailed in our previous study, the untreated LEST-graphene consists of few-layer stacks of turbostratically arranged graphene sheets^[15]. The prominent D peak indicates a high defect density in the graphene basal planes, which is expected for such porous structures. Regardless of the annealing environment, treatment at 500 °C markedly improves graphene quality, as evidenced by the substantial increase in 2D-peak intensity, making it comparable to the G-peak. Ambient annealing produces a greater reduction in D-peak intensity than argon treatment, indicating that environ-

mental oxygen facilitates the removal of highly reactive defect sites, which are of higher reactivity^[30], due to the presence of dangling bonds^[25]. The symmetric and single-Lorentzian spectral shape of the 2D band (Fig. 5b) indicates that the few-layer graphene structure deviates from Bernal-type stacking^[31], suggesting the presence of a turbostratic arrangement of the individual graphitic layers^[32]. Fig. 5(c, d) and Fig. S3 present the deconvoluted C1s spectra of the as-prepared and the annealed films, resolved into 6 components: (1) sp² C—C at 284.4 eV, (2) sp³ C—C at 285.3 eV, (3) C—O bonds at 286.4 eV, (4) carbonyls at 287.7 eV, (5) carboxylates at ~ 289 eV, and (6) carbon's π - π^* shake-up feature at 291.0 eV^[33]. As summarized in Table 1, all annealed samples exhibit very

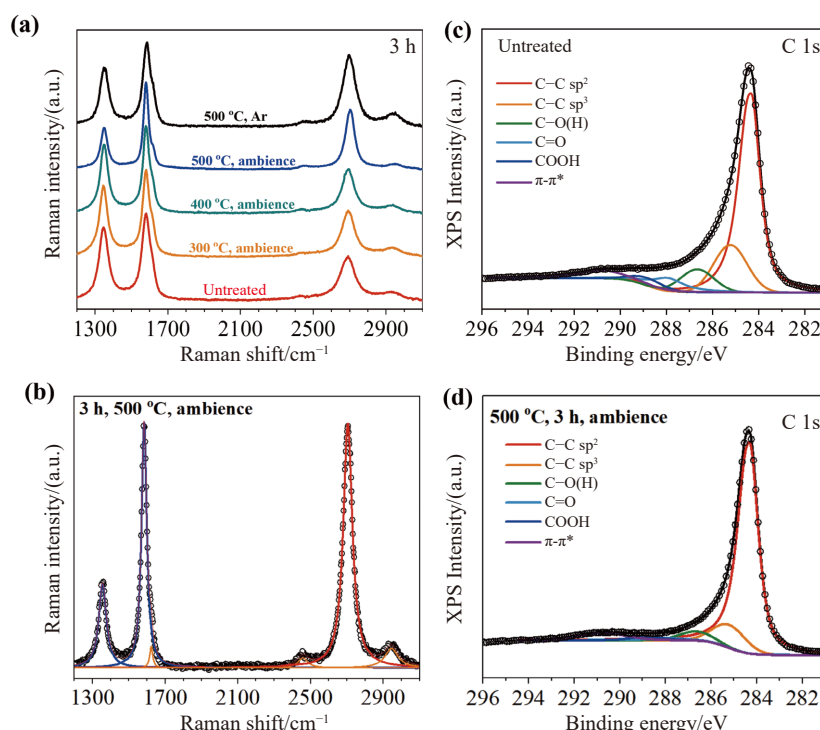


Fig. 5 (a) Representative Raman spectra of LEST-graphene annealed for 3 h at different conditions. (b) Raman spectrum fitting with Lorentzian curves. Deconvoluted C 1s peak of (c) untreated LEST-graphene and of (d) LEST-graphene after a 3h-long ambient annealing at 500 °C

Table 1 Change in surface chemistry of LEST-graphene after annealing (atomic percentage)

Sample	C	O	C—C sp ²	C—C sp ³	C—O(H)	C=O	COOH
Untreated	89.7%	10.3%	64.8%	17.0%	8.2%	6.9%	3.1%
300 °C, 3 h, air	96.2%	3.8%	82.1%	9.9%	4.3%	2.2%	1.5%
400 °C, 3 h, air	96.2%	3.8%	82.1%	10.2%	4.5%	1.6%	1.6%
500 °C, 3 h, air	95.9%	4.1%	82.5%	10.5%	4.1%	1.4%	1.5%
500 °C, 3 h, Ar	96.1%	3.9%	86.2%	6.6%	4.4%	2.0%	0.8%

similar surface chemistries, specifically, their oxygen content drop markedly (raising the C/O ratio from ~ 8.7 to ~ 25.3) and the sp^2/sp^3 carbon ratio improve substantially, with no significant further changes observed above 300 °C.

3.2 Impact of ambient annealing on capacitive performance of laser-assisted graphene electrodes

Fig. 6 compares the electrochemical performance of supercapacitors fabricated with electrodes annealed under the conditions described above. CVs were recorded at scan rates ranging from 0.01 to 0.2 V s⁻¹. From the comparison of the CV curves in Fig. 6(a, b), two key observations emerge: (1) the integrated area under the CV curves increases significantly and monotonically with higher annealing temperatures or longer durations, and (2) all CV curves

exhibit the characteristic behavior of an electric double layer capacitance (EDLC) behavior. Fig. 6(c, d) present the dependence of the devices' areal capacitance on the scan rate, obtained from the corresponding CV curves shown in Fig. S4. The areal capacitance of the device with untreated LEST-graphene electrodes, which is 5.5 mF cm⁻² at 10 mV s⁻¹, rises markedly to 13.9, 22.4, 31.2 and 34.1 mF cm⁻² after annealing the electrodes at 400 °C for 0.5, 1.5, 3 and 6 h, respectively. Similarly, isochronous (3 h) annealing at 300, 400 and 500 °C yields capacitance values of 10.6, 31.2, and 33.3 mF cm⁻², respectively. The data reveal that increasing the annealing temperature from 400 to 500 °C does not significantly enhance capacitance at low scan rates. This is due to the more pronounced graphene mass loss during ambient an-

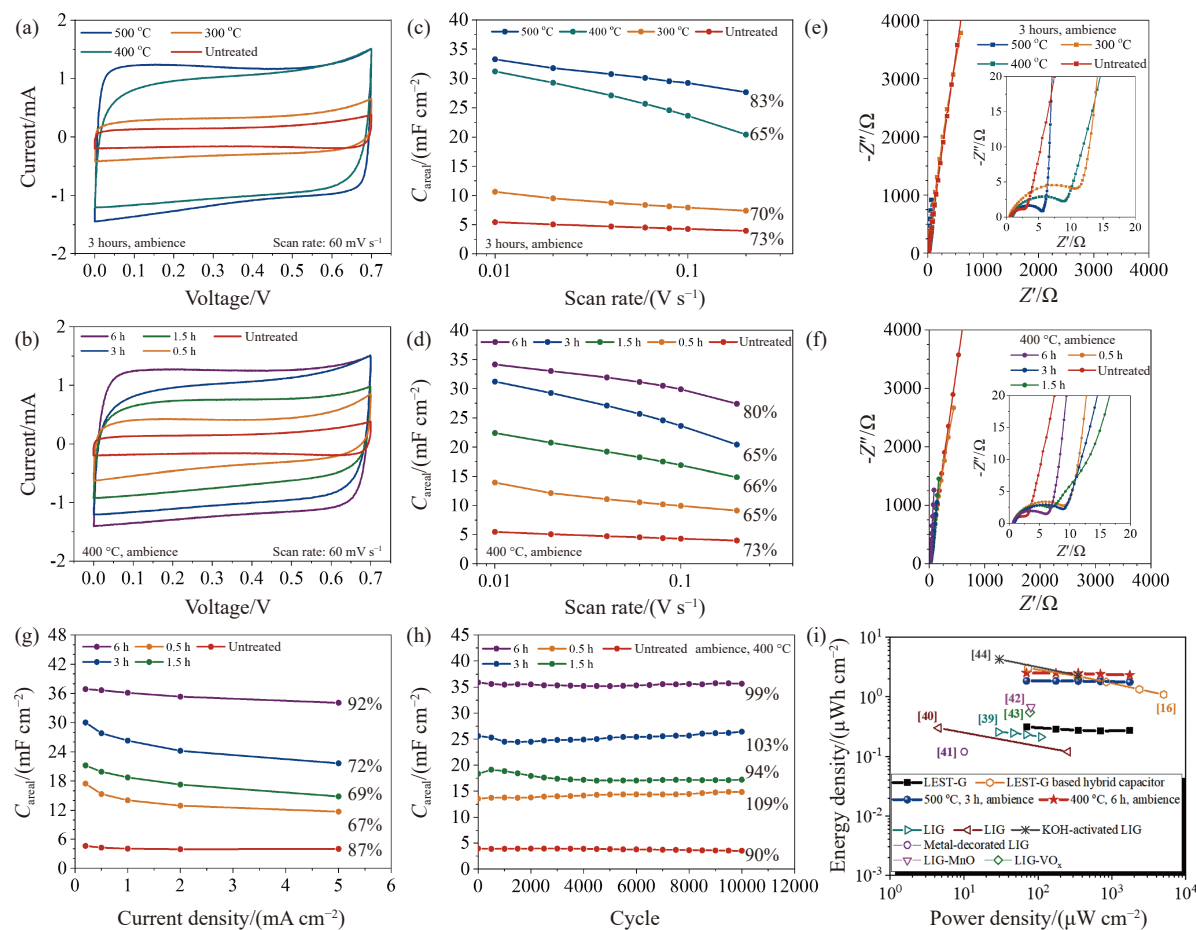


Fig. 6 Comparative CV curves, capacitance vs. scan rate, and Nyquist plots after annealing (a, c, e) at different temperatures for 3 h and (b, d, f) at 400 °C for different durations, respectively. (g) Capacitance vs. current density and (h) cycling stability of supercapacitors using LEST-graphene annealed at 400 °C for different durations. (i) Ragone plot comparison of the herein reported devices against previously reported supercapacitors using laser-assisted graphene electrodes

nealing at 500 °C, supported by the TG profile of LEST-graphene in air environment (Fig. S1). However, high-rate performance improves markedly, with capacitance retention reaching 83% at 200 mV s^{-1} . Similarly, prolonged annealing also benefits rate capability, as the electrodes treated at 400 °C for 6 h retain 80% of their capacitance at 200 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) reveals a non-monotonous evolution of the interfacial charge transfer resistance as annealing intensifies (Fig. 6(e, f)). This behavior is likely due to the interplay of 2 competing factors: (1) the removal of oxygen-containing functional groups, and (2) the improvement of electronic percolation after the removal of defect-rich amorphous carbon. XPS analysis suggests that a low temperature of 300 °C is sufficient to decrease the oxygen content from 10.3% to 3.8%, which increases

the hydrophobicity of LEST-graphene and decreases its wettability by the aqueous KOH electrolyte, translating to an enlargement of the high-frequency semicircle of the Nyquist plots^[34]. While the intensification of annealing does not further affect the oxygen content of LEST-graphene, it promotes the removal of amorphous carbon and improves the electronic percolation of graphene flakes, decreasing interfacial polarization and shrinking the high-frequency semicircle of the Nyquist plots^[35].

The GCD curves for current densities from 0.2 to 5 mA cm^{-2} are presented in Fig. S5. At 0.2/5 mA cm^{-2} , the cell with untreated graphene electrodes yields a capacitance of 4.6/4.0 mF cm^{-2} . Air annealing at 400 °C for 0.5, 1.5, 3 and 6 h increases capacitance to 17.4/11.7, 21.2/14.8, 30.0/21.6 and 36.9/34.1 mF cm^{-2} , respectively (Fig. 6g). Moreover, 3 h an-

nealing at 300, 400 and 500 °C achieves a capacitance of 8.4/6.6, 30.0/21.6 and 27.2/25.9 mF cm⁻² at the same current densities (Fig. S6), and good cycling stability (Fig. S7), which becomes optimum at the temperature of 400 °C. As presented in Fig. S8, the areal capacitance values of LEST-graphene annealed at 300/400 °C are correlated to a good extent with the corresponding SSA values. On the contrary, samples annealed at 500 °C deviate from this correlation due to the significant loss of active material at this elevated temperature (Fig. S1).

Annealing for 3 h at 500 °C or 6 h at 400 °C resulted in exceptional high-rate performance, with the devices retaining 95% and 92% of their capacitance at 5 mA cm⁻², respectively, due to the annealing-induced microporosity refinement. Such an improved high-rate capability suggests the decreased tortuosity of the porous network^[36], which is also implied from the broader pore size distribution at these annealing conditions. While these 2 annealing conditions achieve similar performance enhancement in terms of capacitance and high-rate capability, the annealing temperature of 400 °C is beneficial for the preservation of a higher LEST-graphene mass (refer to TG profile of Fig. S1). This becomes more evident in the case of prolonged annealing at 500 °C, which is detrimental to the pore structure of LEST-graphene. As shown in Fig. S9(a, b), doubling the annealing time from 3 to 6 h preserves the pore size distribution but significantly decreases the micropore and mesopore content, decreasing SSA to 340 m² g⁻¹. While this value is superior to that achieved after the 6-hour long annealing at 400 °C, the corresponding capacitance is substantially lower (Fig. S9(c, d)), which is reasonable due to the higher LEST-graphene mass loss at 500 °C (Fig. S1). All supercapacitors exhibited excellent cycling stability (Fig. 6h and Fig. S7), as is typical for EDLCs, except for the cell with electrodes treated at 500 °C, which lost 25% of its initial capacitance after 10 000 cycles. This degradation may arise from several factors. For instance, the formation of gaseous electrolyte decomposition products could contribute to the detachment of active material. Further, if these products are trapped at the

electrode–electrolyte interface, they can block pores and reduce the electrode area accessible to the electrolyte^[37]. As shown in Table S1, the capacitance of annealed LEST-graphene at high-rates is superior to the vast majority of EDLC-type laser-assisted graphene structures.

The comparative Ragone plot in Fig. 6i demonstrates the substantial gains and the high potential from the post-processing proposed in the current work. Although supercapacitors with untreated electrodes already perform competitively among laser-assisted graphene EDLCs^[38–41] ambient annealing at 400 °C for 6 h boosts the energy density to 2.51 μWh cm⁻² at 70 μW cm⁻² and 2.32 μWh cm⁻² at 1750 μW cm⁻². Similarly, annealing at 500 °C for 3 h delivers 1.85 and 1.76 μWh cm⁻² at those same power densities, respectively.

This performance markedly surpasses that of recent supercapacitors using MnO₂^[42] or VO_x^[43] decorated laser-assisted graphene electrodes and is comparable with EDLCs fabricated from KOH-activated laser-assisted graphene electrodes^[44], underscoring the efficacy of our simple, environmentally friendly method. As shown in Table S2, although our post-processing approach is relatively time-consuming, it achieves an unprecedented refinement of the laser-assisted graphene porous structure. Moreover, as the first step in the electrode fabrication involves the transfer of graphene from the carbon precursor onto another substrate, our combined LEST/annealing approach can be broadly adopted for the refinement of laser-assisted graphene that originates from heat-sensitive organic or biomass precursors. Notably, the energy density achieved after annealing the 2 LEST-graphene electrodes rivals the energy density achieved by replacing the negative untreated LEST-graphene electrode with a battery-type Zn anode in the form of a Zn-ion hybrid supercapacitor configuration, as recently reported by our group^[16].

3.3 Buckling–unknotting model: an atomic-scale mechanism underlying the pronounced annealing-induced increase in SSA and capacitance

The unusually strong increase in BET-accessible

surface area, together with the noticeable improvement in capacitance after air annealing, calls for an atomic-scale structural interpretation of the annealing effect. Since these large functional changes are accompanied by only moderate spectroscopic modifications (Raman scattering and XPS), the underlying mechanism is more plausibly associated with a reorganization of the porous graphene framework and the release of previously inaccessible internal surface than with extensive carbon etching or erosion alone. In particular, Raman spectroscopy reveals a moderate but systematic narrowing of the *G* and *2D* bands with increasing annealing temperature and duration, together with a decrease in the *D/G* ratio and an increase in the *2D/G* intensity ratio. These changes indicate improved structural order and reduced defect density, consistent with the observed linewidth and intensity evolution. Such trends are commonly associated with increased sp^2 bonding and partial defect healing in graphene lattice. XPS provides a complementary signature, as the sp^3/sp^2 carbon ratio decreases by 50% (from 0.26 in the untreated sample to 0.13 after annealing at 500 °C for 3 h), indicating a pronounced reduction in sp^3 -like bonding contributions.

Based on the above-mentioned facts, a purely etching-driven mechanism is insufficient to account for these experimental observations. Classical oxidative etching mechanisms involve removal of carbon atoms and the formation of etch pits, with basal-plane oxidation in graphite becoming dominant only at much higher temperatures, whereas at moderate temperatures oxidation typically initiates at defect sites^[45]. Moreover, in porous networks, the measured SSA is governed not only by how much surface exists, but also by whether that surface is connected and accessible.

We therefore propose a buckling-unknotting mechanism in which the as-prepared laser-derived material contains metastable “interlayer knots” that locally buckle and tie adjacent graphene layers, particularly within narrow pore corridors. Given the extreme, non-equilibrium conditions of laser conversion, kinetically trapped sp^3 -like interlayer linkages are

plausible. When such knots form at pore throats, they obstruct transport of N_2 during physisorption as well as electrolyte ions during electrochemical cycling. Effectively, such knots can lock surface area inside poorly connected pockets. Annealing at moderate temperatures applied in this work, supplies sufficient thermal energy to relax these knots, converting sp^3 -like linkages into sp^2 connectivity and restoring local planarity. Untying the constrictions opens blocked corridors, which increases the fraction of surface that becomes experimentally accessible. Overall, this mechanism can naturally account for the disproportionate increase in SSA and capacitance without invoking extensive carbon removal or major lattice reconstruction. In particular, it is distinct from the very-high-temperature flash/Joule-heating regime reported for laser-induced graphene on polyimide, where pentagon/heptagon defects can transform into hexagons^[18]. In our case, the moderate annealing treatment is more plausibly associated with the release of metastable interlayer buckling through the cleavage or reorganization of weak interlayer sp^3 -type linkages.

3.4 DFT evidence for relaxation of interlayer knots into untied, lower-energy configurations

To test the structural model proposed in the previous section, i.e., whether plausible interlayer-knot motifs can act as metastable, pore-blocking defects in the as-prepared electrodes, we performed DFT calculations on 2 representative bilayer graphene models. The first motif (A) contains a direct interlayer C—C sp^3 bond between adjacent layers, while the second motif (B) contains an interlayer C—O—C bridge that ties the 2 layers (Fig. 7(a, b)). In both structural models the graphene layers exhibit local out-of-plane distortions for C atoms involved in the interlayer bonding. These local configurations represent candidate atomic-scale “knots” capable of constricting narrow pore corridors.

In motif A, the DFT optimized atomic arrangement reaches a structure where the interlayer C—C crosslink has been broken and the layers relax toward a flatter, untied configuration (Fig. 7c). In motif B, the oxygen atom initially bridging 2 layers relocates dur-

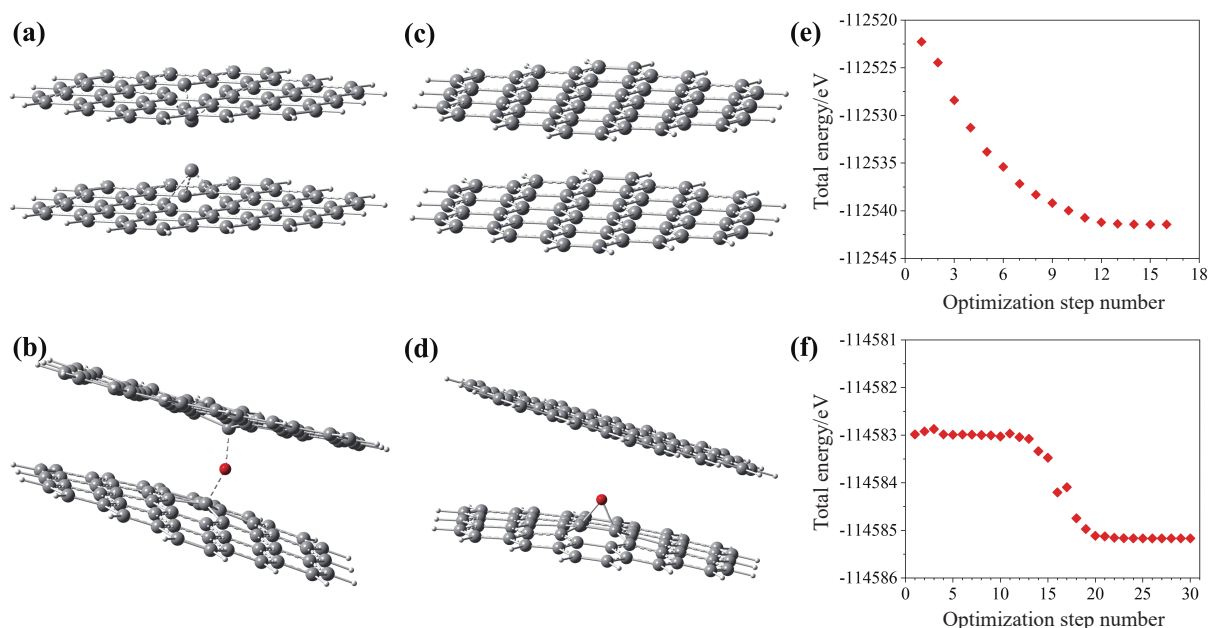


Fig. 7 DFT-based representation of the proposed buckling–unknotting mechanism. (a) Initial metastable Motif A, consisting of a direct interlayer C–C sp^3 linkage between adjacent graphene layers. (b) Initial metastable Motif B, consisting of an interlayer C–O–C bridge. (c) Optimized structure of Motif A, showing loss of the interlayer bond and flattening of the layers. (d) Optimized structure of Motif B, in which the oxygen relaxes into an intralayer epoxy-like configuration, thereby releasing the interlayer constraint. (e) Corresponding total-energy evolution during geometry optimization of Motif A.

(f) Corresponding total-energy evolution during geometry optimization of Motif B

ing relaxation into an intralayer epoxy configuration (both C–O bonds within the same sheet), which also removes the interlayer bridge and releases the layers (Fig. 7d). These relaxation outcomes are consistent with the experimentally observed reduction in sp^3/sp^2 from XPS and with the increased crystallinity (enhanced ordering) trends demonstrated in the Raman spectra. Such structural alterations are also consistent with the known mobility and rearrangement chemistry of epoxy-type oxygen on graphene oxide under thermal/chemical influence^[46]. The DFT optimization pathways show a progressive decrease in total energy from the initially imposed buckled configurations to the final relaxed structures, confirming that the former correspond to metastable, non-equilibrium states (Fig. 7(e, f)). In both geometries examined, structural relaxation removes the interlayer constraint and yields flatter, lower-energy arrangements. This behavior supports our interpretation that the as-prepared LEST-derived graphene may contain kinetically trapped buckled motifs formed under strongly non-equilibrium laser-processing conditions, which relax to more stable states after annealing. Such untying of interlay-

er knots provides a plausible atomic-scale explanation for the marked increase in accessible surface area and capacitance after annealing.

These DFT results provide an atomistic basis for the buckling–unknotting model. In a porous 3D network, the release of even a fraction of such interlayer constraints can reopen constricted pore throats and reconnect previously inaccessible internal domains. This offers a plausible explanation for the disproportionately large increase in BET-accessible surface area and electrolyte-accessible surface, and hence for the strong enhancement in capacitance after annealing.

4 Conclusion

This work shows that post-fabrication annealing is a simple and effective lever to tune the pore network and surface chemistry of LEST-graphene electrodes, leading to substantial improvements in EDLC performance. Mild annealing in air is markedly more effective than inert annealing, yielding a large increase in accessible surface area and a pore architecture that supports both higher capacitance and im-

proved high-rate operation. The best-performing condition, i.e. 400 °C in air for 6 h, led to an almost one order-of-magnitude capacitance increase in comparison to the untreated electrodes, together with outstanding rate capability (92% retention at 5 mA cm⁻²) and excellent cycling stability (99% retention after 10 000 cycles). Spectroscopy confirms that annealing promotes deoxygenation and a higher sp² carbon content, consistent with a more conductive and electrochemically active carbon framework. Consistent with the experiments, DFT indicates that plausible interlayer “knots” are metastable and relax into untied, lower-energy bilayer configurations, supporting a buckling–unknotting mechanism for pore reopening upon annealing. Overall, combining industrially compatible laser processing with a straightforward thermal step provides a scalable, chemical-free route to significantly upgrade laser-derived graphene electrodes, and the established structure–property trends offer clear guidance for further optimization and transfer to related porous carbon architectures.

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