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1	Rapid Joule Heating-Induced Welding of Silicon and Graphene for
2	Enhanced Lithium-Ion Battery Anodes
3	
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33 Abstract

In the pursuit of enhanced energy storage solutions, the application of silicon-based anode materials faces 34 significant hurdles, primarily stemming from the rapid capacity degradation during battery cycles. This study 35 introduces a novel and efficient method for fabricating Si/graphene composites (F-Si@rGO), enhancing the 36 performance and longevity of silicon-based anodes. Utilizing ultra-high-speed thermal treatment, this 37 technique controls the thermal interaction between carbon and silicon phases, leading to the formation of 38 silicon carbide 'riveting points' that firmly anchor silicon nanoparticles within the graphene matrix. This novel 39 method effectively minimizes the problems of phase segregation, which are caused by varying degrees of 40 wettability alteration in the two phases during conventional heat treatments, and guarantees a robust 41 integration of graphene and silicon. This integration results in homogeneous charging and outstanding 42 structural stability of the composites, over extended cycles of use. The resulting Si/graphene composites 43 exhibit exceptional electrochemical performance, achieving a high initial capacity of 1141.3 mAh g⁻¹ at 1C 44 and maintaining a capacity of 894.95 mAh g^{-1} after 1000 cycles with minimal degradation (0.0216% per cycle). 45 This synthesis method, notable for its speed and scalability, offers a potential advancement in battery material 46 technology, suggesting a path towards more resilient and efficient energy storage solutions. 47

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Keywords: Silicon-based anode, Energy storage material, Lithium-ion batteries, Joule Heating, Silicon
carbide, Welding

51

52 **1. Introduction**

The state of the art graphite-based anodes can reach an energy density of $360 \sim 365$ mAh g⁻¹, which 53 is very close to the theoretical specific capacity of graphite at 372 mAh g⁻¹[1]. Further improvements on 54 the overall energy density of the battery packs shall rely heavily on developing new cathode and anode 55 materials. Silicon-based anode materials offer great promise for the next-generation high-density lithium-56 ion batteries due to their exceptionally high theoretical specific capacity (3580 mAh g⁻¹ at room 57 temperature), low delithiation potential (< 0.5 V), environmental sustainability and ample availability in 58 the earth's crust [2]. However, the widespread commercial utilization of silicon-based anodes is often 59 hindered by their rapid capacity degradation during battery cycling [3]. When silicon undergoes lithiation, 60 it experiences significant swelling, leading to the fragmentation of silicon particles and the continuous 61 formation of solid-electrolyte interface (SEI) layers. This process of expansion can result in the 62 detachment of active materials from conductive additives, accelerating the degradation of battery capacity. 63 Furthermore, the uneven expansion of active materials due to lithiation disparities can generate localized 64 stress and strain, eventually causing electrode cracking and detachment from the current collector [4]. 65

To overcome such limitations, nano-structuring silicon particles into different sizes and morphologies such as silicon nanotubes[5], nanowires [6], nanodots [7] are found effective. By reducing the average size of the active material to the nanometer scale, the internal stress generated during lithiation is significantly reduced at the same degree of lithiation [8]. Another strategy for enhancing the electrochemical performance of siliconbased anodes involves the incorporation or encapsulation of silicon nanoparticles within a carbon matrix[9-11]. This carbon matrix serves as a protective layer on the silicon surface, mitigating expansion-induced stress, preventing direct contact with the electrolyte and improving the material conductivity [12].

An ideal carbon matrix should be a continuous phase, completely enveloping the silicon surface. Such 73 an arrangement ensures effective segregation of silicon nanoparticles and provides a stable foundation for the 74 growth of SEI[12]. Typically, realization of such carbon coatings on silicon involves an initial coating with an 75 organic carbon precursor, followed by a carbonization treatment [13-15]. However, due to its brittle nature, 76 these carbon coatings tend to be fragile and can easily fracture when subjected to internal expansion forces 77 [16]. Solving these challenges involves the design and synthesis of complex carbon-silicon hybrid structures, 78 such as hollow [17, 18], hierarchical arrangements [19, 20], and yolk-shell configurations [21]. While these 79 intricate Si-C composites can occasionally yield satisfactory outcomes, the high cost, tedious manufacturing 80 process and use of hazardous materials such as strong acids in manufacturing process limit the production of 81 these materials only at lab-scales, diminishing their commercial applications[22]. 82

Besides such bottom-up approaches, alternative strategies involve incorporating silicon nanoparticles 83 onto pre-existing stable carbon structures or phases, such as porous carbon [10], carbon nanotubes [23], and 84 carbon fibers [24] that can serve as stable pathways for conductivity. However, traditional methods of mixing 85 silicon particles with carbon materials rely on physical blending techniques [25, 26]. This approach often 86 struggles to achieve the necessary uniformity in composition due to issues such as uneven wetting and 87 uncontrollable aggregation of silicon particles within the system. The weak bonding between silicon and the 88 conductive network, along with inconsistencies in these carbon-silicon systems, contribute significantly to the 89 rapid deterioration of conductive connections over extended charge/discharge cycles, thus hindering their 90 widespread commercial adoption[27, 28]. Consequently, there is a pressing need to develop a methodology 91 capable of providing a robust coating layer and establishing a uniform and stable conductive network through 92 scalable production methods. This is essential for practical applications of silicon as lithium-ion anode 93 materials. 94

Among the various carbon-based materials under investigation, graphene attracts significant attention 95 due to its outstanding mechanical strength, low linear expansion coefficient, chemical resistance, and electrical 96 conductivity[29]. Nevertheless, the hydrophobic nature of graphene often leads to severe aggregation in most 97 solvents, making it challenging to create a homogeneous slurry accommodating both silicon and graphene 98 [30]. An alternative is graphene oxide (GO), a graphene derivative featuring oxygen functional groups that 99 greatly enhance its dispersibility in solvents. When silicon and GO are combined in a compatible solvent, they 100 101 can interact through molecular associations facilitated by hydroxyl or carboxyl groups [31]. Subsequent reduction of GO at elevated temperatures results in the formation of silicon-reduced GO (Si-rGO) composites. 102 The electrochemical performance of Si-rGO composites as anodes hinges on the extent to which silicon 103 nanoparticles are enveloped or encapsulated by rGO. Ideally, high-performance Si-rGO composites should 104 meet several structural criteria: 1. Silicon nanoparticles should be extensively covered by rGO to minimize 105 direct contact with the electrolyte. 2. The relative positions of silicon and rGO should remain stable even after 106 multiple cycles of volumetric changes in silicon. This implies that silicon nanoparticles should ideally be 107 anchored to rGO through a specific mechanism to prevent agglomeration of either silicon or rGO particles 108 when external conditions change. 3. rGO should expand and maintain a flexible envelope around silicon 109 nanoparticles when they undergo volumetric changes, providing ample protective shielding against 110 undesirable electrolyte reactions on silicon surfaces. 4. rGO should not readily fold or develop excessive 111 wrinkles that could displace some of the silicon particles from its protective coverage. 112

In a traditional preparation method employing mixing GO and Si together followed by a thermal reduction treatment, these structural prerequisites are not easily met. This difficulty arises from the fact that, within the same thermal environment, silicon and GO typically undergo distinct surface property alterations.
For instance, while silicon consistently maintains a hydrophilic nature during thermal reduction, GO undergoes a significant wettability transition from highly hydrophilic to highly hydrophobic (rGO). These discrepancies frequently lead to pronounced phase segregations between silicon and graphene. As a result, the coverage rate of rGO on silicon diminishes and substantial wrinkling of rGO occurs.

FJH technology is a thermal treatment method based on Joule heating principle. The whole thermal 120 treatment process features exceptionally high heating/cooling rate of up to 10⁵ K/s, with reaction temperatures 121 reaching over 3000 K. This approach enables the synthesis of high-performance electrode materials within 122 minutes[32, 33]. It was found that under specific FJH conditions, formation of silicon carbide at the interface 123 between GO and silicon particles is obvious and can act as "riveting point" to effectively bond rGO and Si 124 particles together. The initial discharge specific capacity of the prepared material reached 1141.3 mAh g^{-1} at 125 a current density of 1C (equivalent to 2280 mAh g⁻¹ or 10.1 A/m²), with a Coulombic efficiency exceeding 126 99% from the second cycle onwards. Remarkably, even after 1000 charge-discharge cycles, the F-Si@rGO 127 composite retained a specific capacity of 894.95 mAh g⁻¹, representing an average capacity degradation of 128 only 0.216 ‰ per cycle. Extended cycling tests demonstrated competitive electrochemical performance and 129 remarkable stability of the F-Si@rGO anode, with a remaining capacity of 651.67 mAh g⁻¹ after 2000 cycles. 130 This synthetic approach not only holds promise for the development of graphene-based energy storage 131 materials but also presents opportunities for broader applications in scenarios requiring graphene surface 132 installation and processing. 133

134 **2. Experimental Procedures**

135 **2.1. Material Preparation**

A homogeneous GO aqueous solution was firstly prepared by diluting a GO solution (Shanxi Institute of 136 Coal Chemistry, Chinese Academy of Sciences) with deionized water to a desired concentration of 4 mg ml⁻¹. 137 Si powders (size ≈ 200 nm, Canrd New Energy Technology Co. Ltd.) were then homogenized into the GO 138 dispersion by ball milling (equipment: MITR, YXQM-4L). A 100ml ZrO_2 jar with ZrO_2 balls (size $\approx 3mm$) 139 and a mass ratio of balls to slurry of 10:1 were used in the milling process, which was conducted at 300 rpm 140 for 12 hours to ensure a stable slurry containing Si-GO assemblies with a silicon content from 30% to 70% 141 wt. To preserve the structural integrity of the already formed Si-GO assembly, the slurry containing Si-GO 142 assemblies was subjected to rapid freezing by placing it in a -55°C cold trap for 12 hours and subsequently 143 freeze-dried under vacuum conditions of 0.01 Pa at -55°C for 24 hours to remove water content. After freeze-144 drying, the material underwent processing using an FJH processor (model HTS-7026D, Shenzhen Joule IC 145

Technology Co., Ltd.), resulting in the production of the F-Si@rGO composite. Within the processor, the 146 material was enveloped in a carbon wrap measuring 3cm by 5cm and positioned between two tungsten carbide 147 electrodes spaced 4cm apart in a gas-tight glass reaction chamber (size of 0.2m x 0.3m x 0.3m). Processing 148 conditions comprised a voltage of 50V and a current of 20A, maintained at 1000°C for 120 seconds with a 149 heating rate of 1000°C s⁻¹. The rapid heating rate was found to be essential for achieving the desired 150 microstructures. To highlight the advantageous effect of fast heating speed, a parallel heat treatment was 151 conducted using the same material in a tube furnace with a significantly slower heat-up rate of 5°C min⁻¹ 152 (approximately 12,000 times slower compared to the FJH process). This slow heat treatment, lasting 120 153 seconds at 1000°C, yielded the S-Si@rGO composite. Both heating processes were performed in an Argon 154 environment with a flow rate of 1.5L/min to prevent oxidation. 155

156 **2.2 Material Characterization**

The microscopic structures and surface morphologies of the prepared materials were characterized by Scanning Electron Microscopy (SEM, GeminiSEM 300, Carl Zeiss Microscopy Ltd., UK) coupled with Energy Dispersive X-Ray Spectrometry (EDS) and a Transmission Electron Microscopy (TEM, FEI Talos F200X).

161 X-Ray Diffraction (XRD, SmartLab XRD, Rikagaku, Japan Inc.) was used to reveal the crystallinity of 162 the samples. The incident radiation used in the XRD testing has a wavelength of 0.1542 nm (Cu K α). The 163 testing is conducted with a voltage and current of 40 kV and 40 mA, respectively. The 2 θ interval is set to 164 24.225 seconds, with a step size of 0.0131303 degrees. The databases employed include PDF#99-0092 and 165 PDF#99-00975.

166 X-Ray Photoelectron Spectroscopy (XPS, XPS Escalab Xi⁺, Thermo Fisher Scientific Co. Ltd, Czech) 167 was used to analyze the changes in the functional groups and surface bonds. A micro-focused monochromatic 168 Al target was used as the X-ray source, with a micro-focus spot size of 500 μ m, and all samples were calibrated 169 with 284 eV (binding energy of sp² hybrid carbon) as C1s. The deconvolution of the spectra was performed 170 by utilizing Gaussian functions within the XPS PEAK program, following the subtraction of a Shirley 171 background.

172 2.3 Electrochemical Characterizations

For the preparation of electrode materials, F-Si@rGO nanoparticles or S-Si@rGO nanoparticles were combined with conductive black (super P) and sodium carboxymethylcellulose (CMC) binder. The mass ratio employed was 8:1:1. These constituents were dispersed in a suitable amount of deionized water to create homogeneous slurries. Subsequently, these slurries were applied onto a Cu foil substrate and subjected to vacuum drying at 80°C for a duration of 12 hours, resulting in the formation of a uniform electrode layer.

To construct standard CR2032-type half cells, the assembly process was conducted in an Argon-filled glove box. Li metal foil was utilized as the counter electrode, while a polypropylene membrane as the separator. The electrolyte employed was $1 \mod L^{-1}$ solution of LiPF₆ dissolved in a mixture comprising ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) with a volumetric ratio of 1:1:1, supplemented with 1% wt. of vinylene carbonate (VC).

The silicon mass loading in the working electrodes was approximately 0.5 mg·cm⁻² for various electrochemical tests, including galvanostatic charging/discharging tests, galvanostatic intermittent titration technique measurements (GITT), cyclic voltammetry tests (CV) and electrochemical impedance spectroscopy tests (EIS). Furthermore, the same anode material was evaluated in an assembled full cell with the cathode being composed of LiFePO₄/super P/Polyvinylidene Fluoride (PVDF) at a mass ratio of 8:1:10n aluminum foil. All electrochemical assessments were carried out at room temperature.

Galvanostatic charging/discharging tests were conducted on a Neware instrument (Shenzhen, China) over a voltage range of 0.01-1.5 V for half-cell and 2.5-3.5 V for full cell. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted using a CHI 660e electrochemical workstation with a standard three-electrode setup. CV curves were generated by scanning voltage in the range of 0 to 3 V at a scan rate of 0.1 mV·s⁻¹, while EIS experiments were performed across a frequency range spanning from 0.01 Hz to 1M Hz.

195 **3. Results and Discussion**



196 **3.1 Synthesis and Material Characterizations**

197

198 Figure 1. Synthesis and material characterization of the prepared composites: a) Schematic of the synthesis routes of F-Si@rGO and S-Si@rGO composites. b) SEM image of S-Si@rGO, inset shows micro-morphology of Si@GO. c) SEM 199 image of F-Si@rGO. d) Partitioning behavior of S-Si@rGO in the binary mixture of heptane and deionized water. e) 200 SEM image of S-Si@rGO at the interface between heptane and deionized water. f) SEM image of S-Si@rGO in the 201 deionized water. g) Partitioning behavior of F-Si@rGO in the binary mixture of heptane and deionized water. h) SEM 202 image of F-Si@rGO in the binary mixture of heptane and deionized water, i) and j) HRTEM image of F-Si@rGO. k) 203 204 and I) HRTEM image of F-Si@rGO in which silicon has been dissolved by sodium hydroxide solution (the inset shows 205 SAED pattern). m) XRD patterns of F-Si@rGO, S-Si@rGO, Si and rGO. n) The XPS spectrum (Si 2p) of the two prepared composites. 206

As depicted in Figure 1a, the synthesis process begins with the mixing of silicon nanoparticles and GO 207 through ball milling. Notably, both silicon nanoparticles and GO sheets exhibit a substantial presence of 208 oxygen-containing functional groups, which can lead to self-agglomeration when dispersed in water. Ball 209 milling can allow sufficient breakup of the GO and silicon particle agglomerates and create enough collision 210 opportunities for the silicon particles to be installed on the surface of GO sheets through interactions between 211 oxygen-containing functional groups [34]. Sufficient time is allowed for the silicon nanoparticles to be 212 anchored onto the GO sheets before the mixture undergoes freeze drying to eliminate water content. This step 213 minimizes the risk of undesirable secondary self-agglomeration between silicon nanoparticles or GO sheets. 214 Freeze drying is selected due to its scalability and industrial applicability, ensuring minimal disturbance to the 215

established installations during water removal. The resulting material from freeze drying (Si@GO) exhibits a fluffy consistency and proceeds directly to the FJH treatment. During FJH, the material is compacted within a soft carbon fabric encasement positioned between two tungsten carbide electrodes. Subsequently, the material undergoes a programed electrothermal processing in Argon as part of the FJH treatment to yield F-Si@rGO composite. For comparison, a traditional slow heat treatment in Argon was used to prepare S-Si@rGO composite from Si@GO.

Figure 1b and 1c present the SEM characterizations of the Si@GO, S-Si@rGO and F-Si@rGO composites. In the case of Si@GO, silicon nanoparticles are evenly distributed on the GO surface (inset in Figure 1b). However, upon subjecting Si@GO to a gradual thermal treatment, pronounced phase segregation becomes evident in the final product (S-Si@rGO). Within S-Si@rGO, rGO sheets display a wrinkled appearance and the silicon nanoparticles agglomerate, no longer maintaining coverage by the rGO sheets (Figure 1b).

Despite the application of freeze-drying to mitigate structural disruption, the slow heating process 228 promotes phase segregation by introducing varying degrees of wettability modification to the silicon and 229 carbon phases. The silicon surface initially possesses hydroxyl groups that can interact with functional groups 230 on GO via non-covalent bonds. As the GO sheets gradually lose their oxygen functional groups, the interaction 231 between silicon and GO diminishes, leading to slow yet irreversible self-agglomeration among the silicon 232 nanoparticles. Simultaneously, with the reduction of oxygen-containing functional groups, interactions within 233 the π -systems of rGO become dominant, resulting in the folding of carbon sheets. This self-agglomeration 234 contributes to the expulsion of hydrophilic silicon aggregates from the carbon matrix. 235

Severe phase segregation can be confirmed by dispersing a portion of the S-Si@rGO composite into a 236 small container containing heptane (at the top) and water (at the bottom). Upon subjecting the container to 30 237 seconds of sonication, a partitioning phenomenon becomes apparent. Specifically, a black layer was formed 238 at the top comprising hydrophobic agglomerates of rGO that migrate into the heptane phase, while a brown 239 aqueous layer was at the bottom which is dominated by uniformly dispersed silicon nanoparticles (Figure 1d). 240 This phase separation is clearly visible through SEM (Figure 1e and Figure 1f). Notably, subjecting F-Si@rGO 241 to the same partitioning tests (sonication in a container filled with heptane and water) demonstrates that such 242 disturbance is insufficient to disengage the silicon nanoparticles from their anchoring points. Furthermore, F-243 244 Si@rGO exhibits surface activity and the capability to stabilize a water-in-heptane emulsion (Figure 1g). This observation conclusively confirms the biwettability of F-Si@rGO particles, an attribute resulting from the 245 coexistence of hydrophobic domains (rGO) and hydrophilic domains (silicon) within the same particle. SEM 246 of F-Si@rGO in the binary mixture of heptane and deionized water also confirms this viewpoint (Figure 1h). 247

On the other hand, the morphology of F-Si@rGO shows that the rGO sheets be more expanded and 248 thinner, with the silicon nanoparticles appeared in smaller domains of agglomerates which are completely 249 wrapped by rGO. The drastic morphological difference between S-Si@rGO and F-Si@rGO is likely 250 dependent on how fast the system can react to surface property change. FJH treatment induces a significant 251 temperature increase within milliseconds, thereby affording minimal reaction time for silicon nanoparticles to 252 migrate within the GO matrix during the electrothermal treatment. Sufficient contacts between silicon and 253 rGO encourages the formation of anchoring points between silicon and rGO, thereby ensuring the relative 254 positioning of silicon nanoparticles within the carbon matrix. These anchoring points are discernible in 255 HRTEM micrographs as diminutive shaded regions (Figure 1i and 1j), featuring a d-spacing of approximately 256 0.256 nm, corresponding to the (111) plane of the SiC crystalline structure [35]. The robustness of these 257 anchoring points arises from the formation of covalent bonds between silicon and carbon. 258

To obtain a clearer perspective on the positioning and distribution of SiC anchor points within the rGO 259 matrix, the silicon phase in the F-Si@rGO composite was selectively removed using a 1 mol/L sodium 260 hydroxide solution. In Figure 1k and 1l, it is evident that, following the removal of the silicon phase, rGO 261 'bubbles' become apparent, signifying the encapsulation of the silicon phase by carbon in the original structure. 262 On the surface of these rGO 'bubbles,' an abundance of dispersed single crystals was observed, resilient to 263 removal by strong base. The Selected Area Electron Diffraction (SAED) test indicates three distinct diffraction 264 rings corresponding to the (113), (022), and (113) crystal planes in silicon carbide crystals according to COD 265 266 1010995 from the Crystallography Open Database (inset in Figure 1k). This finding complements the HRTEM micrographs on the chemical nature of these anchor points. 267

The crystalline phase and structure of the composites were further analyzed by XRD. In Figure 1m, the 268 signature diffraction peaks of silicon (28.44°, 47.30°, 56.12°, 69.13°, 76.37° and 88.03°) and rGO (25.88°) 269 can be easily found. The rGO peak in the XRD pattern of the S-Si@rGO composite is significantly stronger 270 than that of the F-Si@rGO composite, consistent with the observation in SEM micrographs that the rGO sheets 271 are more agglomerated in the S-Si@rGO composite. Figure S1 shows the comprehensive XPS spectrum of 272 the composite anode material. Magnification of the Si 2p spectrum (Figure 1n) for the S-Si@rGO composite 273 displays two distinct peaks at 98.41 eV and 102.86 eV, corresponding to Si-Si and Si-O bonds, respectively. 274 Notably, the Si 2p spectrum of F-Si@rGO exhibits an additional peak at 99.2 eV, indicative of the presence of 275 a Si-C bond, providing additional evidence for the formation of silicon carbide within the F-Si@rGO 276 composite. Be noted that in nanocrystalline silicon, the surface layers can exhibit some degree of amorphous 277 character due to the high surface-to-volume ratio and the presence of defects [36]. This amorphous layer on 278 the surface of nanocrystalline silicon enhances its reactivity, providing ample opportunities for chemical 279

reactions with graphene at elevated temperatures. The disordered structure of amorphous silicon leads to increased surface energy and facilitates the diffusion of carbon atoms from graphene into the silicon lattice and thus can promote the formation of SiC at the graphene-silicon interface.



283 3.2 Electrochemical Performance of F-Si@rGO and S-Si@rGO Electrodes

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Figure 2. Electrochemical performance of the prepared composites: a) CV curves of the F-Si@rGO electrode. b) CV 285 curves of the S-Si@rGO electrode. c) GITT curves of F-Si@rGO. d) GITT curves of S-Si@rGO. e) Capacitive 286 contribution ratio of F-Si@rGO at different scan rates. f) Capacitive contribution ratio of S-Si@rGO at different scan 287 rates. g) Schematic representation of capacitive dominated charging process in F-Si@rGO. h) Schematic representation 288 of diffusion dominated charging process in S-Si@rGO. i) EIS curves of F-Si@rGO. j) EIS curves of S-Si@rGO. k) DRT 289 function plots $\gamma(\tau)$ of F-Si@rGO between 1-10 s and below 10⁻³ s. 1) DRT function plots $\gamma(\tau)$ of S-Si@rGO between 1-290 10 s and below 10⁻³ s. m) DRT function plots $\gamma(\tau)$ of F-Si@rGO between 1-10⁻³ s. n) DRT function plots $\gamma(\tau)$ of S-291 Si@rGO between 1-10⁻³ s. o) Long-term cycling performances of the prepared composites at 1C. p) Comparison of 292 performance of F-Si@rGO with previous reported Si-based materials [37-46] 293

Cyclic voltammetry (CV) analysis at a scan rate of 0.1 mV s⁻¹ between 0 and 3 V (vs. Li/Li⁺) were conducted to illustrate the activation process of F-Si@rGO and S-Si@rGO in the initial five cycles. For F-Si@rGO (Figure 2a), an insignificant reduction peak appeared in the initial cathodic scan at around 0.71 V, corresponding to the formation of SEI layer. Such a reduction peak disappeared in the following cycles, suggesting that SEI layer formed and stabilized in the first cycle discourages further SEI growth. In comparison, three reduction peaks located at 1.98 V, 1.41 V and 0. 68 V are prominent for S-Si@rGO, suggesting that SEI growth happened on different interfaces and was much more severe in the case of S-Si@rGO (Figure 2b).

This observation is consistent with the severe phase segregation observed in the microscopic morphology 302 of S-Si@rGO, that electrolyte consumption and thus SEI growth can happen at various exposed surfaces of 303 S-Si@rGO to electrolyte. Furthermore, the anodic peaks at 0.18 V for F-Si@rGO and 0.12 V for S-Si@rGO 304 are attributed to the reduction of Si to Li_xSi phases, while the cathodic peaks for F-Si@rGO (at 0.35 V and 305 0.52 V) and S-Si@rGO (at 0.39 V and 0.57 V) are related to the phase transformation of Li_xSi to amorphous 306 Si [47]. The potential gap between the anodic and cathodic peaks(ΔE_P) signifies the level of energy required 307 for Li⁺ ions to migrate in or out of the anode materials, and the speed of the electrochemical reaction. Thus, a 308 smaller ΔE_p of F-Si@rGO compared S-Si@rGO (0.17 V vs. 0.27 V) suggests F-Si@rGO bears higher ionic 309 conductivity and electrochemical activity. Higher ionic conductivity ensures F-Si@rGO displays a high initial 310 capacity of 2383.7 mAh g⁻¹ and an impressive initial coulombic efficiency (ICE) of 88.7% at a current density 311 of 0.05 C (Figure S2). 312

The Li^+ diffusion coefficient (D_{Li}^+) was determined using the Galvanostatic Intermittent Titration Technique (GITT). As presented in Figure 2c and 2d, D_{Li}^+ of the F-Si@rGO electrode is always one to two orders of magnitude higher than that of S-Si@rGO electrode. The enhanced Li⁺ diffusion kinetics observed in the F-Si@rGO electrode can be attributed to the presence of silicon carbide anchors, which promote closer contact between silicon and graphene. This establishment of stronger and more efficient pathways for lithiumion diffusion is the key factor behind the observed enhancement.

From a kinetic perspective, measuring the response current (i) of electrode materials at various scan rates 319 (v) is widely considered the most suitable method for identifying electrochemical processes based on battery-320 type (diffusion-controlled) or capacitive (surface-controlled) charge storage. To gain insight into the 321 mechanisms governing the electrochemical performance, cyclic voltammetry (CV) curves of F-Si@rGO and 322 S-Si@rGO are registered at different scan rates, ranging from 0.1 to 0.5 mV s⁻¹ (Figure S3a). By applying the 323 power law, the slope of the plot log(i) vs. log(v) (redox peak current vs. various scan rates) yields the b-value 324 which serves as an indicator of the predominant mechanism governing the energy storage behavior of the 325 active material [48]. Specifically, a b-value of 0.5 suggests a diffusion-controlled redox reaction, primarily 326 involving intercalation/conversion/alloving reactions and b-value of 1.0 indicates a surface-limited 327 electrochemical process, such as a pseudocapacitive storage processes [48, 49]. The calculated b-values for 328

the oxidation and reduction peaks of F-Si@rGO are 0.97 and 0.935 respectively (Figure S3b). (Calculation process detailed in supporting information), suggesting that the lithiation and delithiation cycles in F-Si@rGO are primarily driven by a capacitive process. Furthermore, the contribution of capacitance to the overall capacity (as shown in Figure 2e) increases with higher scan rates, eventually reaching a proportion of 89.2% at a scan rate of 0.5 mV s⁻¹ (Calculation process for capacitive ratios of F-Si@rGO and S-Si@rGO is shown in Figure S4 and S5 respectively). This underscores the remarkable rate performance of F-Si@rGO, which can be attributed to its capacitive behavior.

Conversely, the b-values of S-Si@rGO for the oxidation and reduction peaks of S-Si@rGO are 0.615 and 0.494 (shown in Figure S6a and S6b), which indicates the S-Si@rGO exhibits a diffusion-dominated charging process. The capacitance contribution to the capacity is 43.4% and 63.4% at scan rates of 0.2 mV s⁻¹ and 0.5 mV s⁻¹ (shown in Figure 2f) respectively. These values are notably lower than the capacitance contribution of 56.3% and 89.2% observed in F-Si@rGO when operating at the same scan rates.

To understand the differences in the ratios of capacitance contributions, schematics of the possible storage 341 mechanisms in F-Si@rGO and S-Si@rGO were shown in Figure 2g and 2h respectively. The robust anchoring 342 of silicon nanoparticles within a graphene matrix provides an extensive and uniformly distributed surface area 343 for contact between silicon and carbon in F-Si@rGO. The carbon matrix functions as an ionic-conductive 344 "highway," facilitating the homogeneous transport of electrons and ions to the surface of silicon. This promotes 345 superior ionic spreading on the silicon surface, contributing to energy storage through rapid and reversible 346 redox reactions at the surface and subsurface of the silicon nanoparticles. On the other hand, when such 347 continuous conductive-pathways are lacking, as in the case of S-Si@rGO, charge transport may rely more on 348 diffusive processes within the bulk of the active material. The exchange of Li⁺ and electrons through solid 349 state diffusion can allow for a degree of electric connectivity within the material but is inefficient and may 350 eventually lead to inhomogeneous charging that silicon nanoparticles in contact with the rGO will experience 351 more efficient charge transfer compared to silicon particles that are not in contact with the conductive matrix. 352

Electrochemical Impedance Spectroscopy (EIS) is used to analyze the impedance of the electrode 353 materials. Both Nyquist plots in Figure 2i(F-Si@rGO) and 2j(S-Si@rGO) display two semicircles in the high 354 and medium frequency ranges and an inclined straight line in the low frequency range. The distinct semicircle 355 within the high frequency region is associated to the interface resistance between the electrolyte and SEI on 356 the electrode. The semicircle in the medium frequency range corresponds to the charge transfer process at the 357 interface between the surface layer and the silicon and the inclined straight lines in the low frequency range 358 corresponds to the diffusion-controlled impedance within the silicon phase [47]. For better clarity to see the 359 change in the charge transfer resistance of the SEI, Nyquist plots of the 1st, 5th and 10th cycle of F-Si@rGO 360

and S-Si@rGO respectively are plotted in Figure S7. For both of F-Si@rGO and S-Si@rGO, the initial cycle 361 exhibits a more pronounced charge transfer resistance with its magnitude decreasing as the cycling progresses. 362 This trend suggests a densification of the SEI layer over cycling, thereby enhancing its charge transfer 363 capabilities. The Distribution of Relaxation Times analysis (DRT) conceptualizes an electrochemical system 364 as a combination of an ohmic resistance and an infinite series of polarization processes. This methodology 365 offers a reliable approximation to the impedance model of electrochemical system, delivering insightful 366 kinetic information regarding the anodic electrochemical reactions [50]. Assisted by the DRT tools pioneered 367 by Ciucci's team [51], the peaks observed in the DRT function plots of S-Si@rGO (Figure S8a) and F-Si@rGO 368 (Figure S8b) can be categorized into different electrochemical processes within the electrode based on the 369 value of $\gamma(\tau)$: the signals upon 1 s (frequency below $1/2\pi$ Hz) are associated with the diffusion processes of 370 solid, in which the peaks located at 1-10 s and > 10s represent the region division dictated by the Li-ion 371 diffusion in the surface layer (P_{sl}) and silicon bulk (P_{si}) respectively [52, 53]. Signals located at higher 372 frequencies usually indicates interfacial charge transfers. The peak (Psl-Si) located between 1s and 10⁻³ s 373 (medium frequency) are associated with the charge transfer resistance occurring between the surface layer and 374 the Si bulk, and Peak (P_{E-sl}) in $\gamma(\tau)$ below 10⁻³ s is attributed to the interfacial reaction process between 375 electrolyte and the surface layer [54]. 376

As shown in Figure 2k and 2l, F-Si@rGO exhibits a lower magnitude of P_{E-sl} compared with S-Si@rGO. 377 The value of the P_{E-sl} in F-Si@rGO becomes progressively smaller with cycling (inset in Figure 2k). Be noted 378 379 that the SEI layer start with a porous solid phase with the pores filled with electrolyte [55]. Therefore, in the initial cycles, the magnitude of P_{E-sl} which is attributed to the interfacial reaction between electrolyte and the 380 surface layer predominantly contributes to the total impedance, primarily due to the extensive surface area 381 contacts between SEI and electrolyte. The other part of the contribution arises from the diffusive processes 382 within the surface layer (P_{sl}). Lower starting magnitude of P_{E-sl} with F-Si@rGO and the magnitude decreases 383 along with cycling suggests the starting density of the SEI layer on F-Si@rGO is higher compared with S-384 Si@rGO and the interface between the SEI on F-Si@rGO and the electrolyte becomes increasingly conducive 385 for charge transfer. Be noted that the exceptionally rapid heating capability of FJH ensures that the composite 386 material remains at elevated temperatures for only a brief period, thereby mitigating the risk of crystallization, 387 which can occur if high temperature exposure is prolonged. Unlike amorphous silicon, which undergoes direct 388 lithiation [56], crystalline silicon must first undergo amorphization before full lithiation can occur. In the case 389 of crystalline Si, lithiation predominantly progresses in the <110> direction, leading to additional isotropic 390 stress that may adversely affect early SEI growth [57]. This likely accounts for the observed higher initial 391 density of SEI with F-Si@rGO. In the case of F-Si@rGO, the gradual reduction of P_{E-sl} is accompanied by a 392

mild increase in P_{sl} , indicating a transition from a liquid-phase reaction between the electrolyte and SEI to a solid-state reaction over multiple cycles. This solid-state evolution of the SEI enhances the cycling process by providing the required robustness to maintain the integrity of the SEI in the face of volumetric changes in the active materials.

In contrast, the initial value of P_{E-sl} in S-Si@rGO is notably higher, indicating that the SEI formed in this 397 case possesses a lower initial density and lacks the robustness observed in F-Si@rGO. Both PE-sl and Psl in S-398 Si@rGO exhibit irregular, abrupt increases followed by subsequent decreases during the second, sixth, and 399 eighth cycles (inset in Figure 21). This recurring fluctuation in impedance can be attributed to the significant 400 expansion resulting from silicon lithiation. In scenarios where the SEI formation is less than ideal, such as 401 when it has low mechanical strength or forms directly on the silicon surface, the repetitive volumetric changes 402 in the active material lead to the continuous destruction and reformation of the SEI layers. This, in turn, 403 consumes excessive amounts of electrolytes and results in the formation of unfavorable "dead zones" within 404 the active materials. 405

Peaks of $\gamma(\tau)$ located between 1s and 10⁻³s (medium frequency) are dependent on the electrical contact between silicon and the conductive framework and surface layer. As shown in the Figure 2m (F-Si@rGO) and 2n (S-Si@rGO), F-Si@rGO exhibits a much lower magnitude of P_{sl-Si} and both samples exhibited a similar trend as P_{E-sl}, indicating that the presence of SiC anchors provides more contact points between Si and the carbon conductive framework, significantly enhancing the efficiency of lithium-ion diffusion.

Figure 20 illustrates the long-cycle performance of F-Si@rGO, S-Si@rGO, Si particles and rGO. All test 411 batteries underwent activation with a low current density of 0.05C for the first five cycles before they were 412 tested at a current density of 1C. F-Si@rGO exhibited a high initial capacity of 1141.3 mAh g⁻¹ at a current 413 density of 1C, and demonstrated superior retention compared with S-Si@rGO and Si. Remarkably, after 1000 414 cycles, the capacity of F-Si@rGO remained at 894.95 mAh g^{-1} , corresponding to a capacity retention of 78.41% 415 in 1000 cycles. Furthermore, even after enduring an astonishing 2500 charge-discharge cycles, F-Si@rGO 416 maintained an impressive capacity of 574.47 mAh g^{-1} (see Figure S9). The rate performance of F-Si@rGO, 417 presented in Figure S10, demonstrated excellent performance across a range of current densities (0.1C to 1C). 418

Compared to previous research on silicon-carbon composite materials (Figure 2p and Chart S1), F-Si@rGO prepared via FJH demonstrates superior electrochemical performance across various metrics including ICE, cycle number tested, current density, capacity retention and post-cycling capacity. Additionally, its fast synthesis speed positions it as a viable candidate for industrial-scale production, offering promising potentials for commercialization.



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Figure 3. a) HRTEM image of S-Si@rGO after 500 cycles. b), c) and d) EDS element mapping of S-Si@rGO after 500 cycles. e) HRTEM image of F-Si@rGO after 500 cycles. f), g) and h) EDS element mapping of F-Si@rGO after 500 cycles. i) EIS curves of S-Si@rGO after cycles. j) EIS curves of F-Si@rGO after cycles. k) Microscopic schematic of the cycling process of S-Si@rGO. l) Microscopic schematic of the cycling process of F-Si@rGO m) The SEM images of S-Si@rGO before 500 cycles. n) The SEM images of S-Si@rGO after 500 cycles. o) The SEM images of F-Si@rGO before 500 cycles. p) The SEM images of F-Si@rGO after 500 cycles.

To assess the growth of SEI and integrity evolution of these two different electrodes, the cycled batteries 432 (after 500 cycles) were placed in a glovebox where their shells were opened by pliers and the electrodes within 433 were extracted with care. The electrodes were then soaked and cleaned with anhydrous ethanol to remove the 434 remaining electrolyte before being dried at room temperature in Argon to obtain the cycled electrodes to have 435 their morphology examined. The structures of the active materials within the electrodes were examined by 436 transmission electron microscopy (TEM) imaging and energy-dispersive X-ray spectroscopy (EDS) for 437 elemental mapping. As illustrated in Figure 3a, S-Si@rGO exhibited severe pulverization of silicon particles 438 after 500 cycles. The original spherical shape of silicon was completely lost, transforming the composite into 439 a mixture characterized by a relatively homogeneous distribution of silicon, carbon (C), and fluorine (F) atoms 440 (indicative of SEI growth) (Figure 3b, 3c and 3d). In contrast, F-Si@rGO maintained its structural integrity, 441 with the spherical shape of silicon clearly discernible after 500 cycles (see Figure 3e). Notably, EDS mapping 442

of the F-Si@rGO composite revealed that carbon and fluorine elements were predominantly concentrated at 443 the periphery of silicon particles (as seen in Figure 3f, 3g and 3h). This suggests that SEI growth primarily 444 occurred on the outer layer of rGO, where unnecessary side-reactions were effectively prevented and thus 445 excessive SEI growth as seen in the case of S-Si@rGO avoided. On a microscopic scale, the process of 446 lithiation in silicon is featured by the atomic ledge peeling mechanism that entails the gradual removal of 447 atomic layers from the silicon surface by lithium ions, resulting in the formation of successive layers of an 448 amorphous Li_xSi alloy [57]. As a consequence, the silicon anode experiences non-uniform expansion during 449 lithiation. Within individual silicon nanoparticles, the anchored carbon matrix in F-Si@rGO promotes more 450 uniform lithiation and homogeneous mobility of the interface between the lithiated amorphous LixSi and 451 unlithiated Si core during charging and thus discourage the formation of fractures due to anisotropic swelling 452 in silicon particles after long-term cycling. In S-Si@rGO, on the other hand, charge transport may rely more 453 on lithium diffusion within the silicon bulk, that is, without satisfactory ionic spreading, the average pathway 454 for lithium ions to reach full lithiation of silicon will be significantly longer, leading to uneven lithiation and 455 consequently more fractures and severer SEI growth. 456

This substantial difference in morphology is also reflected in the change of resistance of these two 457 materials. After 500 cycles, the resistance of S-Si@rGO increased by more than two-folds (refer to Figure 3i) 458 due to the extensive growth of SEI, severe phase segregation and silicon pulverization during prolonged 459 cycling. In contrast, the resistance of F-Si@rGO remained largely unchanged due to the sustained integrity of 460 the composite structure and the ideal SEI growth conditions (as shown in Figure 3i). Be noted that the 461 formation of the SEI layer commences during the activation process of the electrodes. This activation involves 462 several initial cycles at a low rate (0.05 C), conducted before cycling the electrodes at high rate of 1C for 500 463 cycles. The absence of a semicircle in the medium-frequency range of the Nyquist plots, as observed in Figure 464 3i and Figure 3j after the activation process, suggests that the densification stage of the initially formed SEI 465 layer is nearly completed within the initial activation cycles. 466

Significant cracks were also observed in the case of S-Si@rGO across the surface of electrode. This is likely due to the severe phase separations between rGO and silicon that leads to non-uniform charging of silicon particles across the electrode. During the electrode's operation, this non-uniform charging state introduces varying degrees of volumetric expansion within the electrode. Regions containing silicon nanoparticles enveloped by rGO experience higher levels of expansion, while areas with concentrated rGO or silicon show less volumetric expansion, due to the limited expansion characteristics of carbon or lack of conductivity in silicon.

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As illustrated in Figure 3k, the surface of the S-Si@rGO electrode is schematically represented as a

checkered patterned box. In this representation, boxes in light yellow depict areas containing effectively 475 charged silicon nanoparticles, while boxes in light blue indicate regions with severe phase segregations. The 476 non-uniform volumetric changes caused by the distinct charging states can result in the development of 477 significant localized stress concentrations (highlighted in red in Figure 3k). These stress concentrations serve 478 as initiation points for the formation of microcracks. The propagation and combination of these microcracks 479 further compromise the conductivity within the electrode, leading to the creation of large "dead zones" where 480 the active material completely loses its conductivity from other areas. On the other hand, F-Si@rGO exhibits 481 a homogeneous charging state throughout different locations within the electrode, primarily due to minimized 482 phase segregation and interfacial sintering (Figure 31). This results in significantly improved ionic wetting 483 during the charging process and ultimately leads to a more uniform volumetric change throughout the 484 electrode. As a result, it alleviates the development of micro-stress concentrations. 485

SEM imagery confirmed formation of numerous large cracks in the electrode of S-Si@rGO (figure 3m and 4n) after 500 cycles. Reginal isolation in the electrode discourages electron and ionic transportation within the electrode and is one of the direct reasons for drastic impedance increase with cycling. In contrast, the surface of F-Si@rGO electrode (figure 3o and 3p) remains remarkably smooth without any visible cracks after 500 cycles. This observation is consistent with the intact integrity of the composite structure in HRTEM after cycling.

492 **3.4 Bench Scale Production and Validation in LiFePO4//F-Si@rGO Full-Cells**

The scalability of this synthesis method for F-Si@rGO particles is exemplified through a bench-scale 493 demonstration, where it successfully treated 1 g of particles sandwiched between two 5cm × 5cm carbon fabric 494 layers (Figure 4a). This setup utilized tungsten carbide electrodes to apply a high electric current to rapidly 495 heat up the materials to 1000°C in ~ 1 second, with a total treatment duration of 100 seconds to produce F-496 Si@rGO. Notably, a total of just three runs, cumulatively lasting for only 5 minutes, produced sufficient F-497 Si@rGO to nearly fill a 100ml glass beaker with ~70ml of material (Figure 4b). It's important to note that this 498 bench-scale process is primarily constrained by the carbon fabric's dimensions. Envisioning in an industrial-499 scale production, significantly larger carbon fabrics can be utilized. For instance, employing a 1.5m × 1.5m 500 carbon fabric could exponentially enhance the production rate by up to 900 times. This scale-up translates to 501 an impressive output of 388.8 kg/day, assuming a 12-hour production cycle. 502



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Figure 4. Bench scale production of F-Si@rGO and its electrochemical performance in full cell tests: a) Bench scale production of F-Si@rGO in the laboratory. b) A jar of F-Si@rGO composites prepared within a total treatment time of 506 5 minutes. c) SEM of the prepared F-Si@rGO in the bench scale production. d) Partitioning behavior of the prepared F-507 Si@rGO in the binary mixture of heptane and deionized water. e) Voltage profiles of the full cell using F-Si@rGO as 508 the anode and LiFePO₄ as the cathode; f) Long-term cyclability of the LiFePO₄//F-Si@rGO full cell at 1 C. g) Schematic 509 illustration of scalable production of F-Si@rGO.

The F-Si@rGO particles produced in this bench-scale test underwent SEM characterization, verifying 510 their morphological consistency with those produced in smaller batches (20 mg). As shown in Figure 4c, the 511 SEM images demonstrate that the bench-scale produced particles retain the key morphological features seen 512 in smaller batch samples, with silicon nanoparticles effectively covered by thin layers of rGO. This consistency 513 in structure suggests that the enhanced performance characteristics observed at a smaller scale may be 514 replicable in larger productions. Furthermore, partitioning tests conducted on the bench-scale produced F-515 Si@rGO particles echoed the emulsion stabilization phenomenon seen in smaller-scale experiments (Figure 516 4d). This consistency is encouraging and suggests a robust silicon-carbon integration in the F-Si@rGO 517 composites, regardless of the batch size. These findings offer evidence of the scalability of this synthesis 518

method and provide a foundation for future work aimed at adapting and validating the process for industrialapplications.

As shown in Figure 4e and 4f, a LiFePO₄//F-Si@rGO full cell was constructed to test the practical application value of F-Si@rGO. The results of the cycle test performed at 1C show that the battery demonstrates satisfactory stability and remains a specific capacity of 120 mAh g⁻¹ after 200 cycles. The rate performance of the as-prepared full cell was also evaluated by testing it at varying charging current densities, and satisfactory results were demonstrated, as illustrated in Figure S13.

Industrialization of such nanocomposites requires exceptional scalability of the proposed synthesis route. Different from most of the other synthetic methods for complex silicon-carbon composites that involves high cost, tedious manufacturing process and use of hazardous materials such as strong acids, the proposed synthesis method here is simple, low cost and has great scale-up potentials.

Figure 4g illustrates an envisioned production line for mass-producing F-Si@rGO integrating freeze-530 drying and FJH treatment. Freez-drying is already a proven industrially viable dehydration method to preserve 531 pharmaceuticals, biologicals, foods, and other heat-sensitive materials. FJH is currently employed in massive 532 production of "flash" graphene and is expected to reach a production scale of 1 metric ton/day [58]. Freeze-533 dried Si@GO particles are fed into the FJH chamber via a carbon fiber weave roller belt. Two movable 534 graphite electrodes compress the particles to achieve desired compactness and resistivity. During 535 electrothermal operation, energy is concentrated on the reactants due to their highest resistivity, following 536 Joule's law. Each batch's operation time can be as short as 100 seconds, and the F-Si@rGO product can be 537 recovered using a rolling splitter that separates the upper and lower carbon fiber weaves. The simplicity, cost-538 539 effectiveness, and scalability of the proposed synthesis method present a promising solution to longstanding challenges associated with the production of silicon-carbon composites. 540

541 **4. Conclusions**

In this work, a simple, fast and scalable synthesis method for high performance silicon anodes of lithium-542 ion batteries is demonstrated. By rapidly sintering Si and graphene together through an ultra-fast heating 543 method based on Joule principle, it was demonstrated phase segregation between silicon nanoparticles and the 544 graphene matrix during a conventional heat treatment was prevented. By introducing localized high 545 temperature, a third phase of silicon carbide was formed between graphene and silicon which serve as "riveting 546 points" to securely anchor the silicon nanoparticles within the graphene matrix, even as repetitive volumetric 547 changes occur during charge and discharge cycles. The robust graphene coverage on silicon also serves as a 548 solid foundation for the controlled growth of SEI, effectively preventing undesirable secondary reactions 549

between the electrolyte and the silicon surface. The synthesized F-Si@rGO composite, as demonstrated in this 550 study, exhibits an impressive capacity of 1141.3 mAh g⁻¹ at 1C and maintains a remarkable reversible capacity 551 of 894.95 mAh g^{-1} even after 1000 charge-discharge cycles, with an average capacity degradation of only 552 0.0216% per cycle. This level of performance and durability is a significant step forward in the development 553 of advanced graphene-based energy storage materials. The proposed synthesis method offers key advantages, 554 including speed, controllability, and scalability, making it a promising avenue for the creation of graphene-555 based energy storage materials with improved performance potentially advancing the use of silicon-based 556 anode materials in commercial applications. 557

558 **CRediT authorship contribution statement**

Fan Yang: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, 559 Supervision, Writing - original draft. Pengcheng Deng: Data curation, Investigation, Methodology, Software, 560 Writing- original draft. Hang He: Conceptualization, Data curation, Investigation, Methodology, Software, 561 Writing- original draft. Ruolan Hong: Data curation, Investigation. Kun Xiang: Investigation. Yuan Cao: 562 Data curation, Investigation. Beibei Yu: Investigation. Zeman Xie: Investigation. Jiming Lu: Investigation. 563 Zikang Liu: Investigation. Danish Khan: Writing - Review & Editing. David Harbottle: Writing - Review 564 & Editing. Zhenghe Xu: Writing - Review & Editing. Qingxia Liu: Funding acquisition, Resources, Writing 565 - Review & Editing. Zeguo Tang: Investigation, Writing - Review & Editing. These authors contributed 566 equally: Fan Yang. Pengcheng Deng. Hang He. 567

568 **Declaration of Competing Interest**

569 There are no conflicts to declare.

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577 Supplementary materials

578 Supplementary material associated with this article can be found, in the online version.

579 Data availability

580 Data will be made available on request.

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