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Supercritical mechano-exfoliation process

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Hao Zhang, Qixuan Xiang, Zhiyuan Liu, Xianglong Zhang, Yaping Zhao
 ${}^{\textcircled{0}}$ \boxtimes & Huijun Tan
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The intricate balance among cost, output, and quality has substantially hindered the practical application of graphene within the downstream industry chain. Here we present a scalable and green supercritical CO_2 -assisted mechano-exfoliation (SCME) process that omits the use of organic solvents and oxidants throughout the production lifecycle, including exfoliation, separation, and purification. The SCME process achieves graphene powder space-time yields exceeding 40 kg/(m³·day) at laboratory (0.06–0.2 kg) and pilot scales (>4 kg), with resultant free-standing films showing conductivities up to 5.26×10^5 S/m. Further kinetic investigations propose general guidelines for grinding-assisted exfoliation: (1) the macroscopic optimizing ability of mechanotechnics for mass transfer frequency and stress distribution and (2) the microscopic multiplication ability of exfoliation medium for sheardelamination. The comprehensive techno-economic analysis also underscores the economic viability of the SCME process for large-scale production.

The tripartite equilibrium among cost, output, and quality has emerged as the paramount challenge impeding the industrial application of two-dimensional (2D) materials, particularly graphene¹⁻¹⁰. We have comprehensively evaluated the predominant processes to date, including mechanical exfoliation (ME)^{1,7}, chemical vapor deposition (CVD)^{2,3}, epitaxial growth on SiC⁴, and liquid-phase exfoliation (LPE, including oxidation-reduction process)^{5,11}, adhering four critical interconnected criteria proposed previously: (1) high yield of products, (2) selectivity towards monolayer graphene, (3) structural integrity and (4) processing efficiency (Supplementary Note 5.3). However, despite numerous groundbreaking achievements¹²⁻¹⁹, no existing process can ideally balance the tripartite constraints of cost, output, and quality, indicating an inherent trade-off. Utilizing the exemplary and promising LPE or mechanical force-assisted LPE (MA-LPE) processes as illustrations, current advancement has significantly augmented the spacetime yields (STYs) to 0.24 kg/(m³·day), a marked increase from previous reports of production rates generally below 0.04 g/h¹⁴. Nonetheless, both LPE and MA-LPE confront considerable hurdles, including a low monolayer rate (usually below 20%)¹⁹ and the requirement to operate in organic or ionic liquids with surface energies akin to graphene (usually $115 \pm 4 \text{ mJ/m}^2$)^{11,14}. This parallels the conventional oxidation-reduction techniques employed in graphene production⁵, indicating that upscaling could render the separation of the product from the liquid phase arduous and costly. Moreover, the equally substantial expense associated with using and detoxifying these organic phases also inevitably inflates the commercialization cost.

Mechanochemistry, characterized by grinding^{12,19-23} or other mechanical actions, has engendered innovative and reliable solventfree methodologies for the exfoliation of 2D materials. The efficiency of transfer for shear-delamination stress, directly resulting from highenergy ball-milling collisions, considerably surpasses that of LPE or MA-LPE^{19,24}. However, numerous reports have acknowledged that the collisions engendered by mechanochemical grinding exfoliation (MGE) could potentially induce size reduction or even amorphization of 2D materials^{19,24-27}. One intriguing approach involves augmenting the viscosity of the liquid phase employed for exfoliation or directly utilizing a high-viscosity solid phase¹⁹. This method offers the benefit of utilizing a high-viscosity medium to mitigate the stress-energy from collisions, thereby maximizing the protection of the lateral dimensions of 2D materials. Moreover, the adsorption energy of high-viscosity media on 2D materials surpasses the interlayer potential energy, creating a substantial shear stress gradient. This mechanism insight aligns with the perspective that exfoliation in LPE or MA-LPE stems from the differential velocity gradient¹⁴ in the liquid phase. Beyond the challenges of size reduction and amorphization, one more pressing issue remains that, despite the solvent-free characteristics emphasized in MGE, the majority of works still depend on the assistance of organic and ionic liquids^{19,21,24,27}. Such a mechanism bears a resemblance to the

School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, PR China. e-mail: ypzhao@sjtu.edu.cn; sophie93@sjtu.edu.cn

earlier proposed liquid-assisted grinding (LAG) techniques^{22,28}, wherein the liquid phase optimizes mass transfer²⁹ and facilitates the acquisition of shear-delamination stress by 2D materials through collisions at an appropriate surface energy state. However, such an approach could induce a slurry condition within the grinding vessels (Supplementary Fig. 4), necessitating intricate liquid phase redispersion-purification to acquire the products, thereby escalating the complexity of post-process handling following the pilot scale. To address the aforementioned issues, an imperative exists to identify a proficient exfoliation medium in MGE that satisfies criteria encompassing low cost, facile separation, and interlayer intercalation.

In recent years, supercritical carbon dioxide (SC CO₂) has been demonstrated to be an effective medium for the exfoliation of 2D materials³⁰⁻³³, particularly graphene. Central to this assertion is the understanding that SC CO₂ exhibits unparalleled permeability at the molecular scale, surpassing conventional liquid/gas phases by orders of magnitude^{34,35}. When reaching the supercritical region, CO₂ with high density could exhibit kinetic behavior similar to solutions but still maintain high diffusion coefficient (D_{SC}) and significantly low dynamic viscosity (μ_{SC}). This mechanism differs entirely from the solvent dispersion approach in LPE (Supplementary Fig. 2), that is, SC CO₂ can form molecular wedges to proficiently infiltrate and intercalate within the graphene layers^{24,36,37}. Furthermore, SC CO₂ can be separated and recuperated without contaminating the product via interphase conversion (supercritical phase to gas phase). More significantly, when viewed from an industrial production standpoint, SC CO₂ unquestionably offers a substantial cost advantage over organic or ionic liquids. The temperature and pressure conditions requisite for the supercritical state are relatively modest ($T_c = 31.05 \text{ °C}$, $P_c = 7.37 \text{ MPa}$, $\rho_c \approx 0.45 \text{ g/cm}^{30}$, and the production apparatus of most major chemical enterprises can adequately meet these requirements (Supplementary Table 1 and Supplementary Fig. 1). Consequently, we have combined the merits of SC CO₂ and MGE to develop a scalable and green exfoliation process - supercritical CO₂ assisted mechano-exfoliation, SCME) - which eliminates the use of organic solvents and oxidants throughout the entire production lifecycle, including exfoliation, separation, and purification (Supplementary Fig. 6). The cost, output, and quality of the SCME process have been extensively investigated at both laboratory scale (0.06-0.2 kg) and pilot-scale (>4 kg) powder feed amounts. Moreover, we have constructed a quantitative model aimed at elucidating the SCME exfoliation mechanism from the perspectives of macroscopic mass transfer optimization and microscopic stress distribution. Critically, the technoeconomic analysis emphatically underscores the significant competitive advantage of the SCME process for large-scale production.

Results and discussion

SCME exfoliation

The SCME exfoliation process at both laboratory-scale (LS- SCME) and pilot-scale (PS- SCME) was meticulously outlined in the methods and supporting information (Supplementary Table 2), offering a comprehensive and typical procedure. As a typical LS- SCME example (from 14 in Supplementary Table 3) with fill factor (φ_{GB}) = 25.3%, density (ρ) = 0.55 g/cm^3 , ball-particle mass ratio (R_{bp}) = 30:1, and rotation-torevolution speed ratio (k) = (-2):1, 12.7 g of graphite and 380 g of ZrO₂ balls with different diameters were loaded into high-pressure vessel (Supplementary Fig. 3). Then about 170.2 g of CO₂ at 30 °C was fed into the vessel (provided by the SC CO₂ system) and milling was conducted at rotation speed (N_r) = 450 rpm. After the grinding time (24 h) was completed, the SCME-exfoliated graphene nanosheets (SGNs) were separated and purified for further use (Supplementary Fig. 5). Before and after exfoliation, it is necessary to assess the mass of the vessels, recovered gases, and products to calculate the STYs of SCME exfoliation (Supplementary Table 5)³⁸. To offer a more intuitive understanding of the dissolution process in SCME, we provide a visual representation using a high-pressure vessel (Supplementary Fig. 7 and

Supplementary Movie 1). The graphite formed a stable dispersion in SC CO₂, occupying the entire vessel space and thereby facilitating more frequent and effective collisions during SCME exfoliation.

Characterization of SGNs

Essentially, the stress-driving shear-delamination originates from the effective collisions among milling balls (Fig. 1a), constituting an inherently complex contact model that includes impact, torsion, shearing, and rolling³⁹. Based on Hertz-Mindlin contact theory⁴⁰, the stresses acting on graphite layers can be simplified to a vector combination of normal (σ_N) and tangential (σ_T) stresses, where the normal component primarily supplies the energy for fracture and the tangential component governs the efficiency of shear-delamination (Fig. 1b). Demonstrating the pivotal role of SC CO₂ density in optimizing stress-distribution, SGNs showcased a substantial volumetric expansion (Supplementary Figs. 8, 9) and both the loose bulk density $(\rho_{\rm I})$ and tap bulk density $(\rho_{\rm T})$ significantly decreased from initial values of 0.65 and 1.80 g/cm3 to 0.08 and 0.37 g/ cm3, respectively (Supplementary Table 4). Powder X-ray diffraction (XRD) patterns (Fig. 1c) affirmed the preservation of SGNs crystal structure, with the intensity of the (002) crystal plane decreasing to a maximum of 21.70% of the initial value and shifting to 26.42°. The directional shear delamination caused by ball collisions, combined with the infiltration and intercalation of highly diffusive, zero-tensile SC CO₂, synergistically leads to a shift in the 2θ value (Supplementary Fig. 10). Considering potential powder re-stacking effects during storage or testing, this volumetric expansion may be more pronounced during exfoliation¹⁹. The SGNs (0.91 g/cm³) possessed relatively low Raman D/G band intensity ratio $(I_D/I_G = 0.27)$ compared to previously reported GO (~1.1)⁵, RGO (~0.7)¹², LPE GNs (~0.4)¹⁴ or MGE GNs (~0.4)¹⁹, revealing slightly defective structural information (Fig. 1d) at the edges of graphene layers induced by ball collisions. The intensity ratio of I_{2D}/I_{G} increased to 0.64, accompanied by a notable shift and normalization of the 2D band (2719–2639 cm⁻¹) (Supplementary Fig. 11). This implies a high percentage of few-laver graphene in the SGNs¹⁰ powder, even without employing any separation or purification measures. Similarly, X-ray photoelectron spectroscopy (XPS) results corroborated the high structural integrity of SGNs (0.91 g/cm³) with a C/O ratio up to 42.45 (Fig. 1e and Supplementary Fig. 18). Approximately 2.30% of trace amount of oxygen atoms derived from -COOH groups were identified, which may originate from physically adsorbed oxygen^{5,12}. Further confirmation of structural evidence was achieved through ultra-small angle X-ray scattering (USAXS) patterns with the resolved objects ranging up to 3 µm. No humps in SGNs (0.91 g/cm³) were observed around 0.05 Å⁻¹ (Fig. 1f), indicating the even distribution region $(d = 2\pi/q_{\text{max}})$ of electron density even post high-energy grinding^{18,41,42}. The formation of fractal structures $(I(q) \propto q^{\alpha})$ with slopes of -2.47 (Supplementary Fig. 12) substantiated the flake-like structure with a fractally rough surface of SGNs powder, indicating a minor proportion of potential aggregation induced by incompletely-exfoliated graphite particles without purification⁴³. Field emission scanning electron microscope (FESEM) images provided an intuitive display of the sheardelamination induced interlayer-slip morphology in SGNs with lateral size distribution of 1-3 µm (Fig. 1g and Supplementary Fig. 13). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) further revealed SGNs possessed lateral size distribution of 1–3 μm with typical six-fold symmetry and characteristic fingerprint of few-layer (Fig. 1h)^{13,14,16}. The SGNs exhibited a characteristic thick center and thin edge (Supplementary Figs. 14, 15), indicating that exfoliation induced by grinding consistently initiated at the layer edge^{12,19}. Atomic force microscopy (AFM) images revealed a platform distribution consistent with the lateral dimensions observed in SEM and TEM images. When dispersed in ethanol and deposited onto mica, the SGNs exhibited uniform apparent heights of approximately 3.1 nm, with deviations of less than 0.5 nm (Fig. 1i). Considering the interlayer



Fig. 1 | **Structural and morphological evolution of SGNs. a**, **b** Schematic diagram of SCME and neat milling in a planetary ball mill (**a**), Simplified representation of ball-collision contact type, where the actual stress direction is vectorially comprised of normal (σ_T) and tangential (σ_T) vectors (**b**). **c**-**f** XRD patterns (**c**), Raman spectra (**d**), high-resolution C1s spectra (**e**), and ultra-SAXS patterns (**f**) of SGNs powder. The samples illustrated in (**c**-**f**) correspond to 3, 11–17 from Supplementary Table 3 with identical grinding conFig.urations (t = 24 h, $N_r = 450$ rpm, $R_{\rm bp} = 30:1$, $\varphi_{\rm GB} = 25.3$ and k = (-2):1) but different densities. The grey arrows signify an increment in grinding density in (**c**, **d**) and an shift of the humps in (**f**). The shading in **c** represents the enlargement of neat milling graphite at 26.54°, and in

g-i Morphology of SGNs (sample 17 from Supplementary Table 3) with high crystallinity after exfoliation. FESEM images of pronounced flipping in the graphene layer due to shear-delamination stress of ball milling, with yellow arrows indicating the flipping direction (g). TEM and HRTEM images of few-layer SGNs dispersed by ethanol, including insets displaying selected area electron diffraction (h). AFM image and corresponding thickness depicting few-layer graphene, dispersed by ethanol and deposited on mica sheets (i). Unless noted otherwise, all data were reported for powder and had not undergone additional purification to reflect the true state after exfoliation. Source data are provided as a Source Data file.

(d) highlights the shift of the peak positions (see Supplementary Fig. 11 for details).

expansion resulting from exfoliation, it is believed that the majority of the as-prepared SGNs powder consists of layers with a thickness of fewer than 10 layers.

Exfoliation mechanism

As previously described, the σ_N used for fragmentation always leads to the pulverization of graphene (Fig. 1b), posing a significant challenge that most MGE processes must confront directly^{19,21,24-27}. Indeed, as the SCME densities gradually diminished towards near-vacuum (neat milling), the size of graphite decreased progressively and ultimately converted into highly amorphous particles (NGPs), with lateral dimensions ranging from 100 to 200 nm and a characteristic height of about 50 nm (Supplementary Fig. 16). The nearly vanishing (002) peak at 26.54° (Fig. 1c), accompanied by an exceedingly high I_D/I_G ratio (1.61, Fig. 1d), also substantiated this trend towards amorphization²⁵. In contrast, SGNs possessed good crystallinity (Fig. 1c) and a significantly low I_D/I_G ratio (Supplementary Fig. 11). These results indicated that once the density of SC CO₂ reached a critical threshold (potentially influenced by overall system parameters, including φ_{GB} , R_{bp} , k, t, and N_r), the infiltration-intercalation-supporting effect of SC CO₂ into the layers sufficiently counteracted the normal stress (σ_N) from ball milling collisions. Consequently, in this state, SGNs were more likely to delaminate directionally rather than continuously reduce the lateral size.

(Supplementary Fig. 15), which showed that as the density of SC CO₂ increased, graphite gradually transitioned from NGPs to SGNs with lateral dimensions of 1-3 um. Another phenomenon that accompanies amorphization is that, upon opening the vessel, these NGPs exhibited intense combustion, persisting for three hours (Supplementary Fig. 17 and Movie 2). Additional evidence of oxidation caused by combustion in NGPs was further provided by XPS spectra (C/O ratio of 8.16) and Fourier transform infrared spectroscopy (FTIR) (Supplementary Figs. 18, 19). These results collectively suggested that the outcome of crushing-amorphization versus shear-delamination is critically dependent on the specific normal/tangential stress distribution and the collision energy magnitude, both dictated by the SC CO₂ density. Hence, we conducted macroscopic computational fluid dynamicsdiscrete element method (CFD-DEM) simulations of a heterogeneous SCME exfoliation (mill with 0.06 kg feed amount) and complemented involved microscopic scenes with molecular dynamics (MD) simulations of SC CO₂ intercalation, aiming at unraveling this intricate tradeoff (Supplementary Note 3).

In comparison to neat milling (Fig. 2a), the graphite demonstrated the ability to form a stable dispersion in SC CO₂, filling the entire vessel space, and thereby facilitating more frequent and effective collisions in SCME (Fig. 2b and Supplementary Fig. 24). These findings aligned with our prior observations within the visible vessel (Supplementary Fig. 7 and Supplementary Movie 1), suggesting enhanced mass transfer optimization during grinding. Besides collision frequency, the distribution of stress energy associated with each collision was also crucial^{39,40}, as the combination of the two factors often determined the total energy transferred to graphite. To delineate stress conditions, the concept of stress energy per collision can be employed⁴⁴. Stress energy quantifies the energy transferred to feed graphite in a single stress event such as the collision of grinding balls, determined by the relative velocity and masses of the colliding entities. In SCME, the translational velocity of balls was reduced from 3.53-3.83 to 3.22-3.27 m/s due to the presence of macroscopic buoyancy and drag force induced from high-density CO₂ (Fig. 2c). This reduction resulted in a significant order-of-magnitude difference (from 2.21×10⁴ to 1.47×10³ l/hit) in stress-energy corresponding to the maximum collision frequency (Fig. 2d), and influence the kinetic energy transferred to the graphite. Given that the grinding duration typically exceeded 24 h, the cumulative energy contrast between neat milling and SCME is substantial, which also elucidated the pronounced amorphization and even combustion observed in neat milling (Supplementary Fig. 17-19). Next, we extracted $\sigma_{\rm N}$ and $\sigma_{\rm T}$ distributions from approximately 10⁴ collisions between neat milling and SCME in the simulation, revealing a noticeable transformational distribution (Fig. 2e). Further precision was attained by calculating the average σ_N/σ_T (k_{σ}) through statistical analysis of the average stress magnitude within each time step. The k_{σ} in neat milling (3.47) significantly surpassed that in SCME (2.55), suggesting that SCME exhibited greater shear-delamination capability. It should be noted that cross-scale simulations often exhibit non-replicability, particularly given the challenges in accurately describing the zero-tension and high-permeability characteristics of SC CO₂ at the microscopic level through the CFD-DEM method. Consequently, we proceeded to integrate the actual stress distribution (k_{α}) into MD simulations. Under identical stress conditions, the topmost layer in SCME exhibited significant exfoliation and displacement from its initial conformation, whereas the topmost layer in neat milling solely demonstrated marginal oscillations localized at the layer edges (Fig. 2f and Supplementary Fig. 25). The calculated PMF curves concerning the collective variable d illustrated that with the increasing distance, the growth rate of PMF for SCME intercalation gradually slowed down, remaining consistently lower than that of neat milling during all stages (Fig. 2g)^{36,37}. The reduction in the radial distribution function (RDF) of SCME around 3 Å also illustrated structural alterations such as exfoliation or rearrangement of the graphene layers (inset in Fig. 2g and Supplementary Figs. 26, 27)³⁷. To further and

conveniently facilitate the determination of configuration parameters crucial for practical SCME exfoliation, we established a straightforward parameterization method to define the requisite conditions for exfoliation (Supplementary Note 3.3). Central to this approach was the development of a modified collision stress energy that takes into account supercritical density:

$$\Delta E = \frac{1}{2} m_b^* \omega_R^2 \left[\left(\frac{\omega_r}{\omega_R} \right)^2 \left(\frac{d_v - d_b^*}{2} \right)^2 \left(1 - 2 \frac{\omega_r}{\omega_R} \right) - 2R \left(\frac{\omega_r}{\omega_R} \right) \left(\frac{d_v - d_b^*}{2} \right) - \left(\frac{\omega_r}{\omega_R} \right)^2 \left(\frac{d_v - d_b^*}{2} \right)^2 \right]$$
(1)

$$\Delta E^* = \varphi_h \Delta E \tag{2}$$

$$E_{cum} = \frac{\Delta E^* N f t}{m_p} \tag{3}$$

Where m_b^* and d_b^* are the equivalent mass and diameter of a ball, d_v is the diameter of the vessel, R is the revolution radius, ω_R and ω_r are the angular velocity of the revolution and rotation. ΔE and ΔE^* are the stress energy and corrected stress energy (J/hit), calculated employing the theoretical-empirical equations proposed by Burgio et al.⁴⁵ φ_h represents the hindering factors originating from containers, grinding balls, and SC CO₂, N is the number of balls in the vessels and f is the frequency at which balls are launched against the opposite wall of the jars. t represents grinding time and m_p is the feed amount of graphite in grams. The ΔE^* calculated via the parameterization method (Supplementary Table 8) closely aligned with the simulation results (Fig. 2d). Consequently, in practical production scenarios, facile modification of these parameters enabled precise control towards either shear-detachment or crushing-amorphization. For instance, increasing the density of SC CO₂ consistently led to larger-sized SGNs (Supplementary Fig. 15), while extending t or raising φ_{GB} typically resulted in heightened combustion (Supplementary Fig. 28). Even if the vessel was opened post 12-hour milling, such combustion still occurred (Supplementary Fig. 29). Evidence from edge FTIR and Raman spectroscopy indicated that combustion likely arised from the activation of carbon species resulting from the disruption of interlayer non-covalent bonds, which is induced by stress energy at the edges of the layers, aligning with prior findings by Jeon et al. (Supplementary Figs. 30, 31)¹². Such oxidized NGPs demonstrated dispersibility in various polar or non-polar solvents, e.g., up to -68.4 mV of zeta potential in aqueous (Supplementary Fig. 32).

In contrast, combustion phenomena were absent in any category of SCME exfoliation. Firstly, the notable decrease in collision stress energy at the macroscopic level $(1.47 \times 10^{-3} \text{ to } 2.21 \times 10^{-4} \text{ J/hit})$ diminished the presence of highly reactive fracture edges, known to induce combustion. Simultaneously, the intercalation effect of high-density SC CO₂ redirected grinding towards a microscopic delaminationfavorable direction. The synergistic impact of these factors yielded SGNs with structural integrity and substantial layer size. These findings above suggested that apart from optimizing the actual stress distribution (k_{σ}) of collisions due to macroscopic density or viscosity, the infiltration-intercalation of SC CO2 at the microscopic level also played a crucial role in SCME exfoliation. In other words, this infiltrationintercalation effect appeared to enhance the shear-delamination in the tangential direction of the ball collisions. Hence, we proposed a universal benchmark encompassing two critical interconnected criteria, applicable not only to SCME but also to all MGE exfoliation mechanisms: (1) the macroscopic optimizing ability for mass transfer frequency and stress distribution induced by mechanical process and (2) the microscopic multiplication ability for shear-delamination resulting from exfoliation medium (SC CO₂).



Fig. 2 | **Inference of exfoliation mechanism. a**, **b** Balls velocity magnitude and flow field of CO₂ distribution at the same simulation moment ($t_s = 0.96$ s) in neat milling (**a**) and SCME (**b**). The CFD-DEM simulations were set with the same initial grinding conditions, namely, k = (-2):1, $\varphi_{GB} = 25.3\%$, $R_{bp} = 30$:1, and $N_r = 450$ rpm, and graphite was simulated as a shape of $1500 \times 500 \times 500$ µm. The density of CO₂ in (**b**) was set as 0.91 g/cm³. Specifically pointed out, limited by the bottleneck of cross-scale simulation, we appropriately scaled up the shape of a single graphite bulk (Supplementary Fig. 20). **c**-**e** Influence of SCME with different SC CO₂ densities on translational velocity of balls motion (**c**), collision stress energy (**d**), and σ_{N} - σ_{T} distribution (**e**) in the absence of graphite. The vertical dashed lines in (**d**)

emphasise the significant order-of-magnitude difference in collision energy corresponding to the maximum collision frequency. **f** MD simulations before and after applying stress in neat milling (upside) and SCME (downside, 0.70 g/cm³). The dimension of the box was set to $21 \times 51 \times 51$ Å, containing seven layers of graphene stacked with AB stacking. The topmost graphene layer was dragged with stress in the vertical (z-direction) and a slight stress originating from the y-z plane for simulating the vectorial stress originating from grinding. **g** The PMF per unit area between two parallel graphene sheets as functions of the intersheet separation d corresponding to **f**, with the inset illustrating the change in radial distribution function (RDF) of SGNs after 500 ps. Source data are provided as a Source Data file.

Process optimisation

Hitherto, we have established a robust correlation between the structural integrity of SGNs and the density of SC CO₂. Parameterized model calculations revealed that the E_{cum} in neat milling per unit time exceeded that of SCME by 42%-284% (Supplementary Table 8). Given the absence of SC CO₂ intercalation, we inferred that this stress energy predominantly contributed to layer fragmentation. This suggested that, within the same timeframe, neat milling significantly outperformed SCME in terms of both capability and efficiency for generating edge defects. It is important to note that a minor quantity of defects does not equate to amorphization, which necessitates prolonged accumulation of stress energy^{12,19,21,26}. Contrarily, it is widely accepted that the presence of a moderate amount of defects facilitates further SC CO₂ infiltration-intercalation^{30,33,36,37}. Hence, we proposed a feasible and convenient optimization strategy for the SCME process, entailing an initial phase of defect generation via short-term neat milling or low-density SCME, succeeded by high-density SCME exfoliation. The merit of this density-gradient approach lies in its capacity to maximize the exploitation of stress distribution (k_{α}) and stress energy transfer (Ecum) characteristics. The significant increase in BETspecific surface area substantiated this strategy (Supplementary Fig. 33). Utilizing identical or merely half the grinding time, the BETspecific surface area of SGNs processed using this method rose from 599.37 to 606.13 and 683.10 m²/g, respectively. Most importantly, this process optimization was continuous and highly straightforward to implement in pilot-scale production. We can control the exfoliation effect in real-time by continuously adjusting the density of SC CO₂ within one process cycle, an approach generally not achievable by altering other process parameters such as $N_{\rm r}$, $\varphi_{\rm GB}$, k, and $R_{\rm bp}$ based on our calculations (Supplementary Figs. 21, 23).

Pilot-scale production and techno-economic analysis

To establish a pathway to industrial applications, we have scaled up the production of the SCME exfoliation process (Supplementary Note 4.1 and Supplementary Figs. 34–36), obtaining key evidence that supports the reliability of exfoliation at a feed amount of kilograms. The pilotscale SGNs (PS-SGNs, $\varphi_{GB} = 21.07\%$, $\rho = 0.55$ g/cm³, $R_{bp} = 15.1$ with feed amount of 4 kg) produced by process optimization strategy exhibited a lateral size of 1-3 µm (Supplementary Fig. 37) and a thickness of approximately 3.5 nm (Supplementary Fig. 38), comparable to those of laboratory-scale SGNs (LS-SGNs, Fig. 1g-i). Raman spectra of graphene powder from six different batches showed an I_D/I_G ratio of about 0.32 and an I_D/I_{2G} ratio of about 0.49 for PS-SGNs (Supplementary Fig. 39), convincing that the majority of the powder consisted of fewer than 10 layers. In addition to evaluating the structure and morphology, we fabricated and tested the conductivity of LS-SGNs and PS-SGNs conductive films to further assess the reliability of pilot-scale production. Test results from 33 SGN films across different batches demonstrated that the films exhibited flexible and self-standing characteristics, maintaining integrity even after bending or flipping (Supplementary Fig. 40). This indicated a robust conductive network composed of large lateral dimensions within the SGNs films. Conversely, NGPs were unable to form films due to the crushing-amorphization-induced granular morphology (Supplementary Fig. 41). The conductivity of both LS-SGNs and PS-SGNs films exceeded 105 S/m (highest of 5.26×10^{5} S/m, Supplementary Fig. 42), representing an increase of two orders of magnitude compared to the raw graphite (Supplementary Fig. 43 and Supplementary Table 9). PS- SCME exfoliation of different raw graphite (100, 200 mesh flake graphite and 500 mesh expanded graphite) was also attempted. The conductivity of these films fabricated from exfoliated PS-SGNs ranged from 1.55 to 2.56×10^5 S/m. Upon purification, the conductivity could increase further, reaching values from 1.65 to 3.24×10^5 S/m (Supplementary Table 9). We also purchased commercial graphene for comparison. The results indicated that while the electrical conductivity of commercial graphene

 $(9.50 \times 10^4 \text{ S/m})$ is close to the same order of magnitude as that of the SGNs. it accounts for only 18.4% of LS-SGNs and 49.8% of PS-SGNs. highlighting the significant potential for SGNs to compete in the marketplace. To provide a more intuitive illustration of the superior conductivity of SGNs, we directly mixed them with an acrylic emulsion (5 wt% SGNs) to create a conductive binder, which was then uniformly coated onto insulating PA-6 mesh fabrics using a metal rod (Supplementary Fig. 44). The resulting PA-6/SGN mesh fabric displayed a low surface resistance of 90–130 Ω over a distance of 5–10 cm, with a mass gain of less than 20%. Furthermore, we incorporated PS-SGNs into the insulating engineering plastic polyamide 6 (PA-6) to prepare a conductive polymer (SGNs/PA-6) composite (Supplementary Fig.45-46). With the addition of only 5 wt% PS-SGNs, the composite exhibited a significantly higher conductivity of 1.46 S/m (Supplementary Fig. 47), compared to neat insulating PA-6 ($\sim 5 \times 10^{-13}$ S/m). In addition, the thermal conductivity (k) of SGNs was 4.67 times that of raw graphite and was 17.0% higher than that of commercial graphene (Supplementary Fig. 48). The above evidence convincingly demonstrated the practical industrial application value of SCME exfoliation.

Hence, we conceptualized the production scale reaching an annual capacity of 4.8 metric tonnes of SGNs at the PS- SCME scale and thoroughly assessed its economic competitiveness against other processes (Supplementary Tables 10, 11)^{46,47}. Among the three main process modules (exfoliation, separation, and purification), the exfoliation and purification stage incurred the highest equipment, energy, and material costs (Fig. 3a), with manufacturing and loading costs amounting to US \$620k. Conversely, the separation and stage costs were minimal due to the complete elimination of organic liquid phases (Fig. 3b and Supplementary Note 1.4). Assuming a 10-year operational period with a 10% discount rate, the net present value (NPV) of SCME was US \$4.04 million at the selling price of US \$500/kg for regular graphene and US \$1000/kg for purified graphene, yielding a high internal rate of return (IRR) of 28.45%. Furthermore, a 10% or 30% increase in the selling price raised the NPV to US \$4.62 million and US \$5.79 million, respectively, with IRR of 33.12% and 46.20% at the break-even point (Fig. 3c). Sensitivity analyses indicated that the annual sales volume and sales price of graphene were critical for sustained profitability (Fig. 3d and Supplementary Table 12-13). These findings suggested that reducing operating costs through optimization of the exfoliation process and increasing the proportion of purified SGNs in total production were essential. Additionally, aggressive marketing measures were recommended to boost sales volume. To more intuitively demonstrate the investment prospects of the SCME process, we compared the cost, output, and quality with CVD (representing D-T synthesis) and MA-LPE process (representing T-D exfoliation) in detail based on reasonable assumptions (Fig. 3e and Supplementary Tables 14, 15). Notably, while the CVD approach entailed higher costs and superior quality, it yielded less, contrasting with the SCME and MA-LPE processes, which generally yielded more at comparatively lower costs and quality levels. Specifically, the production costs exhibited a clearer and more comparable distinction between SCME and MA-LPE processes, amounting to 69.49 and 220 USD/kg, respectively (Supplementary Table 16 and Supplementary Fig. 49). This substantial cost disparity predominantly arose from the utilization, separation, and harmless treatment of organic phases, underscoring the substantial competitiveness of the SCME process.

To summary, the SCME process was established, eliminating the use of organic solvents and oxidants throughout the entire production lifecycle. An in-depth kinetic study has identified two key interconnected criteria critical to the design of this grinding-assisted exfoliation process: the macroscopic optimizing ability of mechanical techniques for mass transfer frequency and stress distribution, and the microscopic multiplication ability of exfoliation medium for sheardelamination at the molecular scale. As calculated by the parametric



Fig. 3 | **Techno-economic analysis of the SCME production process. a** The overall block flow scheme for the SCME production process is divided into three modules including exfoliation, separation, and purification. The rectangular areas indicated the approximate cost share of each corresponding module. All subsystems utilized an integrated design for easy assembly and transportation. **b** Specific costs associated with each module of the SCME production process. **c** *NPV* of the SCME production business operating for 10 years with an *IRR* of 28.45% and the *IRR* at the

break-even point for a range of SGNs prices. **d** Sensitivity analysis on the *IRR* at the break-even points, highlighting parameters with significant influence on the IRR value. The production ratio denoted the ratio of regular SGNs (R-SGNs) to purified SGNs (P-SGNs). **e** Comprehensive evaluation on SGNs in terms of cost, output, and quality (integrity, size, and layers). The specific scoring criteria can be found in Supplementary Note 5.3. Source data are provided as a Source Data file.

model, optimal exfoliation efficiency can be obtained by adjusting various parameters (φ_{GB} , R_{bp} , k, t, and N_r), particularly by continuously fine-tuning the density of SC CO₂ within one process cycle. Both laboratory-scale and pilot-scale productions validated these assumptions, demonstrating the significant industrial potential of the SCME process. The comprehensive techno-economic analysis highlighted the competitive advantages of SGNs in a highly competitive market, further enhancing its potential for application in the downstream industry chains.

Methods

Typical procedure of SCME process

SCME exfoliation. as a typical example (from 14 in Supplementary Table 3) with $\varphi_{GB} = 25.3\%$, $\rho = 0.55$ g/cm³, $R_{bp} = 30:1$, and k = (-2):1, 12.7 g of graphite and 380 g of ZrO₂ balls with different diameters were loaded into high-pressure vessel. Before grinding, N₂ was used to exhaust air three times and then a 5–10 min vacuum pumping process was usually necessary to make the vessel close to vacuum. Then about 170.2 g of CO₂ at 30 °C was fed into the vessel (provided by SC CO₂

system) and then milling was conducted at $N_r = 450$ rpm. The temperature of the grinding chamber was set at 45 °C to achieve a supercritical state. After the grinding time was (24 h) completed, the products were separated and purified for further use.

SCME separation. SC CO₂ was released, transitioning from supercritical to the gas phase, and subsequently recycled through the SC CO₂ system. This method was environmentally benign, preserved the integrity of the product, and achieved efficient separation. To verify that SC CO₂ did not cause structural alterations to graphene, such as the formation of carboxylated species, the mass of the high-pressure reactor was recorded before and after grinding (Supplementary Table 4). All SCME exfoliation experiments confirmed that the introduced CO₂ was successfully recycled into the SC CO₂ system, with no increase in product mass.

SCME purification. The design of the SCME purification system is informed by the principles of fluidized beds. It features a tank equipped with a stirrer and a separation column used for fluidization. Post-milling, SGNs were loaded into the tank, where the SC CO₂ system provided the necessary flow rate for fluidization (Supplementary Fig. 5). Within the separation column, SGNs were subject to the combined forces of gravity, buoyancy (provided by SC CO₂), and drag, allowing thinner SGNs to be separated and purified from the top of the column. Milling conFig.uration and grinding conditions can be found in Supplementary Note 1.4.

All the reagents mentioned (details in Supplementary Note 1.1) were obtained from commercial vendors and used as received unless otherwise noted.

Computational methods for kinetic investigation of SCME

CFD-DEM coupling calculations. The heterogeneous SCME process was mathematically described using CFD-DEM coupling methods (Supplementary Table 6). DEM was employed to precisely model the milling process and apply Newton's second law for assessing the motion of individual particles. Meanwhile, the continuous liquid phase flow was characterized by the generalized Navier-Stokes equations.

MD calculations. To elucidate the underlying microscale mechanisms of SCME exfoliation, comprehensive molecular dynamics (MD) simulations were conducted to investigate the intercalation of SC CO₂ molecules (Supplementary Table 7). Seven graphene layers arranged in an AB stacking were positioned in the yz plane within a box of lateral dimensions set to 21 × 51 × 51 Å, sufficiently large to mitigate interactions between adjacent graphene layers. Subsequently, the box was filled with SC CO₂ molecules to simulate the intercalation effect. Periodic boundary conditions (PBC) were applied in three directions throughout the simulation. A time step of 1 fs was employed during production runs, with data collected every 1 ps. The system was minimized (atomic positions and unit cell size) while maintaining isotropy in box dimensions. The topmost graphene layer experienced a stress in the vertical (z-direction) and a slight stress originating from the yz plane for simulating the vectorial stress originating from grinding, all with magnitudes of 0.001 kcal/(mol·Å). System pressure and temperature were controlled using a Nose'-Hoover barostat and thermostat. All simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).

More necessary parameters and calculations can be found in Supplementary Note 3.

Process design details of pilot-scale. During the pilot-scale production of SCME, all aspects of the manufacturing process were tested and validated. All subsystems utilize an integrated design that allows for easy assembly and transportation (Supplementary Fig. 6). The design and manufacturing processes conform to established standards, cited

as ASME Boiler and Pressure Vessel Code (ASME BPVC)⁴⁸ and Chinese industry standard (GB 150-2011, Pressure vessel)⁴⁹. More necessary details can be found in Supplementary Note 4.

Techno-economic analysis and sensitivity analysis. Technoeconomic analysis (TEA) of the SCME exfoliation process based on the LS- SCME and PS- SCME and sensitivity analysis on the internal rate of return at the break-even point were conducted. The costs of infrastructure, energy consumption, and raw materials have been thoroughly assessed, accounting for market fluctuations (Supplementary Tables 10, 11). Assumptions regarding the production capacity, pricing, and sales volume of SGNs have been rigorously evaluated to reflect the high demand for graphene in both Chinese and international markets, particularly in the sectors of coatings, composite materials, and energy materials. Additionally, the SCME process was compared to that of existing exfoliation processes to evaluate its economic competitiveness. More necessary details can be found in Supplementary Note 2.

Data availability

All data generated or analyzed during this study are included in this published article (and its supplementary information files). The experimental data generated in this study have been deposited in the Figshare database under the accession code https://doi.org/10.6084/m9.figshare.27129876. Source data are provided as a source data file. Source data are provided with this paper.

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Author contributions

H.Z., Methodology, data curation, and writing-original draft preparation. Q.X., Conceptualization and discussion. Z.L. and X.Z., Discussion. Y.Z., funding acquisition, supervision, writing, reviewing, and editing of the original draft, H.T., Discussion and writing-original draft revision.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Yaping Zhao or Huijun Tan.

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