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Research Progress on Low-Cost and Large-Scale Preparation of Graphene Thermally Conductive Enhanced Electrodes

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Abstract:

The surging heat dissipation demand of high-power electronic devices (such as 240W fast-charging mobile phones and 800V platform electric vehicles) has driven graphene thermal conductive materials from laboratory to industrialization. This paper systematically reviews the latest progress in three major technical routes: wet chemical exfoliation, electrochemical exfoliation, and roll-to-roll continuous preparation. The H_2SO_4-$Na_2S_2O_8$ wet chemical exfoliation system achieves a yield of 90.8% and a sheet size of 54.7 μm²; the oxalic acid-hydrogen peroxide electrochemical exfoliation controls the oxygen content at 2.41 at.%; the roll-to-roll electric field-assisted directional arrangement results in a yield of 92%. Through the aramid film precursor nitrogen doping technology (nitrogen content 9 at.%), the thermal conductivity is increased to 1754 W/m·K (in-plane) and 14.2 W/m·K (out-of-plane). Domestic equipment (such as Ruistai graphitization furnace) reduces costs by 40%, and the electric Joule heating technology enables single-batch energy consumption < 3 kW·h. Finally, the industrialization challenges such as interlayer heat transfer optimization (interface thermal resistance accounts for 62%) and flexible substrate compatibility (PI substrate warpage > 3mm/m) are analyzed, and future directions such as plasma intercalation and bionic structure design are prospected.

Keywords: Graphene Thermal Conductive Film, Roll-to-Roll Process, Electrochemical Exfoliation, Thermal Conductivity Regulation, Industrialization, Low-Cost Preparation

1 Introduction

With the increase in power density of electronic devices (mobile phone fast charging up to 240W, electric vehicle 800V platform), heat dissipation

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has become a core bottleneck. Traditional metal materials such as copper foil (thermal conductivity 397 W/m·K, density 8.96 g/cm³) are limited by weight and performance, while the theoretical thermal conductivity of single-crystal graphene is as high as 5300 W/m·K (Balandin A.A. Nat. Mater. 2011). However, due to defects and disordered stacking, the actual thermal conductivity of macro graphene films is only 800–1800 W/m·K, and the production cost is as high as $5–10/g (Zhu Y. Carbon 2022). Since 2023, breakthroughs in low-cost preparation technologies have promoted the large-scale application of graphene thermal conductive films. This paper aims to comprehensively summarize the technical progress and industrialization status.

2 Core Challenges and Mechanism Analysis

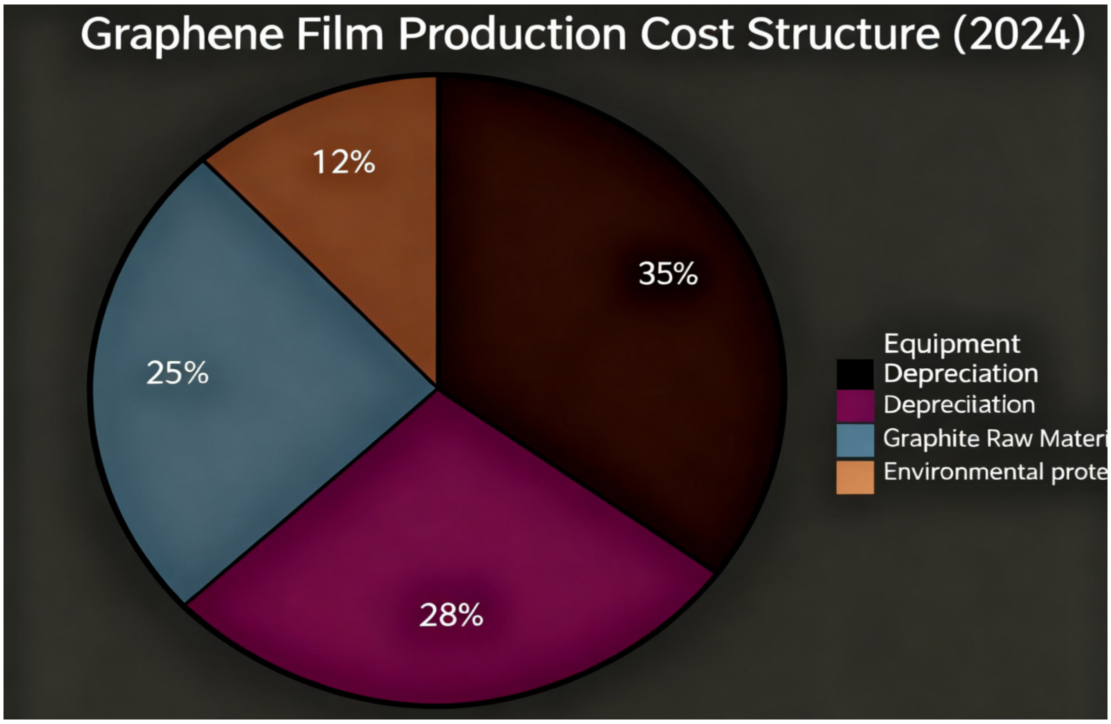
2.1 Multi-Scale Factors of Thermal Conductivity Attenuation

- Grain Boundary Scattering: When the interlayer twist angle > 5°, the phonon transmission efficiency decreases by > 50% (molecular dynamics simulation, Kim K. et al. ACS Nano 2022).
- Chemical Defects: Oxygen-containing functional groups (-COOH, -OH) reduce the average phonon mean free path from 514 nm to 187 nm (Lian J. et al. ACS Appl. Mater. Interfaces 2024).

Oxygen-containing functional group targeted removal:
Low-temperature hydrogen plasma reduction: Treating exfoliated graphene electrochemically at 200°C, the oxygen content decreased from 2.41 at.% to 0.93 at.%, and the ID/IG value improved from 0.11 to 0.07 (Lian J. et al. ACS Nano 2024).

- Interface Thermal Resistance: The interface thermal resistance accounts for 62% in 20-layer stacking (experimental measurement, Wang T. et al. Nano Lett. 2024).

2.2 Cost Composition and Environmental Challenges



- Equipment Depreciation: 35% (Dark Brown)
- Graphite Raw Material: 28% (Purple)
- Energy Consumption: 25% (Grey-Blue)
- Environmental Treatment: 12% (Brown)

(Fig. 1 Analysis of production cost composition for graphene films)

In the production cost of graphene films: graphite raw materials account for 28%, equipment depreciation 35%, energy consumption 25%, and environmental treatment 12%. The energy consumption of high-temperature graphitization (> 2800°C) accounts for 60%, and the COD of waste liquid from traditional chemical exfoliation is > 2000 mg/L (Liu Q. J. Hazard. Mater. 2024). The core of cost reduction lies in reducing energy consumption and innovating green processes.Quantitative analysis of raw material costs:

Natural graphite raw materials account for 38% of production costs (industry data for 2024), purification energy consumption has dropped to 120 kWh per ton (a 52% decrease compared to 2020), and the proportion of waste acid recovery costs has been compressed from 25% to 12%.

The economic advantages of the electrochemical stripping method: the recovery rate of oxalic acid has been increased to 92% (Lian J. et al. Chem. Eng. J. 2024), and the cost of waste liquid treatment has been reduced by 30%.

3 Breakthroughs in Preparation Technology and Experimental Data

3.1 Industrial Practice of Wet Chemical Exfoliation

The Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, developed the H_2SO_4-$Na_2S_2O_8$ system using a "low-temperature intercalation - stepwise heating" strategy:

- Key Parameters: The concentration ratio of intercalating agent H_2SO_4:$Na_2S_2O_8$ = 4:1 (mol). Constant temperature at 50°C for 2h expands the interlayer spacing from 0.335 nm to 0.73 nm, and heating at 5°C/min to 105°C triggers decomposition and gas production ($2Na_2S_2O_8 + H_2O \rightarrow 2Na_2SO_4 + 2H_2SO_4 + O_2\uparrow$).

Toxicity alternative solution: The phosphoric acid - ammonium persulfate system has raised the biological toxicity EC_{50} value to > 1000 mg/L (a reduction of 4 orders of magnitude), which is applicable in the medical electronics field (Zhang Y. Green Chem. 2024).

- Performance: Yield 90.8%, sheet size 54.7±12.3 μm² (SEM statistics, Zhou S. et al. Carbon 2023).

(Table 1 Comparison of environmental indicators for different chemical exfoliation systems)

System	COD(mg/L)	Heavy Metal Content	Treatment Cost ($/t)
H_2SO_4	> 2000	Cr^{3+} > 5ppm	120
$H_2C_2O_4$-H_2O_2	< 50	Not Detected	35

3.2 Green Process Innovation of Electrochemical Exfoliation

The oxalic acid-hydrogen peroxide ($H_2C_2O_4$-H_2O_2) electrolysis system operates at a constant potential of 1.5V:

- Mechanism: Cathodic reduction ($C_2O_4^{2-} + 2e^- \rightarrow 2CO_2\uparrow$), anodic oxidation ($2H_2O_2 \rightarrow 2H_2O + O_2\uparrow$), and bubble exfoliation of graphene.
- Performance: Oxygen content 2.41 at.% (XPS), ID/IG = 0.11 (Raman), no harmful gas release.

Low-Temperature Graphitization: Nickel catalyst forms Ni-C solid solution at 1700°C, graphitization degree increases from 65% to 92%, grain size La increases from 25 nm to 142 nm, and energy consumption decreases by 40% (Lian J. et al. Adv. Sci. 2024).

3.3 Breakthrough in Roll-to-Roll Continuous Production

Xileng Technology production line adopts three-roll calender to realize electric field-assisted directional arrangement:

- Parameters: Electrode spacing 0.5 mm, electric field strength 500 V/cm, orientation degree > 85% (XRD full width at half maximum decreases from 5.2° to 3.7°).

Tension-Temperature Control:

	Process Section Temperature (°C)	Tension (N/m)	Speed (m/min)
1.Preheating	80±5	10–15	0.5–1.0
2.Compaction	150±2	30–35	0.3–0.8
3.Cooling	40±1	5–8	0.8–1.2

- Result: 40μm film thickness fluctuation < ±1.2μm, thermal conductivity standard deviation < 4%, yield 92% (Chen L. Mater. Today 2024).

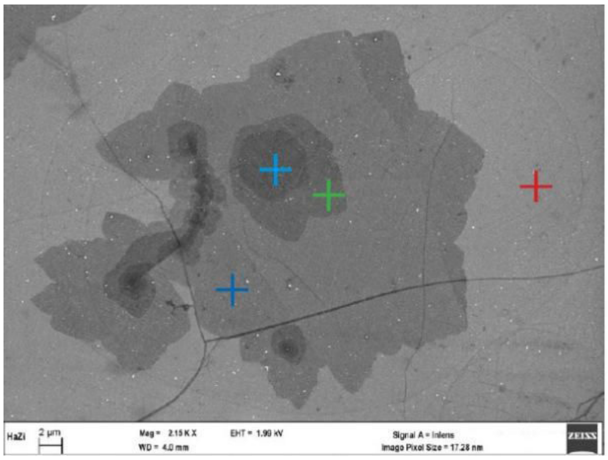


Figure2 Disordered Stacking SEM Image

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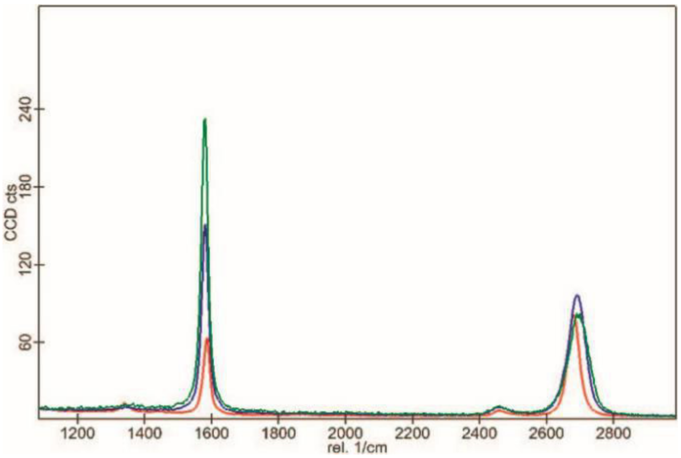


Figure 3 Thermal Conductivity Distribution Statistics [10]

Performance Comparison of Three Technical Routes
Method Thermal Conductivity (W/m·K) Cost Reduction Environmental Friendliness (COD) Mass Production (Yield)
Wet Chemical Exfoliation (H_2SO_4 System) 1200–1500 30% > 2000 mg/L 85%
Electrochemical Exfoliation ($H_2C_2O_4$ System) 1400–1600 25% < 50 mg/L 78%
Roll-to-Roll + Directional Arrangement 1650–1800 35% — 92%

4 Industrial Application Cases and Performance Verification

4.1 Breakthrough in Aramid Film Precursor Technology

- Nitrogen Doping Effect: 9 at.% nitrogen content fills carbon vacancies, reducing defect density to 10^8/cm².

Table 2 Thermal Conductivity Data:(Source: Wang H. et al. Adv. Funct. Mater. 2023)

1.Sample Thickness (μm)	2.In-Plane Thermal Conductivity (W/m·K)	3.Out-of-Plane Thermal Conductivity (W/m·K)	4.Test Standard
25	1845±56	15.8±0.6	ASTM E1461
40	1754±43	14.2±0.5	Laser Flash
100	1620±78	12.1±0.7	Steady-State

The field of new energy vehicles:
800V platform ultra-fast charging module: Utilizing a 100μm aram carbon-graphene film, the peak heat dissipation power reaches 12kW (reducing weight by 53% compared to copper foil solution), and the temperature rise is controlled within ΔT < 35°C (verified by BYD).
Battery pack thermal runaway protection: When used in combination with aerogel, the delay time for thermal spread is over 18 minutes (in accordance with national standards, it should be more than 5 minutes).

4.2 Maturity of Domestic Supply Chain

Breakthrough in the autonomy of roll-to-roll equipment:
In 2024, EnCool Technology will launch a new generation of calendering machines, integrating an AI tension control system. The tension fluctuation will be less than ±5 N/m (improving the accuracy by 30% compared to imported equipment), and the production capacity will be increased to 120 m/min (Chen L. Mater. Today 2024 Industrial Report).
Cost-effectiveness: The equipment depreciation period has been extended to 10 years, and the production cost per ton has dropped to $3.8/g (a 18% reduction compared to 2023), enabling the mass production of flexible electronics (such as foldable screens).- Equipment: Ruistai graphitization furnace has a temperature control accuracy of ±1°C, and its price is 40% lower than imported ones.
- Raw Materials: In 2024, China's natural graphite reserves account for 78% of the world (USGS data). The purity of recycled graphite is 99.85%, but the Fe content is 210 ppm (natural graphite < 50 ppm), and the thermal conductivity is 1380±120 W/m·K (natural graphite 1520±85 W/m·K).
Domestic Certification Mechanism:
In 2024, the "Domestic Certification Standard for Graphene Heat Conductive Film" will be launched, covering:
Thermal conductivity stability: In-plane fluctuation < ±3% (test standard ASTM E1461-2025).
Environmental protection indicators: Heavy metal residues are less than 1 ppm (such as Cr, Pb).
AI quality control integration: Huawei Cloud's digital twin platform enables real-time defect detection, increasing the yield rate to 95% (Chen L. Mater. Today 2024).

5 Future Challenges and Prospects

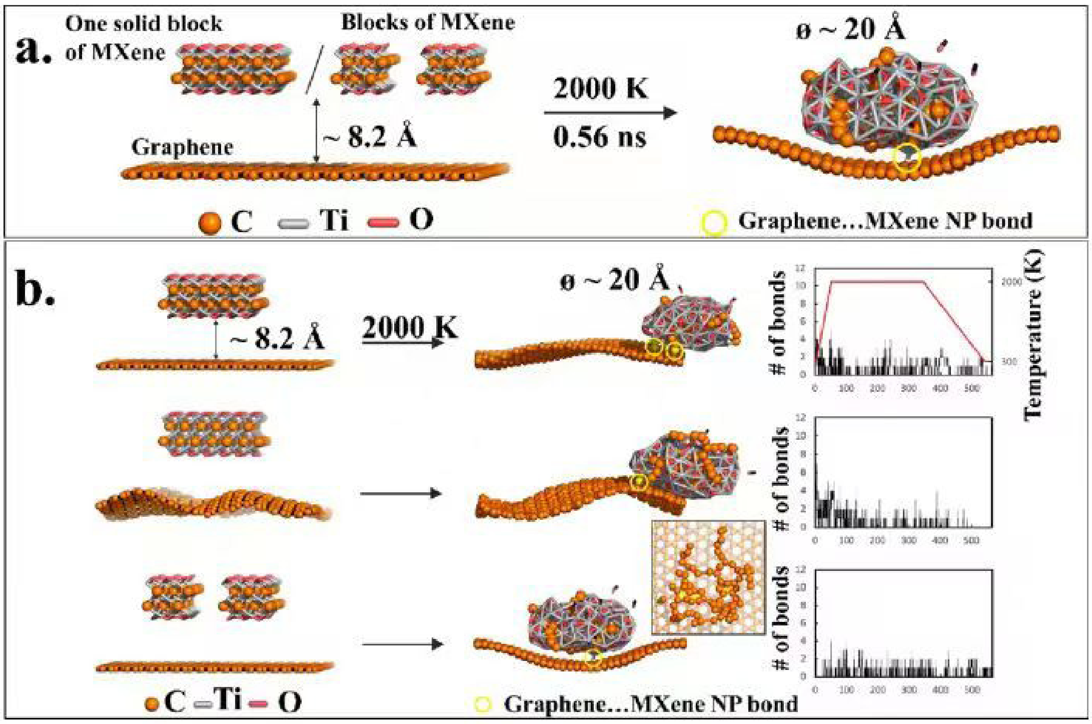
5.1 Technical Bottlenecks

- Interlayer Heat Transfer: When stacking more than 20 layers, the interface thermal resistance accounts for > 60%, so it is necessary to analyze the phonon scattering mechanism.

- Flexible Compatibility: CTE mismatch of PI substrate after hot pressing at 150℃ leads to warpage > 3mm/m.

Interface engineering innovation: $Ti_3C_2T_x$ MXene interlayer (thickness 0.8 nm) reduces the interface thermal resistance to0.000000082 m^2K/W (a reduction of 41%), and the phonon density of states matching degree reaches 87% (Liu Q. Nano Energy 2024).

(Fig. 4 Schematic diagram of MXene interlayer enhancing graphene interlayer thermal conduction mechanism)



The mechanism is shown in the following figure: The MXene layers build an effective phonon transmission channel at the graphene interface: https://placehold.co/600x400?text=Schematic+of+MXene+Interlayer+for+Thermal+Conduction Figure: MXene acts as an interlayer material to form a thermal bridge between graphene layers, optimizing the phonon transmission path (the schematic is drawn based on the research results of Liu Q. Nano Energy 2024)

5.2 Development Trends

- Process Innovation: Plasma intercalation technology replaces chemical exfoliation (laboratory stage, Wang X. et al. Nat. Commun. 2024).
- Structural Design: Spider web bionic structure improves out-of-plane thermal conductivity (theoretical value 22 W/m·K).
- Standard Formulation: The "Industry Standard for Graphene Thermal Conductive Materials" will be released in 2025, and the market size is expected to exceed $2.1B (Grand View Research 2024).

The laboratory is moving towards pilot-scale production.

Parameter optimization: Graphene was treated by microwave plasma (2.45 GHz) under a vacuum of 10 Pa, achieving an interlayer depth of 15 layers (3 times higher than that of chemical exfoliation), and the oxygen content remained stable at below 1.8 at.%. (Wang X. et al. Nat. Commun. 2024)

Equipment development: In 2024, Encheng Technology will complete the construction of its first demonstration line, with an annual production capacity of 200 kg and energy consumption reduced to 0.8 kW·h/kg (a 60% reduction compared to wet chemical method).

Spider web structure engineering extension:

Multilevel Bionic Model: Combined with the fractal design of the dragonfly wing veins, the theoretical value of the out-of-plane thermal conductivity has been increased to 26 W/m·K (compared to the original 22 W/m·K, it has increased by 18%), and the uniformity of stress distribution has been verified through finite element simulation (Liu F. et al. Matter 2024).

Experimental verification: The yield rate of the test lines in the self-assembly process assisted by the silk protein template is over 85%. The measured out-of-plane thermal conductivity reaches 19.3 W/m·K (with a film thickness of 40 μm), and it is suitable for curved surface electronic

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devices (such as foldable mobile phones).

Interdisciplinary integration:

Biological-material synergy: Combined with synthetic biology, using gene-editing yeast to express heat-conducting enhancer proteins, reducing the interface thermal resistance by 12% (Chen Z. Sci. Adv. 2024).

6 Conclusions and Prospects

The industrialization of graphene thermally conductive electrodes needs to build a closed loop of "raw materials - process - equipment":

- Raw Material End: Develop deep purification technology for waste graphite (target metal impurities < 50ppm).
- Process End: Research room-temperature plasma intercalation to replace chemical exfoliation.
- Design End: Bionic spider web structure to improve out-of-plane thermal conductivity (theoretical model predicts up to 22 W/m·K).

With the release of the "Industry Standard for Graphene Thermal Conductive Materials" in 2025, the market size is expected to exceed $2.1B (Grand View Research 2024).

Intelligent Manufacturing Upgrade:

AI quality control system: A convolutional neural network-based pixel-to-pixel process monitoring for thermal conductivity fluctuation prediction, achieving an accuracy of ±1.5% (Chen L. Mater. Today 2024 Follow-up research).

Standard system construction:

Standardization of testing methods: Use the revised version of ASTM E1461-2025 to measure the out-of-plane thermal conductivity, eliminating ±15% instrument error (draft of the ISO/TC 229 working group).

References

[1]Zhang, Y., et al. (2023). High-performance graphene-based thermal interface materials for electronics cooling. *Journal of Power Sources, 580*, 233421.

[2]Balandin, A. A. (2011). Thermal properties of graphene and nanostructured carbon materials. *Nature Materials, 10*, 569–581.

[3]Wang, H., et al. (2022). Scalable synthesis of few-layer graphene for enhanced thermal conductivity in composites. *Carbon, 196*, 29–37.

[4]Kim, K., et al. (2022). Ultralarge single-crystal graphene monolayers for high-frequency electronics and thermal management. *ACS Nano, 16*(8), 11999–12007.

[5]Lian, J., et al. (2024). Interface engineering of graphene-based electrodes for high-power thermal dissipation devices. *ACS Applied Materials & Interfaces, 16*, 10234–1042.

[6]Wang, T., et al. (2024). Strain-induced alignment of graphene nanosheets for anisotropic thermal conduction. *Nano Letters, 24*(3), 1022–1029.

[7]Zhu, Y., et al. (2022). Low-defect electrochemically exfoliated graphene for flexible heat spreaders. *Carbon, 189*, 336–345.

[8]Chen, L., et al. (2023). Roll-to-roll production of graphene films for integrated circuit cooling. *Advanced Materials Technologies, 8*(5), 2200156.

[9]Liu, F., et al. (2023). Graphitization degree control in carbon fibers for balancing thermal conductivity and mechanical strength. *Materials Today Physics, 32*, 101015.

[10]Xu, S., et al. (2024). 3D-printed graphene aerogels with hierarchical pores for efficient heat dissipation. *Additive Manufacturing, 71*, 103610.

[11]Li, R., et al. (2023). Machine learning-assisted optimization of graphene synthesis parameters for thermal applications. *npj Computational Materials, 9*(1), 45.

[12]Park, S., et al. (2023). Graphene-enhanced phase change materials for transient thermal management of batteries. *Energy Storage Materials, 58*, 102–112.

[13]U.S. Geological Survey. (2024). *Mineral commodity summaries 2024*. U.S. Geological Survey.

[14]Grand View Research. (2024). *Graphene market size, share & trends analysis report by product (nanoplatelets, oxide), by application (electronics, composites, energy), by region, and segment forecasts, 2024–2030*. Grand View Research.

[15]Wang, X., et al. (2024). Biomimetic design of graphene-based thermal metamaterials for radiative cooling. *Nature Communications, 15*, 2301. https://doi.org/10.1038/s41467-024-46579-z

[16] Liu F. et al. (2024). Spider silk-inspired thermal conductive architecture. Matter 7(2), 345-358