

Article

Study on the Cumulative Effect of Femtosecond Laser Ablation at the Graphene/Aluminum-Based Interface

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Abstract

The present study aims to investigate the cumulative effects of multi-pulse femtosecond laser etching at the graphene/aluminium interface. In addition, the study seeks to achieve accurate prediction of the ablation threshold and process optimisation at this interface. In this study, a 1.5 μm graphene coating was first deposited onto the surface of a pure aluminium substrate. In the ensuing experiment, the graphene/aluminum interface was subjected to femtosecond laser etching, with the laser parameters varying in both frequency and energy. The present study investigated the ablation process of the graphene/aluminum interface under the action of repeated laser pulses at different frequencies. A model of the cumulative effect of femtosecond lasers at the graphene/aluminum interface was established, and the influence of the cumulative effect on the ablation threshold of the graphene/aluminum interface was analysed. The results indicated that with increasing laser fluence and frequency, the dimensions of the ablation grooves increased significantly and the edge sharpness improved. The square of the ablation diameter showed a linear correlation with the logarithm of the laser fluence. The ablation threshold of graphene decreased gradually with an increase in the effective number of pulses, with a pronounced reduction when the effective pulse number was below 80, and a gentler decline when it exceeded 80. A fitting analysis based on the cumulative model indicates that the cumulative effect coefficient, designated as δ , which was intended to illustrate how the graphene damage threshold changes with the number of pulses, was as low as 0.16. This finding suggested that there was a significant cumulative effect. Through this investigation of the femtosecond laser cumulative effect, an accurate description of the multi-pulse ablation threshold for graphene/aluminum was achieved, providing a theoretical basis and process reference for high-precision femtosecond laser processing of graphene.

Keywords: femtosecond laser; graphene; cumulative effect; ablation threshold; multi-pulse irradiation



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1. Introduction

Etched aluminum foil is a key material in the production of aluminum electrolytic capacitors, and its specific surface area is one of the core factors determining the capacitance of such capacitors [1,2]. However, conventional chemical etching processes produce irregular and randomly distributed corrosion pores on the surface of aluminum foil, which limits the improvement of specific surface area and directly compromises the overall performance of aluminum electrolytic capacitors [3,4].

Graphene is a new type of two-dimensional material that exhibits excellent electrical conductivity and strong corrosion resistance. This makes it highly suitable for use in chemical industries such as the production of hydrochloric and acetic acids. By coating graphene onto aluminum foil, femtosecond laser processing can be employed to fabricate regularly arrayed micro-holes on the graphene surface, forming directional etching channels. This approach enables precise micro-/nano-scale regulation of capacitor structures, effectively improves electrode interface characteristics, and significantly enhances the electrochemical performance and system integration density of the devices [5,6]. Compared with conventional processing methods, the non-contact nature of femtosecond laser processing allows for high-precision patterning on various substrate materials without the need for mask assistance, and complex three-dimensional structures can be flexibly fabricated through computer programming [7]. He et al. applied laser printing technology to fabricate electrode templates on polymer substrates, followed by electron beam evaporation to prepare patterned gold films, and then electrochemically deposited electrode materials onto the gold films to produce cross-linked polyaniline-based micro-supercapacitors (PANI MSC) [8]. After thermal treatment in an argon atmosphere, the flexible PANI MSC exhibited a high areal capacitance of $54 \text{ mF} \cdot \text{cm}^{-2}$ at a current density of $0.3 \text{ mA} \cdot \text{cm}^{-2}$. Wang et al. [9] fabricated electrode-shaped templates via laser technology and applied a doctor-blading method to uniformly coat semi-solid electrode materials onto the surface of an expandable balloon. Upon deflation of the balloon, the electrode dimensions shrank accordingly, enabling the successful fabrication of flexible supercapacitors with tunable sizes and adjustable performance. Khodabandehlo et al. processed graphene by laser scribing and synthesized polyaniline (PANI) via electrodeposition to construct a flexible integrated system [10]. Park et al. developed a laser-induced synchronous modification strategy by compositing MXene nanosheets with graphene oxide (GO), achieving in situ thermal reduction in GO and selective oxidation of MXene simultaneously during laser irradiation [11].

Current research on femtosecond laser processing of graphene primarily focuses on the ablation characteristics and processing precision control under single-pulse irradiation. Although single-pulse irradiation enables deterministic removal of graphene, it fails to adequately account for the coupled effects of thermal accumulation and defect evolution during multi-pulse interaction, making it difficult to accurately predict the material removal threshold in practical processing. Furthermore, although the fluence-based damage threshold methodology can establish a basic processing window, its description of the pulse-number dependence remains incomplete. In addition, the synergistic damage mechanisms of laser-induced plasma behavior and thermal stress accumulation on the graphene lattice structure have yet to be systematically investigated.

In this paper, the cumulative effect of femtosecond laser on graphene is taken as the research object. The damage evolution process of graphene under multi-pulse irradiation is systematically analyzed, and the influence of pulse number and fluence on the damage threshold is investigated. Finally, from the perspectives of thermal accumulation effects and defect density, the modification characteristics and damage mechanisms of graphene induced by femtosecond laser under different pulse numbers are evaluated.

2. Materials and Methods

2.1. Sample Preparation

The substrate material was 1060 commercial pure aluminum with dimensions of $30 \text{ mm} \times 30 \text{ mm} \times 8 \text{ mm}$. The specimens were sequentially ground and polished using 80 to 2000 grit sandpaper. After surface treatment, the specimens were placed in an ultrasonic cleaning tank filled with analytically pure anhydrous ethanol. Ultrasonic cleaning

was performed at a power of 100 W and a constant temperature of 60 °C for 20 min to thoroughly remove residual abrasive particles and organic contaminants from the surface. After each treatment, the specimens were dried with high-purity nitrogen gas and stored in a desiccator for subsequent use.

A graphene/polyurethane (PU) composite coating was prepared using polyurethane. First, 40 mg of graphite was added to a 50% ethanol solution and ultrasonically dispersed for 15 min to obtain a 0.2% graphene ethanol solution. Separately, 4 mL of 1% polyurethane emulsion was added to 16 mL of deionized water and ultrasonically dispersed for 15 min to prepare 0.2% polyurethane solution. Subsequently, the graphene ethanol dispersion was mixed with the polyurethane solution at a solid content mass fraction of 0.2%, and the mixture was stirred thoroughly to ensure uniform dispersion, yielding a 50% graphene/polyurethane hybrid solution, the graphene coating is approximately 1.5 µm thick.

A femtosecond laser direct writing system was employed in the experiments (Pharos PH1-15W, air, Beijing Guangliang Technology Co., Ltd., Beijing, China). The laser source had a central wavelength of 1030 nm and delivered pulsed laser beams with a maximum pulse energy of 15 µJ at a repetition frequency of 1 MHz. The laser pulse was split into two beams by a polarization beam splitter, and the S-polarized beam was used as the writing laser. A 5× objective lens with a numerical aperture (NA) of 0.14 was used to focus the beam to a diameter of 6 µm (at the 1/e² level). The sample was positioned on an air-bearing translation stage with a resolution of 0.5 nm and a maximum scanning speed of 300 mm/s. The detailed experimental parameters are listed in Table 1.

Table 1. Experimental parameters of femtosecond laser processing.

Pulse Energy (µJ)	Scanning Speed	Repetition Frequency (KHz)	Pulse Duration	Spot Diameter (µm)
0.031	1 mm/s	1/2/4/8/10/12.5	290 fs	6
0.497	1 mm/s	1/2/4/8/10/12.5	290 fs	6
0.607	1 mm/s	1/2/4/8/10/12.5	290 fs	6
1.051	1 mm/s	1/2/4/8/10/12.5	290 fs	6

The pulse repetition frequency directly affects the number of pulses incident on the same region and the spot overlap ratio, thereby inducing cumulative effects. The lattice defects induced by cumulative effects can form new energy level structures within the material bandgap [12]. These defect energy levels provide additional energy absorption channels for subsequent laser pulses. As the number of irradiation pulses increases, the defect density within the material exhibits a progressive rise and eventually reaches a saturation level [13]. During this process, the continuous accumulation of defects significantly enhances the effective absorption coefficient of the material [14], consequently leading to a reduction in the surface ablation threshold. When the defect density approaches saturation, the ablation threshold stabilizes accordingly.

Since the laser pulse duration (290 fs) is much shorter than the pulse interval, the temporal cumulative effect can be neglected, allowing the dynamic ablation process to be simplified as a static geometric superposition model, as schematically illustrated in Figure 1. In this model, by calculating the overlap ratio of adjacent laser spots, the number of repetitions in the same area can be determined, which represents the number of effective pulses, and its relationship to the laser frequency is shown in Table 2.

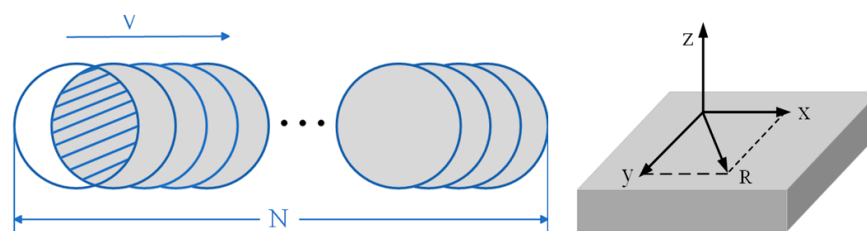


Figure 1. Calculation model of spot overlap ratio. Reprinted from Ref. [15].

Table 2. Repetition frequencies and effective pulse numbers.

Test No.	Repetition Frequency/kHz	Effective Number of Pulses
1	1	12
2	2	24
3	4	48
4	8	96
5	10	120
6	12.5	150

2.2. Morphology Observation and Characterization

The thickness of the graphene coating on the aluminum substrate surface was measured using a DR330 coating thickness gauge to be 1.5 μm . A portable German-made μsurf mobile laser confocal microscope was employed to characterize the grooves formed after laser ablation. Three-dimensional topographic images were reconstructed to characterize the morphology features and surface roughness of the ablation grooves, and the three-dimensional surface morphology of the grooves processed by femtosecond laser was measured (Nano Focus, Oberhausen, Germany).

2.3. Numerical Simulation

Abaqus finite element analysis software was employed to establish a three-dimensional model of the graphene/aluminum-based interface under femtosecond laser irradiation. To improve the simulation accuracy of the geometric dimensions of the ablation grooves, the model comprehensively considered heat conduction, convection, and radiation effects. The geometric model dimensions were optimized based on the actual temperature field distribution characteristics of the material. The model dimensions were set as 150 $\mu\text{m} \times 150 \mu\text{m} \times 30 \mu\text{m}$, with the graphene coating thickness set to 1.5 μm . The element type was DC3D8R, and the global mesh size of the model was 2.4 μm , with a minimum mesh size of 0.4 μm and a maximum of 16 μm . To enhance the accuracy of the simulation analysis, a finer mesh was employed in the region adjacent to the coating–substrate interface, as shown in Figure 2. The total number of mesh elements was 21,469.

The ambient temperature was set to 25 $^{\circ}\text{C}$, the film heat dissipation coefficient was 0.02, and the Stefan–Boltzmann constant was $5.67 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$. The bottom surface was defined as a convective heat transfer interface. During laser loading, the heat flux required for each element was calculated and applied as a surface load on each element. Accordingly, the element birth-and-death technique was employed to achieve dynamic computation: when the element temperature exceeded the critical value of graphene, the element was removed, and the underlying element became the new surface for thermal load application. By invoking the Deflux user subroutine, variables such as laser energy and pulse number were defined, with the pulse duration fixed at 290 fs and the laser spot

diameter set to 6 μm . The laser fluence was described using a Gaussian heat source model, expressed as follows [16]:

$$Q = (3\eta \frac{P}{\pi w_0^2}) \exp(-3 \frac{R^2}{w_0^2}) \quad (1)$$

where Q is the heat flux density at any point within the laser spot, with units typically expressed as W/m^2 or $\text{J}/(\text{cm}^2 \cdot \text{s})$; η is the energy absorption rate ($0 \leq \eta \leq 1$), representing the efficiency of the material in absorbing the incident laser energy; w_0 is the laser spot radius; P is the total laser power (unit: W); and R is the distance from any point to the center of the heat source.

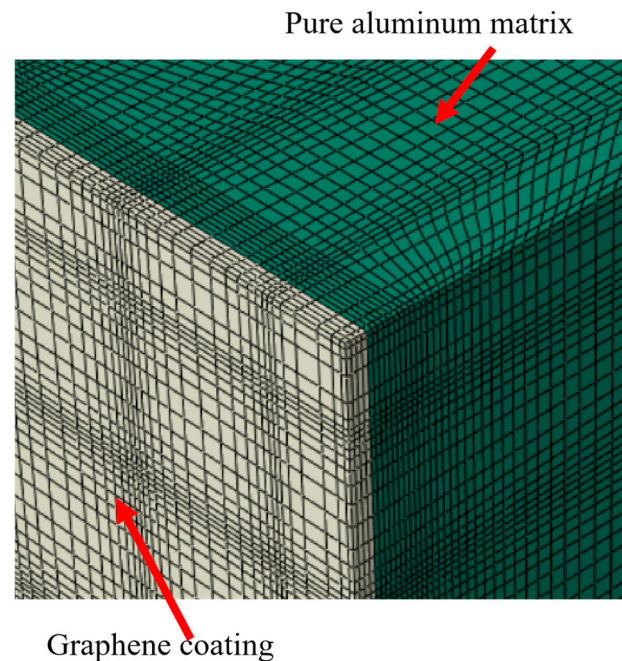


Figure 2. Local mesh refinement of the finite element model for the graphene-coated aluminum substrate. Reprinted from Ref. [15].

The waveform of the laser pulse is shown in Figure 3a,b. In the experiment, the pulse wave is an even function with a period of T (the sum of the laser energy loading time and the loading-off time), an amplitude of $A_{\max}$, and a pulse width of αT . Its Fourier series expansion over the interval $[-\frac{T}{2}, \frac{T}{2}]$ is given as follows:

$$f(t) \sim \alpha A_{\max} + \frac{2A_{\max}}{\pi} \sum_{n=1}^{\infty} \frac{\sin(\alpha n \pi)}{n} \cos(\alpha \omega t), \quad n = 1, 2, 3 \quad (2)$$

In the moving heat source simulation of the graphene-coated aluminum model for investigating the variation in the femtosecond laser ablation groove width, a three-dimensional coordinate system was established at the lower-left corner of the top surface of the model. The distance from any point to the center of the heat source was denoted as R , and the coordinates of that point were denoted as x and y . The moving heat source formula was then defined as follows:

$$R = \sqrt{x^2 + (z - z_0)^2} \quad (3)$$

z is the Z -axis coordinate in a three-dimensional Cartesian coordinate system; z_0 is a fixed offset in the Z direction, representing the Z -coordinate of a fixed point on the axis of symmetry.

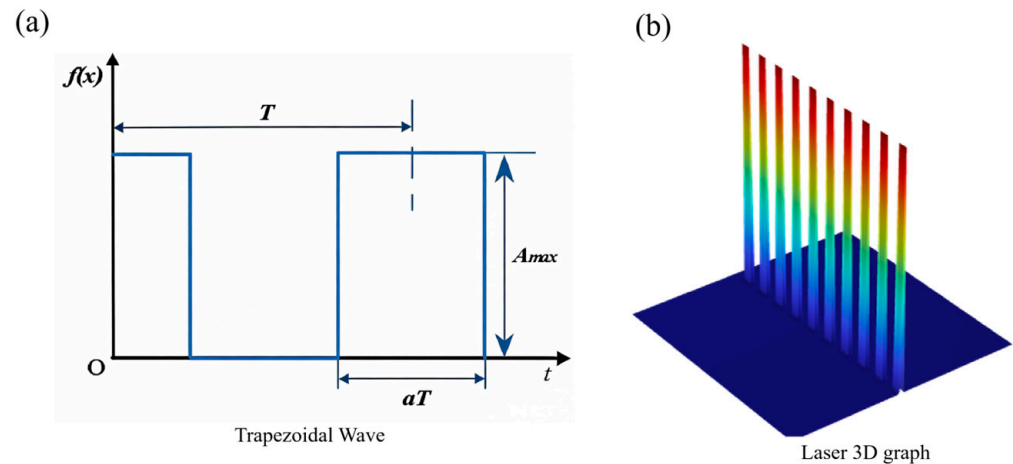


Figure 3. Laser pulse waveform in finite element simulation, (a) Trapezoidal Wave; (b) Laser 3D graph. Reprinted from Ref. [15].

2.4. Damage Threshold Fitting Method

The quantitative relationship between the ablation threshold and the pulse number can be characterized by the following cumulative effect models:

$$F_{th}(N) = F_{th}(1) \cdot N^{\delta-1} \quad (4)$$

By performing a logarithmic transformation on the above equations, the following linearized expressions can be obtained:

$$\ln(NF_{th}(N)) = \delta \cdot \ln(N) + \ln(F_{th}(1)) \quad (5)$$

where N is the cumulative pulse number, and δ is the incubation factor, representing the dependence of the material ablation threshold on the pulse number. Generally, the δ value for metallic materials ranges from 0.3 to 0.5, while that for semiconductor materials is approximately between 0.1 and 0.3 [17].

From Equation (3), it can be seen that the natural logarithm of $\ln(NF_{th}(N))$ is linearly related to the natural logarithm of $\ln(N)$, with the slope being δ , which represents the incubation coefficient of the material damage threshold varying with the pulse number. When δ equals 1, the pulse number has no significant effect on the material ablation threshold; a smaller δ indicates a stronger cumulative effect.

3. Results and Discussion

3.1. Morphology of Femtosecond Laser-Ablated Grooves

Figure 4 shows the three-dimensional topography of a graphene surface that has not undergone laser ablation, the surface is relatively uniform and flat, with a surface roughness of $R_a = 0.136 \mu\text{m}$ as measured by a laser confocal microscope. Here, the roughness R_a is defined as the arithmetic mean deviation of the contour:

$$R_a = \frac{1}{l} \int_0^l |Z(x)| dx \quad (6)$$

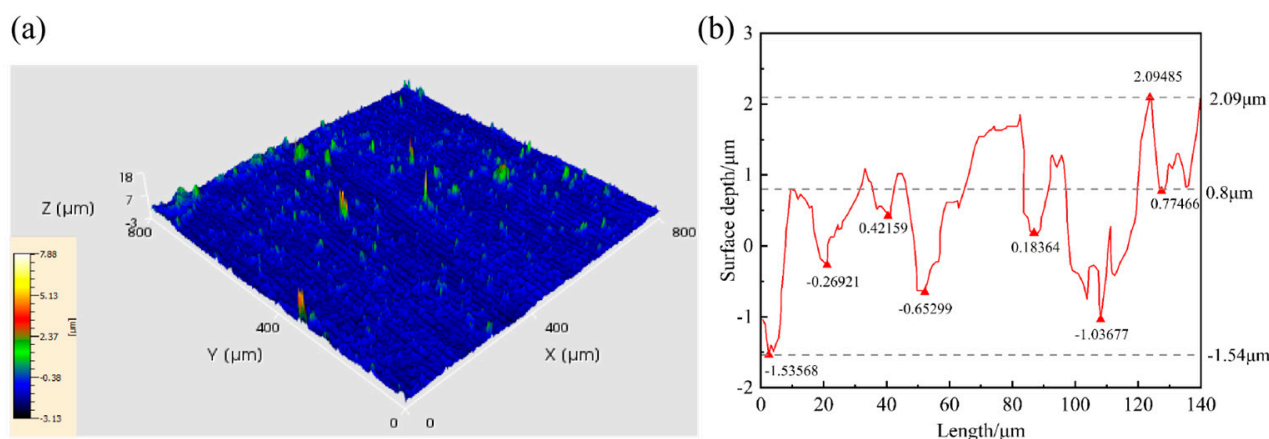


Figure 4. Surface Topography of Untreated Graphene Coatings. (a) 3D topographic map; (b) Specific contour map.

Here, 1 represents the sampling length, and the ordinate value is the arithmetic mean of the absolute values $Z(x)$.

Figure 5 shows the groove profiles formed by femtosecond laser ablation of the graphene coating at different pulse energies. It can be seen that the graphene coating formed relatively uniform groove structures during the ablation process. Around the ablated regions, ripple-like propagation traces resulting from ablation were observed [18]. When the laser energy increased from 0.031 μJ , the groove profiles gradually became clearer. At a laser energy of 1.051 μJ , as shown in Figure 5d, melting and vaporization of the material led to an increase in the lateral dimensions of the machined grooves. As the laser energy continued to increase, the extent of the surface heat-affected zone gradually decreased.

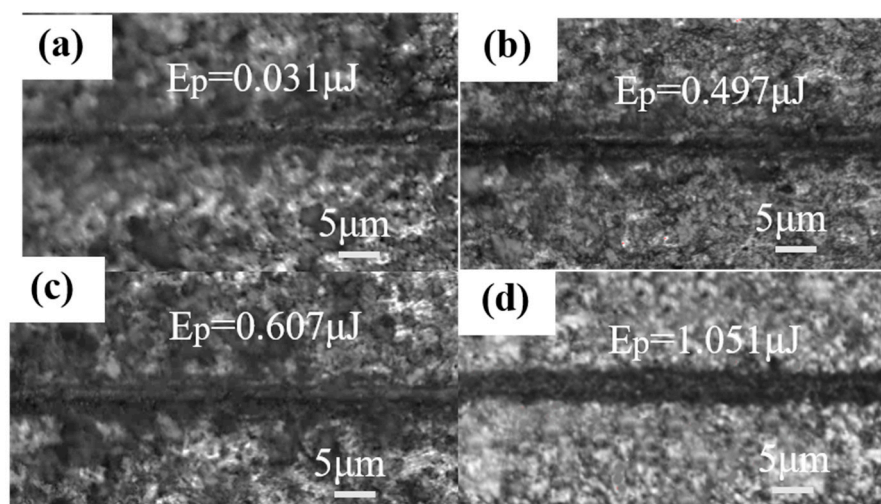


Figure 5. Groove structures formed on the graphene surface at different laser pulse energies (a) $E_p = 0.031 \mu\text{J}$; (b) $E_p = 0.497 \mu\text{J}$; (c) $E_p = 0.607 \mu\text{J}$; (d) $E_p = 1.051 \mu\text{J}$. Reprinted from Ref. [15].

The cross-sections of the laser-ablated grooves are shown in Figure 6. It can be observed that the groove cross-sections exhibit an inverted triangular shape. This is attributed to the fact that the molten liquid-phase graphene inside the groove cannot be expelled in time, causing the melt to accumulate at the groove edges and form an uneven recast layer. With increasing pulse energy, both the width and depth of the ablation grooves gradually increase. This is because, under constant scanning speed and scanning number, the interaction time between the laser and the material remains the same. When the pulse fluence is close to the ablation threshold of the material, the degree of ablation is relatively

low and insufficient to reach the temperature required for melting or vaporization, resulting in a limited material removal volume. In this case, the heat is mainly concentrated on the material surface and does not transfer downward. As the laser energy increases, more heat is deposited downward, leading to an increase in the ablation depth. Simultaneously, the energy absorbed on the material surface diffuses outward into the interior, forming a heat-affected zone at locations away from the laser spot.

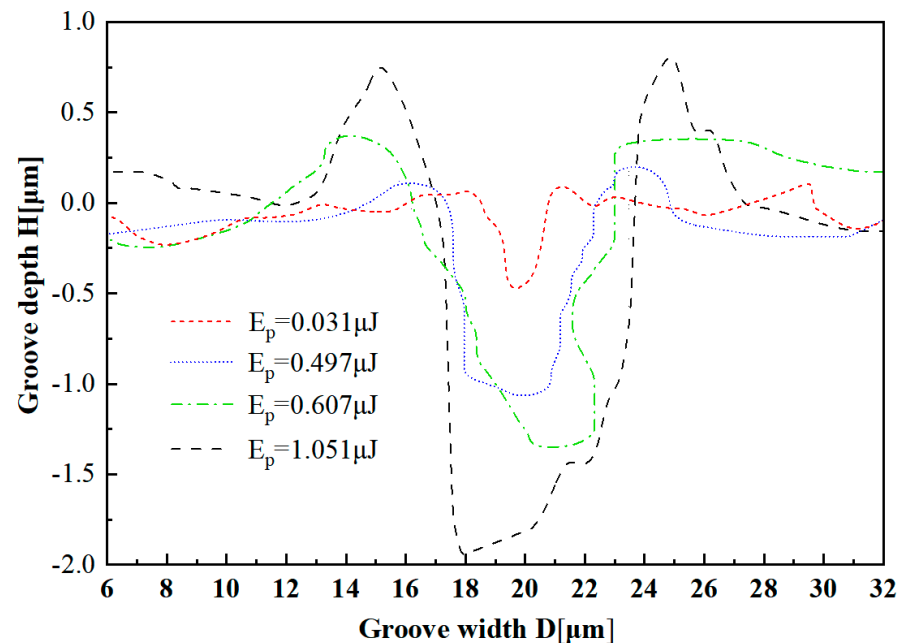


Figure 6. Cross-sectional morphologies of the ablated grooves on the graphene/aluminum-based interface. Reprinted from Ref. [15].

Figure 7 shows the morphologies of the ablated graphene grooves at a laser pulse energy of $0.607 \mu\text{J}$ under different repetition frequencies. With increasing frequency, the diameter of the ablation grooves increases accordingly.

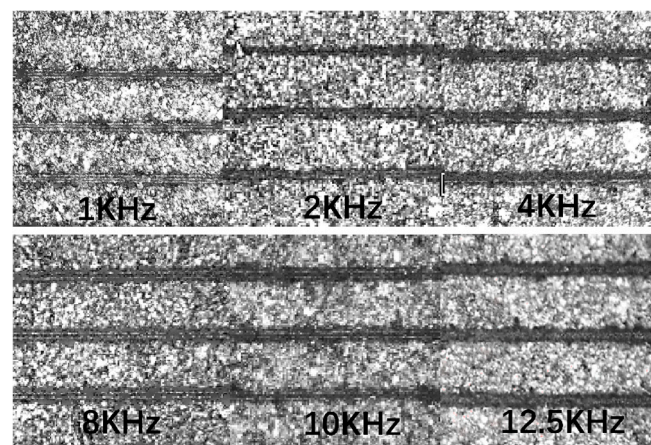


Figure 7. Morphologies of ablated graphene grooves at different laser repetition frequencies.

Figure 8 shows the specific cross-sectional morphologies of the ablation grooves at repetition frequencies of 4 KHz and 12.5 KHz). It can be seen that, at lower frequencies, the diameter of the ablation grooves is relatively small. With increasing frequency, i.e., with an increase in the effective number of pulses, the diameter of the ablation grooves increases correspondingly and eventually tends to reach saturation, at which point the

influence of the effective pulse number on the diameter increase becomes significantly diminished. Experimental results indicate that the variation in ablation morphology under low pulse number conditions is considerably more pronounced than that under high pulse number conditions. This difference originates from the nonlinear characteristics of the pulse cumulative effect: during the initial stage, the random surface modifications induced by individual pulses significantly alter the energy coupling efficiency for subsequent laser pulses. Once the pulse number exceeds a critical value, thermal accumulation effects dominate the process, leading to a stabilization of the ablation morphology.

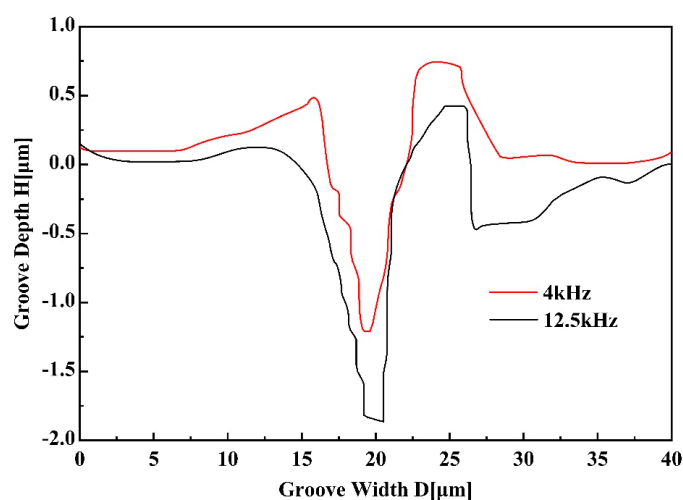


Figure 8. Cross-sectional morphologies of ablated graphene grooves at different laser repetition frequencies.

3.2. Laser Ablation Threshold Fitting

The fitting results of the square of the ablated graphene groove width D^2 versus the logarithm of laser pulse energy $\ln E_p$ are shown in Figure 9. When the pulse number increased from 12 to 150, the influence of laser energy on the ablation diameter gradually decreased and eventually tended to reach saturation. By performing linear fitting of this relationship, the ablation threshold of the material can be accurately determined. The detailed calculation results are summarized in Table 3.

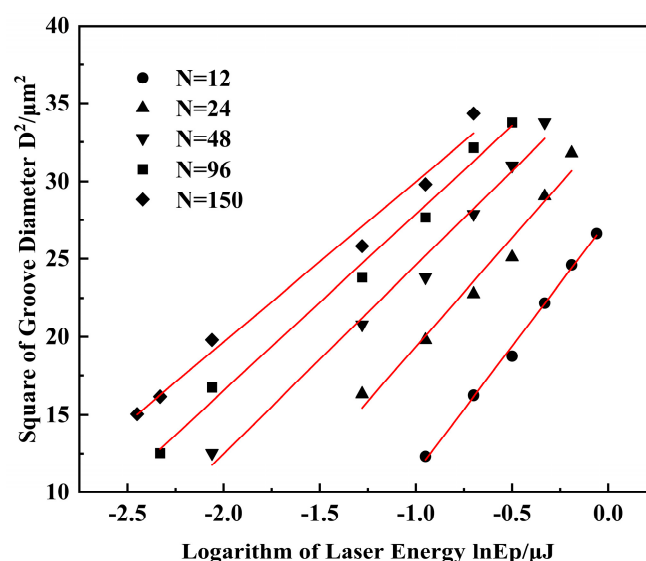
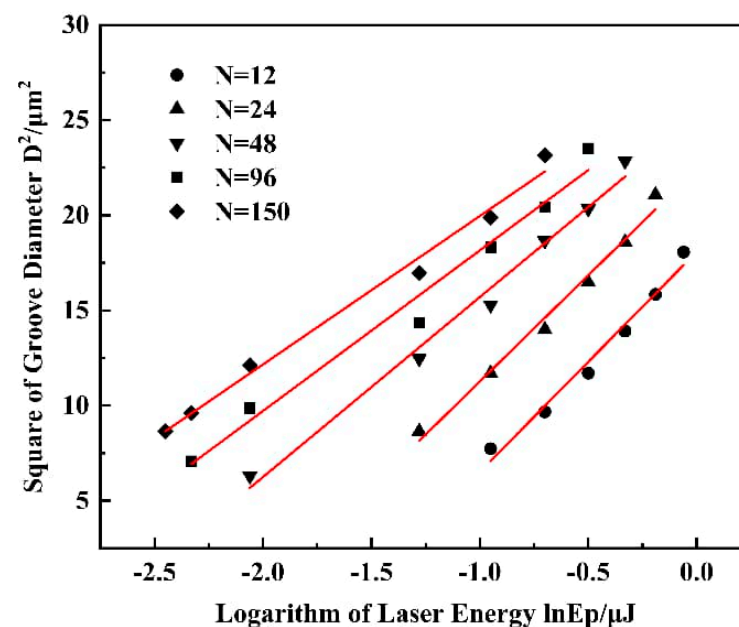


Figure 9. Fitting curves of the square of ablation groove diameter versus the logarithm of laser pulse energy at different pulse numbers (simulation results).

Table 3. Simulated ablation thresholds and corresponding effective pulse numbers.

Effective Number of Pulses N	Minimum Laser Pulse Energy/ μJ	Simulated Ablation Threshold/ (J/cm^2)
12	0.183	0.323
24	0.092	0.163
48	0.048	0.085
96	0.031	0.055
150	0.020	0.035

The fitting results of the experimentally measured square of the ablated graphene groove width D^2 versus the logarithm of laser pulse energy $\ln E_p$ are shown in Figure 10. When the number of laser pulses was relatively small, the groove edges exhibited blurring, which may have affected the accuracy of diameter measurement and consequently reduced the significance of the linear fitting relationship. With increasing pulse number, the edge sharpness of the ablation grooves improved significantly, leading to enhanced measurement precision. It can be observed from the figure that with increasing pulse energy and pulse number, the ablation groove diameter increased correspondingly, while the ablation threshold decreased markedly. In the red fitting curves, the relative spacing between the curves was relatively large at pulse numbers of $N = 12$ and $N = 24$, whereas the spacing between $N = 96$ and $N = 150$ was considerably reduced. This phenomenon can be explained as follows: at a small number of pulses, the ablation threshold of the material decreases sharply. As the pulse number continues to increase, the rate of increase in the spacing between the fitting curves slows down significantly, indicating a gradual weakening of the threshold reduction trend. When the pulse number exceeds a critical value, the fitting curves nearly overlap, suggesting that the ablation threshold has essentially reached a stable state [19].

**Figure 10.** Fitting curves of the square of ablation groove diameter versus the logarithm of laser pulse energy at different pulse numbers (Experimental results).

According to the fitting curves of the square of the ablation groove width versus the logarithm of laser pulse energy shown in the above figure, the experimental femtosecond

laser ablation thresholds at different pulse numbers can be obtained, as summarized in Table 4.

Table 4. Experimental ablation thresholds at different effective pulse numbers.

Effective Number of Pulses	Minimum Laser Pulse Energy/ μJ	Experimental Ablation Threshold/ (J/cm^2)
12	0.209	0.370
24	0.134	0.237
48	0.070	0.124
96	0.041	0.066
150	0.028	0.050

Both the numerical simulation and experimental results indicate that cumulative effects exist during the laser ablation process [20]. As the effective number of laser pulses increases with increasing repetition frequency, the surface ablation threshold of the graphene material gradually decreases and eventually levels off. The cumulative effect can be understood as follows: the interaction between the material and the initial pulses induces temperature rise and defect generation, which enhances the absorption of subsequent pulse energy until saturation is reached, ultimately leading to a reduction in the ablation threshold with increasing pulse number.

3.3. Incubation Factor Calculation

The variation in the material ablation threshold with the number of pulses is shown in Figure 11. It can be observed from the figure that when the pulse number $N < 80$, the ablation threshold decreases significantly; when $N > 80$, the ablation threshold tends to level off, and the rate of reduction becomes notably smaller.

The logarithmic relationships are shown in Table 5 below.

Table 5. Logarithmic relationship between the effective pulse number and the product of the pulse number and the ablation threshold.

Independent Variable $\ln(N)$	Dependent Variable $\ln(NF_{th}(N))$
2.48	1.49
3.18	1.74
3.87	1.78
4.56	1.85
4.79	1.92
5.01	2.01

Figure 12 presents the cumulative effect curve of the experimental data, with a linear fitting goodness-of-fit R^2 of 0.92. From Figure 10, it can be determined that the incubation factor for femtosecond laser ablation of the graphene coating in the experiments is 0.17, indicating that graphene exhibits a significant cumulative effect under low pulse number conditions. Specifically, when the pulse number is relatively small ($N < 80$), the ablation threshold of the graphene material decreases rapidly. As the pulse number continues to increase ($N > 80$), the ablation threshold gradually levels off and tends to stabilize.

To improve the fitting accuracy, the saturation points of the threshold were excluded, and the corrected curve is shown in Figure 13, with a goodness-of-fit $R^2 = 0.85$. It can be seen from the figure that the incubation factor of graphene after correction is 0.16. In addition, the data in both Figures 11 and 12 exhibit fluctuation characteristics caused by measurement errors.

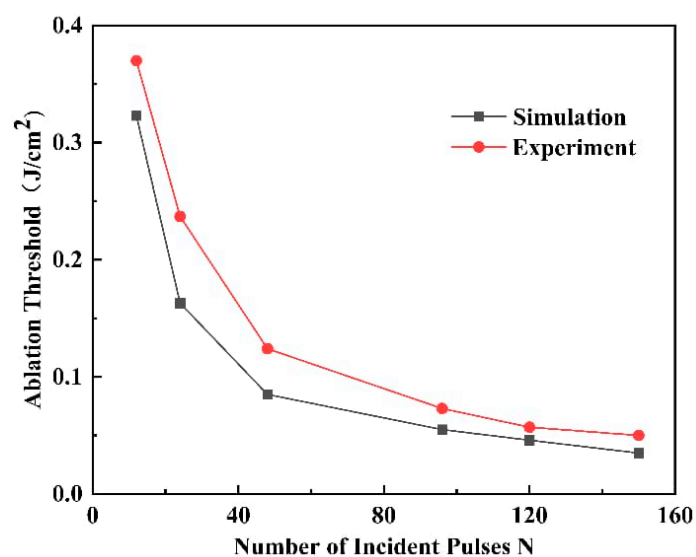


Figure 11. Ablation threshold as a function of pulse number.

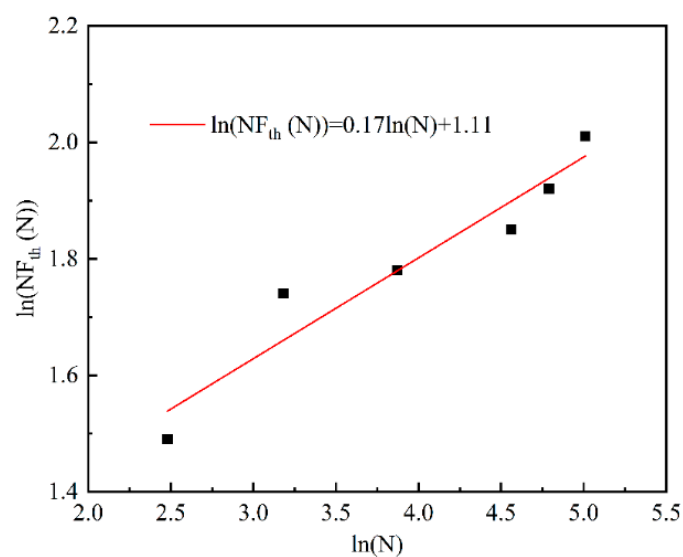


Figure 12. Incubation factor of graphene before correction.

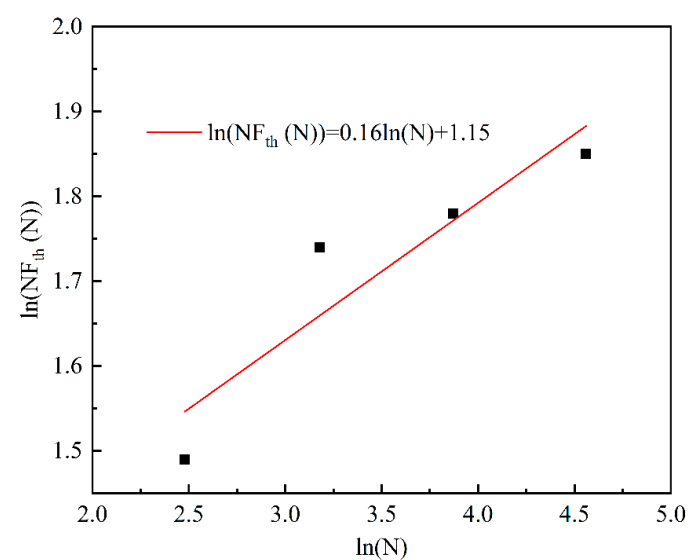


Figure 13. Post-correction incubation factor of graphene.

Due to the differences in ablation mechanisms among various materials, the cumulative effect exhibits significant variations across different materials. In metallic materials, the cumulative effect primarily originates from plastic deformation, with the incubation factor ranging from 0.3 to 0.5 [12,21]. When the tested material is a non-metallic material, laser irradiation induces continuous accumulation of internal defects. This progressive damage mechanism leads to a decreasing trend in the ablation threshold with increasing pulse number. Compared with metallic materials, non-metallic materials generally exhibit lower incubation factor values, typically ranging from 0.1 to 0.3 [22].

To address the complex process of multi-pulse laser–material interaction, researchers have developed various cumulative effect models to accommodate the requirements of different experimental conditions. Hernandez et al. [23] established three typical theoretical models, which have been widely applied to the study of multi-pulse ablation behavior in dielectric and semiconductor materials.

The above cumulative effect model (Model I) is expressed as follows:

$$F_{th}(N) = F_{th}(1) \cdot N^{\delta-1} \quad (7)$$

Di Niso et al. [24] optimized the basic model by introducing a threshold saturation correction term and proposed a modified Model II, as shown in Equation (5):

$$F_{th}(N) = F_{th}(\infty) + (F_{th}(1) - F_{th}(\infty)) \cdot N^{\delta-1} \quad (8)$$

Rosenfeld et al. [25] introduced a threshold offset parameter based on Model II and established an improved exponential cumulative effect Model III, the mathematical expression of which is given as follows:

$$F_{th}(N) = F_{th}(\infty) + (F_{th}(1) - F_{th}(\infty))e^{-k(\delta-1)} \quad (9)$$

The difference between Model III and Models I and II lies in the introduction of the parameter k , which characterizes the cumulative effect coefficient of the exponential function.

Based on these three model frameworks, a systematic investigation of the cumulative effect during femtosecond laser multi-pulse ablation was conducted using numerical analysis in Matlab, and the results are presented in Figure 13. From the red curve in Figure 13, it can be seen that by introducing the cumulative coefficient δ , the multi-pulse ablation threshold $F_{th}(N)$ and the single-pulse ablation threshold $F_{th}(1)$ were correlated. Through fitting with Model I, $F_{th}(1) = 2.57 \text{ J/cm}^2$ was obtained. Model I demonstrates good fitting accuracy under low pulse number conditions. Given that the instability of the ablation crater morphology at low pulse numbers introduces relatively large measurement errors, the application of this model can effectively improve the accuracy of ablation threshold determination in this pulse number regime.

As shown by the blue curve in Figure 14, Model II exhibits excellent fitting performance, with a coefficient of determination $R^2 = 0.993$. Compared with Model I, Model II significantly enhances the descriptive accuracy of the multi-pulse cumulative effect by introducing an asymptotic saturation term $F_{th}(\infty)$. As the pulse number increases, Model II demonstrates superior fitting performance for the cumulative saturation phenomenon, effectively describing the underlying physical mechanisms, including defect-state saturation effects, nonlinear thermal accumulation, and plasma shielding.

The cumulative effect coefficient δ , which describes the variation in the graphene damage threshold with the number of pulses, serves as a material property parameter. Its numerical range is capable of effectively characterising the intensity of the cumulative effect during the multi-pulse ablation process induced by femtosecond lasers [26]. Fitting data

analysis indicates that the incubation coefficient δ in both Model I and Model II satisfies the physical constraint of $0 < \delta < 1$. Notably, in Model I, a smaller δ value corresponds to a stronger cumulative effect. When δ approaches 0, the ablation threshold $F_{th}(N)$ exhibits a rapid logarithmic decrease with increasing pulse number N , indicating a pronounced cumulative effect. When $\delta = 1$, the material exhibits no cumulative effect, and its ablation threshold remains constant regardless of the pulse number. Model I was originally established for the study of cumulative effects in metallic materials; however, its theoretical assumptions have obvious limitations: the model does not account for saturation effects, leading to unrealistic predictions that the threshold approaches zero under infinite pulse number conditions. To address this issue, Model II was improved by introducing a saturation threshold parameter, providing a more accurate description of the cumulative saturation phenomenon in practical processing. Theoretical analysis shows that the initial threshold $F_{th}(1)$ in Model II is lower than that in Model I, which is attributed to the fact that the introduction of saturation effects enhances the actual manifestation of the cumulative effect.

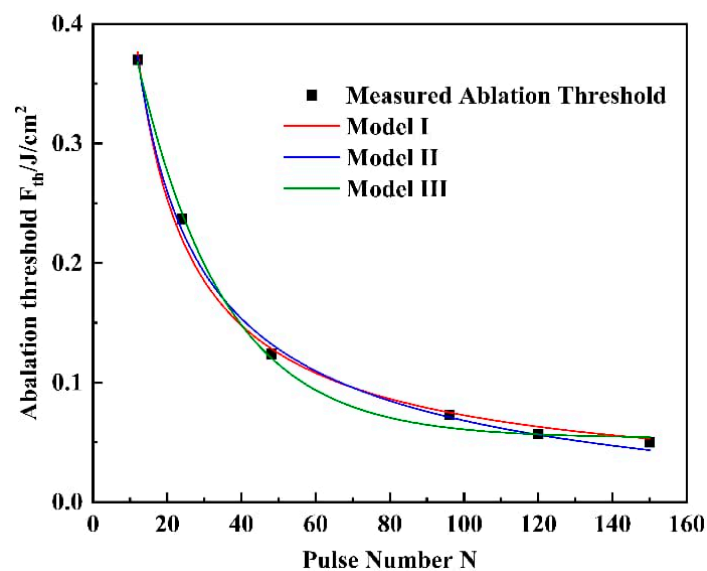


Figure 14. Experimental fitting results of the ablation threshold versus the number of laser pulses under multi-pulse femtosecond laser irradiation.

Model III (shown as the green curve in Figure 12) comprehensively incorporates the defect-state density distribution and thermal diffusion length, enabling the model to accurately describe the wide-range damage accumulation behavior from single-pulse to multi-pulse conditions, and its fitting results are accordingly more precise. The empirical coefficient k in Model III is closely related to the intrinsic properties of the material, with a theoretical value greater than 0, and its specific value needs to be determined through experimental calibration. Studies have shown that the k value directly reflects the damage accumulation sensitivity of the material: when $k > 1$, the material exhibits an enhanced response to repetitive irradiation; $0 < k \leq 1$ corresponds to linear accumulation behavior; and the special case of $k \ll 1$ suggests that the material possesses damage self-healing characteristics. This parametric characterization provides a quantitative basis for evaluating the laser tolerance of different materials. Therefore, a larger k value indicates a more significant cumulative effect. As the pulse number increases, the ablation threshold decreases at an increasingly rapid rate, requiring fewer pulses to reach cumulative saturation. Experimental data show that this phenomenon is in good agreement with the theoretical predictions of Model III: once the ablation threshold drops to a critical value, further increases in pulse

number only cause minor changes in the threshold. This model demonstrates excellent applicability in the field of dielectric materials (such as quartz, calcium fluoride, and gallium nitride), with a goodness-of-fit superior to other cumulative models.

Table 6 compares the fitting parameters of the three cumulative models, where the R^2 value represents the degree of agreement between the model and the experimental data. Data analysis indicates that, after excluding the low-pulse-number regime, Model III exhibits the optimal fitting performance, with its R^2 value significantly higher than those of the other two models.

Table 6. Fitting results of the three cumulative effect models.

Parameter	Model I	Model II	Model III
$F_{th}(1)/J/cm^2$	2.57	1.91	0.57
$F_{th}(\infty)/J/cm^2$	-	0.04	0.05
δ	0.22	0.38	-
k	-	-	0.043
R^2	0.994	0.993	0.999

Experimental investigations indicate that different cumulative models exhibit distinct applicability differences in describing material ablation behavior. In this study, a femtosecond laser system with a wavelength of 1030 nm and a pulse duration of 290 fs was employed to systematically determine the ablation threshold of graphene. By comparatively analyzing the fitting accuracy of the three typical cumulative models across different pulse number regimes, it was found that the prediction accuracy of each model for the ablation threshold exhibits significant range-dependent characteristics. Through a combination of models, more accurate threshold predictions can be achieved. This approach facilitates the selection of optimal parameters for the preparation of graphene/aluminum foil composite electrodes, enabling the fabrication of deep and uniform grooves, thereby effectively increasing the specific surface area of miniaturized capacitors and realizing large-scale production of graphene/aluminum-based capacitors via femtosecond laser processing.

4. Conclusions

Femtosecond lasers with different repetition frequencies were applied to the graphene coating, and the grooves formed on the graphene coating under different effective pulse numbers were characterized. The ablation thresholds of the graphene surface at different pulse numbers were determined through combined simulations and experiments, and the cumulative effect of the ablation threshold was verified. The following conclusions can be drawn:

1. Increasing the laser fluence and repetition frequency significantly increases the ablation groove dimensions and improves edge sharpness, and the square of the ablation diameter exhibits a linear correlation with the logarithm of the laser pulse energy.
2. The ablation threshold of the graphene material gradually decreases with increasing effective pulse number. When the effective pulse number is less than 80, the threshold reduction is very pronounced. Once the effective pulse number exceeds 80, the ablation threshold decreases at a relatively slower rate and eventually tends to stabilize.
3. Fitting analysis based on the cumulative model and its modified versions indicates that graphene exhibits a significant cumulative effect, with an incubation factor δ as low as 0.16. To investigate the threshold evolution behavior under multi-pulse irradiation, the applicability of three cumulative models was systematically evaluated in this study. Experimental data show that Model I demonstrates the best fitting performance for

predicting the single-pulse ablation threshold, while Model III exhibits the optimal overall fitting performance under multi-pulse conditions.

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