

Selective laser reduction of graphene oxide reveals the chemical origin of fatigue degradation

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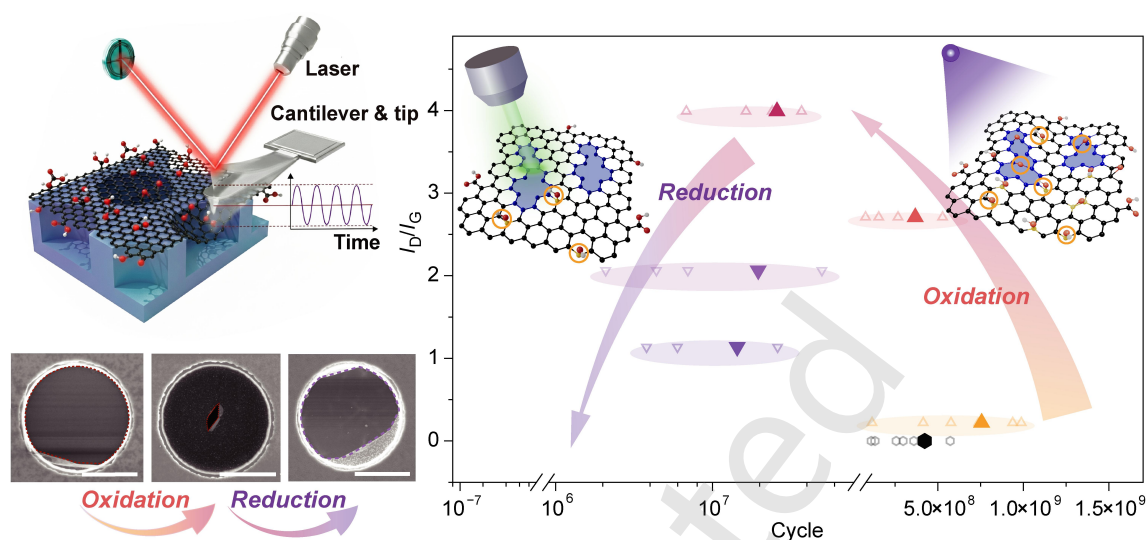
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ABSTRACT: Laser-induced reduction is widely used to modify graphene oxide, yet the chemical origin of fatigue degradation induced by such processing remains poorly understood. Here, we show that Raman laser irradiation acts not only as a characterization tool but also as a controllable reduction stimulus. Combined Raman and nano-infrared spectroscopy reveal that laser exposure preferentially removes sp^3 -type oxygen functional groups, particularly epoxide groups, while vacancy-type defects progressively accumulate. Atomic force microscopy-based fatigue experiments further demonstrate that laser-reduced graphene oxide exhibits inferior fatigue resistance compared to oxidized samples. This degradation arises from the combined effects of vacancy accumulation and the loss of epoxide-enabled crack-arresting mechanisms, driving a transition from localized damage to brittle fracture. These findings establish that fatigue reliability in graphene oxide is governed by chemical identity and defect evolution history, rather than defect density alone, highlighting the limitations of single-parameter Raman metrics for predicting mechanical performance in functionalized two-dimensional materials.

KEYWORDS: graphene oxide; laser reduction; Raman spectroscopy; functionalization; defect; fatigue failure

1 Introduction

Graphene oxide (GO) occupies a unique position among two-dimensional (2D) materials, as its properties can be continuously tuned through chemical functionalization. The incorporation of oxygen-containing functional groups not only modifies the electronic and chemical activity [1-3] of graphene, but also fundamentally alters its mechanical response by introducing sp^3 bonding, local compliance, and damage-tolerant deformation pathways [4-7]. Conventional functionalization strategies, such as UV/ozone treatment [8], plasma exposure [9], thermal annealing [10], and chemical reduction [11, 12], typically operate over large areas and provide only spatially averaged functionality. In recent years, laser-induced reduction has emerged as a promising route for spatially selective and programmable chemical engineering of GO [13-16]. By adjusting laser wavelength, power, and exposure time [17, 18], reduction can be confined to micrometer-scale regions, enabling patterned property modulation [19]. Raman spectroscopy is frequently employed in this context, both as a characterization technique and, often unintentionally, as a reduction stimulus [20-22]. While previous studies have documented changes in Raman signatures during laser exposure and attributed them to removal of oxygen-containing functional groups and partial restoration of the sp^2 carbon network, the evolution

of specific oxygen functionalities and their coupling to defect formation during laser reduction remain poorly resolved, particularly under localized or highly confined modification conditions.

This ambiguity has important consequences for mechanical reliability. Fatigue behavior in pristine graphene and vacancy-engineered 2D materials has been studied extensively, revealing brittle failure governed by defect-driven crack propagation [23-25]. In contrast, GO introduces an additional degree of freedom, as oxygen functional groups can act as extrinsic bonding centers that promote plastic deformation, crack arrest, and progressive damage accumulation [5]. Atomistic simulations have predicted that epoxide groups, in particular, may enhance damage tolerance under cyclic loading [7, 26]. However, direct experimental validation linking functional group chemistry, defect evolution, and fatigue behavior remains scarce, largely due to the lack of techniques capable of resolving chemical heterogeneity at the relevant length scales.

Here, we address these challenges by establishing Raman laser irradiation as a controllable, localized chemical stimulus for graphene oxide, directly resolving its chemical selectivity using nano-infrared spectroscopy (nano-IR), and elucidating how such chemically distinct states translate into fundamentally different fatigue behaviors under cyclic

loading. Defect evolution, spatial distribution, and selective removal of oxygen-containing functional groups during laser-induced reduction are directly correlated using Raman spectroscopy and nano-IR analysis. We demonstrate that laser treatment preferentially removes sp^3 -type epoxide groups, whereas vacancy-type defects persist and progressively accumulate. Building on this mechanistic understanding, we further investigate the fatigue behavior of chemically engineered GO using atomic force microscopy (AFM)-based cyclic loading experiments. Our results reveal that fatigue performance cannot be inferred from Raman defect metrics alone, since GO and laser-reduced GO with comparable I_D/I_G ratios exhibit fundamentally different fatigue lifetimes and failure modes. These findings establish a direct experimental link between functional group chemistry, defect evolution pathways, and mechanical reliability in graphene oxide, providing a framework for the rational design of durable, functionalized 2D materials.

2 Material and experiments

2.1 Preparation of graphene oxide samples

The bulk graphite crystals were purchased from ~~were purchased from~~ Shanghai OnWay Technology Co., Ltd. Monolayer graphene was mechanically exfoliated onto 285 nm-thick SiO_2 substrate using the micromechanical cleavage method [27]. Graphene oxide (GO) was produced by controlled oxidation of exfoliated graphene via ultraviolet/ozone (UV/O_3) treatment in a UV chamber (Jelight Company Inc.) with power of 230 W or oxygen plasma treatment (CIF) with maximum power of 300 W. By adjusting the treatment duration and power, GO samples with different degrees of functionalization were obtained. These samples were used for Raman characterization and nano-infrared (nano-IR) analysis. For mechanical testing, monolayer graphene was exfoliated onto SiO_2 substrates patterned with arrays of circular holes (diameter: 2 μm ; depth: 500 nm), fabricated by nanoimprint lithography followed by reactive ion etching [28]. Oxidation and laser reduction were subsequently performed on the suspended membranes prior to atomic force microscopy (AFM)-based static and fatigue measurements.

2.2 Raman characterization and laser treatment

Raman spectroscopy was performed using a Renishaw inVia confocal Raman microscope equipped with a 532 nm laser (maximum power: 50 mW). A 100 $\times$ objective lens was used, yielding a laser spot size of approximately 0.8 μm . All Raman measurements and treatments were conducted under ambient conditions at room temperature. Raman spectra were analyzed by fitting individual peaks with Lorentzian functions, including the D-band ($\sim 1330\text{ cm}^{-1}$), G-band ($\sim 1580\text{ cm}^{-1}$), D'-band ($\sim 1610\text{ cm}^{-1}$), and G'-band ($\sim 2663\text{ cm}^{-1}$) [29]. Peak intensity ratios (I_D/I_G and $I_D/I_{D'}$) were extracted to quantify defect evolution during oxidation and laser reduction.

2.3 Nano-infrared spectroscopy characterization

Nano-infrared (nano-IR) measurements were carried out using a photothermal infrared AFM system (nanoIR3, Bruker Inc.) operating in photothermal-induced resonance (PTIR)

mode [30]. In this technique, pulsed infrared radiation is absorbed by the sample, inducing localized photothermal expansion that excites resonant oscillations of the AFM cantilever. Then, nano-IR spectra are obtained by applying a Fourier transform to extract the cantilever oscillation amplitude and correlating it with the wavelength of the incident radiation. By illuminating at a fixed wavelength while raster-scanning the AFM cantilever across the sample surface, absorption maps were acquired, enabling nanoscale chemical mapping of oxygen-containing functional groups. GO samples for nano-IR analysis were mechanically exfoliated onto SiO_2 substrates and subsequently subjected to oxidation and laser reduction without additional transfer steps, in order to minimize surface contamination.

2.4 AFM-based fatigue testing methodology

AFM-based static and fatigue tests were performed using a Cypher ES atomic force microscope (Asylum Research) equipped with diamond-coated probes (Adama Cone) (nominal spring constant $\approx 5\text{ nN/nm}$, tip radius $\approx 20\text{ nm}$). Suspended GO membranes were indented at the center of the circular holes to evaluate their mechanical response. Prior to the fatigue tests, the fracture force (F_{Frac}) of the samples was first measured in different functionalization degrees as a baseline. Then fatigue tests were performed on the intact, untested membranes with the same functionalization degree. A constant static force was applied, followed by cyclic dynamic loading generated through tip oscillation. Fatigue failure was identified by a sudden change in the cantilever oscillation amplitude or static deflection signal, indicating loss of load-bearing capability.

3 Results and discussions

3.1 Raman signatures of oxidation and laser-induced reduction in graphene oxide

Five monolayer graphene samples were first oxidized using UV/ozone treatment and characterized by Raman spectroscopy (laser wavelength: 532 nm, maximum power I_0 : 50 mW) with integration time of 4 s and power of 0.1 I_0 . As shown in **Fig. 1a**, prolonged oxidation time leads to the emergence and growth of the D and D'-bands, accompanied by a weakening and broadening of the G'-band [31, 32]. Unexpectedly, when Raman spectra were repeatedly acquired at the same location on a highly oxidized GO sample under otherwise identical characterization conditions, the G'-band intensity increased while the D-band intensity decreased, exhibiting a trend opposite to that associated with oxidation (**Fig. 1b**). Quantitative analysis of the intensity ratios reveals that I_D/I_G initially increases to a maximum value (where $I_D/I_{D'} \approx 7$) and then decreases, while $I_D/I_{D'}$ increases monotonically with laser exposure (**Fig. 1c**). Such Raman characteristics are reminiscent of defect annihilation rather than defect generation [8, 33].

Laser-induced reduction process was further examined with Raman mapping analysis. With precisely controlled laser power and irradiation time, **Fig. 1e** shows that increasing treatments lead to continuous intensity loss of D-band. Moreover, Raman mapping was performed before and after localized laser exposure. As shown in **Figs. 1d and 1f**,

the D-band intensity is spatially uniform across the oxidized GO surface prior to laser treatment, whereas after repeated laser irradiation on the selected area (white rectangle), a distinct reduction region with suppressed D-band intensity emerges. Further experiments demonstrate that the reduction effect originates mainly from laser-sample interaction, rather than preparation artifacts or sample aging (Electronic Supplementary Material (ESM) Section S1). Detailed Raman parameters are presented in ESM Section S2.

These observations demonstrate that Raman laser irradiation can induce a localized reduction of graphene oxide during measurement. Importantly, because Raman scattering probes the material state after laser exposure, the recorded spectra accurately reflect the chemically modified state of GO rather than a transient intermediate. By carefully controlling laser power and exposure time, the reduction

induced by a single characterization scan can be effectively minimized, thereby preserving the reliability of Raman spectroscopy as a diagnostic tool. At the same time, this phenomenon establishes Raman laser irradiation as a controllable and spatially precise stimulus for chemical functional engineering of graphene oxide. Therefore, GO samples with micron-scale, region-specific patterns featuring tunable degrees of functionalization can be achieved (**Fig. 1g**). Such spatial control is particularly relevant for 2D materials, where local defect populations and functional group chemistry can dominate mechanical response and failure pathways [34], providing a critical experimental platform for probing structure-property relationships under spatial confinement, especially for disentangling the respective roles of functional groups and lattice defects, as explored in the following sections.

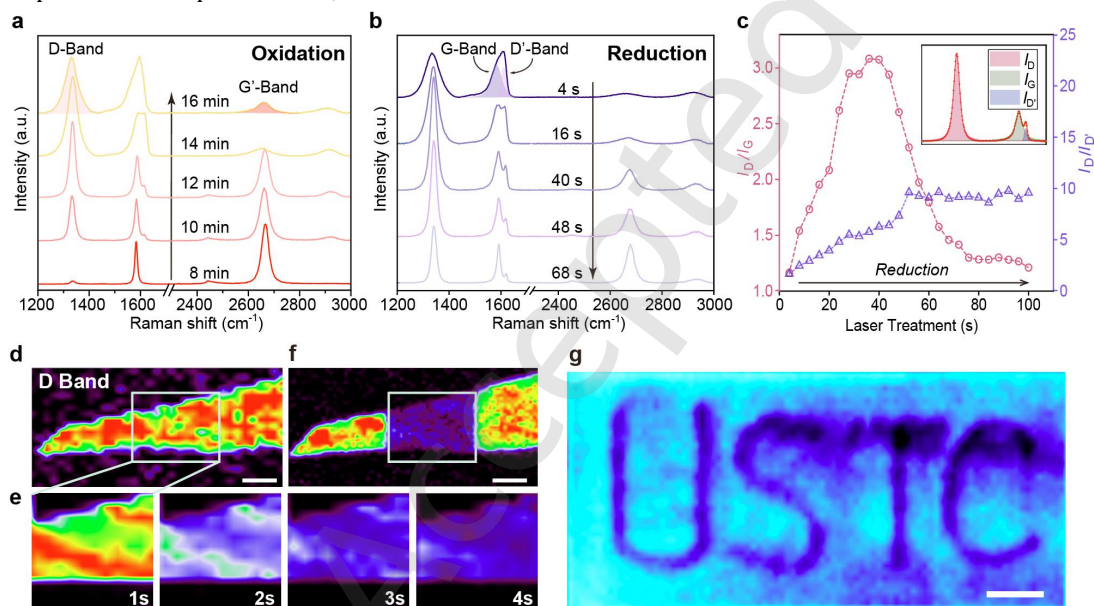


Figure 1 (a) Raman spectra of GO with increasing UV/ozone oxidation time. (b) Raman spectra of reduced graphene oxide (rGO) obtained after accumulated Raman laser exposure. (c) Evolution of the I_D/I_G (red) and $I_D/I_{D'}$ intensity ratios (blue) during laser-induced reduction. The inset illustrates the origin of the Raman bands used in the analysis. (d) Raman mapping of the D-band intensity of an oxidized GO sample prior to laser treatment. (e) Evolution of the D-band intensity within the laser-treated region in (d) with increasing exposure dose. (f) Raman mapping of the D-band intensity over the entire GO sample after localized laser treatment. (g) Raman contour maps of D-band intensity illustrating spatially controlled chemical modification of GO enabled by Raman laser irradiation. Scale bars in (d), (f) and (g): 5 μm

3.2 Non-reciprocal defect evolution during oxidation–reduction cycling

To further elucidate the nature of the laser-induced reduction process observed in Raman characterization, we systematically analyzed the evolution of Raman defect metrics during controlled oxidation and subsequent laser reduction. Because the frequencies and intensities of the D-, G-, and D'-bands are closely related to defect type and density in graphene-based materials, the intensity ratios I_D/I_G and $I_D/I_{D'}$ are widely used to characterize functionalization and disorder in graphene oxide [31, 33, 35, 36]. **Figure 2a** summarizes the evolution of intensity ratios I_D/I_G and $I_D/I_{D'}$ during a single oxidation–reduction cycle. Each UV/ozone treatment was characterized via Raman spectroscopy with precisely controlled laser power to minimize the effect of laser reduction. The non-monotonic trend of I_D/I_G is consistent with the well-known two-stage defect evolution in graphene (See ESM Section S2.3).

Specifically, at relatively low defect density, the introduction or redistribution of sp^3 -type functional groups increases the number of Raman-active scattering centers, leading to an increase in I_D/I_G . With further oxidation, continued lattice disruption decreases the average sp^2 domain size below a critical length scale, decreasing the D-band activation efficiency and resulting in a reduction of I_D/I_G [37, 38]. This transition reflects a shift from functionalization-dominated disorder toward increasing vacancy-type contributions at higher defect densities. In parallel, $I_D/I_{D'}$ decreases progressively during oxidation, further indicating the evolution of defect structure. Importantly, the initial $I_D/I_{D'}$ values are exceptionally large because the pristine graphene contains very few defects and the D'-band is near the detection limit (See ESM Section S2.3). As oxidation proceeds, D'-band grows and $I_D/I_{D'}$ correspondingly drops, eventually approaching values characteristic of more vacancy-like disorder in the high-defect regime [39]. It should also be noted that $I_D/I_{D'}$ is used here as a qualitative indicator of defect evolution rather than a strict quantitative

metric for assigning a unique defect type, as multiple defect species (e.g., sp^3 functionalization and vacancy defects) may coexist in graphene oxide.

Upon Raman-laser exposure (reduction stage), Raman spectra were collected multiple times with laser beam acting as the reduction source to reduce the GO sample. The defect metrics do not retrace the oxidation path: I_D/I_G shows a slight increase and then decreases monotonically, finally approaching a plateau at higher laser doses. Meanwhile, $I_D/I_{D'}$ initially increases and then approaches a plateau during laser treatment. This trend indicates that defect type of the GO sample has turned from vacancy-dominated to sp^3 -dominated [40]. Notably, although laser irradiation removes part of the oxygen functionalization, it does not restore the structure to its initial pristine state. The incomplete recovery evidence highlights the intrinsic asymmetry between oxidation-induced defect generation and laser-induced reduction, indicating that certain defect components are not readily reversible under the present conditions.

The irreversibility of this evolution is further illustrated in **Fig. 2b**, which compares the reduction behavior of GO samples with different initial defect states. GO with 12 min UV/ozone oxidation exhibits a pronounced decrease in I_D/I_G upon laser treatment, approaching values characteristic of pristine graphene. The initial $I_D/I_{D'}$ value (~ 7.42) indicates a defect state with substantial lattice disorder, arising from the coexistence of multiple defect species. In this regime, laser irradiation leads to a significant reduction in I_D/I_G , indicating that a considerable fraction of defect sites associated with sp^3 functionalization can be effectively removed. In contrast, GO subjected to 16 min UV/ozone oxidation ($I_D/I_{D'} \sim 3.15$) shows a substantial irreducible component, since I_D/I_G remains elevated despite extensive laser exposure. This behavior suggests the presence of more stable and less reversible lattice defects that are not readily removed under laser irradiation. As a control, monolayer graphene treated with nitrogen plasma (CIF, model CPC-G) with 1 W plasma power and 1 sccm gas flow for 2 s—known to predominantly introduce vacancy defects [41]—shows

negligible change in I_D/I_G during laser exposure, confirming that laser-induced reduction selectively removes oxygen-related sp^3 defects rather than vacancy-type lattice damage.

Additional oxidation–reduction cycling experiments (See ESM Section S3) further reveal that the irreducible portion of I_D/I_G increases progressively with repeated treatments, accompanied by a diminishing reduction efficiency. This behavior demonstrates that, while sp^3 -type defects can be removed by laser irradiation, vacancy-type defects accumulate irreversibly and increasingly dominate the defect landscape at higher functionalization levels, as schematically illustrated in **Fig. 2c**. Therefore, Raman spectroscopy captures the coexistence and competition between reversible chemical functionalization and irreversible lattice damage during the modification of graphene oxide. Detailed parameters in the Raman experiments above are presented in ESM Section S2.

Although Raman analysis provides valuable insights into defect evolution, it does not allow direct discrimination between oxygen functional groups and lattice vacancies, with I_D/I_G and $I_D/I_{D'}$ serving only as semiquantitative descriptors of mixed defect populations [42]. Previous studies have investigated laser-induced reduction of graphene oxide using techniques such as Fourier transform infrared spectroscopy (FTIR) [17], X-ray photoelectron spectroscopy (XPS) [43], and Electron energy loss spectroscopy (EELS) [44–46], demonstrating that laser-induced reduction of graphene oxide generally involves coupled photothermal and photochemical processes, resulting in both oxygen-functional-group removal and structural reconstruction of the carbon network [43, 47] (see ESM Section S4). However, these methods either probe spatially averaged chemical information or suffer from sample preparation-induced contaminations [48–50], hindering their ability to resolve localized chemical heterogeneity introduced by focused laser irradiation. Consequently, direct experimental characterization of the spatial distribution and selective evolution of individual functional groups is indispensable.

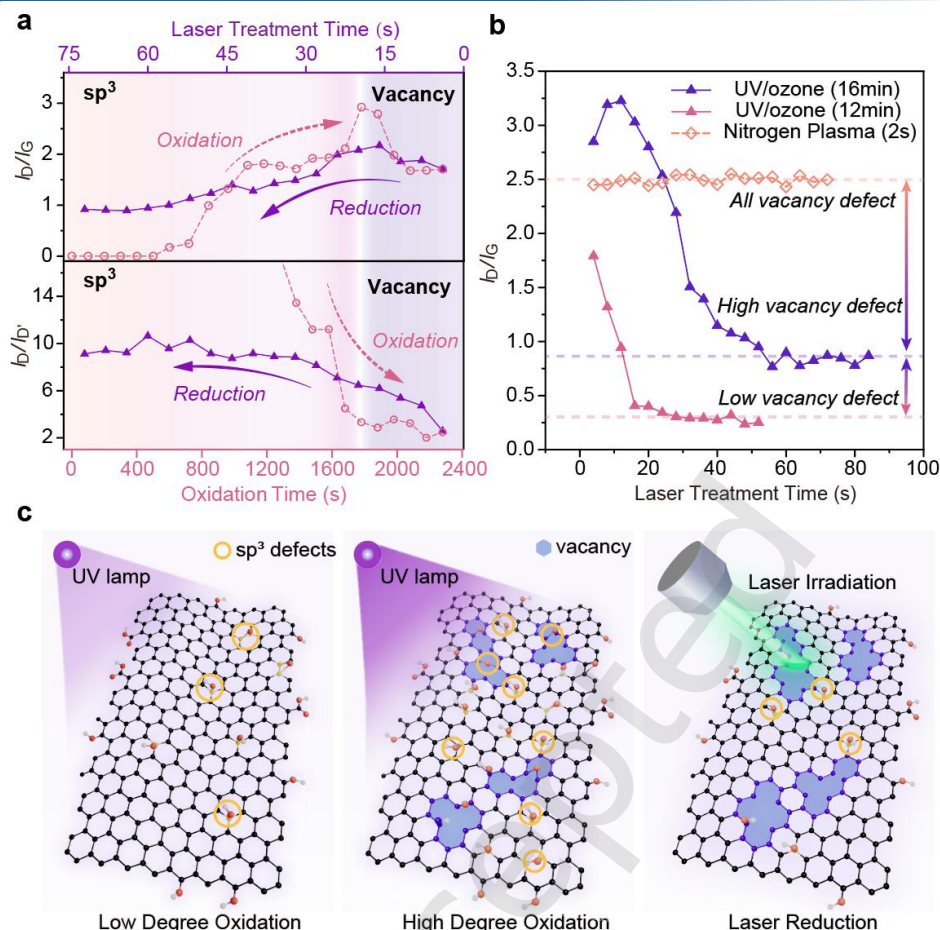


Figure 2 (a) Evolution of the Raman intensity ratios I_D/I_G and $I_D/I_{D'}$ during a single oxidation and subsequent laser reduction process. (b) Comparison of laser reduction behavior for GO samples with long UV/ozone oxidation time (16 min), short oxidation time (12 min), and nitrogen plasma treatment (2s). (c) Schematic illustration of the evolution of oxygen functional groups and vacancy defects during oxidation and laser-induced reduction.

3.3 Selective removal of epoxide groups probed by nano-IR spectroscopy

To directly resolve the chemical origin of the reversible and irreversible components inferred from Raman analysis, we employed nano-infrared (nano-IR) spectroscopy to directly probe the chemical identity, spatial distribution, and evolution of oxygen-containing functional groups in graphene oxide during laser reduction. Unlike Raman spectroscopy, which provides an indirect, defect-based description of disorder, nano-IR offers chemically specific vibrational fingerprints with nanoscale spatial resolution, enabling direct identification of individual functional groups under localized modification conditions [30]. This capability is particularly critical in the present context, where focused laser irradiation is expected to introduce pronounced chemical heterogeneity that cannot be reliably captured by spatially averaged spectroscopic techniques.

Figure 3a shows the AFM topography of a monolayer GO sample, in which a square region was subjected to localized laser treatment. No apparent topographical damage is observed, indicating that laser exposure primarily induces chemical rather than morphological modification. Representative nano-IR spectra acquired inside and outside the laser-treated region are shown in **Fig. 3b**. Three characteristic absorption peaks are observed at

approximately 1080 cm^{-1} , 1440 cm^{-1} and 1730 cm^{-1} , corresponding to C-O bands (epoxide and hydroxyl) [51, 52], O-H bending (hydroxyl) [53] and C=O stretching (carboxyl or carbonyl) vibrations, respectively [54]. For comparison, a control nano-IR spectrum of pristine monolayer graphene under identical measurement conditions shows no detectable oxygen-related vibrational bands (**Fig. S9** in the ESM), confirming that the nano-IR signals originate from oxygen-containing functional groups rather than instrumental background or substrate contributions. Spatially resolved nano-IR absorption maps at these characteristic frequencies reveal a striking chemical selectivity. As shown in **Fig. 3c**, the absorption intensity at 1080 cm^{-1} is significantly reduced within the laser-treated region, closely matching the spatial footprint of Raman laser exposure. In contrast, the absorption maps at 1440 cm^{-1} and 1730 cm^{-1} (**Figs. 3d** and **3e**) show no pronounced contrast between treated and untreated areas, aside from minor edge effects attributable to intrinsic functional group distribution [51].

While the 1080 cm^{-1} band contains contributions from both epoxide- and hydroxyl-related C-O vibrations, the hydroxyl-related nano-IR response at 1440 cm^{-1} exhibits little variation between the GO and laser-treated regions, suggesting that hydroxyl groups are largely preserved after laser treatment. In contrast, a pronounced and spatially localized suppression is observed at 1080 cm^{-1} within the

laser-treated area. Combined with the complementary XPS results (see ESM Section S5), these observations suggest that the dominant chemical change induced by laser reduction is the removal of epoxide-related C–O–C functionalities. These results provide direct experimental evidence that laser-induced reduction selectively removes epoxide groups from the GO surface, while hydroxyl and carboxyl groups remain largely unaffected within the sensitivity limits of the measurement. This finding further advances our understanding of the chemical pathways involved in laser-induced reduction [16].

Apart from the photochemical effect, it should be noted that local heating during the laser treatments is also anticipated to contribute to the reduction process. A rough estimate based on the laser power and spot size used in this work suggests a local temperature rise on the order of several tens to a few hundred Kelvin, which is sufficient to induce the photothermal effect under laser reduction [43] (see ESM Section S4). However, a purely thermal process would be expected to induce concurrent attenuation across multiple oxygen-related vibrational modes [55]. Instead, the nano-IR maps reveal a pronounced and spatially localized suppression of the C–O stretching mode, while the hydroxyl-

and carboxyl-related modes remain largely unchanged. This selective response indicates that laser-induced reduction proceeds through functionality-dependent pathways, consistent with complementary XPS measurements (see ESM Section S5).

Taken together, the combined Raman and nano-IR results delineate a coherent picture of functionalization and defect evolution in graphene oxide. Oxidation initially increases the population of oxygen-containing functional groups, whereas continued oxidation promotes the formation of lattice defects such as vacancies that eventually dominate the defect landscape. In contrast, laser-induced reduction does not act symmetrically on these two components, wherein epoxide groups are preferentially removed, while vacancy-type defects are not healed. Consequently, graphene oxide reduced by laser irradiation represents a chemically and structurally distinct state from graphene oxide oxidized to a comparable I_D/I_G ratio, underscoring the non-equivalence between functional group removal and defect healing and providing a mechanistic basis for interpreting the mechanical behavior examined in the following section.

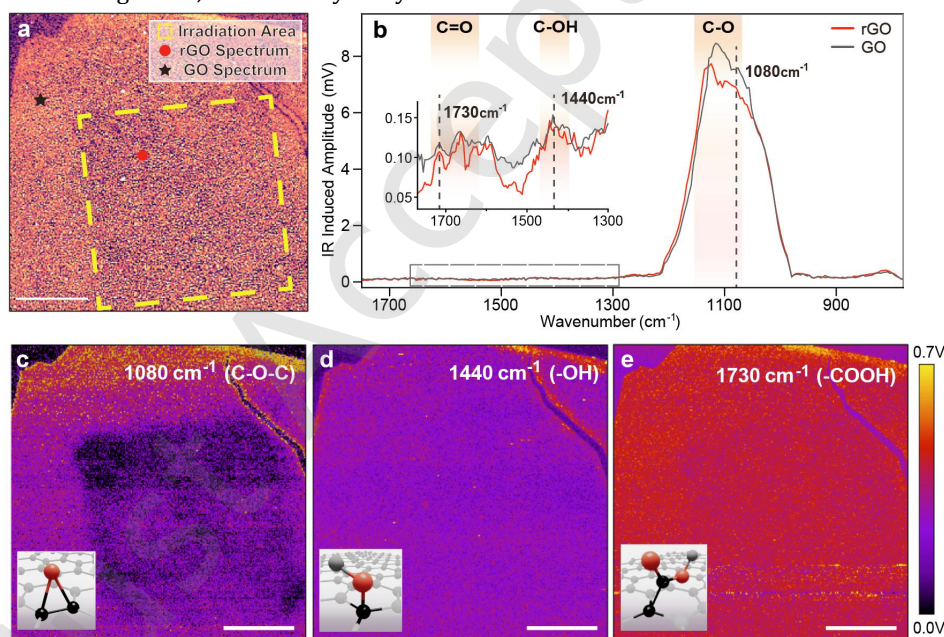


Figure 3 (a) AFM topography of a GO sheet, with the yellow dashed box indicating the region subjected to localized laser treatment. (b) Representative nano-IR spectra acquired from the laser-treated region (red) and the untreated region (black) marked in (a), measured over the wavenumber range of 780–1780 cm^{-1} . The inset shows a magnified comparison of the spectra in the 1300–1780 cm^{-1} region. (c–e) Nano-IR absorption maps acquired from the same area as in (a) at wavenumbers of (c) 1080 cm^{-1} , (d) 1440 cm^{-1} , and (e) 1730 cm^{-1} , corresponding to characteristic vibrations of oxygen-containing functional groups. Scale bars in (a) and (c–e): 2 μm .

3.4 Fatigue behavior governed by chemical selectivity

Motivated by the chemical and structural non-equivalence revealed above, we next examine how these distinct modification pathways manifest in the mechanical reliability of graphene oxide under cyclic loading. Static mechanical properties primarily reflect the instantaneous response of the weakest load-bearing pathway and are therefore insufficient to distinguish these chemically distinct states. In contrast, fatigue behavior probes the evolution and stability of damage under repeated loading and is inherently sensitive to defect type, chemical identity, and dissipation

mechanisms. Although the nano-IR measurements were performed on substrate-supported GO, the suspended fatigue samples were subjected to the same laser irradiation protocol used for the nano-IR characterization. While supported and suspended membranes may exhibit different thermal dissipation conditions, potentially leading to quantitative differences in the extent of reduction, the laser-induced preferential removal of epoxide-related functionalities is expected to reflect the general chemical evolution occurring in the laser-treated fatigue samples as well.

AFM-based cyclic loading experiments (**Fig. 4a**) were

used to compare the fatigue lifetime and failure modes of oxidized and laser-reduced GO membranes (see ESM Section S6). Fatigue tests were performed on the intact, untested monolayer membranes suspended on 2 μm -diameter circular holes (**Fig. 4b**). All samples were subjected to a constant static force ($F_{\text{dc}} = 50\%F_{\text{frac}}$), followed by cyclic dynamic loading at a frequency of 100 kHz and amplitude of 5 nm. AFM nanoindentation analysis revealed no systematic variation in membrane pre-stress after chemical treatments, suggesting that the observed fatigue behavior is not primarily governed by changes in residual tension especially in such a large-deflection regime (see ESM Section S6) [56, 57]. Compared with pristine graphene, GO membranes exhibit pronounced amplitude fluctuations during cyclic loading (**Fig. S7** in ESM) [23], suggesting progressive damage accumulation. **Figure 4c** summarizes the fatigue lifetimes of pristine graphene, oxidized GO with different functionalization degrees, and laser-reduced GO samples, plotted as a function of the Raman defect metric I_D/I_G . All experimental data are plotted as hollow triangles, while the mean fatigue lifetimes are plotted as solid triangles. Despite the expected sample-to-sample variability, the overall trend in fatigue lifetime remains consistent across independent measurements. Detailed fatigue data for each specific test condition are presented and analyzed in ESM Section S6. Pristine graphene ($I_D/I_G \approx 0$) exhibits the longest fatigue lifetime, exceeding $\sim 10^9$ cycles. Upon oxidation, the fatigue lifetime of GO decreases markedly with increasing functionalization. Specifically, lightly oxidized GO with $I_D/I_G \approx 0.22$ fails after $\sim 7.5 \times 10^8$ cycles, whereas heavily oxidized GO with $I_D/I_G \approx 4.0$ exhibits a dramatically reduced fatigue lifetime of $\sim 2.6 \times 10^7$ cycles, corresponding to a reduction of more than one order of magnitude. In addition, oxidized GO displays significantly increased data dispersion compared with pristine graphene, reflecting the heterogeneous distribution of oxygen-containing functional groups and associated local defects. Laser-reduced GO exhibits markedly different fatigue behavior despite reduced Raman defect metrics. rGO samples obtained from highly oxidized GO ($I_D/I_G \approx 4$) show I_D/I_G ratios of approximately 2.1 and 1.1 after laser treatment. Nevertheless, their fatigue lifetimes remain consistently lower than those of oxidized GO samples with comparable I_D/I_G achieved through oxidation alone. Even when reduced GO reaches a low I_D/I_G level close to that of lightly oxidized GO, its fatigue lifetime remains nearly an order of magnitude lower, demonstrating that I_D/I_G ratio alone is insufficient to evaluate the fatigue reliability.

The differences in fatigue lifetime are accompanied by pronounced changes in failure morphology, as revealed by the SEM images shown in the insets of **Fig. 4c**. Specifically, pristine graphene and lightly oxidized GO fail catastrophically under cyclic loading, exhibiting global membrane rupture without clear evidence of progressive

damage. In contrast, moderately and highly oxidized GO exhibit localized fatigue failure, where only the region beneath the AFM tip is punctured while large portions of the membrane remain intact. This localized failure mode becomes more pronounced with increasing oxidation level, indicating progressive damage accumulation and crack arrest. This transition is aligned with the role of oxygen functionalization in enabling plasticity/toughening mechanisms in GO, where epoxide groups in particular have been suggested to promote crack-arresting and damage-tolerant deformation, as predicted by molecular dynamics (MD) simulations [5, 7]. By comparison, laser-reduced GO exhibits larger failure regions and more extensive crack propagation, resembling the brittle, global failure mode of pristine graphene. Given that nano-IR identifies epoxide removal as a primary outcome of laser reduction, the loss of epoxy-assisted toughening provides a mechanistically consistent explanation for the brittle failure of reduced GO, in line with previous simulation-based predictions [7, 26]. Although laser reduction simultaneously alters several material characteristics, including oxygen content, functional-group distribution, and defect structure, the selective removal of epoxide functionalities represents the most distinctive chemical change observed in the present study and correlates closely with the transition from localized to brittle fatigue failure.

The discrepancy between Raman defect metrics (I_D/I_G) and fatigue performance highlights a fundamental distinction between static structural descriptors and dynamic damage-evolution probes. While Raman spectroscopy captures an averaged projection of coexisting defect populations, nano-IR analysis reveals that laser reduction selectively removes epoxide groups without healing vacancy defects, leading to chemically distinct states that collapse onto similar Raman signatures. Fatigue testing, which interrogates the stability and evolution of load-bearing pathways under repeated stress, is inherently sensitive to defect type, chemical identity, and evolution history. As a result, vacancy defects primarily govern fatigue lifetime by serving as crack initiation sites, whereas epoxide functionalization controls failure mode by enabling crack arrest and damage-tolerant deformation. While the present experiments do not independently isolate every variable altered during oxidation and reduction, the combined Raman, nano-IR, XPS, fatigue, and failure-morphology results consistently support a dominant role of functional-group chemistry in governing fatigue behavior. These findings demonstrate that chemical identity and evolution pathway, rather than defect density alone, govern the mechanical reliability of graphene oxide, underscoring the necessity of combining chemical-specific characterization with fatigue-based reliability assessment in functionalized 2D materials.

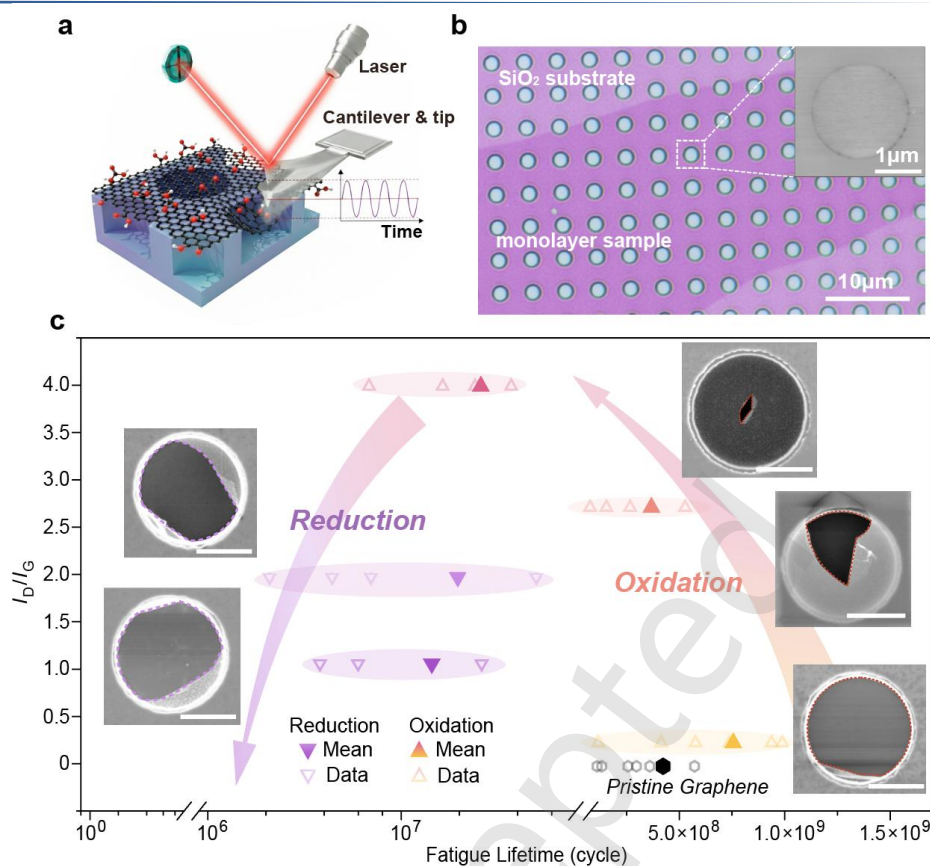


Figure 4 (a) Schematic of the AFM fatigue testing setup on graphene and GO samples. (b) Optical microscopy image of a monolayer sample, with an inset showing the AFM morphology, used for static and dynamic fatigue tests. (c) Fatigue lifetime of GO as a function of the I_D/I_G ratio for oxidized and laser-reduced samples. As indicated by the hollow triangles, 14 oxidized GO samples were measured (6 at $I_D/I_G = 0.22$, 4 at $I_D/I_G = 2.7$, and 4 at $I_D/I_G = 4.0$). After laser reduction, 7 samples were measured (4 at $I_D/I_G = 2.1$, and 3 at $I_D/I_G = 1.1$). Solid triangles represent the corresponding mean fatigue lifetimes. Despite comparable Raman defect metrics, oxidized and reduced GO exhibit markedly different fatigue lifetimes and failure morphologies, as shown by the representative SEM insets.

4 Conclusions

In summary, this work demonstrates that Raman laser irradiation serves not only as a characterization tool but also as a controllable and spatially precise stimulus for reducing graphene oxide. By integrating Raman spectroscopy, spatially resolved Raman mapping, and nano-infrared analysis, we show that laser reduction proceeds through a chemically selective pathway, preferentially removing sp^3 -type oxygen functional groups (particularly epoxide groups) while vacancy-type lattice defects remain largely intact and progressively accumulate. AFM-based fatigue experiments further reveal that, although both oxidation and laser reduction decrease the fatigue lifetime of graphene oxide, laser-reduced graphene oxide exhibits markedly inferior fatigue resistance compared to oxidized graphene oxide with comparable Raman defect metrics. This degradation arises from the combined effects of increased vacancy defect density and the loss of epoxide-enabled crack-arresting and damage-tolerant mechanisms. These results establish that the mechanical reliability of functionalized graphene oxide is governed by chemical identity and defect evolution history rather than defect density alone, thereby providing a unified framework linking laser-induced chemical modification, defect engineering, and fatigue reliability in 2D materials. Importantly, they also suggest that in laser-patterned graphene oxide devices, such as flexible electronics or

micro-electromechanical systems (MEMS), durability requires deliberate control of defect type in addition to defect density [58]. Strategies that mitigate vacancy accumulation or preserve mechanically beneficial functional groups may be essential for achieving long-term reliability under cyclic mechanical loading.

Electronic Supplementary Material: Supplementary material (control experiments, Raman parameters, XPS, fatigue testing details) is available in the online version of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Zhehan Xue: Conceptualization, Methodology, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing. **Yafei Wang:** Methodology, Validation, Formal analysis, Investigation, Writing – Review & Editing. **Guorui Wang:** Conceptualization, Writing – Review & Editing, Supervision, Project administration, Funding acquisition.

Use of AI statement

None.

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Selective laser reduction of graphene oxide reveals the chemical origin of fatigue degradation

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This file includes:

Section S1. Validation of sample quality and control experiments

Section S2. Raman analysis of defect evolution and reliability of I_D/I_G and I_D/I_D'

Section S3. Laser-induced oxidation–reduction cycling behavior

Section S4. Estimated calculation of the local temperature rise under laser irradiation

Section S5. XPS characterization for chemical evolution of oxygen functional groups

Section S6. Fatigue testing data interpretation

Section S1. Validation of sample quality and control experiments

Prior to UV/ozone oxidation, Raman mappings of D-band and G-band were captured, showing that the graphene sample was defect-free and defects and functional groups were introduced only by UV/ozone treatment (**Fig. S1**). In addition, controlled experiment using oxygen plasma oxidized GO was conducted. Treatment times were 10 s (low degree), 15 s (middle degree) and 26 s (high degree), with power of 1 W and gas flow of 50 sccm. Then, three graphene oxide samples were laser reduced with 4 s exposure time and 5 mW power ($0.1I_0$). GO samples with different degrees of functionalization also show the reduction tendency under Raman laser treatment, confirming that the observed reduction behavior is independent of the oxidation method (**Fig. S2**). To exclude the influence of spontaneous reduction at room temperature [1], a series of control experiments were conducted. First, the GO samples were not subjected to laser treatment and characterization until after 20 hours of settling at room temperature. This step aims to confirm their reducibility even after extended rest. As shown in **Fig. S3a**, settling GO sample remained the same reduction phenomenon. Moreover, reduction area in **Fig. 1f** was characterized again after 160 h and the reduction area was still distinguishable (**Fig. S3b**). Both experiments show that settling reduction has less effect than laser reduction during and after the reduction process. The intensity contrast on the GO sample during the mapping characterization, erasing the effect of temporal evolution, directly proves the Raman laser reduction effect.

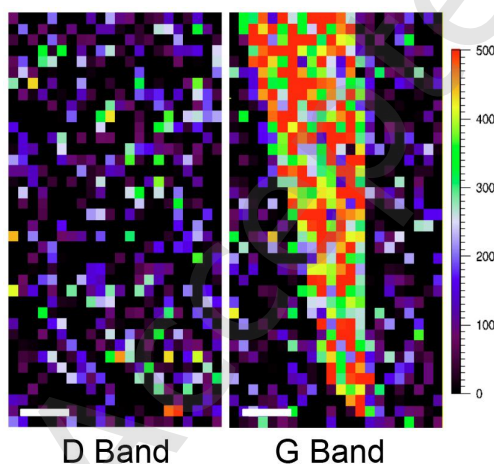


Figure S1 Raman mapping of the pristine graphene before oxidation, shows no defect with negligible D-band signal in the sample area. Scale bars: 5 μm.

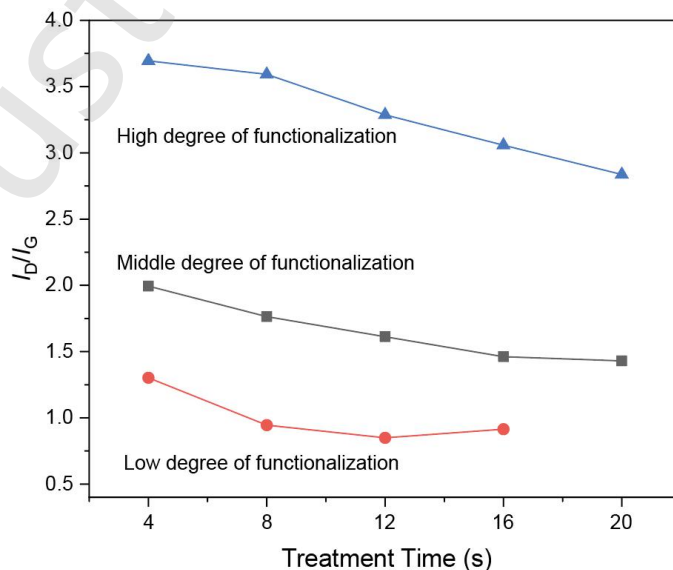


Figure S2 Oxygen plasma treatment of GO shows the reduction in I_D/I_G ratio under Raman laser treatment.

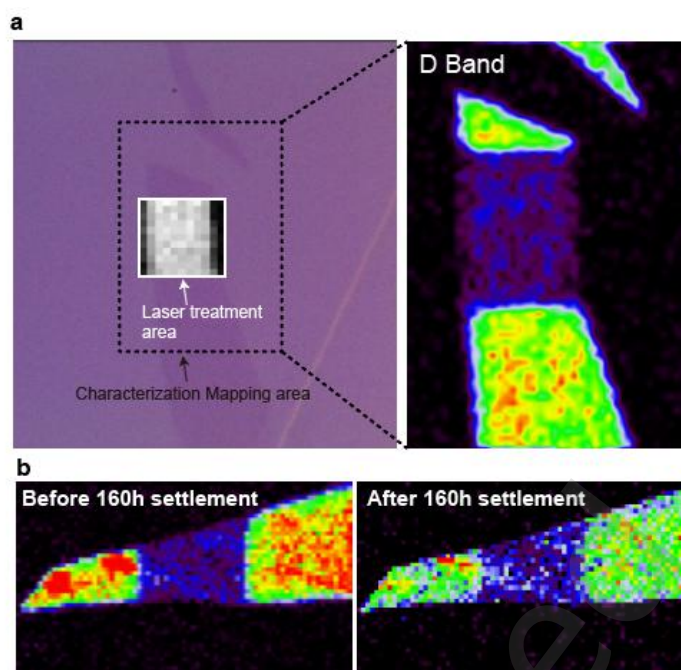


Figure S3 (a) Laser reduced process and Raman mapping of GO samples after 20 hours of settling in ambient condition. (b) Raman mapping of the reduced GO samples before and after 160 hours of settlement.

Section S2. Raman analysis of defect evolution and reliability of I_D/I_G and $I_D/I_{D'}$

S2.1. Raman measurement parameters during mapping characterization and treatment

After oxidation, within the range of $22 \times 40 \mu\text{m}$ on the GO sample and mapping acquisition interval of $1 \mu\text{m}$, spectra at different positions on the sample were acquired (**Fig. 1d**). In order to minimize the laser effect caused by the short distance intervals of the laser interaction during mapping characterization, the laser exposure time was limited to 0.1 s and power was $0.1I_0$, with maximum power I_0 of 50 mW. Then, a rectangular area of $12 \mu\text{m} \times 12 \mu\text{m}$ within the characterization area was selected to be laser reduced (**Fig. 1e**) with much larger exposure time (1 s) and power ($0.5I_0$). After multiple laser treatments of the selected area, Raman mapping of the D-band was acquired again (**Fig. 1f**), in which, to illustrate more clearly the comparison of different sample area, mapping parameters were set with a smaller acquisition interval of $0.5 \mu\text{m}$ and a higher power of $0.5I_0$ than the initial D-band mapping of **Fig. 1d**.

S2.2. Raman measurement parameters during oxidation–reduction cycling

Mechanism of the laser reduction is first studied based on Raman data. Because peak frequencies, intensities, linewidths and areas of the Raman bands of graphene are deeply related to the defect density [2], intensity ratios of D-G bands (I_D/I_G) and D-D' peaks ($I_D/I_{D'}$) are widely used to quantify the functionalization degrees of graphene [3-5].

During oxidation, after exposure to UV/ozone treatment, each treatment was characterized via Raman spectroscopy with 4 s laser exposure time and $0.1I_0$ power to minimize the effect of laser reduction. During reduction, Raman spectra were collected multiple times with 4 s laser exposure time and $0.1I_0$. Each characterization was conducted at intervals of 5 min to avoid the thermal effects accumulated with laser processing.

It should be noted that Raman characterization parameters mainly affect the absolute intensity and the signal-to-noise ratio of the spectra rather than the relative intensity of different vibration modes. Therefore, different parameters in different experiments were used only to achieve particular experimental purposes without severely affecting the accuracy of the Raman characterization. Specifically, longer exposure time and higher power were used as laser reduction stimulus (e.g., **Fig. 1e**), and relatively shorter exposure time and lower power were used to balance the laser effect and good spectral signals during Raman characterization (e.g., **Figs. 1a-1d** and **Fig. 2a**).

S2.3. Raman I_D/I_G and $I_D/I_{D'}$ evolution with respect to defect density and defect type

As the oxidation continues, I_D/I_G exhibits a non-monotonic trend, which rises continuously at early oxidation stages until $I_D/I_{D'}$ approaches ~ 7 and subsequently decreases at longer oxidation time. It has been reported that the I_D/I_G turning point at $I_D/I_{D'} \approx 7$ marks the transition between sp^3 -type defects and vacancy-type defects [6]. At early oxidation stage, D-band first strengthens as new scattering centers are introduced which are mainly attributed to the oxygen functional group bonded to the graphene surface. At high oxidation stage, vacancy-type defects dominate, where the oxygen functional groups progressively distort and disrupt the graphene lattice, leading to the formation and growth of vacancy defects [7, 8].

Section S3. Laser-induced oxidation–reduction cycling behavior

In a subsequent experiment, we re-oxidized the previously reduced sample and subjected it to multiple cycles of laser reduction and oxidation. Meanwhile, the sample was characterized using Raman spectroscopy under the same ultra-low laser power conditions as in the earlier experiments, and the results were plotted in **Fig. S4**. At different oxidation levels, the irreducible portion of the I_D/I_G ratio is different. Based on the data extracted from **Fig. 2b** and **Fig. S4**, we quantified both the initial and plateau I_D/I_G values and defined the ratio $(I_D/I_G)_{\text{plateau}}/(I_D/I_G)_{\text{initial}}$. The results show that the plateau I_D/I_G value, representing the irreducible component, progressively increases with repeated cycling treatments. Correspondingly, the relative decrease in I_D/I_G , during laser reduction, quantified by $[(I_D/I_G)_{\text{plateau}}]/[(I_D/I_G)_{\text{initial}}]$, becomes progressively weaker.

Table S1. Irreducible portion of I_D/I_G at different oxidation levels in Fig. 2b

	$(I_D/I_G)_{\text{initial}}$	$(I_D/I_G)_{\text{plateau}}$	$[(I_D/I_G)_{\text{plateau}}]/[(I_D/I_G)_{\text{initial}}]$
UV/ozone (12 min)	1.79	0.25	0.14
UV/ozone (16 min)	2.85	0.87	0.31
Nitrogen Plasma (2 s)	2.45	2.47	1.01

Table S2. Irreducible portion of I_D/I_G at different oxidation levels in Fig. S4

	$(I_D/I_G)_{\text{initial}}$	$(I_D/I_G)_{\text{plateau}}$	$[(I_D/I_G)_{\text{plateau}}]/[(I_D/I_G)_{\text{initial}}]$
Cycle 1	0.72	0.32	0.45
Cycle 2	1.51	0.83	0.55
Cycle 3	1.62	1.03	0.64
Cycle 4	1.51	0.91	0.61
Cycle 5	1.22	1.02	0.83
Cycle 6	1.46	1.13	0.73
Cycle 7	1.55	1.39	0.89
Cycle 8	1.68	1.52	0.91

Defect density was also calculated using the equation[4]:

$$n_D(\text{cm}^{-2}) = \frac{(1.8 \pm 0.5) \times 10^{22}}{\lambda_L^4} \left(\frac{I_D}{I_G} \right),$$

where λ_L is the laser wavelength of 532 nm, revealing the same trend.

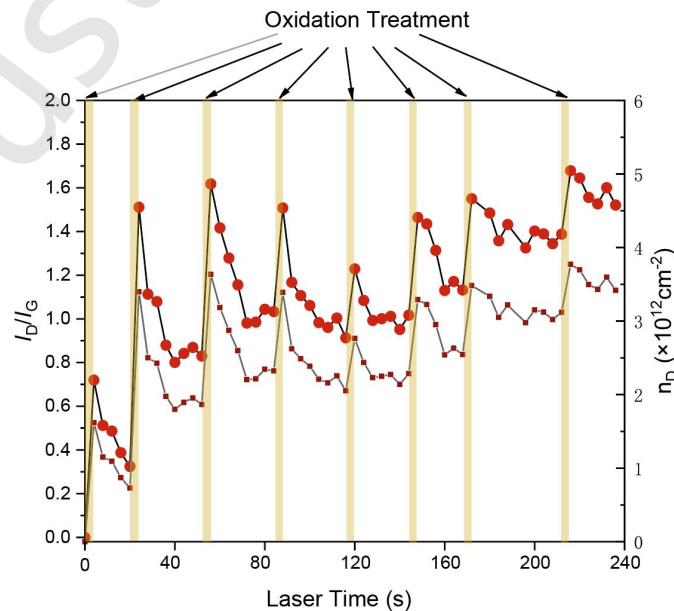


Figure S4 I_D/I_G ratio and defect density evolution under multiple cycles of laser reduction and oxidation treatment.

Section S4. Mechanism study of laser irradiation and estimated calculation of the local temperature rise

Previous studies have shown that laser reduction of graphene oxide involves coupled photothermal and photochemical processes rather than two completely independent mechanisms [9-11]. Local heating generated by laser irradiation can promote the removal of oxygen-containing functional groups and structural reconstruction of the carbon network, while photon-induced bond breaking and electronic excitation may further facilitate the reduction process. As a result, both mechanisms contribute to the restoration of the sp^2 carbon framework.

Apart from the photochemical effect, which is associated with the selective removal of epoxide groups, we have also analyzed the photothermal effect and estimated the local temperature rise on the GO surface under laser irradiation. For supported two-dimensional materials, heat dissipation is strongly influenced by substrate coupling due to phonon leakage across the sample–substrate interface.[12] Taking pristine graphene as an example, the heat generated under laser excitation can be efficiently dissipated into the substrate owing to the finite interfacial thermal conductance g ($\sim 25\text{--}50 \text{ MW/m}^2 \cdot \text{K}$) [13-15]. Consequently, the steady-state temperature profile is primarily determined by the balance between local optical absorption and vertical interfacial heat transfer, whereas the contribution of in-plane thermal conduction becomes negligible. The steady-state temperature rise ΔT at the center of the laser spot can be simplified to a one-dimensional heat balance approximation [16]:

$$\Delta T \approx \frac{q}{g} = \frac{\alpha \cdot P_{inc}}{\pi r_0^2 \cdot g}$$

where α is the optical absorption fraction, q represents the absorbed power density, P_{inc} is the incident laser power, πr_0^2 is the effective area of the laser spot, and g is the interfacial thermal conductance. Given an incident power of 5-25 mW and a spot size of 0.8–1 μm , the calculated local temperature rise of graphene ($\alpha \approx 2.3\%$) [17] is within a range of 2.9–45.7 K.

In contrast, for graphene oxide (GO), local temperature rise would be much higher owing to (i) enhanced optical absorption fraction α ($\sim 10\%$), depending on the degree of oxidation [18] and (ii) suppressed thermal conductance g because of the distorted lattice structure. Estimated local temperature rise is on the order of several tens to a few hundred Kelvin, which is sufficient to contribute to thermal reduction [19].

The present work does not attempt to quantitatively separate the photothermal and photochemical contributions. Instead, our objective is to identify the chemical evolution occurring during laser reduction. The nano-IR and XPS results reveal a preferential suppression of epoxide-related functionalities, indicating that laser reduction proceeds through chemically selective pathways rather than uniform oxygen removal.

Section S5. XPS characterization for chemical evolution of oxygen functional groups

It should be noted that the relative intensity of peaks in nano-IR spectra does not directly correspond to the concentration of functional groups, as the signal amplitude is also influenced by the coupling efficiency between molecular vibrations and the tip-enhanced near field [20, 21].

To further examine the evolution of oxygen-containing functional groups during laser reduction, XPS measurements were performed as a complementary characterization technique. Due to the millimeter-scale sample size required for XPS, highly oriented pyrolytic graphite (HOPG) flakes were used and subjected to the same UV/ozone oxidation and laser treatment conditions. As previously reported, UV/ozone treatment is largely confined to the surface layers, while the probing depth of XPS is limited to only a few atomic layers [22]; thus, the measured signal primarily reflects surface functionalization. It is therefore reasonable to assume that, under comparable UV/ozone treatment durations, graphite flakes exhibit functionalization trends similar to those of monolayer graphene oxide during laser processing.

Two HOPG samples were first oxidized for 12 min using UV/ozone. One sample was subsequently exposed to Raman laser irradiation (4 s exposure per scan, $0.1I_0$), while the other was kept as a reference. XPS analysis was then performed on both samples. As shown in **Fig. S5**, oxidized graphite exhibits a higher relative abundance of C–O species compared to C=O and C–OH groups. After laser treatment, a more pronounced decrease in the C–O component is observed, while the C=O and C–OH signals show comparatively smaller changes. These results provide complementary evidence that laser reduction preferentially affects C–O–related functionalities.

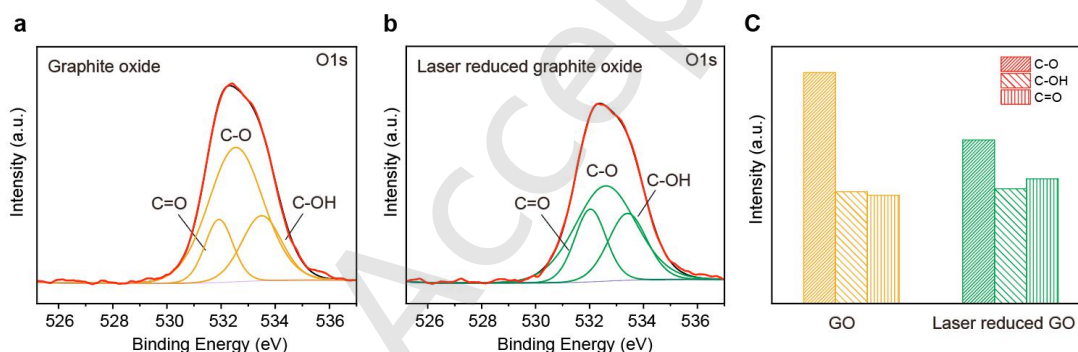


Figure S5 (a) O 1s spectrum for oxidized graphite. (b) O 1s spectrum after laser reduction. (c) Relative concentration of oxygen-containing functional groups, showing a preferential reduction of C–O–related species after laser treatment.

Section S6. Fatigue testing data interpretation

Nanoindentation and fatigue tests were performed under ambient conditions. First, nanoindentation test on suspended monolayer graphene oxide samples with different functionalization degrees was carried out and load–displacement curves were recorded, where fracture force (F_{Frac}) was extracted. The in-plane Young's modulus and pre-stress were obtained by fitting Equation [23]:

$$F(\delta) = \pi\sigma_0\delta + \frac{E^{2D}}{a^2}\delta^3,$$

where δ represents the membrane displacement under an applied force F , σ_0 represents the pretension of the sample, E^{2D} represents the two-dimensional elastic modulus of the material, and a is the radius of the circular hole. **Figure S6a** shows representative load–displacement curves for samples with $I_D/I_G = 0.22$. Fracture force of the oxidized GO and laser-treated GO samples, together with the corresponding loading parameters, are summarized in Table S3.

We analyzed the pre-stress of GO samples under different functional degrees (**Fig. S6b**). The extracted pre-stress values are comparable to previously reported measurements for graphene [24] and do not exhibit any significant variation with the chemical treatments, indicating that the chemical treatments do not introduce substantial changes in the residual tension state of the membranes.

Then fatigue tests were performed on the intact, untested membranes with the same functionalization degree. All the samples were subjected to a constant static force ($F_{\text{dc}} = 50\%F_{\text{Frac}}$), followed by cyclic dynamic loading at a frequency of 100 kHz and amplitude of 5 nm. According to Table S3, the smallest static force ($50\%F_{\text{Frac}} = 344.39$ nN) was applied to laser reduced samples in $I_D/I_G = 2.06$. As the indentation depth increases, the mechanical response transitions from a pretension- or surface-tension-dominated linear regime to an elasticity-dominated cubic regime [25, 26]. This crossover has been reported to occur at loads of approximately 20–60 nN for atomically thin membranes. Therefore, the observed failure behaviors of both oxidized and laser-reduced GO membranes are expected to be governed primarily by their intrinsic elasticity rather than residual tension or surface tension. Fatigue failure was identified by a sudden change in the cantilever oscillation amplitude or static deflection signal, indicating loss of load-bearing capability (**Fig. S7**).

It should be noted that the Raman and nano-IR characterizations were performed on substrate-supported GO, whereas fatigue tests were conducted on suspended membranes. Differences in thermal boundary conditions may influence the quantitative extent of reduction. Nevertheless, the present study focuses on the qualitative evolution of oxygen functionalities induced by laser irradiation, which is expected to remain applicable to both sample configurations.

Besides oxygen-functional-group chemistry and defect structure, laser reduction may also influence other material characteristics, including residual stress, local thermal history, and spatial heterogeneity. However, several observations suggest that these factors are unlikely to dominate the fatigue behavior observed in this work. First, fatigue tests were performed after laser treatment and thermal equilibration under identical ambient conditions, minimizing direct temperature effects during testing. Second, Raman mapping and nano-IR mapping reveal relatively uniform chemical modification within the laser-treated regions, indicating limited spatial heterogeneity. Finally, although residual stress may influence the mechanical response of suspended membranes, the fatigue experiments were conducted at loading levels corresponding to 50% of the fracture force, where the response is primarily governed by material failure rather than small variations in initial membrane tension. Therefore, while multiple factors may evolve during oxidation and reduction, the observed fatigue transition is most consistently correlated with the coupled evolution of oxygen-functional-group chemistry and defect structure revealed by Raman, nano-IR, and XPS characterization.

Additional SEM images of the failure behavior in samples of $I_D/I_G = 2.71$, 3.99 and 2.06 (laser reduced) are presented in **Fig. S8**. The observed morphologies consistently exhibit the same transition from brittle, global failure to plastic, localized failure and subsequently back to brittle failure, confirming the reproducibility of the fatigue failure behavior.

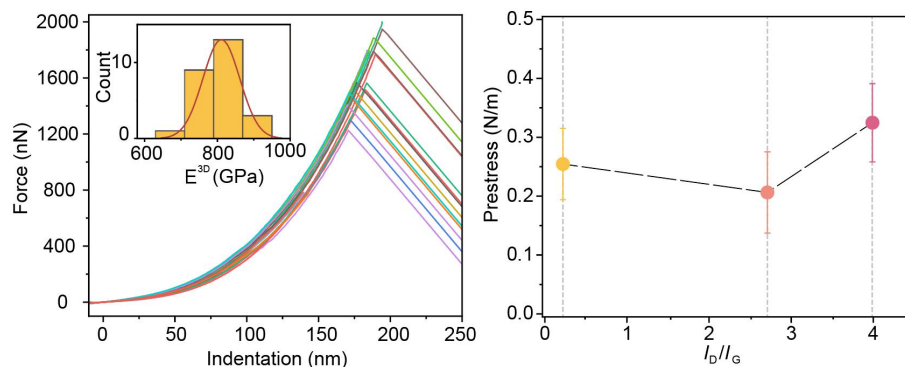


Figure S6 (a) Representative load–displacement curves in $I_D/I_G = 0.22$. (b) Pre-stress values in $I_D/I_G = 0.22, 2.71$ and 3.99 extracted from the load–displacement curves.

Table S3. Fatigue test data and loading parameter settings.

Stage	I_D/I_G	F_{Frac} (nN)
Oxidation	0	2174.55
	0.22	1578.13
	2.71	1140.43
	3.99	995.89
Reduction	2.06	688.78
	1.14	774.88
Loading settings	Static Force (nN)	$0.5 F_{\text{Frac}}$
	Amplitude (nm)	5
	Loading Frequency (kHz)	100

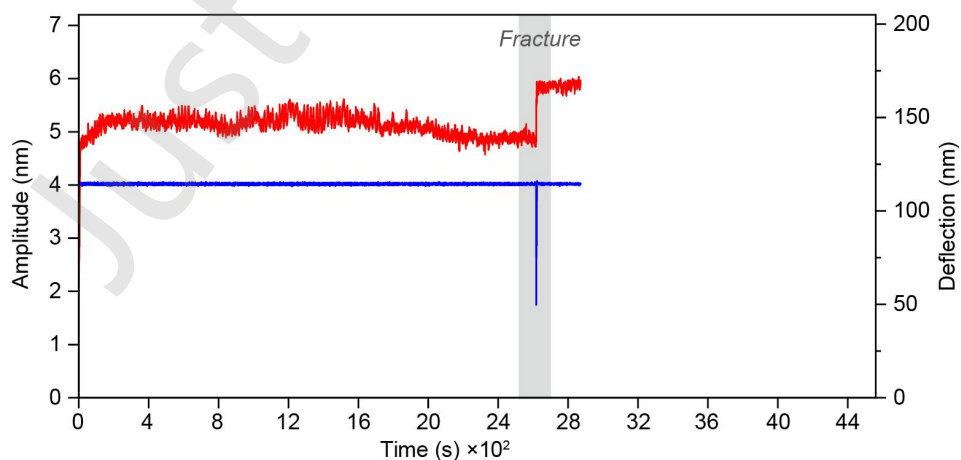


Figure S7 Real-time cantilever's oscillation amplitude and deflection signals during fatigue test.

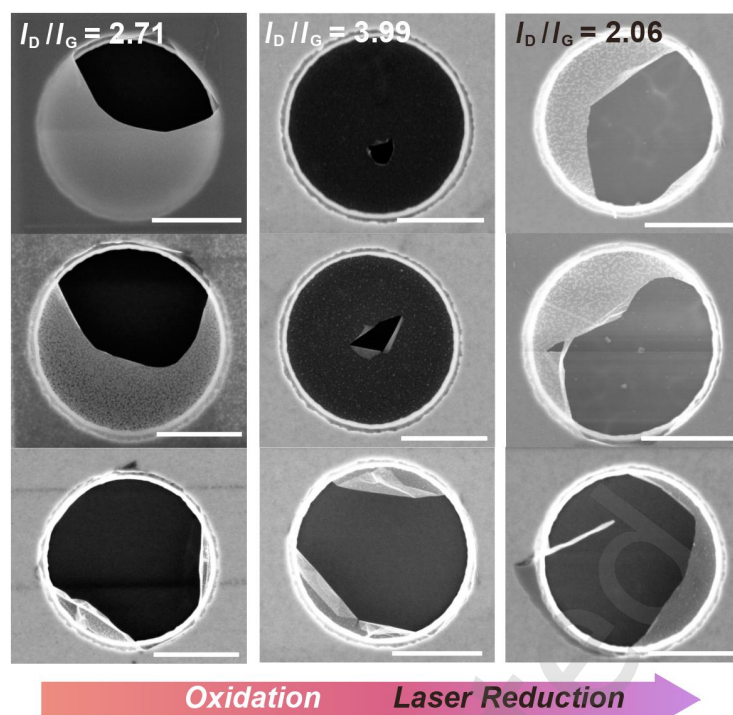


Figure S8 Fatigue failure morphologies in $I_D/I_G = 2.71$, 3.99 and 2.06 (laser reduced).

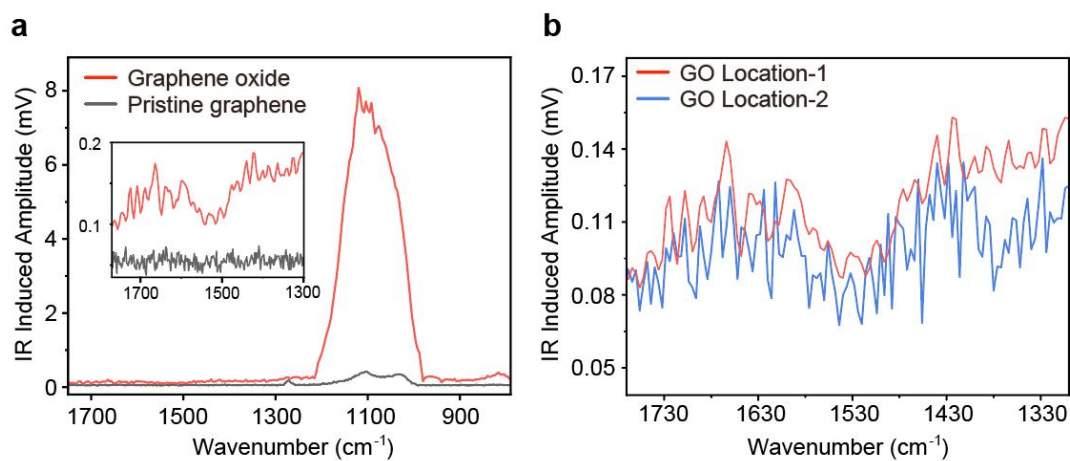


Figure S9 (a) Pristine graphene shows no detectable oxygen-related vibrational bands in the $1000\text{--}1800\text{ cm}^{-1}$ range, in contrast to the pronounced C–O, O–H, and C=O features observed in GO. (b) Single-scan nano-IR spectra acquired at different locations on the same sample show similar oxygen functional groups responses in $1300\text{--}1770\text{ cm}^{-1}$, showing similar O–H and C=O responses with spectral fluctuations due to local heterogeneity.

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