

Scalable enhancement of graphene oxide properties by thermally driven phase transformation

Priyank V. Kumar^{1†}, Neelkanth M. Bardhan^{1,2†}, Sefaattin Tongay³, Junqiao Wu³, Angela M. Belcher^{1,2,4*} and Jeffrey C. Grossman^{1*}

Chemical functionalization of graphene is promising for a variety of next-generation technologies. Although graphene oxide (GO) is a versatile material in this direction, its use is limited by the production of metastable, chemically inhomogeneous and spatially disordered GO structures under current synthetic protocols, which results in poor optoelectronic properties. Here, we present a mild thermal annealing procedure, with no chemical treatments involved, to manipulate as-synthesized GO on a large scale to enhance sheet properties with the oxygen content preserved. Using experiments supported by atomistic calculations, we demonstrate that GO structures undergo a phase transformation into prominent oxidized and graphitic domains by temperature-driven oxygen diffusion. Consequently, as-synthesized GO that absorbs mainly in the ultraviolet region becomes strongly absorbing in the visible region, photoluminescence is blue shifted and electronic conductivity increases by up to four orders of magnitude. Our thermal processing method offers a suitable way to tune and enhance the properties of GO, which creates opportunities for various applications.

Graphene oxide (GO) is a versatile, solution-processable candidate material for next-generation, large-area, ultrathin electronics^{1,2}, optoelectronics³, energy conversion and storage technologies^{4–7}. GO is an atom-thick sheet of carbon functionalized with several oxygen-containing groups dominated by the epoxy and hydroxyl functional groups on the basal plane, with carboxyls and lactols at the sheet edges⁸. The ability to tune and spatially control the oxygen functionality in GO structures is a critical factor in opening up bandgaps comparable to those of silicon (~1 eV) for applications in electronics and photonics^{3,9}. Such control is desirable for many future technologies based on green and sustainable catalysts^{10,11}, metal/semiconductor composites^{12–15} and chemical/biological sensors³ that can utilize the rich and interactive oxygen framework in GO in a number of ways. However, the central issue currently limiting GO's direct deployment in these devices is the material's inherent chemical inhomogeneity and structural disorder caused by the harsh chemical environments employed during current synthesis protocols, and the inability to exercise spatial control over oxygen groups in these processes^{16–18}. These limitations result in large optical gaps (~5.6 eV) and poor electronic conductivity that affect device performance unfavourably^{3,19,20}. Given the high impact of controlled oxygen functionalization on the increasing number of applications that utilize GO, it is of prime importance to develop methods that preserve the oxygen functionality and yet enhance the optical and electronic properties.

A standard approach used to produce GO structures on a large scale is the Hummers method, which typically renders oxygen concentrations of 30–35 atomic per cent (at%)¹⁶. To date, a number of methods to improve the sheet characteristics of as-synthesized GO structures have been reported, but almost all of these improvements come at the expense of oxygen content. One such procedure

is to produce reduced GO (rGO) with 5–8 at% oxygen^{19,20}. Alternatively, several groups have attempted careful hydrothermal treatments under alkaline or acidic conditions and achieved partial success in conserving oxygen functionality (15–20 at%) with improved sheet properties^{10,21–23}. Other approaches include controlled chemical functionalization methods, such as dissociation of oxygen molecules in an ultrahigh vacuum to achieve selective epoxy functionalization²⁴, the use of local reduction methods with nanometer resolution²⁵ and thermal annealing at 750 °C to produce graphene monoxide²⁶. However, these techniques require expensive ultrahigh-vacuum equipment and high-temperature systems, which makes them less amenable to the large-scale processing of GO sheets. Also, high-throughput and easily scalable protocols that aim to enhance the sheet properties and still retain the oxygen content of as-synthesized GO are yet to be developed fully.

In this work, we demonstrate a straightforward mild thermal annealing procedure (50–80 °C) with no chemical treatments involved, to manipulate as-synthesized GO structures on a large scale by facilitating transformation of mixed sp^2 – sp^3 hybridized GO phases into distinct oxidized and graphitic phases. With this approach, oxygen functionality is preserved, and we obtain large improvements in the optical and electronic properties of GO. We demonstrate a strong increase in the visible absorption characteristics compared with those of as-synthesized GO samples, and an opening up of optical gaps in the range 0.5–2.5 eV. We also show enhanced electronic conductivity, by up to four orders of magnitude, and photoluminescence (PL) modulation in annealed GO structures. To understand our experimental results, molecular dynamics (MD) and density functional theory (DFT) calculations were performed on a large set of realistic, disordered GO structures. We show that as-synthesized GO structures are metastable and

¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA, ²The David H. Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA, ³Department of Materials Science and Engineering, University of California, Berkeley, California 94704, USA, ⁴Department of Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA, [†]These authors contributed equally. *e-mail: belcher@mit.edu; jcg@mit.edu

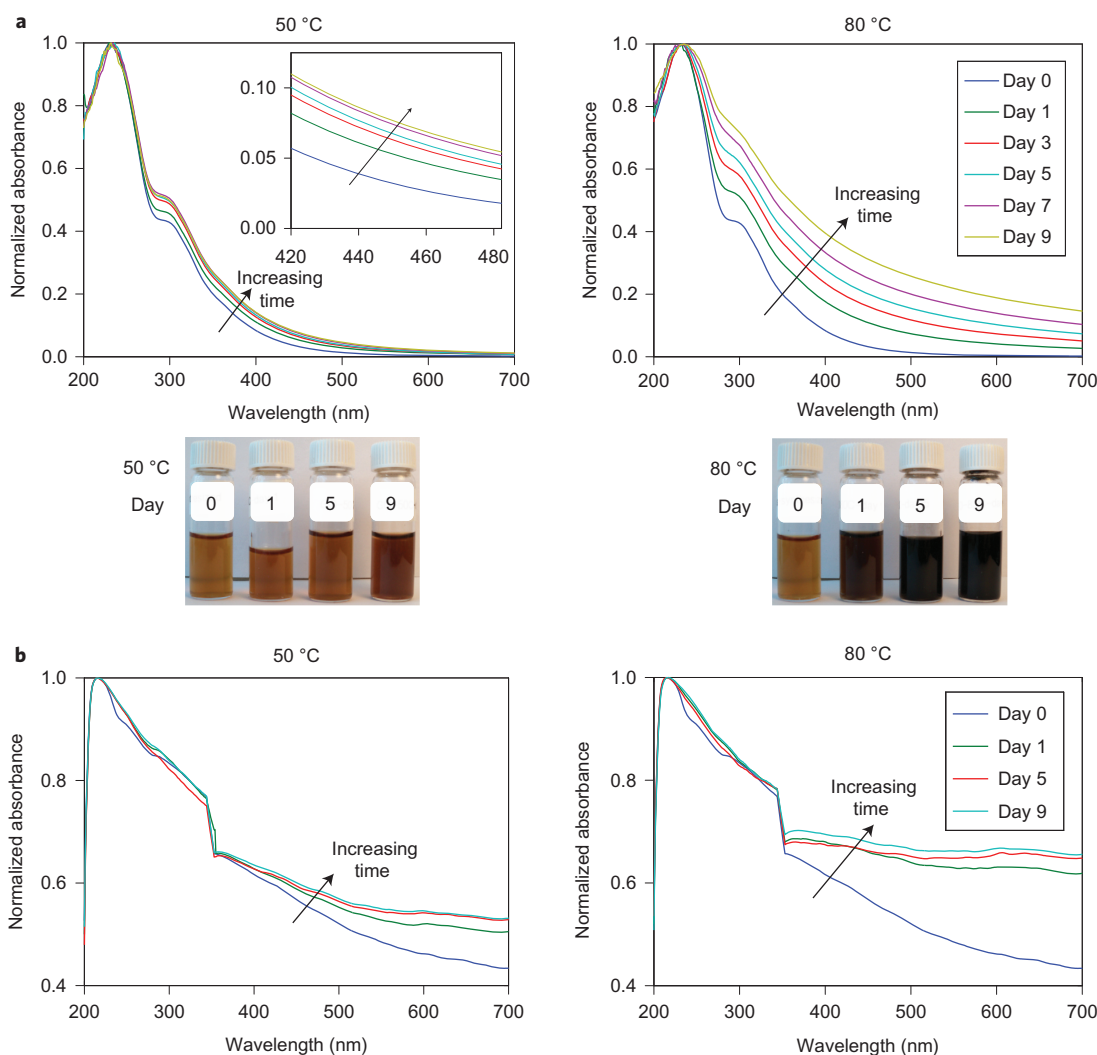


Figure 1 | Improvement in the optical properties of annealed GO structures. **a**, Normalized UV-vis absorption spectra of GO suspensions aged at 50 and 80 °C at different time intervals show increasing visible absorbance with thermal annealing. The inset in the 50 °C case shows the trend at a higher magnification (for clarity). Also shown are photographs that compare the colour change of GO suspensions under continuous annealing at 50 and 80 °C. **b**, UV-vis measurements on fd-GO samples show a similar increasing trend, but a much stronger visible absorbance with thermal annealing. The bump near 360 nm results from the change of detectors (from visible to ultraviolet).

undergo phase separation under the influence of temperature that drives oxygen diffusion by overcoming the associated kinetic barriers^{27–29}. Taken together, our results shed light on the structural stability of GO and open new opportunities for large-scale processing of as-synthesized GO sheets in a wide range of applications.

Results and discussion

GO sheets were synthesized by the Hummers method¹⁶. We performed thermal annealing studies on both GO suspensions and freeze-dried GO (fd-GO) samples to discount the effects of the solvent environment. GO suspensions were prepared by thoroughly exfoliating GO sheets in water (~0.5 wt% solids). Two stock solutions were prepared by diluting this solution (10×) and annealing for a course of nine days, one at 50 ± 1 °C and the other at 80 ± 1 °C in a temperature-controlled oven. We chose to perform annealing at two different temperatures so as to understand the impact of kinetics on the resulting phase-transformation processes. Aliquots were retrieved at regular intervals of one, three, five, seven and nine days, and stored in a vacuum desiccator at room temperature for further characterization. We also performed a similar annealing procedure

with fd-GO samples (see Methods and Supplementary Information for more details on sample preparation and characterization).

The evolution of the ultraviolet–visible (UV-vis) absorption spectra of GO suspensions with thermal annealing is shown in Fig. 1a. The as-prepared GO samples (day 0) showed typical characteristics of a main absorbance peak at ~230 nm, attributed to π - π^* transitions of C=C in amorphous carbon systems, and broad absorption in the visible region. The main absorbance peak remained intact at ~230 nm on annealing at both 50 and 80 °C, in contrast to a clear red shift to ~260 nm reported in rGO samples³⁰, which indicates no major reduction in covalently bonded oxygen at these temperatures. In addition, a broad shoulder at ~300 nm, attributed to n - π^* transitions of C=O, was observed during the entire course of thermal annealing. Although a weak monotonic increment in the visible absorption was recorded with increasing annealing time at 50 °C, GO samples annealed continuously at 80 °C became strongly absorbing in the visible region, consistent with the stronger darkening of these GO samples. UV-vis absorption measurements on fd-GO samples yielded similar trends, but the observed effects were much stronger, as shown in Fig. 1b (also see Supplementary Fig. 1). To put these results in

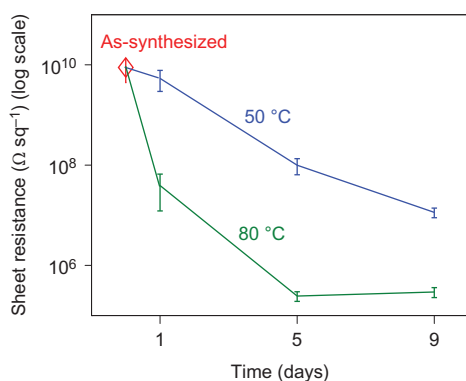


Figure 2 | Enhanced electrical properties of annealed GO thin films. Sheet resistances of GO thin films prepared from fd-GO samples annealed at 50 and 80 °C show a reduction by up to four orders of magnitude compared with the sheet resistance of the as-synthesized GO film. The error bars represent standard error of the mean from at least three different locations on the film.

perspective, in applications that involve light absorption, for example, we estimate that this increase in absorption corresponds to a significant 38% increase in the collection of photons in the wavelength range 350–800 nm, relative to as-synthesized GO (see Supplementary Fig. 2).

We investigated the electrical properties of thin films prepared from annealed GO samples using four-point probe transport measurements at room temperature. Films prepared from GO suspensions annealed at 50 °C showed no appreciable changes in the sheet-resistance values, and those from GO suspensions annealed at 80 °C showed a reduction by up to two orders of magnitude over the nine days, compared with as-synthesized GO samples ($\sim 9 \times 10^9 \Omega \text{ sq}^{-1}$, comparable to $2\text{--}20 \times 10^9 \Omega \text{ sq}^{-1}$ reported previously²⁷). In the case of films prepared from fd-GO samples, even further reductions in sheet resistance values were observed (Fig. 2). Significantly, low sheet resistances of $\sim 3 \times 10^5 \Omega \text{ sq}^{-1}$ were measured in the case of fd-GO samples annealed for five and nine days at 80 °C, respectively, which are four orders of magnitude lower than the resistance of the as-synthesized GO samples and indicate superior electrical characteristics of annealed GO samples. These results are consistent with stronger changes observed in the UV-vis absorption data of fd-GO samples compared with those of GO suspensions (Fig. 1). Overall, this simple annealing procedure is effective in opening up new possibilities for fabricating thin-film devices with better electron-transport characteristics than those afforded by as-synthesized GO.

Although previous reports show enhanced electronic properties of GO under relatively low-temperature annealing, between 25 and 150 °C, combined with suitable chemical treatments^{21–23,31}, such improvements come at the expense of oxygen content, which leads to the formation of rGO. In this work with a simple thermal annealing procedure, such control in optical and electronic properties is obtained without a compromise in the covalently bonded oxygen content, and without being subjected to any chemical treatments. To confirm this, we used thermogravimetric analysis (TGA) to monitor the level of reduction of our GO samples during the 80 °C annealing run (Fig. 3a). Although the annealed sample showed an expected slight weight loss ($\sim 10\%$) over the entire course of annealing, attributed to the elimination of physisorbed and interlamellar water²², the thermogram of a typical as-synthesized GO sample shows an additional significant weight loss ($\sim 32\%$) at an onset temperature of 150 °C, attributed to loss of covalently bonded oxygen from the GO sheets. This result shows that our GO samples are not reduced during the entire course of

thermal annealing, an observation additionally supported by X-ray photoelectron spectroscopy (XPS) measurements (see Supplementary Figs 3–5) and also in agreement with previous reports at these temperatures^{22,23}. Collectively, these results suggest that the measured enhancement in optical and electronic properties does not come at the expense of oxygen atoms, which indicates that instead we are observing a distinct structural transformation inherent to GO.

To probe the fundamental mechanism responsible for the enhancement in the visible absorption and electrical conductivity of annealed GO samples, we carried out Fourier transform infrared (FTIR) spectroscopy measurements of GO samples during the annealing (Fig. 3b). Importantly, the recorded FTIR spectra clearly show the presence of oxygen functional groups for the entire course of annealing, which again confirms no major removal of oxygen groups from the graphene basal plane. In the case of samples prepared from GO suspensions annealed at 50 °C, the absorption peak at $1,620 \text{ cm}^{-1}$, assigned to the C=C skeletal vibrations of graphitic domains or the deformation vibration of intercalated water (scissor mode), remains more or less unchanged. In the case of annealing at 80 °C, this peak intensity decreases, which indicates a loss of intercalated water consistent with our TGA results, and a new peak appears with increasing intensity at $1,580 \text{ cm}^{-1}$, attributed to the formation of prominent graphitic domains in GO, consistent with previous studies^{20,22,23}. Our FTIR measurements for fd-GO samples produced similar results, in addition to reflecting a stronger property enhancement in these samples (see Supplementary Fig. 6). Further, we observed a blue shift in our PL spectra measurements on GO suspensions annealed at 80 °C, as shown in Fig. 3c, which is attributed to the formation of confined graphene domains in GO^{30,32}. The absence of a clear blue shift in the PL spectra of GO suspensions annealed at 50 °C correlates well with the FTIR spectra, and suggests a lack of prominent graphitic domains in these samples. XPS, Raman and additional PL analyses on annealed GO samples also support the clustering and formation of prominent graphitic domains (see Supplementary Figs 3–5 and 7–9). An increase in the stacking of GO sheets was also observed during annealing experiments, consistent with increasing π -conjugation and graphitization in the system (see Supplementary Fig. 10). Taken together, our experimental results suggest that an increasing formation of the graphitic phase in annealed GO samples (with no loss in oxygen content) is the critical factor responsible for the observed improvements in sheet properties.

As a means to probe directly the structural transformations taking place in GO, we performed Auger electron spectroscopy (AES) on as-synthesized and annealed GO thin films (see Methods). The presence of carbon and oxygen on the surface was detected using this technique (Fig. 4a). Figure 4b compares the elemental composition maps (oxygen-rich regions indicated by white spots) of as-synthesized and annealed GO thin films. Clearly, the as-synthesized GO film shows a uniform oxygen composition, and the annealed film shows sharper and segregated regions of oxygen. These results further establish the process of oxygen clustering and development of well-defined graphene-rich domains on annealing as-synthesized GO.

To interpret our experimental results, we propose that as-synthesized GO structures are metastable and have the potential to separate gradually into two distinct phases, graphitic and oxidized domains, under temperature-driven oxygen diffusion on the basal plane. Figure 4c shows a schematic of the phase separation process of an as-synthesized mixed sp^2 – sp^3 GO phase into distinct graphitic and oxidized phases, which results in the formation of larger, well-defined graphitic domains confined in both dimensions. With longer annealing times, some of these domains may further interact and coalesce, which leads to percolation and greater

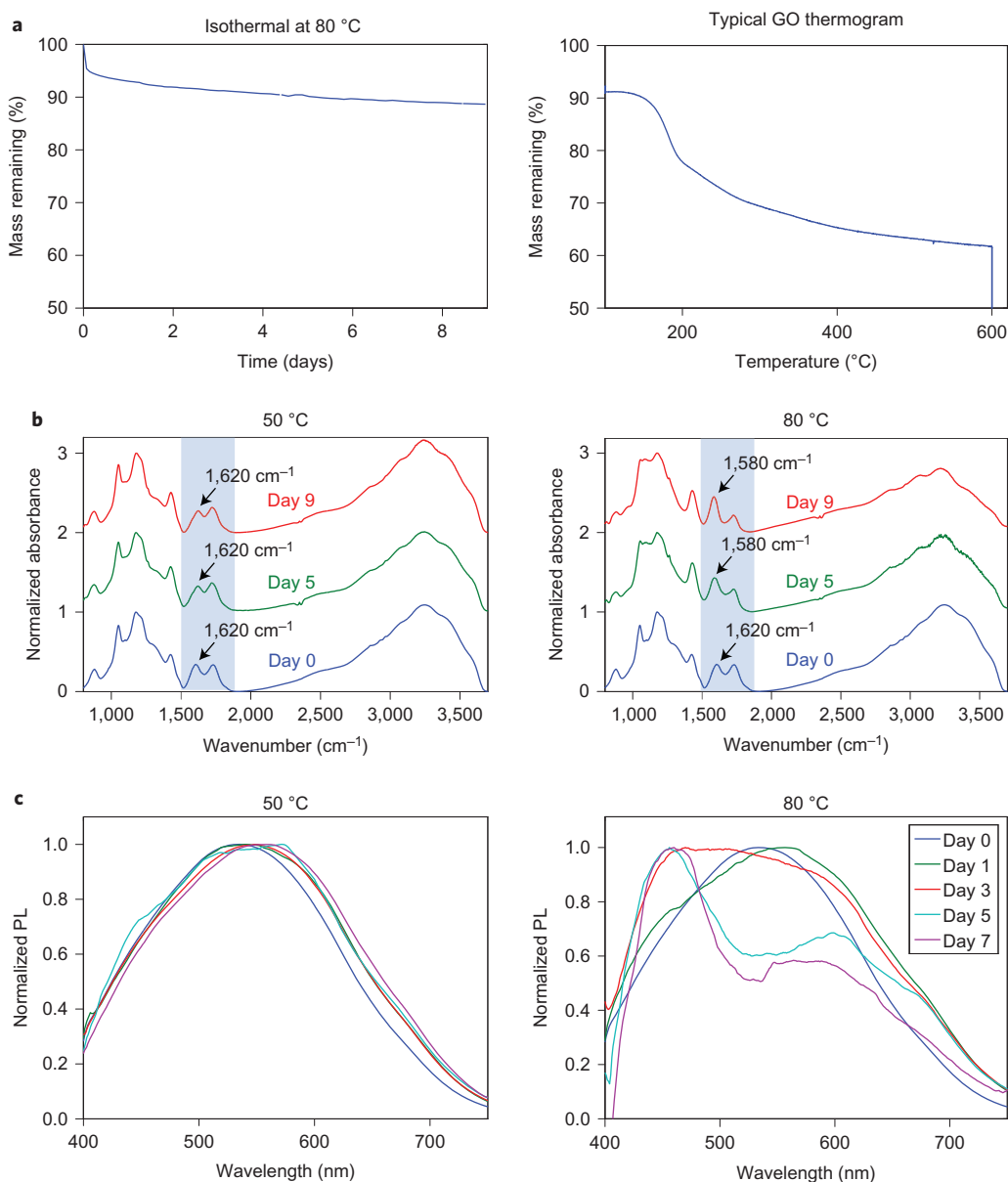


Figure 3 | TGA, FTIR and PL spectra of annealed GO structures. **a**, Recorded mass loss of a GO sample annealed at 80 °C for nine days shows only a slight reduction in mass (~10%) compared with a typical TGA thermogram of GO that shows an additional significant mass loss of ~32% because of the removal of oxygen from the basal plane. This indicates that GO is not reduced during the entire course of thermal annealing. **b**, FTIR spectra of the GO structures reveal increasing absorption intensities near 1,580 cm⁻¹ attributed to C=C bonds in the case of thermal annealing at 80 °C. This correlates with the increasing UV-vis absorbance and decreasing sheet resistance, which suggests the formation of prominent graphitic domains within the *sp*³ matrix. **c**, PL emission from GO suspensions annealed at 50 and 80 °C show a blue shift in the peak PL emission wavelength in the latter case.

connectivity among neighbouring domains. Such prominent graphitic domains in an *sp*³ matrix have been predicted to open up optical gaps in the visible^{30,32}, which explains the increasing visible absorbance and blue shift in PL observed here. Furthermore, this model explains the increasing electrical conductivity of GO thin films with annealing because of graphitization and greater connectivity among the developed *sp*² domains, with no loss in the overall oxygen content.

To further support our hypothesis of a temporal phase separation, we carried out a combination of classical MD simulations based on reactive force fields (ReaxFF)³³ and DFT calculations. Model GO structures with different sizes of oxidized and graphitic domains (none, three and six graphene rows) were prepared with the oxygen concentration kept fixed to mimic the phase-separation process (Fig. 5a). Initially, the oxidized domains consisted of

randomly distributed epoxy and hydroxyl groups attached to both sides of the graphene sheet, consistent with previous work that shows the dominant presence of such functional groups in GO^{3,8,19}. To account for local variations in oxygen concentration and fraction of functional groups on the GO sheet, we studied oxygen concentrations of 10 and 20 at% in the initial GO structures and prepared samples with epoxy to hydroxyl ratios of 3:2 and 2:3 (ref. 19). GO structures were then annealed at 300 K using MD simulations (see Methods for further details).

Our MD simulations produced GO structures that consisted of bare graphitic domains in conjunction with oxidized domains that largely contained epoxy and hydroxyl functional groups with a small amount of carbonyls and water molecules, consistent with previous computational work²⁷. The generation of ten samples for each composition allows us to present meaningful averages of the

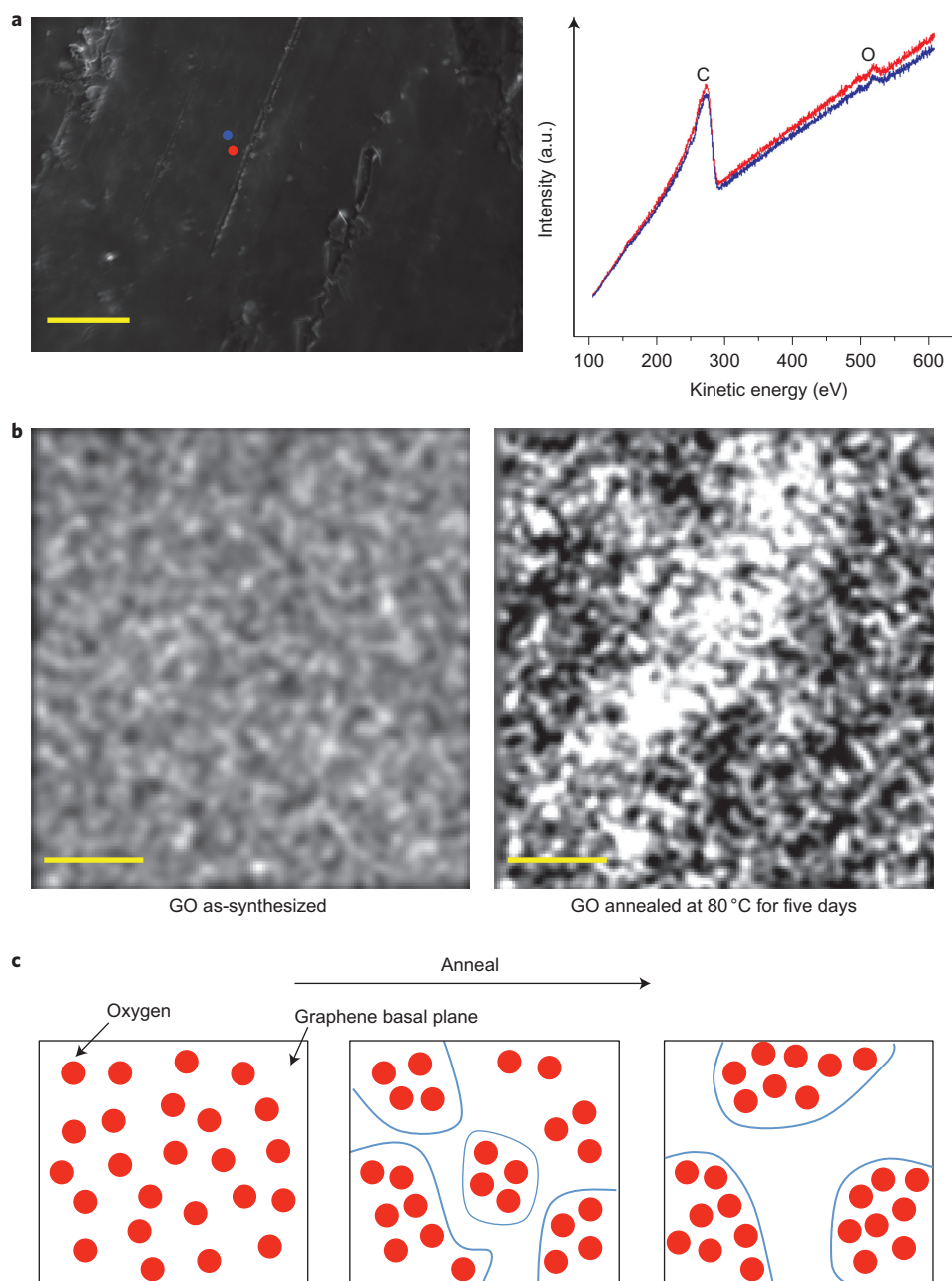


Figure 4 | Direct evidence of phase separation in annealed GO structures. **a**, SEM (left) and AES (right) of as-synthesized GO. The KLL peaks at 256 and 510 eV, respectively, show the presence of C and O. This was confirmed at two different locations (red and blue spots) on the film as indicated in the SEM image. Scale bar, 10 μm . **b**, AES oxygen mapping of as-synthesized and annealed GO films. The white spots indicate oxygen-rich regions and the black spots indicate oxygen-poor regions or, in other words, carbon-rich regions. Scale bar, 2 μm . **c**, Schematic depicting our proposed phase-separation process in as-synthesized GO structures. Synthetic protocols of GO structures lead to a mixed sp^2 - sp^3 phase that has the potential to separate into two distinct oxidized and graphene phases through diffusion of oxygen atoms on the graphene basal plane under the influence of an external stimulus. a.u., arbitrary units.

computed properties. Figure 5b shows the total energy of the phase-separated GO structures computed from our MD simulations (internal energies at 300 K). We observe that the total energies decrease with increasing phase separation, that is, with increasing graphitic domain size, which suggests that the process of phase separation is thermodynamically favourable in GO structures. Additional calculations performed using chemically homogeneous and ordered phases of GO indicate similar trends and favourability of the phase-separation process (see Supplementary Fig. 11). We attribute this favourability to strain compensation and hence strain relief in the GO structures. For instance, although two isolated oxygen groups attached on either side of the graphene sheet increase

strains in their vicinity, the same oxygen groups can partially cancel these strains when present in proximity to one another, and thus favour phase separation and clustering of oxygen atoms on graphene^{34–37}.

A key mechanism involved in the phase-separation process during annealing is the diffusion of epoxy and hydroxyl functional groups along the graphene basal plane. Our calculations show that diffusion of an isolated epoxy group is limited by an activation barrier of 0.83 eV, and the barrier for diffusion of an isolated hydroxyl group is 0.30 eV, much lower than that in the epoxy case (see Fig. 5c). Although diffusion of oxygen atoms at room temperature has been observed in GO multilayers previously, the

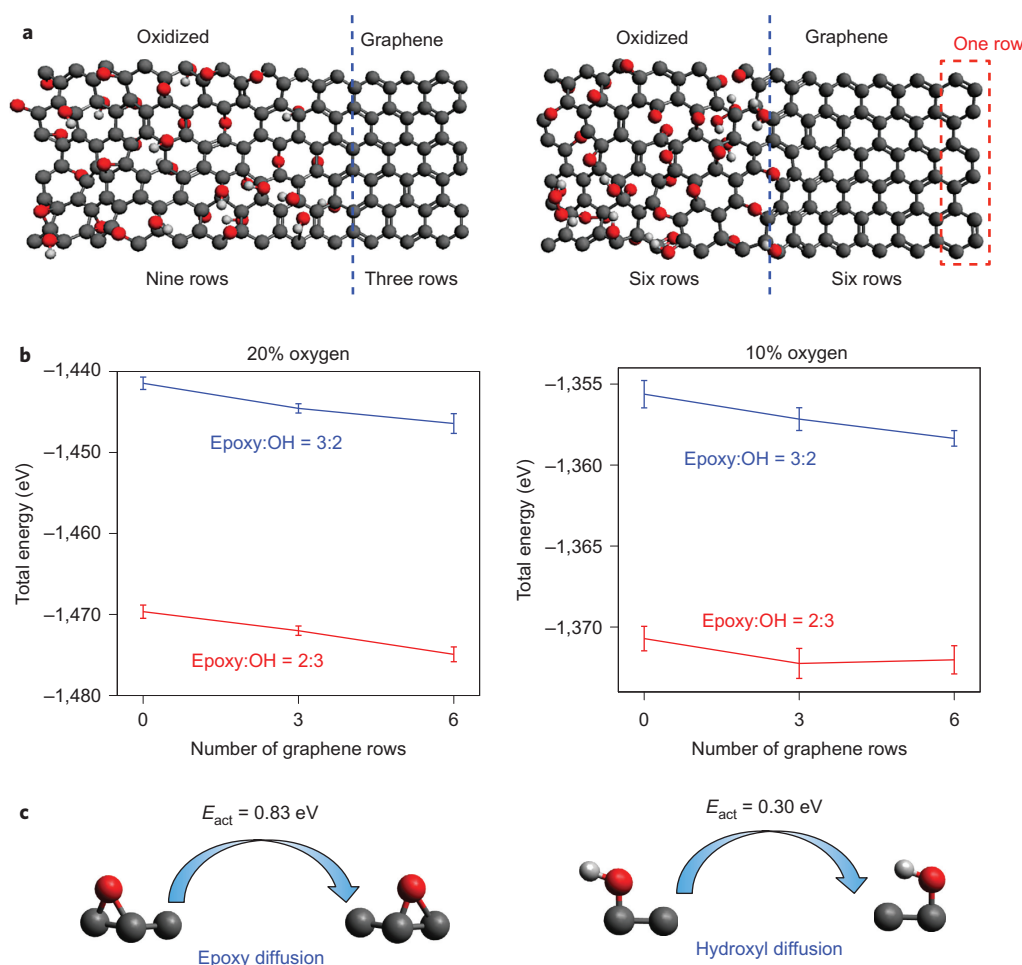


Figure 5 | Favourable energetics of phase separation predicted by atomistic modelling. **a**, Representative model GO structures used to compute the energetics of the phase-separation process. Each structure consists of two distinct oxidized and graphene phases with different domain sizes. Carbon, oxygen and hydrogen are represented as grey, red and white spheres, respectively. **b**, Total energy values of phase-separated GO structures as a function of the graphene domain size for different oxygen contents (in at%) and epoxy to hydroxyl functional group ratios. The total energies decrease on phase separation, which indicates the process to be thermodynamically favourable. In each plot, the results are obtained by averaging over ten GO structures for each data point, and the error bars shown represent the standard error of the mean calculated for the same set of structures. **c**, Computed activation barriers for the diffusion of epoxy and hydroxyl functional groups on the graphene basal plane.

structural changes were discernible only after months, which implies extremely low diffusion rates²⁷. Using the Arrhenius formula $k = k_0 \exp(-E_{\text{act}}/k_B T)$, where E_{act} is the computed activation barrier and k_0 is the attempt frequency (assumed to be constant), we estimate the hydroxyl and epoxy diffusion to increase by one and two orders of magnitude, respectively, at 80 °C (353 K) compared with their diffusion at room temperature (300 K), which correlates well to the fact that structural changes were observed over 1–5 days in our work, rather than the months for reported stock solutions preserved at room temperature, which hence warrant the application of external stimuli, such as elevated temperatures, to activate these structural changes.

We carried out additional analyses to estimate the range of domain sizes in annealed GO samples. Analogous to the case of phase separation in hybridized carbon boron nitride monolayers³⁸, our calculations also indicate that larger graphitic domains are thermodynamically preferred to decrease the number of interfaces and the associated interfacial energy between oxidized and graphitic domains (see Supplementary Fig. 11). To understand the structural evolution of GO on annealing, we first note that the as-synthesized GO structure consists of two distinct features: (1) small sp^2 fragments (or chains) that correspond to no specific structure and (2)

larger unoxidized graphitic domains on the order of ~ 3 nm in size³⁰. On progressively annealing GO, we expect the small sp^2 fragments to interact and coalesce (or, in other words, undergo the process of phase separation), which leads to well-defined graphitic domains. On the basis of Raman and additional PL spectra from GO thin films, we conclude that most of the domains are on the order of 1–2 nm (see Supplementary Figs 7–9) and are mainly responsible for the observed blue shift in the PL (2–2.5 eV).

In parallel, it is reasonable to expect that the ~ 3 nm domains already present in as-synthesized GO will grow further on annealing. We expect these domain sizes to extend from ~ 3 nm to tens of nanometres, similar to the range of domain sizes observed in carbon boron nitride monolayers³⁸. Our DFT calculations show that such large domains formed within the sp^3 matrix open up optical gaps continuously up to 2 eV (see Supplementary Fig. 12), which helps explain the continuous increase in the optical absorption spectra in both the visible and infrared regions. Further, these estimates also explain why certain regions are relatively oxygen rich compared with other regions in our AES maps. Although formation of such larger domains on the order of tens of nanometres requires considerable diffusion of oxygen groups, we found that such mean diffusion lengths can, nevertheless, be

achieved at the temperatures considered in this work (see Supplementary Section 5). Although we show these results for our as-synthesized GO samples with an oxygen content of ~30%, we expect these domain sizes to be tunable depending on the oxygen concentration, temperature and anneal time, and so provide additional opportunities for controlling the properties of oxidized graphene.

Conclusion

In summary, we present a highly scalable, easily controllable, mild thermal annealing procedure that involves no chemical treatments to manipulate as-synthesized GO suspensions and solids through a phase-separation process. We demonstrate that such phase-transformation processes have significant impact on the sheet properties by (1) making GO strongly absorbing in the visible region, (2) reducing the electrical resistance by four orders of magnitude and (3) producing a blue shift in PL emission, without compromising the oxygen content. Atomistic calculations support our experimental results and show that the phase separation of the mixed sp^2 - sp^3 hybridized GO phase into prominent oxidized and graphitic domains is energetically favourable and kinetically accelerated at slightly elevated temperatures compared with room temperature. In addition to shedding light on the thermal stability of GO nanostructures when employed in devices that operate above room temperature, these results open up novel opportunities for bulk processing of as-synthesized GO structures, and highlight pathways to tune the sheet properties of GO for their application in next-generation functional devices.

Methods

Synthesis of GO. GO was prepared from synthetic graphite powder (~325 mesh, 99.9%, Alfa Aesar) using the Hummers approach¹⁶. The yellowish-brown filter cake obtained was suspended in 320 ml of water to give a GO suspension of ~0.5 wt% solids. The suspension was put in a sealed glass bottle and kept in a vacuum desiccator for long-term storage. It was observed that the stock suspension is stable at room temperature, without the addition of any surfactant.

Preparation of fd-GO samples. To study the effects of long-term thermal annealing on GO alone, and discount the effects of the solvent environment, we prepared dried samples from the stock suspension. The stock suspension was diluted to 10× and 1 ml of this diluted suspension was taken in several Eppendorf tubes, which were solidified rapidly by plunging into liquid nitrogen. The frozen samples were put in a lyophilizer (Labconco FreeZone 2.5 Plus), and kept at 0.008 mbar pressure for a day for complete extraction of the water content from the samples. These samples were stored in a vacuum desiccator.

Time-course annealing of GO samples. We studied the effects of thermal annealing on both GO suspensions and fd-GO samples. For GO suspensions, 1 ml of the 10× diluted stock solution was taken in ten Eppendorf tubes. For the fd-GO samples, the lyophilized samples were used as is in ten Eppendorf tubes. One batch of five samples (both suspension and solids) was placed in a vacuum oven at 50 °C, and another similar batch at 80 °C. Both batches were started simultaneously at $t = 0$. Then, at $t = 1, 3, 5, 7$ and 9 days, we retrieved one Eppendorf tube from each oven (both solid and liquid samples), and these were stored in a vacuum desiccator at room temperature for further characterization.

UV-vis absorbance spectroscopy. GO suspensions obtained from annealing experiments were subjected to a vortex treatment and further sonicated for 20 minutes. They were then diluted to 160× (of the stock suspension) for absorbance measurements. The sample (100 μl) was taken in a glass cuvette of path length 1 cm. UV-vis absorbance was measured using a DU-800 Spectrophotometer (Beckman Coulter) with respect to a water (blank) baseline. The scan range was 200–1,100 nm at a scan rate 600 nm min⁻¹. For the UV-vis absorption measurements on fd-GO samples, we used a Cary 300 spectrophotometer (Agilent Technologies) with a solid-state sample accessory with z -height adjustment, operating in diffuse reflectance mode. The fd-GO samples were scanned from 200 to 800 nm at a scan rate of 1 nm s⁻¹. The reflectance measurements were converted into corresponding absorbance data after suitable background subtraction.

Four-point probe measurements. Electrical transport measurements of GO films prepared from annealed GO samples were carried out using a four-point probe technique (Model 2525, The Micromanipulator Company) at room temperature. GO samples were drop-cast into 1 cm² area films on an insulating glass substrate. Measurements were taken by varying the applied voltage from -1 to +1 V.

Infrared spectroscopy. GO suspensions obtained from annealing experiments were freeze dried and the FTIR spectrum (800–4,000 cm⁻¹) was measured using a Thermo Fisher Continuum FTIR Microscope in the transmission mode. A spot size of 100 μm was used. The transmission measurements were converted into corresponding absorbance data and a suitable five-point baseline correction was applied to all spectra.

PL measurements. PL from the GO samples was measured using a NanoLog spectrofluorometer (HORIBA Jobin Yvon). The GO samples were diluted in water to 500× the stock concentration. A continuous-wave xenon lamp with a monochromator was used for the excitation source and the samples were excited at 350 nm. The fluorescence was measured in the range 400–750 nm, using a FluoroHub single photon counter (HORIBA Jobin Yvon), with an integration time of 0.1 s nm⁻¹.

TGA. We characterized the thermal properties of GO by TGA (TA Instruments Q500 TGA). GO solids were equilibrated initially at 30 °C for 30 minutes, followed by a ramp-up to 80 °C where they were held isothermally for nine days to record mass loss during the annealing run. Typical GO thermograms were obtained by similar equilibration, followed by a ramp-up to 800 °C. All measurements were taken at a nitrogen gas flow rate of 40 ml min⁻¹ and a ramp rate of 5 °C min⁻¹ was used.

Nano-AES measurements. Auger spectroscopy was performed using a field emission electron source and a multichannel detector at ultrahigh vacuum ($2\text{--}5 \times 10^{-10}$ mbar) with 100 nm spatial resolution. Increasing resolution beyond this limit resulted in weaker signal collection and poor elemental contrast. As a result, this technique provides direct evidence of oxygen clustering and/or segregation, but to obtain quantitative information on the domain size is rather difficult. A series of Auger spectra were measured on several different regions with a minimum scan area of $3 \times 3 \mu\text{m}$. The AES scanning was performed to detect the oxygen concentration. To eliminate the native oxide contribution on conventional substrates, such as SiO₂, Si and Al₂O₃, GO was transferred onto non-oxidizing MoS₂ substrates.

Computational methods. MD simulations used to prepare realistic GO structures were carried out using the LAMMPS package³⁹ with the ReaxFF reactive force field, chosen here for its ability to describe accurately the bond-breaking and bond-formation events in hydrocarbon systems³³. We employed a time step of 0.25 fs and the NVT Berendsen thermostat¹⁹. To assess the energetics of the phase-separation process into oxidized and graphitic domains, we considered 3×1.3 nm periodic graphene sheets with different oxidized and graphitic domain sizes. The oxidized domains contained randomly distributed epoxy and hydroxyl groups^{40,41}. The temperature of the GO sheets was increased from 10 K to 300 K over a time interval of 250 fs. The system was then annealed at 300 K for 250 ps to allow for structural stabilization. Such MD thermal anneal runs have been employed previously by us and other groups to generate both GO and reduced GO structures^{19,27,41}.

In all the DFT calculations presented in this work, the structures were relaxed to less than 0.03 eV Å⁻¹ residual atomic forces using DFT with a plane-wave basis set as implemented in the VASP package^{42,43}. We used the projector augmented wave method to describe the core electrons⁴⁴ and the Perdew–Burke–Ernzerhof exchange-correlation functional⁴⁵. Isolated epoxy and hydroxyl groups were modelled on a periodic graphene sheet with 120 carbon atoms using a gamma-point k -grid. The wave function and charge density were expanded in plane waves with a wavefunction kinetic energy cutoff of 500 eV. A vacuum region of 16 Å was used in the direction normal to the sheets. To compute the activation energies used to determine the kinetics of oxygen diffusion, we employed nudged elastic band calculations as implemented in VASP with 9–13 image structures between the reactant and the product.

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Author contributions

P.V.K., N.M.B., A.M.B. and J.C.G. conceived and designed the experiments, P.V.K. and N.M.B. performed the experiments, calculations and co-wrote the manuscript with input from J.C.G. and A.M.B., and S.T. and J.W. performed AES, and contributed to Raman and PL mapping.

Additional information

Supplementary information is available in the [online version](#) of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to A.M.B. and J.C.G.

Competing financial interests

The authors declare no competing financial interests.

Scalable Enhancement of Graphene Oxide Properties by Thermally Driven Phase Transformation

Priyank V. Kumar,^{1,§} Neelkanth M. Bardhan,^{1,2,§} Sefaattin Tongay,⁴ Junqiao Wu,⁴ Angela M. Belcher,^{1,2,3,*} and Jeffrey C. Grossman^{1,*}

¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

²The David H. Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, MA, USA

³Department of Biological Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

⁴Department of Materials Science and Engineering, University of California, Berkeley, CA, USA

[§]These authors contributed equally

*To whom correspondence should be addressed

jcg@mit.edu

belcher@mit.edu

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1. UV-Vis data on GO suspensions and freeze-dried (fd-GO) samples

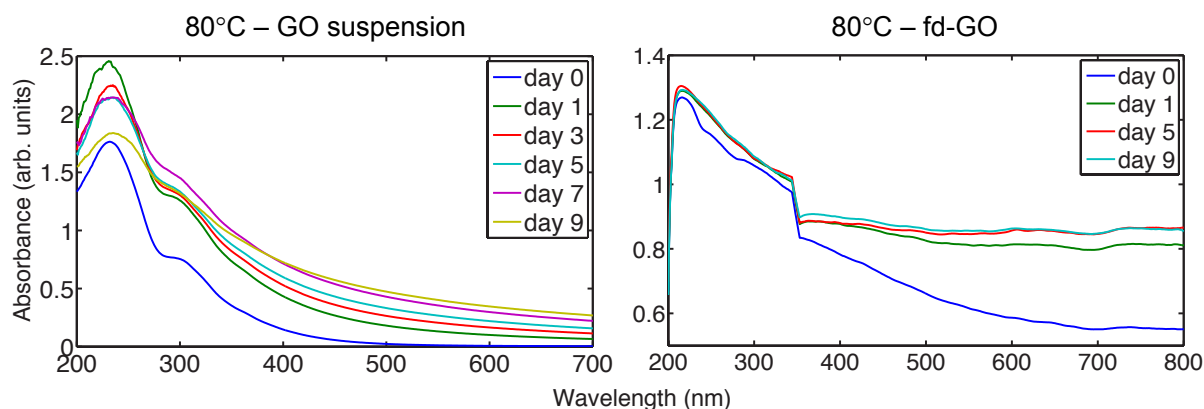


Figure S1: The un-normalized UV-Vis absorption data is shown for both GO suspensions and fd-GO samples annealed at 80°C. The concentrations were kept the same for comparison over different time intervals of annealing. The steep bump near 360 nm in case of the fd-GO sample is due to the change of detectors (from visible to UV).

We note that all of the annealed samples show an increase in the UV-Vis absorption spectra in comparison with the as-synthesized GO sample. Further, the UV-Vis data on both sets of samples with anneal time show a similar increasing visible absorption (400–700 nm) and decreasing UV absorption trend (200–300 nm). While the absorption peak at 230 nm is attributed to the amorphous nature of GO (which leads to an optical gap of ~ 5.6 eV), the absorption in the visible can be attributed to the graphitic regions confined within the sp^3 matrix^[S1]. The increasing visible absorption characteristics thus suggest prominent formation of these graphitic domains with annealing. Importantly, the overall increase in the visible absorption over the entire visible wavelengths suggests that these confined graphitic domains can be of various sizes and shapes.

Our results also show stronger changes in optical and electrical properties of fd-GO samples compared to GO suspensions. We attribute this effect to likely higher kinetics of phase separation in the fd-GO samples, where the solvent environment (water) is absent. The water molecules present in the solvent are known to stabilize GO sheets by forming interactive networks with the oxygen functional groups *via* hydrogen bonding^[S2], which could be the likely cause for slower diffusion of oxygen molecules in exfoliated GO

suspensions. This effect is largely absent in the case of fd-GO samples, which promotes faster diffusion of oxygen groups.

2. Calculation of enhancement in sunlight absorption

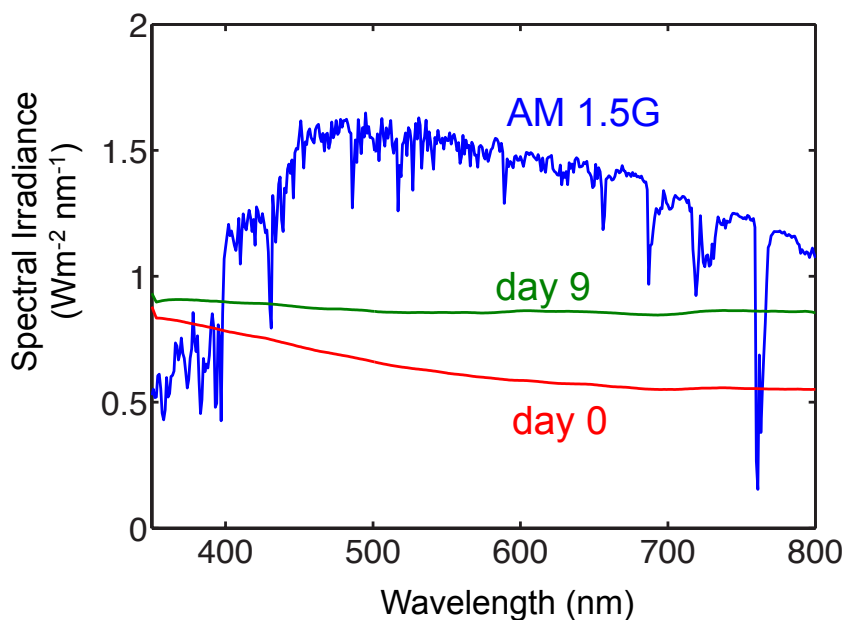


Figure S2: Using AM 1.5G solar irradiance data (denoted as G), and absorbance data (denoted as κ) of fd-GO samples annealed at 80°C, we estimated the enhancement in sunlight absorption of annealed GO samples compared to as-synthesized GO samples. We calculated the net absorbance for day 0 and day 9 cases using the formula:

$$P = \int_{350}^{800} G(\lambda) \cdot \kappa(\lambda) d\lambda$$

The ratio obtained showed an absorption enhancement of about 38% in the day 9 sample compared to the as-synthesized sample within the wavelength range 350-800 nm. We expect this value to increase further if a wider wavelength range (including the infrared) is considered. Such an enhancement has a significant impact on optoelectronic devices making use of GO.

3. X-ray photoelectron spectroscopy (XPS) measurements on annealed GO samples

X-ray photoelectron spectroscopy measurements were done using a PHI VersaProbe II Scanning XPS microprobe (Physical Electronics Inc., MN, USA). Al K_{α} source was used, with an incident X-ray photon energy of 1486.7 eV. The spot size was 200 μm , with a sample tilt of 45° and a hemispherical analyzer with a pass energy of 23.5 eV. The samples used for XPS were prepared by drop-casting GO suspensions on a clean Si substrate. In the case of fd-GO samples, in order to maintain consistency, we dispersed annealed fd-GO samples in water, and then drop-casted them on to a Si substrate.

All the XPS spectra reported in this paper were acquired under the same acquisition conditions. After acquiring the scans, we employed the CasaXPS software (Casa Software Ltd.) for spectral data analysis. After a Shirley background subtraction and applying a Savitzky-Golay smoothing filter, and correction for the different X-ray cross-sections using the Scofield sensitivity factors, we fitted peaks to the spectra. The C 1s spectra were fitted to 3 Gaussian-Lorentzian peaks (C=C-C, C-O-C and C=O/HO-C=O) using the constraint of equal Gaussian-Lorentzian pre-factors, while leaving the full-width at half maximum (FWHM) of the peaks to be freely variable. A similar fitting technique was used for the O 1s spectrum.

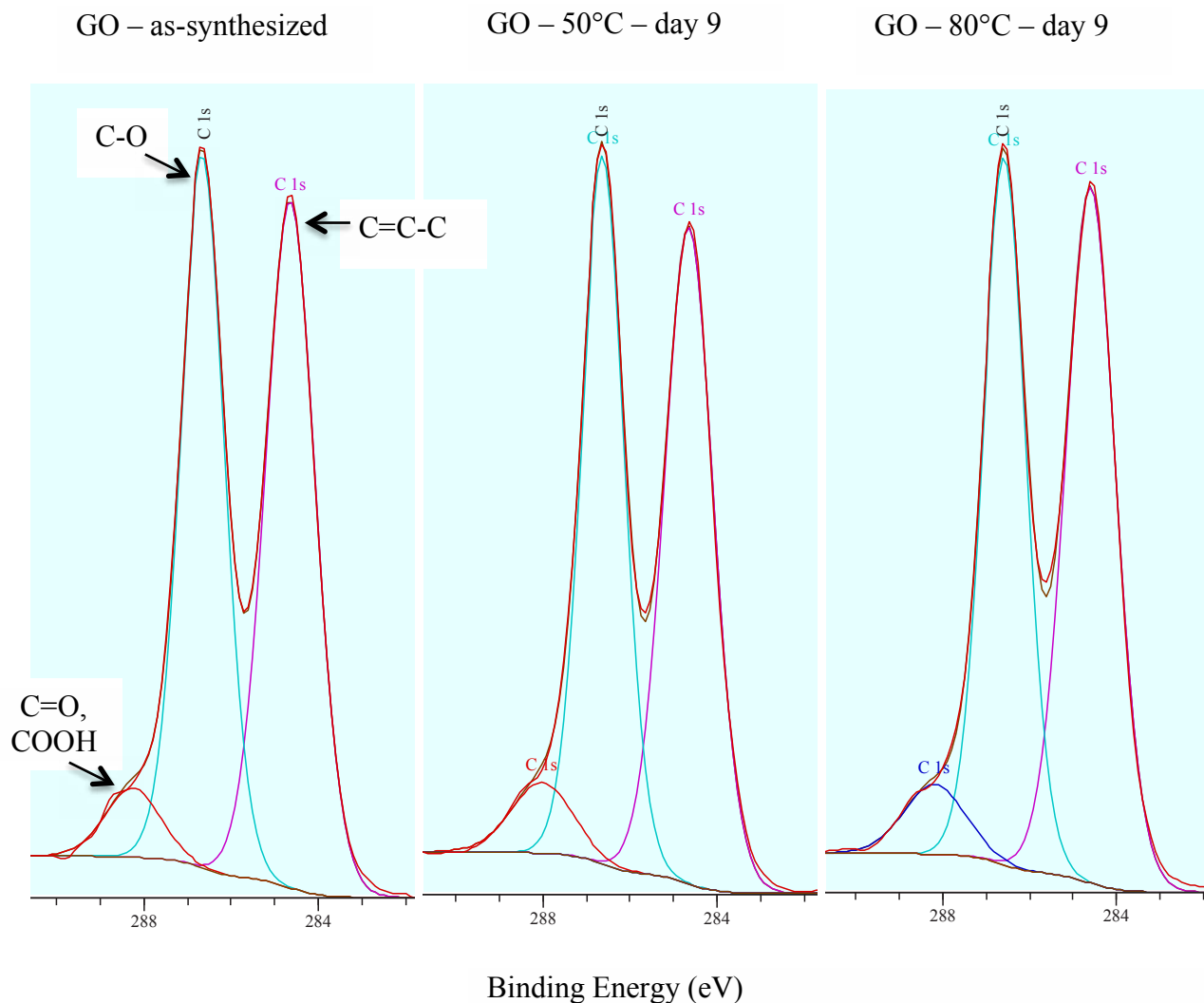
(a) XPS results on GO suspensions

Figure S3: XPS data comparing C1s spectra of GO suspensions annealed at 50 and 80°C show weak changes in the peak intensities compared to the as-synthesized sample even after the entire course of annealing, indicating weaker structural transformations and lower kinetics of phase separation in annealed GO suspensions. The calculated oxygen contents were ~34, 33 and 31 at.% for as-synthesized GO, GO-50°C-day-9 (annealed at 50°C for 9 days) and GO-80°C-day-9 samples, respectively.

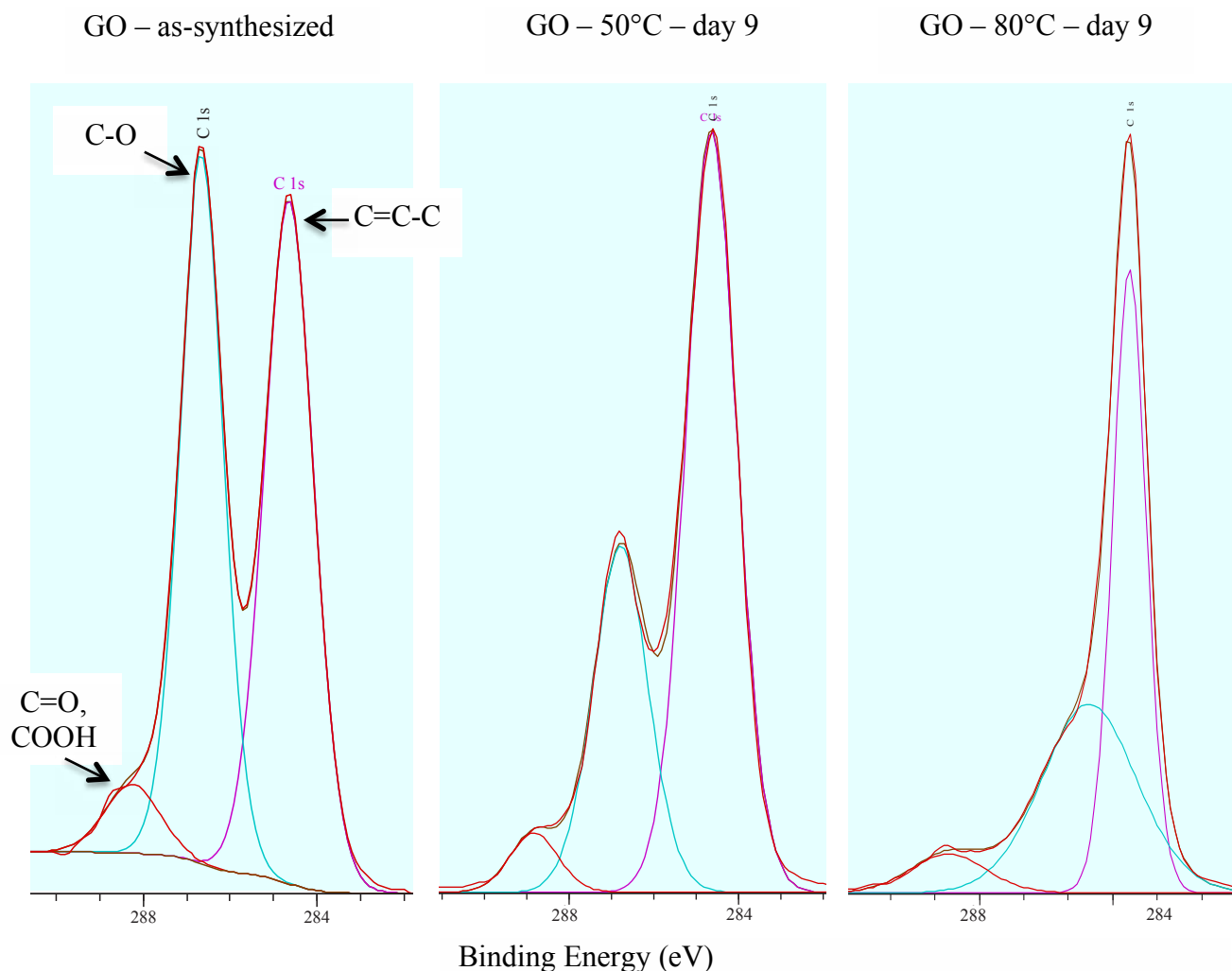
(b) XPS results on fd-GO samples

Figure S4: XPS data comparing C1s spectra of fd-GO samples annealed at 50 and 80°C show stronger relative changes in the peak intensities compared to the as-synthesized sample. Particularly, the C=C-C intensity increases relative to the C-O and C=O, COOH intensities, indicating prominent formation of graphitic regions in annealed fd-GO samples and supporting our hypothesis of phase separation in annealed GO. At the same time, we monitored the O1s spectra of annealed fd-GO samples as shown in Figure S5, which indicated no changes covalently bonded oxygen network in annealed GO. The calculated oxygen contents were ~27 and 28 at.% for GO-50°C-day-9 and GO-80°C-day-9 samples, respectively.

O 1s spectra

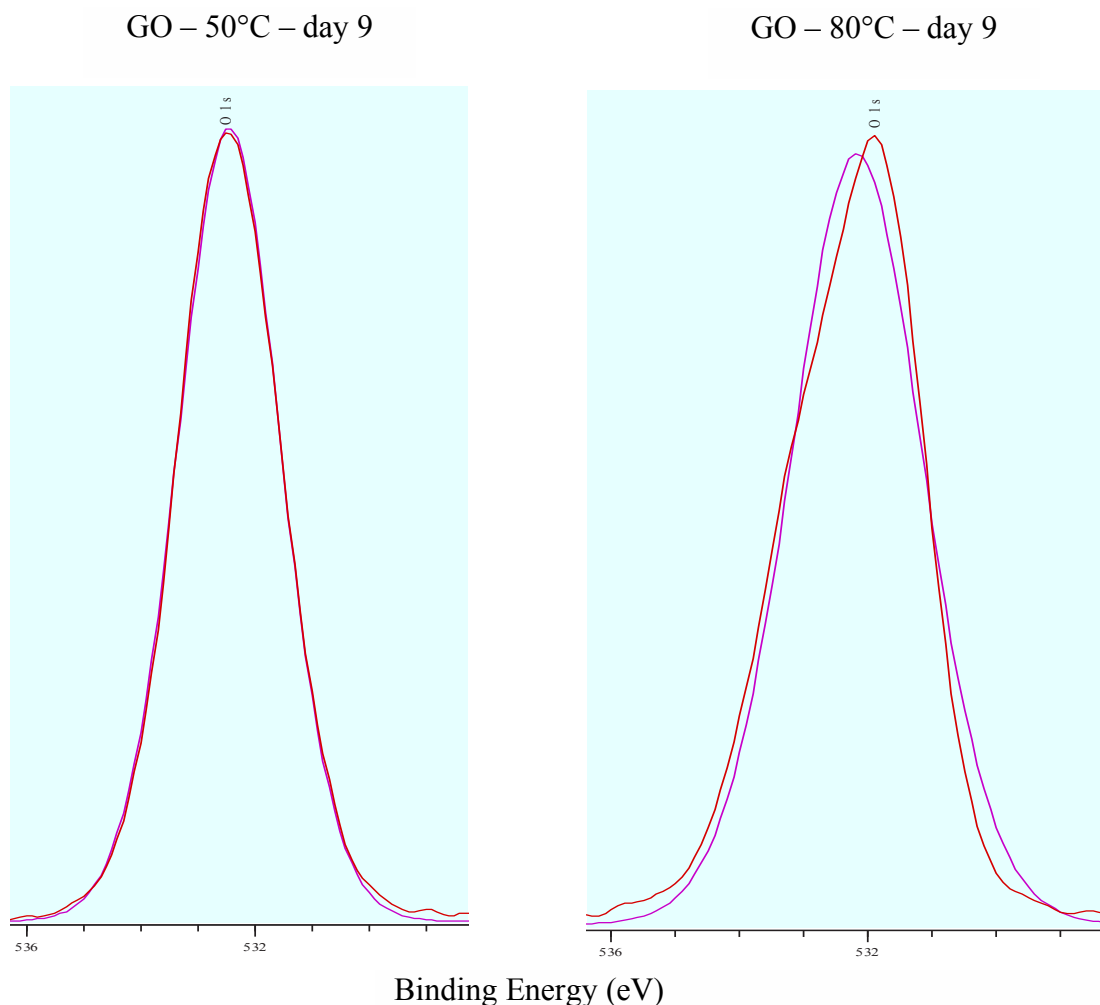


Figure S5: O 1s spectra of annealed fd-GO samples.

Kim *et al.*^[S3] have previously shown that as-synthesized GO structures are metastable and can undergo a small amount of reduction with time due to the interaction between oxygen and chemisorbed H atoms at room temperature. They observed GO samples with an O:C ratio of 0.44 to get reduced to an O:C ratio of 0.38, which corresponds to a slight ~3 at.% reduction in oxygen. We could certainly expect this reduction process to be accelerated at the temperatures used in our experiments, and hence the slight reduction in oxygen content observed in our experiments can be attributed to this process. However, this reduction process is shown to be limited by the amount of C-H species and attain a steady state. Hence, we expect this process to play a minor role in the structural transformations observed in our work that shows continuous changes over 5 to 9 days at 80°C.

4. FTIR measurements on fd-GO samples

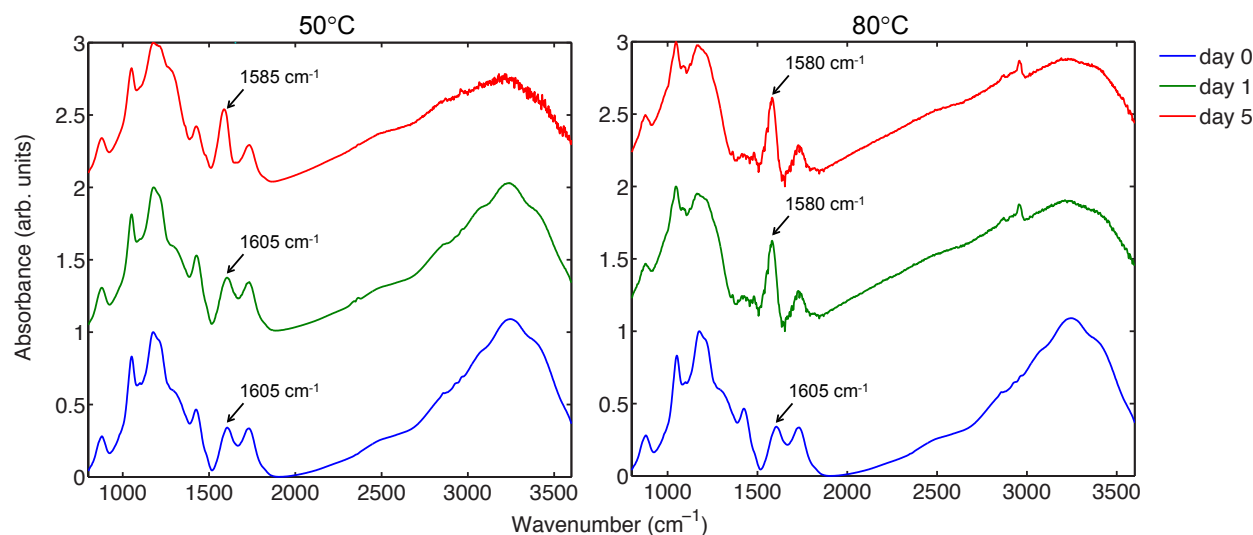


Figure S6: FTIR measurements were performed on fd-GO samples during the course of annealing to discount the effects of the solvent environment (water in this case). As noted in the main text, the effect of thermal annealing on fd-GO samples are much stronger compared to the case of GO suspensions, i.e. the structural transformations are accelerated in the fd-GO case. This fact is evident from the visible absorbance spectra (see main text, Figure 1a and Supplementary Figure S1) and is further supported by the FTIR spectra of fd-GO samples. For example, FTIR spectra of fd-GO annealed at 50°C for 5 days already shows the C=C peak at 1585 cm⁻¹ which was not observed in the corresponding GO suspensions even after 9 days of annealing at 50°C.

These FTIR spectra further illustrate the disappearance of the water peak, usually observed above 1600 cm⁻¹ [S3,S4,S5], which is consistent with the TGA experiment that reveals loss of water (~10%, see main text). The formation of a new peak at around 1580 cm⁻¹, which has been previously observed^[S4, S5], is thus attributed to the formation of prominent C=C domains.

5. Additional evidence for phase separation and estimation of graphitic domain size

In order to further corroborate our hypothesis on clustering and prominent formation of sp^2 domains during thermal annealing, we performed Raman analysis on fd-GO samples, where the effects of annealing on structural transformations were much stronger. Unpolarized Raman spectra were recorded at room temperature on GO films prepared from annealed fd-GO samples on a glass substrate. Mapping images were acquired using Renishaw Raman / PL system with moving stage (100nm precision) using 488 nm laser source and 100x short working distance optical lens (Olympus 100x).

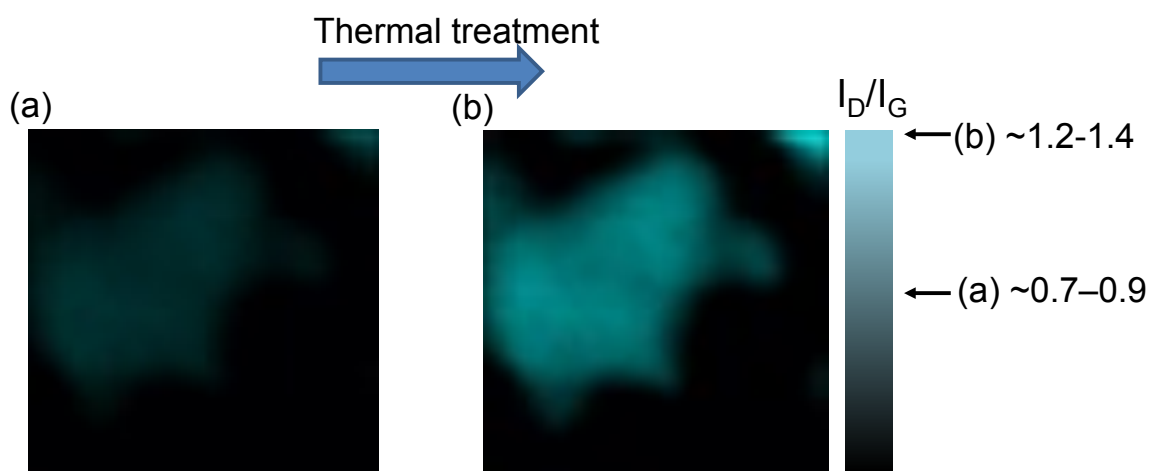


Figure S7: Raman mapping on as-synthesized and annealed GO flakes (at 80°C for 5 days). The mapping is performed in such a way that the brightness corresponds to the I_D/I_G ratio. Clearly, the annealed sample is brighter and corresponds to a higher I_D/I_G ratio.

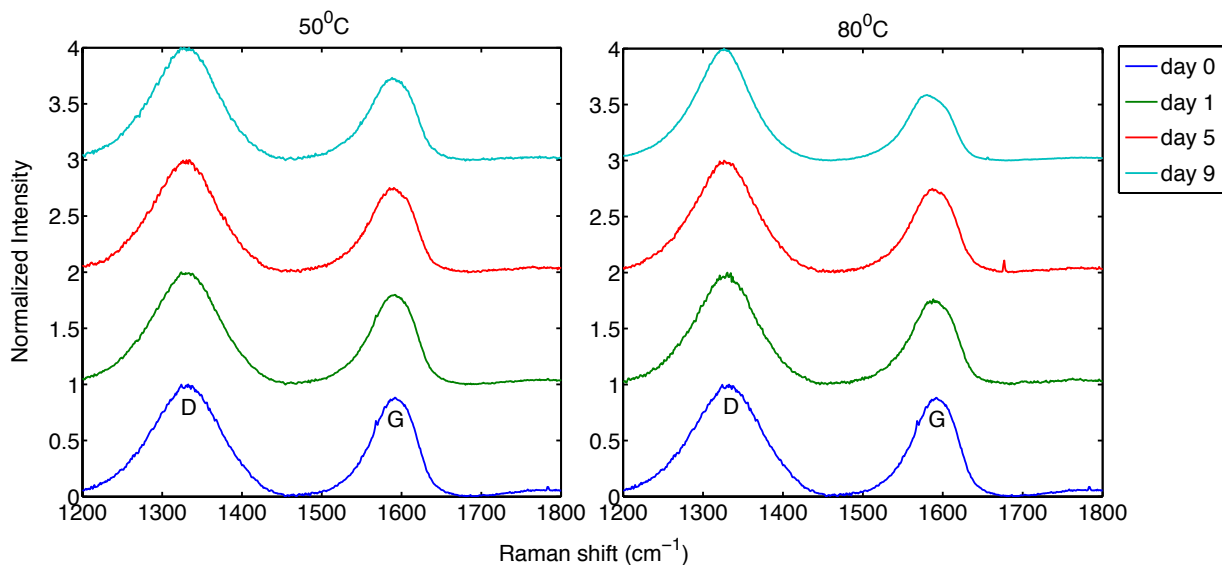


Figure S8: Raman measurements on annealed fd-GO samples at different anneal times. The I_D/I_G ratio increases from 1.14 to 1.37 for the 50°C case, while the same increases from 1.14 to 1.75 for the 80°C case.

The two prominent features obtained from GO samples (D and G peaks, as shown) were used to analyze our hypothesis of phase separation in annealed GO samples. In a seminal paper by Ferrari and Robertson^[S6], it is reported that in amorphous carbons, the development of a *D* peak indicates ordering and clustering of sp^2 domains, exactly opposite from the case of graphite. This trend is observed in the high-defect regime in an amorphous carbon structure. Considering that GO is a 2D amorphous carbon nanomaterial, indeed, our Raman analysis shows an increasing I_D/I_G ratio upon annealing GO samples at both 50 and 80°C, indicating ordering and prominent formation of graphitic domains upon thermal annealing. These changes are also more prominent at 80°C, showing the effect of annealing temperature on the kinetics of phase separation.

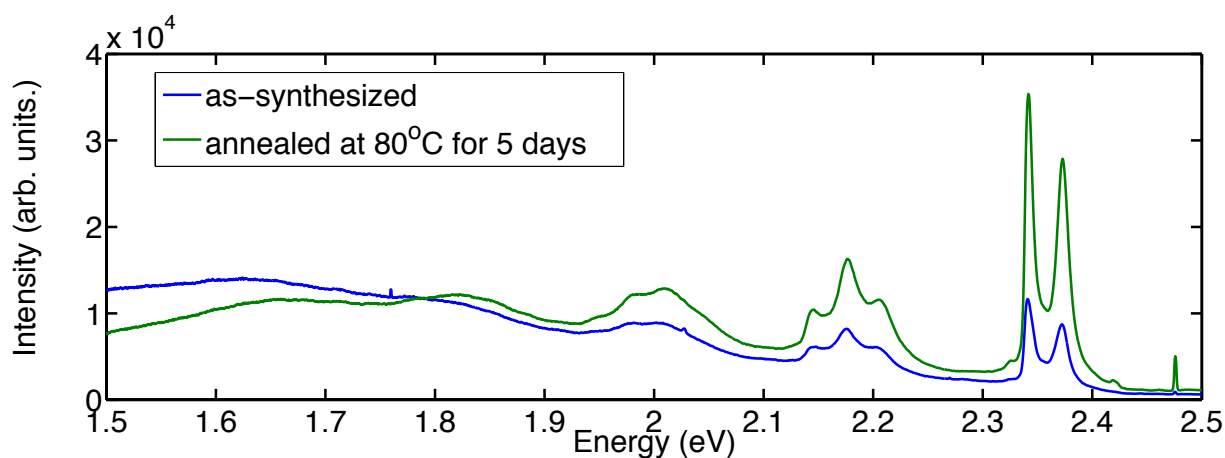


Figure S9: PL measurements on as-synthesized and annealed GO thin films. Clearly, the PL emission is enhanced in the blue upon annealing. A new broad peak at 1.83 eV appears, while the peaks at 2, 2.17 and 2.3-2.4 eV are enhanced significantly.

We can estimate the graphitic domain size from Raman and PL analysis. The I_D/I_G ratio indicates the graphitic domain size in an amorphous carbon sample^[S6]. In the high-defect regime, the Tuinstra-Koenig relation is not applicable, and the domain sizes do not exceed 2 nm in size^[S6]. Comparing the I_D/I_G ratio to the empirical data presented in Ref. S5, we obtain a domain size of ~ 1.8 nm for fd-GO samples annealed at 80°C for 9 days. Thus, we expect the domain sizes to be on the order of 1-2 nm.

We also note a significant enhancement in PL emission of annealed GO samples within the energy range 2-2.5 eV as seen in Figure S9, and also at ~ 450 nm (2.75 eV) for annealed GO solutions as shown in the main text. This emission (2-2.75 eV) corresponds to confined graphitic domains consisting of about 15-35 aromatic rings as detailed in Ref. S1, that in turn translates into a domain size of 1-2 nm, in good agreement with the domain sizes predicted from our Raman analysis.

Regarding diffusion of functional groups, it should be noted that phase separation is limited by the diffusion of epoxy functional groups due to their higher activation barrier of 0.83 eV compared to 0.30 eV of hydroxyl groups. To confirm the possibility of nanometer scale diffusion of epoxy groups, we estimated the diffusion length of the epoxy groups over the period of annealing. By assuming an Arrhenius expression for the rate of hopping of the epoxy groups, we can obtain the diffusivity relation as follows:

$$D = \frac{1}{4} d^2 k_0 \exp\left(\frac{-E_a}{kT}\right)$$

$$L \sim \sqrt{Dt}$$

Using the values for parameters from Ref. [S7], i.e. jump length, $d = 1.23 \text{ \AA}$, attempt frequency, $k_0 = 26 \text{ THz}$, the computed activation barrier, $E_a = 0.83 \text{ eV}$, and a total time period of 9 days; we obtain diffusion lengths on the order of 330 nm at 80°C and 90 nm at 50°C. Although these values are ideal and should be considered as the upper limit of diffusion lengths, these nevertheless justify the fact that the oxygen functional groups have the potential to diffuse considerably to open up graphitic domains on the order of 1-2 nm as estimated from Raman and PL analysis.

6. Stacking of GO layers

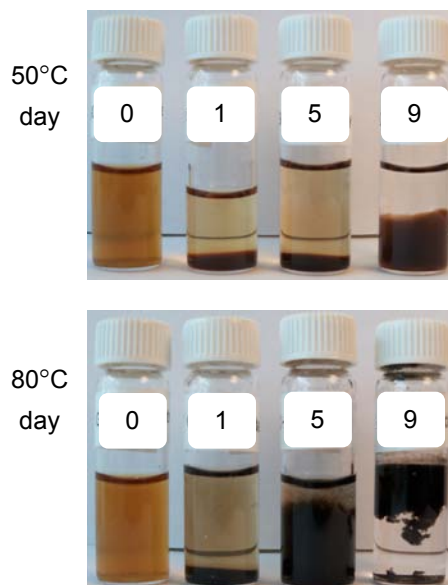


Figure S10: During the course of annealing GO suspensions, we observed increasing stacking and formation of multilayer GO samples as shown above, which indicates π -conjugation and increasing graphitization in individual GO layers^[S8]. Clearly, stacking was more pronounced in the case of samples annealed at 80°C. Settling of GO samples was also observed in the case of fd-GO samples re-dispersed in water. Although GO suspensions are unstable upon annealing and have a tendency to settle down over a time of few hours, they can nevertheless be suspended for longer after being subjected to vigorous vortexing followed by sonication. This procedure was used to characterize GO suspensions.

7. Energetics of the phase separation process considering ordered and chemically homogeneous oxidized phases

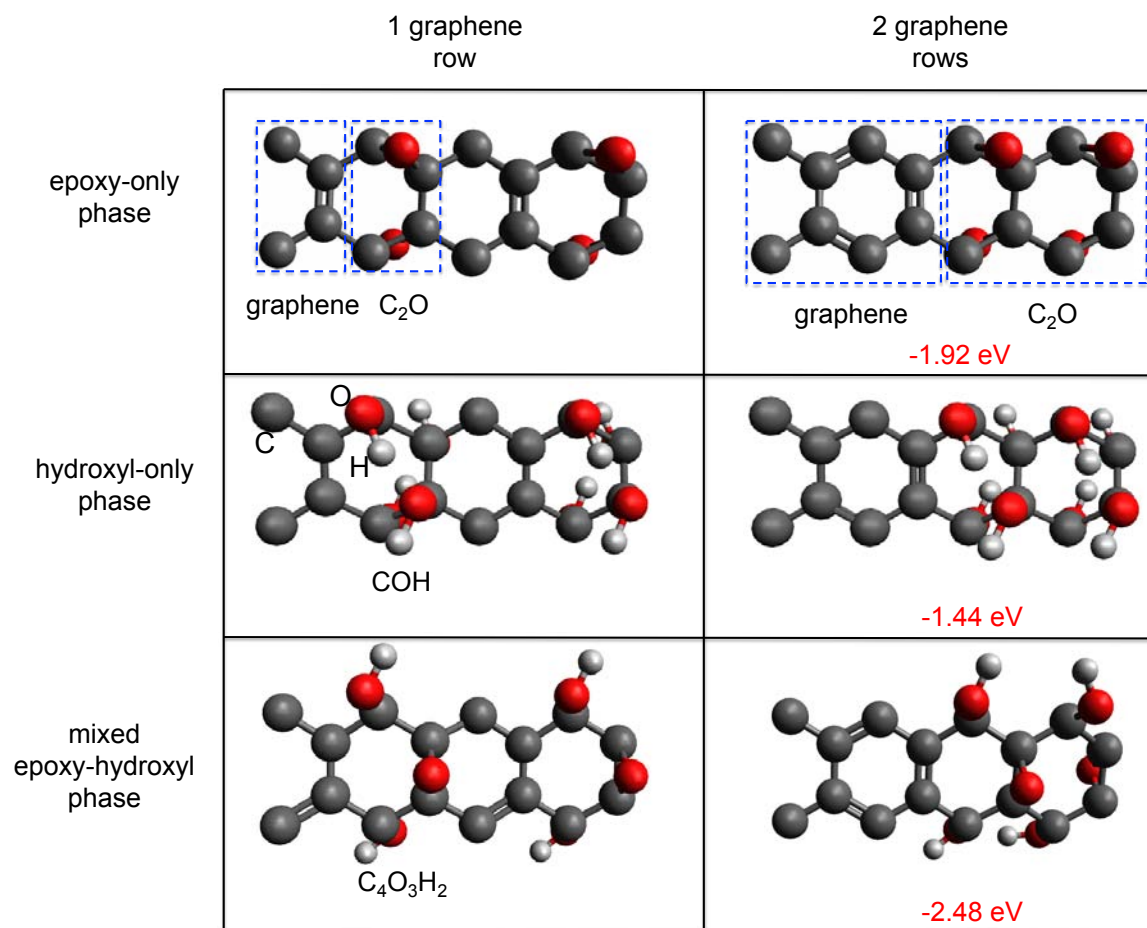


Figure S11: We have performed additional DFT calculations to test our hypothesis of phase separation in GO structures. Our calculations in the main text were performed on disordered GO structures (where oxidized domains are chemically inhomogeneous and oxygen groups are randomly positioned), which are more realistic. However, here we show that phase separation is thermodynamically favorable even when we consider ordered phases of idealized oxidized domains. As shown in the figure above, we have considered 3 different ordered phases: epoxy-only phase (C₂O), hydroxyl-only phase (COH) and a mixed epoxy-hydroxyl phase (C₄O(OH)₂). In all three cases we observe that phase separation is favorable, i.e. structures with two graphene rows together are more

favorable than the structures where they are separated by the oxidized phase. The stability of the phase-separated structure (2 graphene rows) relative to its counterpart on the left (1 graphene row) is also reported in red text.

Another way of looking at this picture is to note the number of interfaces between oxidized and graphene domains. The structure is more favorable when the number of interfaces is lower (two on the right structure compared to four on the left structure). Although this is a preliminary observation, the impact of interface composition on the stability of GO structures deserves further attention.

8. Estimation of optical gaps in phase separated GO structures

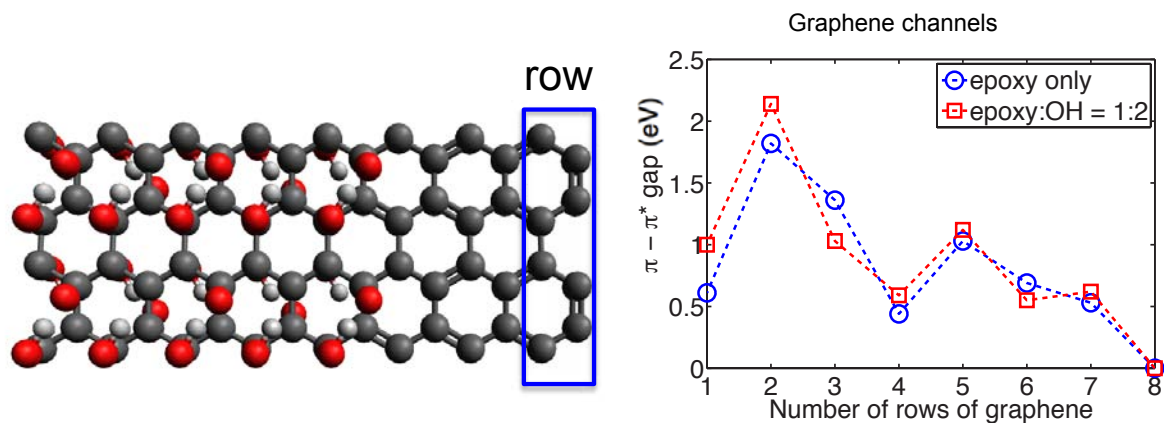


Figure S12: To estimate the optical gaps in phase separated GO structures with varying degree of phase separation, we prepared GO structures formed by alternating one-dimensional stripes of laterally confined graphene domains of different widths within oxidized domains. We computed the optical absorption spectra of these GO structures within the random phase approximation (RPA) at the DFT level of theory^[S9].

These structures represent different levels of confinement of sp^2 graphene domains within the sp^3 matrix. In addition to the well-known case of confined graphene dots^[S1], this result shows that the phase separation process can open up a wide range of optical gaps (~ 0.5 - 2.5 eV), which are found to be responsible for the increasing visible absorption and the blue shift in PL observed in annealed GO structures. These results suggest opportunities in patterning alternating graphene/GO stripes and enabling the fine-tuning of the PL peak frequency in the visible, by controlling the size of these domains and oxygen composition of the GO domain.

9. Additional details on synthesis of GO

(a) Detailed synthesis procedure

Graphite oxide was synthesized using the Hummer's approach. Briefly, 1 gm of synthetic graphite powder (-325 mesh, 99.9%, Alfa Aesar, MA, USA) was used as the starting material. To this, 0.5 gm of NaNO_3 (99%, Alfa Aesar, MA, USA) was added with 23 mL of H_2SO_4 (ACS reagent grade, 95-98%, Sigma-Aldrich, MO, USA) in a pre-cooled beaker kept at 0°C in an ice bath. 3 gm of KMnO_4 (99%, Alfa Aesar, MA, USA) was added to the mixture under vigorous stirring using a magnetic stir plate, taking care that the temperature does not rise above 20°C . After the addition was complete, the suspension was removed from the ice bath and heated at 35°C for 30 min. At the end of the reaction, the paste thickened to a brownish grey color, with reducing gas evolution. Thereafter, 46 mL of deionized water (18.2 $\text{M}\Omega\text{-cm}$ at 25°C , EMD Millipore, MA, USA) was added, causing an exothermic reaction with violent effervescence and an increase in temperature to $\sim 95^\circ\text{C}$. The diluted suspension was maintained at 95°C for 15 min. It was further diluted by adding 70 mL of warm water, and treated with 3% H_2O_2 (Sigma-Aldrich, MO, USA) to reduce the unreacted KMnO_4 and MnO_2 to colorless soluble MnSO_4 . As soon as peroxide was added, the suspension turned bright yellow. This suspension was filtered using a filter paper (grade 597, 4-7 μm , Whatman, NJ, USA), while still warm, resulting in a yellow-brown filter cake. The filter cake was washed 3 times with a total of 140 mL of warm water to remove unreacted salts. Finally the graphitic oxide residue cake on the filter paper was resuspended in 320 mL of water, to give a GO suspension of $\sim 0.5\text{wt.}\%$ solids. The suspension was put in a sealed glass bottle and kept in a vacuum desiccator for long-term storage. It was observed that the stock suspension is stable at room temperature, without the addition of any surfactant, and negligible settling of solids was observed over 6 months.

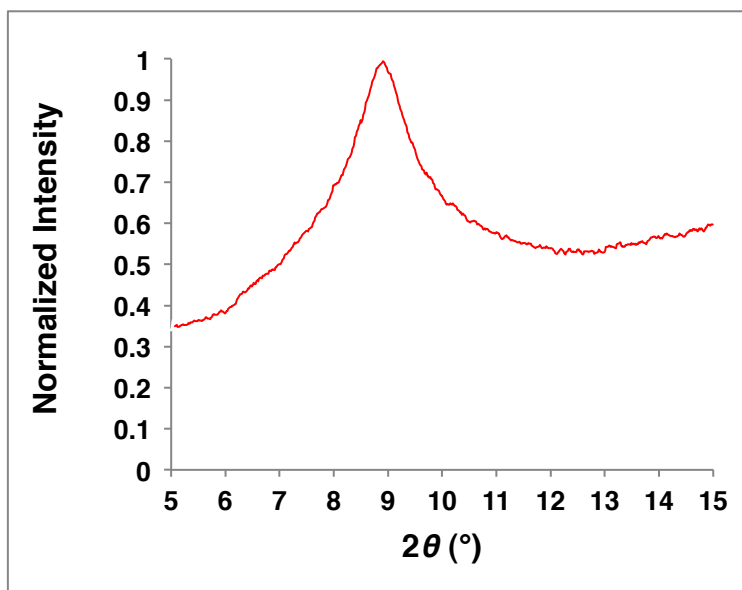
(b) XRD data of as-synthesized GO

Figure S13: Using the relation $n\lambda = 2d\sin(\theta)$, and related parameters: $n = 1$, $\lambda = 1.5406$ Å and $2\theta = 8.87837^\circ$, we obtain the interlayer spacing in our GO samples, $d = 9.95$ Å, in agreement with previously reported values on the order of ~ 9 Å. ^[S10]

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