Exploiting the Surface Properties of Graphene for Polymorph Selectivity

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S1. Crystallisation set-up

Figure S1 shows the experimental set-up used for the crystallisation of glycine. Crystallisations were carried out in the following way: a substrate was placed in the centre of a plastic box, a 2 μL droplet of glycine solution was deposited on the substrate and then it was covered by a clean glass slide, without any contact between the droplet and the cover. The glass slide allowed a 1 mm gap to be present at the front of the sample box. All crystallisations were carried out in an incubator kept at 21 °C.

![Image of the crystallisation set-up.](image)

S2. Raman spectrum of glycine

Glycine crystallises in three distinct polymorphic forms at ambient conditions, denoted as $\alpha$, $\beta$, and $\gamma$. The relative stabilities of these polymorphs are: $\gamma > \alpha > \beta$. The most commonly obtained metastable $\alpha$-form crystallises from aqueous solution; the stable $\gamma$-form can be obtained from acidic or basic solutions; while the unstable $\beta$-form crystallises from mixtures of ethanol or methanol with aqueous glycine solutions and it readily transforms to the $\alpha$-form upon contact with humid air. It has been shown that all three polymorphs of glycine crystallise simultaneously upon evaporation of aqueous solution microdroplets, which makes polymorphs of glycine classified as concomitant polymorphs.

Figure S2.1 shows the distinct Raman spectra of the CH region (2900-3050 cm$^{-1}$) of the three polymorphs of glycine. These peaks represent the symmetric (lower shift) and asymmetric (higher shift) stretches of the C-H bonds. The positions of these modes are distinct for each polymorph, which were found to be at 2972 cm$^{-1}$ and 3007 cm$^{-1}$ for the $\alpha$-form, at 2953 cm$^{-1}$ and 3008 cm$^{-1}$ for the $\beta$-form and at 2962 cm$^{-1}$ and 3000 cm$^{-1}$ for the $\gamma$-form. Only $\alpha$- and $\beta$-forms were considered in our study as $\gamma$-form was not detected.
A Raman map was obtained by scanning the whole area of a crystallised glycine droplet to ascertain the overall distribution of the polymorphs within the product crystal, as shown in Figure S2.2. This map shows the intensity ratio for the symmetric C-H stretch of the β-form (2953 cm$^{-1}$) to α-form (2972 cm$^{-1}$): a low ratio corresponds to α-form, while a high ratio corresponds to β-form. Raman spectroscopy confirms that the bulk of the droplet exclusively consists of the metastable α-form, while the unstable β-form preferentially nucleates at the edge of the droplet, as expected from literature. To be more quantitative, ~10% of the crystals grown at the contact region are α- and ~90% are the β-form. This outcome has been attributed to the higher supersaturation rate generated at the droplet contact region, which should allow formation of a less stable polymorph. Since Raman mapping on such a large scale is extremely time consuming, the analysis of the polymorphic outcome in this work has been performed by taking individual measurements of each crystal at the droplet contact region.

**S3. Graphene dispersion characterisation**

After the electrochemical exfoliation process (see Methods), the graphene dispersions were characterised with several techniques. Figure S3.1a shows the typical UV-vis spectra of graphene dispersions. The concentration of the dispersions was calculated from the absorbance value taken at a wavelength of 660 nm and applying the Beer-Lambert Law.
A detailed Raman characterisation of graphene produced by ECE has been recently provided by our group,\textsuperscript{10} hence we only provide a brief overview of the results in this section. Figure S3.1b compares the Raman spectra taken from isolated flakes of ECE(NH$_4$) and ECE(K) samples. The Raman spectra show the characteristic peaks of solution processed graphene:\textsuperscript{11} the G, D, D’ and 2D peaks, which are observed at ~1580 cm$^{-1}$, ~1350 cm$^{-1}$, ~1620 cm$^{-1}$ and ~2690 cm$^{-1}$, respectively, can be seen for both samples. The D peak, a defect activated feature,\textsuperscript{12,13} is also observed in graphene produced by liquid phase exfoliation\textsuperscript{11} as these flakes have a size smaller than the laser spot, so the edges act as defects.\textsuperscript{14} However in our case, the average size of the flakes is a few micrometers,\textsuperscript{15} so the D peak is likely to be activated by structural defects (e.g. formation of C-O bonds), which are known to form during the intercalation process, resulting in the partial oxidation of ECE graphene.\textsuperscript{15,16}

The Raman spectrum of defective graphene can be described with a phenomenological three-stage amorphization trajectory.\textsuperscript{12} In stage 1, starting from pristine graphene, the Raman spectrum evolves as follows: the D peak appears and the intensity ratio between the D and G peaks ($I_D/I_G$) increases; the D’ appears; all the peaks broaden and G and D’ begin to overlap. In this stage, $I_D/I_G$ can be used to estimate the amount of defects,\textsuperscript{12,17} while $I_D/I_{D'}$ can be used to distinguish between different type of defects.\textsuperscript{13} At the end of Stage 1, the G and D’ peaks are no longer distinguishable and $I_D/I_G$ starts decreasing. As the number of defects keeps increasing, the Raman spectrum enters Stage 2, showing a marked decrease in the G peak position and increase broadening of the peaks; $I_D/I_G$ sharply decreases towards zero and
second order peaks are no longer well defined. Stage 3 describes amorphous materials with increasing sp$^3$ content.$^{12}$

![Graph showing UV-vis spectra](image)

**Figure S3.1** (a) UV-vis spectra of a 5x diluted ECE(K) dispersion (black) and a 10x diluted ECE(NH$_4$) dispersion (red). (b) Raman spectra of ECE(K) graphene and ECE(NH$_4$) graphene samples measured with a laser wavelength of 514.5 nm, 100x magnification and a 2400 l/mm grating.

Figure S3.2 shows representative fits of the Raman peaks, obtained by using a Lorentzian function. Table S1 shows the results of the fits. From the full width at half maximum (FWHM) of the peaks, we can conclude that the samples are defective and belong to Stage 2, so defects quantification is not possible. However, all the Raman peaks are broader for the ECE(NH$_4$) sample compared to the ECE(K) sample: in particular the FWHM of the G peak is $\sim$35 cm$^{-1}$ for ECE(K) and $\sim$65 cm$^{-1}$ for the ECE(NH$_4$) (Table S1). Furthermore, the G and D' peaks are still distinguishable for ECE(K), whereas they overlap considerably for the ECE(NH$_4$) sample. These observations indicate that both samples are highly defective, but ECE(NH$_4$) graphene contains, on average, a higher concentration of defects than the ECE(K) sample.$^{12}$ The defects are likely to be oxygen-containing functional groups which are formed during the ECE process.$^{16}$
Figure S3.2 Raman spectra showing the fittings of (a) D, G and D’ peaks and (b) 2D peak of ECE(NH₄) graphene sample. Raman spectra and related fittings of (c) D, G and D’ peaks and (d) 2D peak of ECE(K) graphene sample.

Table S1 | Fitting results of Raman spectra of ECE(NH₄) and ECE(K) samples. The position and the fullwidth at half maximum (FWHM) of the peaks are reported.

| Sample   | Peak | Position / cm⁻¹ | FWHM / cm⁻¹ |
|----------|------|-----------------|--------------|
| ECE(NH₄) | D    | 1349.4          | 70.4         |
|          | G    | 1585.9          | 64.9         |
|          | D’   | 1616            | 20.7         |
|          | 2D   | 2698.3          | 125          |
| ECE(K)   | D    | 1348.1          | 39.9         |
|          | G    | 1584.6          | 34.4         |
|          | D’   | 620.8           | 15.8         |
|          | 2D   | 2689.4          | 79.4         |
**S4. Surface area and volume ratio calculations**

Figure S5 shows an example of a spherical cap. The surface areas of glycine droplets on different substrates were calculated by applying the obtained contact angles (see Section 5.2) as cap angles ($\theta$) to the spherical cap model. The fixed volume ($V$) of 2 $\mu$L and the cap angles were applied to Equation 1 in order to obtain the radius ($r$) values:

$$V = \frac{\pi}{3} r^3 (2 + \cos \theta)(1 - \cos \theta)^2$$  \hspace{1cm} (1)

Following, the surface areas (SA) were obtained using Equation 2:

$$SA = 2\pi r^2 (1 - \cos \theta)$$  \hspace{1cm} (2)

Finally, the surface area values were divided by a fixed volume of 2 $\mu$L in order to obtain Surface area and Volume ratios.

*Figure S4 An example of a spherical cap (red).*
S5. Additive-templated Crystallisation

S5.1 Samples

Figure S5.1 shows the final solutions used for the additive-templated crystallisation consisting of 0.5 M glycine in 3:1 v/v water/IPA with varying concentrations of ECE graphene.

Figure S5.1 Photo of the range of graphene concentrations generated for the additive-templated crystallisation of glycine. The [Gr] ranged from $4.57 \times 10^{-2}$ mg mL$^{-1}$ to $2.63 \times 10^{-4}$ mg mL$^{-1}$.

S5.2 Contact Angle Measurements

Figure S5.2 shows the contact angle measurements for a select few of the graphene/glycine dispersions. The contact angles were found to be $\approx 40^\circ$, $\approx 39^\circ$ and $\approx 40^\circ$ for the three concentrations of ECE(K) shown. For the ECE(NH$_4$) dispersions, contact angles of $\approx 47^\circ$, $\approx 36^\circ$ and $\approx 40^\circ$ were measured.

Figure S5.2 Contact angle measurements of various solutions used in the additive-templated crystallisation experiments. (a) 0.5 M glycine in 3:1 water/IPA; (b) mixtures containing ECE(K) Gr flakes at concentrations: i) $2.6 \times 10^{-2}$ mg mL$^{-1}$; ii) $1.3 \times 10^{-3}$ mg mL$^{-1}$, and iii) $2.6 \times 10^{-4}$ mg mL$^{-1}$; (c) mixtures containing ECE(NH$_4$) Gr flakes at concentrations: i) $4.6 \times 10^{-2}$ mg mL$^{-1}$; ii) $2.3 \times 10^{-3}$ mg mL$^{-1}$, and iii) $4.5 \times 10^{-4}$ mg mL$^{-1}$. 
S5.3 Morphology

The observation noted in the main text regarding the distinct morphologies of the crystals can be rationalised by considering the solubility curve of glycine and relative growth and nucleation rates, $k_G$ and $J$, respectively. Both $k_G$ and $J$ are dependent on the driving force for crystallization, which is typically expressed as the ratio of the actual liquid concentration to the equilibrium/solubility concentration. The solution begins undersaturated and via evaporation of the solvent crosses the supersaturation threshold into glycine’s metastable zone (MSZ).\textsuperscript{19}

In this region, crystal growth dominates over nucleation (a low $J/k_G$ ratio) so if the system were to crystallise, larger crystals would form. If the solvent continues to evaporate, the system will move past the MSZ into high supersaturation, where nucleation events dominate over crystal growth (a high $J/k_G$ ratio).\textsuperscript{20} It must be noted here that the crystals obtained from a pure water system (example shown in Figure S2.2) were always compact, thus implying that the addition of IPA, an antisolvent, causes a widening of the MSZ width, as already observed.\textsuperscript{21,22}

The effect of graphene on the crystal morphology can be seen in Figure 2f-k. At the highest graphene concentrations, the system always crystallises with a compact morphology (Figures 2f and i). With a decreasing graphene concentration, the likelihood of obtaining the larger crystals increased (Figures 2g, h, j and k). We can infer from this result that graphene is narrowing the width of the MSZ meaning that nucleation is always dominant over crystal growth. This conclusion is reinforced by previous work on MSZ width measurements, where additives (such as sea salt and oxalic acid) could reduce the MSZ width with and produce smaller, more compact crystals.\textsuperscript{23,24} Figure 2f and i also show coffee-ring deposits for the high graphene concentration samples.\textsuperscript{25,26}

Figure S5.3 shows high magnification images of crystals formed at the contact region of some of the crystallising systems. They clearly show some graphene deposits underneath the crystals instead of being incorporated into them.

**Figure S5.3** High magnification (100x) images of glycine crystals grown at the contact region of a crystallising system. (a-b) Glycine crystals from Gr ECE(NH$_4$) additive-templated
crystallisations and (c) glycine crystals from Gr ECE(NH₄) substrate-templated crystallisations. The dark blue spots that can be seen are the graphene deposits. Scale bars ≈ 10 μm.

Figure S5.4 shows a representative Raman spectrum of α-glycine generated from the crystallisation experiments undertaken. The lack of any of graphene’s Raman features (i.e. a D or G peak) is further evidence that the graphene flakes do not incorporate themselves into the growing crystals.

![Raman spectrum of glycine crystals](image)

**Figure S5.4** Raman spectra of glycine crystals in the Raman shift range of 750-1800 cm⁻¹. The broad peak at ~900 cm⁻¹ is from the silicon substrate.

### S5.4 Coffee-ring analysis

Figure S5.5 is a Raman spectrum of a deposit in the coffee-ring found after the crystallisation of an ECE(NH₄) solution at the highest graphene concentration available. These rings are formed during the evaporation process due to the shift from a pinned contact line to a constant contact angle.²⁷,²⁸ During the former stage, the droplet has a constant base area allowing the Marangoni effect²⁵ to carry the graphene flakes to the first, outer edge which creates the first coffee-ring. Progressing through to the next stage of a constant contact angle, the droplet's base area decreases, therefore additional coffee-rings are generated at different stages as more graphene is deposited. The Raman retains the characteristic D, G, D' and 2D peaks found prior to crystallisation as well as the heavy overlapping of the G and D' peaks.
Figure S5.5 | Raman spectrum of a coffee-ring deposit from an ECE(NH$_4$) graphene crystallisation sample at a graphene concentration of 4.57 x 10$^{-2}$ mg mL$^{-1}$.

S5.5 Use of GO
The concentration of GO used for this set of experiments were made comparable to those of the ECE graphene samples, ranging from 5 x 10$^{-2}$ mg mL$^{-1}$ to 5 x 10$^{-4}$ mg mL$^{-1}$. All other experimental parameters were kept identical to the ECE graphene additive-templated crystallisations. The resulting crystals are vastly different, in size and morphology, to those obtained from the experiments with ECE graphene. This is attributed to the different geometries of the droplets between ECE graphene, which is hydrophobic, and GO, which is hydrophilic. Polymorph analysis was attempted by Raman spectroscopy, but the signal from GO made the determination of the glycine’s polymorph impossible.
S6. Substrate-templated Crystallisation
S6.1 ECE Graphene
S6.1.1 Coverage Analysis
Figure S6.1 shows representative Raman spectra taken from different areas with no graphene coverage (area 1), as demonstrated by the absence of the G peak, and spectra with weak (area 2) and strong (area 3) G signal which indicates the presence of graphene on the substrate.

The coverages were calculated by subtracting the number of the pixels with no G peak signal from the total number of pixels and then the sum was divided by the total number of pixels and multiplied by one hundred. Table S2 shows the graphene coverage of the Si/SiO₂ substrates for both the ECE(K) and ECE(NH₄) samples.

![Figure S6.1](image)

Figure S6.1 Representative spectra taken from areas covered with ECE(NH₄) graphene (area 2 and 3) and an area without graphene (area 1).

Table S2 | Graphene coverages on Si/SiO₂ substrates.

| Coverage  | ECE(NH₄) % covered | ECE(K) % covered |
|-----------|--------------------|-----------------|
| Low       | ~2                 | ~6              |
| Moderate  | 67-84              | 30-48           |
| Full      | 100                | 100             |

Figure S6.2 shows the optical images and the Raman maps of the samples with different ECE(NH₄) graphene coverages. The coverage was extracted by analysing the areas...
highlighted in the red rectangles. Figure S6.3 shows the optical images and the Raman maps of samples with different ECE(K) graphene coverages. The coverage was extracted by analysing the areas highlighted in the red rectangles.

Figure S6.2 Optical images of (a) low, (b) moderate and (c) full coverages of ECE(NH₄) graphene on Si/SiO₂ substrates, scale bar ≈ 250 μm. Areas of mapping are marked by red dashed rectangles. (d), (e) and (f) are StreamLine™ Raman maps of the G peak intensity corresponding to samples in (a), (b) and (c), respectively (Scale bar ≈ 100 μm; colour bar= G peak intensity, in arb. units).
**Figure S6.3** Optical images of (a) low (b) moderate (c) full coverages of ECE(K) graphene on Si/SiO$_2$ substrates, scale bar = 250 $\mu$m. Areas of mapping are marked by red dashed rectangles. (d), (e) and (f) are StreamLine™ Raman maps of the G peak intensity corresponding to samples in (a), (b) and (c), respectively (Scale bar $\approx$ 100 $\mu$m; colour bar= G peak intensity, in arb. units).

**S6.1.2 Contact Angle Measurements**

Figure S6.4 shows the contact angle measurement results on different substrates. The contact angles were found to be $\approx$61°, $\approx$71° and $\approx$94° for the low, moderate and full ECE(NH$_4$) sample, respectively. For the ECE(K) sample, the contact angles were measured as: $\approx$58°, $\approx$64° and $\approx$77° for the low, moderate and full coverages, respectively. The contact angle for glycine solution on Si/SiO$_2$ (control sample) was measured as $\approx$54°.

![Contact Angle Measurements](image)

**Figure S6.4** Contact angle measurements of glycine solution deposited on different substrates.
S6.1.3 Morphology

Figure S6.5 shows representative optical images of crystals obtained on substrates with different ECE(K) graphene coverages. It can be seen that the morphology of the crystals grown at the edge changes: the size of the crystals extending over the contact region decreases with an increasing graphene coverage, indicating a possible decrease of the $\beta$-form component.

![Optical images of glycine crystallised on Si/SiO$_2$ substrates having (a) 0%, (b) ~6%, (c) ~38% and (d) ~100% coverage of EC(K) graphene (Scale bar = 250 $\mu$m).](image)

S6.1.4 Kinetic Effects

Figure S6.6 shows the kinetic impact of graphene substrates on the crystallisation of glycine. As stated in the main text, the induction times do not follow the expected behaviour if the times were dictated by the geometry of the droplets. The implication from the geometry results of Figure 3a is that droplets should evaporate slower on the graphene substrates than on the bare silicon substrates, thus a longer induction time should be seen.$^{29}$ However, the graphene substrates had a promoting effect on the induction times, which furthers the hypothesis of H-bonding between graphene and glycine. It is unclear at this time why there is a reduction in the induction times for these substrate-templated experiments whilst there was an apparent increase in the times for the additive-templated ones, but it is likely due to the intricacies of the different solvent systems used. It is also important to remember that the induction times are all qualitative.
**Figure S6.6** Induction times for all substrate-templated crystallisations of 0.5 M of aqueous glycine solution.

**S6.2. CVD Graphene**

**S6.2.1 Coverage Analysis**
To investigate the coverage of CVD graphene, we performed Raman mapping of a large area (200 x 200 μm²). Figure S6.7 shows the 2D peak intensity Raman map (in blue) overlapped on an optical image of the same area. The presence of the 2D peak was detected from each point on the map, confirming the full coverage of graphene on Cu.

**Figure S6.7** Large area (200 x 200 μm²) Raman map (in blue) of the intensity of 2D peak of CVD Gr on Cu. Colour bar = G peak intensity, in arb. Units.
A representative Raman spectrum of CVD Gr on Cu can be seen in Figure S6.8, showing the characteristic G and 2D peaks of CVD Gr. The high crystalline quality of the film is demonstrated by the absence of the D peak and the sharp G and 2D peaks.

**Figure S6.8** Representative Raman spectrum of CVD Gr on Cu.

### S6.2.2 Morphology

Figure S6.9 shows a representative optical image of the crystals obtained on CVD Gr substrates. The crystals grown at the contact region are much smaller than that of the control samples (Figure 2d).

**Figure S6.9** Representative optical image of crystals obtained on CVD Gr substrates.
S7. Computer modelling

We computed the interaction of surfaces of α- and β-glycine crystals modelled by slabs of increasing thickness, namely with 1, 2, 3 and 4 molecular layers in vacuo and interacting with pristine graphene and oxidised graphene. The oxidised graphene model had 12.5 % OH groups and was built by adding 30 OH groups in a 240 C atoms graphene surface of 2.6 nm x 2.5 nm in a highly regular fashion, Figure S7.1. The graphene periodic box was chosen as it is approximately square and has dimensions mostly commensurate with the most significant β-form surface: (010). In addition, the β-form (010) surface is highly commensurate with the α-form (010) surface which allows for their direct comparison. To ease this comparison and the comparison of graphene and oxidised graphene, the 2D periodic box dimensions were held fixed during the optimisations. In addition, the periodic dimension perpendicular to the surface was also fixed and set, in all cases, to 10 nm.

**Figure S7.1** Optimised structures for a 2.6 x 2.5 nm² surface of (a) pristine graphene and (b) oxidised graphene (12.5 %) and commensurate 4 layers slabs of the (c) α-form and (d) β-form of the (010) glycine surfaces in vacuum.
Figure S7.2 | Optimised structures for a 2.6 x 2.5 nm² surface of pristine graphene and, from top to bottom, 1, 2, 3 and 4 layers for the (a-d) α-form and (e-h) β-form of the (010) glycine surfaces.
Figure S7.3 | Optimised structures for a 2.6 x 2.5 nm² surface of oxidised graphene and, from top to bottom, 1, 2, 3 and 4 layers of the (a-d) α-form and (e-h) β-form of the (010) glycine surfaces.

The surface energy was computed subtracting the energy of the slab against the energy of an infinite crystal. This value was normalized by the number of molecules on the surface, Table S3. The interface energy was computed subtracting the energy of the slab in vacuum against the energy of the same slab on contact with graphene and graphene hydroxyl normalized by the number of molecules at the interface. The interface energy quantifies how the presence of
graphene or oxidised graphene stabilises the crystalline surface, negative values indicate stabilising interfaces, Table S4.

**Table S3** | Surface energy per molecule for \( \alpha \) and \( \beta \) (010) glycine surfaces with 1, 2, 3 and 4 molecular layers. **All energies in eV.**

| Number of layers | \( \alpha \)-GLY | \( \beta \)-GLY |
|------------------|-----------------|-----------------|
| 1                | 1.25            | 1.24            |
| 2                | 1.58            | 0.96            |
| 3                | 1.25            | 1.05            |
| 4                | 1.47            | 1.11            |

**Table S4** | Interface energy vs. graphene (Gr) and hydroxyl graphene (Gr-OH) per molecule for \( \alpha \) and \( \beta \) (010) glycine surfaces with 1, 2, 3 and 4 molecular layers. **All energies in eV.**

| Number of layers | Gr | Gr-OH | Gr | Gr-OH |
|------------------|----|-------|----|-------|
|                  | \( \alpha \)-GLY | \( \alpha \)-GLY | \( \beta \)-GLY | \( \beta \)-GLY |
| 1                | -0.36          | -0.83          | -0.35          | -0.83          |
| 2                | -0.49          | -0.93          | -0.35          | -0.50          |
| 3                | -0.45          | -0.70          | -0.39          | -0.52          |
| 4                | -0.44          | -0.78          | -0.36          | -0.50          |
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