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Intercalation, decomposition, entrapment – a new route to graphene nanobubbles.

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Graphene Nanobubbles (GNBs) have become the subject of recent research due to their novel physical properties. However, present methods to create them involve either extreme conditions or complex sample fabrication. We present a novel approach which relies on the intercalation of small molecules (NH₃), their surface-mediated decomposition and the formation of larger molecules (N₂) which are then entrapped beneath the graphene in bubbles. Our hypothesised reaction mechanism requires the copper substrate, on which our graphene is grown via chemical vapour deposition (CVD), be oxidised before the reaction can occur. This was confirmed through x-ray photoelectron spectroscopy (XPS) data of both oxidised and reduced Cu substrate samples. The GNBs have been analysed through atomic force microscopy (AFM, after NH₃ treatment) and XPS, which reveals the formation of five distinct N 1s peaks, attributed to N₂ entrapment, N doping species and atomic nitrogen bonded with the Cu within the substrate. This method is simple, occurs at low temperatures (520 K) and integrates very easily with conventional CVD graphene growth, so presents an opportunity to open up this field of research further.

Introduction

Graphene nanobubbles (GNBs) are a phenomenon which arise due to graphene's unique combination of strength, elasticity and gas impermeability ^{1–3}. This allows the entrapment of gas molecules in small, highly pressurised mesoscale bubbles. Pressures within these bubbles have been reported to be in the order of MPa ^{4–7}, with one report achieving up to 1 GPa ⁸. The small volumes of gas contained within GNBs are therefore a route to study gas-phase reactions in small volumes or under high pressures, potentially producing new exotic phases of matter ⁹.

GNBs, and larger micro-scale bubbles, are regularly found between the graphene and silicon-oxide substrate, believed to have formed due to the trapping of air upon the transfer of mechanically exfoliated graphene flakes onto the flat substrate ^{10,11}. In case of chemical vapour deposition (CVD), where transfer is used, bubbles are usually formed due to polymeric residual or contaminants ¹². This characteristic has been utilised to directly measure graphene's adhesion to Si surfaces by intercalating gold nanoparticles underneath these 'blisters' ¹³, and to study graphene under biaxial strain ¹⁴. Accompanying theoretical studies have been made to establish the mechanical properties ⁴ and numerical methods to describe the curvature of GNBs ⁵.

These bubbles are of great interest for both fundamental science and technological applications. The high levels of strain in the GNBs have also been demonstrated to give rise to exotic physics such as strain-induced pseudo-magnetic fields of > 300 T ¹⁵ and non-linear optical behaviour ¹⁶. Furthermore, the production of GNBs has been demonstrated to facilitate lift-off and transfer of CVD graphene ^{17,18} and has been proposed as a mechanism for gas storage ^{10,19}.

Thus far, GNBs have been produced by either electrolysis ^{17–19}, extreme conditions such as intense laser irradiation ¹⁶, or by complex sample fabrication such as lithography ^{14,20}. In this paper we report a new route for the formation of GNBs based upon the intercalation of small molecules under the graphene, their substrate-mediated decomposition, forming larger molecules which are then entrapped by the graphene, creating GNBs. This process is simple, occurs at low temperatures and is easily integrated into the conventional CVD process.

Specifically, we describe the intercalation of N₂ and formation of N₂ GNBs beneath CVD monolayer graphene on Cu substrates via annealing in NH₃ gas. We show that the reaction is governed by the presence of a Cu oxide layer on the substrate. A recent study by Zhao et al. ²¹ attempted to decouple graphene from its substrate via the intercalation of N atoms through thermal treatments with N₂ gas. Their endeavour to intercalate N was chosen as, unlike the intercalation of other atoms, N atoms provide the possibility of achieving graphene charge neutrality. This would allow the same high electron mobilities that are associated with freestanding graphene, as shown using first principles density functional calculations by Caffrey et al. ²². The attempt by Zhao et al. was unsuccessful in the pressure range 1.3×10^{−6} – 0.1 mbar and temperature range of room temperature (RT) – 350 °C on both Ir(111) and Ni(111).

We have chosen NH₃ gas, as Wang et al. ²³ were able to achieve N-intercalation and N-doping through thermal treatments of

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^b Photon Science Institute, The University of Manchester, Manchester M13 9PL, UK. Electronic Supplementary Information (ESI) available: [The ESI includes details and figures on; the life span of N₂ bubbles, raw Raman data at each stage of treatment and details of the background subtractions and Raman analysis of the graphene on Cu.].

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epitaxial graphene on SiC with NH_3 . Their results indicate that the NH_3 dissociates during the thermal reaction (25 ml/min at 500 °C), leaving N atoms at the surface. Similarly to Wang et al., simultaneous N-doping of the graphene also occurs during the treatment shown in this paper. Samples have been analysed using X-ray photoelectron spectroscopy (XPS), Raman and atomic force microscopy (AFM). Raman spectra at each stage of the treatment indicate that the graphene remains intact and of high quality throughout.

Results and discussion

In our work CVD graphene on Cu substrate samples were annealed in NH_3 to a sample temperature of 600 K and a pressure of ~ 0.6 mbar, which was maintained for 20 mins. It was then cooled to 400 K before removing the NH_3 . After NH_3 treatment, XPS was carried out with no air exposure to the samples. Distinct N 1s peaks appear after the NH_3 treatment (Figure 1). In the first region a peak appears at 404.9 eV (N_{A1}) and has a lower binding energy (E_{B}) shoulder feature at 403.4 eV (N_{A2}). These peaks also persist after prolonged exposure to atmospheric conditions (Electronic Supplementary Information, ESI, Figure S1). $\text{N}_{\text{A1,2}}$ are too high E_{B} for any feasible surface bound N species, due to the reducing conditions of heating in NH_3 . Vapour reference peaks were collected for both NH_3 and air (N_2). These were positioned at 401.6 eV and 405.8 eV,

Figure 1. XPS data. A comparison of the N 1s peaks after NH_3 treatment ($\text{N}_{\text{A1,2}}$) in reference to N_2 (405.8 eV) and NH_3 (401.6 eV) vapour peaks. No N 1s peaks are present before NH_3 treatment.

respectively. Neither reference peak corresponded directly with $\text{N}_{\text{A1,2}}$, though only a minor shift of ~ 1 eV can be seen between the $\text{N}_{\text{A1,2}}$ peaks and the N_2 vapour peak. The same N 1s region before NH_3 treatment, shows no apparent peaks. Numerous reports have been made assigning an N 1s peak at ~ 404 – 405 eV to N_2 intercalated within multilayer-carbon nanotubes (ML-CNT) or captured inside the cavity^{24–27}. A study by Tillborg et al.²⁸, demonstrated the effect the substrate has on reducing the molecular nitrogen E_{B} . Using XPS they observed a screening effect through the physisorption of N_2 on highly oriented pyrolytic graphite (HOPG) at 25 K, lowering the E_{B} by up to 1.4 eV compared to free molecules. This shift in E_{B} would account for the difference in $\text{N}_{\text{A1,2}}$ and the N_2 vapour peak. Examining the C 1s shows a peak shift to lower E_{B} after NH_3 treatment (Figure 2), this indicates an electronic decoupling of the graphene from the substrate²⁹, which would also suggest intercalation between the graphene and Cu. Therefore, we propose that the NH_3 intercalates at the graphene/Cu interface, reacts with the Cu substrate and forms N_2 . Hence, the $\text{N}_{\text{A1,2}}$ peaks are ascribed to N_2 intercalated between the graphene and Cu in two different environments.

In order to establish the onset temperature of N_2 intercalation, a near-ambient pressure (NAP) XPS experiment was performed where the XPS spectra were taken in-situ during the heating of a pristine graphene sample in an NH_3 environment. The sample temperature was increased, by incrementing the e-beam heater, to a maximum of 600 K. The $\text{N}_{\text{A1,2}}$ peaks begin to appear above a sample temperature of 520 K (Figure 3a). A peak at ~ 401.2 eV in the N 1s (Figure 3a) can be seen throughout the temperature profile and is due to the NH_3 vapour above the sample. Two other regions also become apparent. The second region has a peak at 398.4 eV (N_{B2}) and the third has a single peak at 396.5 eV (N_{C}). N_{B2} is associated with nitrogen doping of

Figure 2. XPS data collected from CVD graphene samples. A C 1s comparison shows a shift to lower binding energy after NH_3 treatment and back to 284.5 eV upon release of the N_2 after UHV heating

Figure 3(a-b). In-situ XPS data collected of graphene during an NH_3 treatment. (a) The N 1s spectra shows the $\text{N}_{\text{A1,2}}$ peaks (403–405 eV) begin to appear at 520 K. (b) The overall intensity of the O 1s is shown to decrease as a function of increasing temperature. (c) This is also shown in the atomic concentration (at. %) of the individual O 1s components (Cu_2O , $\text{C}=\text{O}$, $\text{C}-\text{O}$) as a comparison to the Cu $2p_{3/2}$, with a corresponding increase in $\text{N}_{\text{A1}+\text{A2}}$ from 520 K.

graphene (specifically pyridinic doping³⁰), whereas N_{C} is attributed to either low levels of atomic nitrogen bonded with the Cu within the substrate^{31–33}, or chemisorbed nitrogen at Cu atoms formed by dissociation of N_2 ³⁴. We expect that the majority of NH_3 intercalated between the graphene/Cu interface during treatment would react with the substrate and decompose. Though trace amounts of NH_3 may remain after treatment, this would be convoluted within an N_{B1} peak (~ 400.5 eV) which is also associated with nitrogen doping (graphitic³⁰). A study by Sueyoshi et al.³⁵ on the coadsorption of NO and NH_3 on Cu(111), demonstrates the desorption of NH_3 at 300 K. This also suggests that it would not remain adsorbed to the Cu surface in our temperature range, as upon cooling after the treatment NH_3 is removed at 400 K. Therefore the assignment of the NH_3 vapour peak has not been made in after NH_3 treated samples.

Similarly, XPS spectra of a NH_3 treated sample were also taken in-situ whilst annealing in vacuum. The sample was annealed over ~ 5.5 hours up to a sample temperature of 625 K. $\text{N}_{\text{A1,2}}$ and

N_{C} begin to diminish above 520 K (Figure 4a). The N_{C} peak is absent above 535 K, whilst the $\text{N}_{\text{A1,2}}$ peaks decrease gradually up to 595 K. This decrease is accompanied by a shift in C 1s peak to higher E_{B} (Figure 4b). The last C 1s scan of the colour map is plotted in Figure 2 and shows the sp^2 peak returns to 284.5 eV, as expected upon the release of N_2 .

Analysis of the O 1s peaks before and after NH_3 treatment reveals a reduction in overall atomic percentage (at. %), compared with the Cu $2p_{3/2}$. This was also seen in the temperature profile of the in-situ NH_3 treatment, where the O 1s components $\text{C}-\text{O}$ (~ 531.6 eV), $\text{C}=\text{O}$ (~ 532.6 eV) and Cu_2O (~ 530.3 eV³⁶) at. % are inversely proportional to the temperature (Figure 3 b-c). This suggests that the intercalation is associated with a reduction mechanism and requires the underlying Cu substrate to be oxidised in order to initiate the reaction.

A common reduction reaction is that of heated copper (II) oxide (CuO) and NH_3 , forming N_2 and water³⁷:

Figure 4. In-situ XPS data collected from a graphene sample heated in vacuum after NH_3 treatment. (a) Colour map tracks the change in N 1s peak intensity as a function of temperature. (b) Colour map indicates a shift in C 1s peak position to higher binding energy with increasing temperature, also shown in the inset.

Figure 5. XPS data collected from CVD graphene samples. (a) A comparison of the O 1s peaks before NH_3 treatment, of oxidised and reduced samples on Cu. (b) Data was also collected after NH_3 treatment, where a significant reduction in intensity can be seen in the oxidised sample. (c) Examining the N 1s peak shows five distinct peaks associated with; N_2 ($\text{N}_{A1,2}$), nitrogen doping ($\text{N}_{B1,2}$) and N bonded to Cu (N_C) in the oxidised sample but no defined peaks appear in the reduced sample after NH_3 treatment providing further validation for the Cu oxide reaction mechanism.

Under ambient conditions, Cu foil oxidises to copper (I) oxide (Cu_2O) and therefore using Equation (1) we propose a similar reaction occurs for Cu_2O :

To test this hypothesis, an oxidised and a reduced sample were also simultaneously annealed in NH_3 . NH_3 treatment shows a dramatic reduction in O 1s intensity (Figure 5b) for the oxidised sample with very distinct $\text{N}_{A1,2}$, $\text{N}_{B1,2}$ and N_C peaks also observed (Figure 5c). Whereas the reduced sample shows no obvious change in the O 1s peak and no discernible N 1s peaks.

This result further validates our proposed reaction, where NH_3 intercalates at the graphene/Cu interface, reducing the oxidised Cu substrate and forming N_2 and H_2O . Our XPS results show that N_2 is trapped between the Cu and graphene, whereas we do not detect any entrapped water. A molecular H_2O peak would occur at ~ 534 eV in the O 1s signal^{38–40}, which was never observed (see Figure 5b).

We propose two possible hypotheses for why N_2 is trapped but H_2O is not. The first argument is based upon the molecules' respective kinetic diameters. Several studies have investigated intercalating molecules between graphene and its underlying substrate^{41–43}. Mu et al.⁴³ and Graiřnās et al.⁴¹ both intercalate CO between graphene/Pt and graphene/Ir, respectively. The atomic distance between graphene/Pt is 3.30 Å and graphene/Ir is 3.51 Å, which are both near to the kinetic diameter (d_k) of CO (3.76 Å). The intercalation is thought to take place through open channels at edge sites. Similarly the atomic distance between graphene and Cu is 2.24 Å⁴⁴ whilst NH_3 has a $d_k = 2.60$ Å⁴⁵. H_2O has a $d_k = 2.65$ Å⁴⁵ however N_2 is a far larger molecule ($d_k = 3.64$ Å⁴⁵).

This suggests that the smaller NH_3 molecules may react with the Cu oxide surface through open channels, whilst the larger N_2 molecules get trapped at the graphene/Cu interface. The

Figure 6(a-c). AFM data collected before and after NH_3 treatment of CVD graphene. (a) AFM image of the height (left) and stiffness (right) of a sample before treatment. (b) A pressurised bubble feature can be seen in the height of an NH_3 treated sample, with an inset at higher magnification. (c) Additional bubbles can be seen highlighted in white in the height (top) and red in the stiffness (bottom) of the NH_3 treated samples. (d) Comparisons of the bubble distribution before and after NH_3 anneals shows that there is a statistically significant increase in bubble coverage after NH_3 anneals. These GNBs are attributed to N_2 entrapment.

second hypothesis is based upon chemical reactivity – water is a comparatively reactive molecule and molecular nitrogen is highly inert. H_2O is known to dissociate at edge sites⁴⁶, with reports that the graphene edge sites may in fact reduce the activation energy for H_2O dissociation, compared to bare Cu⁴⁷. It is possible that this decomposition is followed by hydroxyl diffusion across the surface, providing a route for H_2O to escape. Research into porous graphene has also shown that N_2 has one of the largest diffusion barriers (1.75 eV)⁴⁸. Contrarily, H_2O has a lower diffusion barrier (1.44 eV) which is reduced further (to 0.94 eV) when three C-H pairs, within the pore, are replaced with N atoms⁴⁹. Therefore, another explanation for the absence of water may be due to the difference in chemical reactivity, where H_2O dissociation occurs at graphene edges and subsequent recombinative desorption on areas of bare copper (recall the NH_3 treatment is performed at 600K -) may provide a route for H_2O to be “shuttled” out from underneath the graphene. No equivalent mechanism exists for the N_2 as it is far too unreactive.

To assess changes in morphology after NH_3 treatment, AFM data sets were recorded over ~27 different areas before treatment (Figure 6a) and after NH_3 treatment (Figure 6b-c). Bright features can be seen in the height (Figure 6a, left) of the before NH_3 treated sample which are thought to be contaminants present in the Cu substrate prior to growth as there also appears to be an absence of graphene in their surrounding area. The contaminants show no obvious difference to the rest of the sample in the stiffness (Figure 6a, right). Examining images of samples after NH_3 treatment (Figure 6b-c) shows bubble like structures. The positive contrast in the height (Figure 6c, top), show these features (a selection of which have been highlighted a white circle for clarity) protrude above the surrounding area. Conversely, a negative

Figure 7. Raman data collected from CVD graphene samples. The appearance of the G ($\sim 1580 \text{ cm}^{-1}$) and 2D ($\sim 2700 \text{ cm}^{-1}$) peaks in each scan are characteristic to graphene.

Figure 8. XPS data collected from CVD graphene samples. The graphene was transferred onto a Si wafer. (a) Examining the N 1s peak of the transferred graphene shows $N_{A1,2}$ and N_C are no longer present; however the $N_{B1,2}$ peaks remains. (b) C 1s remains asymmetric towards the high binding energy, indicating the graphene remains intact after transfer.

contrast is seen in the stiffness (Figure 6c, bottom, corresponding red circles) indicating these features are less stiff than the surrounding Cu. Therefore we conclude that these features are in fact GNBS.

Though the appearance of GNBS may be seen prior to treatment ($0.4 \pm 0.3\%$), attributed to the intercalation of ambient atmosphere through defects which consequently accumulate in trenches of the Cu_2O ⁵⁰, a significantly higher distribution of bubbles are formed after NH_3 treatment ($2.0 \pm 0.2\%$). This is estimated through statistical analysis of the relative surface coverage, by masking the GNBS in the stiffness data, shown in Figure 6d. Hence, the N_2 entrapment is not simply distributed uniformly beneath the surface via intercalation, but appears to also be forming pressurised bubbles. This suggests that after NH_3 treatment, there are two species of N_2 coexisting; both a layer of intercalated N_2 (evidenced by the C 1s peak shifting, Figure 2 and Figure 4b) and GNBS (shown in the AFM, Figure 6b-c). These inequivalent N_2 environments give rise to two closely spaced peaks in the XPS, explaining the shoulder feature (N_{A2}) seen in the N_2 entrapment peak of the N 1s spectra (Figure 2, 3a and 5c).

Raman measurements were taken across the surface of each sample and then averaged. Details of the background subtraction are given in the experimental methods, with spectra before background subtraction shown in the ESI, Figure S2. A comparison of the Raman data collected at each experimental phase indicates that the graphene remains intact throughout the NH_3 treatment and Si transfer (Figure 7). Analysis of the average $2D:G$ intensity ratio (I_{2D}/I_G) indicate that the before NH_3 treated sample is monolayer, with $I_{2D}/I_G = 2.4$. The $2D$ full width half maximum ($FWHM_{2D} = 43.0 \pm 0.4\text{ cm}^{-1}$) is higher than that typically quoted for monolayer graphene, likely due to minor defect concentration in the graphene⁵¹. Prior to transfer, a constant broad peak can be seen in the region where the D peak is expected ($\sim 1350\text{ cm}^{-1}$), however this is an artefact of the photoluminescent background removal (see ESI). A D peak arising from defects in the graphene is a much sharper spectral feature, as seen in Figure 7 (Si transfer). An increase in the $FWHM$ of the G peak is seen from before-treatment

($17.0 \pm 0.6\text{ cm}^{-1}$) to after-treatment ($61 \pm 2\text{ cm}^{-1}$). As the $FWHM$ then decreases back to $19.7 \pm 0.9\text{ cm}^{-1}$ after Si transfer, this suggests that the broadening is due to the N_2 entrapment, hence the $FWHM$ decrease as the N_2 is released during Si transfer. Various bubble shapes and sizes were identified in this experiment, with the largest GNBS in the order of 100's nm diameter, far smaller than the Raman spot size ($\sim 1.6\text{ }\mu\text{m}$). Pressurising graphene to form bubbles ($5\text{--}10\text{ }\mu\text{m}$ diameter) has previously been shown to cause a blue-shift in the spectra as a consequence of biaxial strain¹⁴. We hypothesise that the G broadening could be due to an average over the surface (i.e. a distribution of bubble sizes and bubble-free areas).

Finally, an NH_3 treated sample was transferred onto a Si wafer, using the wet polymer assisted transfer (PAT) process, described in the experimental methods. When examining the N 1s peak of the Si transferred sample, $N_{A1,2}$ and N_C are no longer discernible (Figure 8a). $N_{A1,2}$ and N_C were expected to be absent as the process of the wet transfer would allow the N_2 to escape and remove the Cu associated with the N_C peak. As the $N_{B1,2}$ peaks are attributed to nitrogen doping of the graphene they remain after the transfer. As shown by the distinctively asymmetric C 1s sp^2 peak (Figure 8b) and the Raman spectrum (Figure 7) the graphene layer remains intact after transfer.

Experimental

Bluestone Global Tech (BGT) Materials Gratom-M-Cu-04 CVD graphene on Cu ($25\text{ }\mu\text{m}$ thickness) and cut into $\sim 10 \times 10\text{ mm}^2$ samples were used throughout. Monolayer coverage specified by the manufacturer is $>95\%$. The graphene was not transferred prior to NH_3 treatments, and the bubbles were produced on the same Cu foil used during the CVD growth. XPS measurements were performed using a SPECS NAP-XPS instrument. The system consists of two ultra-high vacuum (UHV) chambers (preparation and analysis), and a PHOIBOS 150 NAP Analyser. A NAP cell is docked onto the analyser and the pressure inside it may then be brought up to the mbar range. Photoelectrons were excited using monochromatic Al K_α radiation (1486.6 eV). A large spot size of $\sim 1\text{ mm}$ was used when

scanning in standard UHV conditions, whilst a smaller spot size of $\sim 300\ \mu\text{m}$ was used for all NAP cell scans. For survey/detailed scans E_{pass} of 60/20 eV were used.

In order to anneal samples in NH_3 , CK Gas Ammonia N3.8 (c.99.98 %) was run through the NAP cell and maintained at an in-situ cell pressure ~ 0.60 mbar and up to 600 K for 20 mins. The samples were then cooled to 400 K before removing the NH_3 . Heating was applied using electron bombardment by an e-beam heater (EBH-150). The emission current was increased from 1.00 mA to a maximum of 30.00 mA to achieve the desired temperatures. The sample temperature was measured by a thermocouple attached to the sample plate. When required, oxidation and reduction treatments were performed before NH_3 anneals. Oxidation of samples was achieved by heating on a hot plate in air at $200\ ^\circ\text{C}$ for 20 mins. The presence of Cu_2O post-oxidation of the sample was then confirmed by the high intensity O 1s peak in the XPS at 530.4 eV³⁶ (Figure 5a). Reduction of samples was performed by heating in UHV until the O 1s peak was minimised, whilst ensuring the C 1s sp^2 peak remained. Samples were then annealed in NH_3 as previously described.

Si transfer was performed using the PAT method. The process began by spin-coating a layer of poly(methyl methacrylate) (PMMA) at 500 rpm for 10 s followed by 1000 rpm for 60 s. To set the PMMA, the PMMA/graphene/Cu was baked for 10 mins at $80\ ^\circ\text{C}$. The Cu foil was then dissolved in 0.1 M ammonium persulfate (APS) Cu etchant. Once the Cu underneath was etched, the PMMA/graphene stack was transferred through several deionised (DI) water baths, before being deposited on the Si target substrate. When the sample was dry the PMMA was dissolved in acetone.

Data processing was carried out using CASA XPS processing software. All peaks were calibrated to the Cu $2\text{p}_{3/2}$ peak at $E_{\text{B}} = 932.6$ eV⁵². Although our samples' surface composition is either metallic Cu or a mixture of metallic Cu and Cu_2O , the chemical shift between Cu and Cu_2O is negligibly small (~ 0.1 eV)^{53–56}. Regions and components were fitted to each peak with the appropriate RSF. Generally a Shirley background type was used. In cases where the intensity was flat or higher at lower E_{B} a Linear background type was used. A symmetric Gaussian-Lorentzian product (pseudo-Voigt) line shape was used for all but Cu 2p peaks, where an asymmetric Lorentzian line shape was used.

AFM measurements were carried out at room temperature using a Bruker Multimode8 SPM, operated in Quantitative NanoMechanical mode. A silicon tip on nitride Bruker lever was used (model: SCANASYST-AIR). A variety of parameters were captured using NanoScope 8.2, which were then analysed using Gwyddion. Errors in bubble distribution were calculated using the standard error of the mean, $\sigma_{\text{M}} = \sigma / \sqrt{N}$, where σ is the standard deviation of the original distribution and N is the sample size. N of 25 and 29 were analysed before and after NH_3 treated samples, respectively.

Raman spectra were taken using a Renishaw inVia Raman microscope with a 532 nm laser. The beam was focused using a $20\times$ objective lens, laser power of 3.32 mW and a grating of 1800 l/mm. For the un-transferred samples (i.e. on Cu

substrate), a Raman map over the entire sample ($1\times 1\ \text{cm}^2$) was taken with a 31×31 grid. The photoluminescent background caused by the Cu substrate was subtracted as described in the ESI (Figure S2-3)⁵⁷. These data were then imported into OriginPro and the G and 2D peaks were fitted with Lorentzian peaks to determine their FWHM.

Conclusions

In conclusion, we have demonstrated a novel route to intercalating N_2 and producing GNBs under CVD graphene grown on Cu by a simple substrate oxidation followed by NH_3 annealing. Through a combination of NAP-XPS, Raman spectroscopy and AFM, we reveal that NH_3 intercalates under the graphene and is subsequently decomposed by the Cu oxide to produce molecular nitrogen which is then entrapped, coexisting in two species: a uniform layer of N_2 intercalated between the graphene/Cu layer and GNB formation.

The results demonstrated here show that graphene can be used to confine molecular reactions, the products of which open up the possibility of studying unique material properties. We have demonstrated that transfer is nonessential and GNBs may be produced through reactions with the growth substrate making it easily integrated into the conventional CVD process. These reactions could be studied prior to transfer, in-situ, in systems such as XPS, AFM or environmental scanning electron microscopy (ESEM). Given that the bubbles persist in atmospheric conditions (ESI, Figure S1) the same sample may in fact be studied in various systems prior to their collapse or transfer. Though outside the scope of this paper we anticipate this approach can be generalized and extended to graphene on other catalytic substrates (e.g. Pt, Ni, Ir, Ru) where graphene has been grown directly or transferred. Similarly, graphene may then be used to confine molecular reactions, specific to the desired substrate, where large, unreactive molecules are produced from smaller reactive ones (e.g. oxidation of CO to CO_2 – as CO is known to intercalate intact under graphene^{41,43,58}) – offering up the possibility of tailoring GNBs with different gases or gas mixtures for particular applications.

Conflicts of interest

There are no conflicts to declare.

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