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Control of Grain Boundary Formation in Atomically Resolved Nanocrystalline Carbon Monolayers: Dependence on Electron Energy

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Abstract

In this study, we explore the dynamics of grain boundaries in nanocrystalline carbon monolayers, focusing on their variation with electron beam energy and electron dose rate in a spherical and chromatic aberration-corrected transmission electron microscope. We demonstrate that a clean surface, a high-dose rate, and a 60 keV electron beam are essential for precise local control over the dynamics of grain boundaries. The structure of these linear defects has been evaluated using neural network-generated polygon mapping.

Key words: grain boundaries, nanocrystalline graphene, neural networks, two dimensional materials, transmission electron microscopy

Introduction

Observing, manipulating, and precisely constructing structures down to the levels of single atoms will pave new avenues in nanotechnology, when precise control over every individual atom is achieved. Through hardware spherical (C_s) aberration correction in transmission electron microscopy (TEM) (Rose, 1990; Haider et al., 1998; Jia et al., 2004), sub-Angstrom resolution can be achieved nowadays in both TEM and scanning (S)TEM (Müller et al., 2011). In particular for experiments at lower accelerating voltages, the spherical and chromatic aberration-corrected sub-Angstrom low-voltage electron microscopy (SALVE) instrument (Kaiser et al., 2011; Linck et al., 2016; Börrnert & Kaiser, 2018) has proven extremely useful to image structural dynamics in low-dimensional materials (Skowron et al., 2017; Cao et al., 2020). Here, one of the most suited two-dimensional (2D) materials is graphene, a one atom thick layer of sp^2 bonded C-atoms laid out in a 2D hexagonal honeycomb structure (Novoselov et al., 2004). Graphene is remarkable for its electronic (Castro Neto et al., 2009) and mechanical (Papageorgiou et al., 2017) properties and its thermal conductivity (Balandin et al., 2008). With the focused electron beam for instance, individual Si atoms can be moved on graphene lattice sites (Susi et al., 2014) and holes of only a few atoms in size can be cut precisely (Song et al., 2011). By illuminating the sample with a broad 100 kV electron beam, which is above graphene's knock-on threshold of ~86 kV (Smith & Luzzi, 2001; Meyer et al., 2012, 2013), a growing number of defects are created in the monolayer until finally it is converted into a disordered state

(Kotakoski et al., 2011). On the other hand, graphene's self-healing properties can be leveraged to reduce the number of defects by thermal treatment (Zan et al., 2012; Chen et al., 2013). Moreover, a high dose 80 kV electron beam can—in turn—transform amorphous carbon to nanocrystalline graphene (NCG; Börrnert et al., 2012) or transform small graphene flakes into fullerenes (Chuvilin et al., 2010). Structural changes as minor as the introduction of individual defects can significantly alter the properties of materials, which makes it intuitively understandable why carbon monolayers with minimal long-range order, such as NCG or amorphous carbon monolayers can exhibit vastly different characteristics compared to pristine graphene. These variations will endow the material with new functionalities (Turchanin et al., 2011; Shekhawat & Ritchie, 2016). Reports suggest that pores in graphene, which are carbon rings of varying sizes, can be utilized as filter membrane for applications such as water distillation (Surwade et al., 2015, 2016), DNA/RNA (Garaj et al., 2010; Venkatesan & Bashir, 2011) separation, or as ion filter membrane (Sint et al., 2008). Notably, the inclusion of seven and eight member rings can enhance proton permeability of an otherwise pristine carbon monolayer (Miao et al., 2013; Griffin et al., 2020) without compromising its impermeability to larger atoms and molecules. Grain boundaries, primarily composed of five and seven member rings (Carlsson et al., 2011), are of interest due to their composition and the variability of their sequence, which depends on the angular mismatch between the adjacent grains (Grantab et al., 2010). These boundaries have also been successfully employed to create simple circuitry for sensing

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(Yasaei et al., 2014). As a type of extended defect, grain boundaries significantly influence the structural (Liu & Yakobson, 2010), magnetic (Červenka et al., 2009), chemical (Malola et al., 2010), and electronic (Castro Neto et al., 2009) properties of the carbon sheet. They have been the subject of extensive theoretical and experimental (Kurasch et al., 2012; Ophus et al., 2015) research. Moreover, the structure of grain boundaries can change under electron beam illumination. When enough energy is provided to surpass the activation barriers, a grain boundary may transition to a more energetically favorable structure (Yazyev & Louie, 2010; Kurasch et al., 2012). One result of this is that grain boundaries in graphene can be altered by electron beam exposure. Through this process, small grains may be entirely removed by integrating them into the pristine carbon structure (Kurasch et al., 2012).

The interaction mechanisms between the electron beam and the sample in the TEM are manifold. These include elastic interaction mechanism, often referred to as knock-on damage, where individual atoms are displaced from their lattice site. Inelastic interactions, such as bond rotations, radiolysis and ionization as well as chemical etching can occur and modify the specimen under investigation (Egerton, 2019). The knock-on threshold for graphene has been determined, both experimentally and theoretically, to be slightly above 80 kV (Smith & Luzzi, 2001; Meyer et al., 2012, 2013). Additionally, graphene's high conductivity helps to eliminate the effects of radiolysis.

However, the knock-on threshold for carbon atoms in defective carbon rings and at edge sites is sufficiently reduced (Warner et al., 2010). For example, in the presence of dangling bond, the threshold can drop down to as low as 56 kV (Warner et al., 2009; Rummeli et al., 2019). With high defect concentrations, the knock-on threshold decreases further, and for freestanding

thin amorphous carbon, it can be below 40 kV (Egerton et al., 2006). Additionally, the energy required to move an atom's position within the lattice is lower; for example, the energy needed to rotate bonds in a carbon monolayer is 10 eV (Li et al., 2005) compared to 17 eV, required to remove a carbon atom from pristine graphene (Crespi et al., 1996). According to the McKinley Feshbach formalism, these energies correspond to electron beam energy thresholds of $\sim <52$ kV and <86 kV, respectively. Consequently, extensive examination of NCG and other defective carbon monolayers at 80 kV in high-resolution (HR)TEM mode can lead to structural changes, hole growth, and ultimately, the destruction of the layer.

In this work, nanocrystalline monolayers are studied using C_e/C_s -corrected HRTEM at acceleration voltage of 80, 60, and 40 kV along with varying electron beam dose rates. The aim of this study is to determine whether the properties of grain boundaries can be strategically manipulated to modify a nanocrystalline carbon monolayer and optimize its parameter, such as increasing the number of seven-member rings, without also incurring hole growth. This approach seeks to enhance the structural characteristics of the monolayer while maintaining its integrity.

Experimental

Methods and Materials

All chemicals were purchased commercially and used without purification. The hexaphenyl benzene hexa(terpyridine) monomer (3) was synthesized according to previous literature entries (cf. Fig. 1) (Bauer et al., 2010). ^1H and ^{13}C NMR spectra were acquired on a Bruker AV-400 operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR at 298 K. In some cases,

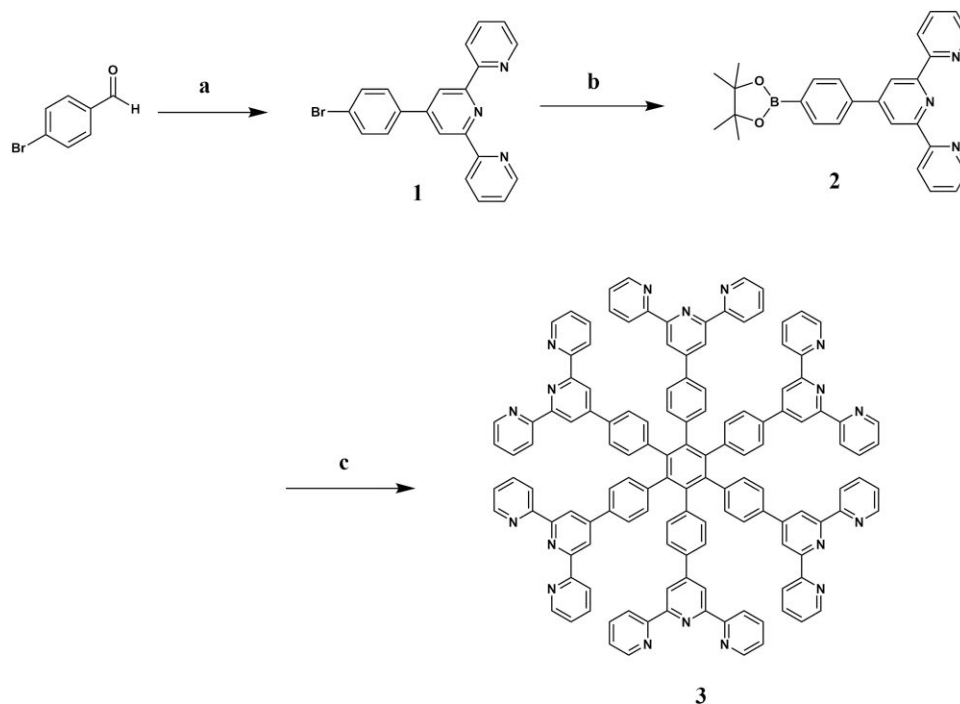


Fig. 1. Synthesis scheme of monomer precursor 3: the synthesis was previously described in (Bauer et al., 2010). Reagents and conditions: (a) 4-bromobenzaldehyde (1.0 eq.), 2-acetylpyridine (2.0 eq.), KOH (2 eq.), $\text{NH}_4\text{OH}_{(\text{aq})}$ (2.5 eq.) in EtOH and 4 h at RT. 47% yield after recrystallization in from hot EtOH. (b) **1** (1.0 eq.), Bis(pinacolato)diboron (1.1 eq.), $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.03 eq.), KOAc (3.0 eq.) in DMSO under Schlenk conditions at 80°C for 6 h. 92% yield from crystallization. (c) **2** (9.0 eq.), hexabromo benzene (1.0 eq.), Na_2CO_3 (16.5 eq.), $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.2 eq.) in Toluene: $t\text{-BuOH}:\text{H}_2\text{O}$ (3.7:1:1.2) under Schlenk conditions at 110°C for 4 d. 25% yield after purification via flash chromatography over Al_2O_3 using DCM:MeOH (0–5%) as eluent. More detailed information on the synthesis of compounds **1–3** can be found below.

spectra were acquired on a Bruker AV-500 operating at 500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR at 298 K. Langmuir monolayers were prepared on a KSV NIMA Langmuir–Blodgett trough. Pyrolysis was performed in a cold wall NanoCVD oven from Moorfield, UK.

Synthesis of Hexaphenyl Benzene Hexa(Terpyridine)

Synthesis of Compound 1

2-Acetylpyridine (5.24 g, 43.2 mmol, 2.0 eq.) was added to a solution of 4-bromobenzaldehyde (4.00 g, 21.6 mmol, 1.0 eq.) in ethanol (EtOH) (108 mL) while stirring. To this solution, KOH pellets (2.43 g, 43.2 mmol, 2.0 eq.) and $\text{NH}_4\text{OH}_{\text{aq}}$ (35%, 1.89 g, 54.0 mmol, 2.5 eq.) was added carefully, which caused a change in the color of the solution from yellow to orange. The reaction was left to stir at room temperature (r.t.) for 4 h during which an additional 50 mL EtOH was added to resuspend the reaction mixture. The off-white colored product was collected by vacuum filtration and washed with EtOH. Recrystallization of the collected solid from EtOH followed by washing with ice-cold EtOH gave the product 1 as a white crystalline solid (2.10 g, 5.40 mmol, 25%) (cf. [Supplementary Fig. S1, S2](#)). ^1H NMR (400 MHz, CDCl_3) δ 8.72 (d, J = 3.8 Hz, 2H), 8.69 (s, 2H), 8.66 (d, J = 7.9 Hz, 2H), 7.88 (td, J = 7.7, 1.8 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.36 (ddd, J = 7.5, 4.8, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.12, 156.07, 149.18, 149.10, 137.44, 136.96, 132.14, 128.93, 123.99, 123.51, 121.42, and 118.59.

Synthesis of Compound 2

An oven-dried Schlenk tube was charged with $\text{Pd}(\text{dppf})\text{Cl}_2$ (113 mg, 5.15 mmol, 0.03 eq.), potassium acetate (1.52 g, 15.5 mmol, 3.0 eq.), bis(pinacolato)diboron (1.44 g, 5.67 mmol, 1.1 eq.), anhydrous DMSO (20.1 mL) and flushed with nitrogen. The reaction mixture was degassed by three freeze-pump thaw cycles after which 1 (2.00 g, 5.15 mmol, 1.0 eq.) was added followed by one final freeze-pump thaw cycle. The mixture was stirred at 80°C for 6 h under nitrogen atmosphere after which it was left to cool. Toluene (200 mL) was added and the resulting mixture was washed with water (3 $\times$ 250 mL) to remove the DMSO and then dried over MgSO_4 . The organic phase was collected by vacuum filtration and the solvent evaporated under reduced pressure to give 2 as dark purple crystals (1.95 g, 4.48 mmol, 87%) (cf. [Supplementary Fig. S3, S4](#)). ^1H NMR (400 MHz, CDCl_3) δ 8.75 (s, 2H), 8.73 (d, J = 4.0 Hz, 2H), 8.66 (d, J = 8.0 Hz, 2H), 7.97–7.90 (m, 4H), 7.87 (td, J = 7.7 Hz, 1.8 Hz, 2H), 7.25 (ddd, J = 7.5 Hz, 4.8 Hz, 1.2 Hz, 2H), 1.38 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.26, 156.00, 150.13, 149.17, 141.00, 136.91, 135.39, 126.60, 123.88, 121.43, 118.93, 84.01, 83.53, 25.05, and 24.94.

Synthesis of Compound 3

An oven-dried Schlenk tube was charged with compound 2 (183 mg, 0.42 mmol, 9.0 eq.), hexabromobenzene (25.8 mg, 0.05 mmol, 1.0 eq.), toluene (3.8 mL) and *t*-BuOH (1.0 mL) under nitrogen atmosphere. Na_2CO_3 (81.7 mg, 0.77 mmol, 16.5 eq.) in UPW (3.0 mL) was added and the reaction mixture was degassed by three freeze-pump that cycles. $\text{Pd}(\text{dppf})\text{Cl}_2$ (6.84 mg, 0.01 mmol, 0.2 eq.) was added and the reaction

mixture was degassed by three additional freeze-pump thaw cycles. The mixture was stirred at 110 C for 4 days. After cooling to r.t., the mixture was extracted with DCM and dried over MgSO_4 . The combined organic layer was collected by vacuum filtration and evaporated under reduced pressure after which the residue was purified by column chromatography over aluminum oxide using DCM and MeOH (0–5 vol% MeOH and 1 vol% TEA) to give 3 as a light pink powder (12.8 mg, 0.01 mmol, 14%) (cf. [Supplementary Fig. S5, S136](#)). ^1H NMR (500 MHz, CDCl_3) δ 8.57 (s, 12H), 8.55 (m, 12H), 8.49 (d, J = 8.1 Hz, 12H), 7.73 (m, 12H), 7.57 (d, J = 7.9 Hz, 12H), 7.19 (m, 12H), 7.14 (d, J = 7.9 Hz, 12H). ^{13}C NMR (125 MHz, CDCl_3) δ 156.4, 155.63, 149.61, 148.98, 141.31, 140.33, 136.59, 135.32, 131.93, 126.06, 123.47, 121.19, and 118.76.

NCG Synthesis

NCG monolayer was prepared following a modified procedure we reported previously with hexaphenyl benzene hexa(terpyridine) as monomer ([Liu et al., 2020](#); [van der Ham et al., 2022](#); [He et al., 2024](#)). To prepare the Langmuir thin-film, a solution of 3 in chloroform (1 mg/mL) was added dropwise onto the air–water interface of a Langmuir–Blodgett trough (KSV Nima, mini trough) equipped with a platinum Wilhelmy plate and temperature control (set to 21°C) for the aqueous subphase. After deposition of the monomer solution, the system was left to equilibrate for 30 min to ensure full evaporation of the solvent. The film was then compressed under constant rate compression (2 mm/min) until the desired surface pressure (15 mN/m), characteristic of a molecular monolayer, was achieved. After the resulting monolayer had stabilized, it was transferred to a plasma-cleaned (100 W, 5 min, 0.3 mbar O_2) SiO_2/Si substrate (285 nm, Sievert Wafer GmbH) via vertical Langmuir–Blodgett transfer (1 mm/min) to yield the desired molecular thin-film. The resulting film was then thermally crosslinked, via pyrolysis under inert conditions (1000°C, 15 min, 1 mbar Ar) in a cold-wall oven (Moorfield, NanoCVD), into the desired NCG film. For structural analysis the nCG film was transferred to a TEM-grid via a modified polymer assisted transfer protocol. We spin-coated (60 s, 4000 rpm) the sample with the transfer polymer (polymethyl methacrylate, PMMA) (M_w = 600 k, Allresist) to protect and stabilize the film during handling, after which the film was released by etching away the substrate on a concentrated potassium hydroxide solution (20 w/v %, 80°C) followed by extensive rinsing on three successive baths containing ultrapure water. After a final rinsing step of 60 min in ultrapure water, the polymer-protected film was transferred onto a TEM-grid using bottom fishing followed by annealing on a hotplate (30 min, 50°C) to ensure sample adhesion. To remove the support polymer, the sample was submerged in acetone for 60 min, after which the sample was blotted dry on filter paper and left to dry overnight. We notice that NCG/amorphous carbon monolayer can also be prepared by plasma enhanced chemical vapor deposition ([Toh et al., 2020](#); [Tian et al., 2023](#)), electron beam induced crosslinking of SAM ([Turchanin et al., 2011](#); [Angelova et al., 2013](#); [Matei et al., 2013](#); [Turchanin & Götzhäuser, 2016](#); [Yang et al., 2018](#); [Neumann et al., 2019](#)), and quenching of metals in organic solvents ([Zhao et al., 2019](#)). The structure of NCG/amorphous carbon monolayer is influenced by the preparation procedures and conditions.

Neural Network (NN) Architecture

The NNs used in this work adopted a modified U-Net architecture (Ronneberger et al., 2015; Madsen et al., 2018; Leist et al., 2022) with convolutional layers. The convolutional layers are implemented with a kernel size of 3 and padding “SAME.” The rectified linear unit was used for the activation function. All convolutional layers were followed by batch normalization. Three convolutional layers and a skip connection formed a residual block. A skip connection concatenated two layers of the same x and y dimensions. In the case of a residual block, these were the input of the last convolutional layer. Downsampling was realized with Max Pooling layers (pool size of 2) to halve the dimensions of a given input layer. The downsampling steps were mirrored with upsampling layers, implemented by deconvolution layers (Conv2DTranspose with kernel size 3 and stride 2). Additionally, dropout layers with a dropout rate of 0.1 were used. These layers were combined to form a NN. As grayscale TEM images were being analyzed, the input was an image with one channel. The downsampling path of the network began with a convolutional layer followed by a residual block and a further convolutional layer. Here all the convolutional layers had eight channels. A downsampling layer followed by a dropout layer was added. After downsampling, this structure was repeated but with doubled channels: that is, a convolutional layer residual block and a convolutional layer with 16 channels each. This process was repeatedly carried out until reaching a total channel number of 128. The upsampling path began with an upsampling layer followed by a skip connection, connecting the upsampling output with the last convolutional layer of the identical dimensions in the downsampling path. In contrast to the downsampling path, the channels for the layers following upsampling were halved for 64 channels in this step. This assembly of layers was repeated three more times so that the final layers had the same dimensions as the original input. Finally, a softmax layer was used to produce a single output image with pixel values between 0 and 1. The layers were initialized with a random normal distribution (mean, 0; standard deviation, 1) with the “RandomNormal” class provided by keras. The network was compiled with MSE for the loss function, the Adam optimizer, and a learning rate scheduler. This scheduler is an exponential decay scheduler with a decay rate of 0.96. The network was trained on normalized grayscale images of 512 by 512 pixels and a minibatch size of 10 with an NVIDIA GeForce RTX 3,060 graphics card with 12 GB VRAM. To convert the NN output into atom positions, we used ndimage.label in conjunction with ndimage.find_objects applied to the difference between the maximum and minimum filtered images. The program iterated through the found objects and determined their centers. The positions were then saved in a list.

Transmission Electron Microscopy

HRTEM images were acquired with an image-side C_c/C_s -corrected SALVE microscope operated at 40, 60, and 80 kV with resolutions of 90, 83, and 76 p.m., respectively (SALVE). The SALVE C_c/C_s corrector adopts a quadrupole-octupole design, which corrects the geometrical axial aberrations up to the fifth order, off-axial aberrations up to the third order, and chromatic aberration (Linck et al., 2016). Data acquisition was conducted with a Ceta16 M CMOS camera and Gatan UltraScan 1000XP fiber-coupled CCD. The dose rate used for recording the images is on the order of $\sim 10^6$

$e\cdot\text{nm}^{-2}\cdot\text{s}^{-1}$. By adjusting (spread and focus) the e-beam, both the dose rate and size of the illuminated area can be rapidly changed, resulting in dose rates of up to $1 \times 10^9 e\cdot\text{nm}^{-2}\cdot\text{s}^{-1}$ and drastically reducing the illuminated area ($\sim 490 \text{ nm}^2$). This ability, combined with control over the beam position allows for fine control over the specific area being illuminated (cf. [Supplementary video 1](#)).

The magnification is set sufficiently high that pixel size in the image is significantly smaller than the resolution of the microscope, so that the resolution is limited by the microscope rather than the detector (0.014 nm pixel size compared to 0.076 nm microscope resolution for 80 kV).

Recording images at such high magnifications and electron dose rates presents significant challenges, primarily due to the risk of damaging the sensitive camera equipment. To mitigate these concerns while utilizing available cameras, the UltraScan@1000XP was used, which is equipped with a fast electrostatic shutter [shutter blanking times as low as $1 \mu\text{s}$ (Gubbens et al., 2010)] and its position in the TEM allows for a large magnification and spread of electron dose on the camera over a broader area. Images are recorded using an illumination time of only 1.5 ms, with a downtime between the frames to minimize the risk of camera damage. However, at these rapid speeds, the system is unable to record and transfer data to the hard drive, and a screen capture script is needed. Consequently, the pixels values in the image are not directly correlating with the detector quantum efficiency, making a straightforward calculation of the electron dose rate from the pixel values in the image impossible. Instead, the dose rate was estimated from the screen current and the illuminated area. For 80 kV acceleration voltage, the high dose rate is estimated to be on the order of $\sim 1 \times 10^9 e/(\text{nm}^2\cdot\text{s})$, for 60 kV on the order of $\sim 6 \times 10^7 e/(\text{nm}^2\cdot\text{s})$ and for 40 kV on the order of $\sim 7 \times 10^6 e/(\text{nm}^2\cdot\text{s})$. The moderate dose rate used in all cases is $\sim 10^6 e/(\text{nm}^2\cdot\text{s})$.

The intense beam focus used to achieve the high electron dose rate introduces a further side effect: The beam's shape diverges from its ideal round form, adding extra aberrations to the image. The employment of the capture script combined with the downtime between images significantly reduces the frame rate, which therefore is much lower than the brief illumination time suggests.

Results and Discussion

80 kV Experiments

When an area of the sample is observed for the first time at high resolution, it initially appears as completely covered by contamination, hiding the individual atomic positions. Eventually, through small holes (1–3 nm in diameter) in the contamination, individual carbon atoms or atom rings can be seen (~ 0 –3 holes per $3,300 \text{ nm}^2$, cf. [Fig. 2a](#)).

When imaging is continued, amorphous contamination disappears, revealing the nanocrystalline material beneath. Composed of small grains, a high percentage of the NCG monolayer consists of grain boundaries. Due to its lower knock-on threshold compared to pristine graphene, holes form and expand, rapidly destroying the monolayer. As a result, no large monolayer regions remain visible at any given time, with the diameters of any visible monolayer seldom exceeding 5 nm (see [Fig. 2b](#)).

Additionally, these samples do not exclusively consist of NCG monolayers; bilayers and few-layers configurations are also present, distinguishable by the presence of moiré patterns (cf. [Fig. 4b](#)).

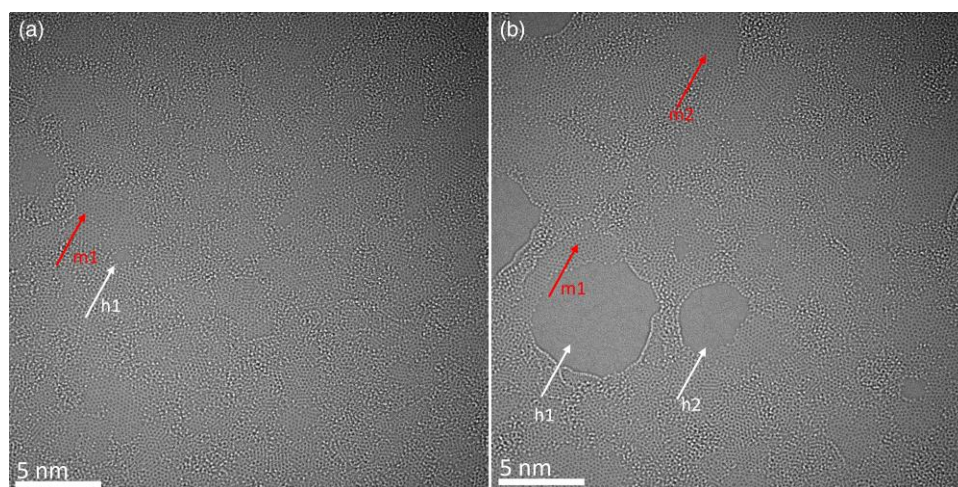


Fig. 2. 80 kV c_d/c_s -corrected HRTEM images of NCG monolayer under moderate electron dose rate [$\sim 10^6$ e/(nm²·s)]: **a)** NCG sample after minimal exposure to electron beam. Small holes are already visible in the monolayer; for example, h1 with a diameter of 1 nm. Small patches of monolayer can also be seen, such as labeled m1 with a diameter of 4 nm. **b)** The same area after continuous illumination at moderate doses for ~ 1 h. Hole h1 has grown from 1 to 7 nm. A new hole, h2, appeared during observation and has grown to 4 nm. Monolayer m2 was revealed during the experiment with a diameter of about 4.5 nm. Monolayer m1 is being dissolved by the growth of hole h1.

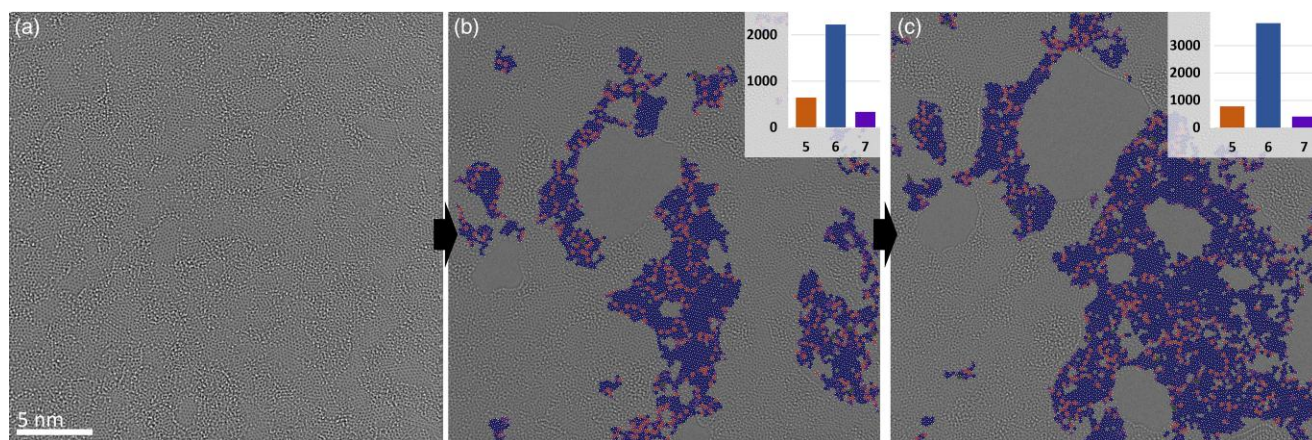


Fig. 3. 80 kV c_d/c_s -corrected HRTEM images of a NCG monolayer treated with high dose rate of $\sim 1 \times 10^9$ e/(nm²·s): **(a)** initial image of NCG. Only in very few places the monolayer is visible. **(b)** The same field of view after exposure to high dose rate 80 kV electron beam. Large areas of the monolayer are revealed, and holes grow. Carbon rings are color coded, to enhance the structural analysis: pentagons in purple, hexagons in blue, heptagons in orange, and octagons in green. Ring statistics are in the upper right corner, showing a pentagon to hexagon ratio of 0.28. **(c)** After more exposure to a high dose rate the monolayer areas and holes have grown. The pentagon to hexagon ratio has further decreased and results in 0.20. The ratio is critical for understanding the molecular geometry and potentially its chemical reactivity and physical properties and highlighting the predominance of hexagonal rings after exposure to high flux.

To further investigate the samples' behavior under the electron beam, the electron dose rate was increased drastically. Two key observations emerge from the high dose rate experiment. First, the high dose rate naturally led to increased damage rate. However, by shifting the beam away from an area as the onset of hole creation is noted, the damage to the material can be minimized. This approach is feasible because, under these conditions, only part of the field of view is illuminated. Consequently, more of the monolayer can be revealed despite the higher damage rate compared to experiments conducted at normal dose rates. Second, as more and more of the monolayer is revealed these areas become large enough that studying their structural development during the experiment becomes feasible. We used NNs (Madsen et al., 2018; Leist et al., 2022) to differentiate between monolayer and contamination and to identify the positions of carbon atoms (cf. Supplementary Figs. S7–S11). The carbon rings can be mapped clearly showing the positions and constituents of

the grain boundaries. Ring statistics were generated and used to detect the changes between frames (cf. Figs. 3b, 3c). By using the NN, the pentagon to hexagon ratio is evaluated for the images, showing that the pentagon to hexagon ratio decreased from 0.23 in Figure 3b to 0.20 in Figure 3c, alluding to structural changes in the monolayer toward a pristine graphene layer.

As the pentagon to hexagon ratio might be skewed by carbon structure at the edges of the holes, we evaluate this value separately for pentagons and hexagons detected at the hole's edge. For Figure 3b, 2% of the pentagons and hexagons are at the edge of a hole with a pentagon to hexagon ratio of 0.63 while for Figure 3c, 4% of the pentagons and hexagons are at the edge of a hole with a pentagon to hexagon ratio of 0.42. Excluding these edge polygons would only change the ratio by 2.2% for Figure 3b and 3.5% for Figure 3c which would not be visible in the final numbers as they are rounded to two decimals.

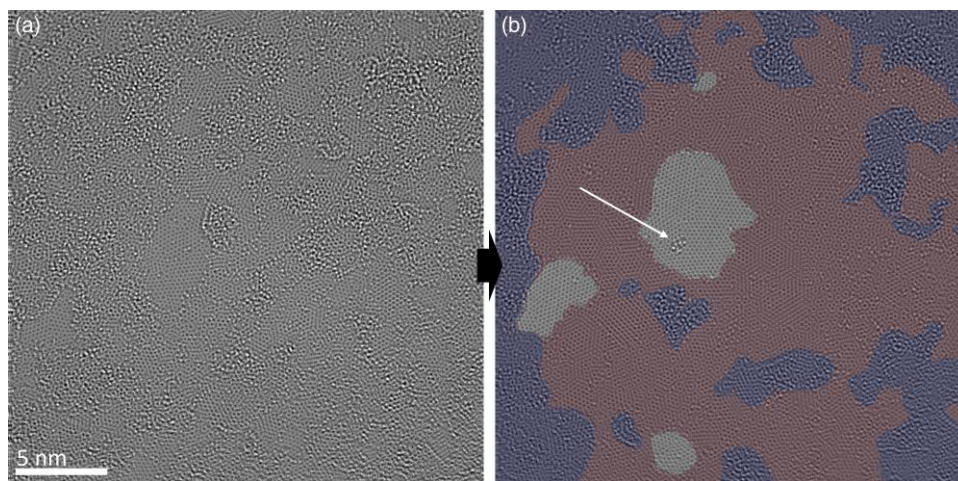


Fig. 4. 60 kV c_d/c_s -corrected HRTEM images of NCG showing changes induced by applying a high dose rate of $\sim 6 \times 10^7 \text{ e}/(\text{nm}^2 \cdot \text{s})$: **(a)** Image taken after high dose rate treatment, a small monolayer area is revealed, no holes were created. **(b)** Further prolonged treatment reveals further parts showing monolayer as well as bilayers as seen in the marked areas (blue: contamination, red: bilayer, and gray: monolayer). Arrow marks the onset of hole growth.

40 kV Experiments

In the effort to derive a method for removing contamination that does not substantially alter the grain structure of the sample, experiments were performed at half the previously used acceleration voltage, specifically at 40 kV. Observation under a moderate electron dose rate [$\sim 10^6 \text{ e}/(\text{nm}^2 \cdot \text{s})$] at this lower accelerating voltage for $\sim 1 \text{ h}$ indicated only minimal changes in the extent of contamination coverage and no hole growth within the sample. However, the maximal dose rate at 40 kV is only $\sim 7 \times 10^6 \text{ e}/(\text{nm}^2 \cdot \text{s})$ as at higher dose rates, radiation safety would be violated. This value at 40 kV is about three orders of magnitude lower than that at 80 kV. As result, the effect of the 40 kV beam on the grain structure could not be explored. We may speculate that a higher dose rate would allow to clear the contamination even at 40 kV and thereby reveal grain boundary structure.

60 kV Experiments

The hole growth caused by the 80-kV electron beam significantly hampers our ability to study the monolayer. At 40 kV, we found that contamination could not be removed effectively. To mitigate knock on damage while still being able to clear contamination, the experiment was performed at 60 kV. Initially, the sample was investigated at a moderate dose rate, similar to the 80 kV experiments. It became clear that under these conditions, hole growth was almost completely halted. Even at high dose rates, holes did not form readily, appearing only after prolonged exposure (cf. Fig. 4). Another factor contributing to the monolayer's increased survivability is graphene's ability to self-heal (Zan et al., 2012). Adventitious carbon can fill small holes, as observed under high dose rate conditions (cf. Supplementary video 3). By strategically moving the beam once the onset of damage becomes noticeable, like the approach used in the 80 kV experiments, the damage can be further reduced, allowing for nearly damage-free imaging at 60 kV.

Under these conditions, it becomes feasible to investigate the monolayer and its response to the electron beam. A high dose rate image series was recorded with a framerate of ~ 5.5 frames per second, with a dose rate of $\sim 6 \times 10^7 \text{ e} \cdot \text{nm}^{-2} \cdot \text{s}^{-1}$. This set up enables tracking grain transformation at atomic resolution and high temporal resolution (cf. Fig. 5 and Supplementary videos 1

and 2). In Figure 5, a neural network-generated overlay for eight frames, selected from a series containing in total 2,339 frames, is presented. These selected frames highlight key stages of the grain boundary dynamics under electron beam. Initially, three distinct grain orientations are clearly divided by a grain boundary and surrounded by contamination (cf. Fig. 5a).

During the experiment, as contamination was removed, the grain boundary partially encircling the center grain becomes visible. The center grain is smaller than the other two grains (cf. Figs. 5b–5d). Over the course of the experiment, the boundary around the center grain initially closes before breaking again. Subsequently, the center grain is absorbed by the lower grain. This process leaves behind the upper part of its grain boundary, resulting in an initially very winding and long grain boundary between the remaining grains (cf. Fig. 5e). This boundary significantly straightens out as the experiment progresses to its end (Figs. 5f–5h). The pentagon to hexagon ratio falls from 0,06 in frame 0 to 0,04 in frame 2327.

To modify the grain boundaries, bond rotations are of predominant interest. If energy, such as heat, is supplied to the sample, the entire structure would undergo a process similar to Oswald ripening. In this process, grains grow larger, defects decrease, and the sample gradually approaches a more pristine graphene structure. This transformation will slow and eventually stop when the grain boundaries become long and straight enough that there is no clear energetically preferred structure or direction (Kurasch et al., 2012). This stabilization occurs because the system reaches a state where further changes do not provide a direct energy advantage.

The 60 kV electron beam can provide the energy necessary for bond rotations in graphene. This energy is delivered locally, enabling transformations only in the areas directly irradiated by the electron beam. Additionally, by adjusting the beam spread, one can quickly modify the dose rate and the size of the irradiated area. This capability provides a tool to control grain movement by only irradiating areas conducive to a set goal.

For example, simultaneously irradiating several grains typically results in the larger grain incorporating the smaller ones. However, the curvature of the grain boundaries significantly affects their behavior under electron beam irradiation. By selectively irradiating outwardly curved parts of a grain boundary, the corresponding grain is encouraged to shrink. Thus,

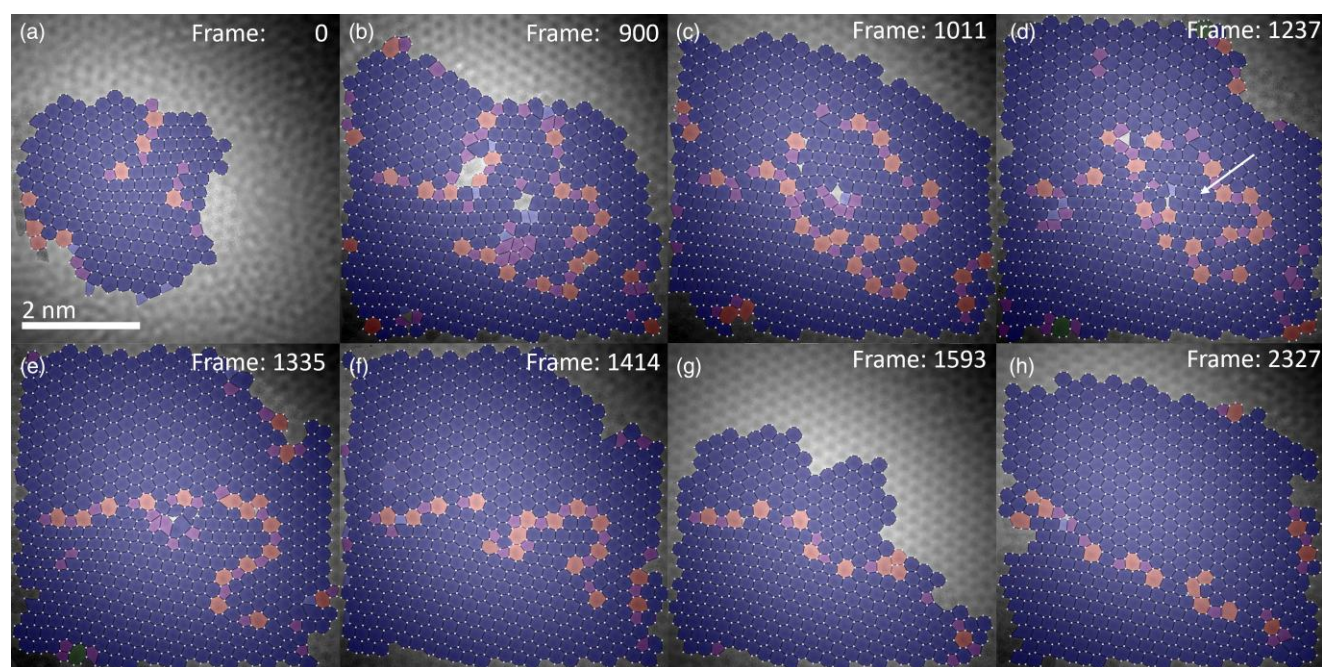


Fig. 5. 60 kV c_d/c_s -corrected HRTEM images showing grain transformation in NCG under 60 kV electron beam examined with neural network-generated polygon mapping: **(a)** Frame 0: NCG surrounded by contamination. A grain boundary coming down the center splits different grain orientations. **(b)** Frame 900: Contamination in the lower part of the frame is removed, center grain is fully visible. Due to out of plane buckling or adatoms some atom coordinates are obscured and therefore cannot be accurately mapped by the NN (cf. [Supplementary Fig. S13](#)). **(c,d)** Frames 1011 and 1237: The center grain (white arrow) is shrinking. **(e)** The center grain is absorbed by the larger grain below it. The grain boundary to the upper grain is retained resulting in a wavy grain boundary. **(f–h)** Frames 1414, 1593, and 2327: The grain boundary straightens. The image series was recorded with a framerate of 5.5 fps at a dose rate of $\sim 6 \times 10^7 \text{ e-nm}^{-2}\cdot\text{s}^{-1}$.

targeting specific areas where the local structure supports the desired change can effectively steer the material's change.

For instance, it is feasible to specifically grow grain boundaries that have a high number of 7 member rings, potentially enhancing the monolayer's proton permeability. Alternatively, this method could be used to create complex circuitry from the grain boundaries. In both cases, the nanocrystalline monolayer needs to initially consist of small grains to compensate for the inevitable and irreversible growth of the average grainsize during the experiments.

The experiments performed here on a nanocrystalline material with such small grains suggest that controlling material changes is indeed possible. However, to fully test this idea, a large area free from contamination is required so that a concrete plan for modifying the sample's structure can be developed based on the initial grain structure. Unfortunately, for both the case of 80 and 60 kV acceleration voltages cannot remove contamination over large areas without also significantly altering the sample's structure. At the dose rates available, a 40 kV electron beam was also unable to remove the contamination.

Conclusion

In this work, NCG was investigated under different acceleration voltages. Our results showed that an 80 kV electron beam destroys the sample; while a 40 kV electron beam fails to produce contamination-free areas. However, imaging with a 60 kV electron beam with a dose rate of $\sim 10^6 \text{ e/(nm}^2\cdot\text{s)}$, the structure of nanocrystalline carbon monolayers can be determined, showing atomically resolved images of the grain boundary structure without causing hole growth. By increasing the dose rate to about $6 \times$

$10^7 \text{ e/(nm}^2\cdot\text{s)}$ and simultaneously reducing the illuminated area, grain boundaries can be selectively modified, and contaminations can be rapidly removed. Neural networks allowed the evaluation of large datasets, enabling mapping, and determination of the distribution of carbon rings in the HRTEM image series. This approach allowed to monitor the dynamics of grain boundary movement and the formation of carbon ring influenced by the electron beam. If this method can be paired with techniques to remove contamination without altering the grain structure, it could lead to precise engineering of grain boundary structure for applications in filter membranes or nanocircuitry.

Availability of Data and Materials

The authors have declared that no datasets apply for this piece.

Supplementary Material

To view [supplementary material](#) for this article, please visit <https://doi.org/10.1093/mam/ozae101>.

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Conflict of Interest

The authors declare that they have no competing interests.

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