Using transmission electron microscopy to stimulate and understand the formation of defects in graphene

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INTRODUCTION

Graphene is a single-layer sheet of carbon atoms arranged in a hexagonal array. The material has many exceptional properties including very high strength, high thermal conductivity and high electrical conductivity when doped. It is nearly transparent and interacts in interesting and useful ways with light and with other materials.

Graphene was first reliably produced in the laboratory in 2004 by Andre Geim and Kostya Novoselov at the University of Manchester. Single-atom-thick crystallites were extracted from bulk graphite by lifting graphene layers from graphite with adhesive tape then transferring them onto a silicon wafer. The material they isolated had the basic properties and structural features of carbon that we see in its other forms, such as graphite and charcoal and, more recently, carbon nanotubes and fullerenes. However, graphene's two dimensional structure, essentially a very large array of aromatic rings, gives the material novel properties. Geim and Novoselov won the Nobel Prize in physics in 2010 for their work.

Researchers have continued to investigate the properties of this material, and high-quality graphene has proven to be relatively easy to produce in ever increasing quantities. This has not only made more research possible but has also allowed the properties being discovered to be exploited and practical uses to be developed. More recently several companies have been formed to develop industrial-scale production processes and investigate commercial applications of graphene.

Potential applications of graphene include: lightweight, thin, flexible, durable display screens; electric circuits and solar cells; as well as various medical, chemical and industrial processes enhanced or enabled by the use of new graphene materials. Some of the most promising applications are in the area of energy storage where, due to its high surface area to mass ratio, graphene has been proposed for the conductive plates of supercapacitors. It has also been suggested for the electrodes in lithium -ion batteries [1].

In another novel application, researchers are exploring graphene's ability to store hydrogen. Hydrogenation-assisted graphene origami (HAGO) causes approximately square graphene sheets to fold into a cage that can store hydrogen. An electric field causes the box to open and close.

EDGES, BOUNDARIES AND VACANCIES

One aspect of graphene that distinguishes it from other carbon nanomaterials, such as nanotubes and fullerenes, is the existence of edges, which make graphene much more reactive.

Graphene created using chemical vapour deposition (CVD) processes is multicrystalline and the edges of adjacent crystal domains form grain boundaries that can be expected to affect the larger-scale properties of the film, such as its thermal and electrical conductivity. The individual grains are readily apparent in darkfield TEM or darkfield STEM images (Figure 1).

At the atomic scale, the presence of defects or vacancies in the crystal lattice can also be expected to affect chemical, physical and electrical properties.

MATERIALS AND METHODS

GRAPHENE SAMPLES

Graphene samples were made available by Graphenea company. The monolayer graphene samples were grown by chemical vapour deposition (CVD) using 25 µm copper foil as the substrate. The monolayer samples were transferred either onto Quantifoil TEM carbon coated grids or on 2000 mesh Au grids using polymethylmethacrylate (PMMA) as the sacrificial polymer layer and ferric chloride as the copper etching agent. In order to prepare the bilayer samples, the transfer process was repeated twice.

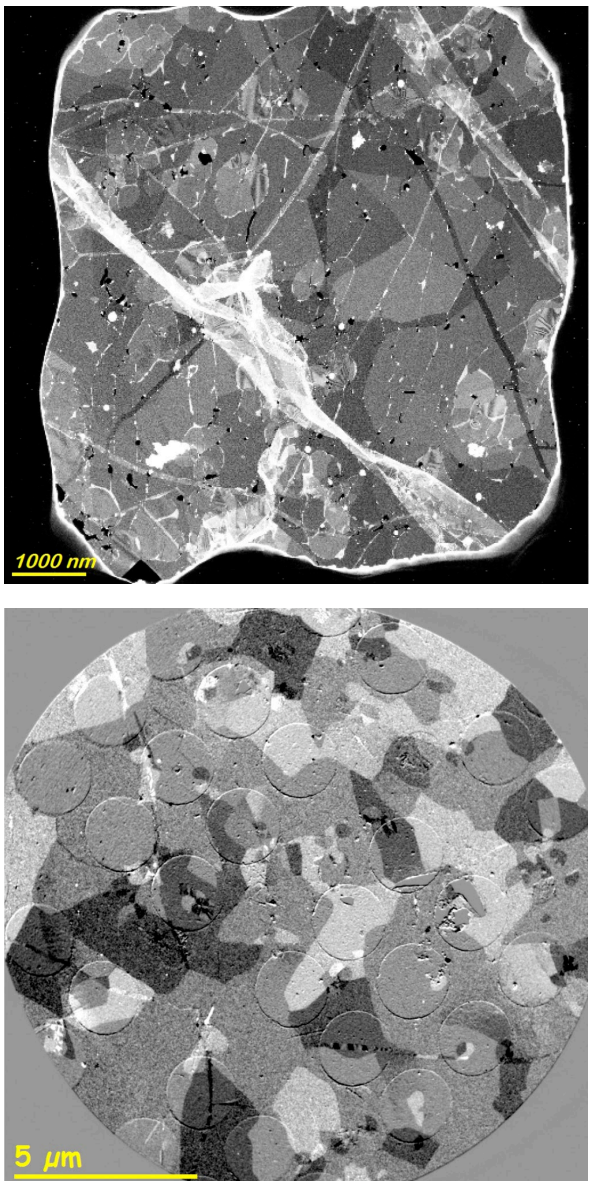


FIGURE 1
Darkfield scanning transmission electron microscopy (top) and differential darkfield TEM (below) images showing individual grains in a CVD graphene film.

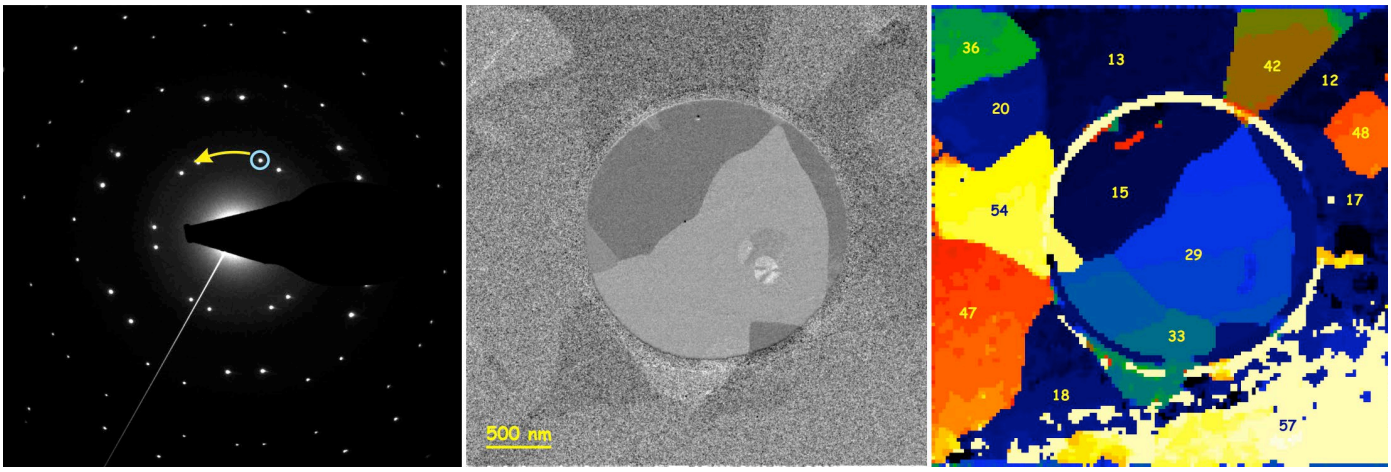


FIGURE 2
Grain orientation can be determined by analyzing multiple darkfield images acquired at different azimuths. The technique can be used to search for boundaries between grains with a specific difference in orientation. Left: Diffraction pattern with a blue circle indicating the position of the objective aperture. Middle: Differential darkfield image showing grains at various orientations. Right: Corresponding map of orientations of the grains determined from 60 dark field images acquired with a step of 1 degree.

HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

High resolution transmission electron microscopy (HRTEM) images were acquired on an FEI Titan 60-300 electron microscope equipped with a high brightness electron gun (xFEG), a monochromator, an imaging Cs corrector and a Gatan UltraScan1000 2k x 2k CCD camera. The microscope was operated at a beam energy of 80 kV; the beam was monochromated to about 100 meV energy spread. Images were recorded on the pre-GIF camera with an exposure time of 1 s.

GRAIN ORIENTATION ANALYSIS

For quantification of grain orientation we used multiple darkfield images obtained at different azimuths. Analysis of intensity versus angle at every point in the image gives grain orientation with an accuracy defined by the angular step and independent of the aperture size. This approach can be used to search for boundaries between grains with a particular difference in orientation (Figure 2).

The angle of mutual rotation of the grains determines the structure of the grain boundary, which in turn contributes to the physical properties of graphene layer. An example of a classical 30 degree boundary composed of a periodic arrangement of 5- and 7-fold rings is shown in Figure 3.

Low-angle boundaries (LAB) are difficult to see in the image but can be detected by the splitting of reflections on the diffraction pattern or on FFT from a high-resolution image (Figure 4). Each LAB is a row of edge dislocations where the separation of the dislocations depends of the mis-orientation angle of two grains. Physically these objects may be interesting as they represent a perfect discontinuous layer with periodically spaced singularities.

DEFECT FORMATION

Understanding the energetics and mechanisms of defect formation, diffusion and transformation in graphene opens the route to control the behaviour of graphitic materials: either to maintain their original properties or to change them in a desired way.

We have been developing approaches to utilize electron radiation in a transmission electron microscope as a controlled stimulus for initiating structural rearrangements in graphene and to observe the pathways and frequency of resulting atomic processes. We use quantum chemistry, molecular dynamics and image simulations in order to unravel the pathway and the rate of observed transformations.

When radiation energy in a transmission electron microscope is exceeds particular threshold value, the formation of vacancies in a graphene sample can be observed. In order to study the formation mechanism of vacancies by *ab initio* molecular dynamics techniques, the static lattice approximation is commonly used, that assumes existence of an abrupt threshold. Below this energy limit, the likelihood of expelling an atom appears to be zero, and thus the creation of vacancies is not possible. In graphene this displacement threshold energy is about 110 keV. In reality, due to thermal vibrations of the atoms the probability of atoms expelling decreases gradually even below the threshold, and even

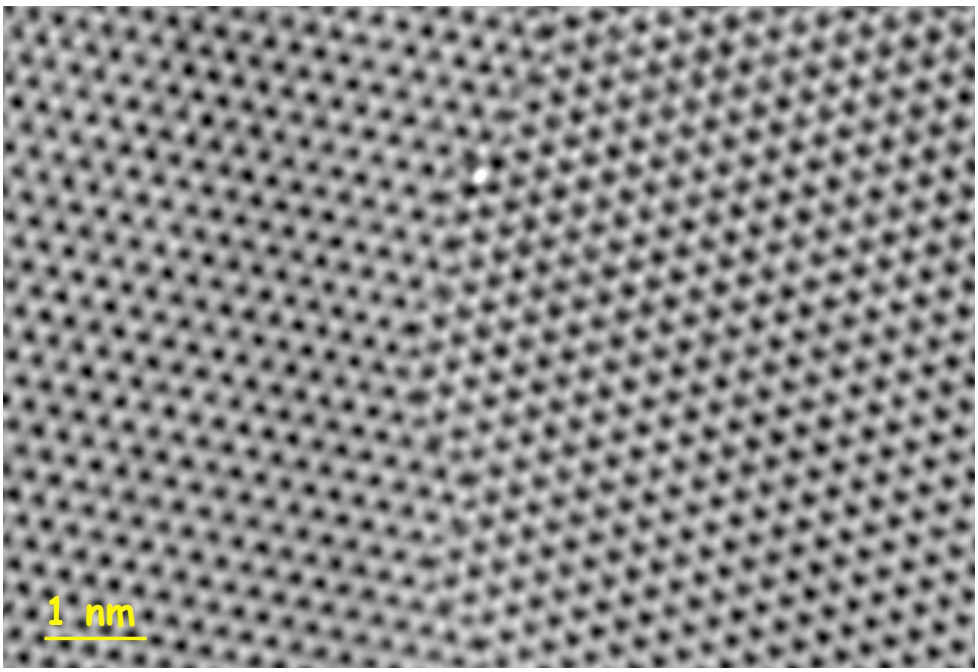
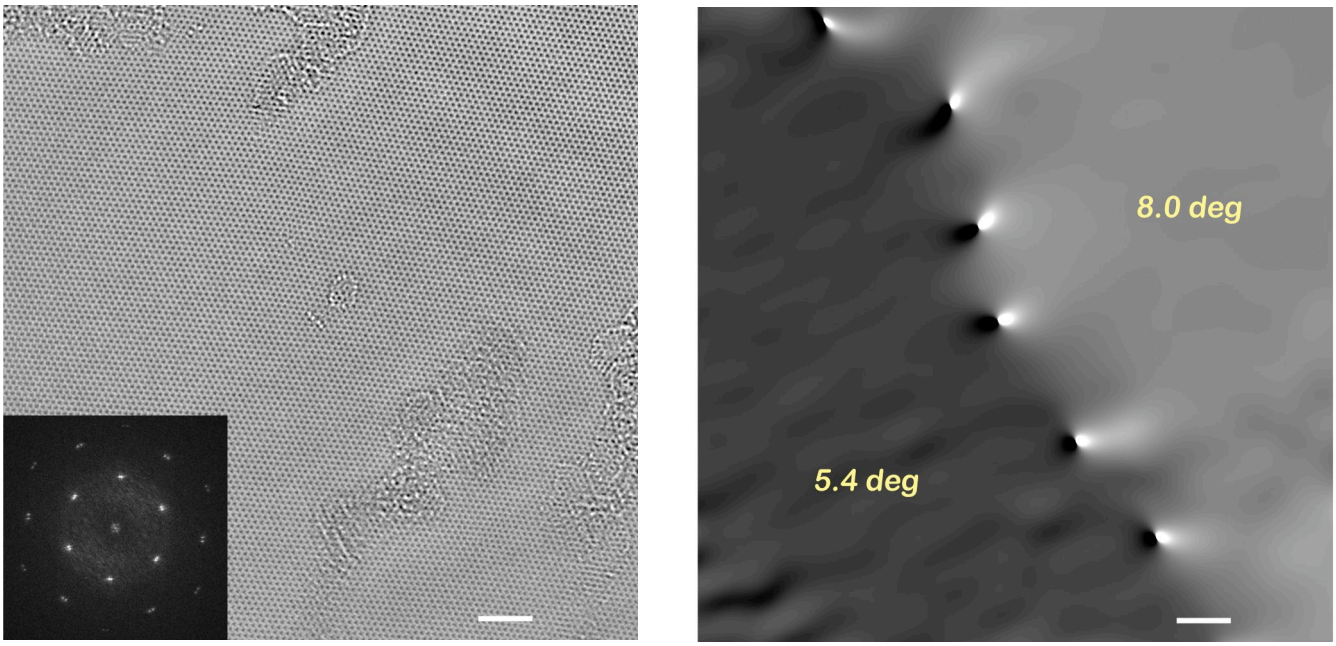


FIGURE 3
Atomic-resolution TEM image of a classic 30 degree grain boundary.



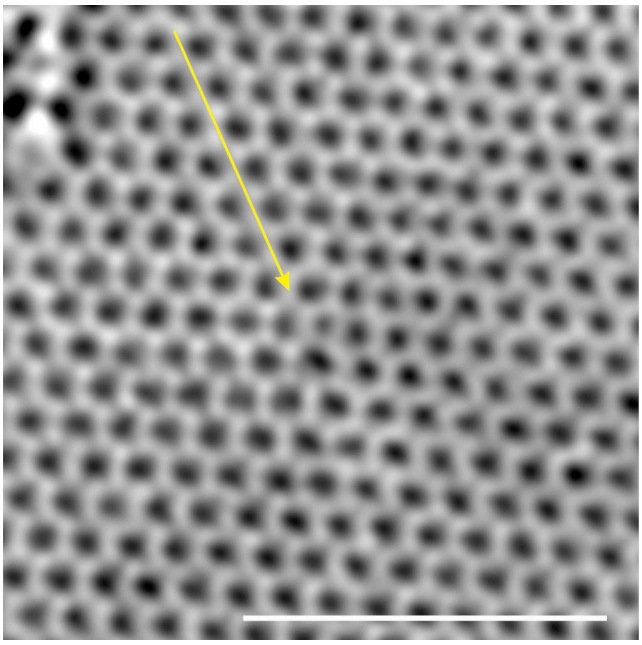


FIGURE 4
Top Left: Low-angle boundaries are difficult to see in the images, however FFT in the insert clearly reveals 2.6 degree reflexions splitting.
Top right: Dislocations can be located by geometrical phase analysis as shown in this rotation map from the image to the left.
Below: High-resolution image of the core of lowermost dislocation in the middle image. The dislocation (arow) is composed of adjacent 5 and 7 member rings.
Scale bars = 2 nm.

for radiation energies of 80 keV this probability is not zero, although it is extremely small.

We have experimentally observed that bilayer graphene shows a substantial increase in the displacement cross-section at this energy with respect to the monolayer graphene. For an electron dose of the order of 10^{10} electrons nm^{-2} the formation of several vacancies is observed in bilayer graphene, while in monolayer graphene the formation of one vacancy is unlikely at this dose.

Figure 5 shows a bilayer graphene sample with a rotation angle between layers of 11.2°. A characteristic hexagonal Moire pattern is observed in high-resolution transmission electron microscopy (HRTEM) images due to this rotational misfit. After extended observation time we start to observe distortions in the Moire figures, which are attributed to radiation-generated defects. Fourier filtering of lattice patterns clearly reveals V2 (5555-6-7777)-type divacancies. Removal of both lattices from the image produces a characteristic signature of a V2 (5555-6-7777) defect in the shape of dumbbell.

The simulation of the observed defect confirms that the formed defects are V2 (5555-6-7777) divacancies, or for simplicity, butterfly defects (Figure 6) [2]. They are characterized by the formation of four heptagonal, four pentagonal, and one rotated central hexagonal carbon rings. If we pay attention to the location of the defects in Figure 5, we observe that they are stabilized close to the edges and corners of the large hexagons of the Moire pattern. This suggests that stacking might influence the stabilization of the defects.

The cross-section σ of C atom sputtering calculated from data is 1.2 x 10^{-3} barn, which is higher by at least two orders of magnitude than the estimated low limit of sputtering cross-section for a single layer. In combination with the fact that the vacancies were only created in one layer, our observation points to a strong synergetic influence of the second layer on the sputtering process.

Extensive density functional theory (DFT) calculations combined with molecular dynamics have led us to conclude that we have observed a multistep process, in which the second underlying layer of graphene serves as a catalyst, stabilizing otherwise metastable intermediate configurations.

Post factum evaluation of the experimental image series really revealed theoretically predicted V2 (5-8-5) and V2 (555-777) configurations needed to stabilize intermediates. As expected, these V2 defects existed only for a short time and then rapidly converted into stable butterfly defects. Detailed kinetic analysis of reversible transformations involved in the mechanism confirmed its validity and allowed us to predict the rate of vacancy formation with a reasonable accuracy.

We have generalized this approach in a workflow, which has been implemented in the software

CompuTEM combining DFT calculations, molecular dynamics and TEM image simulations. The concept provides a combined treatment of perturbation of the electron beam by the sample (elastic electron scattering) and the sample by the electron beam (radiation damage) at one and the same beam conditions. Such treatment results in a realistic determination of the pathway and the rate of the sample evolution under the electron beam along with a realistic estimation of the signal-to-noise ratio achievable for observations of a given atomic process.

Using this approach we were able to reproduce quantitatively in simulation the experimentally observed process of graphene flakes curling into fullerene molecules (Figure 7) [3].

CONCLUSIONS

Transmission electron microscopy, in particular utilizing aberration correction and decreased accelerating voltages, is a powerful technique for studying the structure of novel carbon-based materials including graphene. The technique provides not only unprecedented spatial resolution and contrast allowing for observation of single atoms of light elements, but a decent temporal resolution as well thus giving a unique capability for monitoring atomic processes in real time.

With the example of the atom ejection process from bilayer graphene we show a principal possibility to reveal and describe by means of chemical kinetics complex atomic mechanisms of structural transformations which may include in particular reversible intermediate steps.

Further development of this approach requires understanding and quantitative accounting for the action that the imaging electrons have on the structure under observation. We achieve this understanding by combining advanced quantum mechanical calculations with molecular dynamics and successive image simulations in the software package CompuTEM. The validity of our implemented calculation scheme is proved by quantitative compliance of simulated and experimental data for a test reaction of graphene to fullerene transformation.

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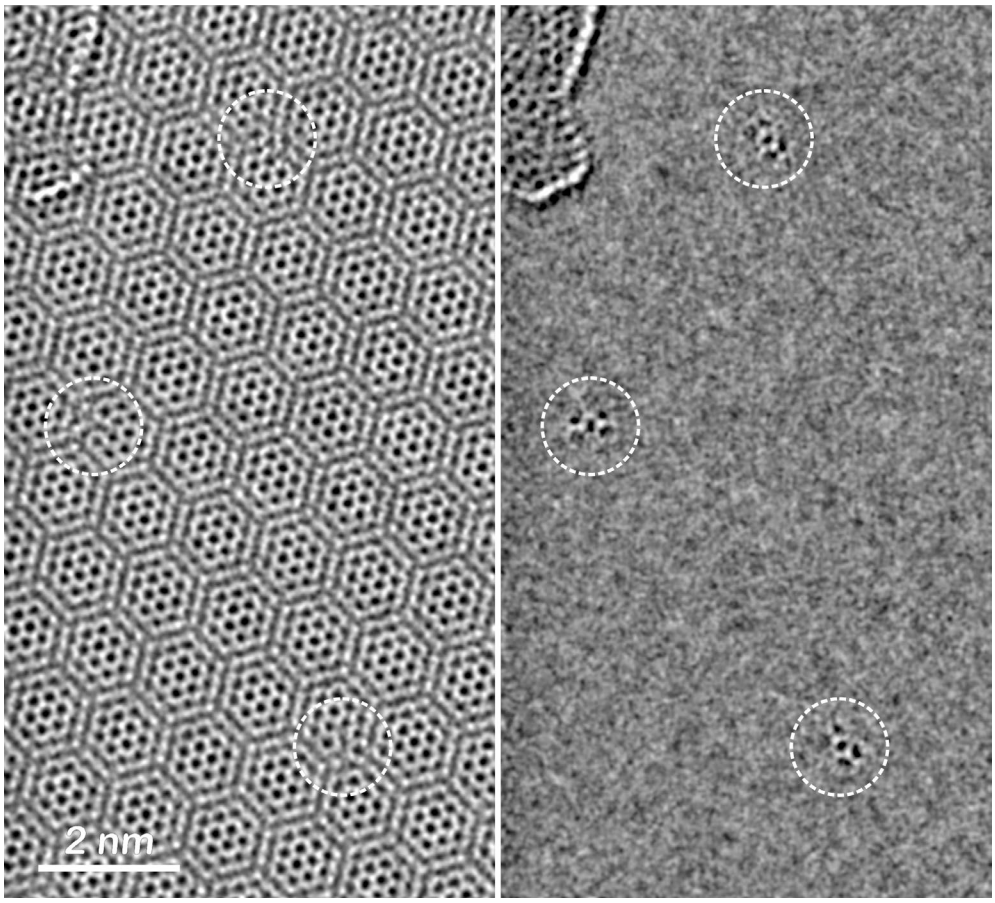

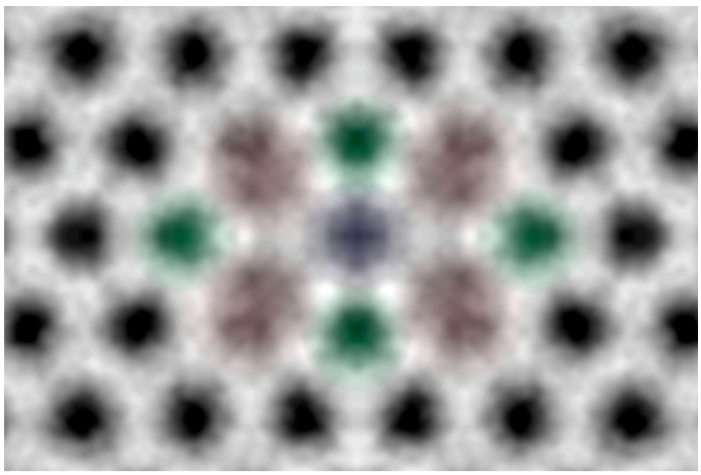

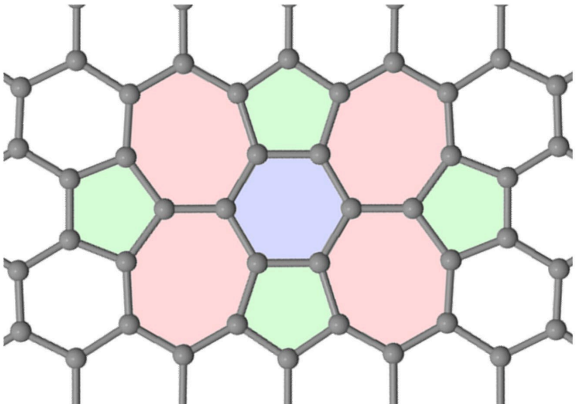

FIGURE 5 (ABOVE)
Left: High resolution image of graphene bilayer with 11.2 degree rotation showing Moire pattern. In the regions marked by the circles the distortions of the pattern are visible. Right: The same area, but the lattices of both layers are removed by Fourier filtering. Characteristic patterns in the shape of double dumbbells appear inside the circles indicating the same type of lattice distortion in all three places [2].

FIGURE 6 (LEFT)
Top: Experimental image averaged over all observed butterfly defects. Below: A corresponding atomic structure of the defect. Four heptagonal (red), four pentagonal (green), and one rotated central hexagonal (blue) rings are formed instead of the original hexagonal lattice [2].
scale bar??

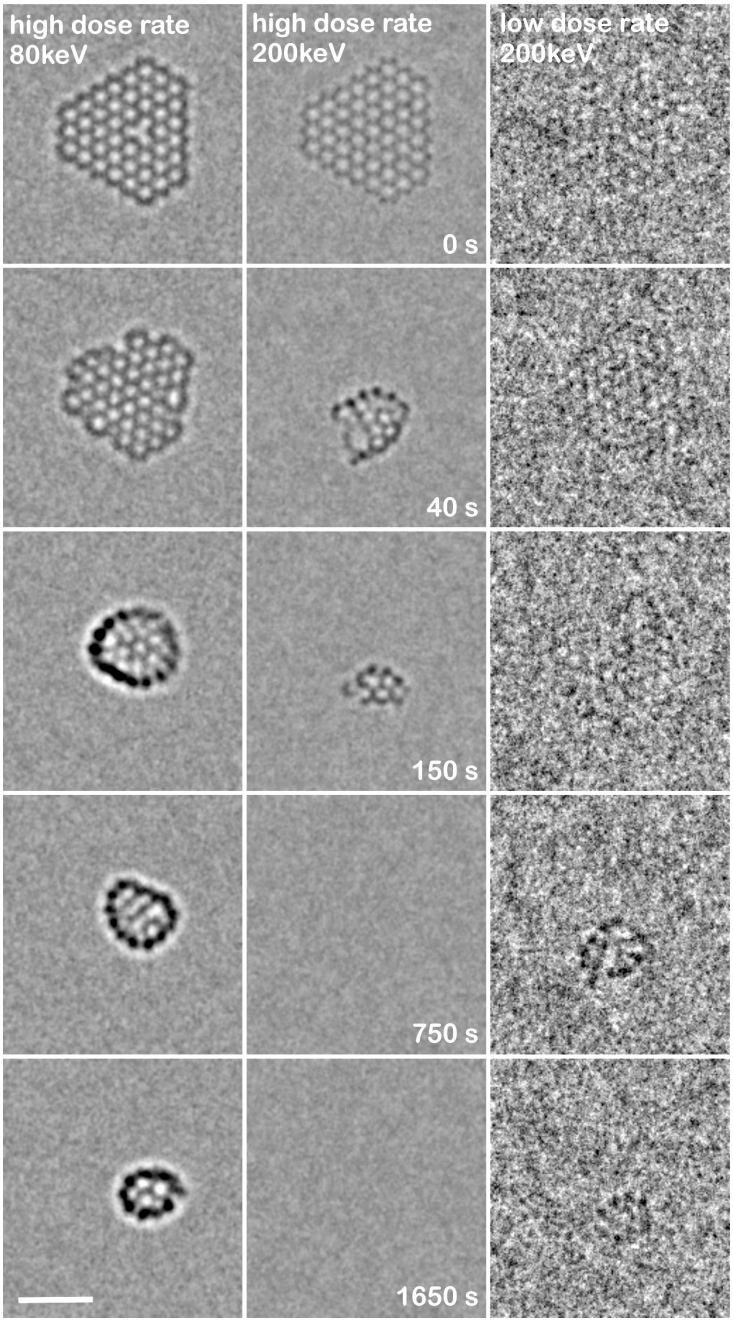

FIGURE 7
CompuTEM simulations of the flake-to-fullerene transformation for three sets of experimental conditions in HRTEM.
Left panel: 80 keV accelerating voltage and 4.1×10^6 electrons s^{-1} nm^{-2} electron flux; these values correspond to the experimental conditions used during the observation of fullerene formation. Middle panel: 200 keV accelerating voltage and 4.1×10^6 electrons s^{-1} nm^{-2} electron flux. Right panel: 200 keV accelerating voltage and 0.25×10^6 electrons s^{-1} nm^{-2} electron flux; this experimental setting determines the same rate of the flake-to-fullerene transformation as in the case shown in the left panel. For all three cases the quality of the imaging system was considered to be the same [3]. Scale bar = 1nm.

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BIOGRAPHY

Andrey Chuvilin has a PhD in physics and mathematics from the Institute of Catalysis in Novosibirsk, Russia. After post-doctoral positions in Novosibirsk, the University of Jena and TU Ilmenau, Germany,earcher in the University of Ulm, Germany, in 2004 he took a post at the University of Ulm, Germany, where he applied low-voltage, aberration-corrected TEM to study the atomic structure of carbon materials. In 2009, Andrey joined an international research team at CIC nanoGUNE in San Sebastian, Basque Country, where he is head of the Electron Microscopy Laboratory. This move diversified his research fields, which now include high-resolution TEM, low-loss EELS of plasmonic structures, electron holography and electron tomography, high-resolution environmental SEM, and FIB nanofabrication.

ABSTRACT
This article discusses the use of time-resolved aberration-corrected transmission electron microscopy imaging in combination with molecular dynamics, quantum mechanical calculations and image simulations to understand topological defect formation and evolution in the graphene flatland. The authors are developing theoretical approaches for the combined treatment of imaging and radiation-induced atomic rearrangements in TEM.

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ABOUT CIC NANOGUNE
The CIC nanoGUNE is a Basque research center set up with the mission to perform world-class nanoscience research for the competitive growth of the Basque Country, fostering high-standard training and education of researchers in this field, and promoting cooperation among the different agents in the Basque Science, Technology, and Innovation Network, and between these agents and the industrial sector. In 2010, nanoGUNE launched a start-up company, Graphenea, as a joint venture of private investors and nanoGUNE with the mission of commercializing good-quality graphene wafers and developing graphene-based technologies. Combining high-end experimental methods using aberration-corrected transmission electron microscopy and advanced quantum mechanical calculations, the nanoGUNE team, in collaboration with the School of Chemistry of the University of Nottingham, is developing an understanding of defect formation and evolution in graphene structures.

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