Direct in situ observations of single Fe atom catalytic processes and anomalous diffusion at graphene edges

Jiong Zhoa,b,c, Qingming Dengd, Stanislav M. Avdoshenkoa, Lei Fu, Jürgen Eckerta,g, and Mark H. Rümmelib,c,1

Abstract

Single-atom catalysts are of great interest because of their high efficiency. In the case of chemically deposited sp2 carbon, the implementation of a single transition metal atom for growth can provide crucial insight into the formation mechanisms of graphene and carbon nanotubes. This knowledge is particularly important if we are to overcome fabrication difficulties in these materials and fully take advantage of their distinct band structures and physical properties. In this work, we present atomically resolved transmission EM in situ investigations of single Fe atoms at graphene edges. Our in situ observations show individual iron atoms diffusing along an edge either removing or adding carbon atoms (viz., catalytic action). The experimental observations of the catalytic behavior of a single Fe atom are in excellent agreement with supporting theoretical studies. In addition, the kinetics of Fe atoms at graphene edges are shown to exhibit anomalous diffusion, which again, is in agreement with our theoretical investigations.

Significance

The single metal atom has been proposed to be a catalyst during the growth of carbon nanotubes; however, this hypothesis is still not confirmed. Our direct in situ transmission EM observation of the restructuring of the graphene edges interacting with an Fe atom directly revealed the intermediate states: pentagon and hexagon structures. In particular, our experiments and simulations show that the single Fe atom behaves differently on the graphene zigzag and armchair edges, giving insights to the growth mechanisms of various sp2 carbon structures.

Author contributions: J.Z. and M.H.R. designed research; J.Z., Q.D., and S.M.A. performed research; J.Z., S.M.A., L.F., J.E., and M.H.R. analyzed data; and J.Z. and M.H.R. wrote the paper.

The authors declare no conflict of interest.

1To whom correspondence should be addressed. Email: mark@rummeli.com.

This article contains supporting information online at www.pnas.org/cgi/doi/10.1073/pnas.1412962111/DCSupplemental.

Previous studies have shown that the 2D behavior of individual atoms over the basal plane in graphene exhibits Brownian motion. From this information, the 2D diffusion coefficient as well as the average Arrhenius activation energy could be extracted (20, 21). The spatial probability of a particle in Brownian motion follows a Gaussian distribution. In this case, the mean square displacement [MSD; \( \langle R^2(t) \rangle \) ] is dependent linearly with respect to time, and the gradient corresponds to the diffusion coefficient (\( D \)) and is written as \( \langle R^2(t) \rangle = 2nDt \) (where \( n \) is dimensionality) (22, 23). Similar to previous observations of an Au atom at graphene edges (11), our in-depth experimental observations reveal that the diffusion of a single (Fe) atom along the edge of single-layer graphene is directly related to the atomic configuration of the graphene edge. Moreover, the random 1D diffusion of an Fe atom along a graphene edge does not follow Brownian motion but exhibits anomalous diffusion (namely, sub- or superdiffusion). Subdiffusion is attributed to the presence of trapping configurations. Without such trapping configurations, superdiffusion (levy flight) is obtained.

Details on the preparation and transfer method of the chemical vapor deposition-grown graphene specimens used in this work can be found elsewhere in the literature (24–26) and SI Appendix. The transferred synthetic graphene is found to occasionally have holes, which can be augmented on electron beam irradiation in a low-voltage Cs aberration-corrected transmission electron microscope (80 kV acceleration voltage). These freshly in situ-derived edges from the augmented holes provide a clean [previous electron energy loss spectrum and TEM study confirmed no oxygen or nitrogen species on these edges (27) as well as no hydrogen (28)] and convenient platform to study the 1D motion of adsorbed Fe atoms. Because of the larger binding energy of an Fe atom at graphene open edges as opposed to binding at the basal plane, Fe atoms tend to reside at the edges. The Fe atoms are present as remnants from the transfer process, in which FeCl3 was used as an etchant to remove the underlying Ni–Mo over which the

Defects in graphene, including vacancies (1), dislocations (2), grain boundaries (3), and edges (4), are currently of interest, because they open up a variety of ways with which to tune the properties of pristine graphene. Dopant atoms in graphene are also of tremendous interest (e.g., transition metal atoms, which substitute carbon in graphene sheets, have theoretically been shown to have unusual magnetic or catalytic properties) (5). Single atoms or small clusters in graphene [e.g., N (6) and Fe (7–9)] have been directly observed with high-resolution transmission EM (TEM). Si dopant species have been directly observed with scanning TEM (10). In these cases, the atoms were embedded within the graphene.

In addition, single Au (11, 12) and Al (12) atoms have also been observed (using TEM or scanning TEM) to be absorbed at the edges of graphene. The interactions between single metal atoms and graphene edges are complicated because of the different types of trapping states at the edges (11). In addition, some theoretical works suggest that the atomic configurations at graphene edges are greatly affected by nearby transition metal atoms (13–15).

Here, we examine individual Fe atoms residing at graphene edges. Single metal atom catalysts have recently been proposed as a means to maximize catalytic efficiency (16, 17). Thus, atoms at graphene edges are of great interest for their catalytic potential, particularly to gain insight to the catalytic growth of sp2 carbon (e.g., graphene) by transition metals. By means of low-voltage aberration-corrected TEM (LVACTEM) (18), the atomic configurations of an Fe atom at a graphene edge can be determined, and in addition, the dynamics of a single Fe atom can be recorded. Pentagon–hexagon transitions are observed and reveal the catalytic addition (growth) or removal processes. These processes are in excellent agreement with our ab initio and molecular dynamics (MD) simulations, which are also in agreement with a previously proposed catalytic growth model for carbon nanotubes (19). In addition, the kinetics of Fe atoms at graphene edges are shown to exhibit anomalous diffusion, which again, is in agreement with our theoretical investigations.

Dopant atoms in graphene sheets have theoretically been shown to have unusual magnetic or catalytic properties (5). Single atoms or small clusters in graphene [e.g., N (6) and Fe (7–9)] have been directly observed with high-resolution transmission EM (TEM). Si dopant species have been directly observed with scanning TEM (10). In these cases, the atoms were embedded within the graphene.

In addition, single Au (11, 12) and Al (12) atoms have also been observed (using TEM or scanning TEM) to be absorbed at the edges of graphene. The interactions between single metal atoms and graphene edges are complicated because of the different types of trapping states at the edges (11). In addition, some theoretical works suggest that the atomic configurations at graphene edges are greatly affected by nearby transition metal atoms (13–15).

Here, we examine individual Fe atoms residing at graphene edges. Single metal atom catalysts have recently been proposed as a means to maximize catalytic efficiency (16, 17). Thus, atoms at graphene edges are of great interest for their catalytic potential, particularly to gain insight to the catalytic growth of sp2 carbon (e.g., graphene) by transition metals. By means of low-voltage aberration-corrected TEM (LVACTEM) (18), the atomic configurations of an Fe atom at a graphene edge can be determined, and in addition, the dynamics of a single Fe atom can be recorded. Pentagon–hexagon transitions are observed and reveal the catalytic addition (growth) or removal processes. These processes are in excellent agreement with our ab initio and molecular dynamics (MD) simulations, which are also in agreement with a previously proposed catalytic growth model for carbon nanotubes (19). In addition, the kinetics of Fe atoms at graphene edges are shown to exhibit anomalous diffusion, which again, is in agreement with our theoretical investigations.

Dopant atoms in graphene sheets have theoretically been shown to have unusual magnetic or catalytic properties (5). Single atoms or small clusters in graphene [e.g., N (6) and Fe (7–9)] have been directly observed with high-resolution transmission EM (TEM). Si dopant species have been directly observed with scanning TEM (10). In these cases, the atoms were embedded within the graphene.

In addition, single Au (11, 12) and Al (12) atoms have also been observed (using TEM or scanning TEM) to be absorbed at the edges of graphene. The interactions between single metal atoms and graphene edges are complicated because of the different types of trapping states at the edges (11). In addition, some theoretical works suggest that the atomic configurations at graphene edges are greatly affected by nearby transition metal atoms (13–15).

Here, we examine individual Fe atoms residing at graphene edges. Single metal atom catalysts have recently been proposed as a means to maximize catalytic efficiency (16, 17). Thus, atoms at graphene edges are of great interest for their catalytic potential, particularly to gain insight to the catalytic growth of sp2 carbon (e.g., graphene) by transition metals. By means of low-voltage aberration-corrected TEM (LVACTEM) (18), the atomic configurations of an Fe atom at a graphene edge can be determined, and in addition, the dynamics of a single Fe atom can be recorded. Pentagon–hexagon transitions are observed and reveal the catalytic addition (growth) or removal processes. These processes are in excellent agreement with our ab initio and molecular dynamics (MD) simulations, which are also in agreement with a previously proposed catalytic growth model for carbon nanotubes (19). In addition, the kinetics of Fe atoms at graphene edges are shown to exhibit anomalous diffusion, which again, is in agreement with our theoretical investigations.
graphene was synthesized. Our electron energy loss spectrum studies previously confirmed that these atoms are Fe (26). In our in situ LVACTEM, the atoms are imaged with dark-contrast conditions to optimize imaging (29). The specific experimental condition can be found in Materials and Methods.

**Results**

In Fig. 1, two ubiquitous configurations of a single Fe atom residing at an armchair graphene edge are provided. The experimental micrographs (Fig. 1 A and D) with false color and magnified sections (Fig. 1 B and E) are overlapped with density functional theory (DFT)-simulated structures (Materials and Methods and SI Appendix have simulation details) (30) to highlight the correspondence between the two. Quantitative comparisons between the experimental images and simulated images can be found in SI Appendix, Fig. S1. In the first case (Fig. 1 A–C), an Fe atom is incorporated into a five-atom ring forming a pentagon. In the second case (Fig. 1 D–F), an Fe atom is incorporated into a five-atom ring forming a distorted hexagon (viz., the Fe atom substitutes a carbon atom in the hexagonal lattice). The respective

---

**Fig. 1.** Identification of hexagon and pentagon structures. (A–C) High-resolution TEM (HRTEM) images (false color), magnified regions of HRTEM with overlaps of the DFT-calculated atomic structures, and DFT-derived structures (top and side views) of a pentagon including an Fe atom. Gray ball, carbon atom; orange ball, Fe atom. (D–F) HRTEM images (false color), magnified regions of HRTEM with overlaps of the DFT-calculated atomic structures, and DFT-derived structures (top and side views) of a distorted hexagon including an Fe atom. (Scale bars: B and E, 0.5 nm.)

**Fig. 2.** One cycle of catalytic growth of graphene edge. (A–D) A series of high-resolution TEM images for 4 s; the Fe atom is highlighted as a red dot, whereas the nearby carbon atoms are highlighted as black dots. The dark shadow line, which is highlighted by the red circle in C, is because of the motion of the Fe atom during exposure time. (Scale bar: 0.5 nm.) (E) The corresponding atomic structures for A–D. (F) The combination of A–D, which shows the trace of the Fe atom during the one-unit cell translocation. (Scale bar: 0.5 nm.) (G) The atomic structure for the whole growth process (two carbon atoms are added).
DFT-calculated structures are shown in Fig. 1 C and F (top and side views, respectively). All of the six energetically favorable configurations for a single Fe atom covalently bonding to graphene edges are provided in SI Appendix, Fig. S2. All of these local Fe–C configurations can be identified in Movies S1 and S2. The pentagon and hexagon structures are of particular interest because of their importance to the catalytic growth of sp² carbon (19).

Exposing the adsorbed Fe atoms at the edges of the graphene to the electron beam triggers an Fe atom to shift to different edge locations, leading to motion along the graphene edge. In Fig. 2 A–D, a typical translocation of one unit cell for the Fe atom is presented. The Fe atom changes from a pentagon structure (Fig. 2 A) to a hexagon (Fig. 2 B and C), and moves toward the right; then, the single-atom motion creates the dark shadow line shown in Fig. 2 C, which is highlighted by a red circle (viz., the Fe atom moves during the camera exposure). It then stops at a nearby position and forms a pentagon again (Fig. 2 D). The atomic structures highlighting this process can be found in Movies S1 and S2. The positions of the Fe atom as well as the carbon atoms can be resolved, which allows us to build matching atomic models like, for example, those shown in SI Appendix, Fig. S4. Right. Intermediate images, which suggest additional atom movement in between captured images, are provided to highlight probable intermediate steps. These images not only show the 1D movement of the Fe atom but also, help elucidate the removal and incorporation of Fe atoms, which are indicated by red and green triangles, respectively, in SI Appendix, Fig. S4. For the most part, Fe atom translocation without the removal or addition of carbon is not observed. The insertion of carbon atoms at the graphene edge through Fe highlights the catalytic properties of Fe at an atomic level. In this process, free carbon atoms in the vicinity diffuse through the assistance of the electron beam (7, 31). Electrons accelerated through 80 kV can transfer up to 16 eV to a carbon atom and 3 eV to a single Fe atom (32). At room temperature, the thermal activation energy for the graphene edges to reconfigure (carbon insertion or removal) is insufficient, whereas carbon atom removal or translocation by the electron beam can occur (4, 11). In this work, we show that Fe atoms at graphene edges are able to both remove and insert carbon species by serving as a catalyst to mediate a transition between pentagons and hexagons.

Compared with armchair edges, the translocation of Fe atoms at zigzag edges (Fig. 3 A), at times, was able to traverse or hop large distances in 1 s, which is shown in Fig. 3 B and C. A typical motion series of a single Fe atom on zigzag edge is shown in SI Appendix, Fig. S5.

By plotting the local displacement of the Fe atom on one graphene edge with respect to elapsed time, it is found to exhibit 1D random motion (Fig. 3 D), consisting of random jumps and random stationary times. Displacements, which are equal or smaller than a single atomic distance (C–C spacing), correspond to hexagon–pentagon transitions. These transitions usually occur rapidly (i.e., at 28 s) (the corresponding TEM image is shown in Fig. 3 F). Long stationary periods are found to occur preferentially at pentagon formations at armchair edges (e.g., from 42 to 58 s) (the corresponding TEM image is shown in Fig. 3 G). Stationary periods also occur for hexagon formations consisting of five C atoms and an Fe atom (Fig. 3 G) for both armchair and zigzag edges. Large displacements or hops are found to occur only along zigzag edges (e.g., at 85 s) (the corresponding TEM image is shown in Fig. 3 G). The DFT calculation data yield the absorption energies for an Fe atom in various configurations at armchair or zigzag edges (SI Appendix, Fig. S2). The DFT data match the experimental observation well, in that the observed trapping state is a high-absorption energy configuration (5.45 eV) compared with other configurations. However, the stability of Fe atoms is dependent on not only the thermodynamics but also, the kinetics, which we elaborate on later. Additional insight can be obtained by evaluating the absorption energies for an Fe atom at armchair and zigzag graphene edges. The data are presented in Fig. 3 A. The dependence of the MSD with respect to time can be characterized by a power law: \( R^2(t) \sim t^\gamma \) (linear on the log–log plot). For the dynamic motion along an armchair edge, \( \gamma = 0.7 \) (linear correlation coefficient is 0.98), whereas for the zigzag edge, \( \gamma = 1.2 \) (linear correlation coefficient is 0.99). These values indicate a deviation from solely thermally activated normal diffusion (\( \gamma = 1 \)). In short, individual Fe atoms undergo subdiffusion (\( \gamma < 1 \)) along armchair edges and superdiffusion (\( \gamma > 1 \)) along zigzag edges. The probability distribution of the displacements (\( \delta \)) between each consecutive snapshot also fits a power law,
P(l) \sim l^{-\mu} \text{ (rather than exponential)}, \text{ where } \mu = 2.2 \text{ on the armchair edges and } \mu = 1.8 \text{ on the zigzag edges (SI Appendix, Fig. S6). The probability distribution of the resting time (time interval between two consecutive jumps) can be fitted by } P(\tau) \sim \tau^{-\nu}, \text{ where } \nu = 0.9 \text{ for armchair and } \nu = 1.1 \text{ for zigzag (SI Appendix, Fig. S7). The divergence of } \langle l^2 \rangle \text{ when } \mu < 2 \text{ and the divergence of } \langle \tau \rangle \text{ when } \nu < 1 \text{ at the time limit will lead to superdiffusion (levy flight) and subdiffusion, respectively (22, 23). In our case, the competition between large hopping distances and long stationary times may lead to cross-overs between the different diffusion regimes. The relationships between } \mu, \nu, \text{ and } \gamma \text{ (according to a continuous time walking model: } \gamma = 2 + \nu - \mu, \nu < 1 \text{, or } \gamma = 3 - \mu, \nu > 1 \text{) (22), where } \mu \text{ and } \nu \text{ are the probability distribution values, can yield the values for } \gamma \text{ along both armchair and zigzag edges in our experiments.}

Moreover, changing the electron beam intensity does not change this anomalous diffusion nature of the Fe atom. We measured the single Fe atom behavior on the same graphene edge (a mixed edge composed of zigzag and armchair sections) under three different beam intensities. The single Fe atom MSD results and beam intensity measurements are shown in Fig. 4C. All of the power law fitting parameters for the MSD as a function of time are shown in Fig. 4C, Inset. The diffusion of the single Fe atom under beams 1–3 exhibits superdiffusive behavior. The fitted power law exponents are 1.15, 1.10, and 1.11 (electron beam intensity from low to high) (the measured beam intensities with respective to lateral positions on the sample are shown in Fig. 4D, independent of the beam intensity. Although the fitted power law exponents are quite close, for the different intensities, the intercepts in the linear fit (prefactor in the power law) do show large differences. We can easily get the generalized diffusion coefficient } K^\gamma \text{ by fitting MSD with the following equation (22):}

\[ \langle R^2(t) \rangle = \frac{2K^\gamma}{\Gamma(1+\nu)} t^{\gamma+\nu-\mu} \]  

(in this superdiffusion case, we can assume } \nu = 1 \). The } K^\gamma \text{ as a function of beam intensity is presented in Fig. 4D, Inset. The generalized diffusion coefficient is linearly correlated with the beam intensity, and by extrapolation, the intercept for the zero generalized diffusion coefficient corresponds to a beam intensity around 60 counts, which is very close to our measured background CCD signal around 65 counts (electron beam blocked).

The MD simulations (33, 34) for zigzag and armchair edges show Fe atom motion very similar to our experimental observations (Movies S3 and S4). A more in-depth analysis indicates the presence of the superdiffusion regime with } \gamma = 1.25, \text{ which is similar to our experimental value of } \gamma = 1.2 \text{ (SI Appendix, Fig. S8). In addition to single atoms at graphene edges, we sometimes observe pairs of Fe atoms at edges. In the case of two Fe atoms,
the observed motion is found to be correlated in that the atoms tend to move coherently as a pair. Moreover, their diffusion rate is significantly smaller than that found for single Fe atoms. These aspects are highlighted in Fig. 4B and SI Appendix, Fig. S9.

**Discussion**

We have previously shown that electrons accelerated through 80 kV are able to sputter C atoms at graphene edges in a zipper-like fashion (1). In the case of Fe atoms at graphene edges, we also observe C atom removal; however, the Fe atom always remains at the interface region at the edge where the last C atom was removed, suggesting involvement of the Fe atom in the process. More importantly, at times, the Fe atom allows carbon atom insertion (viz., we directly observe the catalytic growth of sp² carbon from a single Fe atom at the atomic scale). Examples of this process can be seen in Fig. 2. Initially, the Fe atom is involved in a five-atom ring (pentagon), after which a C atom is inserted, thus forming a six-atom (hexagonal) ring; finally, the Fe atom leaves the hexagonal ring and is replaced by a C atom, forming an all-carbon hexagon. These experimental observations are concomitant with the theoretical predictions by Lee et al. (19). Our observed growth cycle is illustrated in Fig. 5, which includes the DFT calculated energies involved in each step of the cycle. For a deeper understanding, we conducted high-temperature density functional tight binding MD (DFTB-MD) simulations (33) that emulate the catalytic process. Details can be found in SI Appendix, Figs. S10 and S11 as well as Movie S5. In essence, the DFTB-MD simulations highlight the importance of Fe chemical affinity, which enables an Fe atom to absorb nearby C atoms and transfer captured C atoms to nearby growth sites. Many of the translational states (for example, captured C atoms at Fe atoms) are difficult to observe experimentally because of the instrument’s temporal resolution; however, the starting and ending states, which are more stable, are observed. Some intermediate states are also observed (SI Appendix, Fig. S10). These DFTB-MD simulations are carried out at high temperature, enabling one to accelerate the process and thus, make such simulations feasible. Although such simulations are not exactly equivalent to the processes under the electron beam that we observed in the experiments, they do, however, show the possible reaction paths and routes at graphene edges, and the results are in accordance with the lowering of the total energy and the experimental observations where the process is triggered and assisted by the electron beam.

With respect to the removal of carbon atoms, the steps involved are simply the reverse of carbon incorporation (viz., a carbon atom is replaced by an Fe atom in a benzene ring on which another carbon atom is ejected, thus forming a pentagon ring). The repetition of this process, in essence, leads to the unzipping of carbon atoms as experimentally observed (SI Appendix, Fig. S5). For the most part, the unzipping process tends to occur at zigzag edges (Fig. 5B). This preferential unzipping is because when an Fe atom cycle to eject carbon occurs at an armchair edge, the resting position of the Fe atom is inside (not at the edge); thus, a larger activation energy to move to an edge catalytic position is required. This larger activation energy explains the long residence times (Fig. 3F) observed for Fe atoms at nonzigzag edges. These differences between edge types for the energy for Fe atom displacement will affect the Fe atoms diffusion along the edge. In the case of armchair edges, two attachment configurations exist (Fig. 5C). DFT calculations confirm the existence of the two attachment configurations and also show a relatively high energy difference between these two configurations of 1.1 eV. If one compares this attachment configuration with zigzag edges, a single attachment configuration exists (Fig. 5D); the diffusion barrier, as determined from semiclassical MD calculations (SI Appendix, Fig. S12), is ~20% of that for armchair diffusion. This barrier difference is critical for the different diffusion behaviors.

We can now come to a physical picture of the electron beam-induced Fe atom diffusion on the graphene edge. The beam energy is constant at 80 kV, which means the average energy transfer from high-energy electrons to target atoms is constant. In the literature (32), it is already calculated that, under the intensity of the TEM beam, the electrons are basically one by one interacting with the target atoms. Therefore, it is reasonable to assume that the distribution of the jump length of the Fe atom will not be greatly affected by different intensities (because the energy of the electrons does not change; just the flux of electrons changes). However, by varying the beam intensity, the average waiting time \( \tau \) between two movements will be inversely dependent on the beam intensity. In the superdiffusion case, we can assume that \( \tau = 1 \), and from Fig. 4D, Inset, we can see \( 1/\nu \) is linearly dependent on the beam intensity in our experiments, which is in accordance with this e-beam activation model. In addition, without e beam, based on our MD simulations (SI Appendix, Fig. S11), the anomalous diffusive behaviors can still prevail.

In summary, we have shown that, through in situ C\textsubscript{4} aberration-corrected TEM, the diffusion of single Fe atoms at graphene edges is edge-dependent (zigzag and armchair), with subdiffusion being shown for armchair edge termination and superdiffusion being shown for zigzag termination. Supporting theoretical calculations show that this difference is related to different diffusion barriers between the edge terminations. More
importantly, our in situ investigations directly captured the catalytic removal and growth of sp² carbon by a single Fe atom while under electron irradiation. The anomalous diffusion behavior can be expected to influence the growth/catalytic kinetics of synthetic sp² nanomaterials grown using metal catalysts. In short, our in situ observations along with supporting (MD and DFT) theoretical studies provide key insights into the fundamental processes for the growth of sp² nanostructures, such as graphene and carbon nanotubes by metal catalysts.

**Materials and Methods**

**Sample Fabrication and Preparation.** We prepared the synthetic single-layer graphene by chemical vapor deposition over Mo foil coated with 200 nm Ni using methane as the feedstock (25). The as-produced graphene was then coated with poly(methyl methacrylate) and immersed in 1 M FeCl₃ solution. The sample was then thoroughly rinsed with distilled water, dried, and transferred to a standard lacey carbon TEM grid. The poly(methyl methacrylate) layer was then removed with hot acetone vapor, and finally, the graphene sample was annealed at 300 °C in high vacuum (10⁻⁶ mbar) overnight.

**LVACTEM Characterization.** A JEOL 2010F transmission electron microscope equipped with two CEDOS Corrected Electron Optical Systems GmbH spherical aberration correctors was used for the in situ studies. The in situ experiments were conducted at room temperature. The transmission electron microscopy was operated using an 80 kV accelerating voltage. The electron beam current during observations was ~1 pA/mm². The beam intensity was kept constant for all image capture events on a Gatan UltraScan 1000 camera. The exposure time for each snapshot was 0.1–0.3 s, whereas the time interval between two consecutive snapshots was about 1 s. Some TEM images are processed using background subtraction filtering and Wiener filtering to minimize noise.

**Multislice TEM Image Simulation.** The multislice TEM image simulations were performed using JEMS software. For the simulations, an accelerating voltage of 80 kV and an energy spread of 0.3 eV were used. The chromatic aberration Cc was set to 1 mm, and the spherical aberration Cs was set to 1 μm. A defocus between 4 and 5 nm was used, and a defocus spread of 3 nm was implemented. These values are consistent with the experimental conditions used.

**DFT Calculations.** We conducted spin-unrestricted DFT computations through an all-electron method within the generalized gradient approximation with the Perdew–Burke–Ernzerhof function implemented in the DMol₃ program package as available in the Materials Studio software package by Accelrys Inc. (29). The basis set was selected as the double numerical polarized basis set that includes all occupied atomic orbitals with a second set of valence atomic orbitals and polarized d-valence orbitals. The real-space global orbital cutoff radius was set to 4.8 Å, whereas the interlayer distance was set to 3.4 Å. The relaxed geometries were obtained by minimizing the total energies until the energy, maximum force, and maximum displacement were less than 2 × 10⁻⁵ hartree/Å, 0.005 hartree/Å, and 0.005 Å, respectively. The k-points samplings were 3 × 3 × 1 in the Brillouin zone.

**MD Simulations.** Theory at the classical level was achieved by the computation of MD trajectories integration within reax-ff theory with Fe/C parameters as shown by Aryanpour et al. (33) and van Duin et al. (35). The MD trajectories were solved using LAMMPS code (36). The semiempirical DFTB+ self-consistent charge theory (34, 37) (approximate DFT theory with a tight binding model for next nearest neighbor interaction) although less accurate than DFT, is superior to classical schemes. In this case, the calculation scale that we applied was based around 100 atom systems in a time frame of 50 ps. A high temperature (5,000 K) Nose–Hoover NVT (mole (N), volume (V), and energy (T)) ensemble was used to simulate the nonequilibrium states under electron beam irradiation. We considered both spin-polarized and nonpolarized states, and both show similar results.

**ACKNOWLEDGMENTS.** We thank Prof. You-Hua Luo (East China University of Science and Technology) for providing the Dmol3 code. We also thank Leibniz-Institüt für Festkörper- und Werkstoffforschung Dresden and in particular, the Institute for Solid State Research for use of their microscopy facilities. J.Z. thanks the Deutsche Akademische Austausch Dienst, Q.D. thanks the Deutsche Forschung Gemeinschaft (Project PO 1602/1–1). Sino-German Center for Research Promotion Grant GZB71 is acknowledged. This work was supported by Institute of Basic Sciences Korea Grant IBS-R01-D1.
Supporting information for

**Direct in-situ observations of single Fe atom catalytic processes and anomalous diffusion at graphene edges**

Authors: Jiong Zhao\(^{a,f,g}\), Qingming Deng\(^{b}\), Stanislav M. Avdoshenko\(^{c}\), Lei Fu\(^{d}\), Jürgen Eckert\(^{a,e}\), Mark H. Rümmeli\(^{f,g}\)

\(^{a}\) IFW Dresden, Institute of Complex Materials, P.O. Box 270116, D-01171 Dresden, Germany

\(^{b}\) IFW Dresden, Institute of Solid State Research, P.O. Box 270116, D-01171 Dresden, Germany

\(^{c}\) Purdue University, West Lafayette, IN 47907-2045, USA

\(^{d}\) College of Chemistry and Molecular Science, Wuhan University, Wuhan, 430072, P. R. China

\(^{e}\) TU Dresden, Institute of Materials Science, D-01062 Dresden, Germany

\(^{f}\) IBS Center for Integrated Nanostructure Physics, Institute for Basic Science (IBS), Daejon 305-701, Republic of Korea

\(^{g}\) Department of Energy Science, Department of Physics, Sungkyunkwan University, Suwon 440-746, Republic of Korea

Corresponding author. E-mail: mhr1@skku.edu

This material consists of 12 figures (Figure S1~S12) and 5 videos, to present more experimental data and theoretical calculation results.

**Table of contents**

1. Video strategy of the in-situ HRTEM.

2. Quantitative analysis of the HRTEM images and multislice simulation images.

3. The possible atomic configurations for an Fe atom attached to graphene edges as determined by DFT calculations
4. The experimental observations of single Fe atom dynamics at graphene edges

5. The analysis on the frequency distribution of Fe atom jump lengths and waiting times in experiments

6. The electron beam effect

7. Molecular Dynamics (MD) simulations for an Fe atom diffusion along a zigzag edge

8. The motion of two Fe atoms along zigzag edge

9. The DFTB MD simulations of Fe atom catalytic carbon edge reconstruction (growth and removal)

10. Non-equilibrium energy profile of single Fe atom along zigzag and armchair edges

1. **Video strategy of the in-situ HRTEM**

In our in situ studies at room temperature Fe atoms attached to graphene edges appear relatively stable in that on average the Fe atom changes position every 5 seconds. It is natural to assume the electron beam drives this process. When an Fe atom diffuses the process occurs at a time scale of around $10^{12}$ s, far beyond the temporal resolution of our camera. However, this does not affect our diffusion analysis for the mean square displacement ($<R^2(t)>$). If an Fe atom does diffuse during image capture (0.1s) it should leave a trace of the motion on the image which would appear as two Fe atoms (e.g. see Figure S10, snapshot at 2 s). In practice most of the Fe atoms are static during image capture. For the period between two snapshots (1 s), it is possible the Fe atom moves away and then back to its original position (i.e. returns to its point of origin) within one second. We estimate this possibility by using the data in Figure S6. The ratio between the possibility of the Fe atom remaining static and jumping one atomic distance and immediately back is estimated to about 20:1. In the case of two or more atomic distances and back the ratio increases the greater the atomic jump. Thus, it is reasonable to assume that the Fe atoms we observe are on the whole static within a time frame of one second.
2. Quantitative analysis of the HRTEM images and multislice simulation images.

**Fig. S1.** The intensity profiles for the two configurations of a single Fe atom residing at armchair edges. The black and red lines correspond to the black and red lines in the experimental and simulated images in the insets, respectively.

The experimental HRTEM intensity profiles match very well with the intensity profiles from the image simulations based on the DFT derived structures and the experimental imaging parameters. The lateral position at the maximum and minimum of the experimental and simulated images also match. In addition, the contrast ratio between Fe and C is within 1.8~2.0, which is much larger than the contrast ratio between Si (1.4~1.5) which is a common dopant for CVD synthesized graphene samples. Moreover, the ratio is much smaller than the contrast ratio of 3.0 for Mo (CVD substrate) under the current imaging conditions. Further confirmation for atom being Fe is found from EELS elemental analysis which shows a prominent Fe L$_{2,3}$ edge (ref 26) and no other peaks such as Ni and Mo (CVD substrate).
3. The possible atomic configurations for an Fe atom attached to graphene edges as determined by DFT calculations

**Fig. S2.** The six stable configurations for an Fe atom attached to graphene edges as determined through DFT calculations (see main text). The first and third configurations on an armchair edge have a pentagon and hexagon structure, which are core to the catalytic process. The derived configurations from the DFT calculations are used to build the atomic models for the HRTEM images. The DFT calculated Fe atom absorption energies for all configurations are also provided.
4. The experimental observations of single Fe atom dynamics at graphene edges

**Fig. S3.** (a-c) A series of TEM images showing the insertion of two carbon atoms by the Fe atom in 2 seconds. (d-f) The corresponding atomic models for the images in (a-c). In the inset of (f) the three frames are combined (overlapped) to present the dynamics of the Fe atom.
Fig. S4. (Left) A series of images showing an Fe atom diffusing along an armchair edge over an 8 s period. The temporal resolution is 1 s. Frames at 0 s, 1 s, 3 s, 5 s, 7 s, 8 s are shown. Frames 2 s, 4 s, 6 s are the same as 1 s, 3 s, 5 s, respectively. The atomic structure at the edge are highlighted in yellow (carbon) and red (Fe). The red bars on the lower right in each frame indicate the same reference lattice which is determined from a defect in graphene in a larger HRTEM image. The black scale bar is 0.5nm. (Right) The atomic models corresponding to the frames on the left, grey (carbon), orange (Fe). The first model corresponds to the first frame in i and the third corresponds to the second frame, the fifth corresponds to the third frame, and so on. The second model, fourth model, and all other even numbered models are added in between to help highlight intermediate processes. The carbon atoms which are removed in the next step are labeled with red triangles, and carbon atoms have been added in, \textit{viz.} growth steps are labeled with green triangles.
**Fig. S5.** (Left) Image series showing an Fe atom diffusion along a zigzag edge over a time span of 41 s. Displacement occurs at 3 s, 6 s and 41 s. The Fe atom remains static from 6 s to 41 s. The atomic structures are also highlighted. The red bars (bottom right) are for reference and mark the same point on the lattice for all frames. The scale bar is 1nm. (Right) The atomic models built according TEM images in panel. One more steps are inserted into each consecutive frame. The red and green triangles indicate the same nomenclature as in supporting information figure S4. Scale bar is 1nm.
5. The analysis on the frequency distribution of Fe atom jump lengths and waiting times in experiments

**Fig. S6.** The probability distribution of the displacement for each jump for Fe atoms, along the armchair and zigzag edges.

**Fig. S7.** The probability distribution of the waiting time between each jump along armchair and zigzag edges.
6. The electron beam effect

As suggested by the DFT calculations, the Fe atoms are strongly bound to the graphene edges. The absorption energy for stable configurations are typically 2.5~3eV (see Supporting information Figure S2), which is too high for any kind of room temperature diffusion within our observation time scale (100~300s).

During TEM observation energy transfer from (imaging) electrons to the Fe or C atoms is unavoidable. Electrons from the beam interact with specimen atoms for less than 100 fs, including energy dissipation time to the environment. This is much shorter than the time interval between two electron hits under our experimental beam intensity and, thus, the electron beam can be considered to interact with the target one electron at a time (1). The maximum energy (recoil energy) transfer from an 80 kV electron to a Fe atom is about 3eV, just within the range of the absorption energies. To better interpret the effect of the electron beam, we varied the beam intensity and obtained the results shown in Fig.4C,D in the main text.

The generalized diffusion behaviour for a continuous time random walk (CTRW) model can lead to the following equation (ref 22 in the main text), for one dimensional case,

$$< R^2(t) > = \frac{2K_0^\mu}{\Gamma(1+\alpha)\tau^{2+\nu-\mu}}, \hspace{1cm} (1)$$

where $K_0^\mu$ is the generalized diffusion coefficient, defined by

$$K_0^\mu = \sigma^\mu / \tau^\nu,$$

The possibility distribution function (pdf) of the time and jump length are

$$\omega(t) \sim (\tau/t)^{1+\nu},$$

$$\phi(R) \sim 1/(\sigma^\mu R^{1+\mu}).$$

The physical meaning of $\tau$ and $\sigma$ can be understood with the help of the average resting time in the Poisson distribution and standard variance of Gaussian distribution.
In our experiments, we fabricate one graphene edge by electron beam irradiation which becomes a combination of armchair and zigzag edge. We vary the electron beam intensity and can measure the electron beam intensity directly by the CCD camera. Then we measured the single Fe atom behaviour on the same graphene edge (a mixed edge composed of zigzag and armchair sections) under three different beam intensities. The single Fe atom MSD results and beam intensity measurements are shown in Fig.4C,D.

All the fitting parameters for the mean square displacement (MSD) as a function of time are shown in the inset table of Fig.4C. The diffusion behaviour of the single Fe atom under beam size 1,2,3 all exhibit superdiffusive behaviour. The fitted power law exponents are 1.15, 1.10 and 1.11. While the fitted power law exponents are quite close, for the different intensities, the intercept in the linear fit which is the prefactor in the power law shows large difference. We can easily get the generalized diffusion coefficient from fitting using eq.(1) in the main text (in this superdiffusion case, we can assume \( \alpha = 1 \)). The \( K_0^B \) as a function of beam intensity is presented in the inset of Fig.4D. The generalized diffusion coefficient is linearly correlated with beam intensity, even by extrapolation the zero generalized diffusion coefficient (\( K_0^B =0 \)) corresponds to a beam intensity around 60 (linear fitting intercept = 60), which is very close to our measured background CCD signal ~65.

The DFT calculated barriers for Fe atom moving are all relatively high, and our experiments are carried out under room temperature, which is too low for only the thermal excitation inducing the motion of Fe atom on graphene edges in the observation time scale (seconds). Here the electron beam transfers the necessary energy to the Fe atom or neighboring atomic structures which can induce the movement of the Fe atom. To generalize the diffusion on graphene edges, even without electron beam excitation, the super- or sub- diffusion behavior are still no different from the one under electron beam excitation, evidenced by our MD simulations under high temperatures (just thermal excitation). Unfortunately we cannot test this now because we still need the electron beam to "see" and measure. In summary, both our experimental and theoretical investigations have shown that the anomalous diffusion on graphene edges is mainly
caused by the specific energy landscape, probably broken of symmetry both in geometry (one dimension) and history (non-Markovian process). Although the full physics about this still needs further investigation.

The effect of electron beam here is to excite the Fe atom to move, similar to the effect of thermal energy, evidenced by the linear dependence of the generalized diffusion coefficient on the beam intensity. Initially, the stable absorption configurations of single Fe atoms at graphene edges are activated by the electron beam energy as well as by the thermal energy. Using different electron beam intensities can change the activation frequencies accordingly. Secondly, the anomalous diffusion behavior is not affected by the electron beam, but is only related to thermal activation, the energy landscape at the graphene edge, etc.

The catalytic processes we observed should also be assisted by the electron beam. Our modeling (molecular dynamics) at high temperatures can qualitatively resemble the processes we observed in TEM. In these simulations the thermal energy (high temperature) has an equivalent effect as the combination of an irradiating electron beam and room temperature thermal activation.

7. Molecular Dynamics (MD) simulations of Fe atom diffusion along graphene edges

Within conventional MD schemes the TEM-experimental time scale (~100 s) is an inaccessible task, even if an acceleration of sampling by means of meta-dynamics or umbrella sampling techniques were possible. It might help to have a better idea about overall potentials/Gibbs energy profiles, but structural changes as function of time cannot be solved at the second time scale. However, by making an assumption that a short-time behavior can be propagated up to large time scales, one can use a simple MD simulation at high temperature to find the MSD with temperature constrains. An additional kinetic energy given with the same order as the highest possible activation barrier will not change MSD significantly, and should keep the information governed by the actual energetic landscape of potential energy surface provided by the original system.
To illustrate this let’s consider a particle traveling along an edge has an energy landscape \( E_p(x) \) with position variable \(-x\). It would take time, \(-t_o\), to jump over the barrier to explore the phase space further.

Without changing the activation energy, \(-E_a\), we can add energy to a particle \( N \) times \( k_bT \) to effectively change chemical the potential of the particle \( E_p^* \sim E_p + Nk_bT \). This will promote atomic motion along original \( E_p \) profile faster over the barriers within time \( t'(T) \) which is smaller than the original \( t_o \). If the particle interaction is a weak function of the participle kinetic energy, the MSD should not be affected much. It has the position \(-x(t)\) as a random variable with \( \langle x(t)^2 \rangle \) as given. By pulling an additional energy in to the system, \(-Nk_bT\), which is given in terms of kinetic energy \((v_x,v_y,v_z)\), one would expect \( x^*(t) \sim x(t) + \langle v_x \rangle t \); and so \( \langle x^*(t)^2 \rangle = \langle x(t)^2 \rangle + 2\langle v_x \rangle t\langle x(t) \rangle + \langle v_x^2 \rangle t^2 \). Having placed \( \langle x(t) \rangle \) to “0” (as for a zero shifted normal distribution), we have \( \langle x^*(t)^2 \rangle = \langle x(t)^2 \rangle + \langle v_x^2 \rangle t^2 \) where \( \langle v_x^2 \rangle t^2 \) is just a shift of the MSD, and therefore MSD \sim MSD(T)^*, if \( Nk_bT \) is not too big compared to \( E_a \).

Our construction discussed below is based on an immobilized graphene layer with zigzag and armchair edges with Fe-atoms placed randomly at the edge, but in the optimal configurations predicted by DFT.

Considering the motion of the Fe-atom is assisted by the energy transfer from an electron beam in TEM experiments, we started our theoretical study within a classical potential in the MD simulation, which has been proposed as a reactive force field \((2,3)\), and proven to suitable for such cases.

Classical potentials are known to be less accurate than any \textit{ab-intio} models. To understand the energetics in our problem, before the product runs, we have checked the minimal potential energy profile as a function of the position of the Fe-atoms along the zigzag and armchair edges. The results are shown in the Supporting information Figure S8. Apparently, the potential energy barriers are quite different from those predicted from DFT theory in this study. Remarkably the same proportion between zigzag and armchair has been kept, which is similar to DFT prediction of one quarter. Here we can conclude that we can compare behavior of the Fe-atoms around different edges within reax-ff theory, but we cannot make precise prediction for the necessary access energy. It should be scaled and optimized for the problem to
have more predictive power. As we will present later, the same kinetic energy makes transformation rate much higher at the DFTB level of theory.

Despite the issue of incorrect energetics, the classical description allows us to make a sophisticated integration of the MD trajectory up to ~4-5 ns. However, even with this integration length, it is insufficient to produce statistically relevant Fe-rearrangements. Due to the high activation energies at 300K, Fe-atoms are localized. To accelerate the process of structural reconstructions, namely Fe atoms traveling along the edges, we have to make an assumption in the access energy, which can provoke a reaction and help overcome the activations barriers, thus allowing us to explore the phase space further. High-energy electron beams can justify the actual presence of the access energy in these experiments, as we have previously demonstrated (4). The access energy was mimicked by coupling our systems with a Nòse-Hoover thermostat (NVT) and integrating the equation of motion within NVT ensemble with temperature constrains.

Having provided additional kinetic energy, we are now able to follow significant structural changes on time scale of nanoseconds. We have run several ~4-5 ns MD integrations. Below we discuss representative examples. For the model system optimized zigzag or armchair nanoribbons, with two zigzag/armchair edges (~100 Å) with a random distribution of the 2 Fe atoms on each edge (see Supporting information Figure S8) was used. The integration was performed with a time step 0.5 fs with an overall integration time of 4-5 ns. For dynamic acceleration we have used a kinetic energy set to 0.5 (T=6000K)/1.0 (T=12000K) eV. That is approximately half the barrier height in the zigzag case and one quarter in case of armchair edges.

In summary, Supporting information Figure S8 we present structural changes (a,c) and statistics of the changes in MSD and RMSD function (b,d) for zigzag and armchair edges respectively, also see supporting information Video S3 and Video S4. For zigzag edges based on 100 ps sampling we were able to estimate the MSD function, which is shown on Supporting information Figure S8b. It predicts a value
close to the experimentally observed value, $\gamma \sim 1.25$. Additional smoothing of the data points (running average) can increase this number up to 1.4, which highlights the statistical validity of the prediction. In the case of armchair edges, 6000 K is not enough to accumulate any significant structural changes, and so Fe-atoms remained localized up to 12000 K ($\sim 1.0$ eV). At such high temperature simple atomic motion is able to produce a complex RMSD as on Supporting information Figure S8d, but analysis of the diffusion type here is hardly possible. Although, in order to make verification tests to this theoretical data one should conduct more interdependent runs with variation of simulation parameters. It is important to compare the composed trajectory superposition of the zigzag and armchair cases. In the zigzag system the Fe-atoms distribution forms a continuous cloud-like form (Supporting information Figure S8a), while armchair (Supporting information Figure S8c) appears to be discontinuous or jumpy with strong preferential sites for atomic positions/localization, as we observed experimentally.

Fig. S8. a, superposition of the 4 ns trajectory with the sampling rate every 100 ps for zigzag edge case, where solid balls denote the staring position of the two Fe-atoms. b, log-log plot MS(lower right) demonstrates the super-diffusion behavior ($\gamma = 1.25$) with a running average along the RMSD it can increase up to 1.4. c, superposition of the 4 ns trajectory with the sampling rate every 100 ps armchair case, where solid balls denote the staring position of two Fe-atoms. d, RMSD profile for armchair system shows this system to be more localized in nature, even with a thermostat temperature at 12000 K.
8 The dual Fe atoms motion along zigzag edge

Fig. S9. a, The dual Fe atom motion along zigzag edge during 15 s. The two Fe atoms tend to attach together, also see Fig. 3d in the main text. Scale bar is 1nm. b, The corresponding atomic model during 15s, with one frame inserted between each two steps. The green and red triangles represent the growth and removal of carbon atoms same as in the main text.
9. The DFTB MD simulations of Fe atom involved carbon edge reconstruction (growth or removal)

In this section we present our DFTB-based molecular dynamic around an Fe-center where every 4 ps a C atom added and attached to the “catalytic” center (The Fe-atom is consider to have the highest affinity to carbon atoms). As previously we have simplified our system and consider the grapheme zigzag edge to be immobilized with the initial Fe-C and further clusters being mobile. For consistency with the classical study we used a 6000 K kinetic energy in the NVT/NH (with 3000 cm$^{-1}$ coupling strength). Every 4 ps a new C atom is coupled to the Fe center. Figure S10 shows some snapshots of the MD series. Over the running frames in this model we can observe strong similarities between the TEM experimental data (viz. structural changes of a pentagon to a hexagon to Fe being replaced by a carbon atom and the Fe atom then moves to other sites) and MD series. Furthermore, some transitional states (highlighted in Figure S10,S11) can also be occasionally observed in our TEM experiments (Figure S10, 7 ps, 11 ps and 12 ps).

**Fig. S10.** Snapshots of the MD series during 13 ps. At 0 ps the Fe atom sits at the 5 member ring position, while after 1ps one C atom is added into the ring and form a hexagon. At 7 ps another C atom is further added into the ring and forms a seven member ring. After some fluctuations, the Fe atom moves to the nearby site and two complete carbon hexagons are formed. Occasionally our TEM experiments can also capture some of these transitional states. (7 ps: pentagon-heptagon; 11 ps: dangling bonds; 12 ps: large ring cross two lattice distances).
10. Non-equilibrium energy profile of single Fe atom on zigzag and armchair edges

Fig. S11. Some transitional configurations by MD simulations of the single Fe atom on graphene edge bonding with the carbon atoms or clusters. The chemical affinity between Fe-C can be clearly identified.

Fig. S12. The energy profile obtained by reax-ff potentials (semi-classical), the dynamical diffusion barrier of Fe atom on armchair edge (red) is over five times of that on zigzag edge (black).
Supporting information Video legends

**Video S1** The *in situ* TEM series of Fe atom along graphene armchair edge

**Video S2** The *in situ* TEM series of Fe atom along graphene zigzag edge

**Video S3** The MD simulation series of Fe atom diffusion on zigzag edge

**Video S4** The MD simulation series of Fe atom diffusion on armchair edge

**Video S5** The MD simulation series of Fe atom involved graphene edge reconstructions

**Note:** (Video S1 and Video S2 are 10X accelerated as the real observation time, Video S3,S4 and S5 are 10^10X accelerated as the simulated time scale)

**References:**


Supporting Information

Zhao et al. 10.1073/pnas.1412962111

Movie S1. The in situ transmission EM series of the Fe atom along the graphene armchair edge.

Movie S2. The in situ transmission EM series of the Fe atom along the graphene zigzag edge.
Movie S3. The molecular dynamics simulation series of the Fe atom diffusion on the zigzag edge.

Movie S4. The molecular dynamics simulation series of the Fe atom diffusion on the armchair edge.

Movie S5. The molecular dynamics simulation series of the Fe atom involved in graphene edge reconstructions.

Other Supporting Information Files

SI Appendix (PDF)