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Direct visualization of reversible dynamics in a Si₆ cluster embedded in a graphene pore

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Clusters containing only a handful of atoms have been the subject of extensive theoretical and experimental studies, but their direct imaging has not been possible so far, with information about their structure provided mainly by theory. Here we report a direct atomically-resolved observation of a single Si₆ cluster trapped in a graphene nanopore. Furthermore, though electron-beam-induced irreversible atomic displacements have been reported before, here we report a sequence of images that show a reversible, oscillatory, conformational change: one of the Si atoms jumps back and forth between two different positions. Density-functional calculations show that the embedded cluster is exploring metastable configurations under the influence of the beam, providing direct information on the atomic-scale energy landscape. The capture of a Si cluster in a graphene nanopore suggests the possibility of patterning nanopores and assembling atomic clusters with a potential for applications.

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Silicon clusters have been the subject of a large number of theoretical and experimental studies due to their importance both in fundamental science and potential applications. The structural identification of silicon clusters has been primarily a theoretical search^{1–4}, as experiments such as vibrational⁵, photoemission⁶, infrared multiple photon dissociation spectroscopy⁷ and ion mobility measurements⁸ have provided limited and indirect information.

Recently, nanopore technology has emerged as a powerful tool for single-molecule detection and DNA sequencing. Using an electric field, DNA molecules in an electrolyte solution have been pushed through a graphene pore. As the molecules translocate they partially block ion flow through the pore, detected as a transient decrease in ionic current. Significant information (diameter, length and size) about DNA molecules was obtained through this translocation technique using graphene pores^{9–11}.

In this paper, we provide direct, atomically-resolved structure information of a single Si₆ cluster trapped in a graphene nanopore using aberration-corrected scanning transmission electron microscopy (STEM). Contrary to previously reported irreversible beam-induced dynamics^{12–22}, here we report a beam-induced reversible conformational transformation of the trapped Si₆ cluster in a graphene nanopore. Density-functional calculations of an embedded Si₆ cluster are used to probe its bonding to the host graphene lattice and the energy barriers for the conformational transformation. Though the Si atoms are bonded to C atoms with roughly the same bond lengths, the structure of the embedded cluster is only slightly different from that of the free cluster.

Results

Z-contrast images of a Si₆ cluster trapped in a graphene pore.

Figure 1 shows a sequential set of annular dark field (ADF) Z-contrast images of a single Si₆ cluster trapped in a graphene nanopore. Electron-beam-induced ejection of carbon atoms and defect creation/migration has been actively studied in graphene and carbon nanotubes^{12–22}. Contrary to these irreversible dynamics, we find that an oscillatory motion occurs in the trapped Si₆ cluster: one of the Si atoms executes a back-and-forth motion corresponding to the reversible conformational change of

the Si₆ cluster in the graphene pore. The acquisition time for the sequential images was ~6 s per frame, which implies that the conformational transformation occurs reversibly in less than ~10 s.

Three-dimensional structure characterization. The ADF images exhibit two representative stable structures with the oscillating Si atom either at the left or right sites as indicated in Fig. 2a,d. However, the ADF images do not reveal the full three-dimensional (3D) structure of the cluster. To obtain the pertinent structures, we performed density-functional calculations using the following procedure (see Supplementary Fig. S1). (i) The in-plane (xy-plane) atomic positions were extracted from the two fundamental configurations seen in ADF images. (ii) Coordinates in the third-dimension (along the z axis) were assigned to the Si atoms, resulting in nine distinct trial 3D structures for each of the two configurations. (iii) Each trial Si structure was embedded in a graphene pore and in each case the entire system was fully relaxed using first-principles methods. The embedded cluster configuration with the lowest energy corresponding to each of the two fundamental configurations seen in ADF images was then selected (see Supplementary Fig. S2). There exists a small deviation in the Si atomic coordinates between the experimental ADF images (Fig. 2a,d) and the calculated structures (Fig. 2b,e). The average Si-C bond length for two clusters is 1.85 ± 0.1 Å, which is similar to that for Si-C bulk (1.89 Å).

Symmetry identification of three Si₆ clusters embedded in graphene pore. After some time under the electron beam, one C atom was ejected from the pore edge. Another stable structure configuration was observed. From the ADF Z-contrast image and 3D atomic configuration as shown in Fig. 3a–c, we find that it has a higher-symmetry atomic configuration compared with the previous two clusters.

To identify the symmetry of the three observed configurations for the Si₆ cluster trapped in the graphene pore, the graphene matrix was removed and the remaining Si₆ were relaxed in free space. We find that the Si₆ clusters collapse to ground-state configurations with full C_{2v}, C_s and D_{4h} symmetry, respectively, as indicated in Fig. 3d–f.

Figure 1 | Sequential STEM-ADF Z-contrast images of the Si₆ cluster embedded in a graphene pore (a–h) The images have been low-pass filtered in order to reduce random noise. Scale bar, 0.2 nm.

Figure 2 | 3D structure characterization. (a,d) ADF Z-contrast images of two representative stable Si_6 cluster configurations embedded in graphene pore. (b,e) The two- and (c,f) 3D structures obtained from first-principles calculations. Si and C atoms below the graphene plane are shaded. L or R labels are used to highlight when the oscillating Si atom is either at the left or right sites. Scale bar, 0.2 nm.

Figure 3 | Symmetry identification of three Si_6 clusters embedded in graphene pores. (a) ADF Z-contrast image of the Si_6 stable cluster embedded in a graphene after the ejection of one C atom. Scale bar, 0.2 nm. (b,c) The two- and 3D structures obtained from first-principles calculations, respectively. Atoms below the graphene plane are shaded. (d-f) The 3D structures of Si_6 clusters with distorted C_{2v} , C_s and D_{4h} symmetry, respectively. The trapped Si_6 clusters collapse to C_{2v} , C_s and D_{4h} symmetry configurations when the graphene lattice is removed, as shown in the last row.

In the free state, the total energy of the Si_6 cluster is essentially the same for the three different configurations with C_{2v} , C_s and D_{4h} symmetries, and energy barriers between them are small, suggesting a fluxional ground state⁴. However, the present findings show that the clusters trapped in the graphene pore exhibit a distorted version of one of the free-cluster symmetries as the Si atoms are bonded to C atoms at the pore edge.

Energy barrier and transition time for conformational transition. Through a sequential set of ADF Z-contrast images as shown in Fig. 1, we have shown that a Si_6 cluster trapped in a graphene pore undergoes reversible conformational transformation. Here we investigate the trajectory and energy barrier for the transformation process using the nudged elastic band method²³. The initial, three intermediate and the final atomic configurations of the embedded cluster are presented in Fig. 4a–e to show the transformation pathway. The 3D structure of the clusters shows that, though only one Si atom executes an oscillatory motion in the xy-plane, the neighbouring Si and C atoms also move along the z axis in response to the oscillatory motion.

We find that the energy barrier (E_B) for the transformation is 1.44 eV to move out of the ground-state configuration and only 0.8 eV to return to the ground-state configuration as shown in Fig. 4f. According to transition-state theory²⁴, the required time for a transformation is given by,

$$t = \nu^{-1} \exp\left(\frac{E_B}{k_B T}\right) \quad (1)$$

where ν is the characteristic attempt frequency of a Si atom ($\sim 10^{12}$ – 10^{13} Hz), k_B is the Boltzmann constant and T is the temperature. We estimate that the thermal activation over 1.44 and 0.8 eV energy barriers, at room temperature, takes approximately 10^{11} and 10 s, respectively, (Fig. 4g). Thus, the

observed oscillation of the Si atom in a graphene pore, which takes place in < 10 s, is induced by the electron beam.

Calculations for scattering cross section and the number of displacements. We revealed that the observed conformational transformations are not thermal but rather induced by the beam. However, we still need to understand why the back-and-forth motion of a Si atom corresponding to a reversible conformational transition occurs on a similar time scale (~ 10 s). To explore this issue, we calculated the scattering cross sections for the two processes. The pertinent theory is described in ref. 25. The basic point is that during an electron-nucleus scattering event, the energy transfer is given by²⁵,

$$E_t = \frac{E(E + 1.02)}{496A} \sin^2\left(\frac{\theta}{2}\right) \quad (2)$$

where θ is the scattering angle indicated in the inset of Fig. 5, E is the incident electron energy in MeV and A is the atomic mass number ($A \sim 28$ for Si). For both conformational transitions, the energy transfer E_t from the electron beam to the cluster should be greater than the energy barrier E_B separating the two minima of the potential energy shown in Fig. 4f. The scattering cross section for an energy transfer $E_t \geq E_B$ can be calculated by first determining the minimum scattering angle $\theta_{\min}$ for which $E_t = E_B$ using equation (2) (Fig. 5a)²⁵. We expect $E_t \geq E_B$ for all $\theta \geq \theta_{\min}$ so that

$$\begin{aligned} \sigma(\theta_{\min}) &= 2\pi \int_{\theta_{\min}}^{\pi} \frac{d\sigma_{\text{el}}}{d\Omega} \sin\theta d\theta = \frac{4Z^2 R^4 (1 + E/E_0)^2}{a_H^2} \\ &\times 2\pi \int_{\theta_{\min}}^{\pi} \frac{\sin\theta}{[1 + (\theta/\theta_0)^2]^2} d\theta \end{aligned} \quad (3)$$

Figure 4 | Trajectory, energy barrier and transition time for conformational transformation. (a–e) Successive change of the 3D atomic configurations during the conformational transformation. (f) Energy barriers for the conformational transformation. (g) Time required for the transitions from the stable to the metastable Si_6 clusters (red) and from the metastable to the stable (green) to occur as a function of temperature. The required time for a transition to occur at room temperature is highlighted by the horizontal arrows.

Figure 5 | Energy transfer, scattering cross section and the number of displacements. (a) Energy transfer in an elastic electron-nucleus collision as a function of the electron scattering angle. Inset: schematic diagram of an elastic scattering event. (b,c) The scattering cross section as a function of the electron scattering angle, energy transfer. (d) The number of displacements of a Si atom as a function of energy transfer.

in which we use the differential elastic cross section $d\sigma_{el}/d\Omega$ for large-angle scattering and relativistic energies²⁵. a_H is the Bohr radius (5.29×10^{-11} m), Z is the atomic number ($Z = 14$ for Si), E_0 is the electron rest energy, $R = a_H Z^{-1/3}$ and $\theta_0 = \lambda/2\pi R$.

Based on our energy barrier calculations, in order to move a Si atom from the left site to the right site, E_t should be larger than 1.44 eV, for which equation (3) gives $\sigma = 1.2 \times 10^{-5} \text{\AA}^2$ (Fig. 5b). For the reverse process, the cross section is $2.8 \times 10^{-5} \text{\AA}^2$, only a factor of two larger. Experimentally, we observe a factor of two difference in the forward and reverse rates (see Supplementary Fig. S3). As a consequence, the conformational changes induced by electron scattering events occur on the same time scale even though the time scales of the corresponding thermal activations differ by ten orders of magnitude. Figure 5c shows how the scattering cross section depends on the energy transfer E_t (from a 60-keV beam electron to a Si atom), which is simply obtained by inserting equation (2) into equation (3).

The displacement rate p of an atom²⁶ is given by the product of the cross section σ and the beam current density j ($7.53 \times 10^{-11} \text{ A/\AA}^2$). In the STEM experiment, the electron beam scans the specimen from left to the right and from top to bottom staying for 24 μs at each pixel. One Si atom approximately spans 277 pixels. As a result, one can estimate that the electron beam is over a Si atom for about 6.6 ms. By multiplying this dwell time (6.6×10^{-3} s) by the displacement rate (p), we predict 37 displacements of a Si atom from the left site to the right site occurring because of the electron beam. For the reverse process, the number of displacements is expected to be about 87 as indicated in Fig. 5d.

Our calculated value is large compared with our experimental observation for the Si atom movement. However, the calculation does not take into account the need for a momentum transfer to be in the direction required to cause a jump, and is therefore expected to be higher than what we observe experimentally. We note, however, that the ratio of observed forward displacements (left to the right) and reverse displacements (right to the left) is indeed about two (see Supplementary Fig. S3), which is consistent with the calculated displacement ratio.

We further calculated that, under the 60 keV electron beam irradiation, the maximum energy transfer to a Si atom is 4.67 eV, which is lower than the energy for a knock-on displacement of a Si atom out of the cluster, which we calculate to be 6.39 eV. That is why for the most part of the experiment, we observed only reversible conformational transformations instead of ejection of Si atoms from the cluster.

Discussion

We directly observed three stable configurations with different symmetries for Si_6 clusters trapped in a graphene nanopore, and a conformational structural change between two structures induced by energy transferred from the electron-beam in the electron microscope. Specifically, the oscillatory motion of Si atoms between the ground state of the Si_6 cluster and a metastable configuration was directly captured in sequential electron micrographs with atomic resolution.

The observations reported here reveal the possibility of identifying the structure and exploring the energy landscape

of trapped nanoclusters in graphene pores through electron beam excitation, revealing the metastable atomic configurations that a particular cluster may assume. Density-functional calculations then establish the coordinates in the third dimension (the electron beam direction) from which the energies of each configuration and their transformation pathways can be determined. In this way, our method reveals unique information on the true molecular dynamics of ultrasmall atomic clusters.

Though free Si clusters exist in either neutral or charged states, a cluster embedded in a graphene pore cannot exist in a truly charged configuration because of the absence of an energy gap in which a localized state can exist. Nevertheless, we performed calculations to probe the state of an extra electron or hole. In both cases, we find that the extra electron or hole occupies a resonant state at the Fermi energy, but, as expected, there is no charge accumulation at the cluster (see Supplementary Figs S4–S6).

In summary, the combination of STEM imaging and theoretical calculations has led to the identification of the atomic configuration and dynamics of an ultrasmall cluster embedded in a graphene nanopore. In the present case, the trapping of the cluster occurred during routine chemical vapour deposition growth and/or TEM sample preparation. However, recent experiments have shown that an electron beam can be used to generate pores of particular sizes in graphene²⁷. Patterning such graphene pores and subsequently trapping or assembling atomic clusters of specific size or magnetic moment inside them can potentially lead to practical applications.

Methods

Sample preparation. The graphene sample for the study was obtained from Graphene Supermarket. The graphene material was grown on a nickel film on a silicon wafer using a chemical vapour deposition method, and then extracted from the nickel film via chemical etching using concentrated nitric acid, and deposited onto a copper grid. The sample presented single and multi layer graphene regions. The sample then was analysed in the STEM. The trapped Si₆ cluster described in the main text was found in a region of monolayer graphene.

STEM-ADF imaging experiments. Aberration-corrected STEM-ADF imaging was performed with a Nion Ultra STEM 100, equipped with a cold field emission electron source and a corrector of 3rd and 5th order aberrations²⁸. The microscope was operated at 60 kV accelerating voltage, which is below the knock-on radiation damage threshold of graphene. The convergence semi-angle of the incident probe was set to ~30 mrad, and the ADF images were collected from ~54–200 mrad half-angle range. The probe current was set to ~100 pA, containing in a probe of 1.3 Å in diameter. Fast-scan sequential ADF images were acquired from the trapped Si₆ cluster with 24 μs per pixel dwell time, and each frame was recorded with 512 × 512 pixels. The sequential images were then aligned using cross-correlation based on the graphene lattice. All ADF images have been low-pass filtered in order to reduce random noise.

Chemical identification of impurity trapped into graphene pore. Atom-by-atom chemical analysis was performed based on quantitative intensity analysis of the deconvolved ADF image. The intensity from the impurity atoms is about 3.83 times the intensity obtained from the carbon atoms, which is close to the Z^{1.6} ratio of 1:3.87 for Z = 6 (C) and Z = 14 (Si), respectively²⁹. Furthermore, electron energy-loss spectroscopy analysis from a substitutional impurity atom with the same ADF image intensity ratio indicates that the impurities are Si atoms³⁰.

First-principles calculations. First-principles calculations, based on density-functional theory^{31,32}, were performed using the Vienna Ab initio Simulation Package³³. The projector-augmented wave method was used to mimic the ionic cores³⁴, while the generalized gradient approximation in the Perdew–Burke–Ernzerhof parameterization was employed for the exchange and correlation functional³⁵. Atomic positions, as well as lattice parameters were optimized using a conjugate gradient algorithm. Ionic and electronic relaxations were performed by applying a convergence criterion of 5 × 10^{−2} eV per Å per ion and 10^{−4} eV per electronic step, respectively. A rectangular unit cell of graphene containing 75 C atoms and 6 Si atoms was considered to explore the cluster stabilization in the graphene pore, conformational change and energy barrier. The distance between graphene sheets in neighbouring supercells was set to 14 Å to avoid spurious interactions. A k-point sampling of 4 × 4 × 1 was used for the atomic relaxation.

References

- Ho, K. M. *et al.* Structures of medium-sized silicon clusters. *Nature* **392**, 582–585 (1998).
- Zhu, X. & Zeng, X. C. Structures and stabilities of small silicon clusters: AB initio molecular-orbital calculations of Si₇–Si₁₁. *J. Chem. Phys.* **118**, 3558–3570 (2003).
- Tekin, A. & Hartke, B. Global geometry optimization of small silicon clusters with empirical potentials and at the DFT level. *Phys. Chem. Chem. Phys.* **6**, 503–509 (2004).
- Zdetsis, A. D. Analogy of silicon clusters with deltahedral boranes: How far can it go? Reexamining the structure of Si_n and Si_n^{2−}, n = 5–13 clusters. *J. Chem. Phys.* **127**, 244308 (2007).
- Honea, E. C. *et al.* Raman spectra of size-selected silicon clusters and comparison with calculated structures. *Nature* **366**, 42–44 (1993).
- Binggeli, N. & Chelikowsky, J. R. Photoemission spectra and structures of Si clusters at finite temperature. *Phys. Rev. Lett.* **75**, 493–496 (1995).
- Haertelt, M. *et al.* Gas-phase structures of neutral silicon clusters. *J. Chem. Phys.* **136**, 064301 (2012).
- Jarrold, M. F. & Constant, V. A. Silicon cluster ions: Evidence for a structural transition. *Phys. Rev. Lett.* **67**, 2994–2997 (1991).
- Schneider, G. F. *et al.* DNA translocation through graphene nanopores. *Nano Lett.* **10**, 3163–3167 (2010).
- Merchant, C. A. *et al.* DNA translocation through graphene nanopores. *Nano Lett.* **10**, 2915–2921 (2010).
- Garaj, S. *et al.* Graphene as a subnanometre trans-electrode membrane. *Nature* **467**, 190–193 (2010).
- Batson, P. E., Dellby, N. & Krivanek, O. L. Sub-ångström resolution using aberration corrected electron optics. *Nature* **418**, 617–620 (2002).
- Meyer, J. C., Girit, C. O., Crommie, M. F. & Zettl, A. Imaging and dynamics of light atoms and molecules on graphene. *Nature* **454**, 319–322 (2008).
- Girit, C. O. *et al.* Graphene at the edge: stability and dynamics. *Science* **323**, 1705–1708 (2009).
- Meyer, J. C. *et al.* Direct imaging of lattice atoms and topological defects in graphene membranes. *Nano Lett.* **8**, 3582–3586 (2011).
- Kotakoski, J., Krashennnikov, A. V., Kaiser, U. & Meyer, J. C. From point defects in graphene to two-dimensional amorphous carbon. *Phys. Rev. Lett.* **106**, 105505 (2011).
- Kotakoski, J. *et al.* Stone-wales-type transformations in carbon nanostructures driven by electron irradiation. *Phys. Rev. B* **83**, 245420 (2011).
- Chuvilin, A. *et al.* Self-assembly of a sulphur-terminated graphene nanoribbon within a single-walled carbon nanotube. *Nat. Mater.* **10**, 687–692 (2011).
- Kotakoski, J., Santos-Cottin, D. & Krashennnikov, A. V. Stability of graphene edges under electron beam: equilibrium energetics versus dynamic effects. *ACS Nano* **6**, 671–676 (2012).
- Meyer, J. C. *et al.* An accurate measurement of electron beam induced displacement cross sections for single-layer graphene. *Phys. Rev. Lett.* **108**, 196102 (2012).
- Rodriguez-Manzo, J. A. & Banhart, F. Creation of individual vacancies in carbon nanotubes by using an electron beam of 1 Å diameter. *Nano Lett.* **9**, 2285–2289 (2009).
- Rodriguez-Manzo, J. A., Cretu, O. & Banhart, F. Trapping of metal atoms in vacancies of carbon nanotubes and graphene. *ACS Nano* **4**, 3422–3428 (2010).
- Mills, G. & Jonsson, H. Quantum and thermal effects in H₂ dissociative adsorption: evaluation of free energy barriers in multidimensional quantum systems. *Phys. Rev. Lett.* **72**, 1124–1127 (1994).
- Vineyard, G. H. Frequency factors and isotope effects in solid state rate processes. *J. Phys. Chem. Solids* **3**, 121–127 (1957).
- Reimer, L. & Kohl, H. *Transmission Electron Microscopy*. (Springer, 2008).
- Banhart, F. Irradiation effects in carbon nanostructures. *Rep. Prog. Phys.* **62**, 1181–1221 (1999).
- Russo, C. J. & Golovchenko, J. A. Atom-by-atom nucleation and growth of graphene nanopores. *Proc. Natl Acad. Sci. USA* **109**, 5953–5957 (2012).
- Krivanek, O. L. *et al.* An electron microscope for the aberration-corrected era. *Ultramicroscopy* **108**, 179–195 (2008).
- Krivanek, O. L. *et al.* Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy. *Nature* **464**, 571–574 (2010).
- Zhou, W. *et al.* Single atom microscopy. *Microsc. Microanal.* **18**, 1342–1354 (2012).
- Hohenberg, P. & Kohn, W. Inhomogeneous electron gas. *Phys. Rev.* **136**, B864–B871 (1964).
- Kohn, W. & Sham, L. J. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **140**, A1133–A1138 (1965).
- Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
- Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
- Perdew, P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).

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Author Contributions

J.L. and W.Z. contributed equally to this work. J.L. performed the first-principles calculations. The experiments were designed by W.Z., J.-C.I. and S.J.P. Measurements and sample preparation were done by W.Z., J.-C.I. All other activities, including data

interpretation, conclusions and manuscript writing, were carried out collaboratively by J.L., W.Z., J.-C.I., S.J.P. and S.T.P.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

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