

Supplementary material

Effects of Metal Doping on Defect Dynamics in Graphene: In-Situ TEM Observation and Persistent-Homology-Based Structural Analysis

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S1. Comparison between original and Gaussian-filtered HR-TEM images

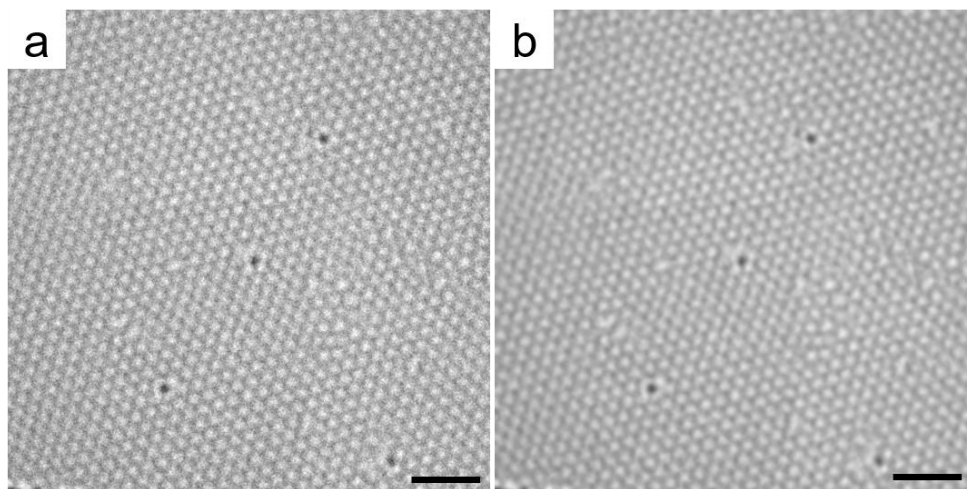


Figure S1. (a) Original HR-TEM image of Cr-doped graphene, which were used for the PH-based analysis. (b) Gaussian-filtered image of (a). Scale bars are 1 nm.

Alt text for FIG. S1

Two panels showing high-resolution transmission electron microscopy (HR-TEM) images of Cr-doped graphene. Panel (a) displays the original HR-TEM image used for the persistent homology-based structural analysis, revealing the atomic-scale contrast of the graphene lattice and dopant sites. Panel (b) shows the corresponding Gaussian-filtered version of the same image to reduce noise and enhance structural visibility. Both panels include a scale bar representing 1 nanometer.

S2. Regions with few Cu and Cr atoms in doped graphene.

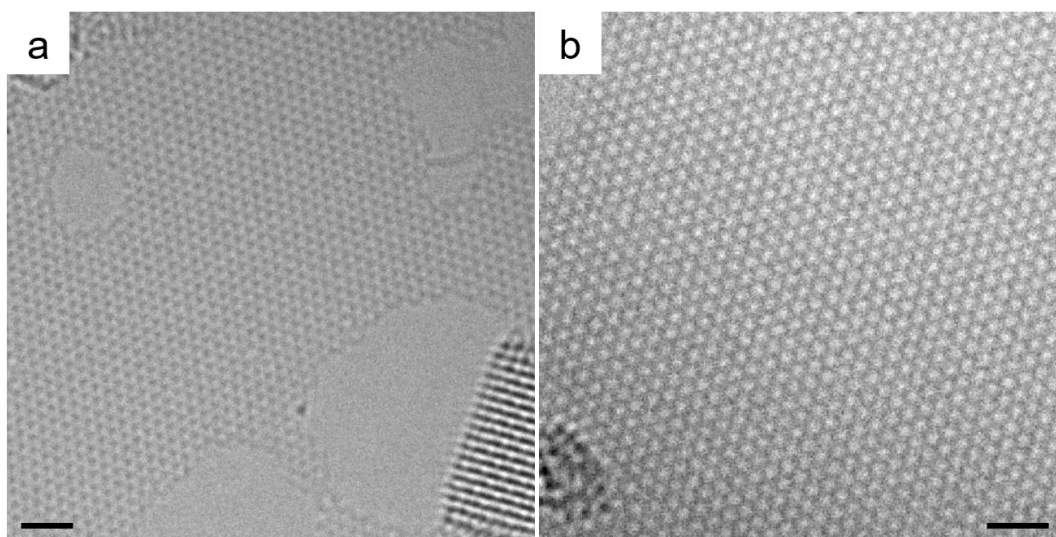


Figure S2. Original HR-TEM images of the regions with few Cu (a) and Cr (b) atoms in the metal-doped graphene, producing negligible defect formation. Comparison with the regions with the metal atoms demonstrates that Cr atoms are the primary factor for defect formation. Scale bars are 1 nm.

Alt text for FIG. S2

Two panels displaying original high-resolution transmission electron microscopy (HR-TEM) images used for a control experiment on metal-doped graphene. Panel (a) shows a pristine lattice region containing few copper atoms, and panel (b) shows a similar pristine region with few chromium atoms. Both regions exhibit negligible defect formation under electron irradiation. These panels contrast with the metal-rich regions to visually demonstrate that the presence of chromium atoms is the primary driver of defect generation. Each panel includes a scale bar representing 1 nanometer.

S3. Suppressed defect evolution at a region with few Cr atoms in doped graphene.

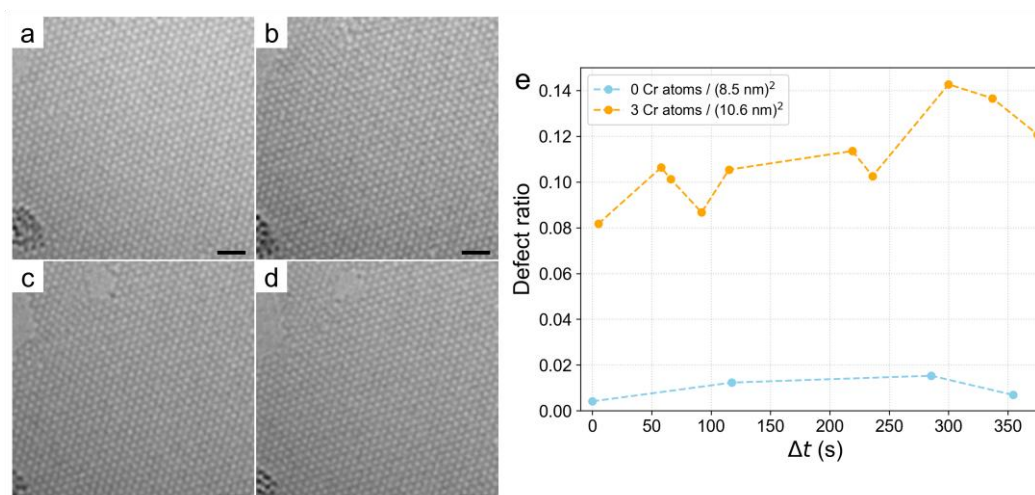


Figure S3. (a)–(d) Filtered HR-TEM image sequence of a region with few Cr atoms in the Cr-doped graphene sample. The images were captured at (a) 116.4 s, (b) 285.4 s, and (c) 354.4 s after the initial image (a). Scale bars are 1 nm. (e) Temporal evolution of the defect ratio under electron beam irradiation. The legend indicates the number of isolated Cr atoms and the area in the initial TEM image (a). Note that the Cr atoms are counted excluding ones within the nanoparticles (left bottom). The blue plots represent the defect ratio calculated from the images (a)–(d), while the orange plots correspond to the defect ratio for Cr-doped graphene in Fig. 3(g).

Alt text for FIG. S3

A multi-panel figure consisting of a transmission electron microscopy image sequence and a corresponding line graph. Panels (a) through (d) display a sequential series of filtered high-resolution transmission electron microscopy (HR-TEM) images showing a graphene region with few chromium atoms under electron beam irradiation. The images capture structural changes over time, specifically recorded at 0 seconds for panel (a), 116.4 seconds for panel (b), 285.4 seconds for panel (c), and 354.4 seconds for panel (d). Scale bars in each electron microscopy panel represent 1 nanometer, and a nanoparticle is visible in the bottom-left corner of the initial frame. Panel (e) features a line graph plotting the temporal evolution of the defect ratio on the vertical axis against the electron irradiation time on the horizontal axis. The graph contains two sets of data points: blue plots representing the defect ratio calculated directly from the image sequence (a) through (d), and orange plots representing the defect ratio for comparison with the Cr-doped graphene data from Figure 3(g).

S4. Filtered HR-TEM image of Cu-doped graphene and its time sequence.

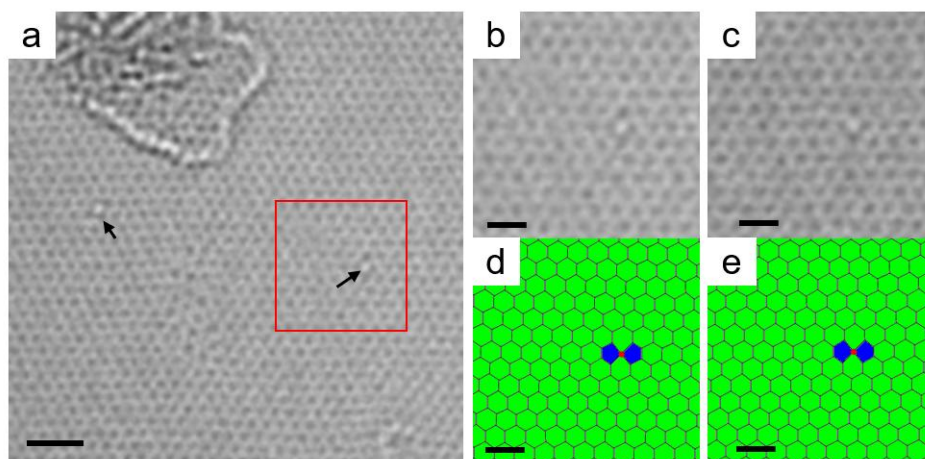


Figure S4. (a) Filtered HR-TEM image of Cu-doped graphene under electron beam irradiation at 80 kV during *in situ* observation. Cu metal atoms are indicated by the black arrows. (b) Magnified view of the red-marked region in (a). (c) Image of the same region with (b), acquired after 80kV-electron-beam irradiation for 150 s. (d), (e) Corresponding atomic models of Cu-doped graphene under electron beam irradiation to the TEM images (b) and (c), respectively. Blue and green regions correspond to pentagons and hexagons, respectively. Red points indicate Cu atoms. Scale bars: (a) 1 nm and (b)-(e) 0.5 nm.

Alt text for FIG. S4

A multi-panel figure containing *in situ* transmission electron microscopy images and corresponding atomic structural models of Cu-doped graphene under an 80 kilovolt electron beam. Panel (a) shows a filtered high-resolution transmission electron microscopy (HR-TEM) image with black arrows pointing to individual copper dopant atoms; the panel includes a 1 nanometer scale bar. Panel (b) is a magnified view of the region outlined in red in panel (a), and panel (c) shows the exact same region after 150 seconds of further electron beam irradiation; both panels (b) and (c) include a 0.5 nanometer scale bar. Panels (d) and (e) display the corresponding atomic models for the states observed in panels (b) and (c), respectively. In these models, copper atoms are represented by red points, while the defect structures are color-coded, with blue regions highlighting pentagons and green regions highlighting hexagons.

S5. Filtered HR-TEM image sequence of Cr-doped graphene and 200kV-electron irradiated graphene.

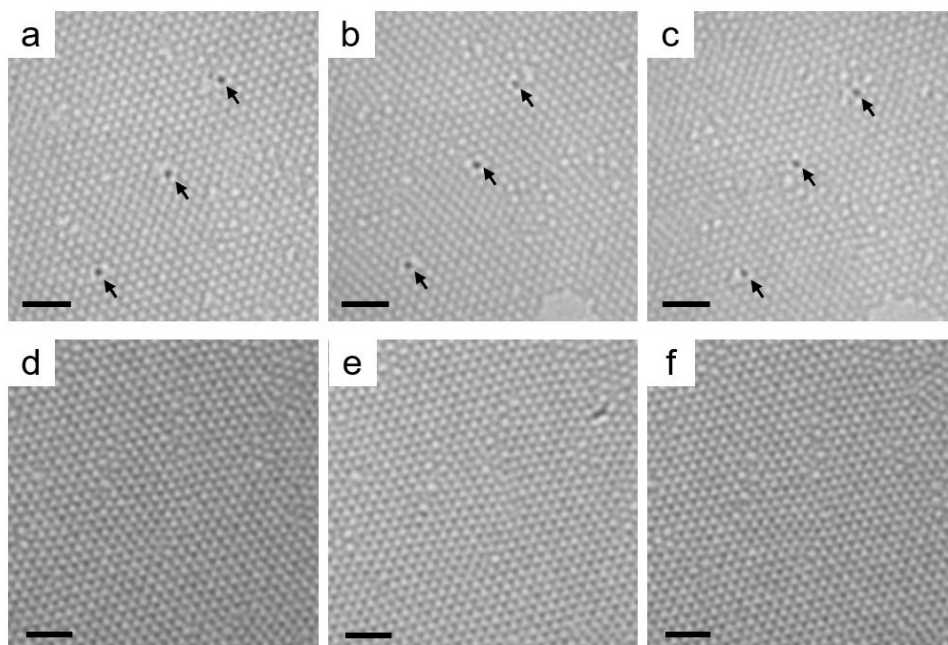


Figure S5. Filtered HR-TEM images. Scalebars indicate 1 nm. (a)-(c) Original images of Cr-doped graphene under electron beam irradiation at 80 kV during *in situ* observation corresponding to Fig. 3(a)-(c). Cr metal atoms are indicated by the black arrows. (d)-(f) Original images of 200-kV-irradiated graphene with defects corresponding to Fig. 3(d)-(f).

Alt text for FIG. S5

A multi-panel figure consisting of six filtered high-resolution transmission electron microscopy (HR-TEM) images of graphene, all including scale bars indicating 1 nanometer. Panels (a) through (c) display original *in situ* TEM images of Cr-doped graphene under electron beam irradiation at 80 kilovolts, corresponding to the sequence shown in Figure 3(a)-(c). Within these panels, individual chromium metal atoms are visually identified and highlighted by black arrows. In contrast, panels (d) through (f) show original TEM images of undoped graphene with pre-existing defects after irradiation at 200 kilovolts, corresponding to the sequence shown in Figure 3(d)-(f).

S6. Structural evolution and connectivity analysis of defect clusters in additional regions (Region 2 and Region 3).

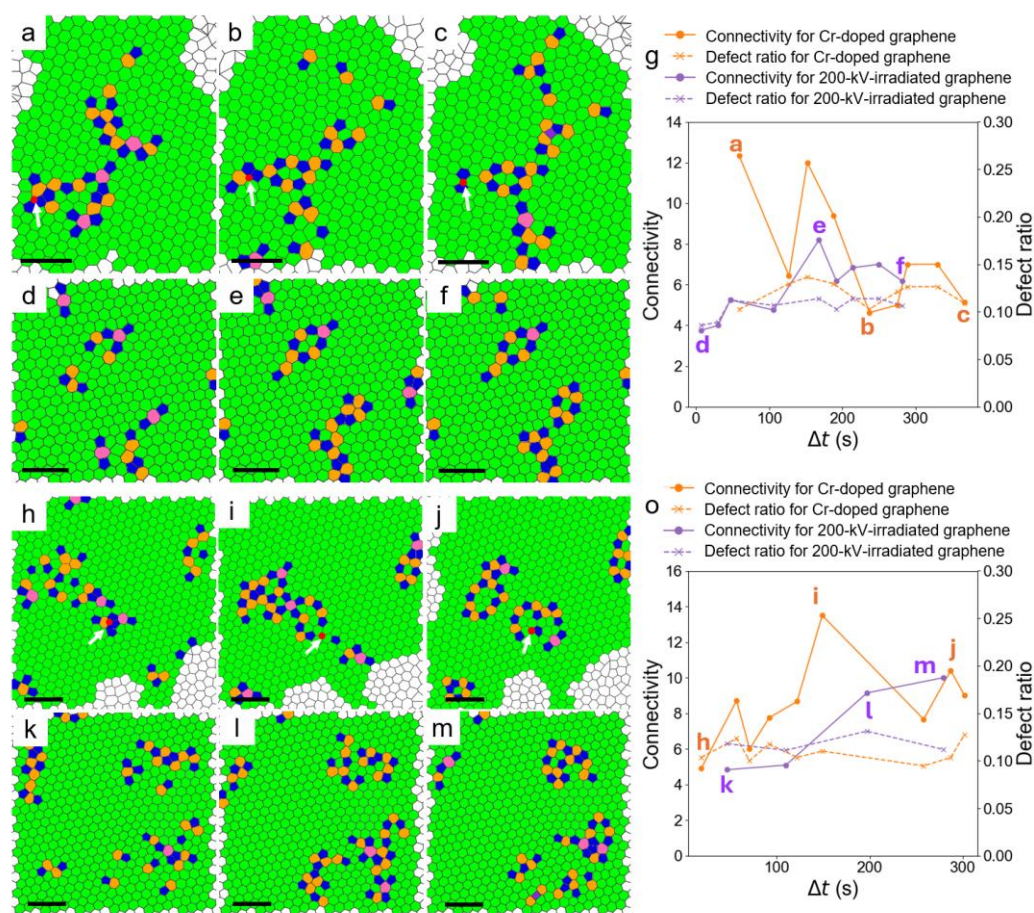


Figure S6. Structural evolution of defect clusters in graphene induced by Cr atoms and 200 kV electron irradiation. Scalebars indicate 1 nm. Comparison 1: (a)–(f) Region 2 with the total number of polygons of 350 ± 10 . (a)–(c): Cr-doped graphene. (d)–(f): 200-kV-irradiated graphene with defects. Comparison 2: (h)–(m) Region 3 with the total number of polygons of 500 ± 10 . (h)–(j): Cr-doped graphene. (k)–(m) 200kV-irradiated graphene with defects. (g), (o) Temporal evolution of connectivity and defect ratio for Region 2 and 3, respectively. The letters a–f and h–m in the graphs correspond to the left images, indicating the TEM observation time, i.e. electron irradiation time after the start of image acquisition. In both Regions 2 and 3, the Cr-doped graphene exhibited a higher mean connectivity and more pronounced temporal fluctuation of the connectivity compared to 200kV-electron-irradiated undoped graphene.

Alt text for FIG. S6

A comprehensive multi-panel figure illustrating the structural evolution of defect clusters in graphene under electron irradiation, comparing Cr-doped graphene and 200-

kilovolts-irradiated undoped graphene across two distinct regions, with all microscopy panels including 1-nanometer scale bars. The top half represents Comparison 1 for Region 2 (350 ± 10 total polygons), where panels (a) through (c) show the time-series TEM images for the Cr-doped sample, and panels (d) through (f) show the corresponding sequence for the 200-kilovolts-irradiated undoped sample; panel (g) is a line graph plotting the temporal evolution of connectivity and defect ratio for Region 2. The bottom half represents Comparison 2 for Region 3 (500 ± 10 total polygons), where panels (h) through (j) display the TEM sequence for the Cr-doped sample, and panels (k) through (m) show the sequence for the 200-kilovolts-irradiated undoped sample; panel (o) is the corresponding line graph showing the temporal evolution for Region 3. The labels (a)–(f) and (h)–(m) are marked within the graphs to denote the specific TEM observation times. In both regions, the line graphs visually demonstrate that the Cr-doped graphene maintains a higher mean connectivity and exhibits more pronounced temporal fluctuations in connectivity compared to the undoped graphene.