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Cu Atoms Reknit the Graphene Structures

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The interactions between metals and graphene have recently been studied in order to control the properties of graphene. Our knowledge about these metal-graphene systems are mainly based on theoretical calculations, except for Fe dimers in graphene vacancies [1] or some metal-mediated etching [2] observed by transmission electron microscopy (TEM). Theoretical studies have predicted that transition metal atoms in graphene vacancies have unique properties depending on its electronic state [3].

In contrast to most transition metals, Cu and Au atoms have filled d shells. These electronic states affect the catalytic properties. Bulk Au doesn't show any catalytic properties, but downsized Au nano-particles attract enormous attention as catalyst of CO oxidation. Bulk Cu is known to be the best catalyst for the synthesis of graphene by chemical vapor deposition, and Cu nano-particles are also able to synthesize carbon nanotubes, though these catalytic growth mechanisms are unclear. Atomic scale observations of the interaction between Cu and graphene could prove the predicted properties and gain understanding how Cu act as catalyst to create nano-carbon structures.

Here we report the structures and dynamics of Cu atoms in a graphene sheet by aberration-corrected TEM (JEM-ARM200F, JEOL). The samples were obtained by transferring monolayer graphene onto *in situ* heating chips (E-chips for Aduro, Protochips). It was cleaned up by heating, and the clean surface area was about 200 × 200 nm. Cu was then deposited by ion beam etching system (PECS, Gatan). The accelerating voltage was 80 kV, and a temperature was kept at 150 °C with an *in situ* heating holder.

When observed at room temperature just after the deposition, Cu didn't form crystals; they were dispersed with a lot of oxygen and hydrocarbons. The sample was heated at 150 °C to remove these contaminants. When we started the heating, some of the contaminants got away and Cu atoms aggregated with each other to form clusters or nanoparticles, as shown in **Fig. 1a**. Some Cu atoms remained on graphene with some contaminants, and then they substituted carbon in a graphene lattice when a high density of electron beam was irradiated. Atoms appeared white in **Fig. 1b** since it was taken at over-focus. More than 10 Cu atoms were embedded closely in graphene, where additional Cu and C had existed (indicated by red arrow in **Fig. 1a**). TEM movies were acquired with a speed of 1-2 frames/s to observe the dynamics of embedded Cu atoms in graphene vacancies. Current density was about 250 A/cm^2 at **Fig. 1b**, which was enough to cause in-plane diffusions of Cu atoms in graphene, and was too large to observe atoms simply adsorbed on graphene because the out-plane diffusion barrier was more than ten times smaller than the in-plane one.

FFT spots of the electron beam irradiated area gradually broadened as shown in **Fig. 2b**, compared with **Fig 2a**. Many small grains were formed which were surrounded by 5-7 defects (**Fig. 2c**). Defects created near Cu atoms moved to form grain boundaries. The area without irradiation didn't change the structure.

These results suggest that the diffusion of Cu atoms was promoted not by heat but by the electron beam irradiations. **Figure 3a-b** show the consecutive snapshots of the movie. One atom of Cu dimer, shown in **Fig. 3a**, replaced neighboring C atoms and changed the structure from **Fig. 3a** to **Fig. 3b.** The corresponding models are **Fig. 3e** and **3f**, respectively. Since single Cu atom in single vacancy (**Fig. 3g**) seems most stable, many Cu atoms embedded in closely gradually diffused to be isolated. It is reported that many kinds of metals etch graphene [2]. Cu atoms, however, switch positions with neighboring C atoms (**Fig. 3a-b**) and reknit the graphene structures rather than etching. Even when small hole-defects were created by irradiation, Cu atoms immediately mended them (**Fig. 3i-j**).

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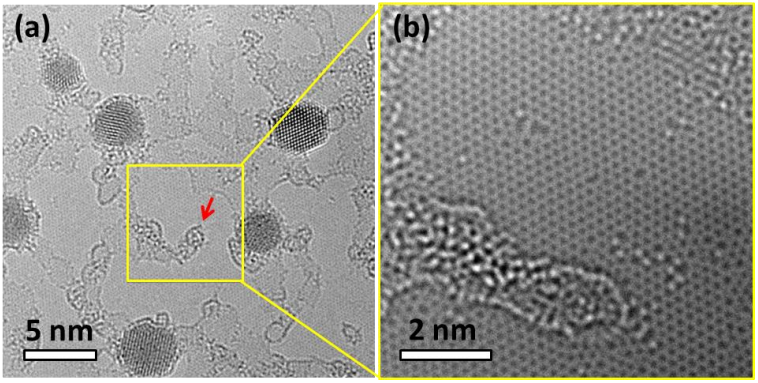

Figure 1. TEM images of Cu/graphene. (**b**) Magnified image of (**a**). White spots are Cu atoms.

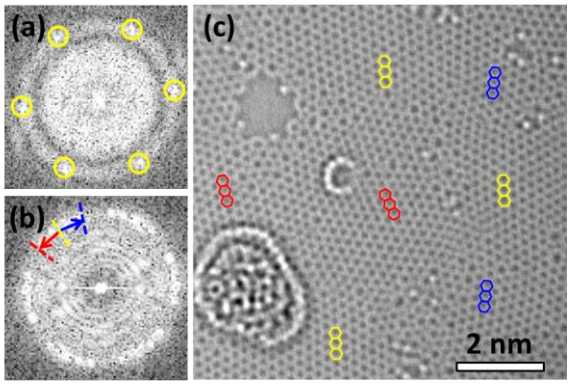

Figure 2. FFT of (**a**) pristine graphene and (**b**) reknitted graphene. (**c**) TEM image of b.

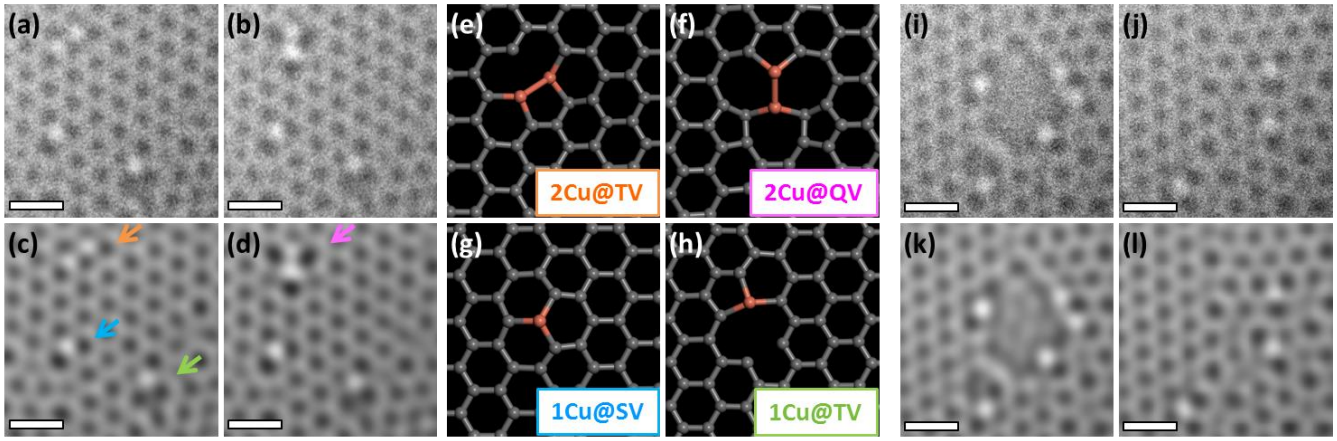

Figure 3. (**a-b**, **i-j**) Consecutive snapshots of TEM movie. (**c-d**, **k-l**) smoothed images of a-b and i-j, respectively. (e-h) atomic models of Cu atoms in graphene vacancies (SV: single vacancy, TV: tri-vacancy, QV: quad-vacancy) shown in (a-d). Scale bar: 0.5 nm.

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