Elementary Process for CVD Graphene on Cu(110): Size-selective Carbon Clusters

Jialin Zhang1, Zhunzhun Wang2, Tianchao Niu3, Shengnan Wang2, Zhenyu Li2 & Wei Chen1,3

1Department of Physics, National University of Singapore, 2 Science Drive 3, 117542, Singapore, 2Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China, 3Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore.

Revealing the graphene growth mechanism at the atomic-scale is of great importance for achieving high quality graphene. However, the lack of direct experimental observation and density functional theory (DFT) verification hinders a comprehensive understanding of the structure of the carbon clusters and evolution of the graphene growth on surface. Here, we report an in-situ low-temperature scanning tunneling microscopy (LT-STM) study of the elementary process of chemical vapor deposition (CVD) graphene growth via thermal decomposition of methane on Cu(110), including the formation of monodispersed carbon clusters at the initial stage, the graphene nucleation and the ripening of graphene islands to form continuous graphene film. STM measurement, supported by DFT calculations, suggests that the carbon clusters on the surface are C2H5. It is found that graphene layers can be joined by different domains, with a relative misorientation of 30°. These graphene layers can be decoupled from Cu(110) through low temperature thermal cycling.

Ever since its mechanical exfoliation from small mesas of highly oriented pyrolytic graphite, graphene has spurred a tremendous of interest because of its exceptional electronic and mechanical properties, such as anomalous quantum Hall Effect (QHE), long-range ballistic transport, high carrier mobility, tunable band gap, high elasticity and intrinsic strength1–3. All these qualify graphene as a promising material for applications in microelectronic and spintronic devices1–3, sensors5, supercapacitors6, building blocks for multifunctional composites7 as well as for structural and mechanical applications8. Motivated by these extraordinary properties and numerous potential applications, a number of graphene fabrication methods have been explored, including the micromechanical cleavage of graphite1, thermal decomposition of SiC8, reduction of chemically functionalized graphene9–12, chemical exfoliation of graphite13 and transition metal (TM)-catalyzed chemical vapor deposition (CVD)14–26, and so on. Graphene prepared by cleavage and exfoliation of graphite shows superior transport properties, but its size is usually limited to micrometers and the productivity of this method is very low1. Epitaxial graphene on SiC allows larger area synthesis27, but this method induces noticeable densities of defects and achieving large graphene domains with uniform thickness remains a challenge28. Transition metal assisted growth of graphene, which provides many unique advantages, such as industrial scalability29, relatively low temperature processing30, easy transferring onto other substrates31, has received the most attention.

The graphene growth on TM surfaces is based on high-temperature pyrolysis of hydrocarbons and different growth mechanisms can be involved according to the carbon solubility limit in the metal. For the growth on TM where carbon is soluble, the graphene forms when the sample is cooled and carbon segregates on the surface (surface segregation)32–34; but for TM with very low carbon solubility, the synthesis is limited to the surface of the catalyst and mainly involves surface diffusion and nucleation of carbon atoms. The growth of graphene can be accomplished by CVD via two approaches: directly cracking the carbon source on TM surface at a high temperature or temperature programmed growth (TPG) via room temperature adsorption of the molecules followed by pyrolysis and graphene growth at a fixed elevated temperature35.

Graphene growth has been demonstrated on a variety of TMs. For example, Li and colleagues reported a CVD method that used copper-foil to produce single crystal graphene with dimensions of up to 0.5 mm36; Bae and colleagues demonstrated a roll-to-roll production of 30 inch graphene films for transport electrodes37; Gao and colleagues showed the repeated growth and bubbling transfer of graphene with millimeter-size single-crystal grains using platinum38. Additionally, intensive theoretical efforts have been devoted to revealing the growth
showed that the core-shell C_{21} is a very stable magic carbon cluster on Cu(111) surface, which represents a more favorable reaction path compared to CH dissociation. By careful optimization of the supported carbon clusters C_{30} on Ni(111), Gao et al. indicated a ground state structure transition from a one-dimensional (1D) carbon chain to a two-dimensional (2D) sp² carbon network at N - 10 – 12; while Wesep and co-workers proposed an energetic preference for the formation of stable 1D carbon nanoarches consisting of 3–13 atoms on Cu(111) surface. Explored by ab initio calculations, Yuan et al. showed that the core-shell C_{41} is a very stable magic carbon cluster on Rh(111), Ru(0001), Ni(111) and Cu(111) surfaces. Zangwill et al. predicted that an immobile island composed of six five-atom carbon clusters as the smallest stable precursor to graphene growth on metals. Despite these inspiring achievements, most of these theoretical studies only address the number of carbon atoms, and the precise determination of hydrogen atoms within the cluster is rare. Moreover, very little of the growth mechanism in the initial nucleation stages of carbon atoms has been revealed experimentally. In this regard, atomic-scale characterization of a complete process of graphene growth in combination with theoretical calculations is of great importance, for both fundamental interest and achieving high quality graphene.

Here, we report an atomic scale characterization of the elementary process of CVD graphene growth via thermal decomposition of methane (CH_4) on Cu(110) using low-temperature scanning tunneling microscopy (LT-STM), including the formation of monodispersed carbon clusters at low temperature, nucleation and ripening of graphene islands at high temperature. Combined with first principles calculations, the monodispersed carbon clusters are identified as C_{2n}H_2. Different domains stitch together to form a graphene layer, with a preference angle of 30° at the grain boundaries. These graphene layers can be decoupled from Cu(110) through low temperature thermal cycling.

**Results**

As shown by the high magnification STM image in Fig. 1a, upon the deposition of CH_4 at room temperature (RT) and subsequent annealing at 480 °C in CH_4 at a pressure of 2 × 10^{-8} mbar for 50 min, the Cu(110) surface was almost decorated with carbon clusters of monodispersed size. Each carbon cluster appears as a bright spot with an identical size of 0.4 nm. Careful inspection of the STM image reveals that the surface is decorated by isolated but well-defined superstructures, where the carbon clusters are adsorbed in an epitaxial relationship with the underlying Cu(110). As indicated by the dashed lines in Fig. 1a, the minimum distance between two neighboring rows is 2a_0 of 0.512 nm; while it is 2b_0 of 0.723 nm between two columns (a_0 and b_0 are the unit cell dimensions of Cu(110)). It can also be revealed that the carbon cluster arrays are aligned precisely with the crystal orientation of the underlying Cu(110). The carbon cluster at this low coverage was referred to as "cluster 1" with a density around 2.70 × 10^{14}/cm^2. Previous theoretical studies proposed that carbon dimers are energetically favorable on the Cu(110) surface. Therefore, we tentatively assign these carbon clusters as carbon dimers (C_{2n}H_2).

Further increasing the coverage of the carbon clusters can result in the formation of a hexagonally close packed structure, as shown in Fig. 1b. The coverage of the carbon clusters can be increased through low temperature thermal cycling as described in the supporting information. Some gaps can still be observed between the ordered domains. However, the carbon clusters in each ordered domain possess the unit cell with a = 0.515 nm, b = 0.500 nm and an inclusion angle of 60°, as indicated by arrows A and B. Upon saturation of the carbon clusters on the surface, they formed highly ordered close packed structure over the surface, as shown in Fig. 1c. The unit cell...
was further reduced to $c = 0.450 \text{ nm}$, $d = 0.480 \text{ nm}$ with an unchanged inclusion angle of $60^\circ$. At this stage, the carbon cluster density was increased to $10.9 \times 10^{15}/\text{cm}^2$, referred to as “cluster 2”. In this regime, the arrangement is supposed to be cluster-cluster interaction dominated. Some brighter lines can be frequently observed, induced by the stress relaxation at high cluster coverage with increased lateral inter-cluster interaction.

Annealing the Cu(110) surface at high temperature at 550°C in CH$_4$ at a pressure of $2 \times 10^{-5}$ mbar for 130 min can promote the nucleation of small graphene flakes. As shown in Fig. 1d, at this stage the carbon clusters co-exist with the small graphene flakes which are indicated as “G”. The high magnification STM image in Fig. 1e reveals that the clusters on Cu(110) are “cluster 2”. The directions indicated as “G”. The high magnification STM image in Fig. 1e shows that the carbon clusters co-exist with the small graphene flakes which are indicated in the lower right corner.

To obtain the atomic structure of the carbon clusters, the adsorption of various carbon clusters on Cu(110) were simulated using DFT. First, the stability of C$_{12}$H$_x$ (0 ~ 4) and C$_2$H$_x$ (0 ~ 6) clusters on Cu(110) were studied. We define the formation energy in equation (1)

$$E_F = E_{\text{tot}} - E_{\text{sub}} - \sum_i n_i \mu_i$$

where $E_{\text{tot}}$ is the total energy of the adsorbed system, $E_{\text{sub}}$ is the energy of clean Cu(110) substrate, $\mu_i$ and $n_i$ (i = C, H) represent chemical potential and the number of atoms in the cluster, respectively. Considering the equilibrium of CH$_4$ and H$_2$, the relationship of $\mu_{\text{CH}_4}$ and $\mu_{\text{H}_2}$ in unit of electron volt can be obtained as equation (2) by the process described in the supporting information:

$$\mu_i = g_{\text{CH}_4} - 4\mu_{\text{H}_2} = -2\mu_{\text{H}_2} - 9.695 + 0.0689\ln \chi$$

where $\chi$ is the ratio of the partial pressures of CH$_4$ and H$_2$.

For each carbon cluster species, the most stable adsorption configuration was found by checking different adsorption sites on Cu(110) surface, including the hollow site (H-site), bridge-long site (B$_0$ long site), bridge-short site (B$_0$ short site) and Top site (T-site). Figure 2 shows the formation energy of various carbon cluster species as a function of the chemical potential of H (thus the partial pressure of H$_2$). The $\chi$ here was set to be 20:1; we also tested $\chi = 1:20$, which gave similar results.

From Fig. 2, it is easy to find that clusters C$_2$H$_6$ and C$_2$H$_5$ are the two most stable species under all physical H$_2$ partial pressure. Although the formation energy of C$_2$H$_6$ is very large, as a close shell molecule, its adsorption energy is expected to be very small, and it’s hence easy to desorb from Cu(110) at high temperature. The average lifetime of C$_2$H$_6$ and C$_2$H$_5$ can be estimated by their adsorption energy $E_a$ via $\tau_a = \frac{1}{\nu_0} e^{E_a/kT}$ where $\nu_0$ is about $10^{13}$ s$^{-1}$. Therefore, their average lifetime on the surface at 480°C is $5.5 \times 10^{-11}$ and $1.2 \times 10^{-10}$ s, respectively. Such a short lifetime makes C$_2$H$_6$ not be able to be observed by STM. Therefore, C$_2$H$_5$ could be the most possible abundant species from the thermodynamic point of view.

Large graphene flakes can be achieved through low temperature thermal cycling process as described in the supporting information. Figure 4a shows a large scale STM image of a flake of graphene film on Cu(110) interconnected by two graphene grains, forming a grain boundary in between as indicated by the red ellipse. Close-up (Fig. 4b) and the corresponding atomic-resolution STM images (Fig. 4c) reveal that the two graphene grains are stitched together to form a continuous film with a relative misorientation of 30°. The detailed atomic structure at the grain boundary cannot be identified.

Figure 2 | Relationship of formation energy and chemical potential of H or the pressure of H$_2$. Relationship of adsorption energy and chemical potential of H or the pressure of H$_2$ during CVD growth of carbon clusters on Cu(110) at $T = 527^\circ C$. The ratio of partial pressures of CH$_4$ and H$_2$ is $\chi = 20$.

Figure 3 | Optimized structures (left panels) and simulated STM images. Optimized structures (left panels) and simulated STM images (right panels) of (a, b) C$_2$, (c, d) C$_3$H$_4$, (e, f) C$_3$H$_5$, and (g, h) C$_3$H$_6$. The integrated density of states from 0.25 V below $E_F$ to the Fermi level is used to simulate the STM image, which represents the HOMO of the carbon clusters.
from our STM image, but it has been theoretically proposed and experimentally conformed as a series of pentagons, heptagons and distorted hexagons. The graphene grows in different orientations with respect to the underlying lattice, resulting in two different moiré patterns. As shown in Fig. 4c, the lower right panel shows a different moiré pattern with a larger periodic modulation and is rotated by 30° from the lower R phase. The graphene lattice of the upper left panel shows a different moiré pattern with a larger periodic modulation and is rotated by 30° from the lower R phase, referred to as R30 phase. Supplementary Fig. S3 on line shows a graphene film joined by multi-domains taken from a different location on Cu(110), which also shows a 30° misorientation. The preference of around 30° misorientation between two domains has also been reported by other groups. For graphene grown on Ru(0001), only one orientation can be observed, due to the strong interaction between graphene and Ru. The two dominating orientations observed here and the fact that graphene can grow continuously across Cu step edges could indicate a weaker graphene-Cu interaction when compared with Ru.

As described in the supporting information, during the experiment, we introduced the low temperature thermal cycling method to increase the carbon cluster coverage. Figure 4d shows the STM image of large flakes of graphene coexisting with carbon clusters on Cu(110). After repeating several cycles of low temperature thermal cycling, the graphene flakes on the surface possess two stripe-shaped contrasts. Comparison between Supplementary Fig. S2 on line and Fig. 4d reveals that the appearance of those bright stripes are same with the previous small graphene islands, while the dark stripes are newly produced during the low temperature thermal cycling. Close up STM image in Supplementary Fig. S4 on line and Fig. 4f reveals that the bright and dark stripes alternated between each other with a continuous boundary. As shown in Fig. 4e, the bright stripes (BG) show moiré pattern resembling the underlying Cu(110); while the dark stripes (DG) display perfect hexagonal graphene lattice. These contrasts result from the modulation by different interactions with the underlying Cu(110). The appearance of the perfect hexagonal graphene lattice in DG suggests that the graphene in this region is physically decoupled from the underlying Cu(110).

The formation of such physically decoupled graphene can arise from the intercalation at the graphene/Cu(110) interface by hydrogen atoms released from CH₄ decomposition, similar to the previously reported hydrogen, lithium, and fluorine intercalation to form quasi-free-standing graphene; or from the strain relief during the annealing/cooling cycles due to the different thermal expansion of graphene film and Cu substrate. More controlled experiment and detailed theoretical calculations will be carried out to unravel the decoupling mechanism.

**Discussion**

Through the combination of the LT-STM and DFT calculations, we reveal the elementary process of graphene growth on Cu(110) surface via thermal decomposition of CH₄. Low temperature annealing (>480 °C) in CH₄ results in the formation of carbon clusters at the initial stage; further high temperature annealing (>550 °C) activates the graphene nucleation; prolonged annealing in the absence of CH₄ propels the diffusion and ripening of these graphene island to form continuous graphene films extended over the surface. Low temperature thermal cycling induced decoupling of graphene from Cu(110) has also been demonstrated. Our systematic investigations identify the fundamental carbidic building blocks by STM measurement, and further elucidate their atomic structures through DFT calculations. Our work could lay the foundation for providing rational design rules for synthesis of large area single crystalline graphene films.

**Methods**

**Growth of graphene on Cu(110).** Graphene was grown on a single crystal Cu(110) via thermal decomposition of CH₄. Prior to the deposition of CH₄, Cu(110) substrate was cleaned by a few cycles of Ar⁺ ion bombardment and subsequent annealing at 530 °C. The CH₄ gas was introduced into the growth chamber through a leak valve, and the pressure was monitored by a cold cathode gauge. A typical growth procedure
as is follow: the Cu(110) substrate was exposed to CH₄ at a pressure of 2 × 10⁻⁹ mbar for 20 min; annealing the sample at 480 °C in CH₄ at a pressure of 2 × 10⁻⁹ mbar resulted in the formation of carbon clusters; further annealing the sample in the absence of CH₄ at 550 °C initiated the graphene nucleation; prolonged annealing without CH₄ at higher temperature up to 720 °C propelled the ripening of graphene islands.

**Characterization of graphene in UHV LT-STM.** The LT-STM experiments were carried out in a custom-built multichamber ultra-high-vacuum (UHV) system with base pressure better than 1.0 × 10⁻¹¹ mbar, housing an omicron LT-STM interfaced to a Nanonis controller. All STM imaging were performed at 77 K using constant current mode with an electrochemically etched tungsten tip. All the bias voltage was applied to the tip.
60. Simon, N. J., Drexler, E. S. & Reed, R. P. Properties of copper and copper alloys at cryogenic temperatures. *International Copper Association, Ltd.*, New York and National Institute of Standards and Technology, Gaithersburg (1992).

**Acknowledgments**
Authors acknowledge the support from Singapore MOE grants R143-000-505-112, R143-000-530-112, R143-000-542-112, R143-000-559-112, NUS YIA grant R143-000-452-101, and NSFC funds 21173202 and 21222304.

**Author contributions**
W.C. conceived and designed the experiments; J.L.Z. and T.C.N. performed the experiments; Z.Z.W., S.N.W. and Z.Y.L. performed theoretical calculations; W.C. and J.L.Z. wrote the manuscript. All authors contributed to writing and revising the manuscript.

**Additional information**
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Zhang, J.L. *et al.* Elementary Process for CVD Graphene on Cu(110): Size-selective Carbon Clusters. *Sci. Rep.* 4, 4431; DOI:10.1038/srep04431 (2014).

This work is licensed under a Creative Commons Attribution 3.0 Unported license. To view a copy of this license, visit http://creativecommons.org/licenses/by/3.0