Direct graphene growth on (111) Cu₂O templates with atomic Cu surface layer

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ABSTRACT

This work explores nucleation and epitaxy of graphene on crystalline Cu₂O templates formed via self-assembly and surface reduction of Cu₂O nanocrystallites on the cubic textured (100) orientation Cu (CTO-Cu) and polycrystalline Cu (poly-Cu) substrates, respectively. It has been found that the presence of sub-surface oxygen causes the reconstruction of Cu surface due to the formation of oriented Cu₂O nanocrystallites at a low H₂ gas flow. Self-assembly of the Cu₂O nanocrystallites into a textured surface template provides direct nucleation sites for graphene growth after the oxygen-sublattice on the template surface is reduced. The atomic Cu surface layer provides advantages of high graphene growth rate due to the catalytic role of Cu and in-plane alignment of graphene nuclei. It is particularly important that the Cu₂O crystallites have predominantly (111) orientation aligned to each other in the plane of the (100) CTO-Cu substrates, which allows epitaxy of graphene with much lower defect density as compared to that in the poly-Cu case. Since Cu₂O (111) templates may be developed on lattice matched (100) surfaces of other dielectric materials, this self-assembly approach provides a promising pathway for large-scale, transfer free graphene epitaxy on nonmetallic surfaces.

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1. Introduction

The recent advance in growth of graphene on Cu foils using chemical vapor deposition (CVD) has opened up a practical route for the fabrication of monolayer graphene on a large variety of metal substrates including Cu, Ni, Co, Fe and Ru [1-5]. Cu is of particular interests since graphene growth on Cu is self-limiting, which leads to monolayer graphene in a large CVD processing window[1], and bilayer or few layer with a control over hydrogen flow [6]. In the CVD process, an annealing treatment of the Cu foils under flowing hydrogen is employed prior to graphene growth to remove copper oxides typically existing on the surface of the Cu foils. The exposure of a clean Cu surface is believed essential to nucleation and evolution of the graphene and the crystallinity and orientation of the Cu surface have been found to have a profound effect on the in-plane orientation and evolution of the graphene grains [7, 8]. A more recent study on the correlation between the orientation of the facets and graphene nucleation has found that the graphene growth rate is the largest on the Cu (111) facet [9, 10]. This is not surprising considering Cu (111) has an almost perfect lattice match with graphene and is therefore ideal for graphene epitaxy. Epitaxial nucleation of monolayer graphene platelets on single-crystal Cu (111) substrates has been confirmed although two types of grains rotated by 7 degrees with respect to each other were observed [11]. The coalesce of the graphene grains leads to grain boundaries (GBs) with much smaller GB angles observed on single-crystal Cu (111) as compared to the case of polycrystalline (poly-Cu) substrates, on which multiple facets of different orientations are present [12].

An additional challenge in development of CVD graphene is associated with the graphene transfer process. For most practical applications, the CVD graphene grown on metal foils must be transferred to nonmetallic surfaces. The transfer process requires multiple steps of chemical treatment to dissolve metal foils and to rinse off residues. Many additional defects may form during this transfer process, not to mention the difficulties in scaling up the process for transferring large size sheets of graphene [13]. Direct growth of graphene on nonmetallic

surfaces with a surface texture control to facilitate graphene epitaxy is therefore desired and important [14]. This has motivated extensive efforts in direct growth of graphene on technologically important nonmetallic substrates such as SiO₂, BN, and Ge [15-17]. Without the metal catalysts, however, graphene growth rate is very slow, often resulting in non-continuous graphene patches of micrometers in dimension and often defective as manifested in appearance of a prominent “D” peak on Raman spectra.

The challenges in direct epitaxy of graphene on functional substrates may be addressed by development of a nonmetallic epitaxial template with atomic Cu (111) surface layer. Such a template may take the advantages of the catalytic surface Cu for nucleation and evolution of high-quality graphene, allowing direct epitaxy of graphene on nonmetallic surfaces and elimination of graphene transfer. Cu₂O is a semiconductor with a bandgap in exceeding 2.1 eV. At a low defect density, Cu₂O behaves like an insulator. In most commercial Cu foils, Cu₂O is native and can form as soon as the Cu surface is exposed to air or oxygen even at room temperature. Consequently, most Cu foils employed for graphene growth in CVD, which is a low vacuum process, have a Cu₂O surface layer due to the presence of oxygen in CVD chambers and outward diffusion of oxygen from sub-surface of Cu foils. Without a proper heat or chemical treatment, the native Cu₂O formed on the surface of the Cu foils is amorphous with thickness typically on the order of hundreds of nanometers [18, 19], and hence cannot be used for nucleation and growth of graphene. However, heteroepitaxy of the Cu₂O (111) layer can occur on (100) oriented Cu facet via moderate oxygen exposure of Cu substrates over 600 °C [20]. On the other hand, other orientations of Cu₂O, such as (110) and (100) may also form on (100) Cu surface at lower temperatures such as 350 °C [21]. The Cu₂O (111) template is particularly interesting to graphene growth due to its alternating Cu and Oxygen sub-lattices [22]. Surface reduction of the crystalline lattice of Cu₂O (111) may allow exposure of the atomic Cu (111) sub-lattice after removing the surface oxygen sub-

lattice, enabling epitaxy of graphene on the surface of these crystalline Cu_2O islands. This may provide a unique scheme for controlling the graphene nucleation and orientation.

In this work, we explore epitaxy of graphene on an atomic Cu (111) facet on a crystalline Cu_2O (111) template self-assembled on cubic textured (100) orientation copper foils (CTO-Cu). We have found that the shape and alignment of the self-assembled Cu_2O crystalline islands are both affected by the structure of the underlying Cu substrates. In contrast to the aligned triangular and square shapes on CTO-Cu, stripe and randomly shaped domains were observed on poly-Cu. CVD growth of graphene on both substrates was investigated and nucleation of graphene was confirmed to only occur on the crystalline Cu_2O islands on both substrates. This observation is important to development of textured nonmetal Cu_2O templates through controlling the crystallinity and orientation of the underneath Cu substrates for transfer-free epitaxy of graphene.

2. Experimental

The CTO-Cu with a thickness of 150 μm was fabricated using thermomechanical processing of base metal Cu [23]. The poly-Cu was obtained commercially from Alfa Aesar, item No.13382. Crystallization of Cu_2O on CTO-Cu and poly-Cu foils was investigated by increasing the sample temperatures to $\sim 1000^\circ\text{C}$ in flowing H_2 gas at different temperature ramping rates. Graphene growth was initiated by introducing a mixture of CH_4 (3.0-25 sccm) and H_2 (0.1-2 sccm) to CVD system at $\sim 1000^\circ\text{C}$ following previously published procedures while no H_2 annealing before graphene was adopted [1, 24]. Low H_2 flow rate below 3 sccm was found critical to obtaining crystallization of the Cu_2O and reduction of the surface oxygen sub-lattice. The reduction rate seems to increase with the H_2 flow rate and at higher flow rate, the surface oxides were removed efficiently, resulting in growth of graphene directly on the copper surface [1, 24]. In order to transfer the CVD-grown graphene films onto other substrates, poly-methyl methacrylate (PMMA) was first spin-coated on the surface of the as-

grown graphene on copper. The film was then placed in iron chloride solution (0.1g/mL) to remove the copper foil, followed by rinsing with deionized (DI) water. The presence of Cu₂O template between graphene and copper foil did not seem to have any effect on the graphene transfer process. The target substrate was then immersed in the DI water and alignment of the graphene film on the substrate was made before the DI water was drained. The sample was then placed in an oven at 80 °C for one hour to eliminate moisture. Finally, the PMMA was removed with acetone.

The structure and morphologies of graphene on Cu substrates were examined with scanning electron microscopy (SEM, Jeol JSM-6380 and Leo 1550 FESEM) with the electron beam accelerating voltage of 2-25 KeV. The electron backscatter diffraction (EBSD) patterns were used to examine recrystallization and grain orientation of Cu substrates during growth of graphene. The samples were placed in the Leo 1550 FESEM and inclined approximately 70° relative to normal incidence of the electron beam for sensitive detection of the EBSD patterns. The detector is actually a camera equipped with a phosphor screen integrated with a digital frame grabber. The Raman spectra were recorded using a Renishaw InVia Raman Microprobe equipped with a Helium-cadmium laser at 442 nm (blue) excitations. The laser spot is ~2 μm in diameter on the sample, and its energy density is ~1 mW/μm². The spectrum was taken by averaging over 10 scans. Raman mapping was taken on a confocal Raman system (WiTec alpha300) with laser excitation of 488 nm. The conductivity of the samples was measured in a four-probe configuration after the graphene sheets of typical dimension of 1x1.5 cm², were transferred onto fused silica substrates. The linear I-V curves observed on all samples in this experiment suggest that Ohmic contacts were made to the graphene samples via Ti(15 nm)/Au(65 nm) electrodes **evaporated through a shadow mask using e-beam evaporation.** **Optical transmittance spectra were also taken on these graphene/fused silica the transmittance data were taken on multiple spots of graphene in the area between the two voltage electrodes.** Atomic force microscopy (AFM) images were obtained in ambient conditions using a

Multimode Nanoscope E Atomic Force Microscope (Veeco Instruments, Santa Barbara CA) operating in contact mode. Veeco silicon nitride tips with a force constant of 0.12 N/m were scanned at 2 Hz with a set point of approximately 1.5 V. Images were flattened before cross section analysis.

3. Results and discussion

Fig. 1 Schematic of self-assembly of textured (111) Cu_2O crystal on (100) Cu.

Figure 1 shows schematically the self-assembly procedure of copper oxides on Cu and the alignment of the Cu_2O (111) lattice over the Cu (100) lattice. Cu_2O comprises a face-centered cubic sub-lattice of Cu^+ ions with O^{2-} ions occupying positions along the body diagonal of the unit cell at $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$ [22]. As an elemental face-centered cubic crystal, the crystal (111) Cu face with its high packing density has the lowest surface energy and greatest thermodynamic stability. Such a crystal face would be energetically favorable to grow along the normal direction of the surface. The Cu_2O oriented in the [111] direction exhibits a triangular morphology [25]. The presence of sub-surface oxygen atoms can cause a reconstruction of the surface of Cu due to the formation of oriented Cu_2O nanocrystallites [26]. The surface temperature was found to be directly relevant to the formation of Cu-O islands [27]. Different morphologies of oxide nanostructures, such as triangular, hut, rod, or pyramid structure, could form depending on the oxidation temperature [28].

The CTO-Cu and poly-Cu foils were heated at a ramping rate of 40 $^{\circ}\text{C}/\text{min}$ to 1000 $^{\circ}\text{C}$ in H_2 flow of 2 sccm followed by cooling back to room temperature immediately to examine the

morphology of the copper oxide surface layer. Different grains can be observed on the two types of Cu substrates. Triangles as well as rectangles of a few μm in dimension were formed on CTO-Cu, as shown in Figure 2a. Energy-dispersive X-ray spectroscopy (EDS) (Figure 2d) demonstrated a uniform distribution of chemical elements Cu (blue) and O (blue), as shown in the line scans (blue line) across a selected triangle in Figure 2a. This suggests the shaped islands are copper oxides with a similar chemical composition to the surrounding amorphous materials, which is anticipated considering both CTO-Cu and poly-Cu foils were stored in air and no heat/chemical treatment was applied to remove the surface oxide layer. EBSD spectra taken on areas away from shapes reveals no crystallinity (Figure 2b) while that on shaped islands illustrate crystalline structures, as shown in Figures 2c, and 2e-2g. The EBSD patterns obtained can be indexed to the Cu_2O (111) using TSL orientation image maps (OIMs) Analysis 5 software as shown in Figure 2c. In particular, the same EBSD patterns were observed on different locations of the same triangle, as shown in Figures 2e and 2g, indicating a single crystalline Cu_2O layer formed within the shaped island on CTO-Cu. In addition, EBSD patterns taken on other shaped grains (not triangular) on CTO-Cu also have (111) orientation, indicating Cu_2O (111) dominating on the surface of CTO-Cu. On the other hand, irregular stripe shaped domains can be clearly seen in the SEM image taken on a representative poly-Cu substrate (Figure 2h). No EBSD patterns can be detected on areas away from stripes (Figure 2i), which is consistent with the observation on CTO-Cu. However, different EBSD patterns were observed on different locations of the same stripe, as shown in Figures 2j-2k, indicating the polycrystalline nature of multiple facets formed within the same island on poly-Cu.

Fig. 2 (a) SEM image of CTO-Cu heated to 1000 °C at the ramp rate of 40 °C/min under 2 sccm H₂ flow followed by cooling to room temperature, (b) EBSD pattern taken away from triangles, (c) EBSD pattern indexed to Cu₂O (111), (d) EDS line scan of Cu, O across the line in the triangles with their EBSD patterns on different facets of a triangle on CTO-Cu (e-g). (h) SEM image of poly-Cu heated to 1000 °C under 2 sccm H₂ flow followed by cooling to room temperature, (i) EBSD pattern taken away from grains, and (j-k) EBSD patterns on different locations of a grain on poly-Cu.

The surface morphology of three CTO samples is compared in Figure 3 after going through a similar thermal cycle, while the temperature ramping rate was varied during heating. At the highest ramping rate of 40 °C/min, square, rectangle and triangle shaped features coexist, as shown in Figure 3a, due to the formation of (100), (110) and (111) facets, respectively, as confirmed by the EBSD analysis. At lower ramping rates of 20 °C/min and 10 °C/min, as

shown in Figures 3b and 3c, respectively, triangular shaped islands of larger dimension and smaller density become dominant. These triangular shaped islands have (111) orientations, suggesting a control over the orientation of self-assembled islands could be achieved by tuning the ramping rate during heating.

Fig. 3 SEM images of CTO-Cu heating to 1000 °C at various ramping rates of (a) 40 °C/min, (b) 20 °C/min, and (c) 10 °C/min.

In order to understand the effect of orientations of the Cu_2O islands on the graphene growth, a set of CTO-Cu and poly-Cu were heated to 1000 °C at the ramp rate of 40 °C/min and kept at this temperature for a selected period in a mixed gas of CH_4 and H_2 . Figure 4 compares the SEM images of graphene grown on CTO-Cu (Figure 4a) and poly-Cu (Figure 4c), respectively, at the growth time of 5 min. The change of the surface morphology of the islands suggests growth of graphene on the islands. A closer look in the region surrounding the island features on both CTO-Cu and poly-Cu reveals attachment of a uniform layer of most probably hydrocarbon, suggesting its physical absorption does not have strong selectivity on the substrate surface, which can be confirmed from the uniform distribution of chemical elements from the EDS line scans of C, O and Cu across a selected graphene nucleus. EBSD mapping was performed on the two samples and the results are included in Figure 4b for graphene grown on CTO-Cu and in Figure 4d for that on poly-Cu. In the former, the oriented pyramidal grains are surrounded by amorphous copper oxides since negligible chemical variation could be observed in EDS shown in Figure 2d. The (111) orientation

appears to be prominent (blue in the figure). The observed pyramidal features suggest that the crystallization of the Cu_2O (111) islands is accompanied by dynamic surface reconstruction. In the latter, the shapes of the graphene grains have random orientation and texture, which differ distinctively from the case of CTO-Cu and could be attributed to the more complicated surface reconstruction pattern due to the presence of multiple facets on poly-Cu foils. However, the surface coverage by oriented Cu_2O islands is larger in the case of poly-Cu as compared to its CTO-Cu counterpart, probably as a consequence of more efficient recrystallization of the Cu_2O on poly-Cu when a large number of grain boundaries are available for nucleation of Cu_2O crystallites.

Fig. 4 SEM images of graphene on (a) CTO-Cu and (c) poly-Cu for the graphene growth time of 5 min at the heating ramp rate of 40 °C/min. EBSD OIM images taken on the same samples of graphene on (b) CTO-Cu with the inset showing single stereographic triangle, and on (d) poly-Cu.

Fig. 5 Raman mapping of (a) G band and (b) 2D band on graphene grown on CTO-Cu for 5 min. (c) Raman spectrum taken on a triangular grain and the inset showing Raman spectrum away from triangular grains. Raman mapping of (d) G band and (e) 2D band of graphene on poly-Cu for 5 min growth time. (f) Raman spectrum taken on a random shaped graphene grain with the inset showing Raman spectrum away from the grains. The wavelength of the Raman excitation laser is 488 nm.

Spatially resolved Raman spectroscopy was employed to confirm the graphene growth on different Cu₂O grains on CTO-Cu and poly-Cu, respectively. Two major peaks are expected from graphene on Raman spectrum: G peak due to the doubly degenerate zone center E_{2g} mode and 2D peak attributing to the second order of zone-boundary phonons [29]. The typical Raman maps of G and 2D bands on graphene grown on CTO-Cu for 5 min are shown in Figures 5a-b. Nucleation and uniform coverage of graphene on triangular islands are confirmed. The Raman 2D to G peak intensity ratio (I_{2D}/I_G) (Figure 5c) is more than two, indicating that the graphene grown on the triangular grains is single layer. No graphene peaks

can be detected on areas away from triangular grains, as shown inset of Figure 5c, which means graphene only grew on triangular grains. The graphene nucleation on poly-Cu occurred also on Cu_2O grains of irregular shapes, as shown in G and 2D maps in Figure 5d-e. The Raman 2D to G peak intensity ratio I_{2D}/I_G (Figure 5f) could be influenced by the number of graphene layer and interlayer strain between graphene grain and Cu substrate due to the presence of multiple grains, which most probably have different crystalline orientations.

Fig. 6 AFM image of triangles of graphene grown on (a-b) CTO-Cu and (c-d) poly-Cu for 5 min.

Figure 6a-b depicts AFM images of graphene grown on CTO-Cu for 5 min, which are consistent with the SEM images of these triangles and allow the shape of the triangle to be investigated in more detail. These triangle features are typically on the order of 80-150 nm tall from edge to center and show clear faceting along different directions. The regions outside the triangular area show very rough topography, again consistent with the SEM images. The roughness in these regions is on the order of 10-15 nm. The surface features of graphene on

the poly-Cu seem to be arranged in a more random orientation, switching alignment direction several times within the micron-size image, as shown in Figure 6c. AFM images of these samples are consistent with the SEM images. The cross-sectional cut through sample image is shown in Figure 6d. These features are typically on the order of ~ 50 nm tall from edge to center and show clear faceting along different directions. The regions outside the grain area show very rough topography, again consistent with the SEM images.

Fig. 7 (a-b) AFM image of the CTO-Cu (a) before and (b) after graphene growth of 30 min. (c) Step height histogram of graphene on CTO-Cu. (e-f) AFM image of the poly-Cu (e) before and after (f) graphene growth of 30 min. (g) Step height histogram of graphene on poly- Cu.

With an increase of the growth time, the graphene grains on poly-Cu and CTO-Cu extend to larger size and merge together. Figure 7 includes typical AFM images for two types of copper substrates and graphene grown on them. In addition, the step height histograms of graphene on these two types of copper substrates are also included. The comparison of Figure 7a-d reveals that the surface of CTO-Cu is considerably flatter than that of the poly-Cu. In particular, the large trenches on the poly-Cu sample lead to a more deeply corrugated surface when compared to the features of the bare CTO-Cu surface. This roughness may influence the subsequent growth of the graphene on these different copper substrates. Significant

differences in surface structure are observable between AFM images of graphene grown on CTO-Cu and on poly-Cu as seen in Figures 7b and 7f. The surface features of graphene on the poly-Cu seem to be arranged in a more random orientation, switching alignment direction several times within the micron-size image. Conversely, the graphene on the CTO-Cu is organized into relatively consistent, straight, ordered steps throughout the entire surface. Not only the orientation, but also the step characteristics appear to be distinctively different on the two copper substrates. Furthermore, the surface roughness and reconstruction can be observed by using the AFM. The histograms in Figures 7c and 7g represent the relative step height distributions of graphene grown on CTO-Cu and poly-Cu, respectively. As can be seen in the histograms, the distribution of step heights is much broadened for the graphene on poly-Cu as compared to the graphene grown on the CTO-Cu substrate. For the poly-Cu, the majority of values falling below a 10 nm height, but a considerable portion of the step heights are larger, up to 25 nm. For the graphene grown on the CTO-Cu substrates, most step heights are below 3 nm with very few values approaching 10 nm. Where large step heights are observed, they could be single steps that are the full height, or multiple very closely spaced smaller steps. The important thing here is that the distributions of the step, both in terms of orientation and height appear to be significantly different for samples grown on the CTO-Cu or the poly-Cu substrates.

Figure 8 compares the representative Raman spectra of the graphene sheets fully covering the poly-Cu and on CTO-Cu substrates respectively after 30 min. CVD growth time. Specifically, two spectra were shown on each sample with one on a graphene grain and the other on the grain boundary. From all the spectra on both samples, the graphene G peak at around 1580 cm^{-1} and 2D peak at around 2700 cm^{-1} are the most intense features. For both samples, the full-width-at-half-maximum (FWHM) is around 50 cm^{-1} due to the absence of interlayer coupling at the excitation wavelength. The 2D peaks for both samples are symmetric and 2 times more intense than the corresponding G peaks, respectively, indicating

the presence of single layer graphene [30]. From the Raman spectrum focused on a grain boundaries area from the graphene growth on poly-Cu (red curve in Figure 8), we found the D peak at $\sim 1350\text{ cm}^{-1}$ due to the breathing modes of sp^2 rings and the active phonons being excited in defective graphene with high intensity, indicating high density of defects on grain boundaries. However, very little D peak (black curve) was observed in the domain area (black curve), which demonstrated the absence of a significant number of defects in the graphene domain area. This proves that the distribution of defects on graphene grown on poly-Cu is nonuniform, in particular, the defect density is higher in regions near the grain boundaries.

Fig. 8 Raman spectra of graphene grown on poly-Cu (black-on graphene grains, red-on grain boundaries, and cyan-whole film) and on CTO-Cu (green-on graphene grains, blue-on grain boundaries, and magenta-whole film)

In the spectra of graphene grown on CTO-Cu (green-on grains and blue-on grain boundaries curves in Figure 8), much less intensive D-peaks at $\sim 1350\text{ cm}^{-1}$ were observed as compared to the poly-Cu case. Also, the D-peak of Raman spectrum on whole film of graphene grown on CTO-Cu (cyan curve) is less intense than that on poly-Cu (magenta curve). This suggests graphene growth on CTO-Cu with considerably lower density of defects, which

may be attributed to the in-plane alignment of the shaped Cu_2O islands and the reduced density of randomly aligned graphene grain boundaries. This argument is consistent with the presence of much lower density of graphene grain boundaries on CTO-Cu as compared to that on poly-Cu revealed in Figure 4. It is particularly worth mentioning that the graphene growth rate on Cu_2O is comparable to that on Cu foils, which is significantly higher than on non-metal surfaces without catalysts. In addition, the I_D/I_G ratio $\sim 20\%$ on graphene/(111) $\text{Cu}_2\text{O}/\text{CTO-Cu}$ is considerably smaller than previously reported on graphene directly grown on SiO_2 [16, 31], suggesting the importance of controlling the in-plane grain alignment in graphene growth.

Fig. 9 (a) Optical transmittance and (b) electrical conductivity measured on graphene grown on CTO-Cu (red) and poly-Cu (black) with crystalline Cu_2O templates. Fused silica was used as the substrate for the optical transmittance and electric transport measurements of graphene.

The density of defects on graphene can significantly affect the optical and electrical properties. The optical transmittance spectra of graphene transferred from CTO-Cu and poly-Cu substrates are compared in Figure 9a and higher transmittance is observed on the former. At 550 nm, the transmittance of graphene transferred from the CTO-Cu substrate is about 97%, which is close to the expected visible transmittance of 97.7% [32]. The presence of the Cu_2O template between graphene and the copper foil did not seem to have any noticeable

effects on the graphene transfer process and on the optical transmittance of graphene after the transfer. In particular, no features of absorption related to the band gap of Cu_2O are observable, suggesting the residues of the Cu_2O are negligible. The slightly lower transmittance of 95% in the latter may be attributed to higher density defects such as in the graphene grown on poly-Cu. The electrical conductivities of graphene growth on poly-Cu and CTO-Cu were also investigated using four-probe method and the results are shown in Figure 9b. The conductivity estimated from the slope of the linear I-V curve of graphene grown on CTO-Cu is up to 20% higher than that of its counterpart on poly-Cu. The observed enhanced conductivity together with the improved optical transmittance indicate controlling the grain alignment and density of the grain boundaries is important to reduce the density of defects on graphene.

4. Conclusions

In conclusion, we have demonstrated that a crystalline Cu_2O film self-assembled on copper foil surface can provide a viable template for single-layer graphene growth in a standard CVD process. The crystallinity of the Cu_2O film has been shown to be essential to nucleation and evolution of graphene, resulting in selective graphene nucleation only on crystalline Cu_2O grains and graphene evolution with the growth of the grains. The orientations of the crystalline Cu_2O grains are strongly influenced by the underlying copper surface crystalline facets. On single-crystalline (100) CTO-Cu, (111)-orientation of the Cu_2O is predominant, which provides the most favorable (111) Cu facets upon oxygen sub-lattice reduction for fast graphene growth with catalytic assistance of Cu. In contrast, multiple orientations including (111), (110) and (100) Cu_2O grains aligned with various different facets on poly-Cu co-exist, resulting in a larger density of graphene nucleation sites and therefore a higher density of grain boundaries of larger grain boundary angles in the latter case. The less defective graphene due to lower density defects on grain boundaries on CTO-Cu is confirmed by

Raman spectra, leading to better optical transmittance and electrical conductivity of graphene as compared to that on poly-Cu. This result is important by not only providing a novel scheme for direct CVD growth of graphene on non-metal surfaces, but also an approach to control the microstructure and orientation of graphene nucleation and evolution for low cost, scalable, transfer-free graphene epitaxy.

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