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Selective Area Oxidation of Copper Derived from Chemical Vapor Deposited Graphene Microstructure

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Abstract

The barrier properties of graphene coating are highly correlated with its microstructure which is then determined by the chemical vapor deposition (CVD) growth history on metals. We demonstrate here an unrevealed selective area oxidation of copper under graphene, which is derived from the implicit-etching-controlled CVD growth mode of graphene. By characterizing and analyzing the selective area patterns of Cu oxidation, an etched pattern trace with nano/microvoids during graphene growth has been proposed to account for this. Based on such selective oxidation of Cu, distributed galvanic corrosion will be triggered and proceed locally at the interface of graphene-Cu system to coalescence together under a continuous corrosion environment, eventually presenting a homogeneous oxidation of Cu and gradual decoupling of graphene-Cu system. This discovery will assist our understanding of the barrier properties of two-dimensional materials and can be extended to other applications related to quality monitoring of grown materials and defects-based chemical modifications.

Supplementary materials for this article are available online

Keywords: Selective area oxidation, Chemical vapor deposition, Growth pattern, Corrosion, Graphene coating

1. Introduction

Protective coating against metal corrosion is of significant importance for the applications of metallic materials[1]. As a two-dimensional material, graphene films directly grown on metal surfaces by chemical vapor deposition (CVD) has been proposed to be a promising protective coating due to its supreme impermeability and the nature of the thinnest layer of coating[2-4]. Moreover, in-situ grown graphene has many advantages in maintaining the topographical conformity with metal surfaces, and in

controlling layers number and large-area uniformity[5-7]. In principle, the dense hexagonal honeycomb structure of perfect graphene lattice would isolate the metals from any corrosive elements[8-10]. However, the structural defects and growth imperfections in graphene are inevitably created accompanying the CVD processes and facilitate the mass transport of corrosive species as a pathway[11]. Recently, many graphene defects such as grain boundaries, vacancies, wrinkles, and the incommensurate coupling of graphene-Cu system[12-17] have been revealed to cause oxidative damages correlated with a galvanic corrosion in the long term[18, 19].

Despite the intensive researches, the barrier properties of graphene coating, either on the oxidation mechanisms or on the corrosion kinetics, have been incongruous and to be developed. Especially, the pattern of triggering oxidation and the corresponding corrosion mechanism are still elusive when it is associated with the preparation details of graphene by CVD.

Here, we investigate the oxidation pattern and understand the corresponding corrosion mechanism of copper-graphene system from the perspective of CVD growth. A selective area oxidation of copper which is strikingly resemble with the graphene growth pattern is disclosed. Further, an implicit-etching-controlled growth of graphene, containing specific patterns (such as dendritic microstructure) of nano/microvoids, has been proposed to account for this selective area oxidation of copper. Based on this oxidative pattern, local electrochemical corrosion then will be triggered and expand around at the interface between graphene and copper surface under oxidative environment, presenting a homogeneous corrosion of Cu with a gradual and uniform decoupling of graphene-copper system. Which is inconsistent with previously published results[20-22], where it was believed that a decoupling of graphene-copper system would proceed

in a preferential path starting from the graphene edges to the center. This work provides insights into a distinctively partial oxidation of copper with selective patterns under graphene grown by CVD which have never been observed before. Importantly it has significant implications in other layered materials involving anti-corrosion, growth-mode-dependent quality detection and defects-based chemical modifications.

2. Experimental methods

2.1 CVD growth of graphene on Cu

Graphene samples of isolated grains and full-coverage films were grown on Cu foils by low-pressure CVD. Cu foils (99.8% purity, 25 μm thick, Alfa Aesar) were used as growth substrates within a hot-wall tube furnace and Aixtron Black Magic cold wall CVD system. After an annealing process in an Ar atmosphere, a changed H_2 flow rate (from 5-100 sccm) diluted CH_4 (1 sccm) feedstock was introduced in the chamber for the growth in varied growth time (from 1-5 hour). Both annealing and growth were carried out at 1020 $^\circ\text{C}$ and low pressure (20 mbar). After growth, CH_4 was turned off, and the Cu foil was cooled down by keeping the other CVD parameters unchanged.

Figure1. a) A schematic processes of CVD growth of graphene with implicit pattern on copper and then followed by a selective area oxidation of Cu under graphene. b) Optical image of a graphene grain grown on Cu surface after 200 $^\circ\text{C}$ annealing in air for 10 min. c) Optical image of the same graphene grain on Cu by a subsequent 50 $^\circ\text{C}$ annealing in air for 24 hours after 200 $^\circ\text{C}$ annealing in air for 10 min. d) Dark-field optical image corresponding with c). e-f) Enlarged optical images taken from the red frame in b), c) and d), respectively.

2.2 Oxidation of graphene-Cu system

Thermal annealing in air at 200 °C was applied to the as-grown samples for 10 min, resulting in the morphology profile of graphene on Cu. Then, the samples were followed by means of other oxidation treatments including 50 °C in air for 24 h, ambient oxidation for 3-12 months, and 50 °C in water for 24 h to study its oxidation behavior.

2.3 Characterization of graphene and Cu oxidation

Graphene domains were observed after Cu oxidation by a Nikon Eclipse L200N microscope. Scanning electron microscopy (SEM) (Zeiss Supra VP 60, 5 kV) was used to characterize the morphology of graphene transferred on Cu grids. Transmission electron microscopy (TEM) (Tecnai G2 F20, operated at 200 kV) then was used to characterize the nano/microvoids defects of the as-transferred graphene domain. Raman spectroscopy was performed with a Thermo Fisher DXR microscope under ambient conditions using a 532 nm excitation laser source. The nominal spot size is 700 nm. The power of the laser is kept below 1 mW. X-ray photoelectron spectroscopy (XPS) was performed on oxidized Cu grown with graphene with an Escalab 220i-XL from Thermo Scientific. A monochromatized Al K-Alpha X-ray source with photon energy 1486.7 eV was used as photon source.

3. Results and discussion

It is well known that optical microscopy provides a convenient method for direct visualization of graphene profile grown on copper by post-annealing[12, 23]. As shown in Figure 1, post-annealing in air at 200 °C for 10 min resulted in an uniform graphene profile on copper substrate (Figure 1b) as previous reports[23]. Interestingly, an explicit pattern of copper oxidation with selective area under graphene appeared when a further annealing (50 °C for 24 h) was applied to the same sample. The graphene bright and dark field optical images (Figure 1c, d and Figure S1) demonstrate a clearly visible pattern with dendritic morphology which here ascribes to the implicit microstructure of graphene. The corresponding Raman spectrum (Figure S2) confirmed the presence of copper oxides, presenting an obvious signal of Cu_2O [24-27] at $\sim 644 \text{ cm}^{-1}$. Figure 1e-g are the enlarged optical images taken from the red-framed graphene surface in b), c) and d), respectively. One can unambiguously see and distinguish that there are some lines of nano/microvoids making Cu oxides visible (Figure 1f, g) after a further annealing.

As well as, the full-coverage graphene on copper, which is well-known composed of different graphene grains, display distributed selective patterns of copper oxidation (Figure S3) by applying a fierce annealing condition. These consistent phenomena of Cu oxidation pattern demonstrate that both

partial- and full-coverage graphene have the same graphene microstructure. In principle, the microstructure of graphene is primarily determined by its growth history. The CVD growth processes then should be taken into accounts herein.

Figure 2. a) Optical image of a graphene grain grown on Cu surface after a 200 °C annealing in air for 10 min. b) Optical image of the same graphene grain grown on Cu surface by a subsequent natural oxidation in air for half year after 200 °C annealing in air for 10 min. c) Raman spectra taken from the graphene grain in a) and b), respectively. d) XPS core-level C 1s spectra of before and after 0.5 year-aged Cu with graphene. e) XPS core-level Cu 2p spectra of before and after 0.5 year-aged Cu with graphene. f) Deconvoluted XPS core-level Cu 2p spectrum of 0.5 year-aged Cu with graphene.

In order to understand such a selective oxidation pattern of copper, the etching-controlled growth pattern of graphene on copper by CVD was proposed to be responsible for this. It is generally believed that there is an accompanying etching process occurred simultaneously in the CVD growth process of graphene, and results in a common fractal etching patterns[28-32]. Figure S4 shows the time- and hydrogen-resolved growth results of graphene by an etching-controlled CVD method[30, 31] where the proportion between etching and growth of graphene can be tuned by the regulation of hydrogen etchant. As shown, the graphene patterns are tuned from dendritic to compact with respect to the increasing of hydrogen flow rate, meanwhile the grain size of graphene is getting larger in the growth time axis. The evolution of

Figure 3. a) Optical image of a graphene corner on Cu surface after immersion in DI water for 24 hours at 50 °C. b) Raman spectrum from the area marked a red cross in a). c) Raman intensity mapping of Cu₂O at ~ 644 cm⁻¹ taken from a).

graphene patterns from dendritic to compact is essentially attributed to the etching effect changed from dominate to recessive. Although there are not visible etching effects in the compact graphene, it inevitably remains the microstructure with recessive etching trace due to the same graphene-branched growth model. It is because the continuous and robust oxidation process (for instance 50 °C for 24 h), making the recessive etching trace microstructure in compact graphene visible by filling the etched nano/microvoids with copper oxides (Figure 1f, g). Therefore, the microstructure of graphene with implicit patterns composed of etched nano/microvoids, which is derived from the etching-controlled growth mode of graphene, should account for this selective area oxidation of copper. In order to directly see the actual nano/microvoids defects, the etching-controlled CVD grown graphene were transferred onto copper grids for the TEM characterization. As shown in their SEM images (Figure S5a, b), graphene with dendritic morphology are clearly seen on the copper grids, indicating the successful transfer of graphene. More important, the corresponding low- and high-resolved TEM image (Figure S5c-f) shows that various growth imperfections including micro/nanovoids (Figure S5c, d), hole defects (Figure S5e), and vacancies (Figure S5f) could be found in the etching-controlled grown graphene, confirming that these defects indeed present there. It is because of this presented micro/nanovoids etc. defects which would serve as oxidative originators and facilitate the mass transport of oxidative species (O₂ and H₂O) as a pathway, causing this selective Cu oxidation along these defects.

It should be noted here that fast annealing conditions (200 °C for 10 min) alone (Figure 1b) is not sufficient to cause this feature of selective area oxidation of copper under graphene. This oxide building up and visualization of the selective pattern is based on an accumulated oxidation of copper via a relative long-time diffusion of oxygen and formation of Cu oxides. Further confirmation from other experiments by naturally oxidizing the graphene samples has been conducted. As shown in Figure 2a b and Figure S6, by exposing the graphene samples in ambient after fast annealing for as long as 6-12 months, a selective oxidation of copper with branched

pattern under graphene appears as expected. Raman spectra (Figure 2c) of the graphene before and after 6 months ambient oxidation show the characteristic 2D and G bands. Distinctive features associated with Cu oxides (typical Cu₂O at ~ 644 cm⁻¹) can be distinguished after 6-month natural oxidation. X-ray photoelectron spectroscopy (XPS) was further employed to analyze the surface composition of the sample before and after aging. Oxygen, carbon, and copper are overall included in their typical survey scan, and the oxygen content is much more in the aged sample than that in not aged sample due to the long-term exposure to air (Figure S7a). In addition, there are clear differences presented in both of C 1s (Figure 2d) and Cu 2p spectrum (Figure 2e) of the aged and not aged sample. Specifically, the aged sample exhibits a broader Cu 2p_{3/2}, 2p_{1/2} peak and C 1s peak with satellite peak as seen in Figure 2d and e. Further analysis is conducted by peak deconvolution for the aged sample. As shown, the C 1s spectrum (Figure S7b) exhibits mostly graphitic sp² carbon peak at binding energy of ~284.5 eV, fitted hydroxyl C-OH (~286.3 eV), and carbonyl C=O (~288.1 eV)[14]. The Cu 2p spectrum (Figure 2f) shows broader peaks which correspond to different copper oxides assigned to Cu/Cu₂O (~932.5 and 952.4 eV), CuO (~933.6 and 953.4 eV), and Cu(OH)₂ (~934.7 and 954.5 eV)[8, 33]. These Raman and XPS data indicate the presence of selective area copper oxides unambiguously after long-term natural oxidation for the samples.

It was reported that water can accelerate the interfacial Cu oxidation and decouple graphene-copper system by intercalation of H₂O due to galvanic corrosion[20, 34]. Here the graphene sample immersion in water was conducted as well to test our selective area oxidation of copper-graphene system. Figure 3a is an enlarged optical image of graphene sample after immersion in water for 24 hours at 50 °C, showing clear observation of selective oxidation of Cu with much more severe oxidation level. This is confirmed by the very strong Cu₂O Raman intensity at ~ 644 cm⁻¹ (Figure 3b) from the area marked a red cross in Figure 3a. Moreover, the Raman intensity mapping of Cu₂O (Figure 3c) and graphene 2D peak (Figure S8) illustrate regions with different colors, which are related to the selective oxidation pattern of copper

grown with graphene. All the experimental results from different oxidative conditions confirmed an intrinsic oxidation behavior of Cu under graphene with selective area patterns.

Figure 4. a) Raman spectra of graphene grown on Cu after a 200 °C annealing in air for 10 min followed by different oxidation conditions. b-d) Evolution of Raman D peak and Cu₂O intensity with respect to time as graphene-Cu systems are oxidized by different oxidation conditions.

It is necessary to point out that the different Cu oxidation extent (corresponding to different oxidation conditions) would

cause the generation of graphene defects with different levels. Extracted Raman spectra for the oxidation conditions utilized above, which correspond to 50 °C in air for 24 h, ambient oxidation for half year, and 50 °C in water for 24 h, respectively, exhibit obvious difference for graphene D peak which assigned to the graphene defects[35] (Figure 4a). As shown, the Raman spectra show a strong D peak for 50 °C in water for 24 h, and a moderate D peak for 50 °C in air for 24 h, while no detected D peak for ambient oxidation for half year. Figure 4b, c and d show time evolution of Raman D peak and Cu₂O intensities of graphene-Cu system when the samples were oxidized by the aforementioned oxidation conditions. In the case of ambient oxidation for 0.5 year (Figure 4b), the Cu₂O starts forming after around 50 day and no obvious D peak intensity was detected in the whole duration due to the relative mild oxidation condition. Regarding the other two cases, D peak and Cu₂O formation were initialled from the point of 4.5 hour for 50 °C air oxidation (Figure 4c) and 2.5 hour for 50 °C water oxidation (Figure 4d), respectively. Moreover, the overall oxidation of Cu under graphene in the case of 50 °C in water for 24 hour proceeded much quicker than the others. These results indicate that the Cu oxides would form along the nano/microvoids at their own speed corresponding to each oxidation condition, and vigorous oxidation conditions would further destroy the graphene at the regions of nano/microvoids.

Figure 5. a) Optical image of a graphene grain grown on Cu surface after a 200 °C annealing in air for 10 min followed by an ambient oxidation for 1 year. b) Magnified optical image taken from the up-left corner of the graphene domain on Cu in a), showing almost uniform decoupling of graphene-Cu system. c) Optical image of a graphene grain grown on Cu surface after a 200 °C annealing in air for 10 min followed by a 3 months ambient oxidation, showing edges-towards-center decoupling of graphene from Cu surface. d) The schematic illustration of a selective oxidation pattern-triggered corrosion mechanism. e) The schematic illustration of a corrosion mechanism with conventional corrosion path from edges to center of graphene grain on Cu surface. f) and g) The side view representation of corrosion mechanism corresponding to d) and e), respectively.

Importantly, based on this oxidative pattern, distributed galvanic corrosion will be further triggered locally and expand around at the interface between graphene and Cu surface (Figure S9) under a continuously oxidative environment. With this galvanic corrosion expansion in plane, these distributed corrosion areas proceed together and eventually demonstrate a homogeneous corrosion of Cu with a gradually uniform decoupling of graphene from copper surface (see Figure 5a, b and Figure S10). One can clearly see the whole oxidation pattern (Figure 5a) and the partially enlarged (Figure 5b) oxidation of copper, respectively, after a longer (1 year) natural oxidation. It indeed presents a striking resemblance with the graphene growth pattern shown above, and an almost uniform decoupling of graphene from Cu substrates (also see Figure S9c). In comparison, the compact graphene grown on Cu without selective etching patterns of nano/microvoids would follow a preferential corrosion path where the oxidative front starts from the graphene edges to the center [20-22] as demonstrated in Figure 5c. Based on this analysis, the top view (Figure 5d, e) and side view (Figure 5f, g) of these different corrosion mechanisms are schematically illustrated for comparison, showing the selective oxidation pattern-triggered corrosion and conventional corrosion with path from edges to center of graphene, respectively. This different discovery will enrich our understanding of the barrier properties of two-dimensional materials.

4. Conclusion

In conclusion, we have investigated an unrevealed selective area oxidation behavior of copper under graphene by means of various oxidation conditions including directly heating in air, ambient oxidation, and immersion in water. By characterizing the selective oxidation patterns, we are able to correlate this selective area oxidation of copper with its synthesis history by CVD growth where an etching-controlled growth of graphene with dendrites-etched microstructure has been proposed to be responsible for this. Such oxidative patterns of Cu derived from graphene growth processes have never been observed before. Further, a distinctive corrosion mechanism with homogeneous and gradual decoupling kinetics based on such a selective area oxidation of copper has been demonstrated as a counterpart with respect to the conventional direction-preference corrosion. This discovery provides insights into corrosion mechanisms of graphene coating and correlates its growth history which actually is the fundamental factor determining the barrier properties of two-dimensional materials.

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