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Etching-controlled preparation of large-area fractal graphene by low-pressure CVD on polycrystalline Cu substrate

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ABSTRACT

Fractal graphene can provide more active sites for electrocatalytic reactions due to its unique morphology. The preparation of large-area fractal graphene and the understanding of its morphology evolution are crucial to the improvement of catalytic performance. Chemical vapour deposition (CVD) technology is a unique method to obtain high quality fractal graphene. In this study, low-pressure CVD method was used to prepare fractal graphene on Cu substrate. Through the etching effect of hydrogen in the cooling process, the evolution process of graphene from compact to dentritic was realized and the fractal dimensions of graphene with different morphologies were calculated. It was found that the hydrogen etching reaction of graphene begins at the edges and moves towards the nucleation point gradually until the etching progress is completed. And continuous large-area fractal graphene films were obtained for the first time, which would find potential application in electrocatalysis and other fields.

1. Introduction

The preparation of graphene by CVD has attracted great interest since 2009 [1]. Fractal graphene can be obtained by using the etching effect of hydrogen during the CVD process [2]. The etched graphene has abundant sharp edge-sites which would find potential applications in electrocatalysis and other fields [3,4]. In 2010, Rong Yang et al. [5] observed an anisotropic etching effect on graphene using hydrogen plasma. Dechao Geng et al. [6–8] found that the etched graphene patterns using CVD can be complex and fractal instead of hexagonal that people accepted in common. In 2018, Zewdu M. Gebeyehu et al. obtained the dentritic graphene patterns by a two-step mechanism consisting of growth and subsequent etching [9]. Although several papers reported different morphologies of fractal graphene grains grown by CVD [6–11], the fractal structures are all observed in separate graphene domains with small size (a few microns to tens of microns) and low coverage. And for the analysis of the growth process and fractal geometry of graphene on copper have been developed a few express methods, including qualitative description and calculating the fractal dimension of graphene [1,12,13]. Advances in these areas of research would contribute to further understanding of the formation mechanism of fractal structures during CVD process.

In this paper, fractal graphene was obtained through a two-step process which involved graphene growth and subsequent etching by hydrogen during the cooling process. The evolution process of graphene from compact to dentritic was observed and the fractal dimensions of the graphene with different morphologies were calculated. By the proper control of reaction conditions, for the first time, large-area of dendritic graphene was obtained which may widen the potential applications of graphene in many fields.

2. Experimental details

Cu foils (25 μm, Alfa Aesar) were loaded into the quartz tube mounted inside a CVD furnace (G-CVD Graphene Technology Company Limited, Xiamen). The chamber was pumped to below 0.7 Pa and then heated to 1050 °C with 100 sccm (standard cubic centimeters per minute) argon, followed by an annealing process for 30 min with a mixture gas flow of 20 sccm hydrogen and 320 sccm argon. Next, a small flow rate of 2 sccm methane was introduced for 60 min. After that, the CH_4 flow was turned off and the flow rate of other gases was kept unchanged for an hour. Finally, the system was cooled down by taking the tube out of furnace at 700 °C. To obtain continuous fractal graphene films, the H_2 and CH_4 supply was increased to 80 sccm and 4 sccm respectively during the growth stage with 320 sccm Ar kept unchanged. The growth time was set for 40 min. After that, the tube

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was taken out of the furnace at 1050 °C in the subsequent etching process with 20 sccm H_2 and 320 sccm Ar last for 60 min.

The fractal graphene was transferred onto the SiO_2/Si by using the wet-etching of copper foils. The surface of copper covered with graphene was spin-coated with polymethyl methacrylate (PMMA) and was put into the drying oven at 70 °C for 30 min. Then, the copper foil was etched by 1 M aqueous solution of ammonium persulfate. After that, the graphene adhered with PMMA was transferred onto the silicon substrate with 300 nm thick SiO_2 coating. Finally, the PMMA film was rinsed by acetone.

The scanning electron microscopy (SEM) and optical microscopy were used to observe the morphology of graphene. The Raman spectroscopy and AFM results showed the thigh quality and single layer characteristic of graphene.

3. Results and discussion

Previously, graphene grown on solid polycrystalline copper was mostly irregular shaped. Through repeated experiments, we found that fractal graphene patterns with different morphologies were always observed on the surface of polycrystalline Cu by taking the tube out of furnace at specific temperature (1050 °C–500 °C) during the etching process. The typic series of hexagonal fractal graphene using the fast cooling mode (taking the tube out of furnace at 700 °C) was showed in Fig. 1a–h. The fractal graphene with different morphology can represent different etching stages. In particular, the edges of these grains are found to be predominantly parallel to zigzag directions [14]. Clearly, the etching of graphene begins at the edges and moves towards the nucleation point until the etching process completed. It is showed that the diffusion direction of the carbon atoms along the zigzag is faster than armchair [15]. We believe that the migration and reconstruction of activated carbon atoms along the mental surface under the etching effect of hydrogen resulted fractal graphene. It is similar to the explanation of the final morphology of graphene that the continuous modulation of the competition between adatom diffusion along island edges and surface diffusion process [11,16,17]. Obviously, the role of hydrogen and the environment of the substrate surface are significant for the preparation of fractal graphene.

The fractal dimensions of Fig. 1a–h were calculated using the box-counting method which has been proved to be an effective way to measure the dimensions of fractal images [18,19]. The results are shown in Fig. 2 Here, the SEM images of fractal graphene in Fig. 1a–h were cut into the size of M × M and were binarized to get black and white illustrations as is shown in the upper right corner of Fig. 2. Based on the classical box dimension formula of $D_b = \lim_{r\to 0} \frac{\log N_r}{\log 1/r}$, in which D_b is the slope of a least-squares linear fit to the set $\{(\log 1/r, \log N_r)\}$, r is the box size and N_r is the number of boxes needed to cover the fractal images [13,19,20]. The boxes with different side lengths (2^n, n is an integer) were used to cover the black and white graphs, and the total numbers of boxes (N_r) were calculated. Finally, the least square method is used to fit the set {(log r, log N_r)} and the fractal dimensions of Fig. 1a–h were obtained. Through these processes above, the corresponding fractal dimensions of graphene in Fig. 1a–h are 1.851, 1.877, 1.884, 1.849, 1.820, 1.795, 1.754, 1.742 respectively. These fractal dimensions were found to be in good agreement with the box-counting fractal dimensions of the planar flake-like graphene oxide nanosheets ($D = 1.975 \pm 0.025$) [13] and the fractal Au islands ($D = 1.72 \pm 0.07$) [21]. It seems that the fractal dimensions of fractal graphene tend to decrease with the deepening of etching process.

The optical images of the fractal graphene transferred onto the silicon dioxide substrates were shown in Fig. 3a–f. The Raman spectra (Fig. 3g) of two different areas in Fig. 3a confirm the monolayer characteristic of graphene. In area A, the characteristic 2D and G peak of graphene were observed at 2688 cm^{-1} and 1593 cm^{-1} respectively, with the intensity ratio about 2.04, implying that the graphene is single layer. The 2D peak is sharp and the half peak width is about 37 cm^{-1}. Additionally, peak D is barely visible. The AFM result of the white square inside Fig. 3f further confirmed the monolayer characteristic of the dendritic graphene. The height profile across the dendrite of graphene in Fig. 3f showed that the thickness of transferred graphene is about 0.63 nm, which is consistent with the theoretical thickness of monolayer graphene on substrate. Therefore, these characterization results provide direct evidence of the successful transfer of the fractal graphene.

Previous theoretical studies and experimental results have showed that the C supply will affect the graphene nucleation density [22]. For better transfer and application of fractal graphene, continuous large-area dendritic graphene films (Fig. 4) were obtained by increasing the nucleation density and using the fast cooling method. In these cases, the graphene films were all grown on solid copper surface at 1050 °C with 80 sccm H_2, 4 sccm CH_4 and 320 sccm Ar for 40 min. The tube was taken out of the furnace at 1050 °C in the subsequent hydrogen etching process. The SEM images with typical hexagonal (Fig. 4a) and four-lobed (Fig. 4b) structures illustrate an anisotropy etching and growth velocity. Obviously, the growth mechanism of large-area dendritic graphene is similar to the fractal graphene in a single domain that we discussed above. Fig. 4c and d showed the optical images of large-area dendrite graphene after annealed at 200 °C in air for 10 min. Distinctly,

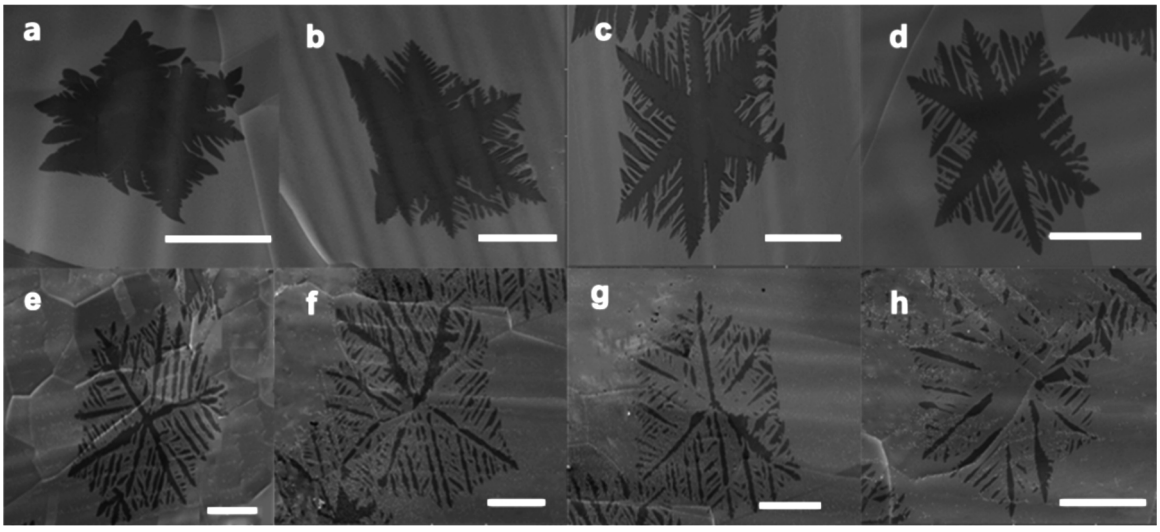

Fig. 1. (a)–(h) A series of SEM images of fractal graphene with different morphology. All scale bars are 50 μm.

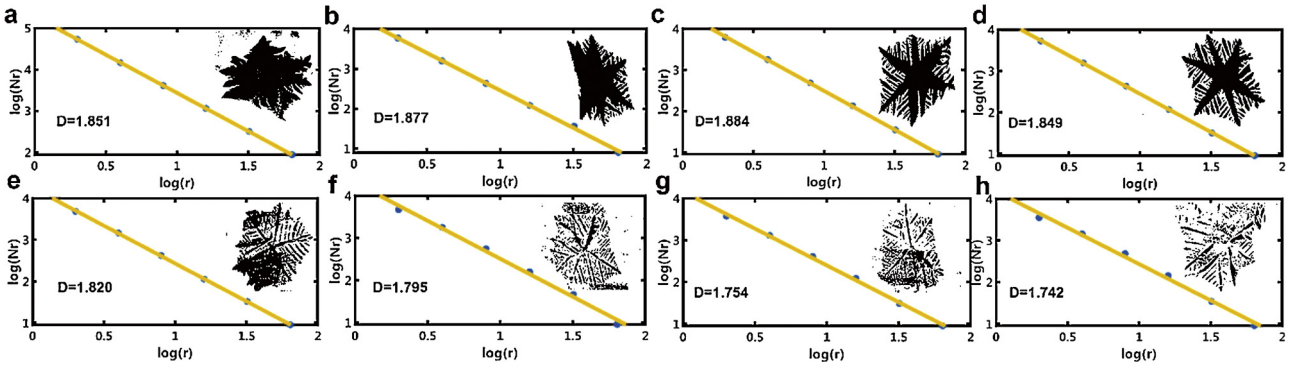

Fig. 2. (a)–(h) Fractal dimension calculation using the box-counting method of the graphene images shown in Fig. 1a–h.

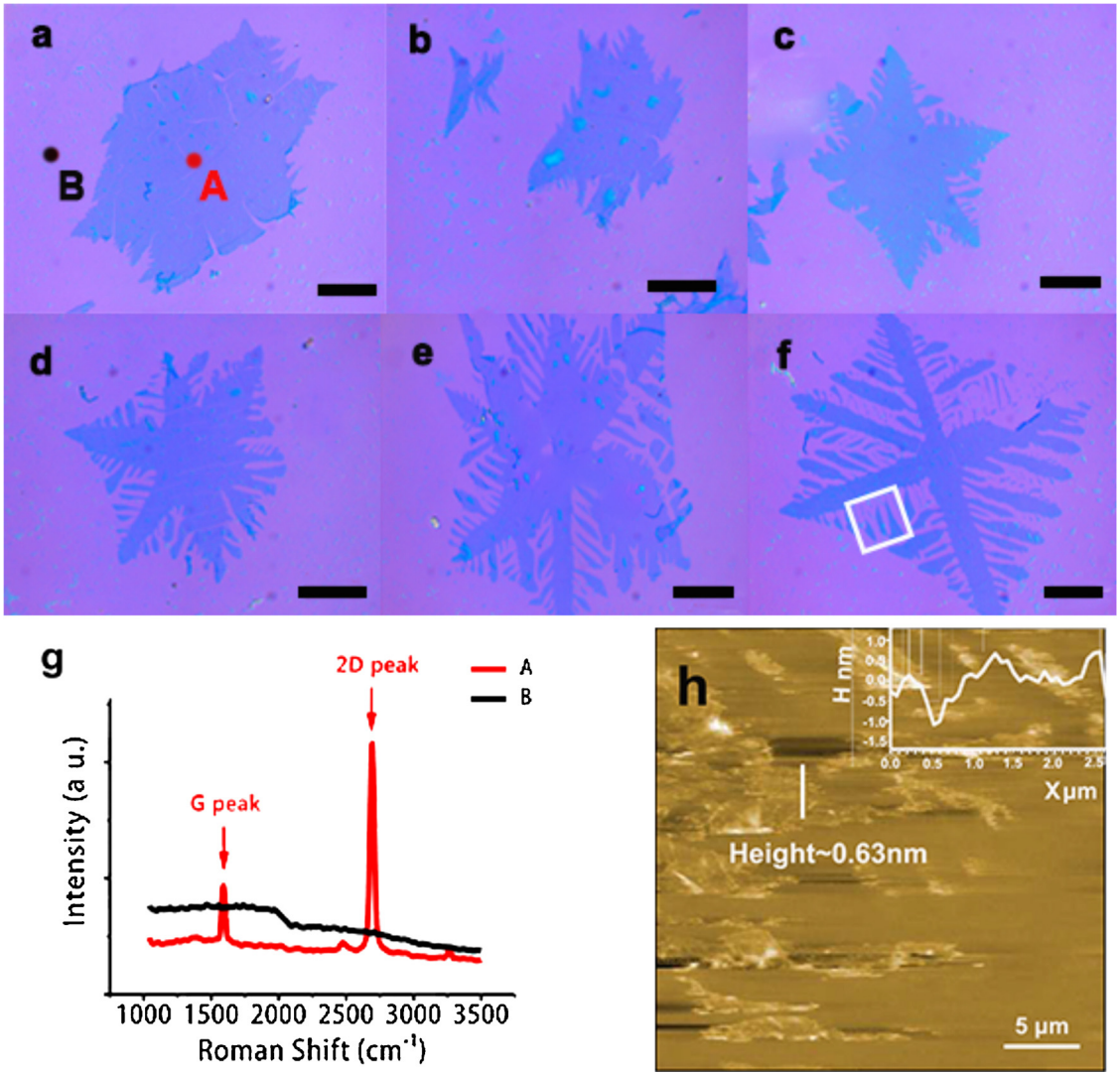

Fig. 3. (a)–(f) Optical images of various fractal graphene transferred onto SiO_2/Si. All scale bars are 20 μm. (g) Raman spectra of different regions (A and B) in Fig. 3a. (h) AFM image of graphene in the white square area of Fig. 3f and a corresponding height profile along the white solid line.

the dark orange region was the oxidized copper substrate without graphene covering. Our results confirm that continuous fractal graphene can be gained under a two-step process, i.e., the growth and subsequent etching process.

4. Conclusion

In summary, graphene from compact hexagon to fractal structures were obtained through the etching effect of hydrogen by CVD on polycrystalline Cu Substrate. It was found that the hydrogen etching reaction of graphene begins at the edges and moves towards the nucleation point. The formation mechanism of fractal graphene is the migration and reconstruction of activated carbon atoms along surface under the hydrogen etching effect. And continuous large-area fractal graphene films were obtained for the first time, which may play an important role in the applications of electrocatalytic and electronic

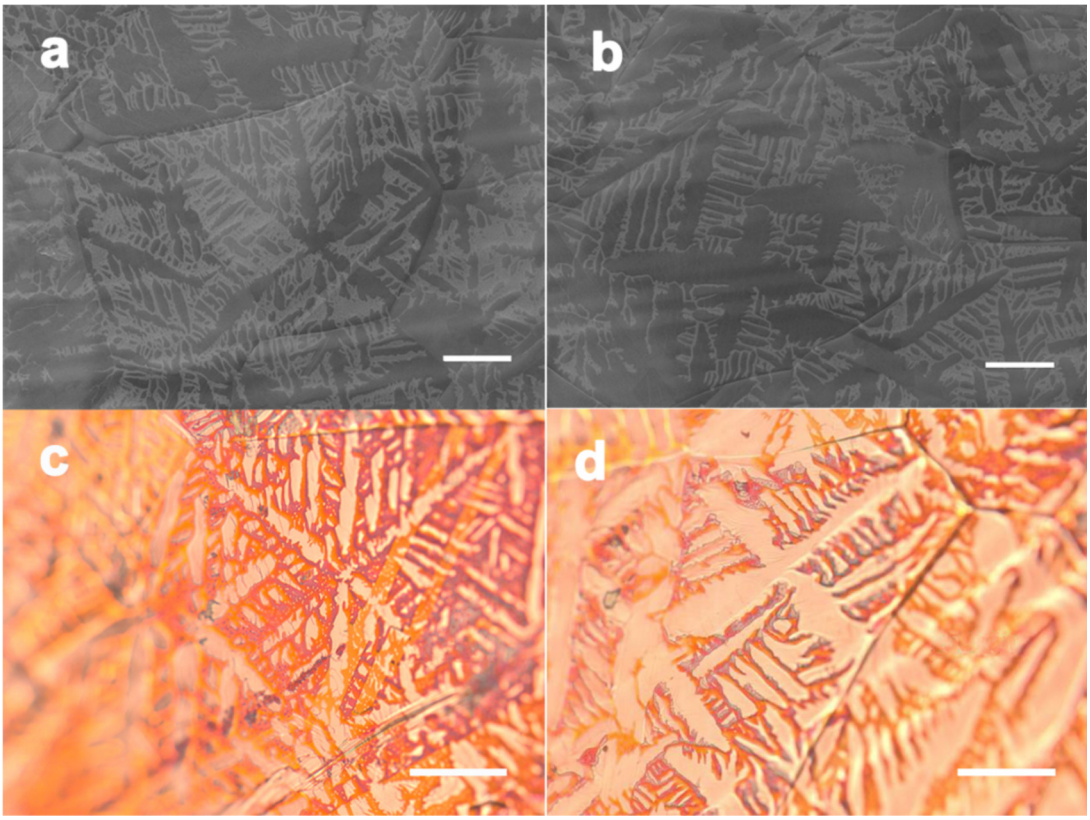

Fig. 4. Images of large-area dendritic graphene. (a) SEM image of hexagonal dendrite graphene. (b) SEM image of four-lobed dendritic graphene. (c) Optical micrograph of hexagonal dendritic graphene after annealed. (d) Optical micrograph of four-lobed dendritic graphene after annealed. All scale bars are 50 μm.

devices fields. Our results proved that the low-pressure CVD method provides an efficient way for preparation of large-area fractal graphene. In addition, the etching mechanism and the preparation method of fractal graphene may provide reference for other two-dimensional materials.

CRediT authorship contribution statement

Xia Zhang: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing, Visualization. **Qian Zhou:** Investigation, Validation, Writing - review & editing. **Miaomiao Yuan:** Investigation, Validation, Writing - review & editing. **Bin Liao:** Resources, Writing - review & editing, Supervision. **Xianying Wu:** Writing - review & editing, Supervision. **Minju Ying:** Conceptualization, Investigation, Resources, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mtcomm.2020.101093.

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