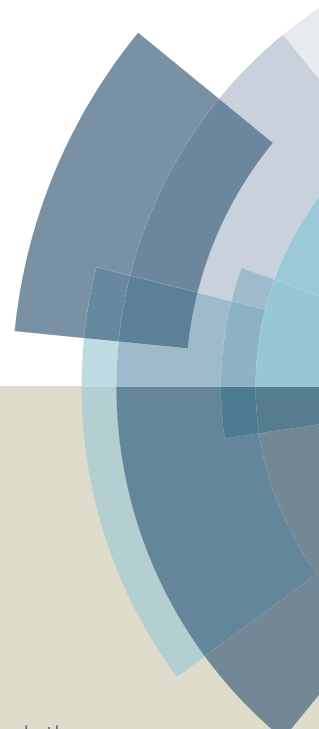
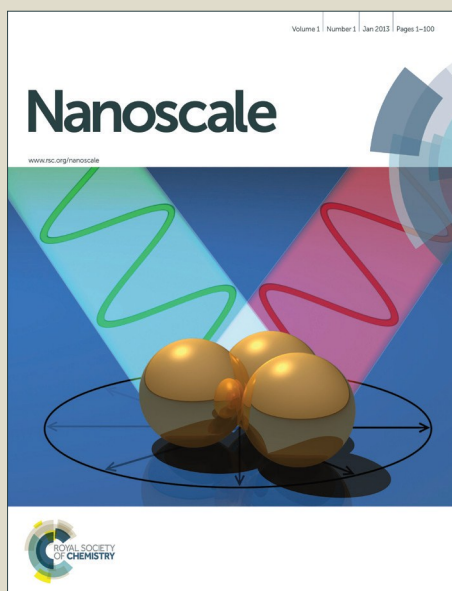


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Double Hexagonal Graphene Ring Synthesized by Growth-Etching Method

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Precisely control the layer number, stacking order, edge configuration, shape and structure of the graphene is extremely challenging but highly desirable in scientific research. In this report, a new concept namely growth-etching method has been explored to synthesize graphene ring with the chemical vapor deposition process. The graphene ring is the hexagonal structure, which contains a hexagonal exterior edge and a hexagonal hole in the centre region. The most important concept introduced here is that the oxide nanoparticle derived from annealing is found to be played dual roles, which firstly acts as nucleation site to grow the hexagonal graphene domain and then works as defect for etching to form a hole. The evolution process of the graphene ring with the etching time was carefully disclosed. In addition, the double hexagonal graphene ring was successfully synthesized for the first time by repeating the growth-etching process, which is not only confirmed the validity and repeatability of the method developed here but also may be further extended to grow unique graphene nanostructure with three, four, even tens of the graphene rings. Finally, a schematic model was drawn to illustrate how the double hexagonal graphene ring generates and propagates. The results shown here may provide valuable instructions for the design and growth unique nanostructure in graphene even the other two-dimensional materials.

Introduction

Graphene, a first discovered two-dimensional (2D) single layer crystal, has attracted a great attention due to its excellent mechanical,^{1, 2} thermal,³ optical⁴ and electronic⁵⁻⁸ properties. These properties are effected by lots of parameters, for instance, layer number,⁹ stacking order,¹⁰ edge configuration, shape and structure¹¹ etc. Controlling these variables is not only highly important for obtaining the desired characteristics but also having a profound impact on our understanding of non-equilibrium growth processes for large-scale production. At present, various approaches have been developed to prepare graphene, such as mechanical cleavage,⁶ chemical method,¹²

epitaxy on SiC,¹³ and chemical vapor deposition (CVD)^{14, 15} on metal foil. Among them, the CVD method has aroused great attention due to it is potential to be a procedure that is not only to manipulate the layer number, stacking order, edge configuration, shape and structure of the graphene and but also to test the validity of the classical theory of nucleation and growth. In fact, various unique graphene structure were synthesized by CVD, for example, Yan et.al¹⁶ have synthesized graphene onion rings using CVD with controllable pressure; Yan et.al¹⁷ have produced large hexagonal bi-and trilayer graphene single crystal with varied interlayer rotations; Liu group^{18, 19} demonstrated a method to grow complex fractal geometric patterns; Ma et.al²⁰ demonstrated an approach to grow graphene with the edge controlled from zigzag to armchair orientations; Ito et.al²¹ even synthesized 3D nanoporous graphene and so on.

In fact, precise controlling over shape and structure of the graphene is extremely challenging but highly desirable in scientific research. However, it relies not only on precise tuning the growth condition, but also on good understanding of growth kinetics. In this report, the hexagonal graphene ring has been successfully synthesized for the first time with the growth-

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etching method explored here by CVD process. The oxide nanoparticle derived from annealing is found to be played dual roles which firstly acts as nucleation site to grow graphene domains and then works as defect for etching to form holes. The size of the graphene ring in the exterior edge gradually shrinks while the hole in the center region quickly broadens as the etching time increasing. In addition, the double hexagonal graphene ring was successfully synthesized for the first time by repeating the growth-etching process, which is further confirmed the validity and repeatability of the method explored here. Finally, a possible schematic model to synthesize the double hexagonal graphene ring was proposed. The results shown here may provide valuable instructions for designing and growing unique graphene nanostructure, which could even extend to other 2D layered materials.

Results and discussion

Synthesis of the hexagonal graphene ring

To observe the morphology of the graphene domains simply and effectively, the Cu substrates grown graphene domains were oxidized at 200 °C in air for 1 min firstly.²² Figure 1(a) shows the typical optical microscopy images of the graphene domains grown on Cu, where the hexagonal shape with six-fold symmetry graphene domains can be observed clearly and the oxide nanoparticle in the centre of the graphene domain was also distinctly illustrated. These results are consistent with our previous reports.²³ To obtain graphene ring, a new concept namely growth-etching method has been explored based on a series experiments. It is found that when the concentration of

the H₂ decreases namely the concentration of the CH₄ is higher, the copper oxide nanoparticle will be reduced by CH₄ to form copper structural defects,²⁴ and it does not continue nucleation and grow graphene layer, contrary to expectation it begins to etch from the nanoparticle. In this experiment, the etching process was performed by decreasing the H₂ flow to 3 sccm and keeping the CH₄ flow at 0.5 sccm for constant in 1070 °C. Figure 1(b), (c), (d), and (e) show the optical microscopy images of the graphene domains after etching for 30 min, 60 min, 90 min and 120 min respectively. After etching process, a hole around the oxide nanoparticle was appeared in the center of the graphene domain. The hole is nearly round with etching for 30 min. But, it is transformed to the hexagonal shape when the etching time increases. Especially, it becomes the quite perfect hexagonal shape after etching for 120 min as shown in Figure 1(e). Furthermore, another important point should be noted is that exterior edge and inner edge of the graphene ring is nearly paralleled, indicating the crystal orientation of the etching process is the same as that of the growth process. To achieve a quantitative understanding of the graphene growth and etching, the size evolution of the graphene ring as a function of the etching time was further counted and the results are shown in Figure 1(f). The diameter of the graphene ring in the exterior edge is about 263.3 μm, 238.4 μm, 226.0 μm and 181.4 μm after etching for 30 min, 60 min, 90 min and 120 min respectively, indicating the shrinking of the graphene ring sharply accelerates at first and then with a nearly linear behavior. While the diameter of the hexagonal hole in the centre regions is about 17.6 μm, 51.3 μm, 57.3 μm and 73.1 μm after etching for 30 min, 60 min, 90 min and 120 min

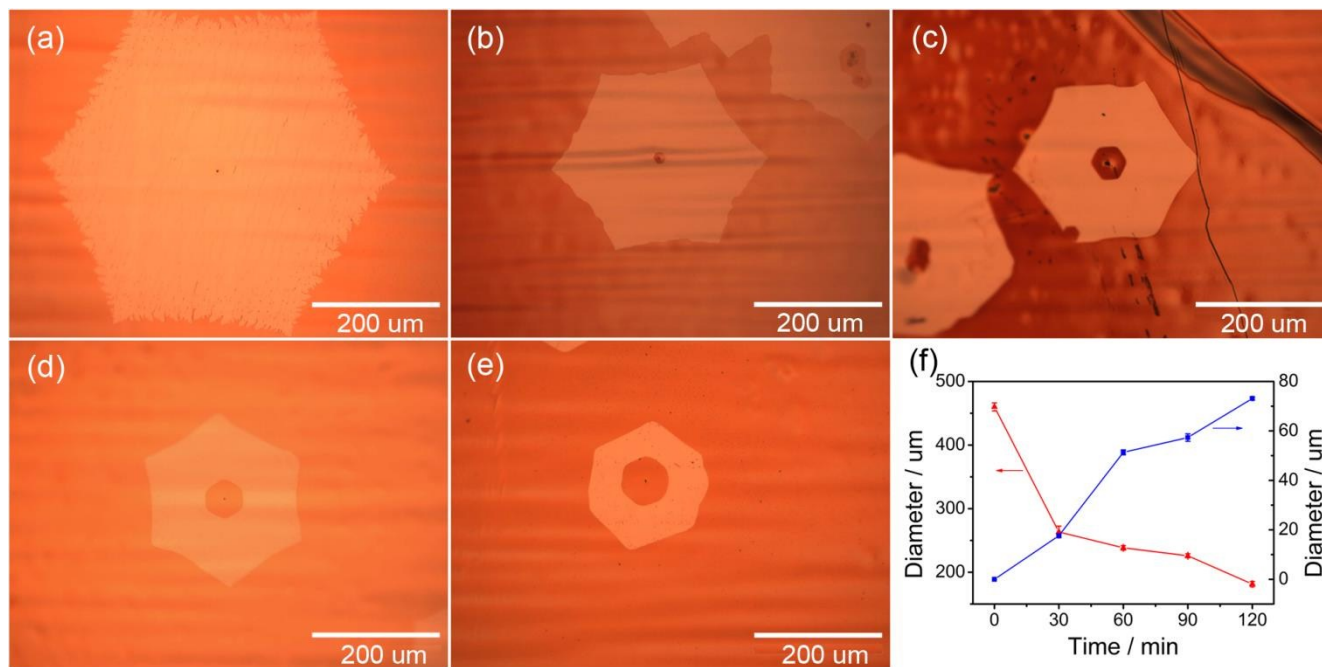


Figure 1. The optical microscopy images of the graphene nanostructure on Cu foil after oxidation. (a) The as-synthesized graphene domain. (b), (c), (d) and (e) The hexagonal graphene ring obtained after etching for 30 min, 60 min, 90 min and 120 min. (f) the statistical data of the diameter of the hexagonal graphene ring in the exterior and inner edge with the time.

respectively, indicating that similar to the etching process in exterior edge, the broadening of the graphene ring also accelerates with a nearly linear behavior. Therefore, it can be concluded that the hexagonal graphene ring can be effectively obtained through growth-etching method introduced here for the first time by the CVD process.

Synthesis of the double hexagonal graphene ring

For the validity of the growth-etching method introduced here to be proved further, the double hexagonal graphene ring was synthesized by repeating the growth-etching process in the CVD. In details, firstly, the graphene ring, obtaining by growth with 0.5 sccm CH₄ and 100 sccm H₂ for 30 min and then etching with 0.5 sccm CH₄ and 3 sccm H₂ for 120 min as shown in Figure 1(e), was used as the precursor. Then, the sample was re-grown with 0.5 sccm CH₄ and 100 sccm H₂ for 15 min. Figure 2(a) illustrates the optical microscopy image of the as-synthesized graphene nanostructure on Cu foil after oxidation. A small graphene domain repeated nucleation on the oxide nanoparticle was clearly distinguished and the diameter is approximately to 45.5 μm. Meanwhile, the precursor graphene ring will be re-grown in this process, namely the exterior edge of the graphene ring broadens from 181.4 μm to 381.3 μm, while the inner edge shrinks from 73.1 μm to 66.5 μm. And later, the sample was re-etched with 0.5 sccm CH₄ and 3 sccm H₂ for 10 min, and the typical results are shown in Figure 2(b). The small graphene domain in the second growth was etched subsequently and a small hole was appeared in the centre regions. The diameter of the second growth graphene ring in the exterior edge is approximately to 22.9 μm, and the size of the hexagonal hole in the centre regions is approximately to 5.9 μm. Simultaneously, the precursor graphene ring will be re-etched in this process, namely the size of the exterior edge of the graphene ring will shrinks and that of the inner edge will broadens. As shown above, the double hexagonal graphene ring has been successfully constructed by repeating the growth-etching method introduced here, and it is natural extended to design and grow unique nanostructure with three, four, even tens of the graphene rings. Therefore, the results illustrated here not only confirm the validity of the concept introduced here but also may have valuable guidance for designing and producing

novel nanostructure even the other 2D materials.

For the quality of the as-synthesized double hexagonal graphene ring to be characterized further, the sample was transferred to the SiO₂/Si substrate²² and characterized by the Scanning Electron Microscopy (SEM). The shape of the double hexagonal graphene ring is viewed clearly with well contrast as shown in Figure 3(a). The hexagonal graphene ring is very smooth, and the diameter of the outside graphene ring in the exterior and inner edge is about 179.7 μm and 42.1 μm respectively, while that of the inside graphene ring is about 27.9 μm and 11.3 μm respectively.

In addition, the Raman spectroscopy was utilized to characterize the double hexagonal graphene ring transferred on the SiO₂/Si substrate due to it is an excellent approach to evaluate the quality, thickness, and uniformity of the graphene.^{25, 26} The typical Raman spectroscopy of the graphene ring with probed position demonstrated in Figure 3(a) is shown in Figure 3(b). The G-peak and 2D-peak are observed clearly and located at ~1585.8 cm⁻¹ and ~2679.4 cm⁻¹ respectively. Meanwhile, the I_{2D}/I_G is about 2.93 and the 2D band exhibits a single Lorentzian curve with a full width at half maximum (FWHM) of ~32.0 cm⁻¹, confirming that it is a single layer graphene. On the other hand, the intensity of the disorder-induced D-peak (~1345 cm⁻¹) is very weak, indicating the quality of the graphene is very high. From the results shown above, it is confirmed that the double hexagonal graphene ring is the monolayer structure.

The electrical property of the graphene ring was further performed on a back-gated field effect transistor (FET) built on a highly doped p-type silicon substrate with 300 nm oxide. The typical FET was fabricated on the individual graphene ring using conventional electron beam lithography. A typical current-voltage (I-V) curve measured for a device is illustrated in Figure 4(a), showing a linear relationship with the resistance of ~13100Ω. The representative transfer curve in Figure 4(b) shows a Dirac point at a positive gate voltage (~27V), indicating that the graphene is p-type doping which may come from the residues or contaminants in the device fabrication process. In addition, the mobility of the as-constructed FET device is approximately to 2600 cm²V⁻¹s⁻¹, which is comparative with those of single-crystal hexagonal graphene

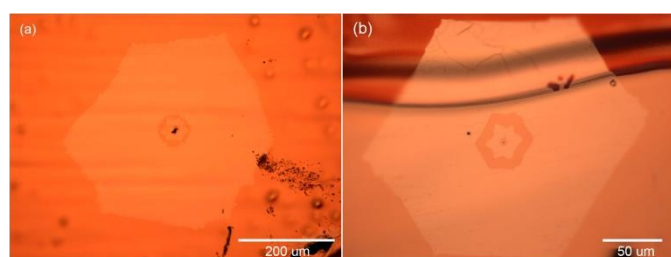


Figure 2. The photograph of the as-synthesized graphene nanostructure on Cu foil after oxidation. (a) The graphene nanostructure obtained with regrowth based on the hexagonal graphene ring. (b) The double hexagonal graphene ring obtained with re-etching based on (a).

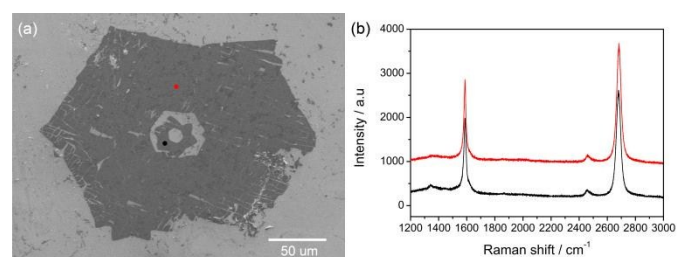


Figure 3. (a) The SEM image of the double hexagonal graphene ring transferred to SiO₂ and (b) Raman spectroscopy of the double hexagonal graphene ring in the inner and outer.

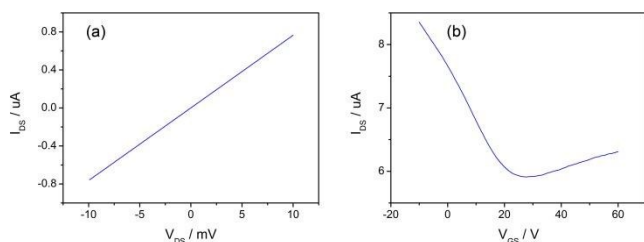


Figure 4. The electrical characterization of the graphene ring nanostructure. (a) Room temperature IDS-VDS characteristics and (b) IDS-VGS curve measured at VDS=0.1V for a representative the graphene ring-based FET device. (The typical length (L) and width (W) of the graphene channel of FET is about 4.80 μm and 0.16 μm respectively)

reported recently.²⁷⁻²⁹ Therefore, the results shown above indicate the double hexagonal graphene ring is of the high quality with the monolayer structure.

For the crystalline structure of the double hexagonal graphene ring to be characterized further, transmission electron microscopy (TEM) has been investigated and the results are shown in Figure 5. Because of the double hexagonal graphene ring is too big, the full view image can't be observed by TEM, so, the SEM (shown in Figure 5(a)) was used to characterize and position it at first. The double hexagonal graphene ring retains their original shape after being transferred onto the TEM Cu mesh. Figure 5(a) shows that two graphene ring arrange orderly, with the edge marked by a dashed line as a visual guideline. To identify the crystallinity of the graphene domains, the selected area electron diffraction (SAED) patterns^{30, 31} were taken from different sites of the outside and inside graphene ring. As shown in Figure 5(b), (c), (d) and (e), only one set of

hexagonal diffraction spots without rotation was observed, revealing the outside graphene ring is a single crystalline film. On the other hand, the inside graphene ring is also a single crystalline as indicating from the one set of hexagonal diffraction spots without rotation shown in Figure 5(f) and (g). However, a rotation (about 6.8 $^\circ$) in the hexagonal diffraction spots was observed in the outside and inside graphene ring, indicating that they have different crystal orientation. Therefore, SAED patterns recorded from arbitrary areas of the graphene domains demonstrate the single-crystalline nature of the outside and inside graphene ring with different crystal orientation.

Growth mechanism

Based on the findings in our experiments and the facts in previous reports,^{22, 28, 32} a possible schematic diagram to grow double hexagonal graphene ring was drawn as shown in Figure 6. In this process, the Cu foil annealed in the high temperature plays significant roles, which not only reduces the impurity and eliminates the sharp wrinkles, steps, and defects effectively, but also more important it produces some oxide nanoparticles^{23, 33, 34} from the mild oxidation residual (shown in Figure 6(b)). The chemical composition of the nanoparticle was further confirmed by energy-dispersive X-ray spectroscopy (EDX) as shown in our previous reported,²³ and it may be the oxide of copper. The oxide nanoparticle derived from annealing plays dual roles, which firstly acts as nucleation site to grow hexagonal graphene domain as shown in Figure 6(c), and the results are consistent with our previous reports.²³ The most important concept introduced here is that the oxide nanoparticle also can be adopted as the defect to graphene which works as

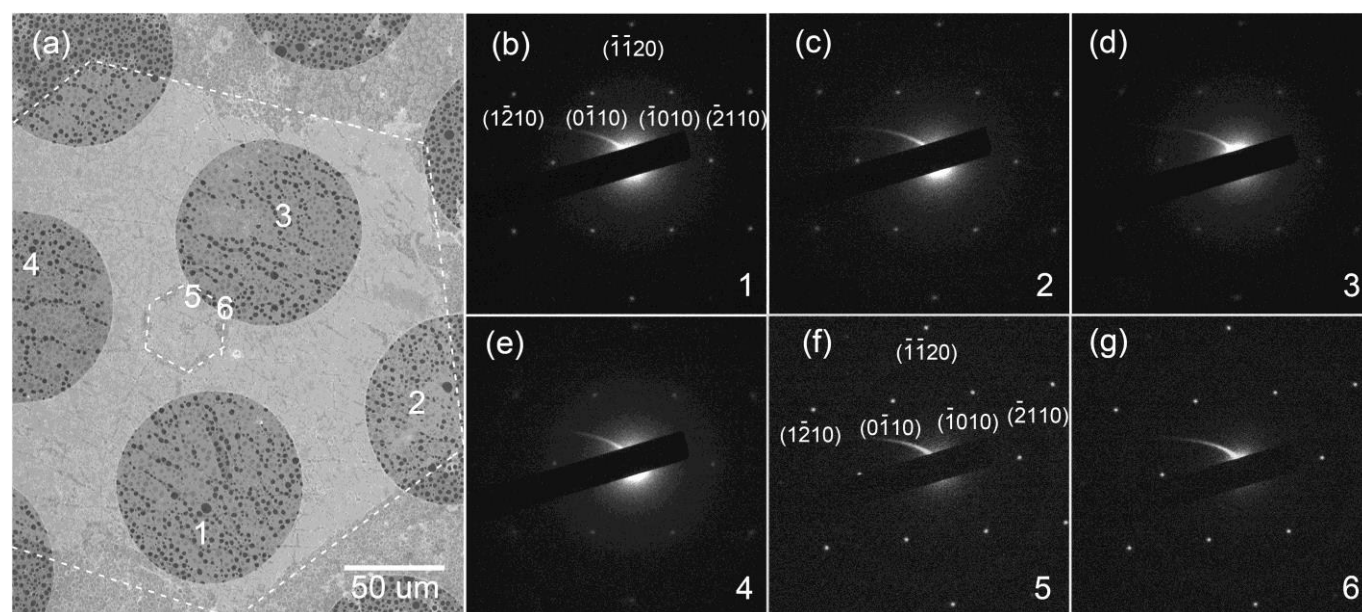


Figure 5. (a) The SEM image of the double hexagonal graphene ring transferred on the TEM Cu mesh. (b), (c), (d) and (e) SAED data from the graphene ring in the outer indicated 1, 2, 3 and 4. (f) and (g) SAED data from the corner of the graphene ring in the inner regions indicated 5 and 6.

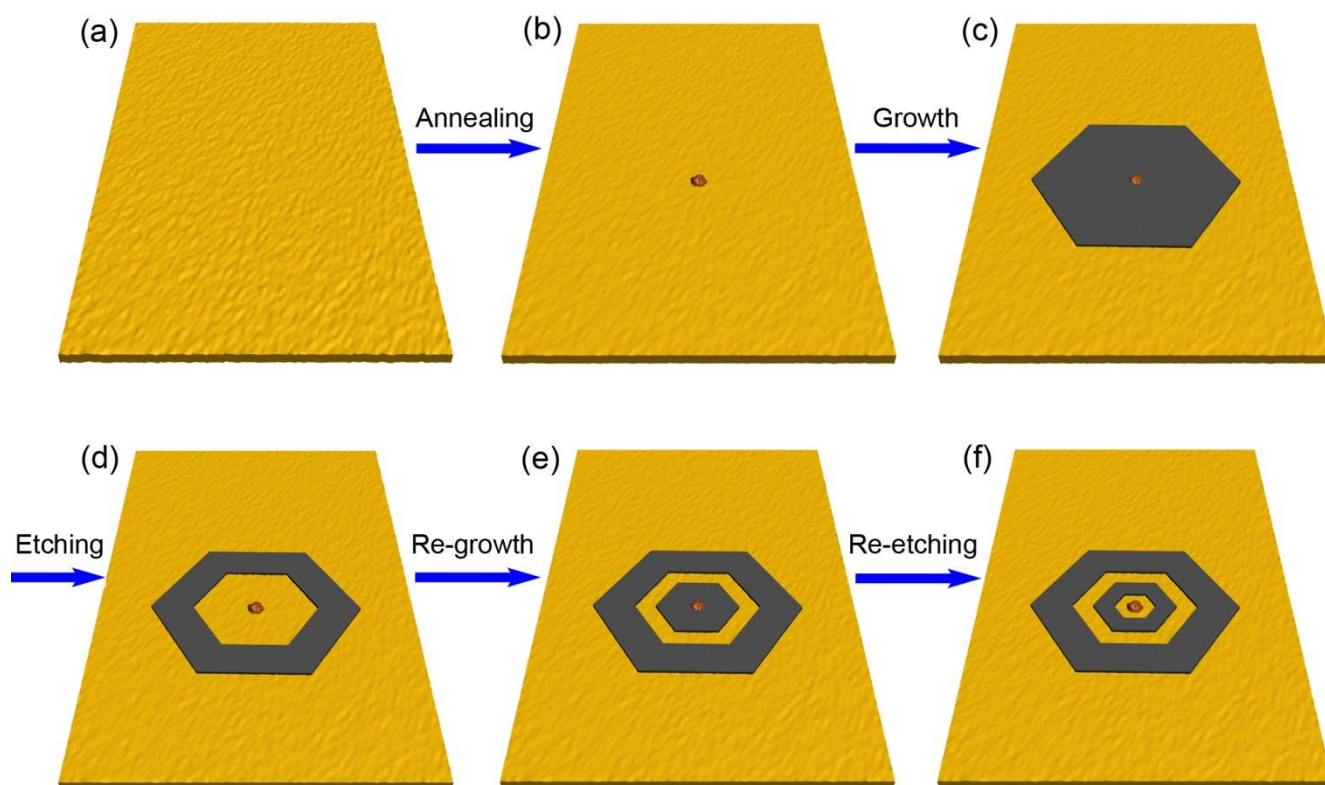


Figure 6. The schematic model for the growth of the double hexagonal graphene ring. (a) The smooth Cu foil was obtained by cleaning with dilute hydrochloric acid and acetone under ultrasonic. (b) Formation of large oxide nanoparticles resulting from the mild oxidation by trace amounts of oxygen in Ar gas on the CVD chamber. (c) The large single crystal monolayer graphene domain synthesizing from nucleated on the oxide nanoparticle. (d) The hexagonal graphene ring obtained with the oxide nanoparticle as the etching site. (e) The graphene nanostructure with a hexagonal graphene ring in the outer and a graphene domain in the center region obtained with re-growth process. (f) The double hexagonal graphene ring obtained after re-etching based on (e).

the initial etching sites. The article reported by Esmail R. Monazam²⁴ shown that the copper oxide nanoparticle will be reduced by CH₄ when the concentration of CH₄ is high (the concentration of H₂ is very low) in the high temperature, and etching process will be driven by the defects/impurities on the substrate surface.^{20, 35, 36} Subsequently, a hexagonal hole around the oxide nanoparticle was obtained after etching process as shown in Figure 6(d), which is further confirmed by a series results shown in Figure 1. If we repeat the growth-etching method under optimized conditions, the double hexagonal graphene ring will be gained as shown in Figure 6(f), which is reported for the first time and further proved the validity and repeatability of the method introduced here. Theoretically, the unique graphene nanostructure with three, four, even tens of the graphene rings can be obtained with the growth-etching method developed here. Therefore, the mechanism shown here may provide valuable guidance for designing and constructing the other unique graphene nanostructure on Cu by CVD.

Conclusions

The double hexagonal graphene ring has been successfully synthesized on Cu based on the growth-etching method

introduced here for the first time by CVD process. The most important concept introduced is that the oxide nanoparticle derived from annealing plays dual roles, which firstly acts as nucleation site to grow the hexagonal graphene domains and then works as defect for etching explored firstly to form holes. In addition, the evolution process of the graphene ring with the etching time was disclosed systemically. By repeating the growth-etching method, the double hexagonal graphene ring has been perfectly synthesized, which is not only confirmed the validity and repeatability of the method developed here but also may illustrated the potential to produce the unique grapheme nanostructure with three, four, even tens of the graphene rings. Furthermore, a possible schematic model was suggested to understand growth process of the double hexagonal graphene ring. The results may hopefully be guidance to design and synthesize other 2D materials and promote their applications.

Experiment section

Synthesis of the double graphene ring

The synthesis of the double hexagonal graphene ring was carried out in a split tube furnace using the CVD method and

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the typical process is shown as follows. The Cu foil (25- μm thick, 99.8%, polycrystalline, Alfa Aesar, #13382) used as substrate was cut into small rectangular shape with size of 2.5 cm. Then, the Cu foil was etched in dilute hydrochloric acid and cleaned by acetone under ultrasonic conditions, and subsequently dried by flowing N_2 gas. Next, the Cu foil was placed in a quartz tube in the furnace and heated to 1070 $^\circ\text{C}$ with flowing 300 sccm Ar, and the temperature was held for 3 h with flowing 300 sccm Ar and 50 sccm H_2 . Graphene domain growth was carried out by starting the CH_4 flow at 0.5 sccm and 100 sccm H_2 in the same tube furnace following completion of the annealing/reduction step of the Cu foil. Subsequently, it switches to etching process by decreasing the H_2 to 3 sccm while keeping the CH_4 flow for constant. The double hexagonal graphene ring was obtained by repeating growth-etching process. Finally, the sample was quickly cooled to room temperature by opening the furnace under 300 sccm Ar and 4 sccm H_2 . The method to transfer graphene grown on copper foils is similar to the previous report.³⁷

Characterization

Raman spectroscopy was recorded at room temperature using HORIBA Jobin Yvon Evolution with laser excitation at 532 nm with power less than 5 mW. Optical microscopy was characterized with the Olympus BX51M in reflection mode at room temperature. Scanning electron microscopy (SEM) was characterized by Hitachi SU-8010. Transmission electron microscopy (TEM) attached with selected area electron diffraction (SAED) was characterized by JEOL JEM-2010 TEM. The graphene ring-based FET device was fabricated by standard electron-beam lithography (EBL) on a Raith e-line system with polymethylmethacrylate (PMMA) as the e-beam resist. The 10 nm thick Ti and 100 nm thick Au were sequentially deposited via electron beam evaporation to fabricate electrodes, followed by lift-off technology. The electrical measurements FET device was carried out using a Keithley 4200 in a LakeShore CRX-4K probe station.

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