Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Effects of carbon-based impurities on graphene growth

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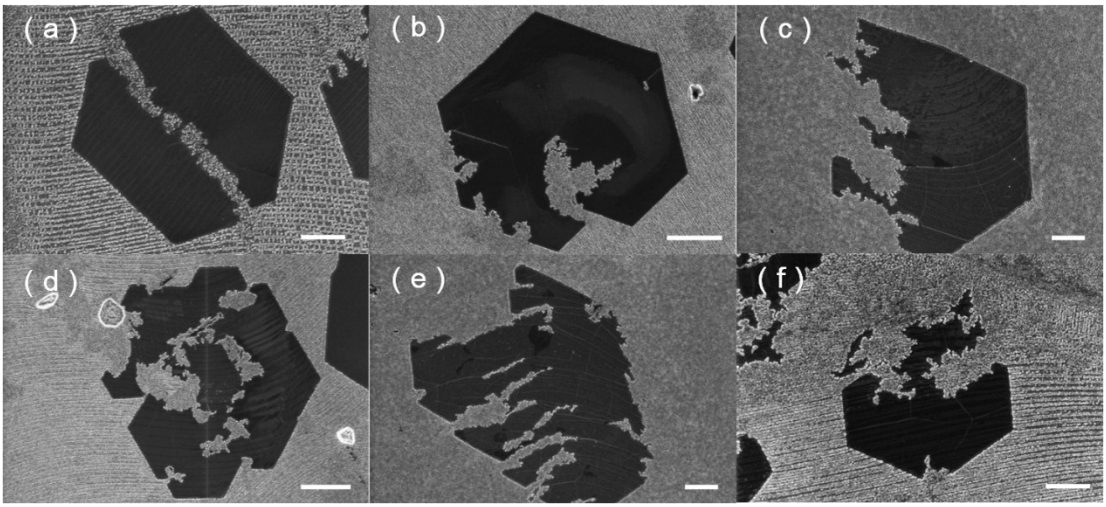
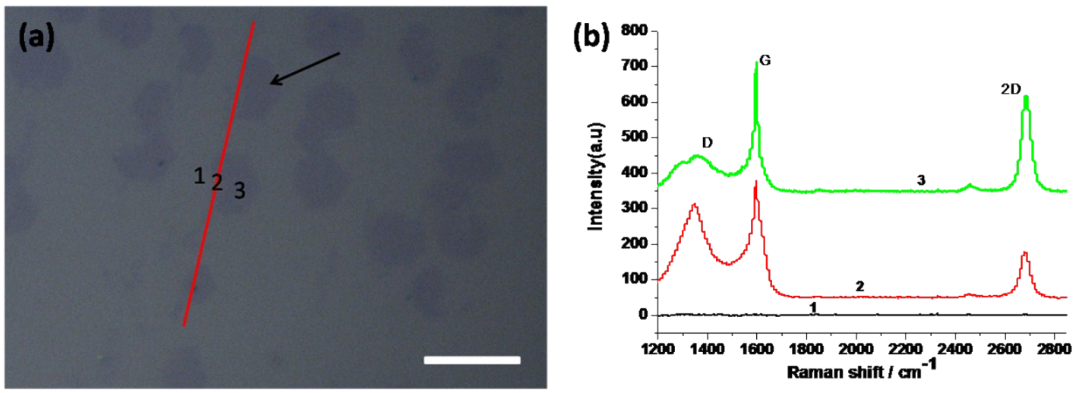


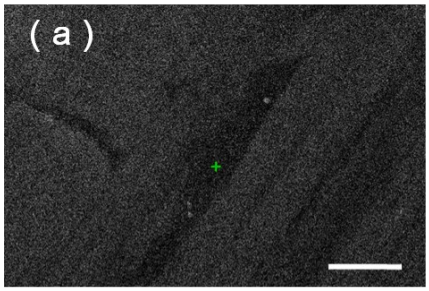
FigureS1. SEM images of graphene domains with various shapes on untreated Cu surface. The bars in the Figures a–f are1, 2, 1, 2, 1, and1μm, respectively.

FigureS1 shows the SEM images of graphene domains with damage on untreated Cu foils. In Figure S1 (a), a graphene domain is divided into nearly equal halves by damage. In Figure S1 (b) and S1 (c), the damages occur mainly on the side of the graphene crystal domain; thus,we can see that the two crystal domains are semi-intact, whereas the other half is severely damaged. In Figure S1 (d–f), the damages are more irregular,and differently shaped damages can be found at the edge and the interior of the graphene domains.



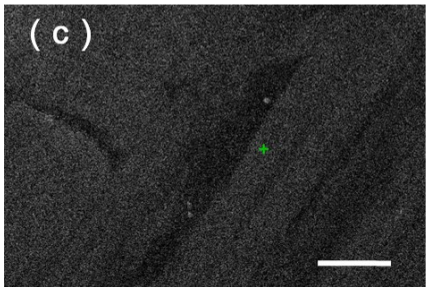
FigureS2. (a)The optical image of graphene domains grown on untreated Cu substrate transferred to SiO_2 /Si, the bar is 10μm. (b) The Raman spectra of the areas 1, 2, 3 in (a).

Figure S2a shows the optical image of graphene domains grown on untreated Cu substrate transferred to SiO_2 /Si, and many damaged graphene domains (noted with arrow) can be found. The red line indicates where the liner impurity exists. Area 1 is the missing part of the damaged graphene domain, area 2 is the part of the damaged graphene domain near the impurity, and area 3 is the part of the damaged graphene far away the impurity. Figure S2 (b) shows the Raman spectra of the three areas in Figure S2 (a). There is no peak of graphene in line 1, which indicates there no graphene exists. In line 2 and 3, D, G and 2D peaks can be found obviously. The ratio of D peak to G peak intensity (Id/Ig) in line 2 is bigger than that in line 3, and the full wave at half maximum(FWHM) of 2D peak in line 2 ($50cm^{-1}$) is bigger than that in line 3($45cm^{-1}$), both of which demonstrate that the graphene quality in area 3 is better than that in area 2. In addition, It is interesting that the height of 2D peak in line 2 and 3 is lower than that of G peak, however, the AFM images (not shown here) and optical images indicate that the graphene domain in Figure S2 (a) is monolayer, the reason is probably that the low quality of graphene leads to the broadening of the 2D peak, which reduces the height of 2D peak.



(b)

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	19.97	19.61	56.34	9.28
Copper	K-series	81.89	80.39	43.66	8.03

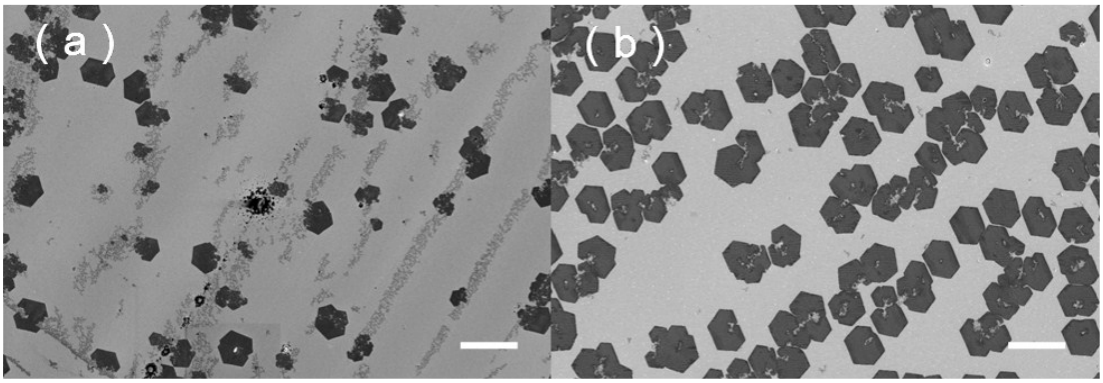


(d)

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	1.39	1.44	7.16	1.14
Copper	K-series	95.53	98.56	92.84	9.34

FigureS3. The EDS results of the impurity on the untreated Cu surface after annealing. The bar in the figure is 20μm.

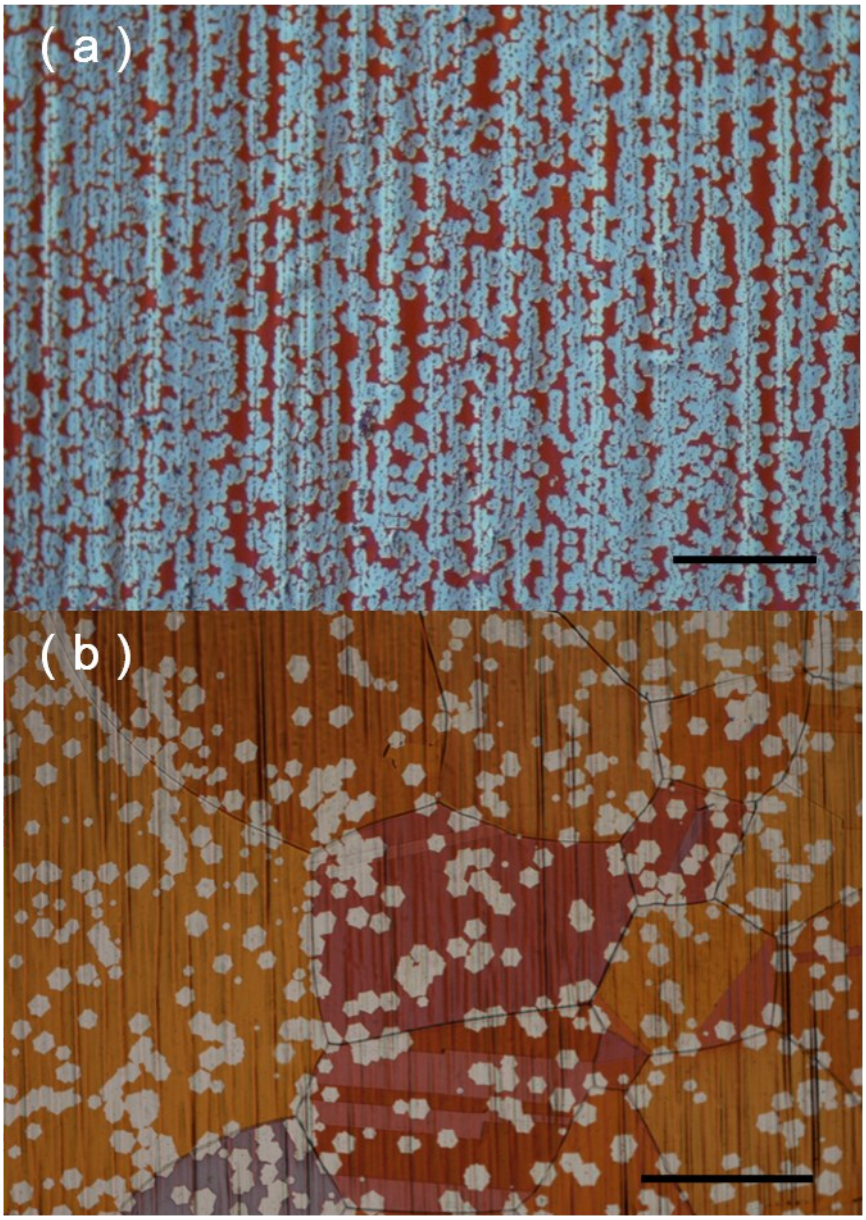
The linear impurity on the untreated Cu surface was measured using EDS, and the results are shown in FigureS3. From Figure S3(a) and S3(b), we can see that the dark impurity region contains56.34% carbon (mass ratio), whereas the carbon content of the next light-colored Cu surface is 7.16 (Figure S3 (c) and S3(d)). Therefore, the impurity on the surface of copper after annealing is a type of carbonaceous impurity.



FigureS4. SEM images of graphene domains on the Cu substrates with annealing at 1050 °C for 10 (a) and 60 (b) min. The bar in the figure is 10μm.

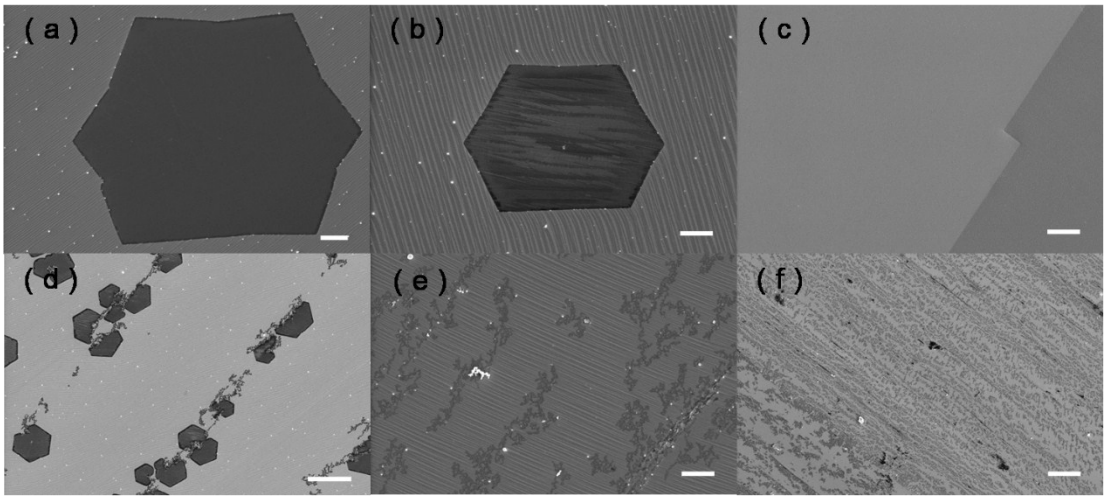
FigureS4 shows the SEM images of graphene domains on the substrates with different annealing degree. As can be seen from FigureS4(a), significant carbon

impurity residues are present on the substrate annealed for 10min, the graphene is seriously damaged, and most of the graphene domains are irregularly shaped owing to large-area damage. Compared with FigureS4(a), Fig. S4(b) shows significantly lower carbon impurity content on the copper surface after annealing for 60min, the extent of the damage of graphene domains was significantly reduced, andmost of the graphene domains are mostly intact.



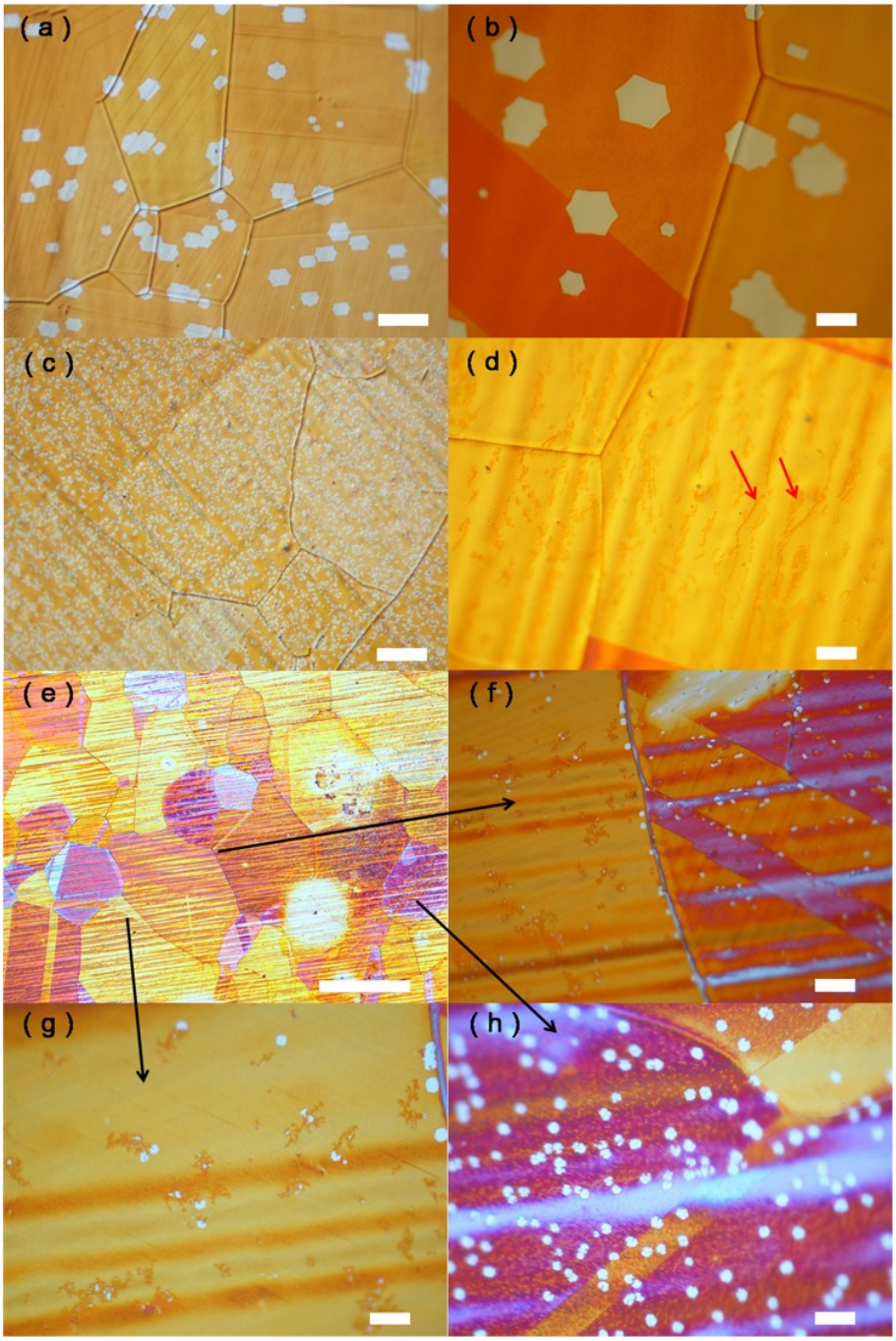
FigureS5. Optical images of graphene domains on (a) untreated Cu foil and (b) oxidized Cu foil in air. The bars in (a) and (b) are100 and 500μm, respectively.

Figure S5 shows the optical images of the graphene domains on different Cu substrates under the same growth conditions, the flow of Ar, H_2 and CH_4 in growth process is 1000, 20 and 1.5sccm, separately, the growth time is 30min. After growth, the Cu substrates were cooled down rapidly (200°C/min). In Figure S5 (a), the Cu substrate is untreated Cu foil. In Figure S5 (b), the Cu substrate is the Cu foil oxidized in air at 300°Cfor 30min. In Figure S5, the white area indicatesthe graphene domains, and the dark area is the exposed Cu surface. As seen from Figure S5 (a), graphene nucleates along the mechanical indentation;owing to high nucleation density, the graphene domains become connected to form a white strip along the indentation. Through careful observation, we can see a dark line in the center of the white strip; these dark lines correspond to the breakage of graphene. In Figure S5 (b), we can see that the mechanical indentation on the Cu surface remains clear after oxidation; however, the density of graphene domains is markedly decreased, the graphene domains do not nucleate along the indentation, and no damage was found in the graphene domains. Therefore, the damage of graphene on the untreated Cu substrate is caused by impurities and not by the indentation.



FigureS6. Amplified SEM images of Fig.6 in the text. The bars in a–f are2, 1, 10, 4, 1, and 10μm, respectively.

As can be seen from Figure S6 (a) and S6 (d), at the hydrogen flow of 20sccm, the graphene domains on the polished Cu substrate were without damage and possessed lower density, whereas the graphene domains on the untreated substrate showed obvious damage and higher density. When the hydrogen flow was increased to 40sccm (Figure S6 (b) and S6 (e)), intact graphene domains can still be found on the polished Cu substrate, whereasonly a small amount of impurities and no graphene domains can be found on the untreated Cu substrate. When the hydrogen flow was increased to 60sccm (Figure S6 (c) and S6 (f)), no graphene domains can be found on both the polished and untreated Cu substrate, and the dark areas on the untreated Cu substrate are impurities.



FigureS7. Optical images of graphene domains on the polished and untreated Cu substrates under the same growth conditions. Optical images of polished Cu surface after graphene growth at (a) 1035 and (b) 1020 °C; optical images of untreated Cu surface after graphene growth at (c) 1035 °Cand 1020 °C (d);optical image of the untreated Cu surface after graphene growth at 1020 °C (f), (g), and (h) are the amplified images (noted with arrows)in(e). The bars in a and c, b and d, e and f – h are 60, 20, 500, and 10 μ m, respectively.

The decomposition of methane is related to temperature; therefore, altering the growth temperature can alter the ratio of effective carbon source and hydrogen, which indirectly changes the etching ability of the growth atmosphere. In Figure 6, the flow

of Ar, H_2 and CH_4 in growth process is 1000, 20 and 1.5sccm, separately, the growth time is 30min.As seen from Figure S7 (a)and S7 (c), the density of graphene domain on untreated Cu substrate is markedly higher than that on the polished Cu substrate at 1035 °C, indicating that the carbon atoms can nucleate around impurities at 1035 °C; under this growth condition, impurity promotes graphene nucleation. However, as seen from Figure S7 (b) and S7 (d), no graphene domains are evident on the untreated Cu substrate at 1020 °C, and the darker areas (noted with arrows) are impurities; these findings indicate that the carbon atoms cannot nucleate around impurity. Consequently, the density of graphene domain on the untreated Cu substrate is markedly lower than that on the polished Cu substrate at 1020 °C; under this growth condition, impurity suppressed graphene nucleation. Figure S7 (e–h) show the optical images of untreated Cu surface after graphene growth at 1025 °C. In Figure S7 (e–f), the graphene density and impurities show a gradual change from left to right. In the left area (Figure S7 (g)), the graphene domain and the impurities show low and high densities, respectively; by comparison, in the right area (Figure S7 (h)), the graphene domain and the impurities show higher and lower densities, respectively. These findings indicate that the impurity suppressed graphene nucleation at 1025 °C.