Supplementary Information

In-Situ Chemical Probing of Hole Defects and Cracks in Graphene at Room Temperature

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Fig. S1 Photo of the reaction setup before sealing and injection of dilute H_2SO_4 solution. The double vials ensure that the graphene sample is only exposed to H_2S gas which is generated in situ, not any liquids or solids. Scale bar: 1 cm.

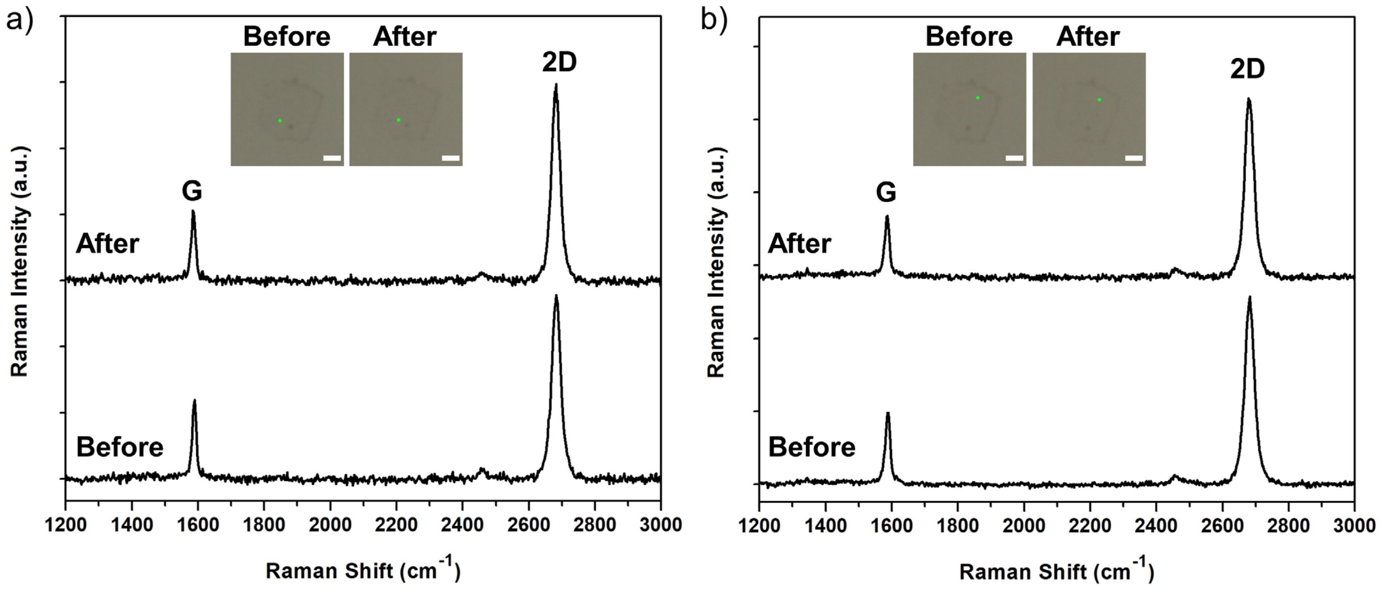

Fig. S2 Representative Raman spectra of the monolayer graphene domain transferred onto Si wafer. (a) Raman spectra on the same region of the first spot in the same graphene domain on Si wafer before (bottom) and after (top) 15 min of H_2S treatment. (b) Raman spectra on the same region of the second spot in the same graphene domain on Si wafer before (bottom) and after (top) 15 min of H_2S treatment. There is little change of Raman features of monolayer graphene after H_2S treatment. Inset: Microscopic optical images of the graphene domain on Si wafer and the green dots showing the first and second spots where the Raman spectra were taken, respectively. Scale bar: 2 μm.

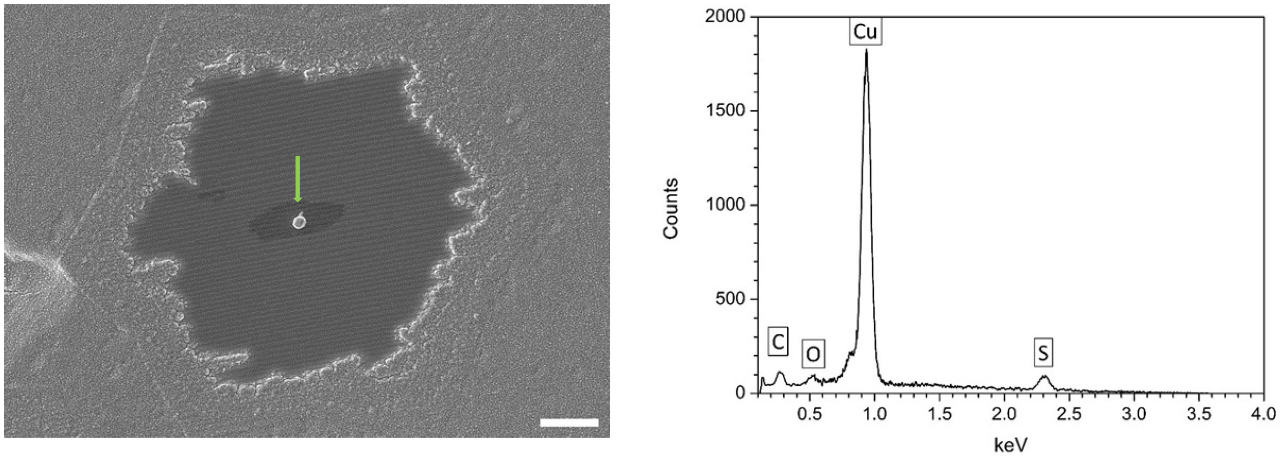

Fig. S3 EDX spectrum (right) of a nanoparticle formed on graphene domain after the H_2S treatment. Electron beam was focused on the center of the nanoparticle (indicated by the green arrow) in the SEM image (left). Scale bar: 3 µm.

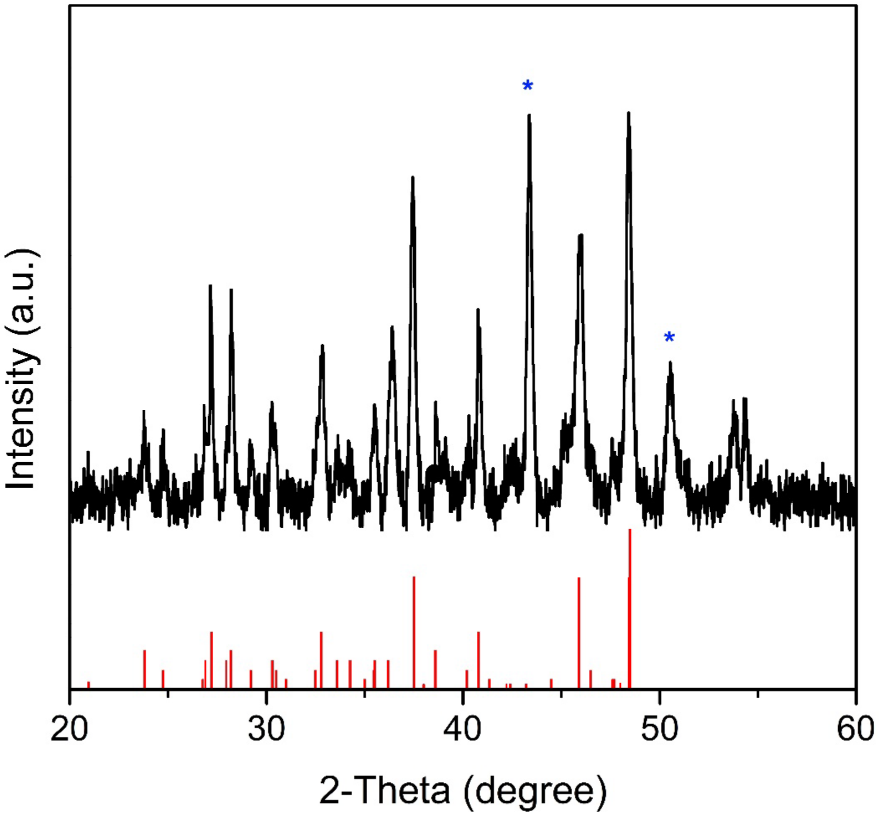

Fig. S4 XRD pattern of Cu_2S nanoparticles scraped off from the copper foil surface. The asterisks indicate diffraction peaks coming from copper particles.

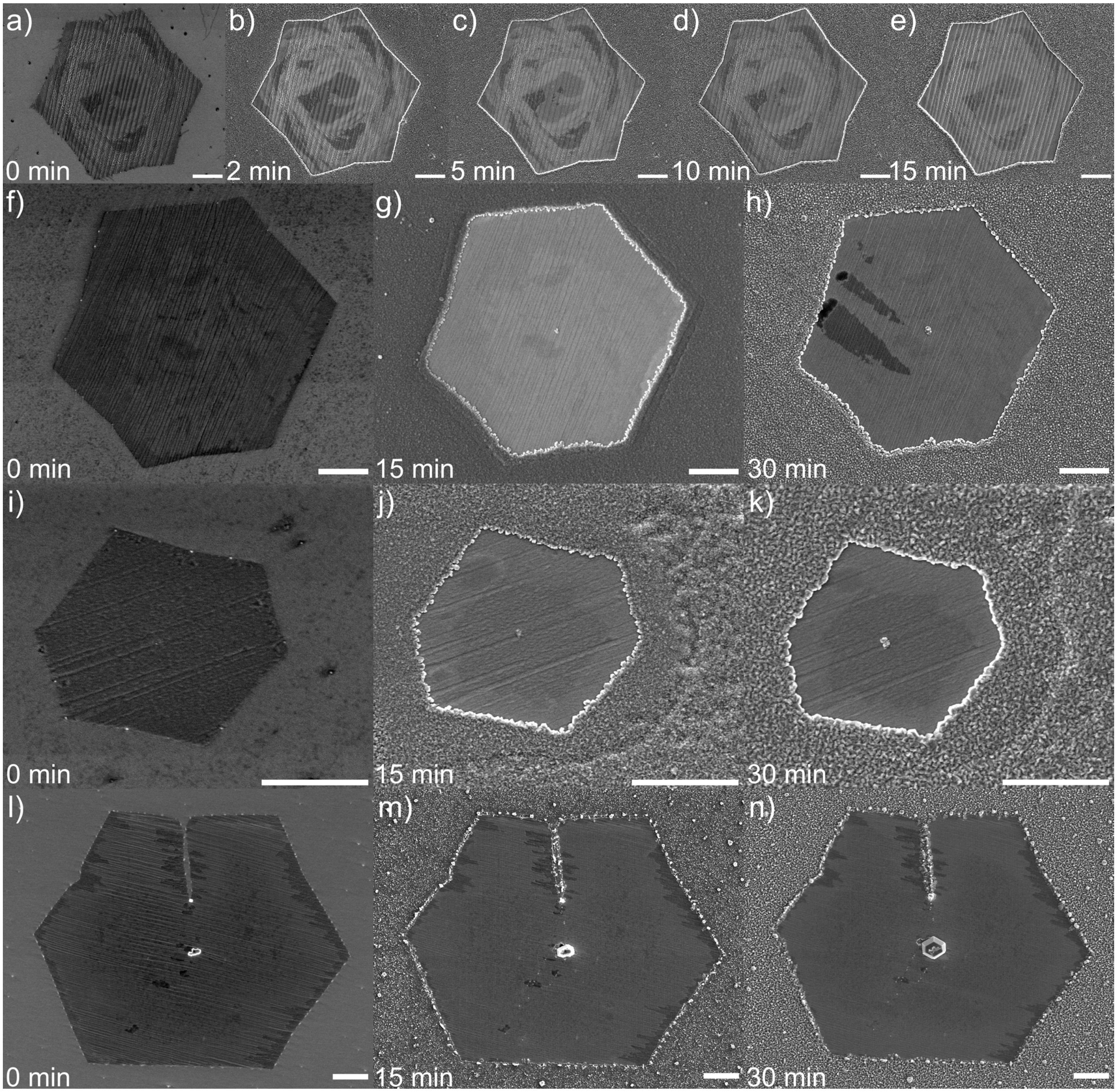

Fig. S5 SEM images of graphene domains before treatment (0 min) and after repeated H_2S treatment. The total amount of H_2S treatment time is denoted in each SEM image. (a-e) No Cu_2S nanoparticle formation after repeated treatments. (f-k) The size of the Cu_2S nanoparticle formed at the nucleation center of domain increases with reaction time. (l-n) The Cu_2S nanoparticle emerges from a pre-existing impurity nanoparticle at the center and grows much larger with additional reaction time. In addition, a large straight crack is easily visible even before the H_2S treatment. Scale bar: 2 μm.

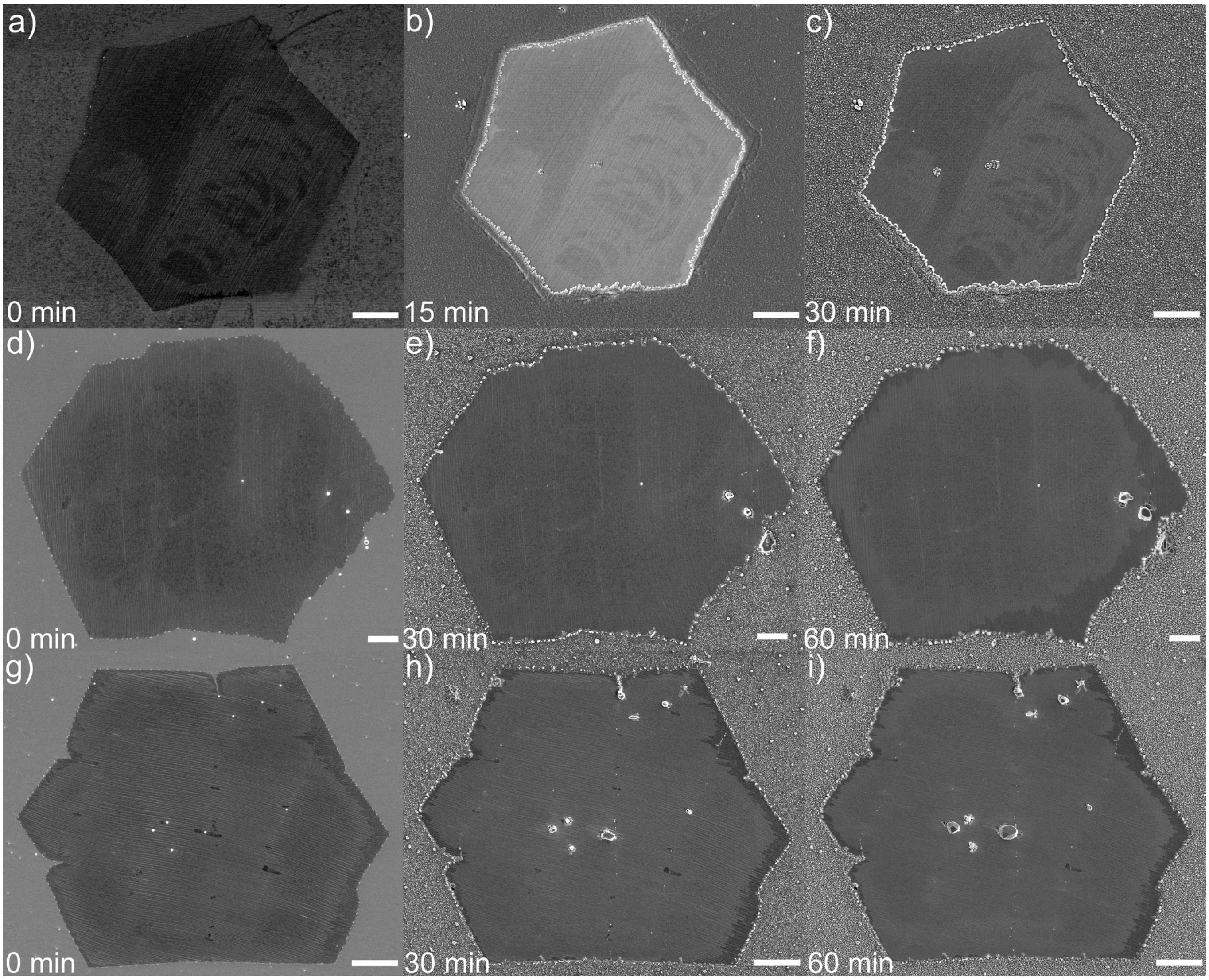

Fig. S6 SEM images of graphene domains before treatment (0 min) and after repeated H_2S treatment. The total amount of H_2S treatment time is denoted in each SEM image. Multiple Cu_2S nanoparticles are formed in each graphene domain. Although the sizes of the Cu_2S nanoparticles generally increase with reaction time, some Cu_2S nanoparticles grow much faster than others within the same graphene domain. The different growth rates may originate from either the difference in vacancy defect sizes, or tight or loose binding of pre-existing SiO_x nanoparticles with surrounding defective graphene. Scale bar: 2 μm.

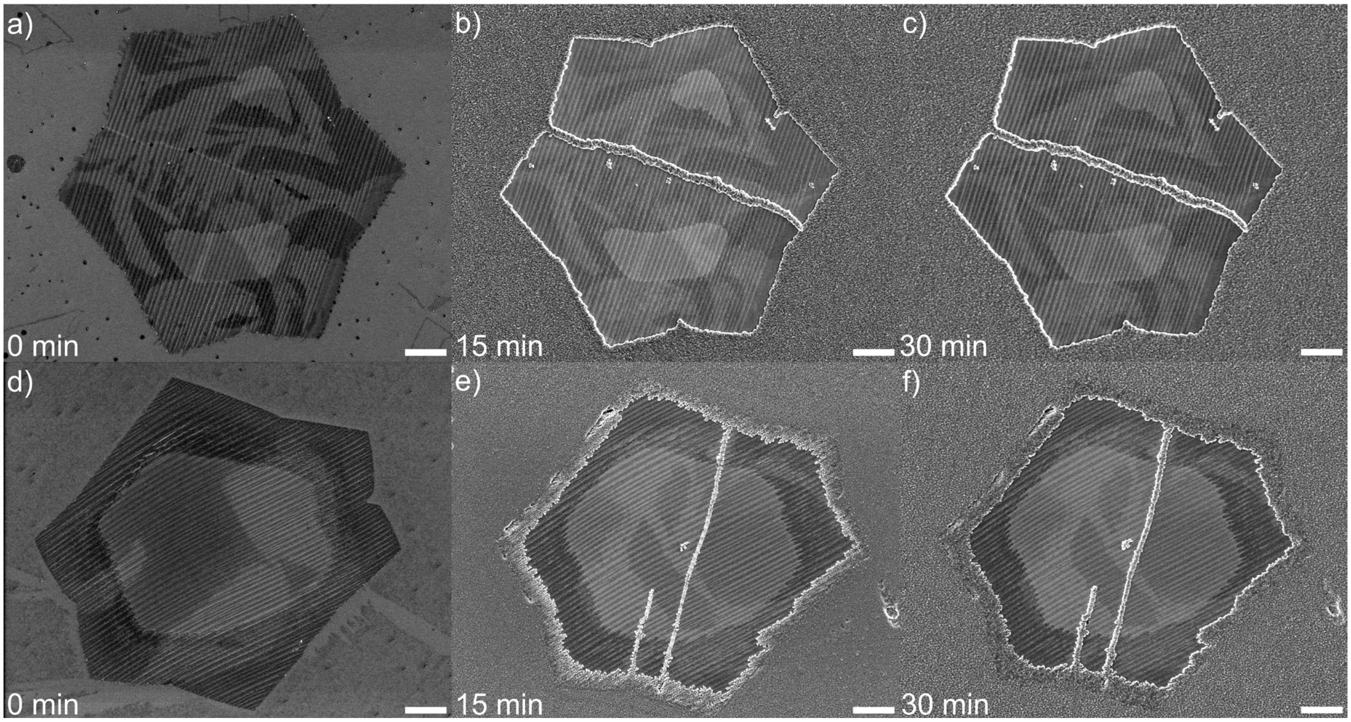

Fig. S7 SEM images of graphene domains before treatment (0 min) and after repeated H_2S treatment. The total amount of H_2S treatment time is denoted in each SEM image. Both kinked and straight cracks can be visualized with formation of Cu_2S nanoparticles in the crack regions. The reaction time-dependent study shows that Cu_2S nanoparticles form rapidly and occupy all of cracked areas within 15 min of H_2S treatment. Further chemical treatment does not change the lengths of 1D Cu_2S nanowires, only increases their widths slightly. Scale bar: 2 μm.

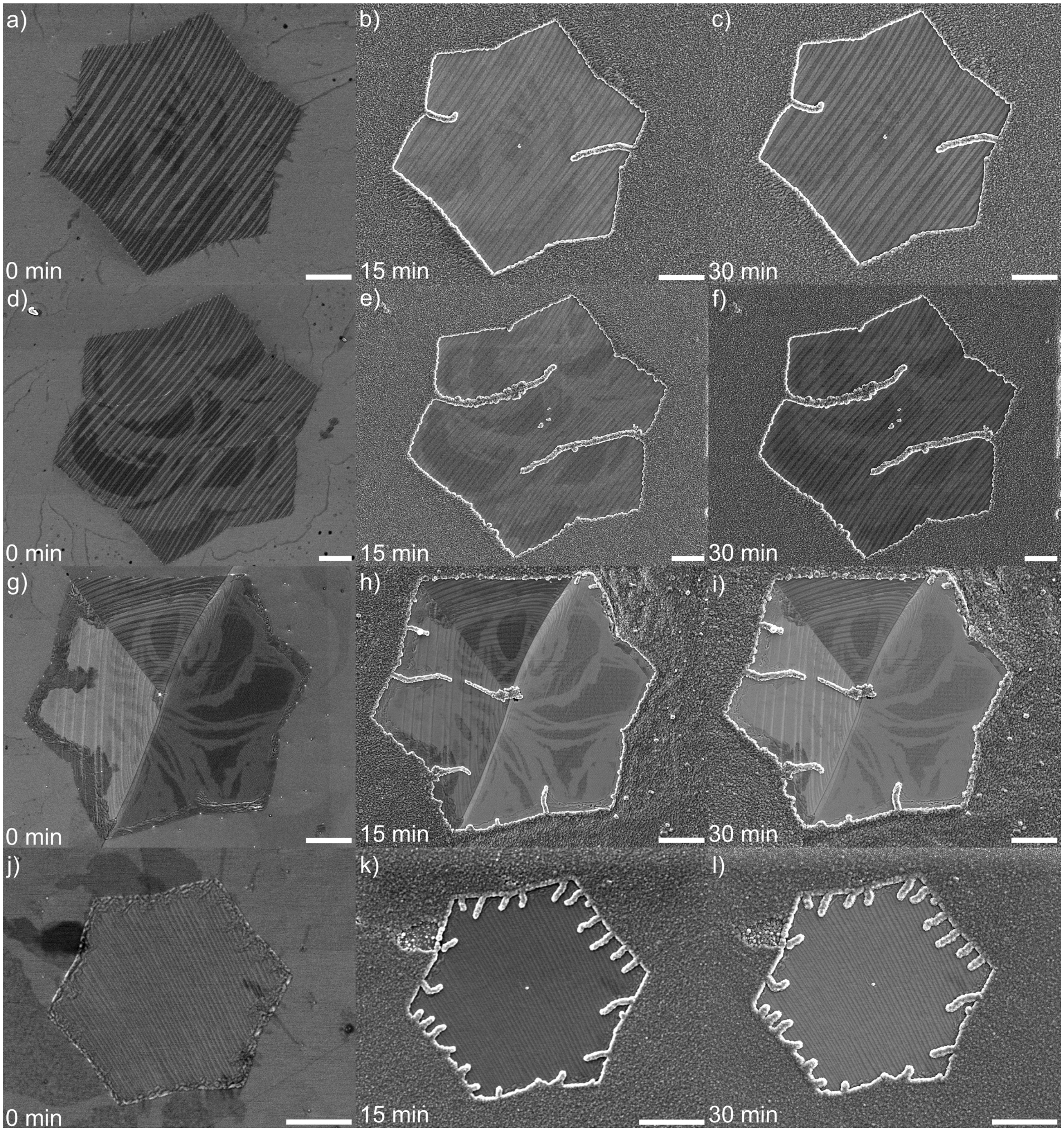

Fig. S8 SEM images of graphene domains before treatment (0 min) and after repeated H_2S treatment. The total amount of H_2S treatment time is denoted in each SEM image. Both kinked and straight cracks can be visualized with formation of Cu_2S nanoparticles in the crack regions. The reaction time-dependent study shows that Cu_2S nanoparticles form rapidly and occupy all of cracked areas within 15 min of H_2S treatment. Further chemical treatment does not change the lengths of 1D Cu_2S nanowires, only increases their widths slightly. Scale bar: 2 μm.

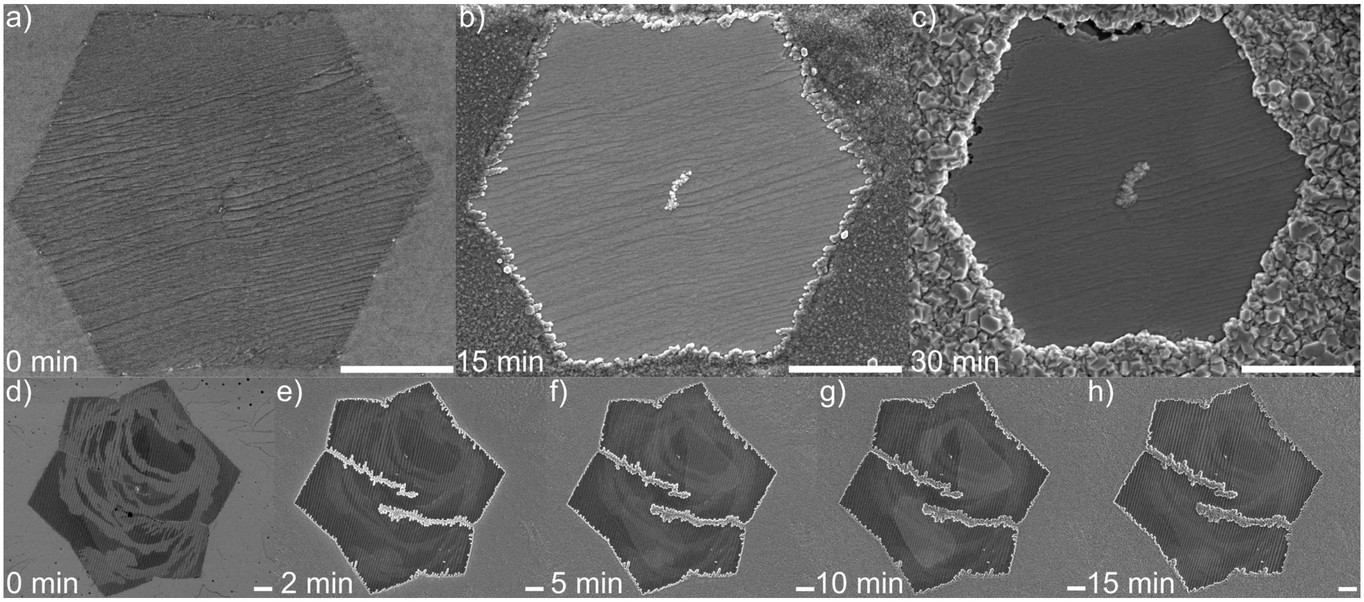

Fig. S9 SEM images of graphene domains before treatment (0 min) and after repeated H_2S treatment. The total amount of H_2S treatment time is denoted in each SEM image. Cracks can be visualized with formation of Cu_2S nanoparticles in the crack regions. (a-c) Two cracks originate from domain center, resembling hour and minute hands in a clock. (d-h) Branched cracks. Scale bar: 2 μm.

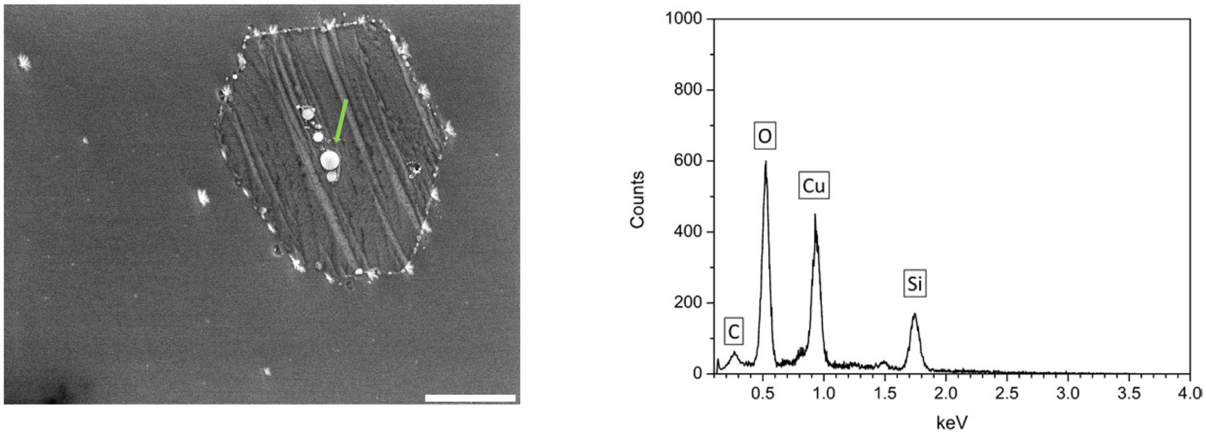

Fig. S10 EDX spectrum (right) of a pre-existing nanoparticle in hexagonal graphene domain before the H_2S treatment. Electron beam was focused on the center of the nanoparticle (indicated by the green arrow) in the SEM image (left). Scale bar: 2 µm.

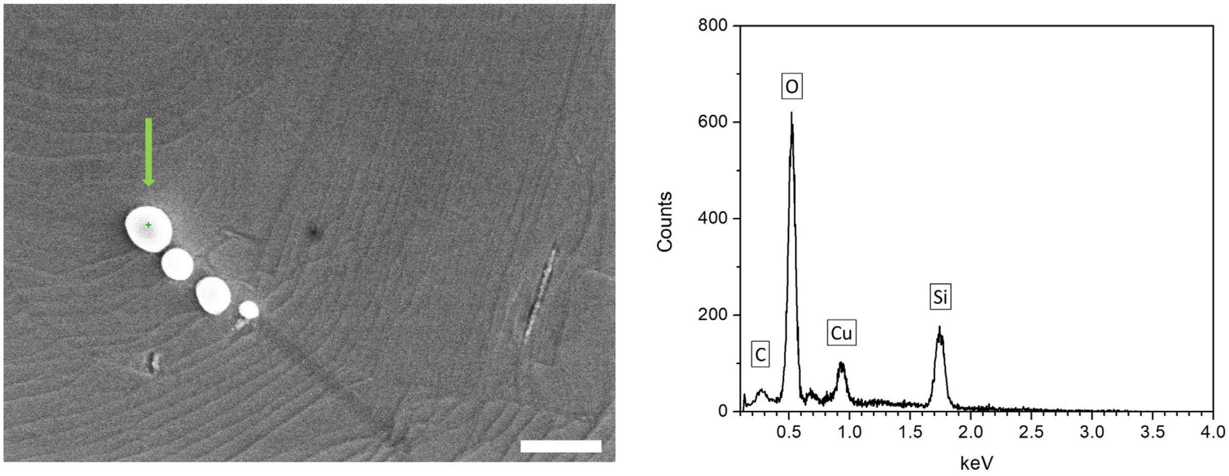

Fig. S11 EDX spectrum (right) of a pre-existing nanoparticle in polycrystalline graphene film before the H_2S treatment. Electron beam was focused on the center of the nanoparticle (indicated by the green arrow) in the SEM image (left). Scale bar: 0.5 µm.

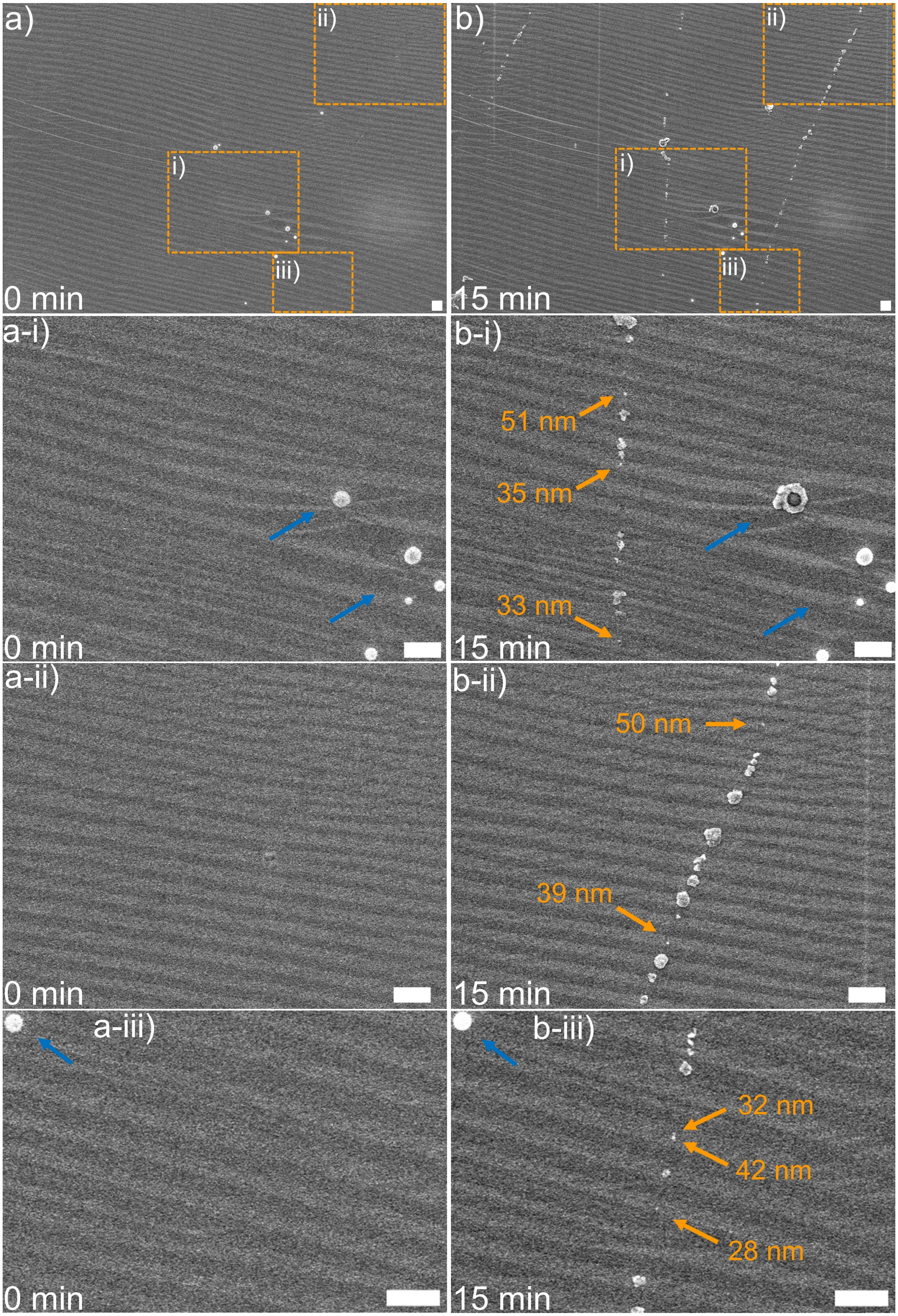
a)
ii)
i)
iii)
0 min
b)
ii)
i)
iii)
15 min
a-i)
0 min
b-i)
51 nm
35 nm
33 nm
15 min
a-ii)
0 min
b-ii)
50 nm
39 nm
15 min
a-iii)
0 min
b-iii)
32 nm
42 nm
28 nm
15 min

Fig. S12 SEM images of polycrystalline graphene films on copper foil before and after H_2S gas treatment. (a,b) SEM images from Fig. 5g and Fig. 5h in the main text with three highlighted zoom-in regions. (a-i,b-i) SEM images from the zoom-in region i. (a-ii,b-ii) SEM images from the zoom-in region ii. (a-iii,b-iii) SEM images from the zoom-in region iii. Pre-existing SiO_x nanoparticle sites are indicated by blue arrows. The Cu_2S nanoparticle size analysis was performed in original SEM images using the ImageJ software. Scale bar: 500 nm.

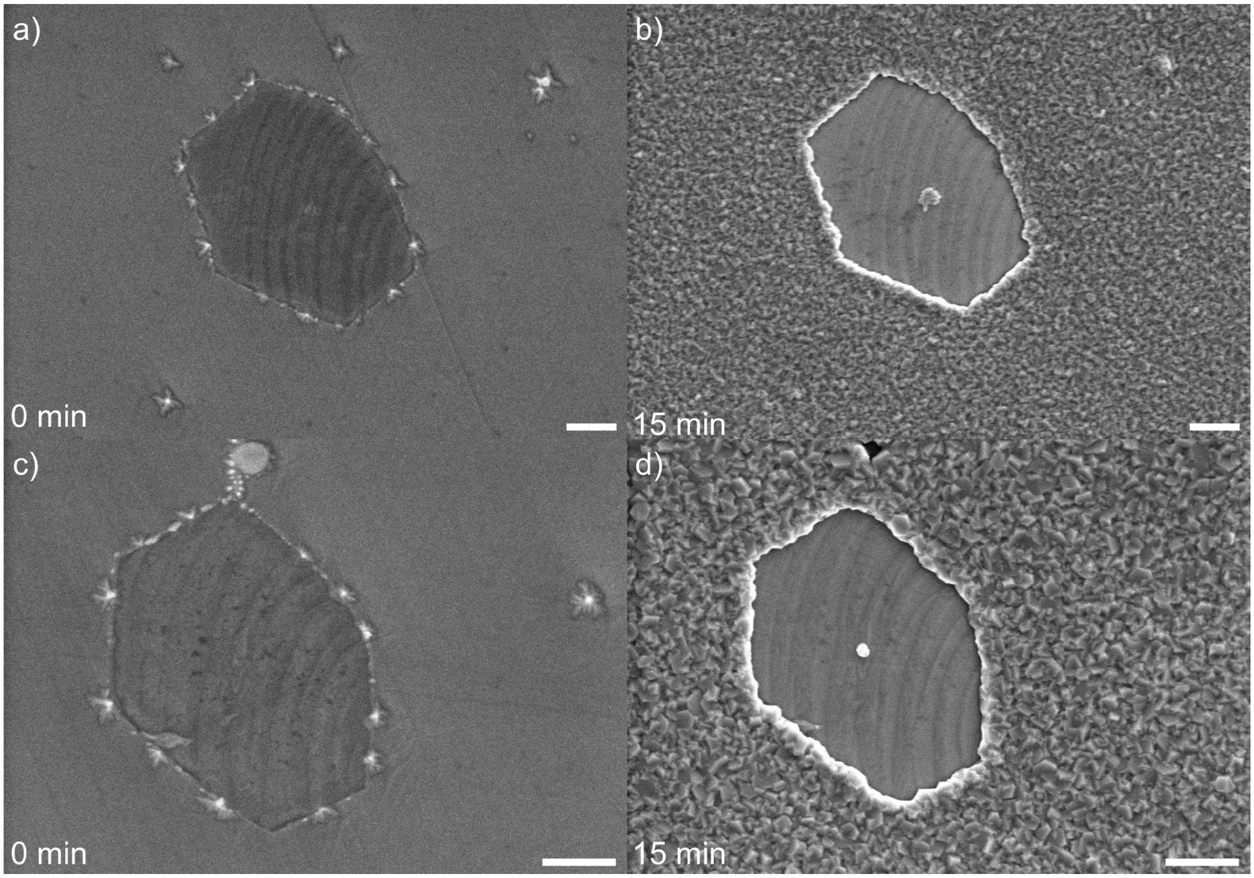

Fig. S13 SEM images of graphene domains before treatment (0 min) and after 15 min of H_2S treatment using the minimum amount of H_2S gas produced in situ, corresponding to 0.02 mg of H_2S/cm^2 of graphene. A Cu_2S nanoparticle appears at the nucleation center of each of two graphene domains, respectively. In addition, the exposed copper substrate outside the graphene domain is fully covered with numerous Cu_2S nanoparticles, suggesting 0.02 mg of H_2S/cm^2 of graphene is sufficient for chemical probing of graphene vacancy defects. Scale bar: 0.5 μm.