

# CHEM**ELECTRO**CHEM

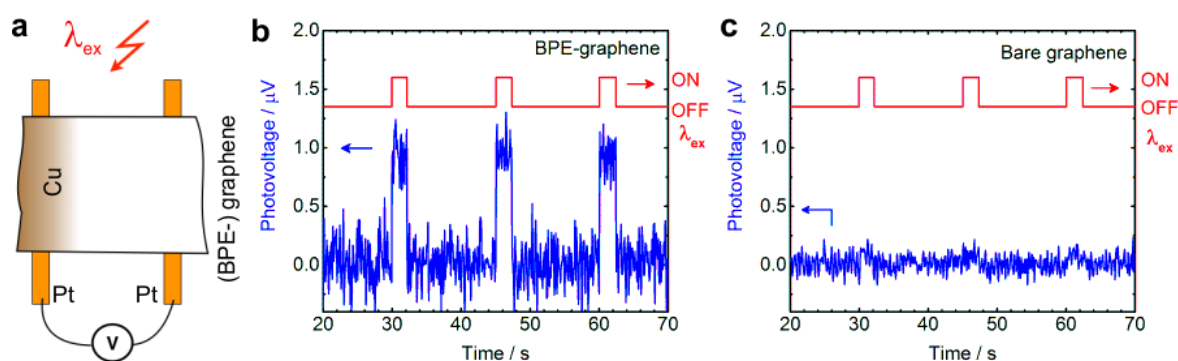
## Supporting Information

### **Selective Functionalization of Graphene Peripheries by using Bipolar Electrochemistry**

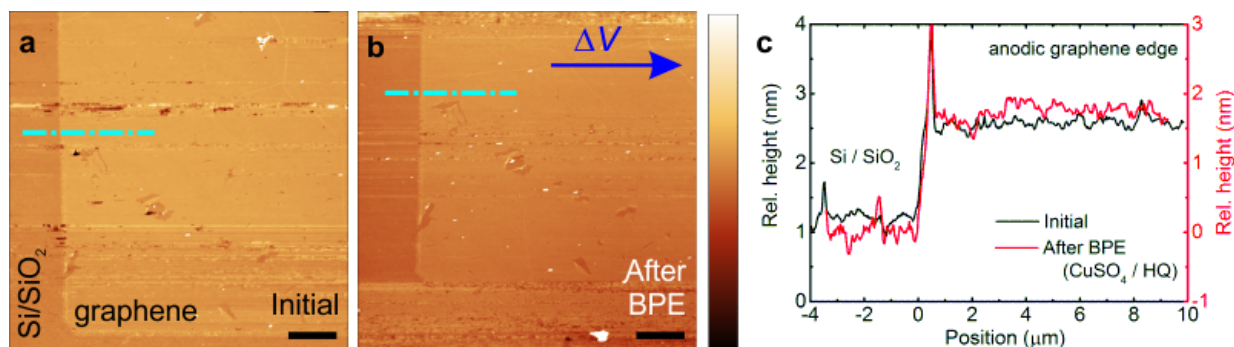
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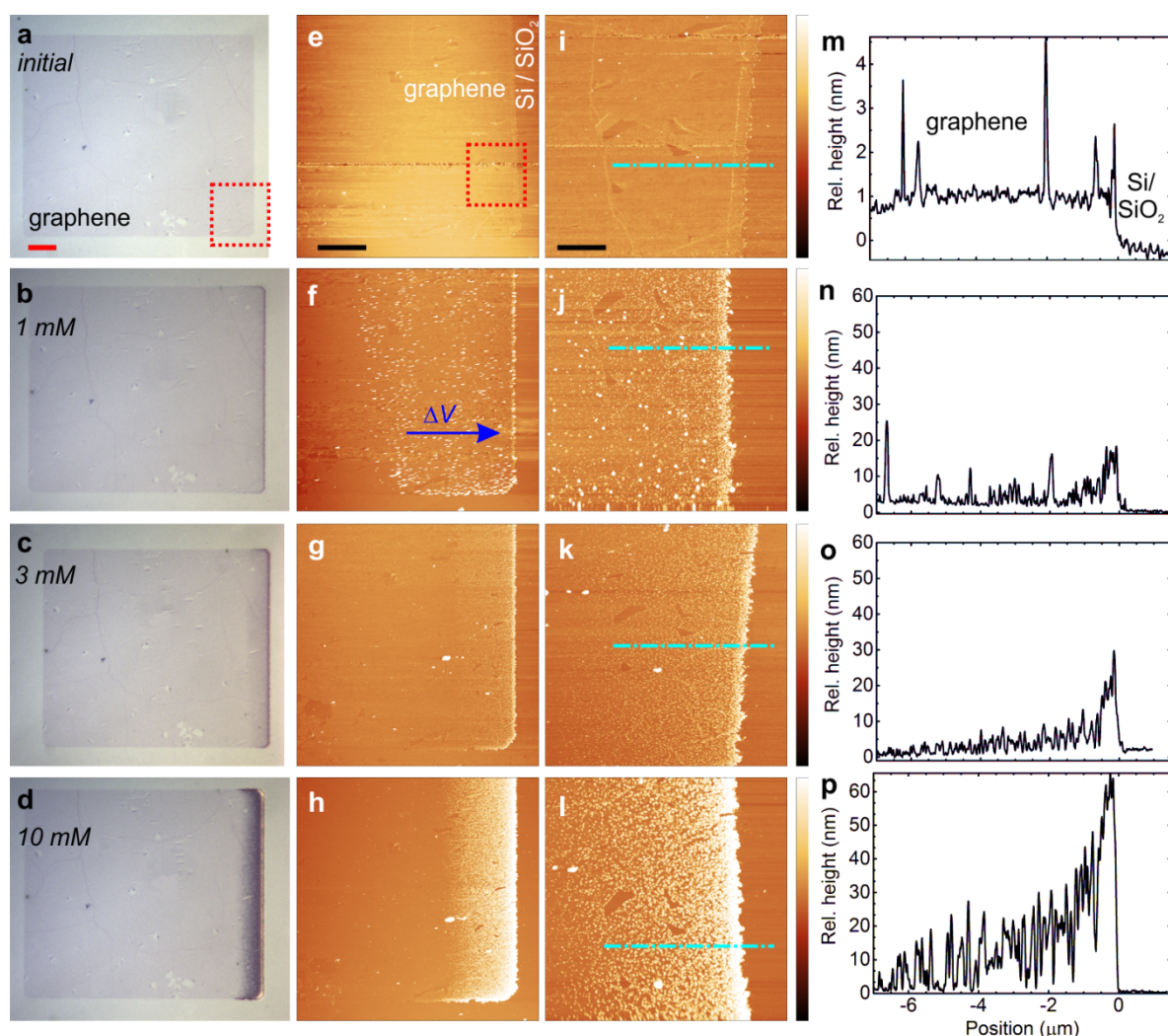
**Figure S1.** Photovoltage generation in graphene modified by bipolar electrochemistry. (a) Scheme showing the measurement configuration wherein bare graphene or graphene modified by bipolar electrochemistry (BPE-graphene) is contacted by pre-patterned Pt electrodes spaced 1 mm apart. The voltage across bare graphene or BPE-graphene is measured with or without global photoillumination from a laser diode ( $\lambda_{\text{ex}} = 638 \text{ nm}$ ). (b) Photoresponse of a graphene sheet asymmetrically modified with copper at one periphery similar to the case of fig. 1. The sheet is around 2 mm long and the conditions used are 10 mM  $\text{CuSO}_4$ , 10mM HQ, 15 V/cm, 10s. A clear photoresponse is visible upon laser illumination attributed to asymmetric contacts formed at the ends of the sheet. The mechanism of the response may be attributed to photovoltaic or photothermal effects whose magnitude is different at the two contacts leading to a net photovoltage. (c) Photoresponse of a bare graphene flake without any modification. Here there is only a negligible photoreponse, which can be understood by considering that the contacts are symmetric.



**Figure S2.** (a,b) AFM images of the anodic edge of the graphene sheet of figure 1 before (a) and after (b) BPE using 3 mM of  $\text{CuSO}_4$  and HQ. The other parameters are shown in figure 1. (c) Line profile along the cyan lines drawn across the graphene edge in (a) and (b). There is almost no change in height signifying that the anodic edge is intact after the BPE procedure.  $x,y$ -scale bars: 5  $\mu\text{m}$  in (a) and (b);  $z$ -scale bar is 30 nm in (a) and (b).



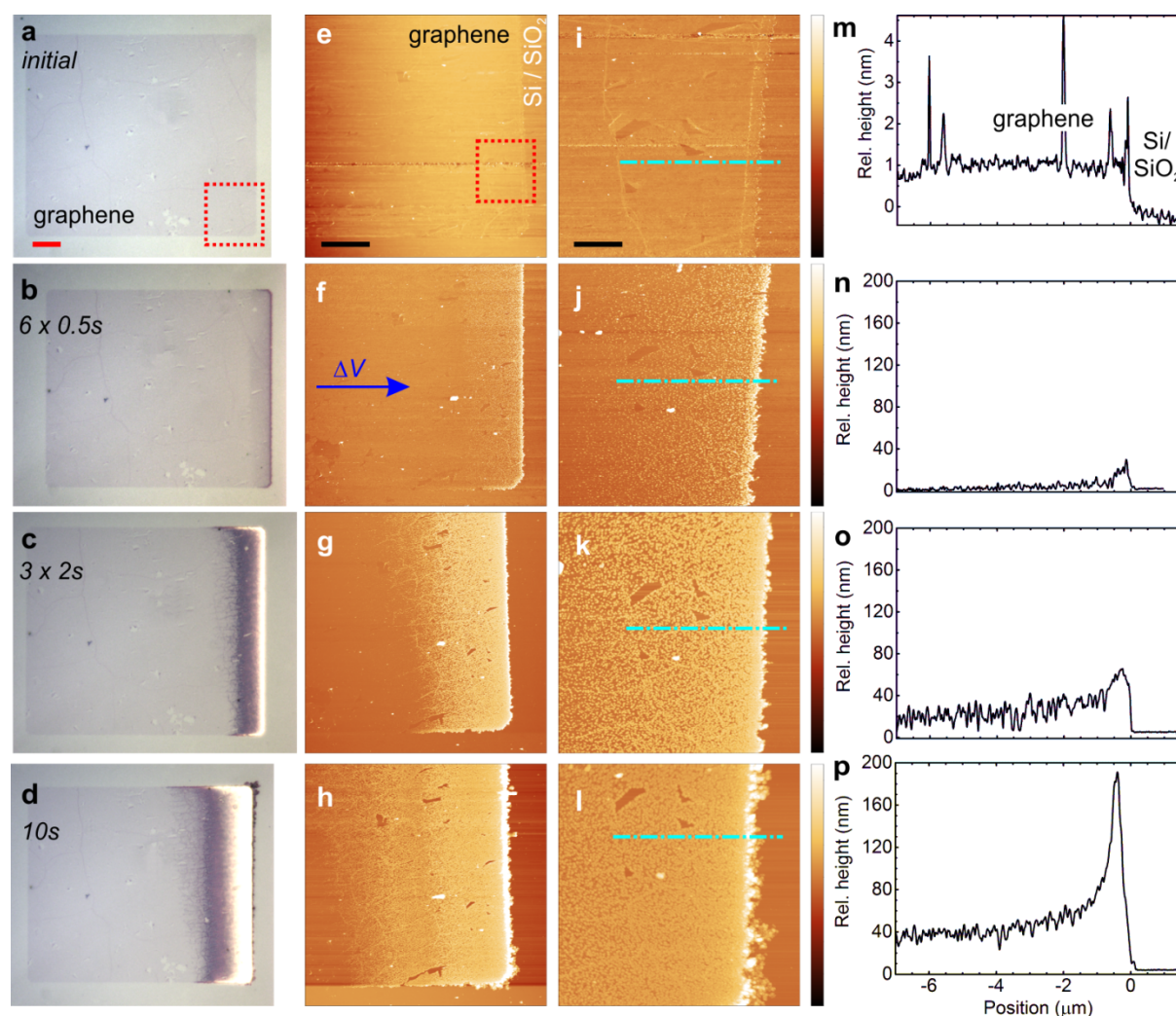
**Figure S3. Effect of varying concentration of precursors.** A data series collected on one graphene sheet showing the effect of varying precursor concentration ( $\text{CuSO}_4$  and HQ, molar ratio 1:1) on the copper deposit obtained using BPE. (a-d) are optical images, where the concentration values are denoted (1 mM implies 1 mM  $\text{CuSO}_4$  with 1 mM HQ); (e-h) are AFM images of the square region marked in (a), (i-l) are zoomed-in AFM images of the region marked in (e), while (m-p) are line profiles along the lines marked in the corresponding AFM images in the same row. The four images in every row constitute a set of data obtained at the initial step (a,e,i,m) or after a BPE experiment with the concentration values shown on the optical images on the left. Before every BPE run, the copper deposit is etched away to recover bare graphene (as in (a)). Other conditions of BPE were kept constant



for the 3 runs at a field of 18 V/mm, and a deposition time of  $6 \times 0.5$  s. As the concentration increases, the density of particles is seen to increase, with little effect on the spatial extent of functionalization. Below 1mM almost no copper deposits are visible, while concentrations above 10 mM lead to a quick fouling of the feeder electrodes due to copper electrodeposition on the Pt wires. Moreover, higher concentrations lead to an increase in solution conductivity

having a detrimental effect on the efficiency of graphene modification.  $x,y$ -scale bars: 10  $\mu\text{m}$  in (a-d) , 5  $\mu\text{m}$  in (e-h) and 2  $\mu\text{m}$  in (i-l);  $z$ -scale bar is 35, 50, 70, and 100 nm in (e) to (h) (and ((i) to (l)) respectively. The direction of electric field is marked with a blue arrow, the right graphene edge is the cathodic edge.

**Figure S4. Effect of varying deposition time.** A data series collected on one graphene sheet showing the effect of varying deposition time on the copper deposit obtained using BPE. (a-d) are optical images, where the deposition times are denoted; (e-h) are AFM images of the



square region marked in (a), (i-l) are zoomed-in AFM images of the region marked in (e), while (m-p) are line profiles along the lines marked in the corresponding AFM images in the same row. The four images in every row constitute a set of data obtained at the initial step (a,e,i,m) or after a BPE experiment with the deposition times shown on the optical images on the left. Before every BPE run, the copper deposit is etched away in order to recover bare graphene (as in (a)). Other conditions of BPE were kept constant for the 3 runs at a field of 18 V/mm, and 3 mM of  $\text{CuSO}_4$  and HQ. As time increases, the predominant changes are the



increase in size of the particles as well as their density. The spatial extent also seems to increase with time, however this might be only due to the fact that the particle density is increasing and therefore the visibility of the layer gets better.  $x,y$ -scale bars: 10  $\mu\text{m}$  in (a-d), 5  $\mu\text{m}$  in (e-h) and 2  $\mu\text{m}$  in (i-l);  $z$ -scale bar is 35, 60, 130, and 180 nm in (e) to (h) (and ((i) to (l)) respectively. The direction of electric field is marked with a blue arrow, the right graphene edge is the cathodic edge.

**Figure S5.** Line profiles along the left (a) and right (b) edges of the bimetallic graphene hybrid shown in figure 5. The profiles were taken at the middle of the region shown in the AFM images of (e) and (f). NP : nanoparticles

