Supporting Information

Pristine Graphene Electrode in Hydrogen Evolution Reaction

Aozhen Xie,[†] Ningning Xuan,[†] Kun Ba,[†] and Zhengzong Sun[,†,‡]*

[†]*Department of Chemistry, Fudan University, Shanghai 200433, P. R. China;*

[‡] *Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China*

*Correspondence to: zhengzong_sun@fudan.edu.cn

Full Methods

Synthesis of single-layer graphene. 10-μm thick-Cu foils were used as growth substrates. A standard -inch tube furnace was used as the CVD chamber. The copper foils were annealed under a hydrogen atmosphere (200 s.c.c.m. hydrogen and ~ 76 torr total pressure) at 1,050 °C for 60 mins prior to the growth. Then methane was introduced into the tube to synthesize SLG at 1,050 °C for 30 min (29 s.c.c.m. CH_4 and 10-100 s.c.c.m. H_2, 0.15-1 torr total pressure).

Synthesis of single-layer h-BN film procedure. Single-layer h-BN film was grown on the Cu substrate (Alfa Aesar, 99.8%, 25 μm) by using PECVD method. The Cu substrate was covered with a Cu foil, placed in a 4-cm diameter quartz boat, and loaded into the PECVD furnace. Subsequently, another quartz boat containing 20 mg ammonia borane (Alfa Aesar, 97%) was placed into the furnace. The Cu substrate was annealed at 1,050 °C for 60 mins under H_2 flow (532 Torr). The distance from the plasma generator to ammonia borane and copper was ~ 24 cm and 75 cm, respectively. The power of the frequency generator was set to 100 W to initiate the growth and the temperature was kept at 1,050 °C (200 s.c.c.m H_2). After 2 h, the quartz boats containing Cu foil was quickly cooled down to room temperature under the H_2 atmosphere.

Transfer process. 300 nm SiO_2/Si wafer was washed with ultrapure water and blow-dried by N_2 before any use. PMMA substrate was prepared by spin-coating 10% PMMA/anisole solution on SiO_2 wafer at 5,000 rpm for 10 s and then dried at 120 °C on hot plate. Rectangular Cu/graphene foil was spin-coated with 4% PMMA/anisole solution and then the foil was pressed on PMMA substrate with wet PMMA solution

as adhesive. The adhesion was done by placing the wafer on 120 °C hot plate for 10 mins.

The graphene on Cu foil was pre-etched in 0.6 M Marble solution to remove unwanted graphene. After that the wafer was immersed in 0.1 M ammonium persulfate solution till complete etching of Cu. Bilayer graphene was transferred similarly. Another layer of graphene was transferred to pristine Cu/graphene foil to fabricate bilayer graphene. For graphene electrodes in electrochemical characterization, another layer of PMMA was deposited on top of Cu foil by dabbing 4 % PMMA/anisole solution after adhesion between Cu and PMMA. Here this additional PMMA layer served as a mask to expose a small portion of Cu foil (Detail in Supplementary Information). This provided convenience for the later electrochemistry since active area of graphene can be measured and Cu lowered electrical resistance as electrode. For higher transfer yield, it is recommended that the edges of the Cu foil should be sealed with 10% PMMA additionally to prevent penetration of etchant and then anisole was evaporated on hot plate.

Graphene and h-BN electrode fabrication. To minimize the electrode areas and resistance caused by large SLG sheet, a modification was made from the transfer. After the adhesion of Cu on PMMA substrate, 10% PMMA/anisole solution was again used to mask most of the Cu, leaving only a small area of unprotected Cu. Then exposed Cu was pre-etched in Marble solution and further immersed in APS solution for complete etching. After washing and drying, epoxy resin was used to mask the exposed Cu edge around the graphene region. After 24 h, part of the PMMA on Cu was scratched away and the Cu can be used as current collector.

HOPG electrode fabrication. An area of 0.5 × 0.5 cm freshly-cleaved HOPG was exposed by masking the other part with silicon or epoxy resin.

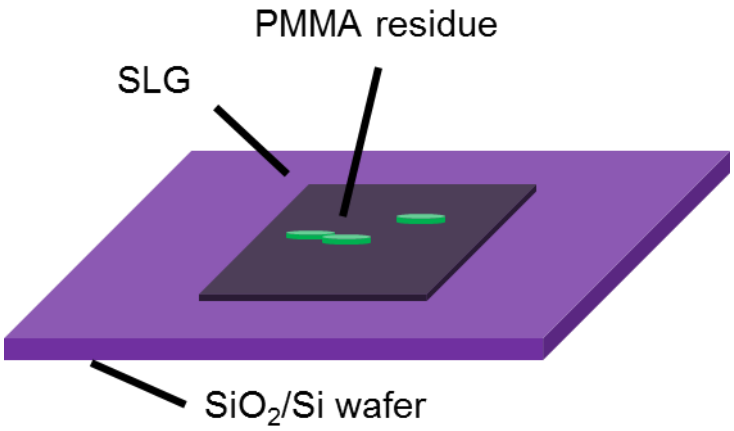

Figure S1. One disadvantage of traditional PMMA transfer. Electrochemical active sites of SLG were occupied with PMMA residues.

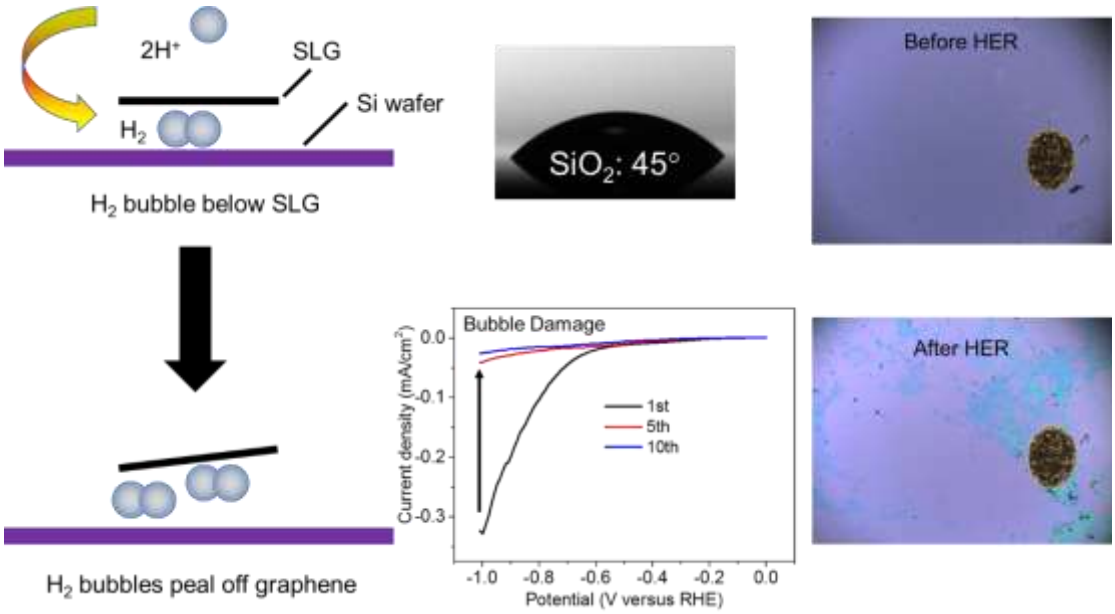

Figure S2. Another disadvantage of traditional PMMA transfer. Protons easily intercalates into the gap between SLG and SiO_2 wafer, due to the hydrophilicity of SiO_2. The bubble generation during HER damages the SLG, jeopardizing the electrode's HER performance soon.

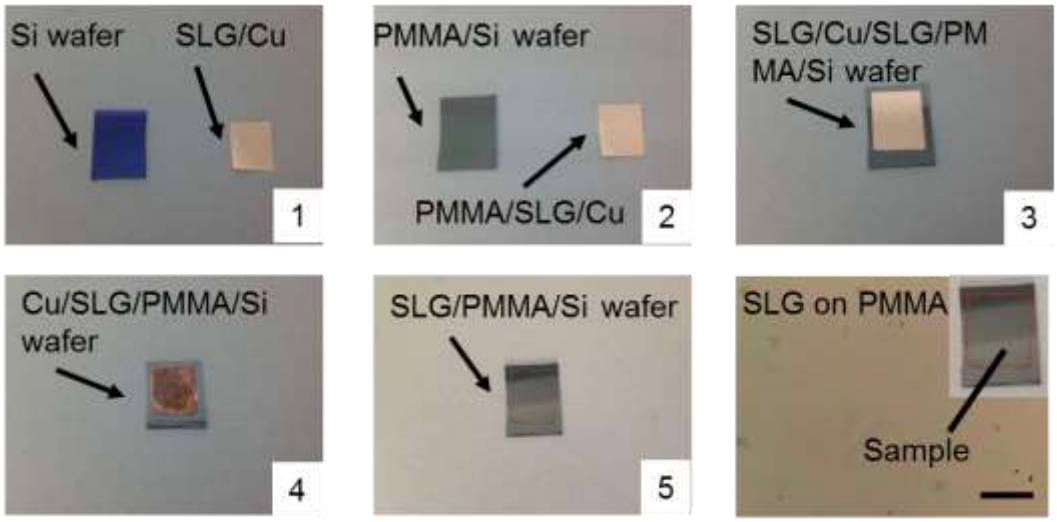

Figure S3. Optical images of the PMMA-assisted, flipped transfer process. As demonstrated in step 1, a 300 nm SiO_2/Si wafer and a graphene film on Cu (1.5 × 1 cm) are the starting materials. In the 2nd step, PMMA is spincoated on wafer as substrate (dried upon heating) and on graphene as the adhesive (without drying). The two parts in step 2 are stacked together with PMMA sides facing with each other to obtain sample in the 3rd step. Then in the 4th step the graphene/Cu on upper side is pre-etched with Marble solution to remove the top covered graphene film. The rest Cu is etched in APS solution overnight before we got the final electrode displayed in step 5 and a zoomed-in optical image in the last image. Graphene cannot be directly seen due to lack of contrast.

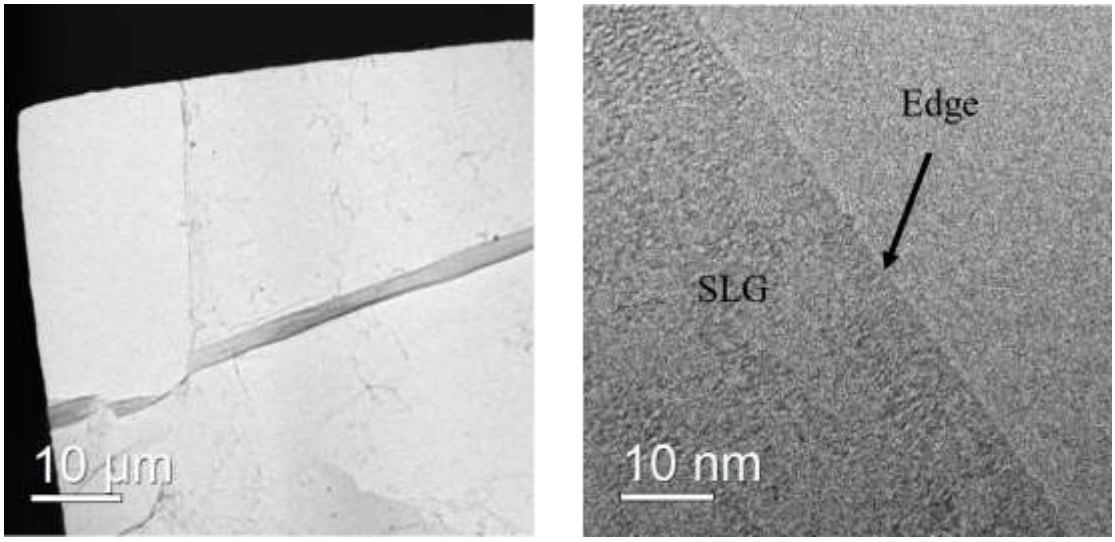

Figure S4. TEM images of typical SLG in this experiment. Folding and PMMA residue

can be seen under TEM because traditional PMMA transfer to TEM grid was used.

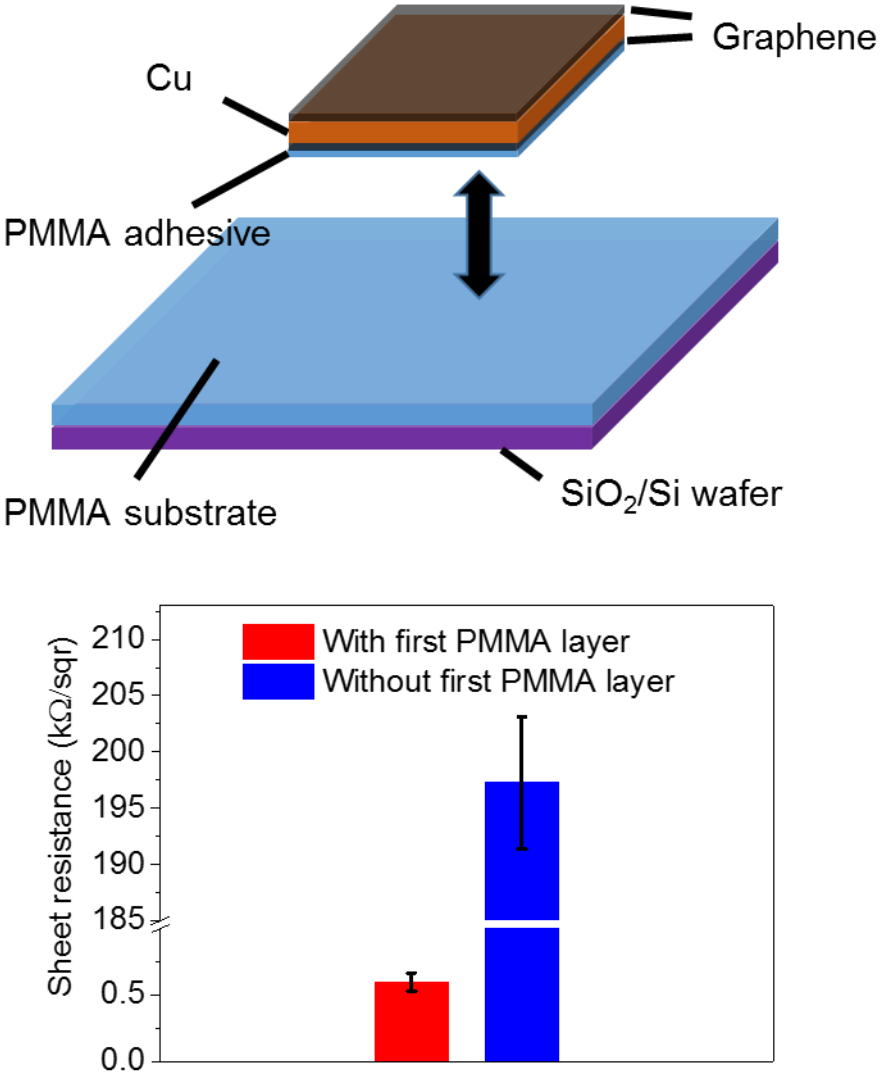

Figure S5. Influence of first PMMA layer. From sheet resistance comparison, we can see that with the spincoated PMMA layer, the quality of SLG is much better. The reason behind it is not clearly understood so far.

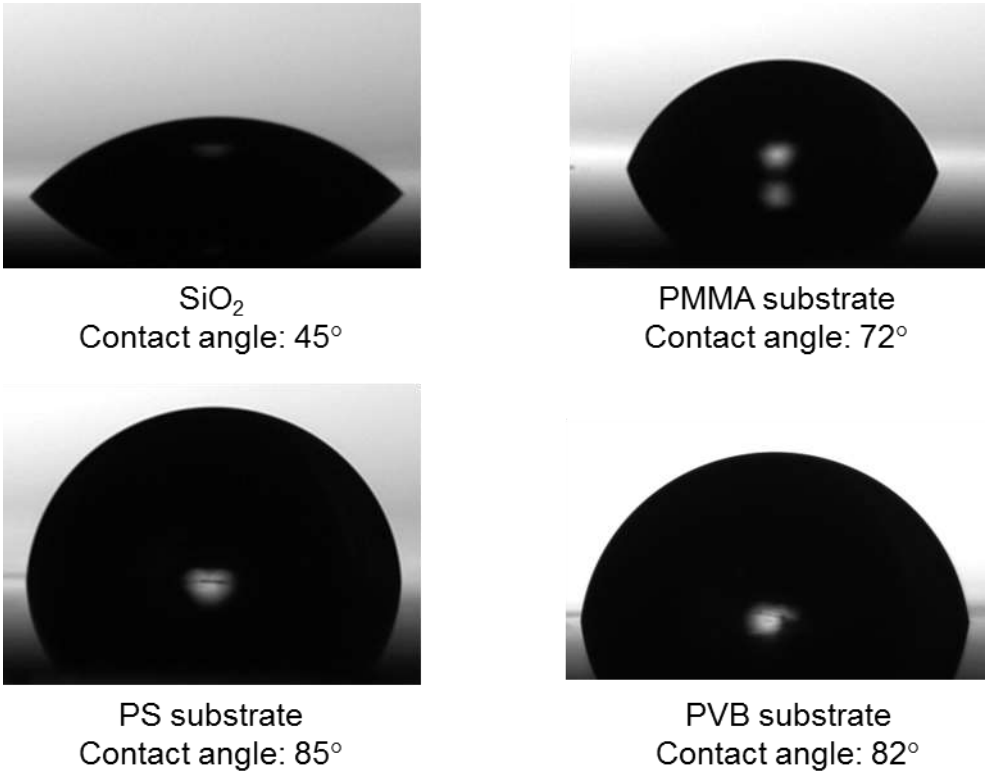

Figure S6. Contact angle measurement of water on different substrates. All polymers in this experiment with higher contact angle than SiO_2 wafer allow characterization of graphene for HER performance. However, according to our sheet resistance result, PMMA offers the lowest sheet resistance though it has the lowest contact angle.

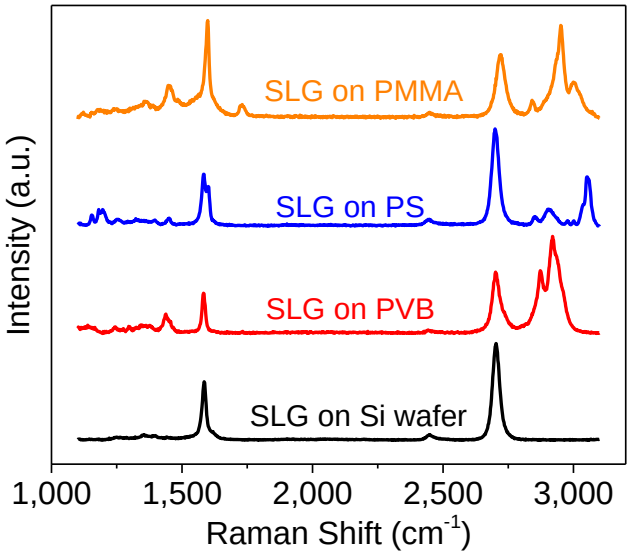

Figure S7. Raman spectra of SLG on different insulating substrates. SLG on PMMA shows different Raman spectrum from that on SiO_2 wafer, where $I_G/I_{2D} \geq 1$, wider FWHM and blueshift of 2D peak. From our result, SLG on PMMA behaves uniquely. Almost all of samples (more than 20 samples) showed the similar Raman spectra while they were confirmed to be SLG.

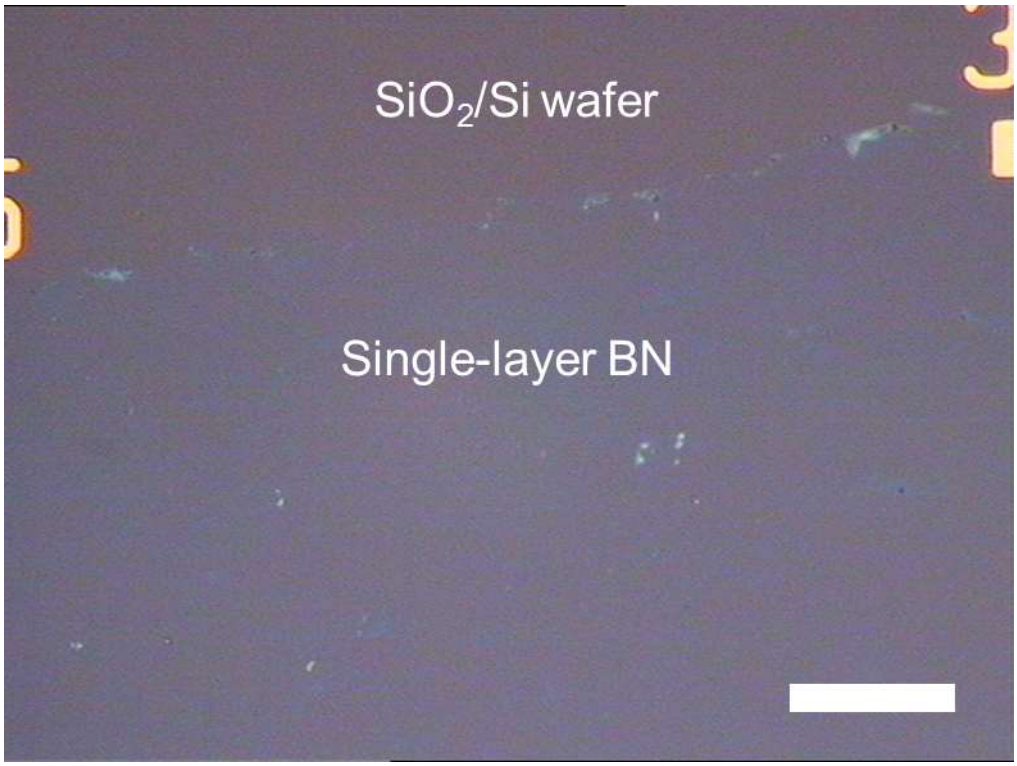

Figure S8. Optical image of transferred h-BN film on SiO_2 wafer. h-BN film on PMMA substrate can be hardly seen similar to SLG on PMMA. However, due to its weak Raman signal and strong PMMA background, Raman spectroscopy is not effective in this case. Thus single-layer h-BN was transferred to SiO_2 wafer to verify its continuity. Scale bar, 20 μm.

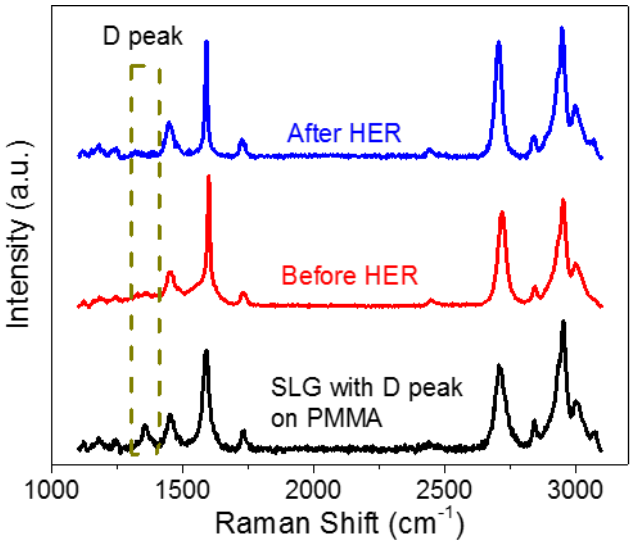

Figure S9. Raman spectra of graphene after HER. SLG with D peak was purposely grow to demonstrate the location of D peak.

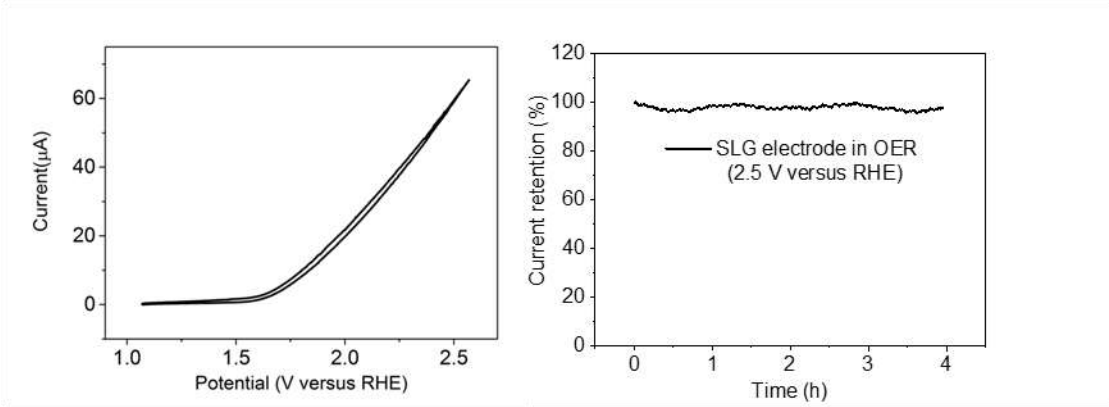

Figure S10. CV and chronoamperometric i-t curve of SLG electrode for OER. SLG electrode can also be evaluated in OER in 1 M NaOH solution. We here simply demonstrate the stability of electrode to prove versatility of our transfer method.

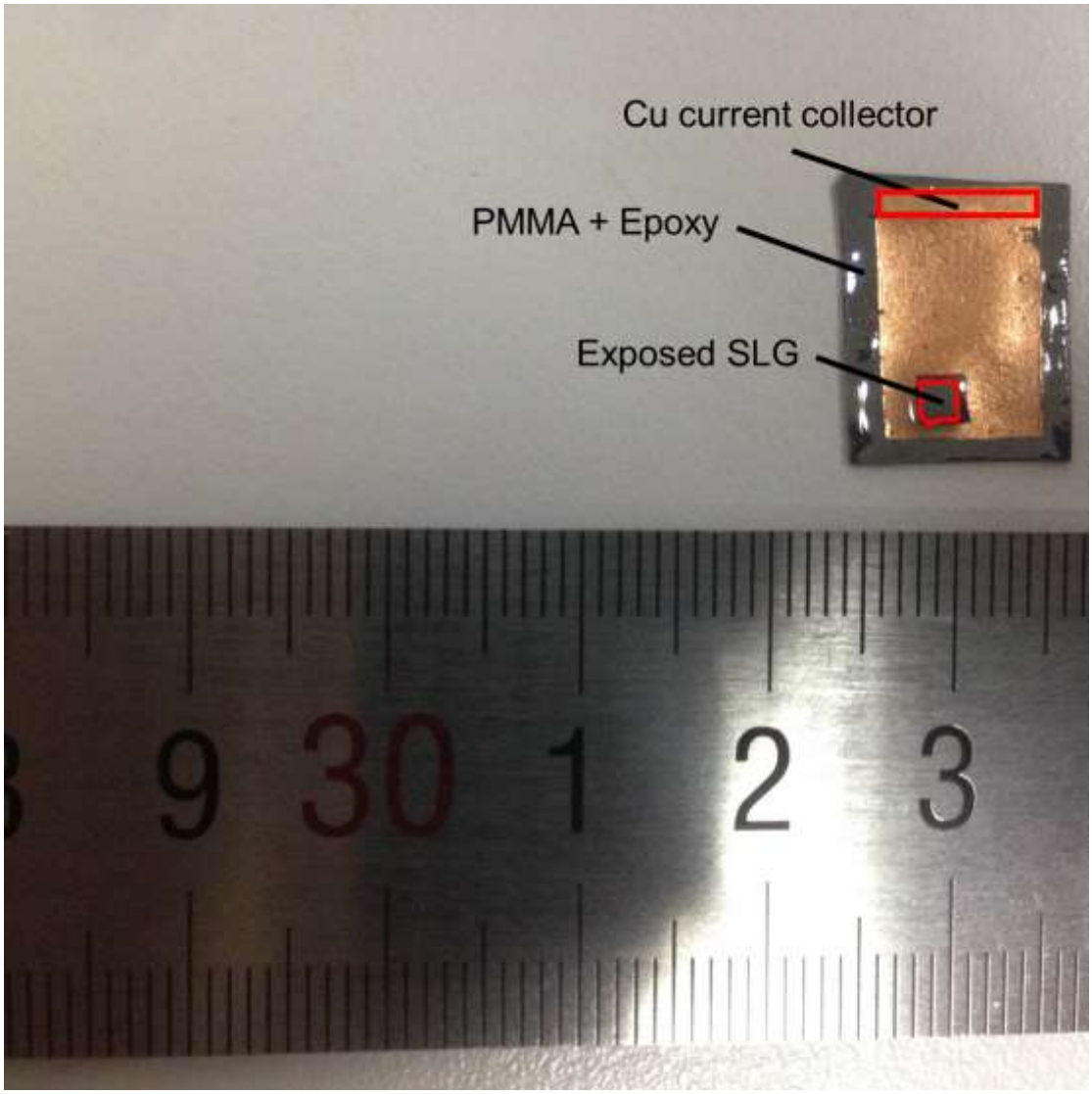

Figure S11. Optical image of modified SLG/BLG electrode. By masking most Cu region with PMMA, only a small SLG/BLG region is exposed. This is beneficial for HER characterization due to lower *iR* drop. The exposed graphene area was calculated by ImageJ.

Table S1. Summary of HER performance of different carbonaceous materials compared with Pt.

Materials	η @ 0.1 mA/cm^2 (V)	Tafel slope (mV/dec)
SLG	0.72 ± 0 .04	147 ± 29
BLG	0.71 ± 0.03	142 ± 21
HOPG	0.64 ± 0.03	122 ± 7
GC	0.76	116
Pt	0.01	40

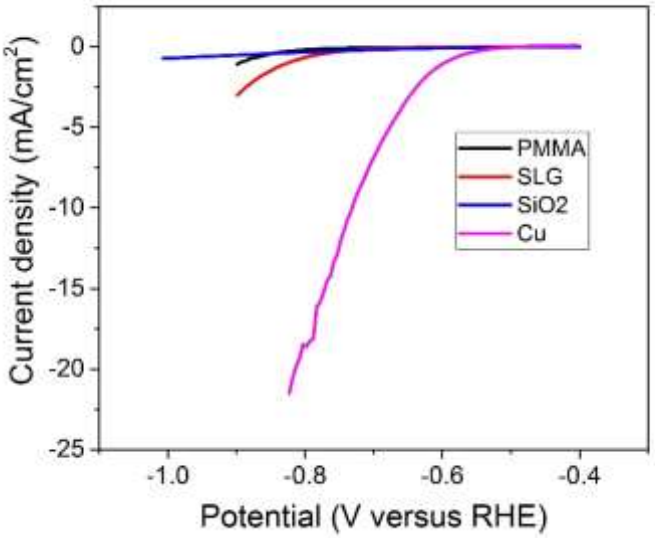

Figure S12. Graphene's HER on different substrates

Table S2. Summary of the HER performance of graphene on different substrates.

SLG on Substrates	Onset potential (V)	η @ 0.1 mA/cm^2 (V)
PMMA	0.63	0.72
SLG	0.63	0.71
SiO_2	0.44	0.63
Cu	0.52	0.52

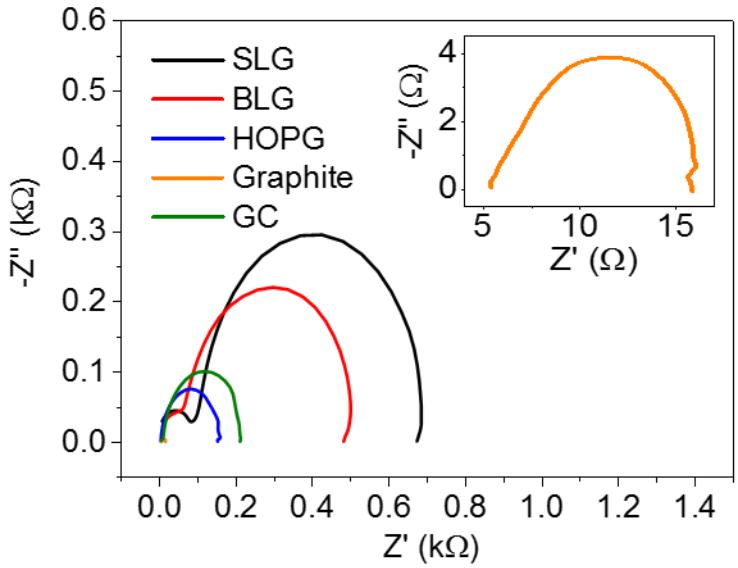

Figure S13. Nyquist plots of different carbonaceous materials. The plots show the smaller charge transfer resistance with increasing graphene layers. No Warburg impedance is observed. Inset is the close-up Nyquist plot for graphite.

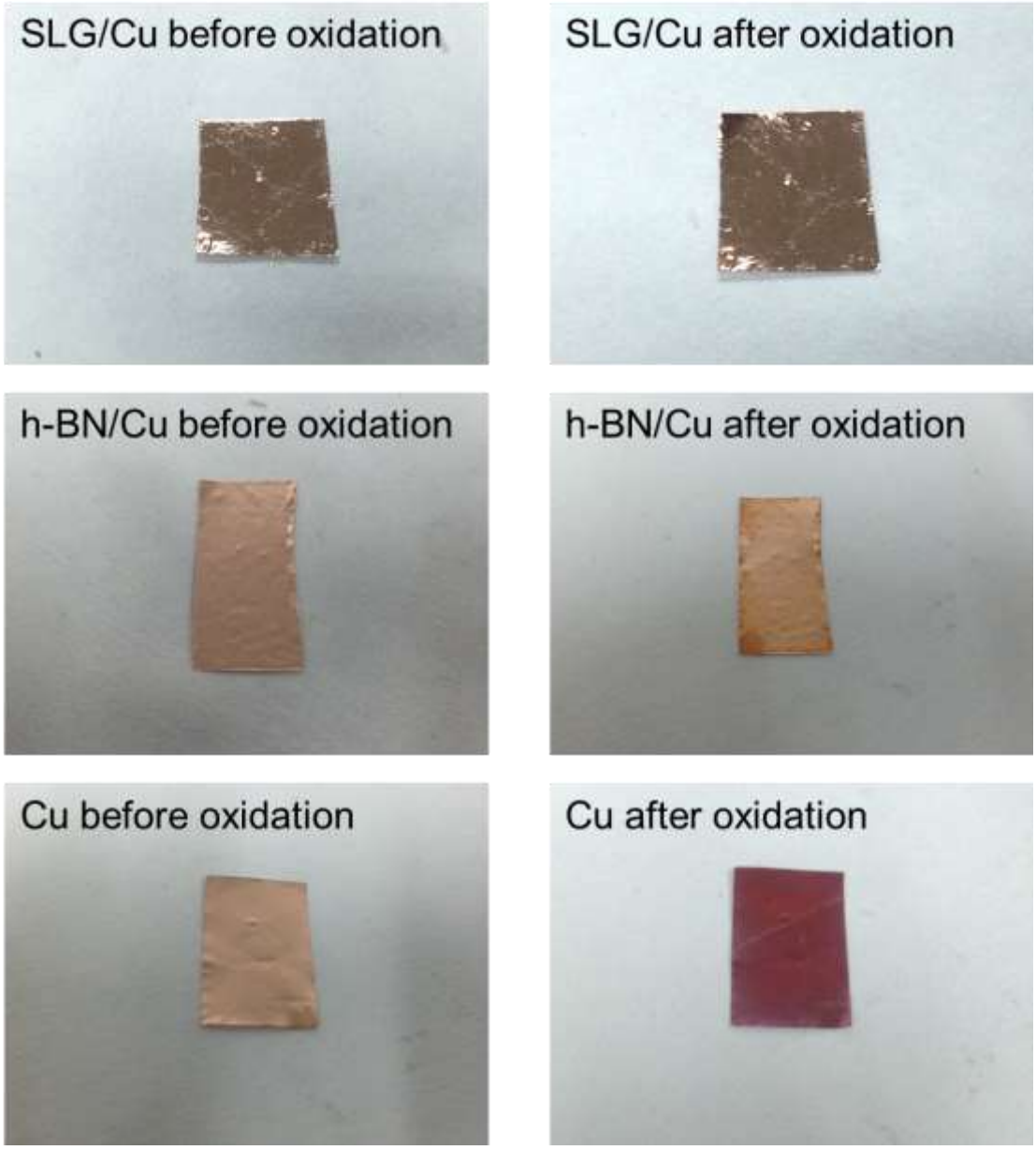

Figure S14. Oxidation of SLG or single-layer BN-terminated Cu and pure Cu. No obvious color change before and after oxidation at 180 °C in air proves the full coverage on Cu after 1 h for SLG/Cu and SLBN/Cu. Without protection, pure Cu is completely oxidized and its color changes a lot.