ELECTRONIC SUPPLEMENTARY INFORMATION

Highly durable graphene monolayer electrode under long-term hydrogen evolution cycling

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METHODS

Materials. HCl (35%), H_2O_2 (33%) and H_2SO_4 (95%) were purchased from VWR, $HClO_4$ from AppliChem, KCl, poly(styrene) (PS) and ferrocenedimethanol (FDM) from Sigma-Aldrich, toluene and *N*-ethylpyrrolidone (NEP) from Roth, acetone and 2-propanol (iPrOH) from BASF. All solutions were prepared with ultra-pure water (Barnstead Easypure II system, 18 MΩcm^{-1}).

Graphene devices. Pt/Ti electrode lines were prepared using photolithography followed by metal deposition on Si/SiO_2 wafers (SiO_2 thickness 500 nm). These samples were cleaned with NEP, acetone and isopropanol before transferring graphene. CVD-grown graphene on copper foil was purchased from Graphenea or Grolltex Inc. and cut into rectangular pieces (a few mm^2 in size). A solution of PS (50 mg/mL) was drop cast onto the CVD-graphene pieces and dried for 15 min at 75°C. The underlying copper was removed by using a metal-ion free etching solution of hydrochloric acid and hydrogen peroxide (1.4 M HCl and 0.5 M H_2O_2) for 7 minutes. Immediately prior to the transfer, the Si/SiO_2 samples with pre-patterned electrodes were annealed on a hotplate at 120°C for 30 min to optimize the hydrophobicity of the surface. PS-coated graphene was transferred onto the samples and dried at 75°C for 10 minutes. Afterwards, the PS was dissolved in toluene for 5 minutes and dried again at 75°C for 10 min. Next, the devices were annealed in a furnace at 600°C under nitrogen atmosphere for 2 minutes to remove organic traces and improve the adhesion between graphene and substrate. To insulate the electrode lines, PS (600 mg/mL) was applied on top of the electrode fingers and left to dry. To ensure a clean graphene surface, the samples were cycled using an electrochemical etching (e-etching) step in 0.1 M HCl with 20 scans in a potential range from -0.6 to +0.3 V (vs. Ag/AgCl) and a scan rate of $v = 100$ mV s^{-1} to remove organic and metal impurities. (see ref. 18 in main text).

Optical and AFM imaging. The optical images were obtained using a Leica DM4000B fluorescence microscope. AFM images were collected by using a JPK Nanowizard 4 (Bruker) in AC mode. The images were further processed with Gwyddion.

Raman spectroscopy. Raman spectra of graphene were obtained on JASCO NRS-4100 Raman spectrometer equipped with a 1650 x 256 CCD detector (Andor; air/Peltier-cooled, operating temperature: -60°C), a 1800 L/mm grating, a diode laser with excitation of 531.98 nm, and a 100X (NA 0.90) objective. A steady power was maintained at 5.6 mW. Each of the Raman spectra was recorded with exposure time of 5 s with 2 accumulations. The spectrometer of the instrument was calibrated by determining the wavenumber position of Raman line of a silicon substrate at 520.7 cm^{-1} before data acquisition. Raman spectra were processed using Origin 9.1 and plotted after normalization. The characteristic bands of graphene were fitted using Lorentzians.

Electrochemical measurements. The electrochemical measurements were carried out in 100 mM acid ($HClO_4$ or HCl or H_2SO_4) with scan rates of 100 mV s^{-1} or 1 V s^{-1} using an Ivium Compactstat. The electrochemical cell (15 mL) comprised of a single graphene monolayer (on Si/SiO_2 substrate) as working electrode, a Pt wire counter electrode and a commercial Ag/AgCl reference electrode. All measurements were performed under ambient conditions.

X-ray photoelectron spectroscopy (XPS) / Nano Electron Spectroscopy for Chemical Analysis (NanoESCA). XPS data were obtained using an Omicron NanoESCA spectrometer. Using an Al Kα source, we monitored carbon, oxygen, and silicon at the C 1s, O 1s, Si 2s and Si 2p core levels to distinguish chemical states of respective elements via their characteristic chemical shifts. Fitting of the spectra was done using KolXPD software.

Figure S1: A photograph of the electrochemical setup indicating bubble formation at the graphene monolayer electrode during the HER cycling experiments. A Pt counter electrode (CE), an Ag/AgCl reference electrode (RE) and a graphene monolayer working electrode (Gr) were used to perform the HER in 0.1 M $HClO_4$.
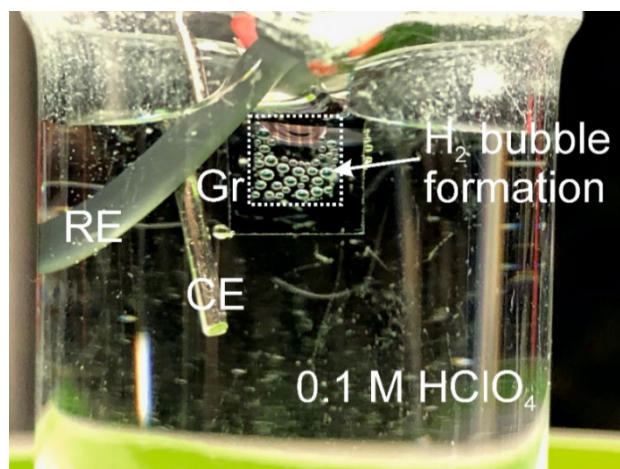

Figure S2: Another location on the graphene monolayer electrode of figure 1 was characterized using AFM before (a) and after (b) performing HER cycling indicating no major changes in the morphology of the graphene monolayer after HER cycling. Lateral scale bar : 2 μm, Height scale: 20 nm.
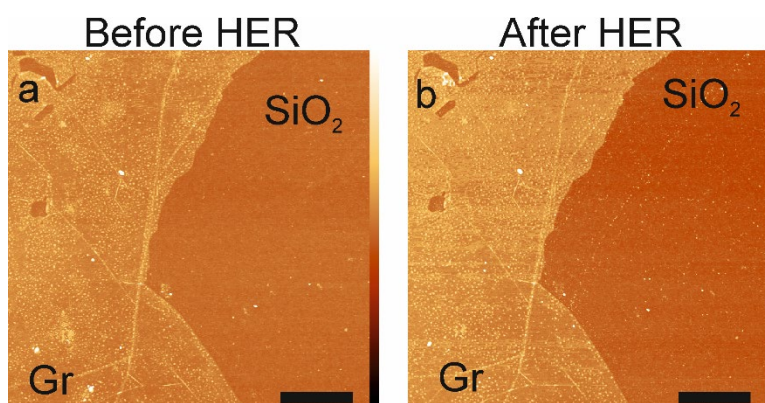
Figure S3: Comparison of HER on a graphene monolayer electrode in different acidic media measured on the same sample. For this, sulfuric acid (a), perchloric acid (b) and hydrochloric acid (c) were used. (d) Cycling voltammograms measured at the same electrode with the redox probe ferrocenedimethanol (FDM) before and after all the HER cycling experiments presented in (a)-(c).
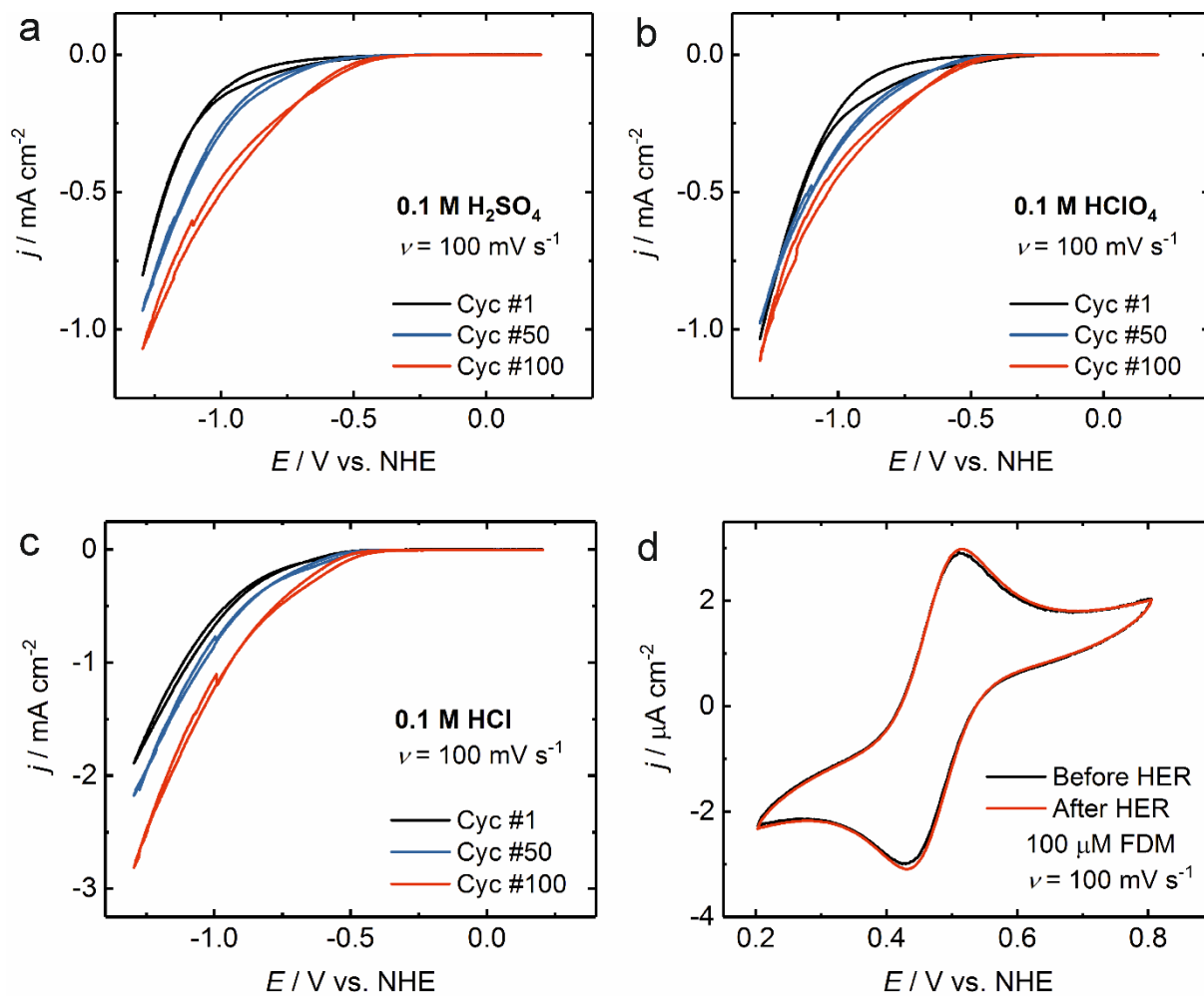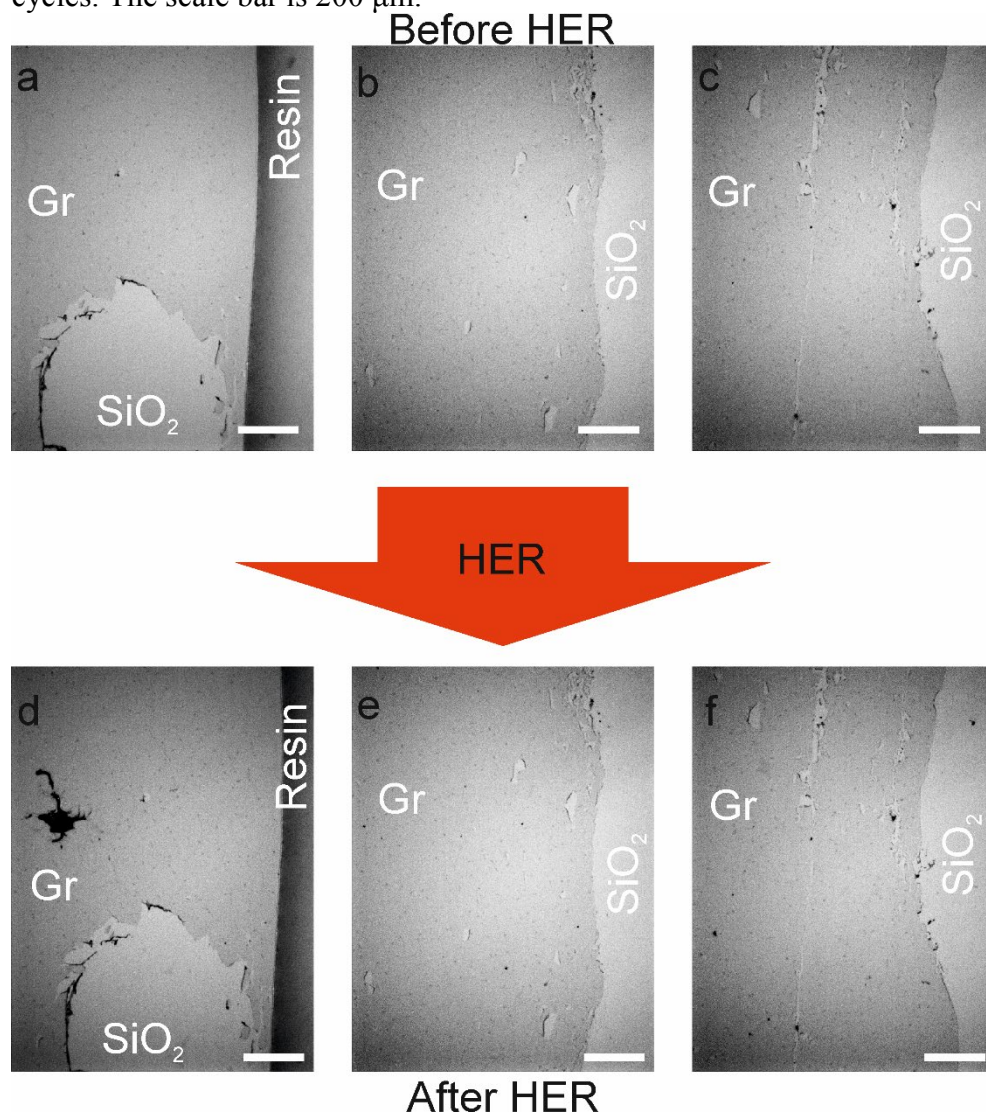
Figure S4: Further optical images of different positions on the graphene monolayer electrode of figure 2 in main text before (top, a-c) and after (bottom, d-f) performing HER for 1000 cycles. The scale bar is 200 μm.

Until now, HER cycling was carried out by cycling the potential down to -1.3 V vs. NHE, analogous to previous reports. (refs. 2 and 3 in main text) In order to evaluate the highest cathodic potential that the graphene sheet can withstand, we carried out systematic measurements with stepwise increase in the vertex cathodic potential of the CVs. Figure S5a shows CVs obtained at a typical electrode during this multi-step experiment. Starting at -0.4 V as the cathodic vertex potential, CV was performed for 10 cycles, followed by successive increase of the vertex potential up to -1.5 V. After every step, the electron transfer with the redox probe FDM was measured to evaluate the integrity of the graphene sheet. Figure S5b shows CVs obtained with FDM at the graphene electrode after every step of 10 cycles of HER. It is clear that the CVs remain unchanged during this entire multi-step HER experiment. Only when the potential reaches -1.5 V vs. NHE, we start seeing a small shift in the formal potential of the redox species. However, the current density remains at the same level even for this extreme vertex potential. This data series attests the extremely high stability of our graphene monolayer electrodes even up to cathodic potentials as high as -1.5 V vs. NHE. Optical images obtained between every step also confirm that the integrity of the graphene sheet is totally guaranteed without the creation of new holes or cracks after applying such a procedure. (see figure S6)

Figure S5: (a) CVs with increasing cathodic vertex potential (as indicated) measured at a graphene monolayer in HCl. At every vertex potential, 10 cycles of CV were carried out. The last cycle is shown. (b) CVs of ferrocenedimethanol (FDM) after each set of 10 cycles, with the corresponding cathodic vertex potential.
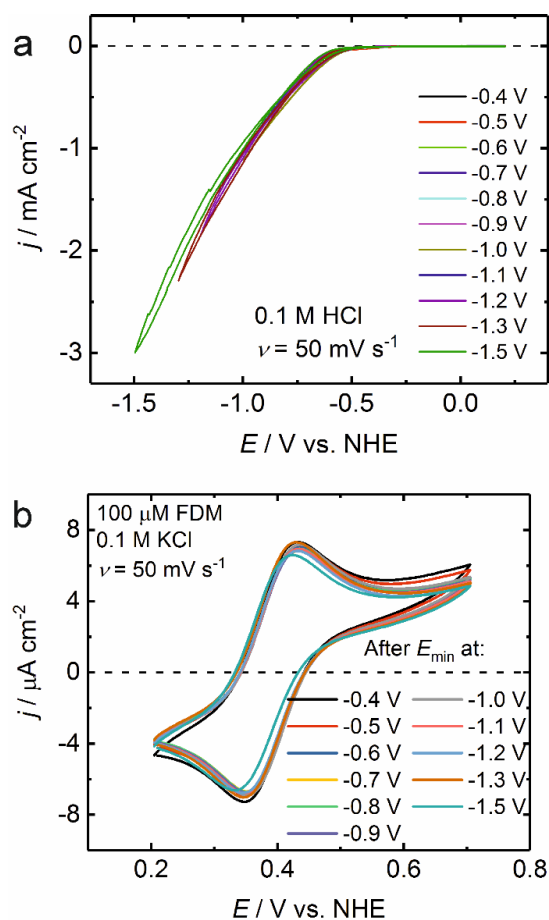
Figure S6: Optical images of the graphene monolayer electrode of figure S5 after HER cycling with a step-wise increasing cathodic vertex potential from -0.4 V (a) to -1.5 V (k) vs. NHE. Cracks as well as wrinkles can be observed from the beginning, which are typical for CVD-grown graphene. After cycling in the different potential windows, the graphene monolayer electrodes do not change and no structural defects are introduced. The scale bar is 50 μm.
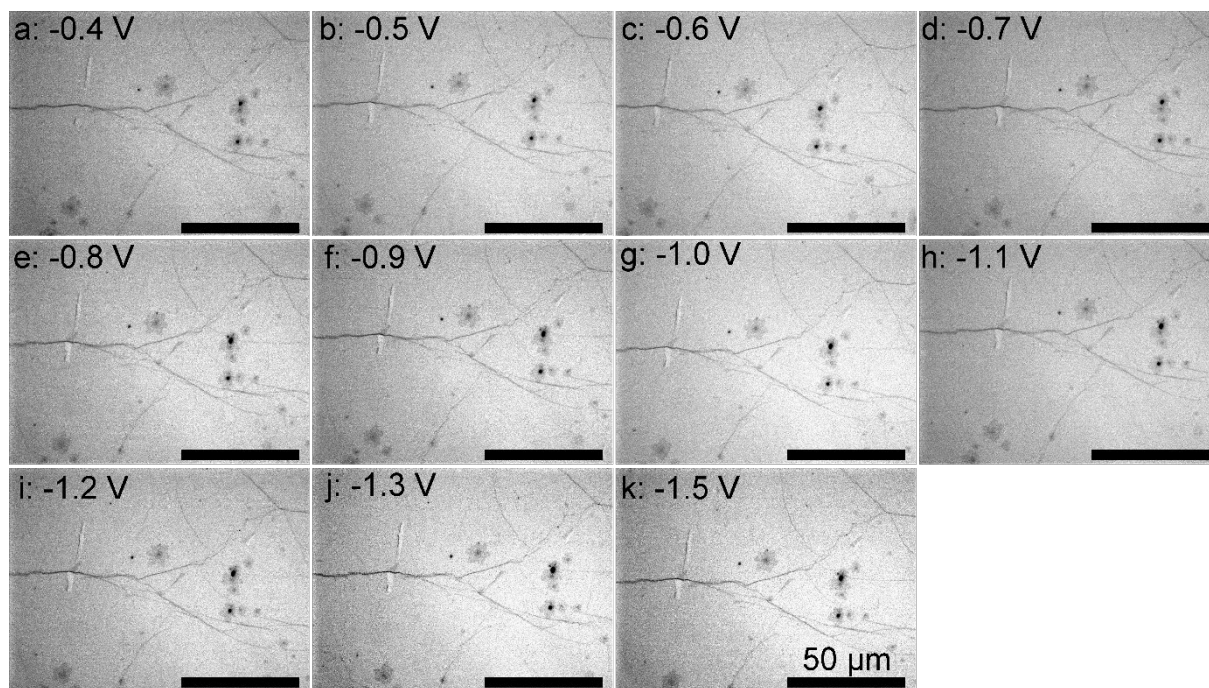
Figure S7: Tafel slope (a) and exchange current density (b) extracted from HER cycling data of figure 1 in main text.
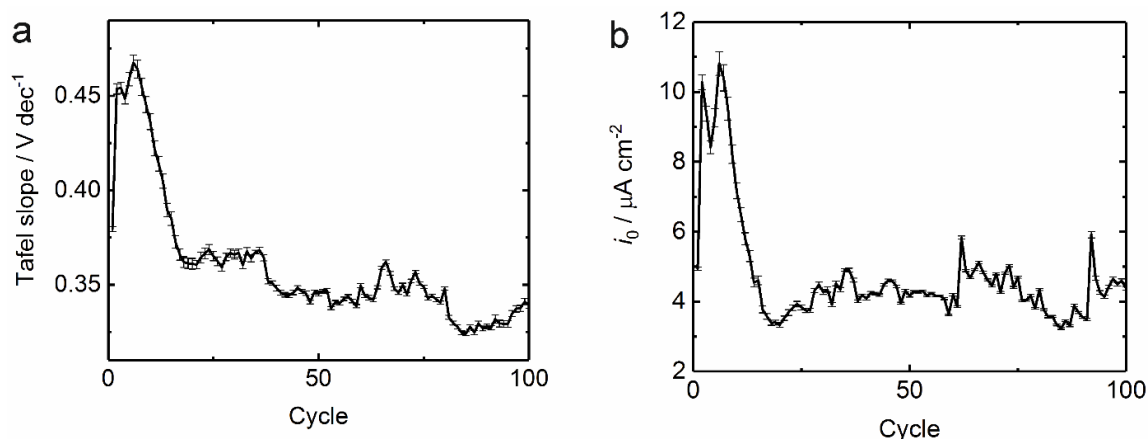

Figure S8: Statistical analysis of Raman spectra measured at 50 different location on the graphene electrode of figure 1 in main text before and after 200 HER cycles: (a) histograms of the *2D*-to-*G* intensity ratio and (b-d) histograms of the position of the *G*-, *D*- and *2D*-peaks. The solid curves are fits to a normal distribution.
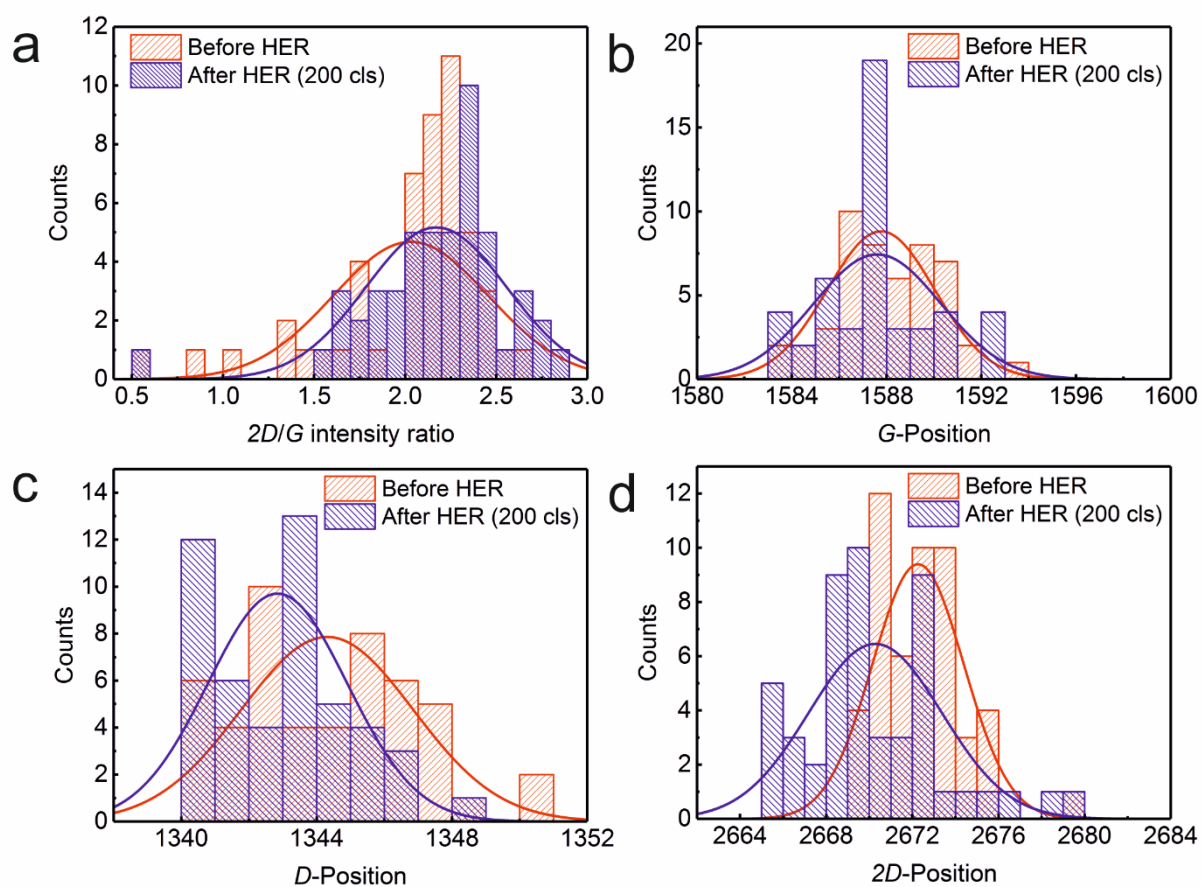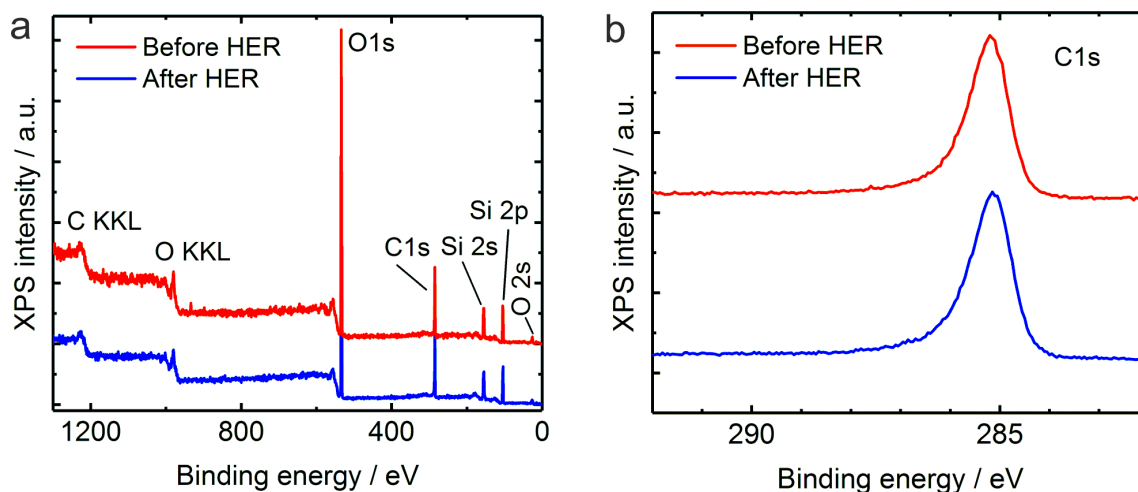
Figure S9: (a) XPS survey spectra and (b) high resolution C1s spectra (same data as in figure 3) are shown for a graphene electrode before and for a graphene electrode after 1000 cycles of HER. The spectra are offset for clarity.

The survey spectra (figure S9a) for both the electrodes show mainly C, O and Si peaks, the latter two arising because of the underlying Si/SiO_2 substrate. The small peak at around 950 eV (0.2%) in the sample before HER cycling is due to copper. As discussed in the main text we perform an elaborate electrochemical etching procedure to remove copper traces, which are left over from the copper substrate on which graphene is grown by chemical vapor deposition. However, it is difficult to remove 100% of the copper in all the samples (see ref. 18 for further details). 0.2% is already an extremely low contamination for such samples. The absence of copper in the samples after HER can be explained by the several runs of electrochemical cycling in acidic solutions performed on this sample. During this cycling, the electrode experiences anodic potentials for longer times, where the copper traces can be slowly oxidized and are removed from the graphene surface.

The fitting of the XPS spectra in figures 3c and 3d in main text was performed using a multicomponent function as shown by the shaded regions. This function includes a standard Shirley background. Since contamination-free unmodified graphene mainly contains sp^2 and sp^3 carbon species, we fit the data using only one Doniach-Šunjić (convoluted with a Gaussian) and one Voigt profile separated in energy by ~0.5 eV (see ref. 17 for further references).