

Electronic Supplementary Information

Selective Electrochemical Functionalization of the Graphene Edge

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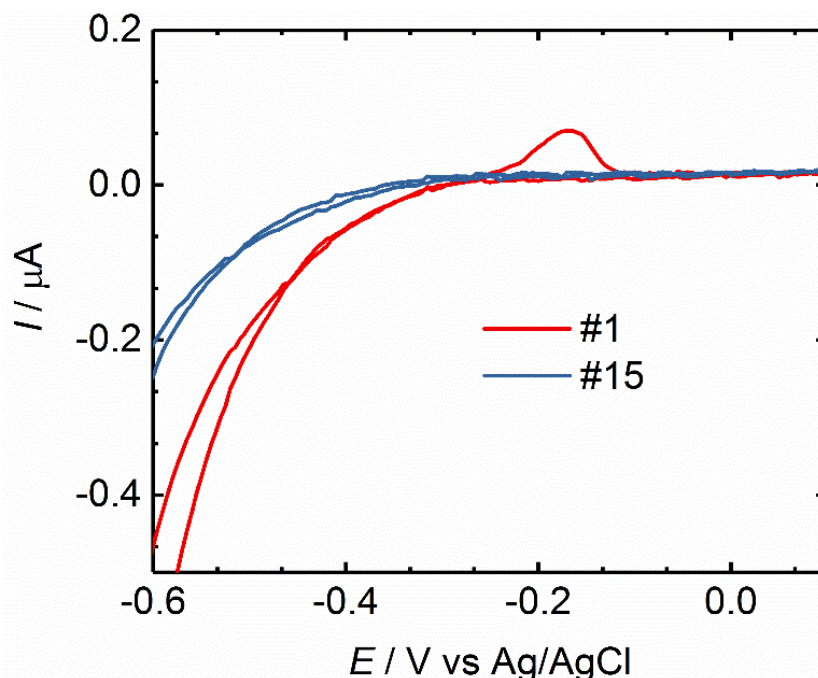


Figure S1. Electrochemical etching of bare graphene. Cyclic voltammograms (CVs) of as-transferred graphene for the first (#1) and the 15th scan (#15). The peak in the red curve corresponds to the oxidation of copper. In the 15th scan, this peak disappears indicating the removal of trace copper impurities. Scan rate 50 mV s⁻¹. Electrolyte: HCl 0.1 mol L⁻¹. T 25 °C. See Ref. 27 (main text) for further details.

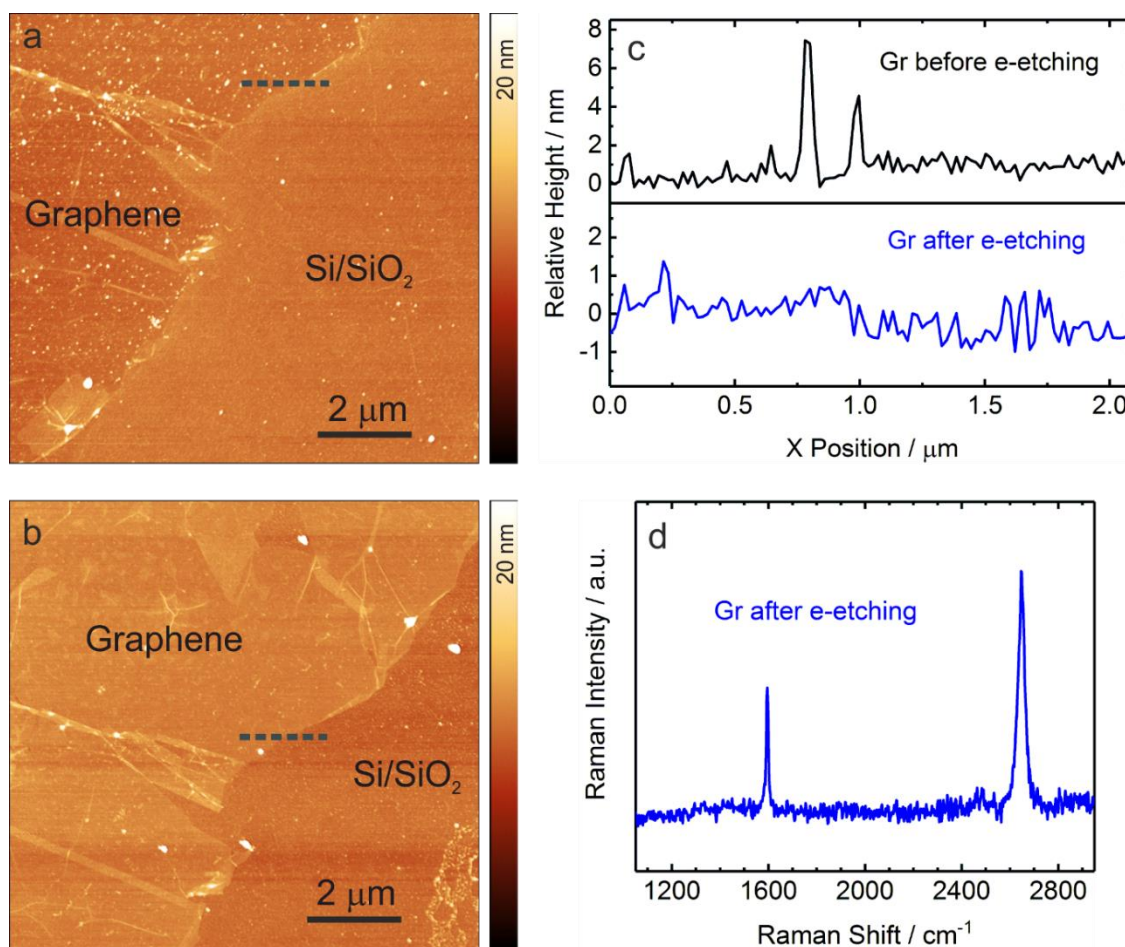


Figure S2. Characterization of graphene after e-etching. AFM of transferred CVD-graphene (Gr) (a) before e-etching and (b) after e-etching (c) Relative height profile of Gr before (in black) and after e-etching (in blue). (d) Raman spectra after e-etching showing the *G* and *2D* peaks and the absence of a *D*-peak, indicating graphene of a high quality. (λ_{ex} : 633 nm, 4.5 mW, 1s)

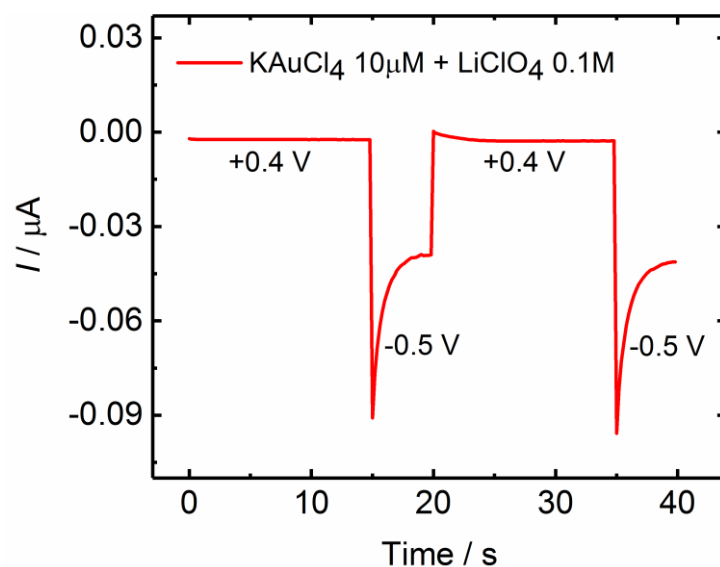


Figure S3. Electrochemical deposition of AuNPs at GrEdge. Chronoamperometric profile for the potentiostatic deposition of AuNPs at a GrEdge electrode with $10 \mu\text{mol L}^{-1}$ KAuCl_4 . Supporting electrolyte: LiClO_4 0.1 mol L^{-1} . T $25 \text{ }^\circ\text{C}$

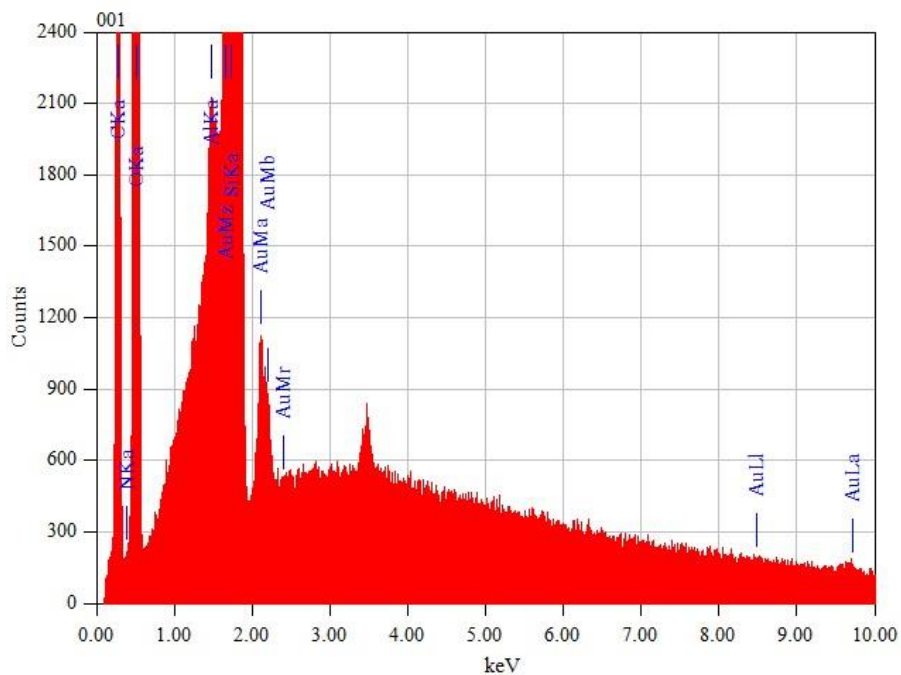


Figure S4. Energy Dispersive X-ray (EDX) spectra obtained at the GrEdge-AuNP-electrodes. The peaks corresponding to the K and M edges confirm the presence of gold.

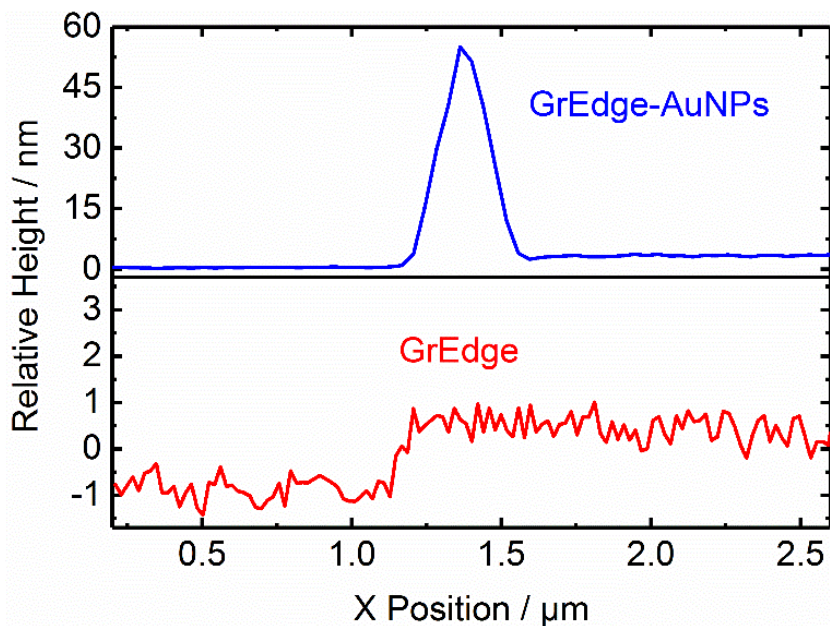


Figure S5. Line profile along the cyan dashed lines shown in figure 1(e) and (f) for GrEdge-AuNPs and pristine GrEdge respectively.

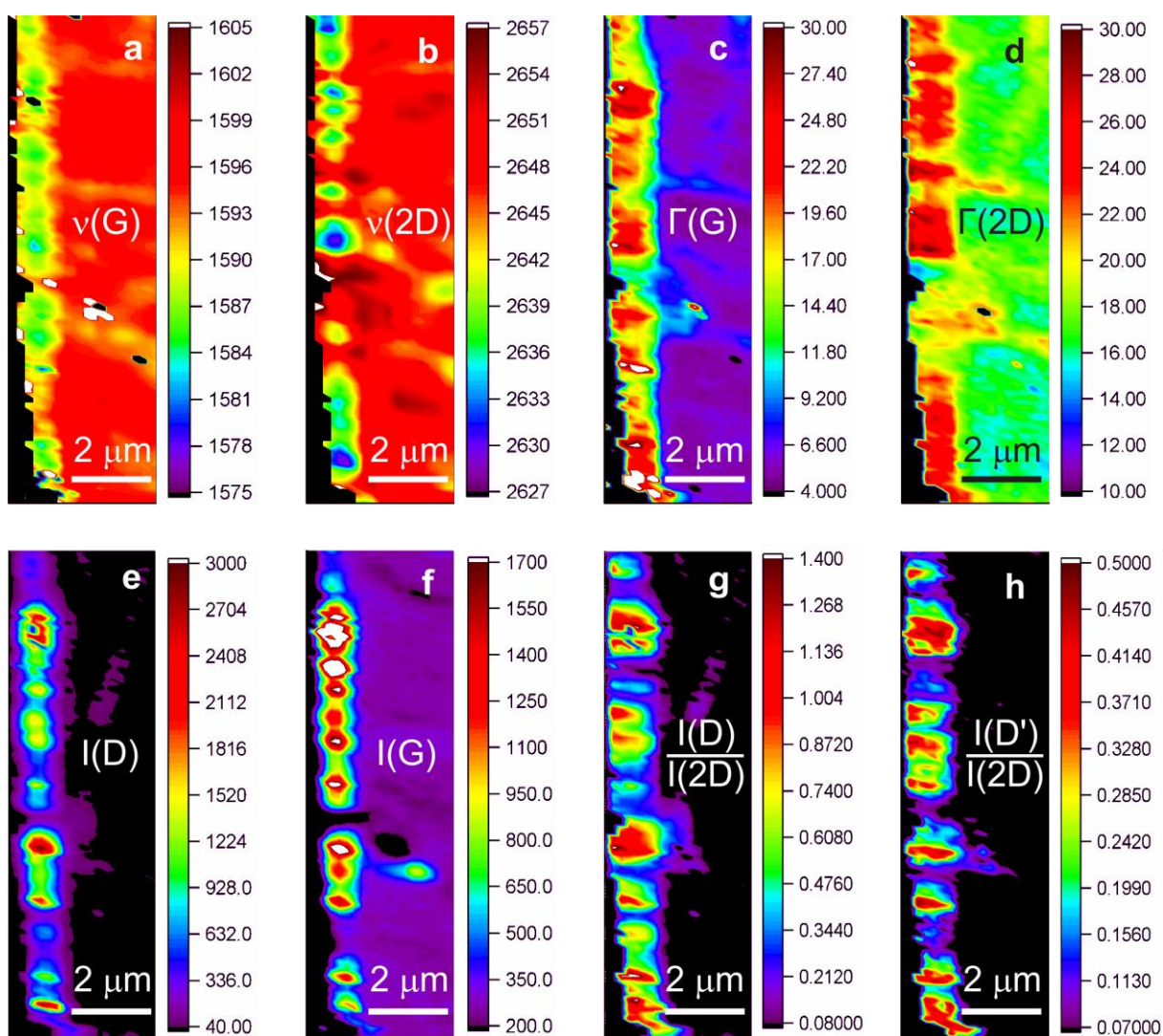


Figure S6. Raman Maps of the mode frequency or peak position (ν) FWHM (Γ), intensity (I) and intensity ratio of the various graphene bands for the sample in figure 3. (λ_{ex} : 633 nm, 4.5 mW, 1s)

Table S1. Mode parameters of graphene-related peaks in the Raman spectra of basal plane, GrEdge and GrEdge-AuNPs ($n = 7$ for GrEdge and 25 for the others).

($\pm\text{cm}^{-1}$)	GrBasal Plane	GrEdge	GrEdge-AuNPs
ν (D)	-	1328.4 (± 0.81)	1329.1 (± 3.9)
ν (G)	1595.5 (± 0.87)	1592.8 (± 1.8)	1588.9 (± 2.5)
ν (D')	-	-	1621.0 (± 1.2)
ν (2D)	2649.0 (± 1.1)	2650.5 (± 1.9)	2639.9 (± 5.4)
Γ (G)	5.5 (± 0.42)	13.2 (± 2.7)	20.0 (± 2.0)
Γ (2D)	16.5 (± 0.84)	29.6 (± 1.2)	22.7 (± 2.2)
$I(2D)/I(G)$	2.06 (± 0.13)	2.5 (± 0.48)	1.9 (± 0.8)

We have also evaluated the effect of the AuNPs on the electronic structure as observed by Raman spectroscopy. The positions and the relative intensities of the *G* and 2*D* peaks are sensitive to charge transfer doping.¹⁻³ Figure S5 presents the Raman maps (for the sample in figure 3) of mode frequency (ν) FWHM (Γ), intensity (*I*) and the intensity ratio for *G*, *D*, *D'* and 2*D* peaks. When we compare the peak positions of the pristine GrEdge with that of the GrEdge-AuNPs, it is apparent that the *G*-peak shifts only slightly, while the 2*D*-peak moves to a lower frequency. The intensity ratio $I(2D)/I(G)$ also decreases. This is consistent with electron transfer from the nanoparticles to graphene,³ as observed earlier on the basal plane, however with a smaller magnitude.⁴ For GrEdge-AuNPs, the interfacial contact area between AuNPs and the edge is considerably smaller, explaining the comparatively weak charge transfer between the particles and graphene. All these observations are consistent with the claim that the particles are exclusively attached to the edge of the graphene sheet.

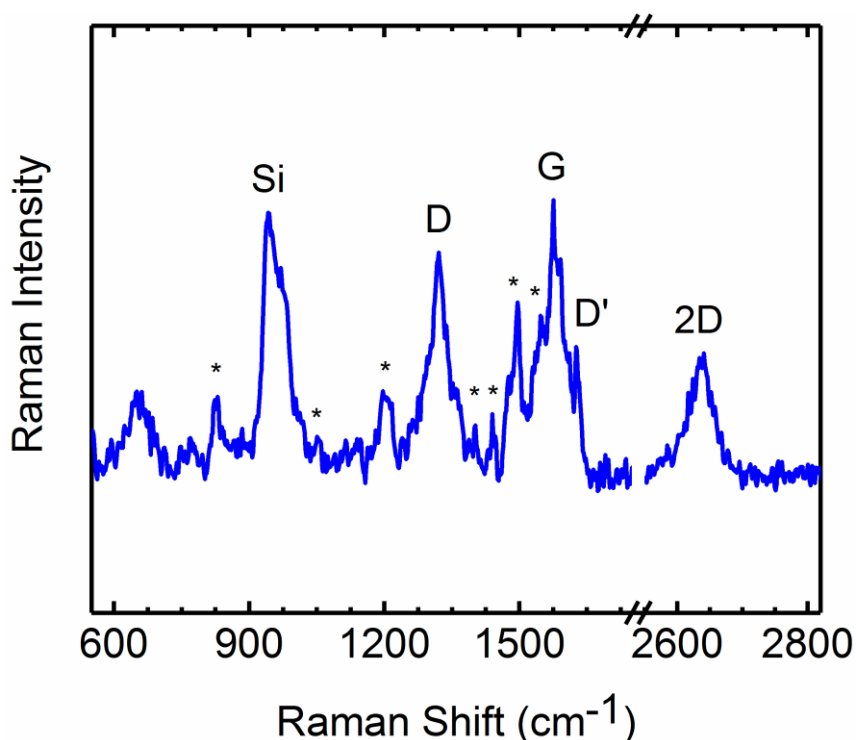


Figure S7. Raman Spectra of GrEdge-AuNPs after the electrochemical oxidation of GrEdge. The spectra shows signature graphene bands (*D*, *G*, *D'* and 2*D*) and various oxidized carbon peaks: epoxide, C-O-C stretching (1052 and 1445 cm^{-1}); hydroxyl, O-H bending (~ 1415 cm^{-1}); C-O stretching (1204 cm^{-1}) and C=C stretching of phenyl rings (1496 and 1548 cm^{-1}) (λ_{ex} : 633 nm, 4.5 mW, 1 s).^{5,6} The electrochemical oxidation of GrEdge was carried out using cyclic voltammetry from 0.8 V to 1.8 V (vs. Ag/AgCl).⁷ Supporting electrolyte: H_2SO_4 0.5 mol L^{-1} . Scan rate: 50 mV s^{-1} .

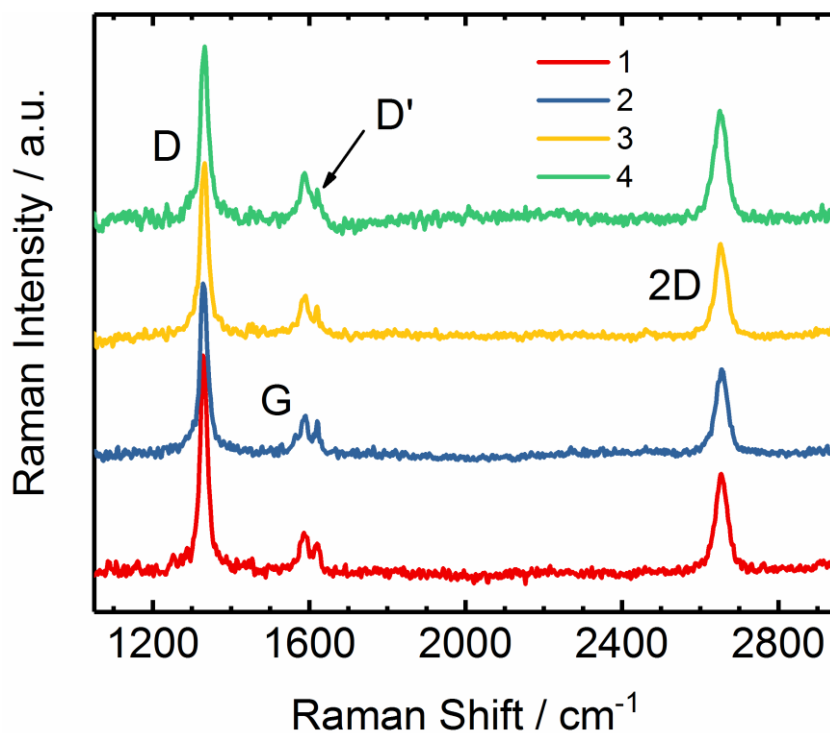


Figure S8. Raman spectra of GrEdge-AuNPs from 4 different devices demonstrating the reproducibility of the peaks and the absence of other modes. The spectra are shifted for clarity. Compare with figure 3a (λ_{ex} : 633 nm, 4.5 mW, 1s)

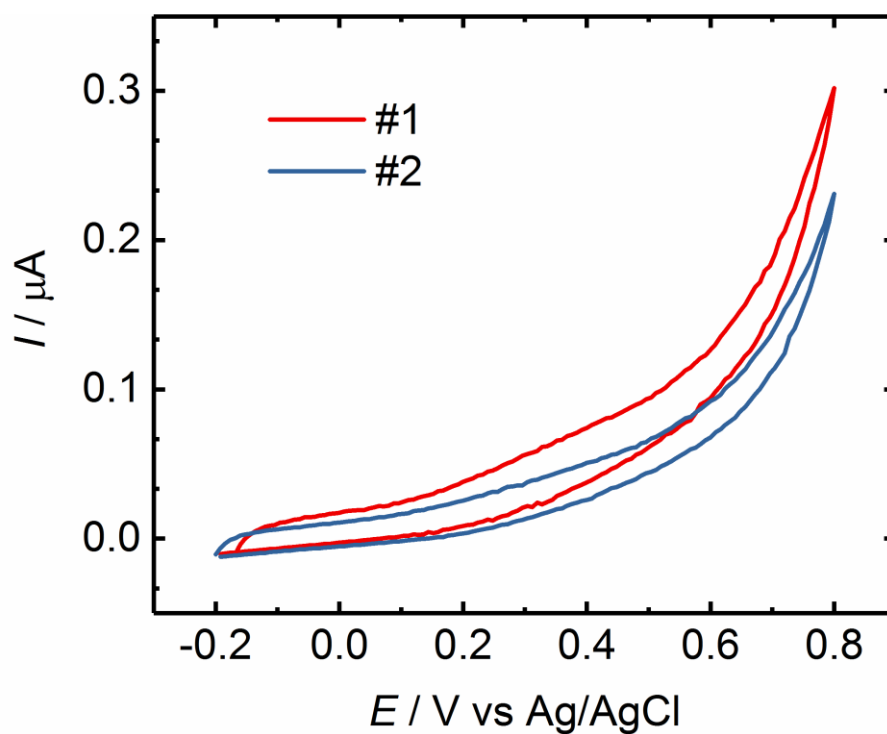


Figure S9. Electrochemical deposition of 4-aminobenzylamine (ABA) at GrEdge electrodes. Cyclic voltammetry at a GrEdge electrode with the precursor ABA (5 mmol L^{-1}) in an aqueous solution. Supporting electrolyte: LiClO_4 0.1 mol L^{-1} . T $25 \text{ }^\circ\text{C}$. Scan rate 20 mV s^{-1} .

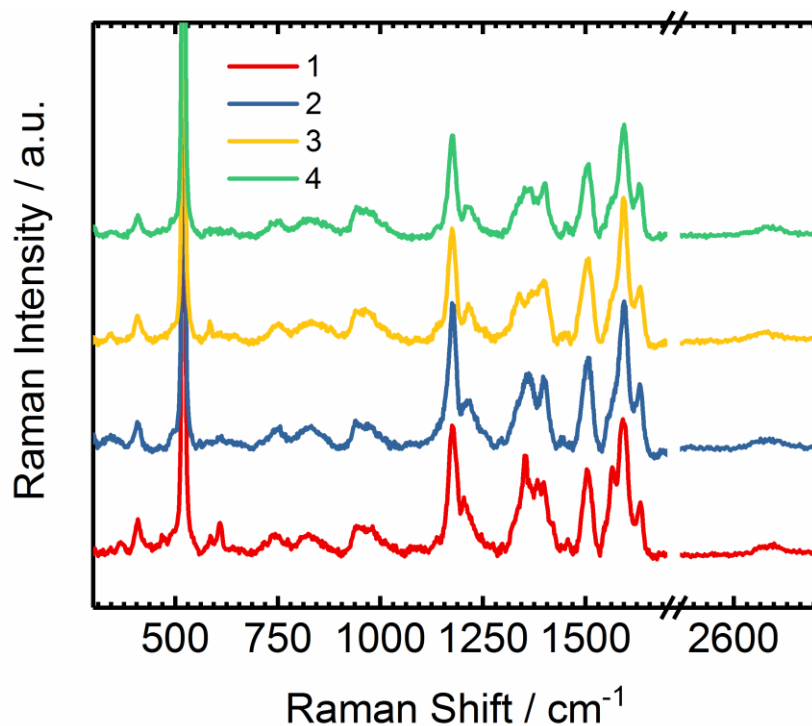


Figure S10. Raman spectra of GrEdge-pABA-AuNPs from 4 different devices showing the reproducibility of the pABA peaks and the essential features in the fingerprint region. The spectra are shifted for clarity. Compare with figure 4c (λ_{ex} : 633 nm, 3.4 mW, 2x1s)

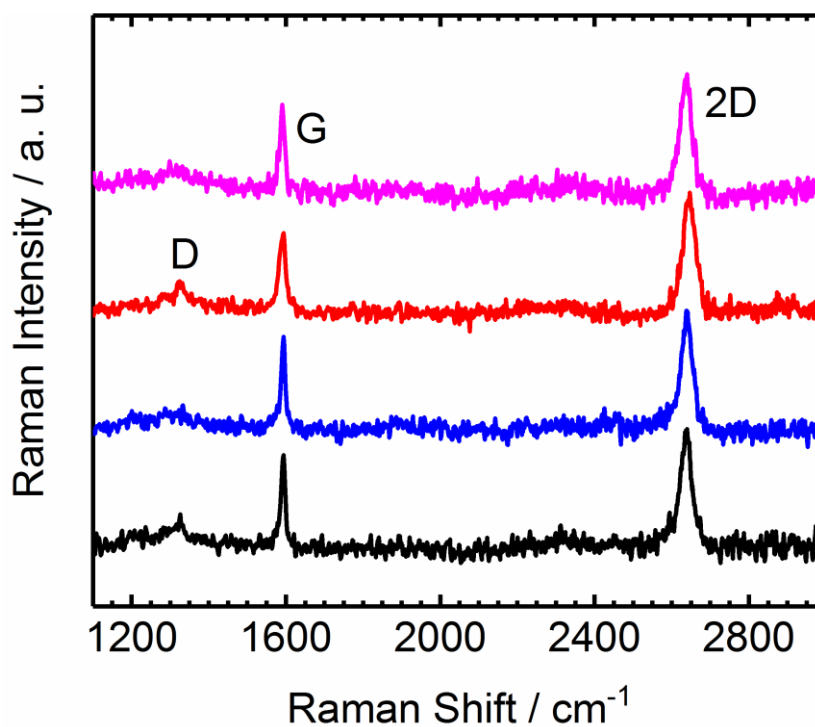
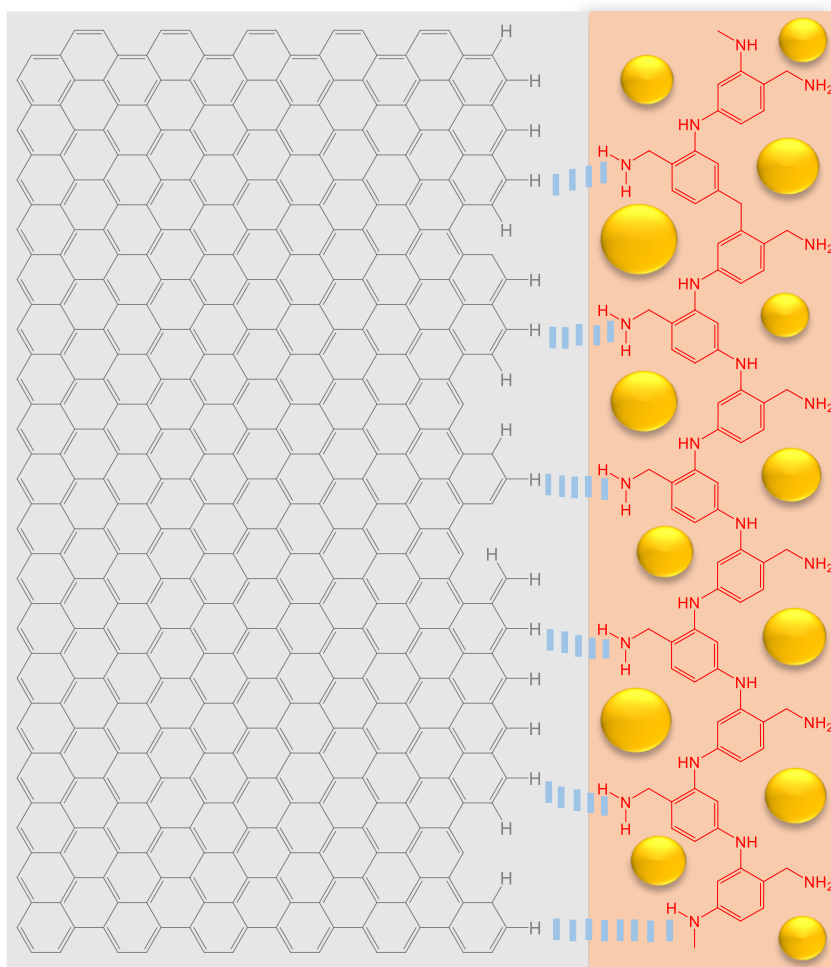


Figure S11. Raman spectra of GrEdge after chronoamperometry in background electrolyte LiClO_4 0.1 mol L^{-1} in the absence of AuCl_4^- ions for 4 different positions, indicating that the edge remains unmodified in the absence of the gold species. The spectra are shifted for clarity.



Scheme S1. A proposed schematic of the functionalized GrEdge-pABA-AuNPs showing a possible chemical structure of the various layers. The blue dashed lines refer to non-covalent interactions.

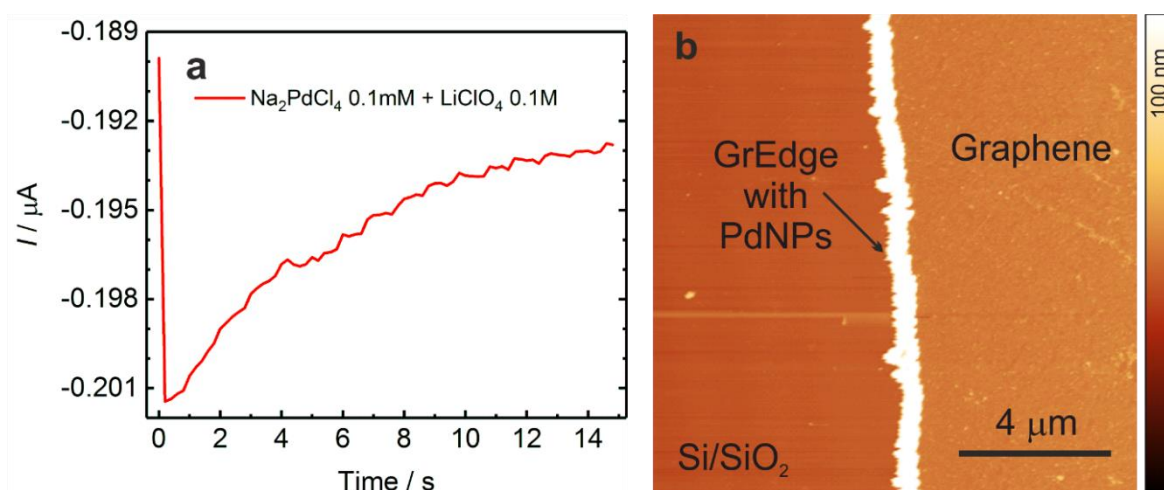


Figure S12. a) Chronoamperometry of GrEdge electrodes in electrolyte solution of Na_2PdCl_4 (0.1 mM) + LiClO_4 (0.1 M). The deposition of PdNPs was carried out in 15 seconds. b) AFM image showing PdNPs at the GrEdge.

References

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