Supporting Information

Electrophilic Radical Coupling at the Edge of Graphene

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Raman characterization.

We monitored the variation of the Raman signature of the embedding polymer to exclude the adsorption of nitrobenzene on the polymeric surface. The edge electrode and the surrounding polymer are rinsed in ultra pure water after electrografting. Figure S1 shows the Raman spectroscopy of the embedding polymer before and after functionalization of the edge electrode. The Raman spectra is not altered by the electrografting reaction, indicating that the reaction happens at the edge electrode.

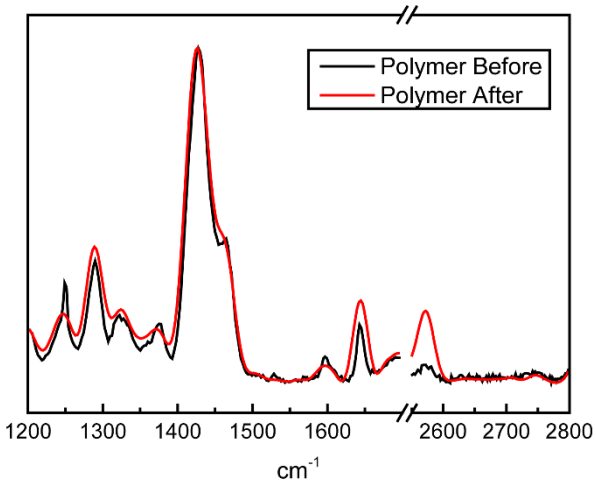

Figure S1. Comparison between the embedding polymer before and after functionalization of the edge electrode and normalized over the peak around 1450 cm^{-1}.

Electrical characterization.

At last, we confirmed the edge selectivity of the electrografting with a control experiment forming an edge on SiO_2 via oxygen plasma etching. Figure S2-a shows the preparation of the sample: a CVD film of graphene is deposited on a SiO_2 substrate and partially covered with the PEMPT-TATATO polymer. Oxygen plasma etches the excess of graphene until covered by the polymer. The polymer protects the graphene, forming an edge at its extremity. Afterwards, the edge is functionalized by electrografting of nitrobenzene diazonium.

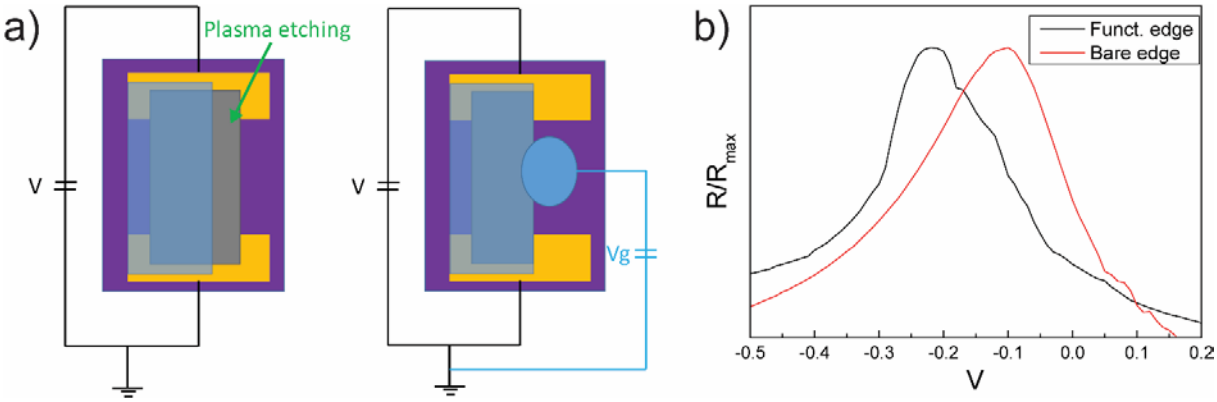

Figure S2. Edge electrode on SiO_2. a) A graphene field effect transistor, GFET, with an exposed edge electrode is formed by coating partially a graphene film with a polymer. An oxygen plasma etches the unprotected graphene, forming an edge at the interface with the protecting polymer. The edge electrode is in contact with an electrolyte solution of 1M KCl and a gate potential V_g is applied to the edge through the solution. b) Conductivity measurements of the GFET before functionalization (red curve) and after functionalization (black curve).

The control experiment suggests a behavior comparable to what was observed with the polymer-embedded graphene edge electrode in figure 3d of the main text. Figure S2-b shows the gating curves of the graphene film before and after functionalization, respectively red curve and black curve. We performed liquid gating in 1M KCl in ultrapure water. The conductivity of the graphene sample is not affected by the electrografting at the edge, indicating the protection of the basal plane. The shift in resistivity at the charge neutrality point is around three

times the minimum in resistivity at negative gating potential, as observed also for the edge electrode within the polymer.

References

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[2] R. L. Mays, P. Pourhossein, D. Savithri, J. Genzer, R. C. Chiechi, M. D. Dickey, J. Mater. Chem. C 2013, 1, 121–130.