Supporting information

Pt Immobilization within a Tailored Porous-Organic Polymer-Graphene Composite: Opportunities in the Hydrogen Evolving Reaction

Ahmed B. Soliman,[a,b,g] Mohamed H. Hassan, [a] Tran Ngoc Huan,[c] Arwa A. Abugable,[a,d] Worood A. Elmehalmey, [a] Stavros G.Karakalos, [e] Manuel Tsotsalas, [f] Marita Heinle,[f] Mady Elbahri,[g] Marc Fontecave,[c] and Mohamed H. Alkordi [*a]

[a] Center for Materials Science, Zewail City of Science and Technology, Sheikh Zayed District., 12588, Giza, Egypt.

[b] Chemistry Department, Faculty of Science, Ain-Shams University, Abbasia, Cairo, 11566, Egypt.

[c] Laboratoire de Chimie des Processus Biologiques, Collège de France, Université Pierre et Marie Curie, CNRS UMR 8229, 11 Place Marcelin Berthelot, 75005 Paris, France.

[d] Center of Genomics, Helmy Institute, Zewail City of Science and Technology, Sheikh Zayed District., 12588, Giza, Egypt.

[e]College of Engineering and Computing, Swearingen Engineering Center, University of South Carolina, Columbia, SC 29208, USA.

[f] Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany.

[g] Nanochemistry and Nanoengineering, School of Chemical Engineering, Department of Chemistry and Materials Science, Aalto University, Kemistintie 1, 00076 Aalto, Finland

*malkordi@zewailcity.edu.eg malkordi@mail.usf.edu

Experimental

All reagents were used as received without further purification. Solvents, catalysts, and common chemicals were purchased from Sigma-Aldrich or Fisher Scientific-UK. Brominated aromatics were purchased from Combi-Blocks. Triethynylbenzene was synthesized as described earlier.[26, 35] Nitrogen gas for sorption were purchased from Airliquide (N_2 AlphaGaz2 (99.9998%), Graphene (Alfa Aesar, catalogue 47312), copper(I) iodide (CuI, 98%, Acros Organics); triethylamine (Chromanorm®, HPLC grade, VWR); Acetonitrile (fischer, analytical reagent grade 99.99%).
Gas sorption analysis was performed on Micromeretics **ASAP2020**. The apparent surface areas were determined from the nitrogen adsorption isotherms collected at 77 K by applying the Brunauer-Emmett-Teller (BET) and Langmuir models. Pore size analyses were performed using a slit NLDFT pore model system by assuming a carbon finite pores surface. CHN elemental analyses were conducted on ThermoScientific **Flash 2000**. Infra-red absorption spectra were recorded on ThermoScientific **Nicolet is-10**. Thermogravimetric analyses were conducted on Thermal Analysis-**Q50** under nitrogen atmosphere. SEM and EDX analyses were done on Nova NanoSEM 450 equipped with EDAX Octane Silicon Drift Detector (SDD). TEM images were acquired on a JEOL JEM-2100, operating at 200 KV.

XPS measurements: X-ray photoelectron spectroscopy measurements were performed using a Kratos AXIS Ultra DLD XPS system with a monochromatic Al Ka source operated at 15 keV and 150W and a hemispherical energy analyzer. The X-rays were incident at an angle of 45° with respect to the surface normal. Samples were placed in small powder pockets on the holder and analysis was performed at a pressure below $1x10^{-9}$ mbar. High resolution core level spectra were measured with pass energy of 40 eV. The XPS experiments were performed by using an electron beam, directed on the sample, for charge neutralization.

ICP-OES measurements

Platinum concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES; OPTIMA 8300DV, Perkin-Elmer). The sample flow was set to 1.5 ml/min. The HF-generator operated at 1300 W. Argon flows were 12 l/min for the plasma, 0.2 l/min for the thrust gas and 0.55 l/min for the vaporizer gas. The platinum bands at 265.945 nm, 214.423 nm, 299.797 nm and 204.937 nm were analyzed.

For the ICP-OES measurements18.3 mg of PyPOP-Pt@G sample was eluded in a mixture of 1.5 mL HNO_3 65%, 1.65 mL $H_2O_2$40% and 0.9 mL H_2SO_4 96% Merck (Suprapur). Afterwards the solvent was evaporated and the sample again eluded in Aqua Regia Merck(Suprapur) and diluted for ICP-OES-measurements.The Pt loading in the PyPOP-Pt@G sample was determined to 54.5 µg /mg +- 4.2%.

Preparation of the GCE electrode

2.25 mg of the PyPOP-Pt@G was dispersed in a solution of 1 mL isopropanol and 40 µl of a Nafion® perfluorinated resin solution (5 wt. % in mixture of lower aliphatic alcohols and water, containing 5% water, Sigma-Aldrich). After sonication, a 40 µl portion of the suspension was drop casted on a 0.07 cm^2 GCE electrode (ALS co., Ltd.) and let to dry in air. Analysis of the LSV made on the GCE of 0.07 cm2 surface area shows a current density of 25 mA/cm^2 At 50 mV overpotential, while it reached 76 mA/cm^2 at 100 mV overpotential.

Based on the above electrode loading, the Pt content was calculated as below:

86µ g * 0.054 (wt. percentage of pt collected from ICP) = 4.67 µg pt / 0.07 cm^2 ~ 66.7 µg Pt/cm^2, ~ 3.4 e-7 mol pt/ cm^2

The mass activity will be;

At 50 mV overpotential = 25 mA/cm^2 /(0.067 mg/cm^2) = 373 mA/mg

At 100 mV overpotential = 76 mA/cm^2/(0.067 mg/cm^2) = 1,134 mA/mg

overpotential	PyPOP-Pt@G GCE preparation and ICP Pt loading of 5.4 wt%	Pt/C Reported in literature	Activity ratio (PyPOP-Pt@G/ Pt@C)	reference
50 mV	25 mA/cm^2 (3.4e-7 mol pt/ cm^2) **373 mA/mg pt**	**270 mA/mg pt**	1.38	[1]
100 mV	76mA/cm^2 (3.4e-7 mol pt/ cm^2) **1,134 mA/mgPt**	18.4 mA cm^{-2} (2.5 × 10^{-7} mol_{Pt} cm^{-2}) **377 mA /mg Pt**	3.56	[2]

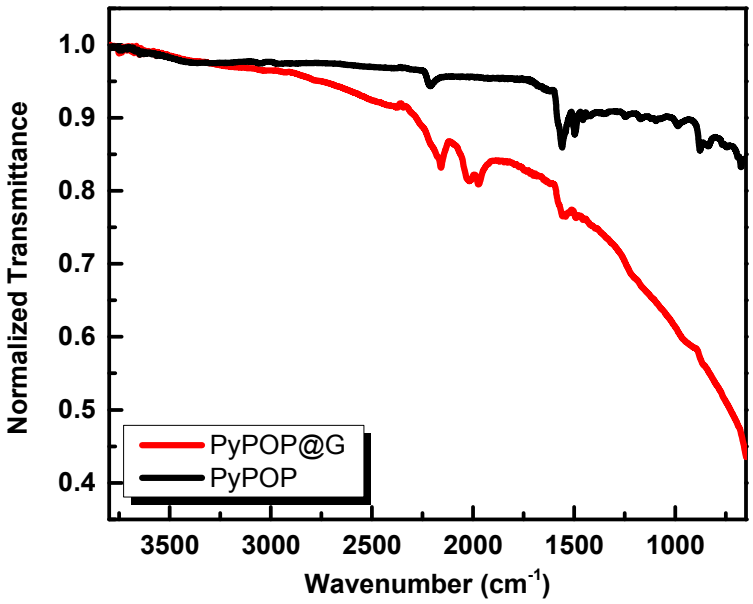


Figure S1. FTIR spectra for the composite PyPOP@G and the PyPOP.

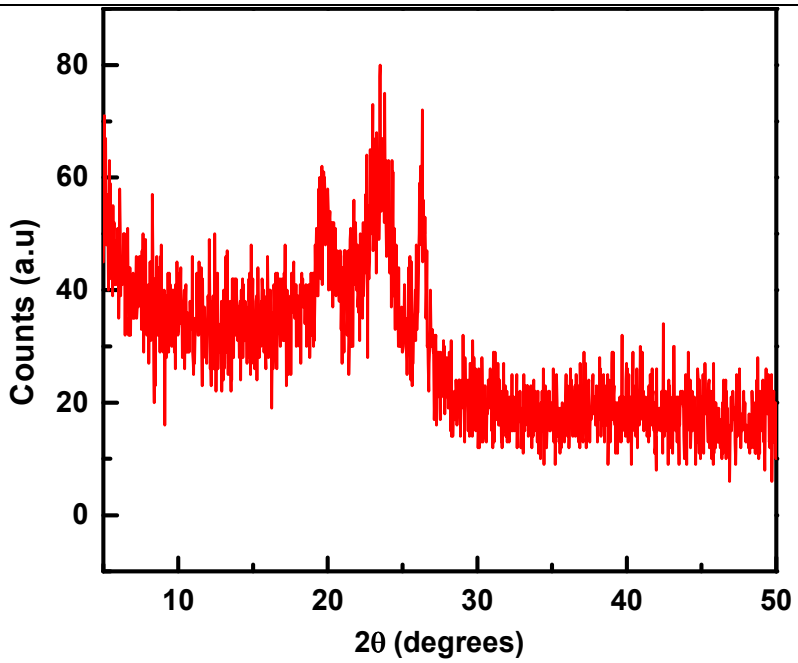


Figure S2. X-ray powder diffraction pattern conducted on the PyPOP-Pt@G after 100 seconds controlled potential electrolysis where Pt nanoparticles peaks expected at 2θ of 40 degrees and above were not observed in the pattern.[3]

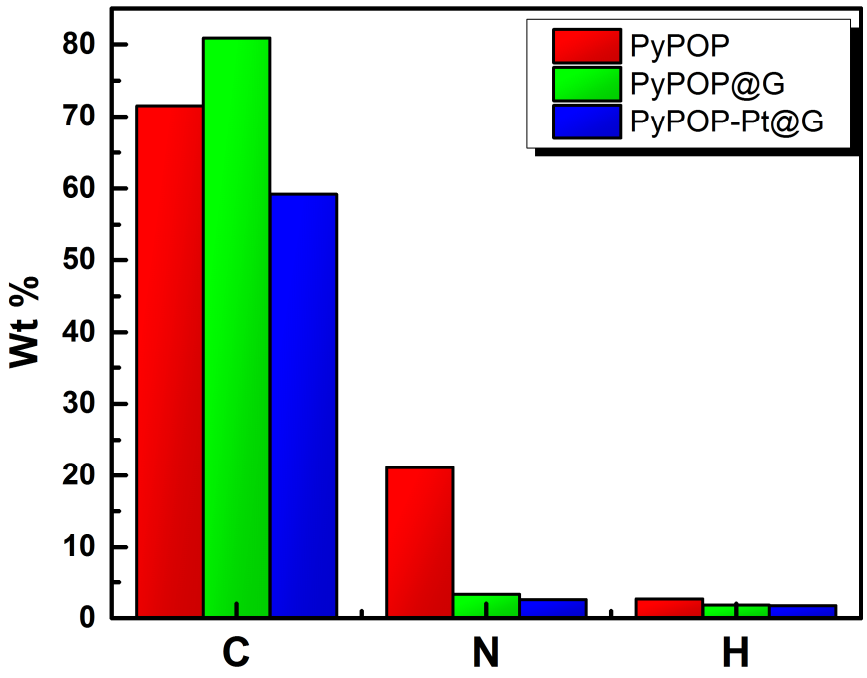
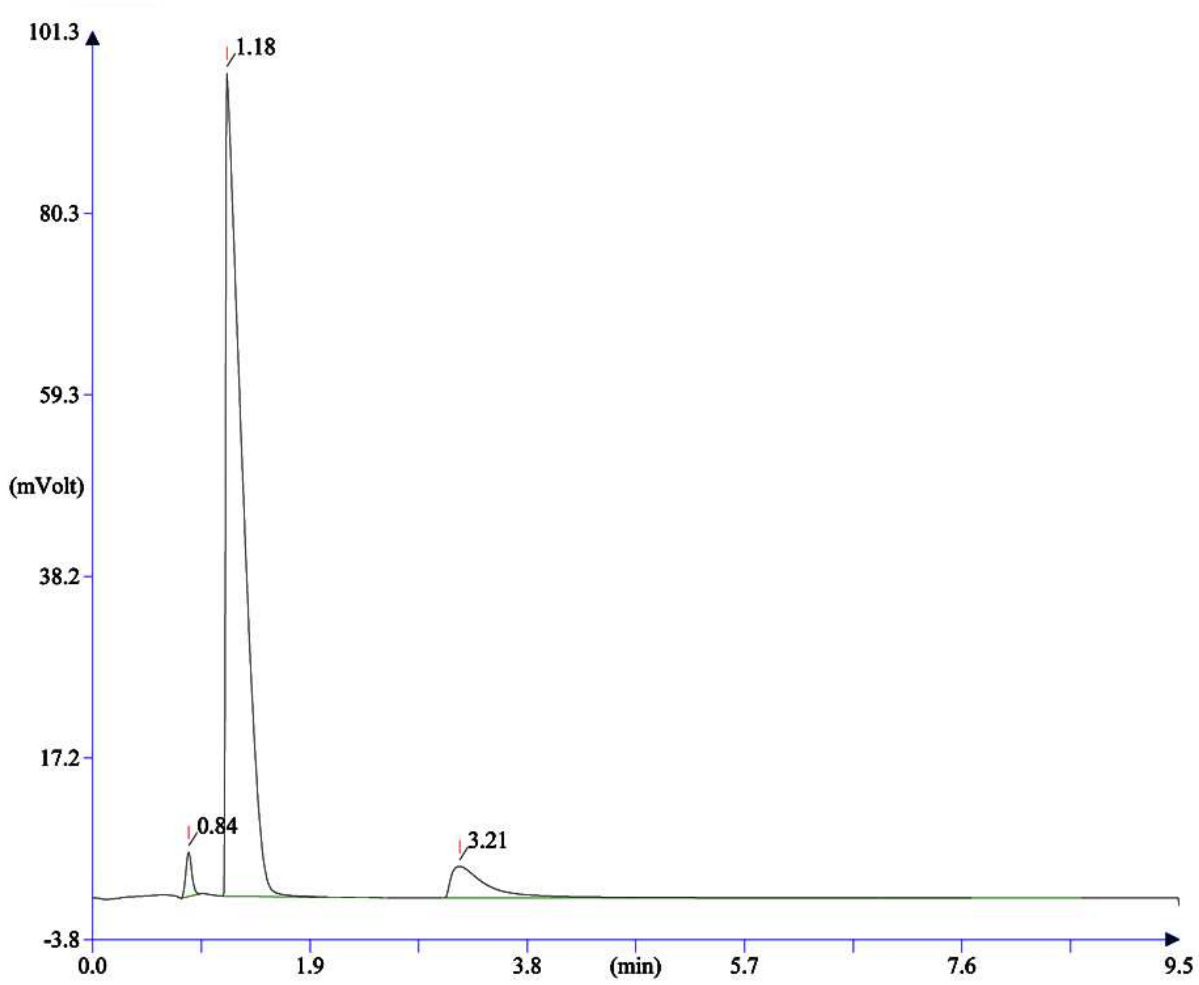
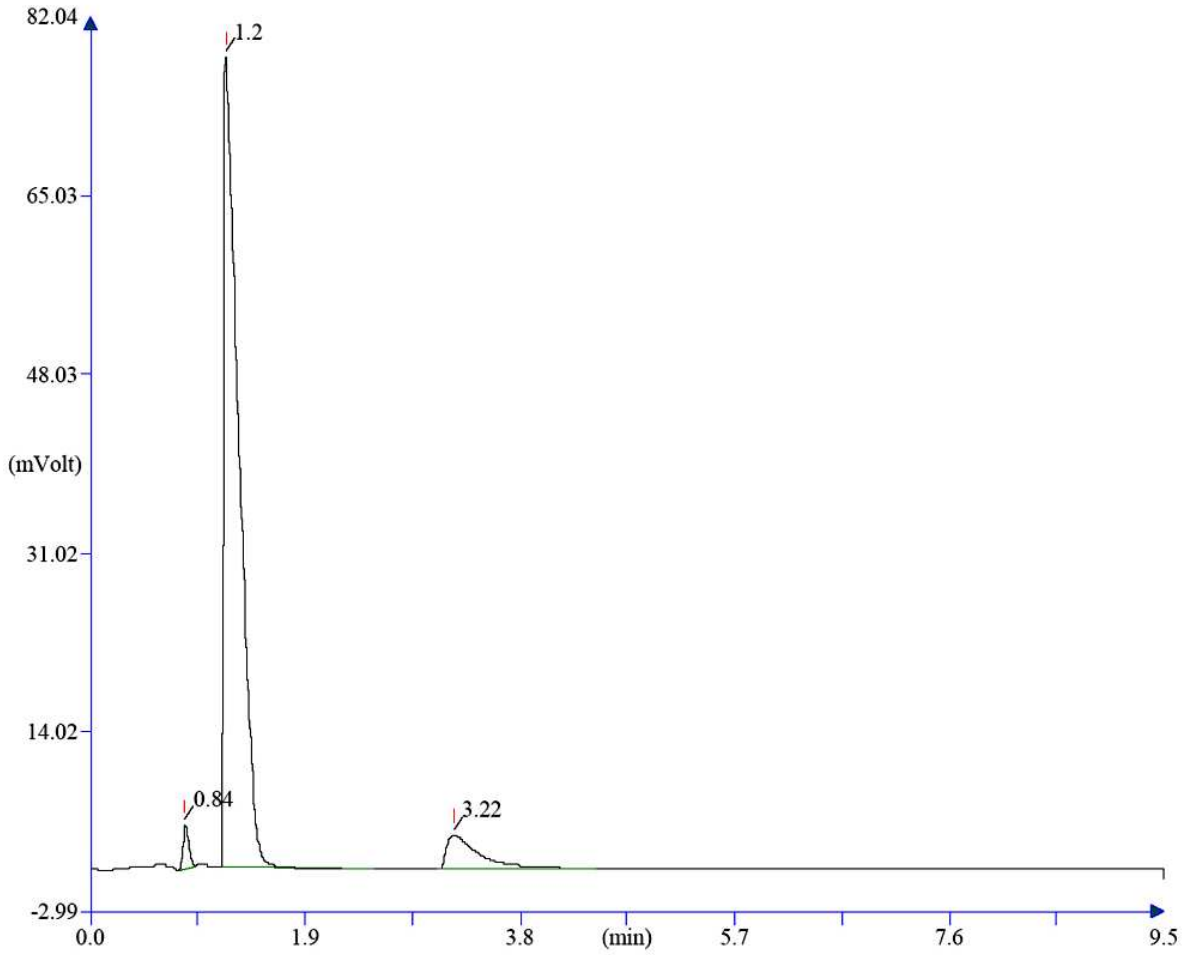


Figure S3. Plot of CHN elemental analysis ratios for the PyPOP, PyPOP@G and PyPOP-Pt@G



Element Name	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	3.3528	51	186697 mi	50.272820	.201309E+07
Carbon	80.3475	71	9385760 mi	1.000000	.490294E+07
Hydrogen	2.1515	193	818860 mi	11.461990	.156434E+08
Totals	85.8518		10391320		

Figure S4. CHN elemental analysis for the PyPOP@G



Element Name		Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	2.5754	51	147013	mi	46.070400	.205568E+07
Carbon	59.2380	72	6772948	mi	1.000000	.500402E+07
Hydrogen	1.7462	193	632483	mi	10.708510	.154241E+08
Totals	63.5595		7552444			

Figure S5. CHN elemental analysis for the PyPOP-Pt@G

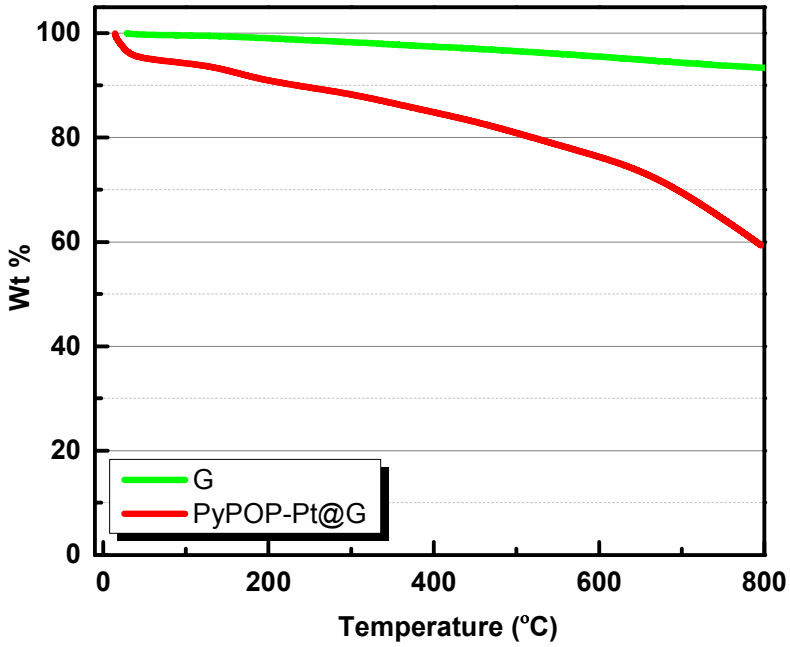


Figure S6. TGA analysis for the G and the PyPOP-Pt@G in N_2 atmosphere

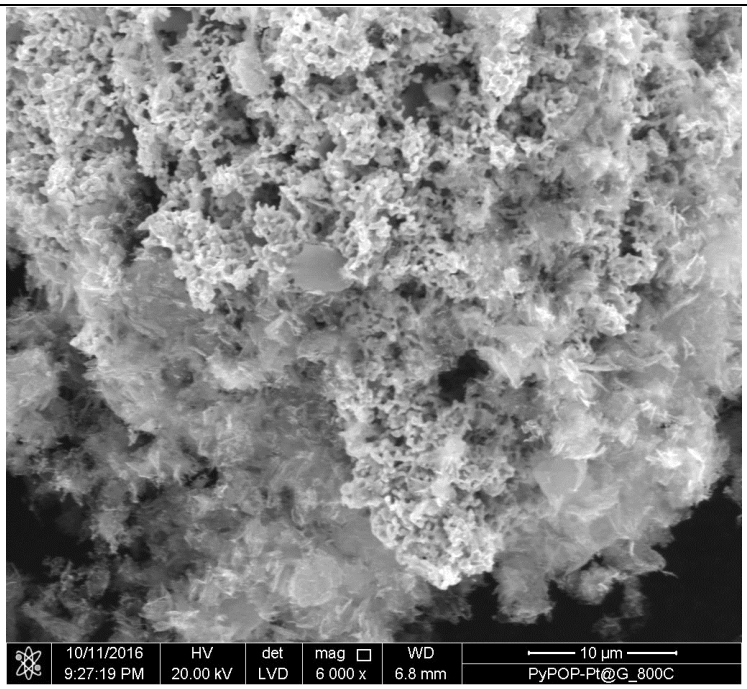


Figure S7. SEM image of the PyPOP-Pt@G composite after conducting the TGA analysis at 800C, showing graphene plates and microstructured Pt.

Table S1. EDX point analysis for the two distinct features of graphene plates and Pt structures in the SEM image above, for the PyPOP-Pt@G after pyrolysis in the TGA analysis at 800°C.

Element	*Weight %*		*Atomic %*	
	G plates	Pt structure	G plates	Pt structure
C K	54.98	3.98	81.61	20.04
O K	13.95	14.45	15.55	54.66
Pt M	31.07	81.57	2.84	25.3

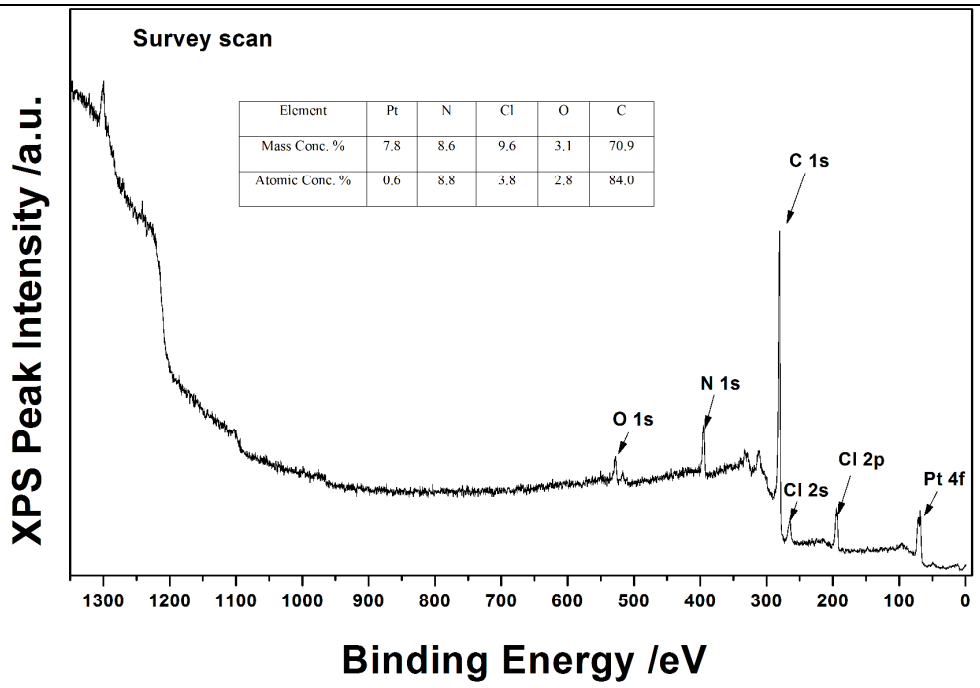


Figure S8. XPS survey spectrum of the PyPOP-Pt@G.

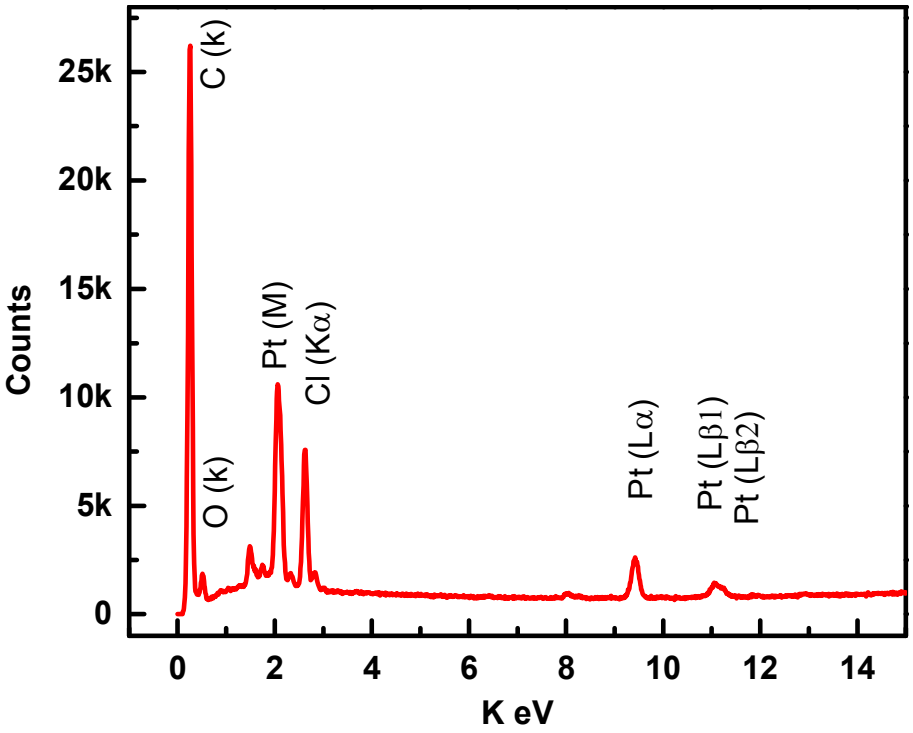


Figure S9. EDX elemental analysis spectrum for the PyPOP-Pt@G

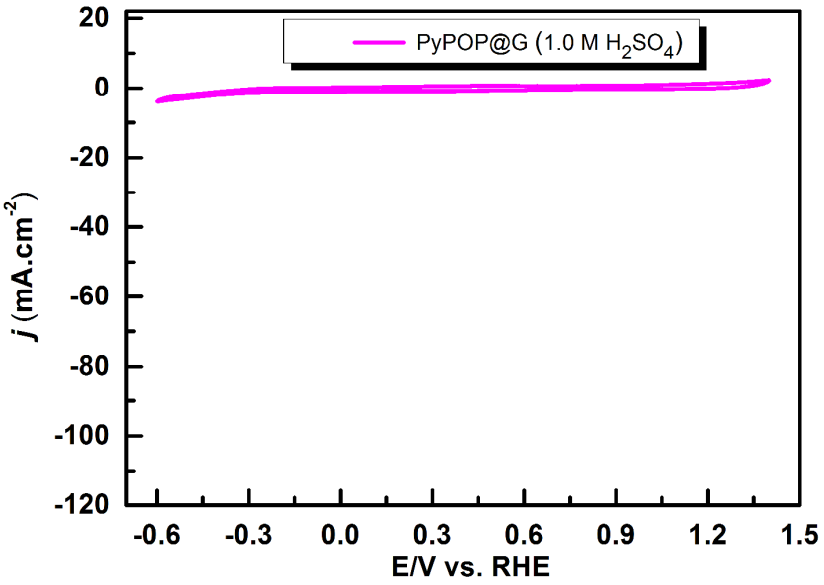


Figure S10. CV scan for the PyPOP@G in 1M H_2SO_4.

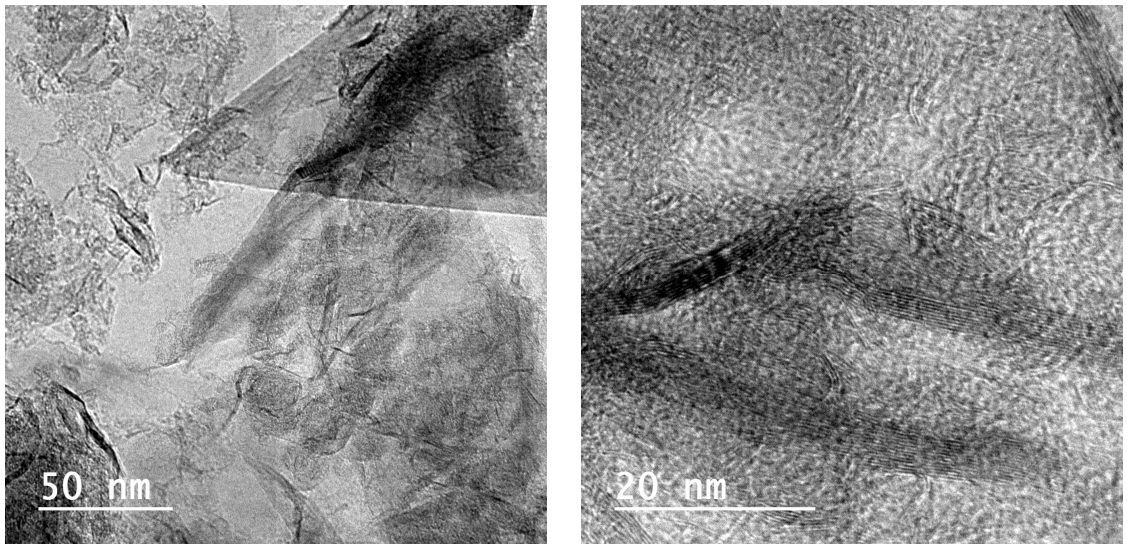


Figure S11. TEM images of the graphene support used in this study.

References

1. Cheng, N.; Stambula, S.; Wang, D.; Banis, M. N.; Liu, J.; Riese, A.; Xiao, B.; Li, R.; Sham, T.-K.; Liu, L.-M.; Botton, G. A.; Sun, X., *Nature Communications* **2016,** *7*, 13638.
2. Huan, T. N.; Jane, R. T.; Benayad, A.; Guetaz, L.; Tran, P. D.; Artero, V., *Energy & Environmental Science* **2016,** *9*, 940-947.
3. Long, N. V.; Thi, C. M.; Nogami, M.; Ohtaki, M., *New J. Chem.* **2012,** *36*, 1320-1334.