Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Ru nanoparticles supported on alginate-derived graphene for the hydrogen evolution reaction

Laura Mallón,[a, c] Christian Cerezo-Navarrete,[b] Nuria Romero,[a] Marta Puche, [b] Jordi García-Antón,[a] Roger Bofill,*[a] Karine Philippot,*[c] Luis M. Martínez-Prieto*[b] and Xavier Sala*[a]

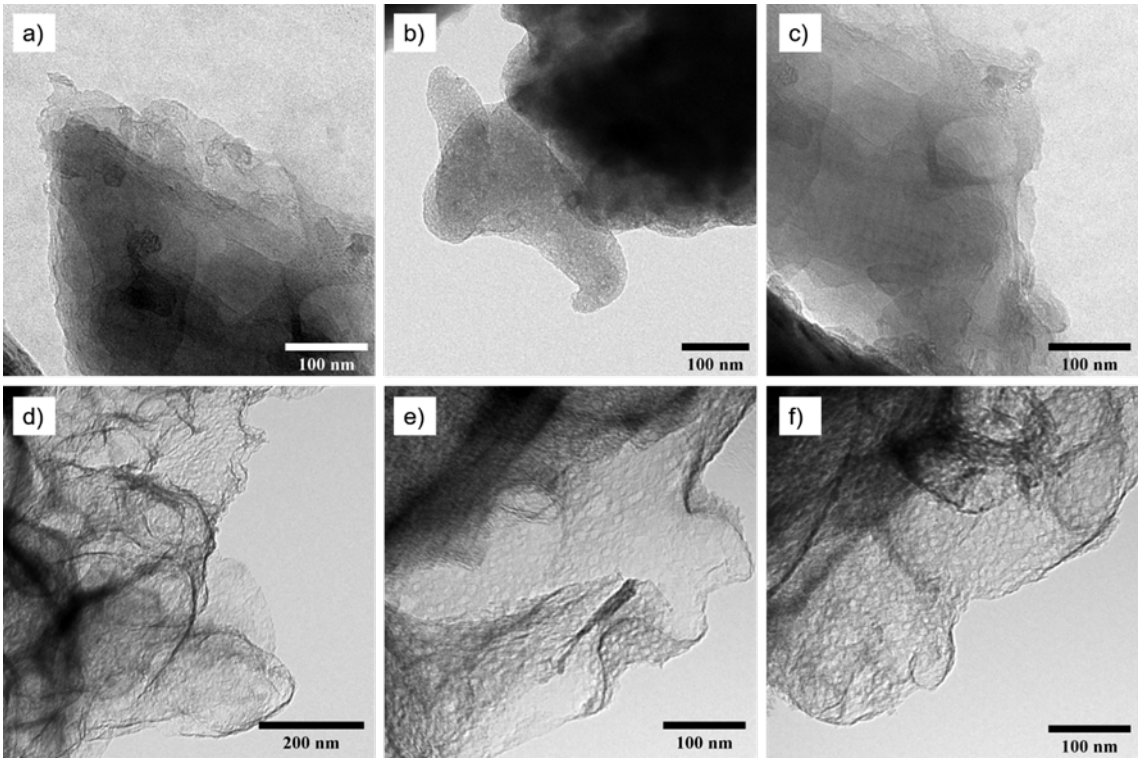

Figure S1. TEM images of **G** (a-c) and **P-G** (d-f) supports.

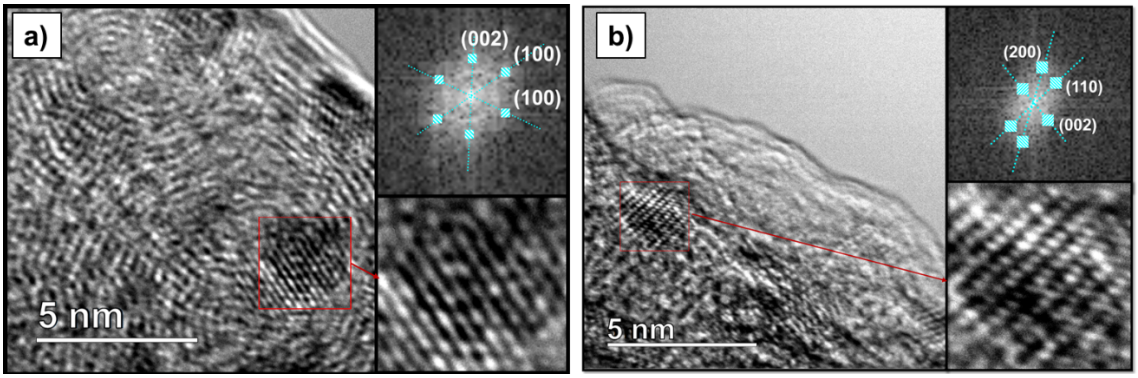

Figure S2. HRTEM images, chosen expanded zone and corresponding Fourier Transform Analysis with planar reflections for **Ru/P-G** (a) and **Ru/G** (b).

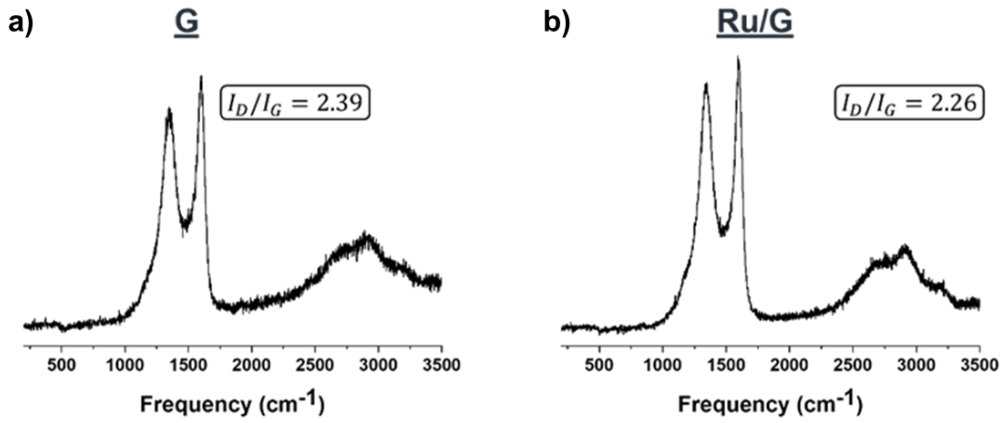

Figure S3. Raman spectrum and I_D/I_G ratio of **G** (a) and **Ru/G** (b).

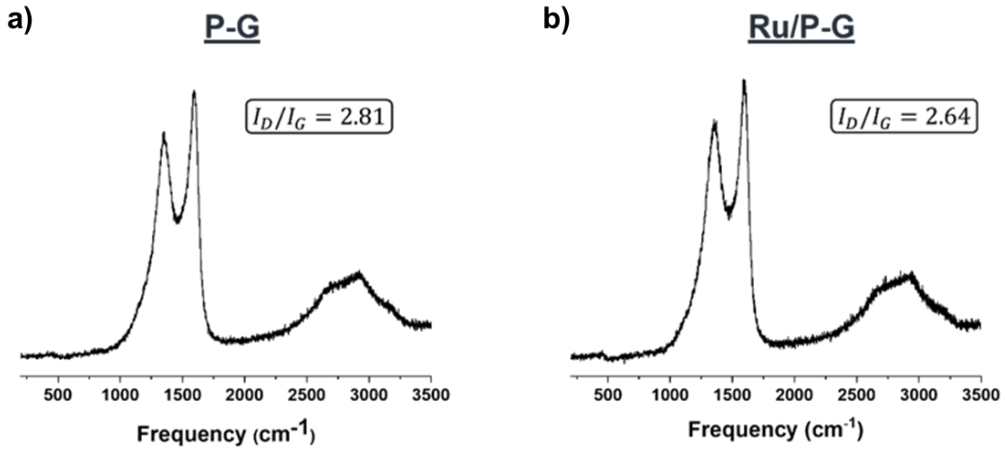

Figure S4. Raman spectrum and I_D/I_G ratio of **P-G** (a) and **Ru/P-G** (b).

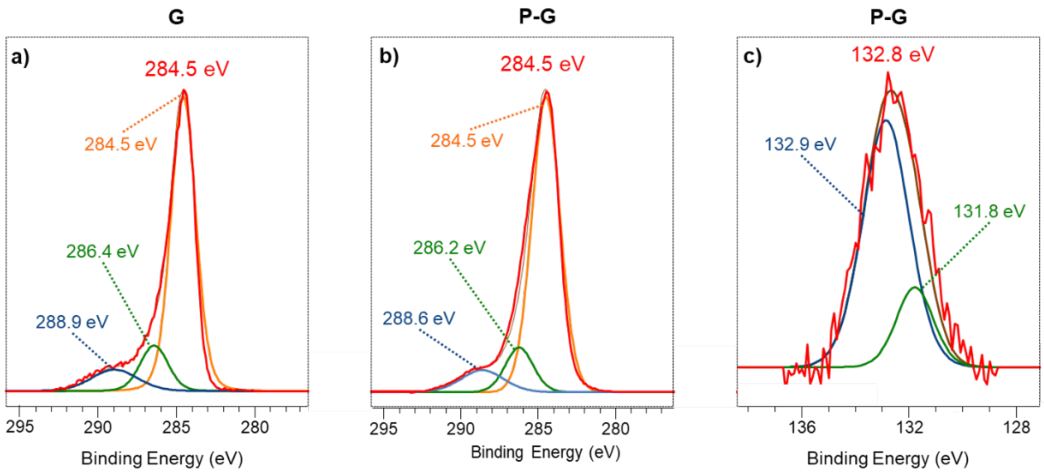

Figure S5. XPS signal of the C 1s bands of **G** (a) and **P-G** (b), and the P 2p band of **P-G** (c). Deconvoluted peak component analysis is shown for each case (baseline as red curve.

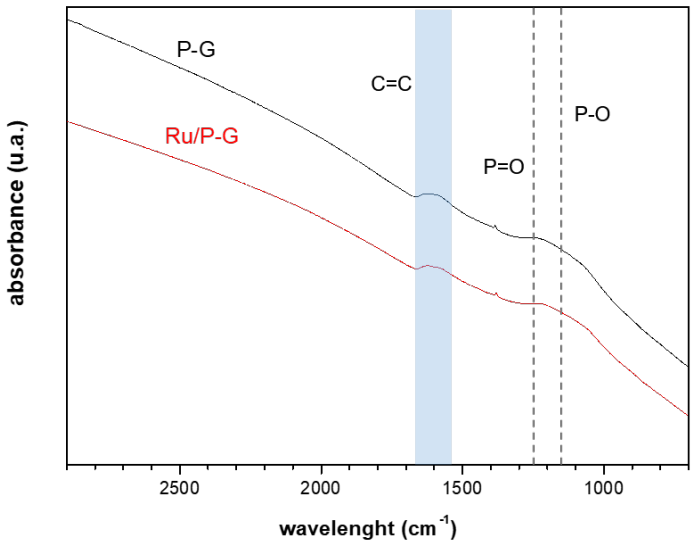

Figure S6 FT-IR spectra of **P-G** (top; black) and **Ru/P-G** (bottom; red).

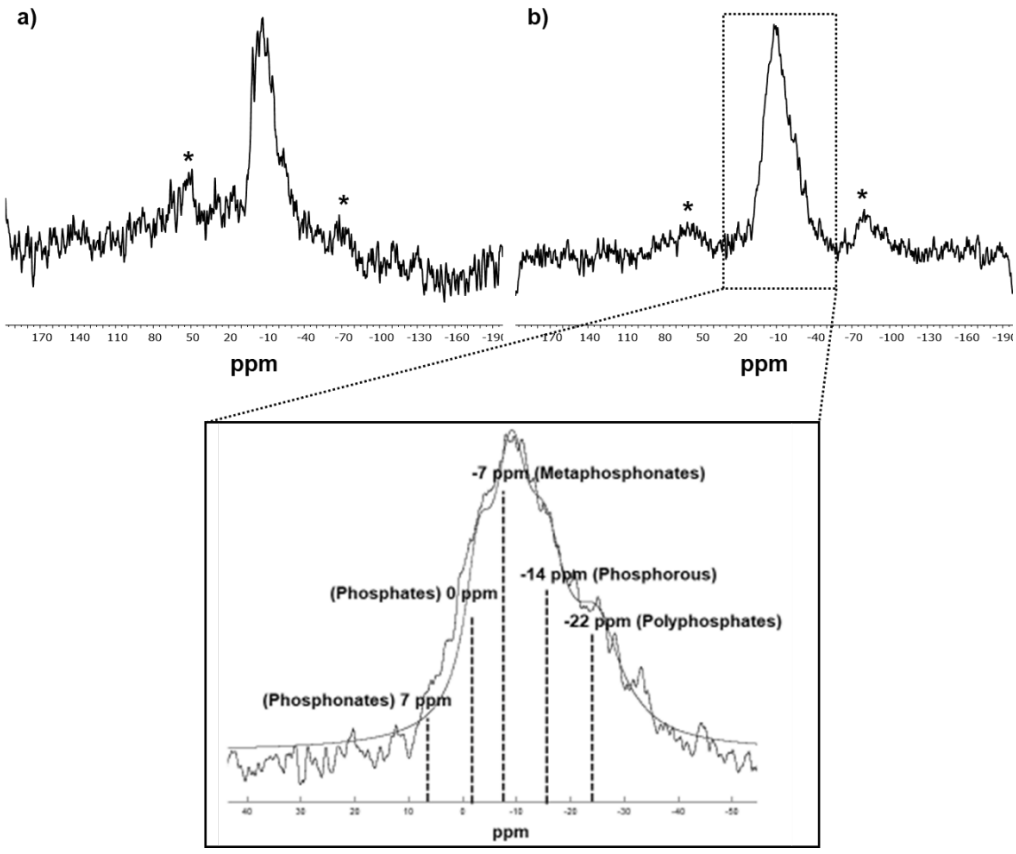

Figure S7. ^{31}P MAS NMR spectra of a) **P-G** and b) **Ru/P-G**. Asterisks (*) mark the spinning side bands. The positions of phosphonate (7 ppm), phosphates (0 ppm), metaphosphonates (-7 ppm), phosphorous (-14 ppm) and polyphosphate (-22 ppm) are indicated on the zoomed part.

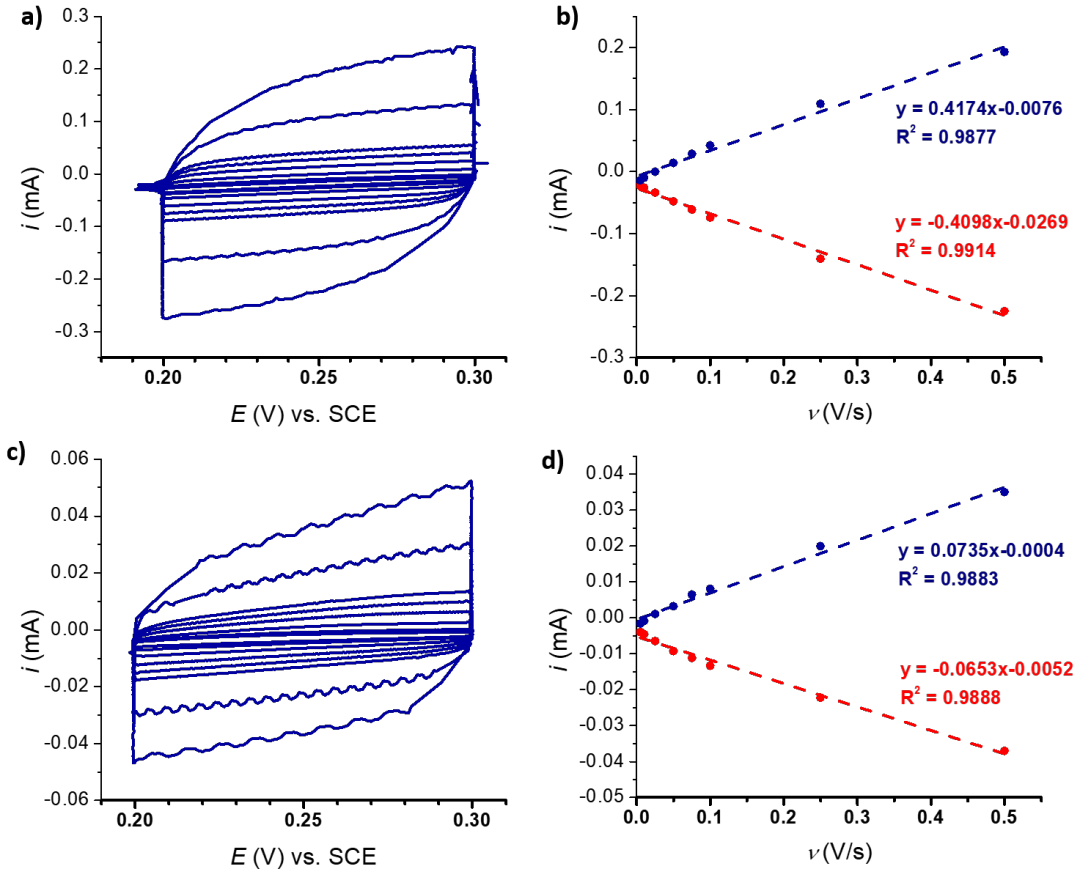

Figure S8. Representative multi CV experiment at different scan rates for C_{DL} determination of **Ru/G** (a) and **Ru/P-G** (c)**.** Plot of current values at 0.25 V (vs. SCE) for the different scan rates in 1 M H_2SO_4 for **Ru/G** (b) and **Ru/P-G** (d).

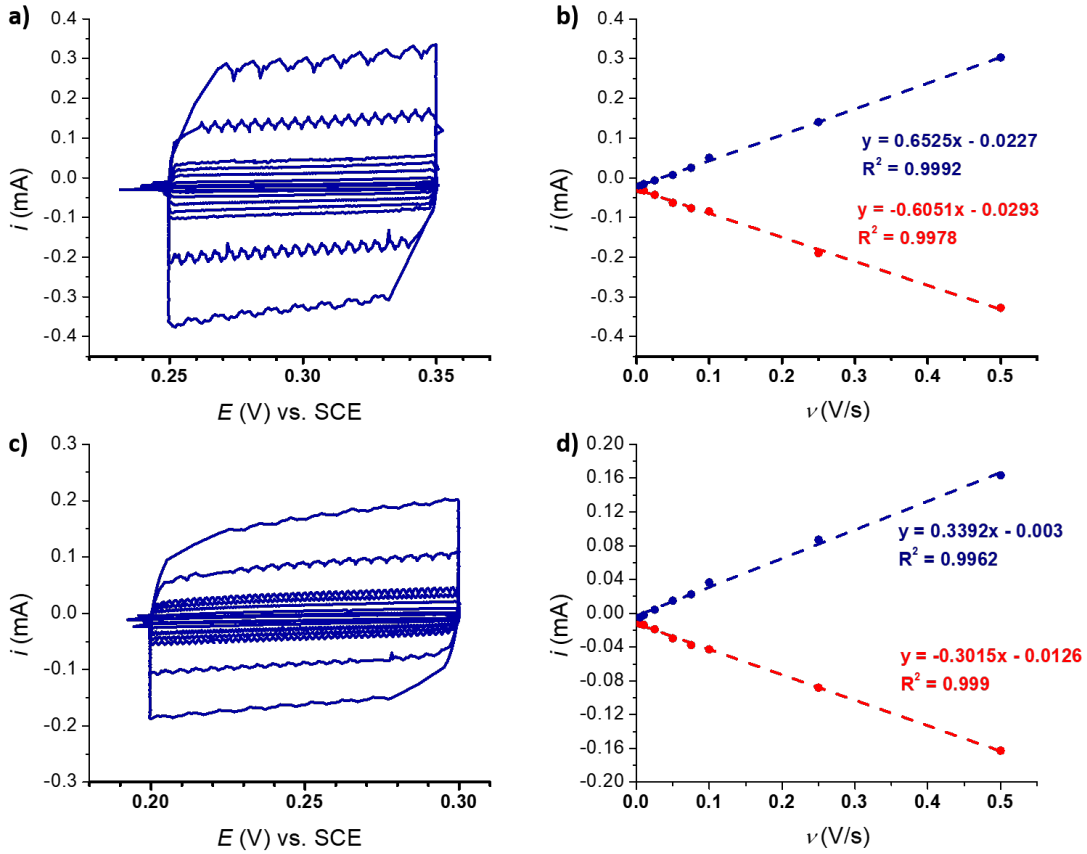

Figure S9. Representative multi CV experiment at different scan rates for C_{DL} determination of **Ru/G-r** (a) and **Ru/P-G-r** (c). Plot of current values at 0.30 V and 0.25 V (*vs.* SCE) for the different scan rates in 1 M H_2SO_4 for **Ru/G-r** (b) and **Ru/P-G-r** (d), respectively.

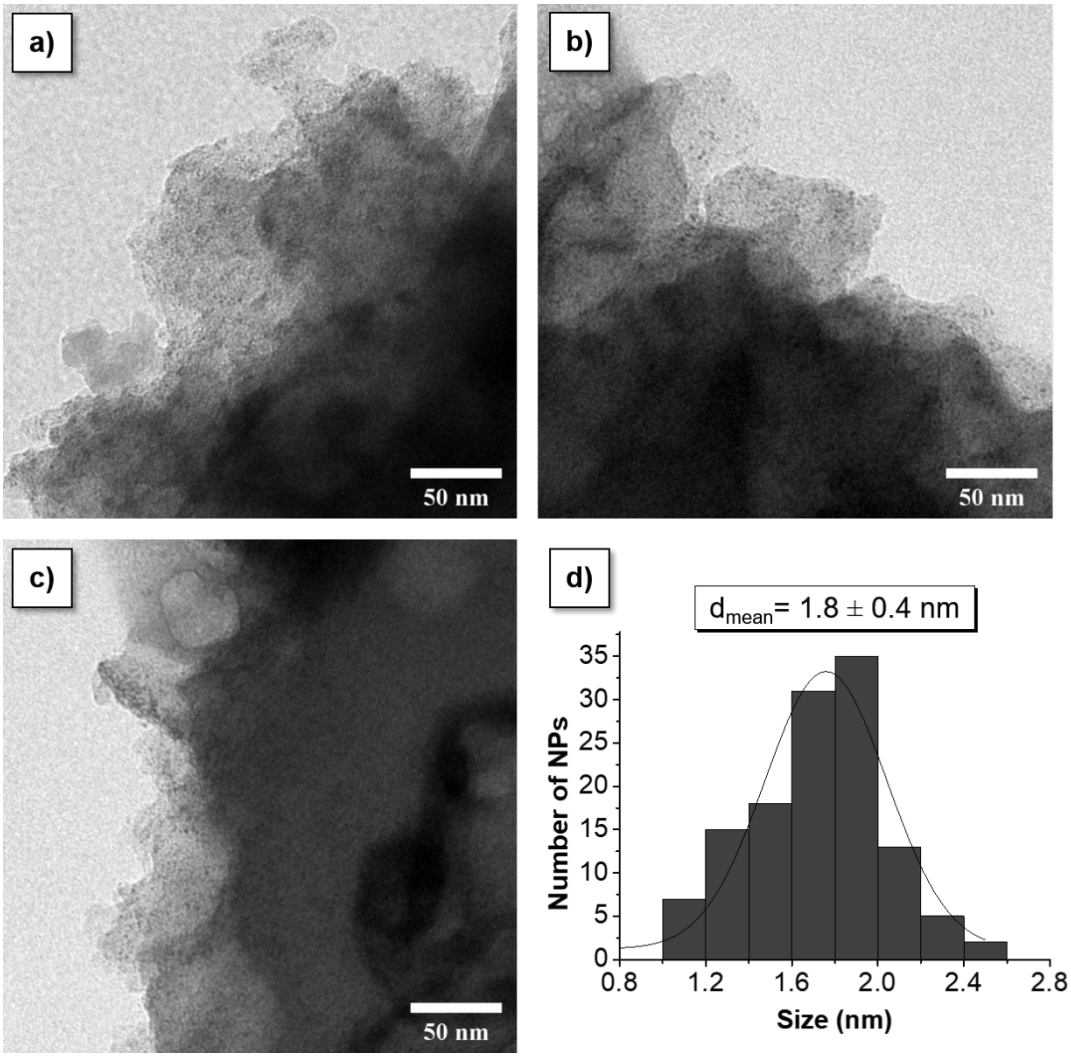

Figure S10. TEM images and corresponding histogram of **Ru/G** after 2 h under catalytic conditions (j = -10 mA/cm^2).

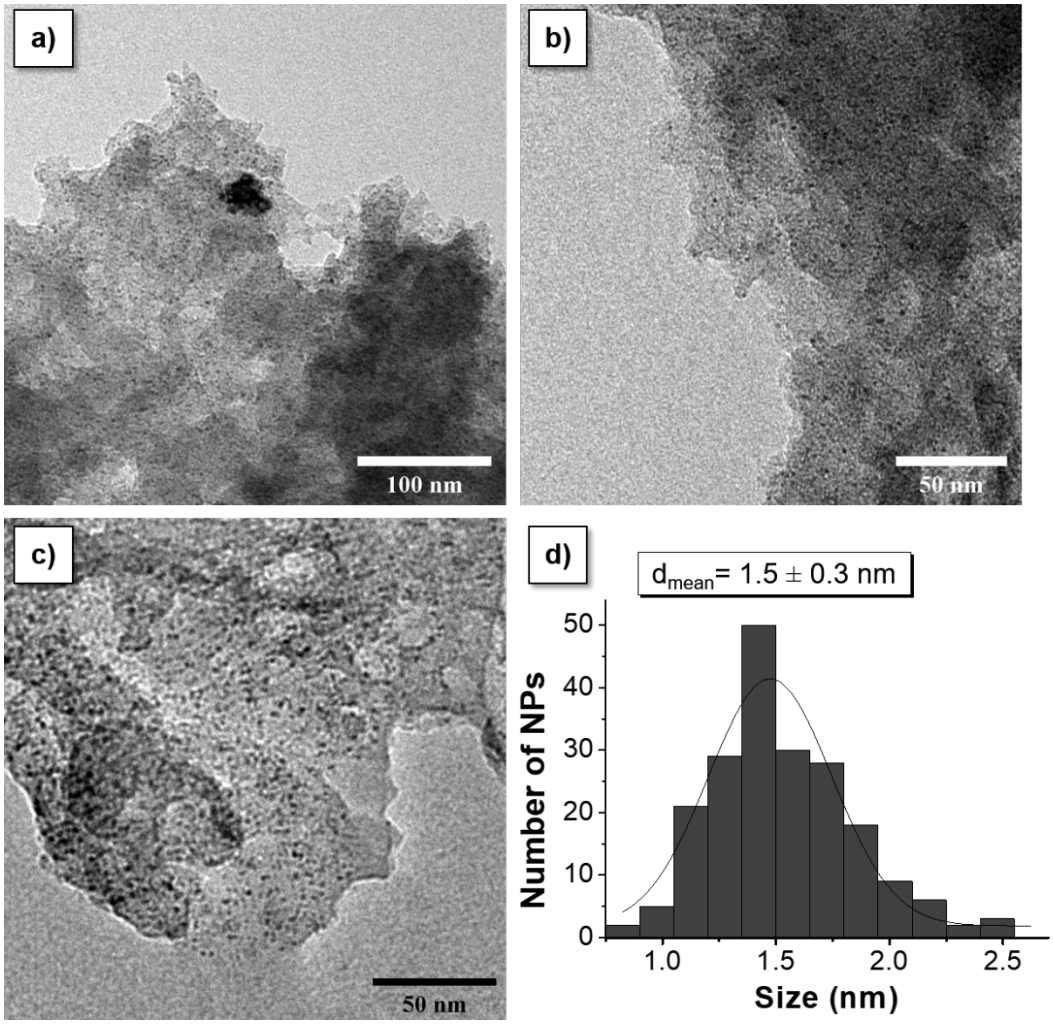

Figure S11. TEM images and corresponding histogram of **Ru/P-G** after 2 h under catalytic conditions (j = -10 mA/cm^2).

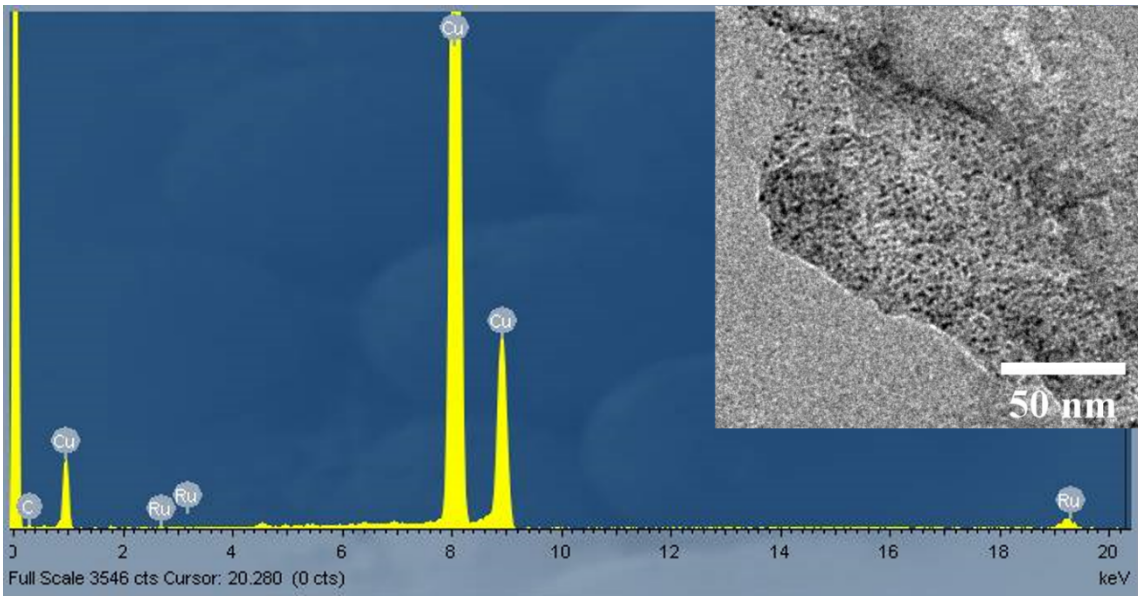

Figure S12. TEM/EDX analysis of **Ru/P-G** after 2 h under catalytic conditions (j = -10 mA/cm^2).

Table S1. Comparison of the most relevant graphene-derived and Ru/graphene-based HER nanoelectrocatalysts under acidic conditions. Parameters: mean diameter (Ø), onset overpotential (η_0, mV), overpotential at $|j|$ =10 mA·cm^{-2} (η_{10}, mV), Tafel slope (b, mV·dec^{-1}), exchange current density ($|j_0|$, mA·cm^{-2}), specific current density ($|j_S|$, mA·cm^{-2}) and turnover frequency (TOF, s^{-1}). Unless otherwise stated, electrolyte is 0.5 M H_2SO_4.

Entry	Catalyst	Ø (nm)	η_0 (mV)	η_{10} (mV)	b (mV·dec^{-1})	$\|j_0\|$ (mA·cm^{-2})	Ref.
1	GCE-S-GNs-1000-CB-Ru	30	≈ 60	80	61 (Tafel) 71 (EIS)	0.541 0.431	1
2	Ru-GLC	2-5	3	35	46	-	2
3	Ru_2P/RGO	<7	≈ 0	22	29	2.2	3
4	Ru@GnP	2	≈ 0	13	30	-	4
5	N-G	-	≈ 250	490	116	-	5
6	P-G	-	≈ 300	550	133	-	5
7	N,P-G	-	≈ 240	420	91	0.00024	5
8	N,B-CN	-	≈ 410	710	198	-	6
9	N-CN	-	≈ 400	620	159	-	6
10	N,P-CN	-	≈ 340	550	139	-	6
11	N,S-CN	-	≈ 100	290	77	-	6
12	N-G	-	499	-	405	86	7
13	N,P-G	-	399	-	565	265	7
14	P-G	-	536	-	348	76	7
15	P,N-G	-	247	380	126	21	7
16	VG	-	≈ 375	-	158	-	8
17	N-VG	-	≈ 200	290	121	-	8
18	Ru/NG-750	3-7	≈ 0	53	44	-	9
19	Ru@CN	2.37	≈ 70	126	-	-	10
20	Ru-NGA	3.5	≈ 15	55	32	-	11
21	Ru@NC	2.1	≈ 10	62	40	-	12
22	Ru/G-r	1.9	≈ 0	29	48	2.50	This work
23	Ru/P-G-r	1.5	≈ 0	15	49	4.97	This work

Legend: GCE-S-GNs-1000=glassy carbon modified sulfur-doped graphene nanosheets heat treated at 1000 °C, GLC=graphene-layered carbon, RGO=reduced graphene oxide, GnP=graphene nanoplatelets. N-G=N-doped graphene; P-G=P-doped graphene; N,P-G=N,P-doped graphene; N,B-CN=N,B-doped carbon nanosheets, N-CN=N-doped carbon nanosheets, N,P-CN=N,P-doped carbon nanosheets, N,s-CN=N,S-doped carbon nanosheets, P,N-G=P,N-doped graphene, VG=vertical graphene, N-VG=N-doped vertical graphene, Ru/NG-750= Ru nanoclusters on N-doped graphene prepared at 750 °C, Ru@CN=Ru NPs over N-doped carbon, Ru-NGA= Ru-modified N-doped graphene aerogel, Ru@NC= Ru NPs embedded in N-doped carbon.

References

[1] R. K. Shervedani and A. Amini, *Carbon* **2015**, 93, 762-773.

[2] Z. Chen, J. Lu, Y. Ai, Y. Ji, T. Adschiri and L. Wan, *ACS Appl. Mater. Interfaces* **2016**, 8, 35132-35137.

[3] T. Liu, S. Wang, Q. Zhang, L. Chen, W. Hu and C.M. Li, *Chem. Commun.* **2018**, 54, 3343-3346.

[4] F. Li, G.F. Han, H.J. Noh, I. Ahmad, I.Y. Jeon and J.B. Baek, *Adv. Mater.* **2018**, 30, 1803676.

[5] Y. Zheng, Y. Jiao, L.H. Li, T. Xing, Y. Chen, M. Jaroniec and S.Z. Qiao, *ACS Nano* **2014**, 8, 5, 5290-5296.

[6] K. Qu, Y. Zheng, X. Zhang, K. Davey, S. Dai and S.Z. Qiao, *ACS Nano* **2017**, 11, 7293-7300.

[7] Y.H. Hung, D. Dutta, Y.J. Tseng, J.K. Chang, A.J. Bhattacharyya and C.Y. Su, *J. Phys. Chem. C* **2019**, 123, 22202-22211.

[8] Y. Li, C. Ai, S. Deng, Y. Wang, X. Tong, X. Wang, X. Xia and J. Tu, *Materials Research Bulletin* **2021**, 134, 111094.

[9] R. Ye, Y. Liu, Z. Peng, T. Wang, A.S. Jalilov, B.I. Yakobson, S.H. Wei and J.M. Tour, *ACS Appl. Mater. Interfaces* **2017**, 9, 3785-3791.

[10] J. Wang, Z. Wei, S. Mao, H. Li and Y. Wang, *Energy Environ. Sci.* **2018**, 11, 800–806.

[11] Y. Shi, W. Dai, M. Wang, Y. Xing, X. Xia and W. Chen, *Chem. Res. Chinese Universities*, **2020**, 36 (4), 709-714.

[12] B. Zheng, L. Ma, B. Li, D. Chen, X. Li, J. He, J. Xie, M. Robert and T.C. Lau, *Catal. Sci. Technol.* **2020**, 10, 4405-4411.