Supporting Information

Shape-Selective Rhodium Nano-Huddles on DNA for High Efficient Hydrogen Evolution Reaction in Acidic Medium

Sangeetha Kumaravel,[†‡] Kannimuthu Karthick,[†‡] Selvasundarasekar Sam Sankar,[†‡] Arun Karmakar[†‡] and Subrata Kundu[†‡*]

[†]*Electrochemical Process Engineering (EPE), CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630003, Tamil Nadu, India.*

[‡] *Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.*

*To whom correspondence should be addressed, *E-mail:* skundu@cecri.res.in *and* kundu.subrata@gmail.com, Tel: +91 4565-241487.

This file contains pages from S1 to S16, where the detailed, reagents and instruments used in the study, figures and Tables corresponding to Rh/DNA has been given.

Number of Pages: 16

Number of Figures: 10

Number of Tables: 03

Reagents and Instruments used

Rhodium chloride ($RhCl_3.H_2O$) and Sodium borohydride ($NaBH_4$) was purchased from Sigma-Aldrich. The Double stranded Deoxyribonucleic acid (DNA) from Herring Testes with a base pair of around 50 k was obtained from Sigma-Aldrich (99%) and used as received. SCE reference electrodes, Pt-foil were purchased from CH Instruments pvt. Ltd. The entire synthesis and the EC studies were performed in DI water. By varied DNA concentration, the two set of Rh/DNA-1 and Rh/DNA-2 was characterized using the techniques such as XRD, UV-Vis, FT-IR, TEM, HR-TEM, EDS, HAADF, and XPS analysis. The Fourier Transform Infrared (FT-IR) spectroscopy analysis carried in the model Nexus 670 (FTIR), Centaurms 10X (Microscope) with the spectral range 4,000 to 400 cm^{-1} with a MCT-B detector. The UV-Visible (UV-Vis) absorption spectrum was recorded in a Unico (model 4802) UV-Vis-NIR spectrophotometer equipped with a 1 cm quartz cuvette holder for liquid samples. The X-ray diffraction (XRD) analysis was carried using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD) with Cu K_α radiation (λ = 0.154178 nm) with a scanning rate of 0.020 s^{-1} in the 2θ range 10-80°. Scanning Electron Microscopy (SEM) analysis was carried with a Hitachi, Japan make model S-3000H instrument having magnification 30X to 300 KX with the accelerating voltage ~ 0.3 to 30 kV. The transmission electron microscopy (TEM) analysis was done with a Tecnai model TEM instrument (TecnaiTM G2 F20, FEI) with an accelerating voltage of 200 KV. The morphological studies and the HAADF color mapping of both the electrocatalyst was carried in HR-TEM, (TecnaiTM G2TF20) working at an accelerating voltage of 200 kV. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was done with the HR-TEM with a separate EDS detector (INCA) connected to that instrument. The X-ray photoelectron spectroscopic (XPS) analysis was done to check the state of elements present in the outermost part of materials and analysed by using Theta Probe AR-XPS System, Thermo Fisher Scientific (U.K).

Preparation procedure for pure Rh NPs

For comparison study, we have prepared pure Rh NPs by using same wet-chemical approach. At first, the 5 ml of 0.1 M $RhCl_3{\cdot}H_2O$ solution was taken with 10 mL of DI water and further reduced with 1 ml of 0.1 M $NaBH_4$ (ice-cold condition). The formed Rh NPs gets settle-down within a short time after synthesis where collected and centrifuged thoroughly to remove the excess of $NaBH_4$ if any. Then the collected mass was kept for drying overnight and the same were used in the electrocatalytic studies.

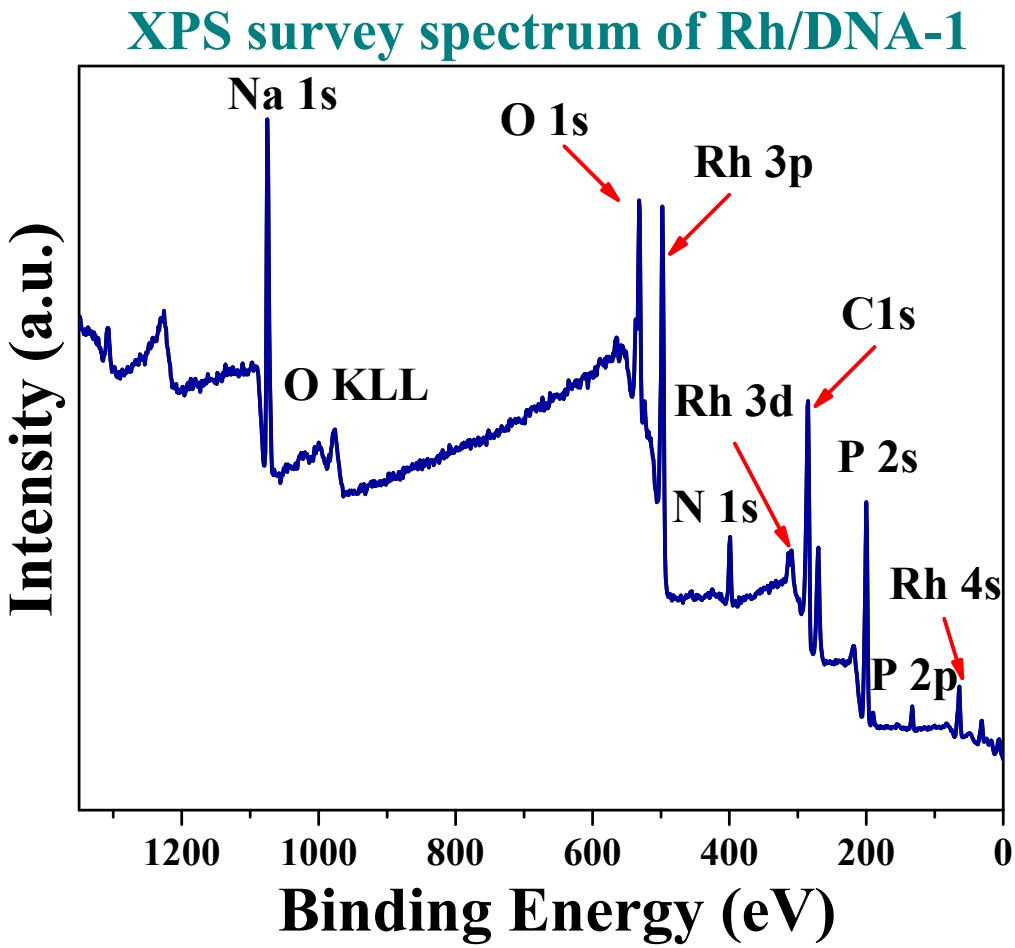

Figure S1. X-ray photoelectron (XPS) survey spectrum of Rh/DNA-1.

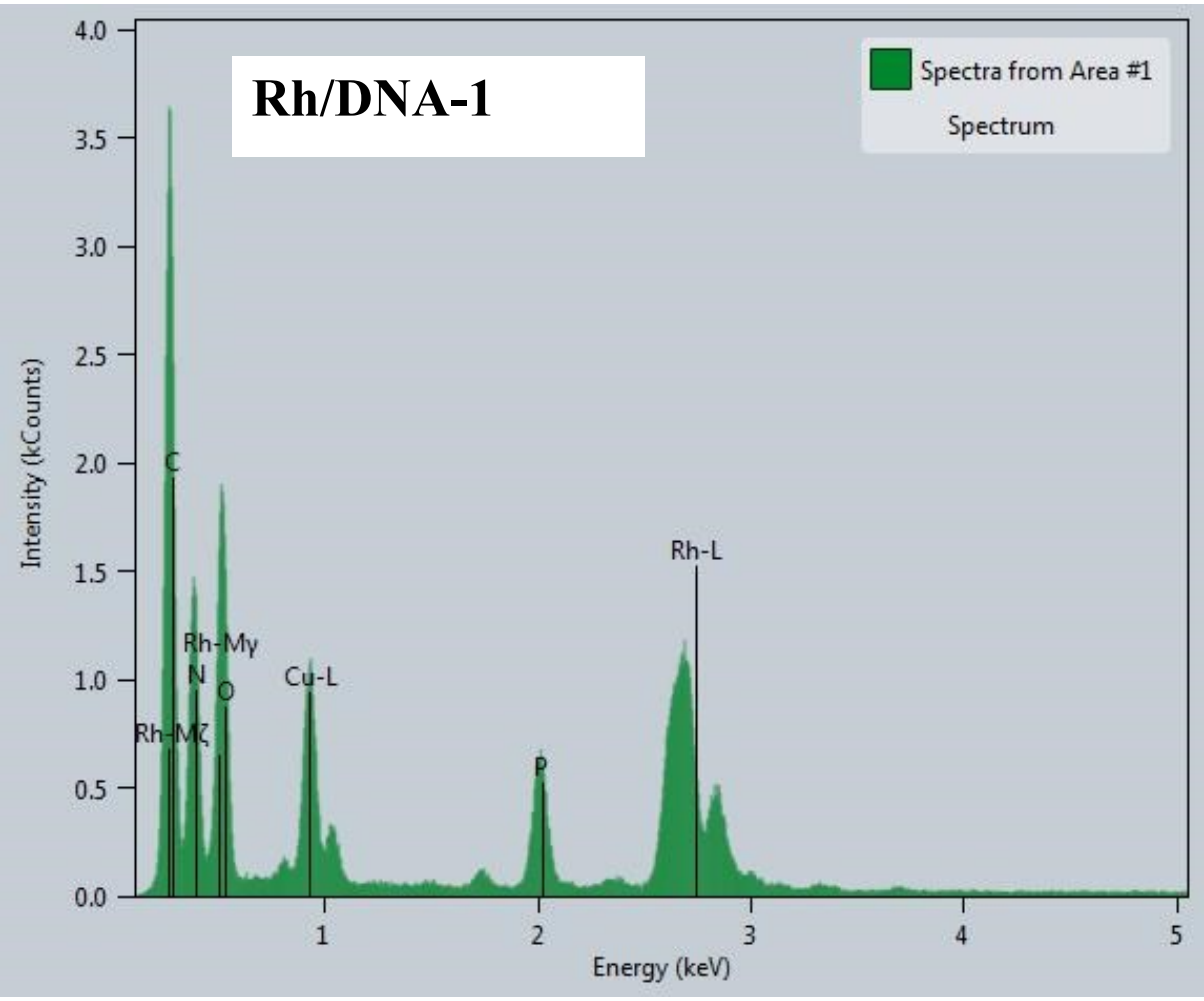

Figure S2. Energy dispersive X-ray spectrum of Rh/DNA-1 nano-huddles shows the elemental presence of Rh, O, C, N and P.

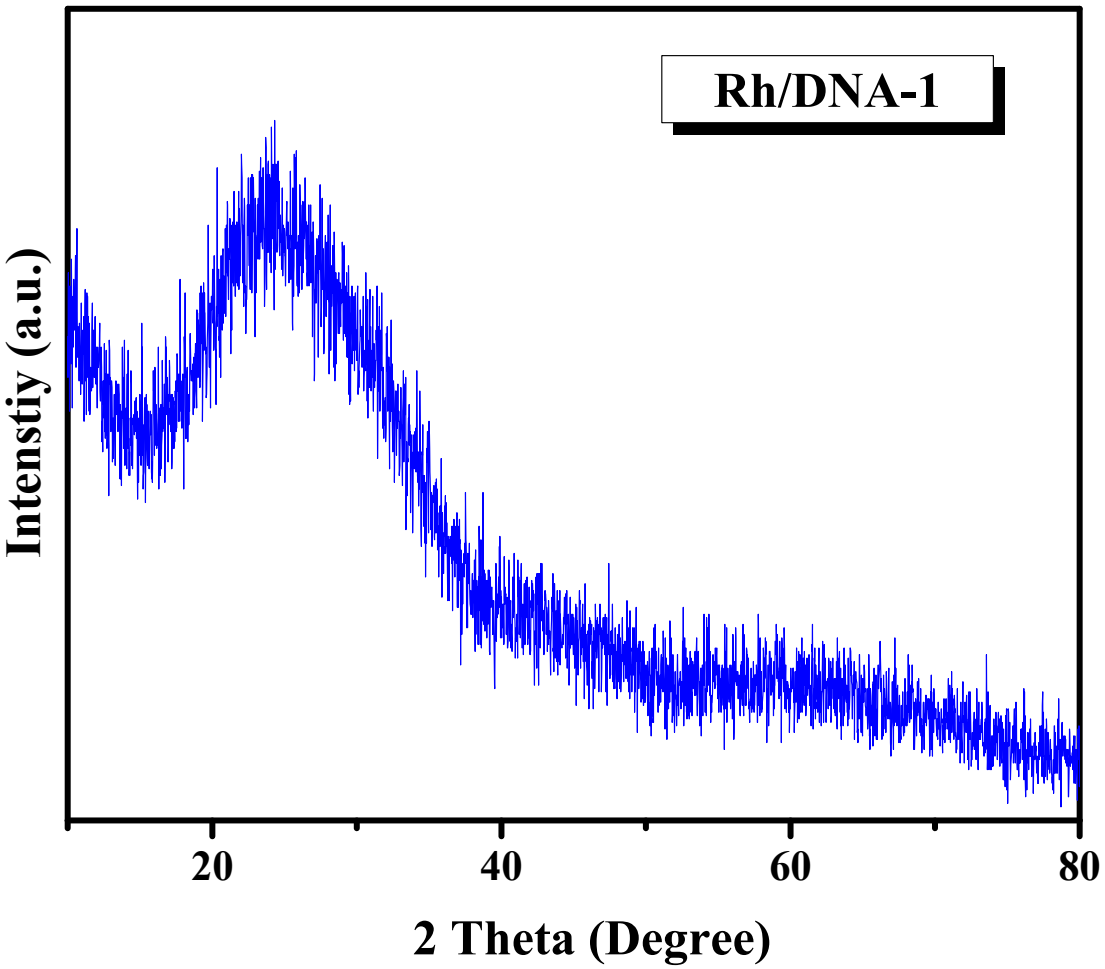

Figure S3. XRD pattern for Rh/DNA-1 nano-huddles.

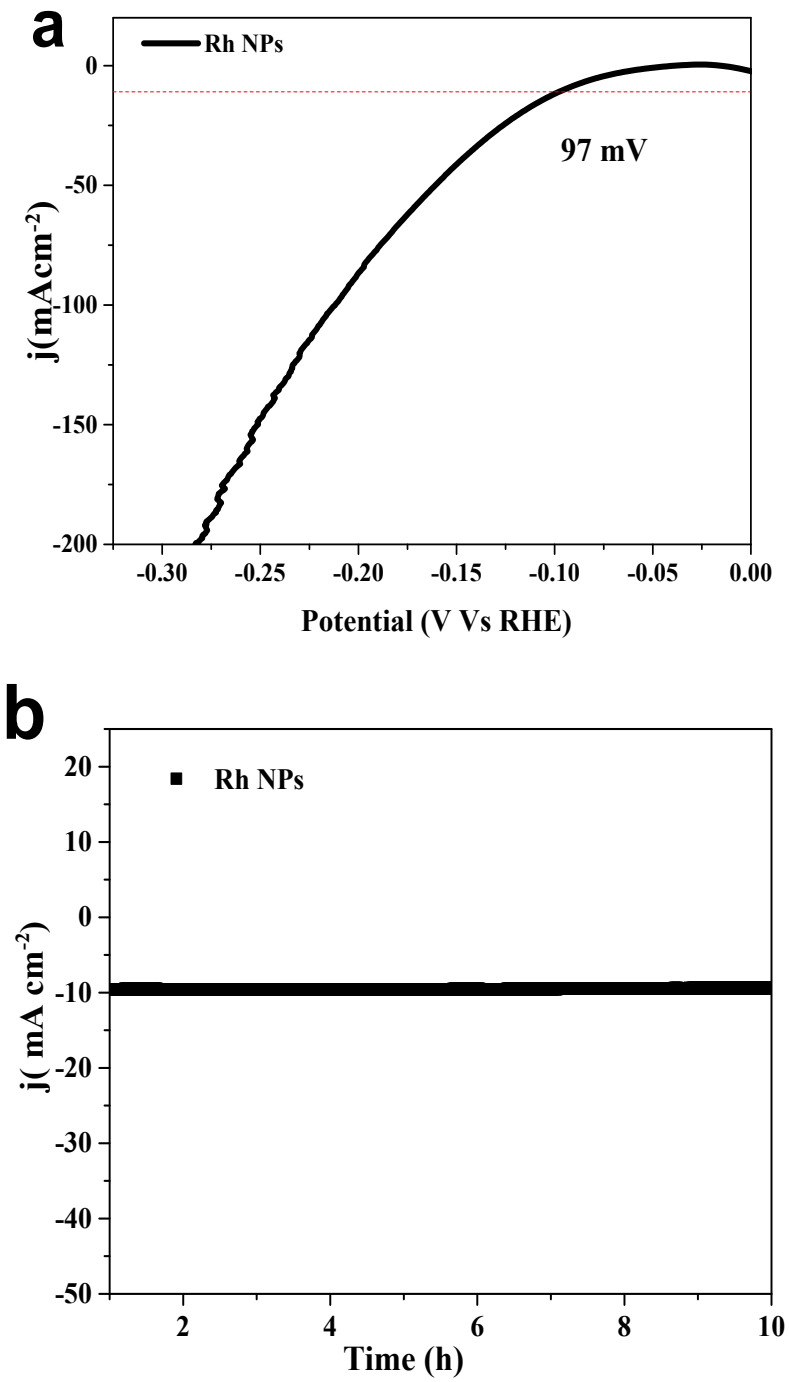

Figure S4. (a) The LSV analysis of pure Rh NPs and (b) their corresponding chronoamperometry study carried for 10 h at 10 mA cm^{-2}.

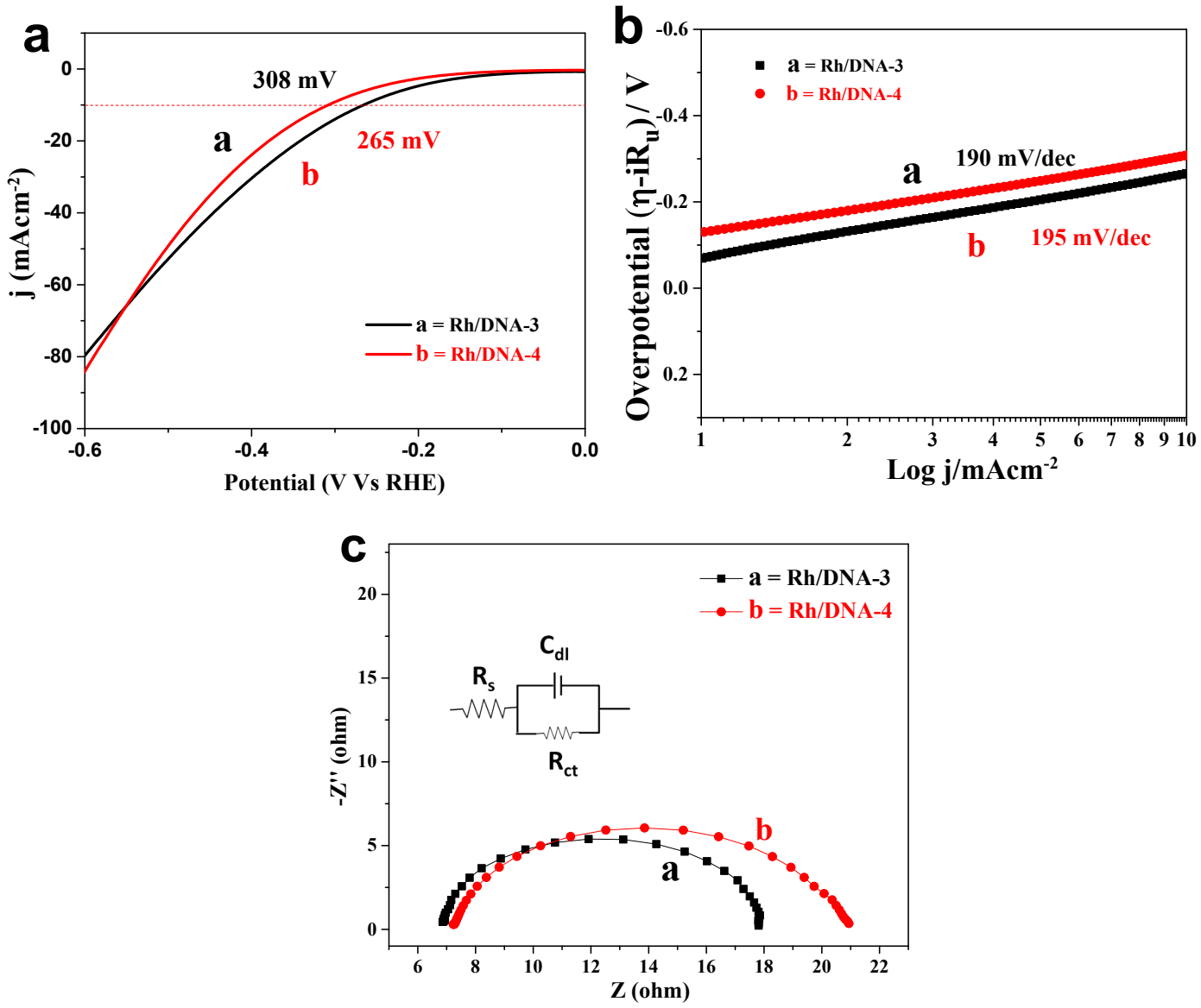

Figure S5. (a) The LSV analysis increased DNA concentrated catalysts Rh/DNA-3 and Rh/DNA-4, (b) their corresponding kinetic study from Tafel slope and (c) the electrochemical impedance spectrum.

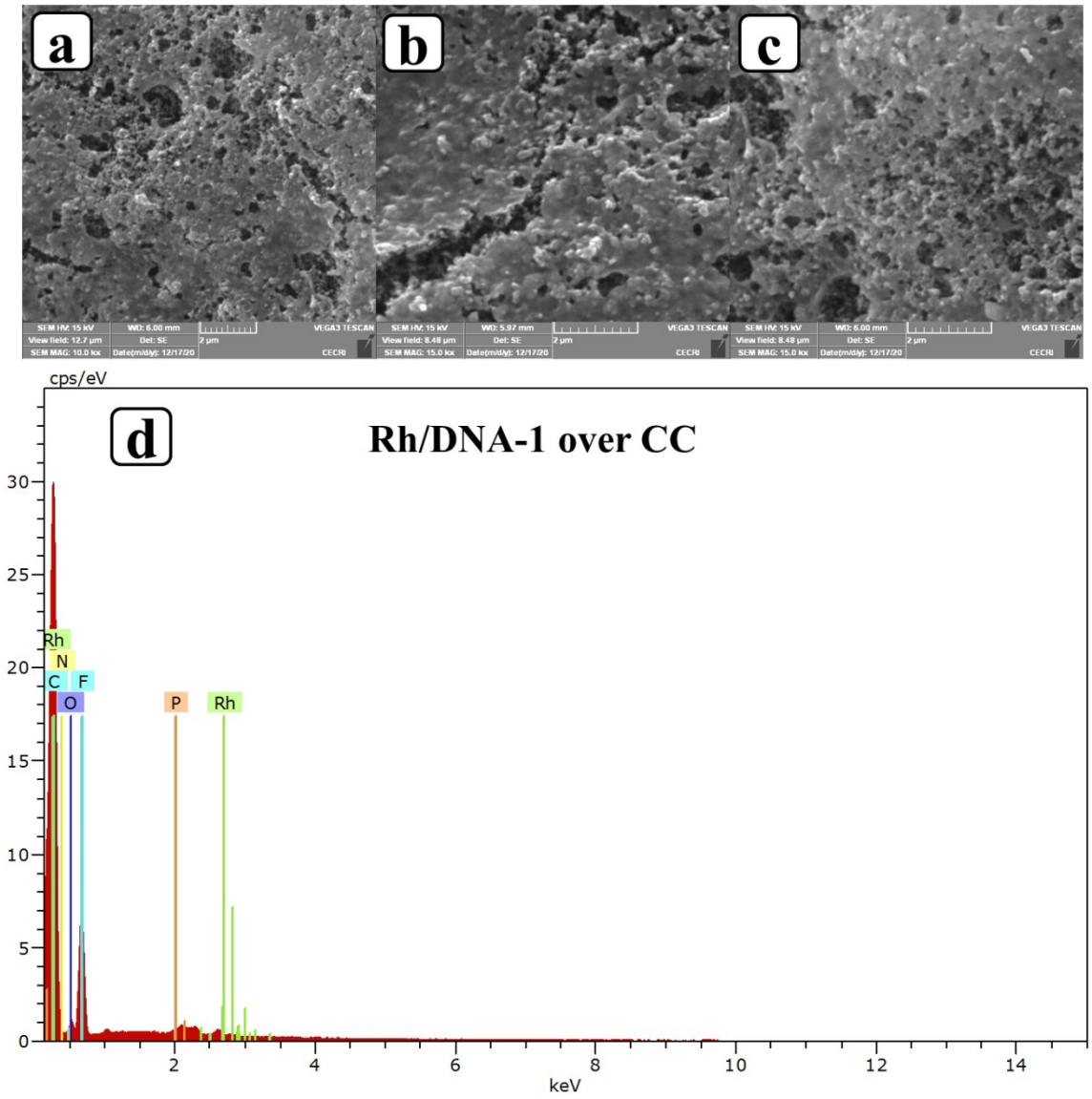

Figure S6. (a-c) SEM images of Rh/DNA-1 at different places after fabricating in CC electrode; (d) EDS pattern of the same indicating the presence of DNA components.

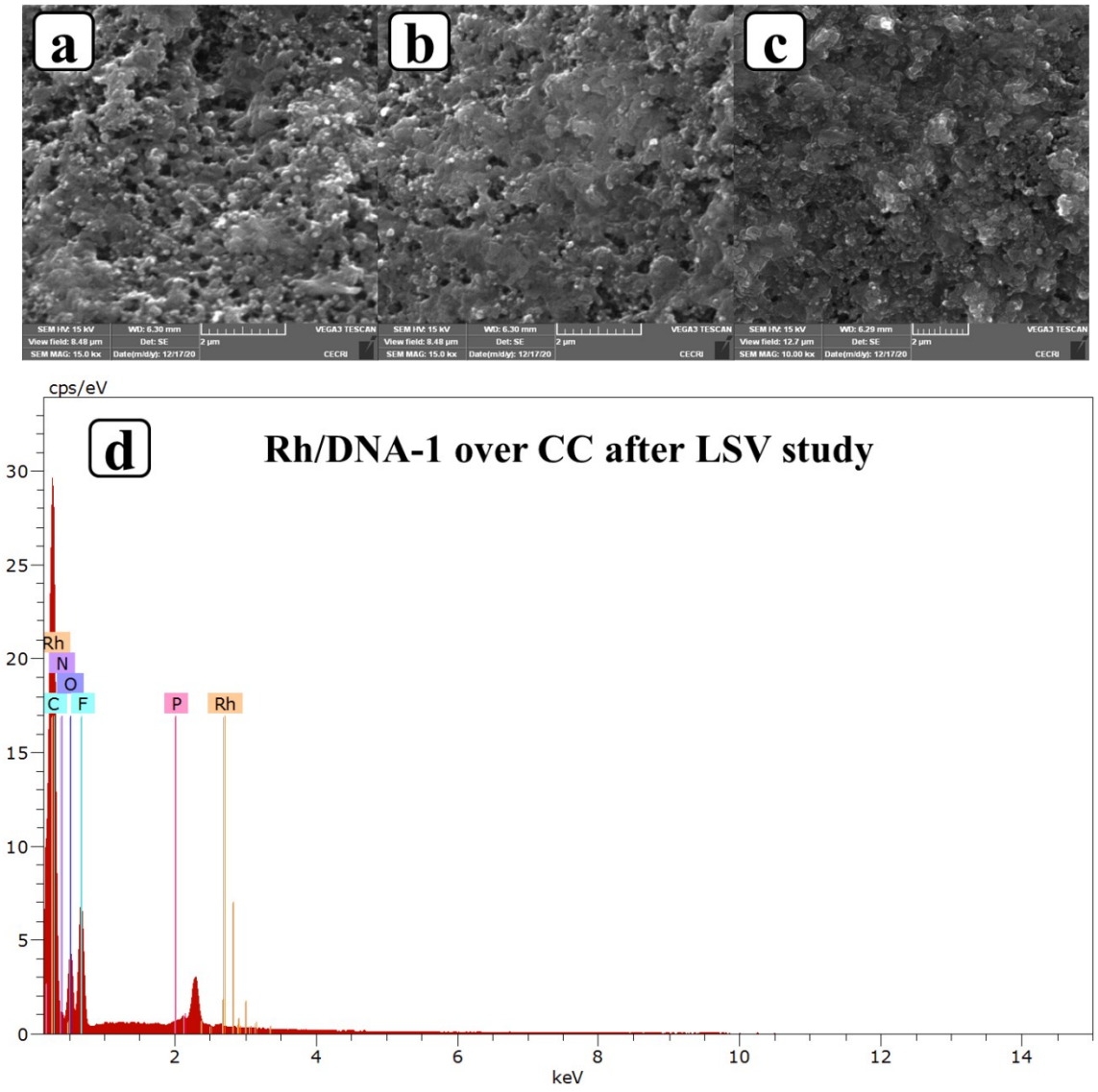

Figure S7. (a-c) SEM images of Rh/DNA-1/CC at different places after LSV study; (d) EDS pattern of the same confirming the presence of DNA components after cathodic polarization.

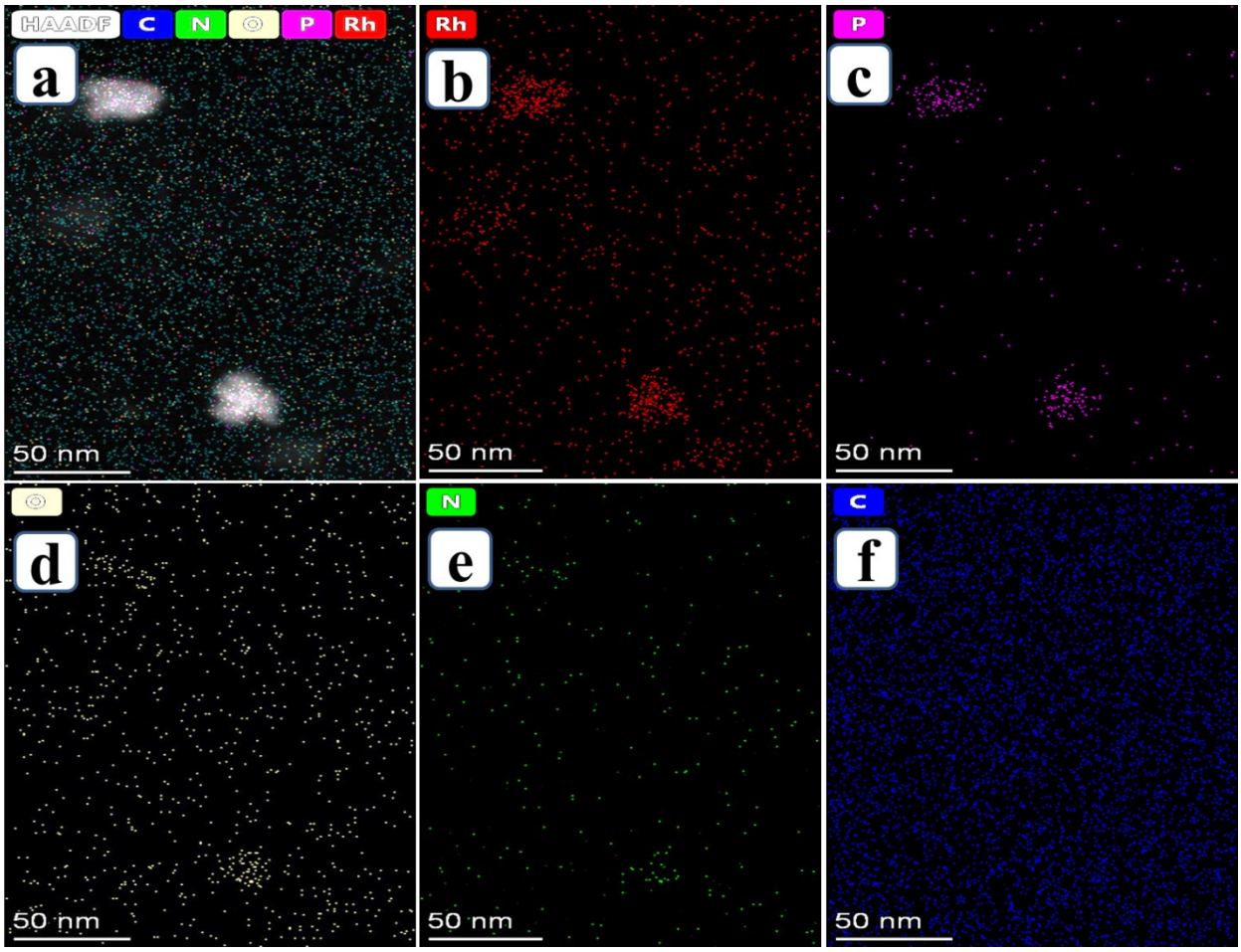

Figure S8. Post HAADF colour mapping of Rh/DNA-1 shows the elemental conformation of Rh, N, P, O and C, respectively

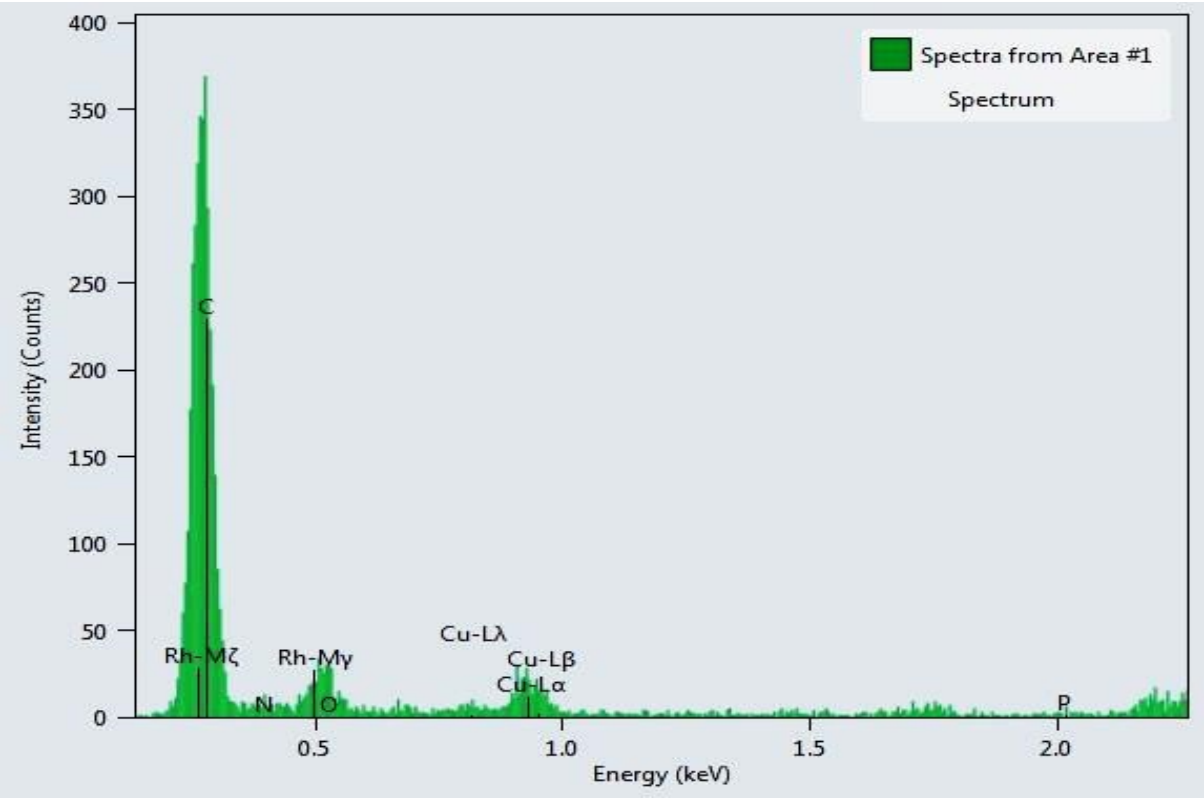

Figure S9. Post Energy dispersive X-ray spectrum of Rh/DNA-1 nano-huddles shows the same elemental presence of Rh, O, C, N and P.

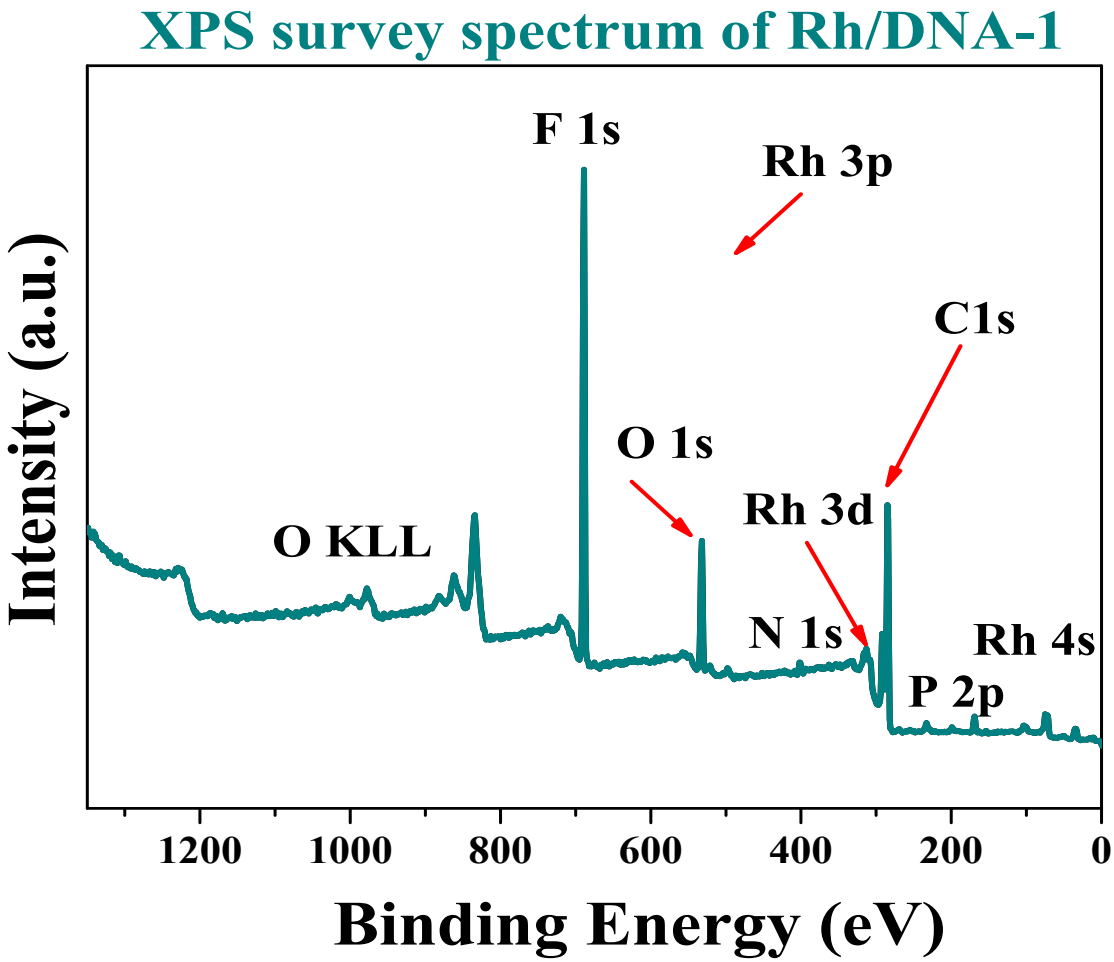

Figure S10. X-ray photoelectron spectroscopy (XPS) analysis survey spectrum of Rh-DNA-1 carried after cycling study.

Table S1. Optimization in the formation of stable Rh NPs over biomolecule DNA.

S. No	Volume of 10^{-2} M $RhCl_3.XH_2O$ Solution (mL)	Volume of DNA(mL)	Volume of 0.1 M $NaBH_4$ solution (mL)	observation	Solution state
1.	1	2	1	Brown	Not stable
2.	1	4	1	Brown	Stable
3.	1	6	1	Brown	Stable
4.	1	8	1	Brown	Not stable
5.	2	1	1	Orange	Not stable
6.	3	1	1	Orange	Not stable
7.	4	1	1	Orange	Not stable
8.	5	1	1	Orange	Not stable
9.	1	10	1	Brown	Stable
10.	1	12	1	Brown	Stable

Table S2: The standard values of the vibrational bands of DNA compared with the vibrational band of the DNA used for stabilizing Rh.[1]

S. No	Types of bonds & vibrational modes of DNA	Standard vibrational bands of DNA (cm^{-1})	Vibrational bands of DNA (used in this work) (cm^{-1})
1.	Stretching vibration of -OH group from the aromatic ring & ribose sugar	3100-3750	3308
2	Stretching vibration of C=O	1732-1595	1698
3	Asymmetric stretching of PO_{2-} group	1260-950	1259
4	Fundamental deformation modes of DNA	500-960	526, 624

Table S3. Comparison of electrocatalytic activities of Rh/DNA-1 catalyst with other Rh based catalyst in terms of current density, overpotential and Tafel slope.[2–11]

S. No.	Catalyst	Loading mg cm^2	Current density mA cm^{-2}	Overpotential (mV)	Tafel slope (mV dec^{-1})	References
1	Rh_2PuNSs	0.1143	10	300	33.4	*Applied Catalysis B: Environmental.* **2020***,270,*118880
2	Rh/F-graphene	20	10	46	30	*Sci. Rep.***2019**, *9,* 17027
3	Rh@CTF-1	0.003	10	58	37	*J. Mater. Chem. A* **2019**, *7,* 11934
4	S-Rh/C	0.05	60	109	45.9	*Applied Catalysis B: Environmental.* **2019***,255,*117737
5	rGO/CoP-Rh	0.218	10	72	43	*J. Energy Chem.* **2018**, 34, 72
6	Rh-doped PbS/C	0.26	10	187.4	68.9	*J. Energy Chem.* **2018**, 10, 9845
7	Rh_2S_3_Thick HNP/C	0.918	10	175	65	*Energy Environ. Sci.* **2016**, 9, 850
8	Rh/SiNW	0.193	100	180	24	*Nat. Commun.* **2016**, *7*, 12272
9	Rh/CQD	0.122	10	176	126.6	*Electrochim. Acta,* **2019**, 299, 828
10	Rh_2S_3 and RhS_2	0.02	20	460	-	*Electrochim. Acta,* **2014**, 1*45*, 224
11	**Rh/DNA-1**	**0.007**	**10**	**105**	**68**	**This work**

References

1 M. Banyay, M. Sarkar and A. Graslund, *Biophys. Chem.*, 2003, **104**, 477–488.

2 Y. Zhao, N. Jia, X. Wu, F. Li, P. Chen and P. Jin, *Appl. Catal. B, Environ.*, 2020, 118880.

3 N. Singh, J. Hiller, H. Metiu and E. Mcfarland, *Electrochim. Acta*, 2014, **145**, 224–230.

4 L. Zhu, H. Lin, Y. Li, F. Liao, Y. Lifshitz, M. Sheng and S. Lee, *Nat. Commun.*, 2016, **7**, 12272.

5 A. Begum, M. Bose and G. Moula, *Sci. Rep.*, 2019, **9**, 17027.

6 M. Siebels, C. Schlusener, J. Thomasn, Y.-X. Xiao, X. Yang and C. Janiak, *J. Mater. Chem. A*, 2019, **7**, 11934–11943.

7 Q. Dang, F. Liao, Y. Sun, S. Zhang, H. Huang, W. Shen, Z. Kang, Y. Shi and M. Shao, *Electrochim. Acta*, 2019, **299**, 828–834.

8 H. Zheng, X. Huang, H. Gao, W. Dong, G. Lu, X. Chen and G. Wang, *J. Energy Chem.*, 2018, **34**, 72–79.

9 D. Yoon, B. Seo, J. Lee, K. S. Nam, B. Kim, S. Park, H. Baik, H. Joo and K. Lee, *Energy Environ. Sci.*, 2016, **9**, 850–856.

10 J. Lu, Z. Tang, L. Luo, S. Yin, P. K. Shen and P. Tsiakaras, *Appl. Catal. B, Environ.*, 2019, **255**, 117737.

11 T. Kim, J. Park, H. Jin, A. Oh, H. Baik, S. H. Joo and K. Lee, *Nanoscale*, 2018, **10**, 9845–9850.