

Supplementary Information

Non-covalent Functionalization of Graphene Oxide Supported 2-Picolylamine-based Zinc(II) Complexes as Novel Electrocatalysts for Hydrogen Production

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S1. Syntheses

S1.1. Synthesis of zinc(II) complexes **Zn1** and **Zn2**

Zinc(II) complexes [(2-PA)₂ZnCl]₂(ZnCl₄) **Zn1** and [(2-PA)₂Zn(H₂O)]-(NO₃)₂ **Zn2** were prepared in a 1:2 molar ratio by mixing methanolic solutions of ZnX₂ (X = Cl or NO₃) and ligand 2-PA. For 2h, the reaction mixtures were stirred. By slow diffusion of the reaction mixture, single crystals suitable for X-ray crystallography were obtained. Filtered off, washed with ether, and dried *in vacuo*. [(2-PA)₂ZnCl]₂(ZnCl₄) **Zn1**: Anal. For C₂₄H₃₂Cl₆N₈Zn₃ (841.43): Calcd. C, 34.26; H, 3.83; N, 13.32; Cl, 25.28; Zn, 23.31; Found C, 34.38; H, 3.92; N, 13.22; Cl, 25.7; Zn, 23.24. ¹H NMR (D₂O, 298 K): δ = 8.27 (d, J = 8.2 Hz, 2H, Py-H_a), 7.89 (m, 4H, Py-H_{b,c}), 7.59 (m, 2H, Py-H_d), and 3.81 (s, 2H, -CH₂-). IR: ν(cm⁻¹): 3068 [ν_{st}(N-H)], 1606 [ν_{st}(C=N)], 950 [ν(Ring breathing)], 775 [δ(Py)], 429 [ν(Zn-N)]. [(2-PA)₂Zn(H₂O)](NO₃)₂ **Zn2**: Anal. For C₁₂H₁₈N₆O₇Zn (421.67): Calcd. C, 34.18; H, 3.82; N, 19.93; Zn, 15.50; Found C, 34.08; H, 3.88; N, 19.98; Zn, 15.62. ¹H NMR (D₂O, 298 K): δ = 8.24 (d, J = 8.2 Hz, 2H, Py-H_a), 7.91 (m, 4H, Py-H_{b,c}), 7.57 (m, 2H, Py-H_d), and 3.80 (s, 2H, -CH₂-). IR: ν(cm⁻¹): 3072 [ν_{st}(N-H)], 1608[ν_{st}(C=N)], 946 [ν(Ring breathing)], 771 [δ(Py)], 435 [ν(Zn-N)].

S1.2. Synthesis of hydroxo zinc(II) complex **Zn3**

Solution of Zn(NO₃)₂·6H₂O (0.372 g, 1.0 mmol) and ligand 2-PA (197 μl g, 2.0 mmol) in methanol (10 mL) were mixed with a solution of NaOH (40 mg, 1 mmol) in methanol (5 mL). The mixture was further stirred for 2 hrs. Colorless crystals were collected upon standing for several days. Filtering and drying in vacuum [(2-PA)₂Zn(OH)](NO₃) **Zn3**. Anal. For C₁₂H₁₇N₅O₄Zn (360.68): Calcd. C, 39.96; H, 4.75; N, 19.42; Zn, 18.13; Found C, 40.15; H, 4.72; N, 19.38; Zn, 18.29. ¹H NMR (D₂O, 298 K): δ = 8.13 (d, J = 8.2 Hz, 2H, Py-H_a), 7.68 (m, 4H, Py-H_{b,c}), 7.40 (m,

2H, Py-H_d), and 3.69 (s, 2H, -CH₂-). IR: $\nu(\text{cm}^{-1})$: 3069 [$\nu_{\text{st}}(\text{N-H})$], 1604 [$\nu_{\text{st}}(\text{C=N})$], 945 [$\nu(\text{Ring breathing})$], 766 [$\delta(\text{Py})$], 431 [$\nu(\text{Zn-N})$].

S1.3. Functionalization of graphene oxide (GO)

A solution of the hydroxide zinc(II) complex **Zn3** (20 mg) in distilled water (10 mL) was added to GO (200 mg) suspended in ethyl alcohol (4 mL). The pH of the solution was raised to ~12 using ammonia solution. The suspension formed was heated for 5 h at 70 °C. The pH was raised again to ~12 with ammonia solution. The solid part was then filtered out, washed with ethanol and dried to form the hybrid form **Zn3/GO**.

Table S1. Crystal data, data collections and structure refinement of zinc(II) complex **Zn1**.

| | Zinc(II) complex (Zn1) |
|--|--|
| Empirical formula | C ₂₄ H ₃₂ Cl ₆ N ₈ Zn ₃ |
| Formula weight | 841.38 |
| Temperature [K] | 100(2) |
| Wavelength [Å] | 0.71073 |
| Crystal system | Triclinic |
| Crystal colour | Colorless |
| Crystal size [mm] | 0.070 x 0.150 x 0.310 |
| Space group | P -1 |
| Z | 2 |
| Volume [Å ³] | 1613.6(4) |
| a [Å] | 7.0781(9) |
| b [Å] | 13.6526(19) |
| c [Å] | 17.137(2) |
| α [°] | 86.756(3) |
| β [°] | 82.505(3) |
| γ [°] | 79.531(3) |
| Density(calc.) [g/cm ³] | 1.732 |
| Absorption coefficient [mm ⁻¹] | 2.739 |
| F(000) | 848 |
| Θ -range [°] | 1.90 to 28.41 |
| Index ranges | -9 \leq h \leq 9, 18 \leq k \leq 18, 22 \leq l \leq 22 |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on F^2 |
| Refinement program | SHELXL-2014 (Sheldrick, 2014) |
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$ |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0182P)^2+1.0720P]$, where $P=(F_o^2+2F_c^2)/3$ |
| Reflections collected | 29556 |
| Independent reflections | 7995 [R(int) = 0.0146] |
| Max. and min. transmission | 0.8310 and 0.4840 |
| Data /restraints / parameters | 7995 / 0 / 402 |
| Goodness-of-fit on F^2 | 1.050 |
| Final R indices | 7598 data; $I > 2\sigma(I)$: R1 = 0.0181, wR2 = 0.0439 |
| R indices (all data) | R1 = 0.0196, wR2 = 0.0445 |
| Largest diff. peak [$e\cdot\text{\AA}^{-3}$] and hole | 0.678 and -0.399 |
| R.M.S. deviation from mean [$e\text{\AA}^{-3}$] | 0.054 |

S2. Electrochemical measurements

S2.1. Materials and solutions

Analytical grade chemical reagents (Sigma-Aldrich) were freshly prepared using water purified by a Millipore Milli-Q method (resistivity: 18.2 M Ω cm). First a homogeneous, well-dispersed electrocatalyst ink was prepared by dispersing 4 mg of complex **1** in a 4:1 ratio (v/v) mixture of deionized water and ethanol. Then 80 mL Nafion was then added to the mixture. A homogeneous ink from the electrocatalyst is produced after 30 minutes of mixture sonication. On a well-polished glass carbon (GC) electrode (3 mm in diameter), 5 mL of this homogeneous ink was dropped and then dried in the air, creating a mass load of 0.2 mg cm⁻². To prepare two other GC-loaded complex **1** electrodes with mass loading densities of 0.4 and 0.8 mg cm⁻², the same procedure was repeated.

S2.2. Cell and apparatus

In deaerated 0.1 M KOH aqueous solution using a typical jacketed three-electrode cell, electrocatalytic behavior of the synthesized **Zn3** and **Zn3**/GO cathodes towards the HER was examined. The cell's inner compartment has a volume capacity of 200 mL, large enough to resolve

any major changes in composition that may occur during the run. To maintain the temperature of the test solution constant ($25 \pm 0.2^\circ\text{C}$) during the run, temperature-controlled water is permitted to circulate through the outer jacket of the cell. The cell consists of three electrodes, an auxiliary electrode (graphite rod, Sigma-Aldrich, 99.999%), and a reference electrode (saturated calomel electrode, SCE), the working electrode (GC-loaded complex 1).

Potentials were referenced against a reversible hydrogen electrode (RHE). Conversion to RHE was done using the via the Nernst equation: $E_{\text{RHE}} = E_{\text{SCE}} - E^\circ_{\text{H}_2/2\text{H}^+} + 0.244$, where $E^\circ_{\text{H}_2/2\text{H}^+}$ is the reversible hydrogen potential, given by Nernst equation ($E^\circ_{\text{H}_2/2\text{H}^+} = -0.059 \text{ pH}$); a pH value of ~ 13 was measured for the test solution (0.1 M KOH). The number +0.244 in Eq. (1) denotes the standard potential (in Volts) of the used SCE {Cl⁻ (4M) | Hg₂Cl₂(s) | Hg(l) | Pt @ 25 °C}.

Various electrochemical techniques were applied to the electrocatalyst/OH⁻ interface by connecting the three cell terminals to an AUTOLAB (PGSTAT30) potentiostat/galvanostat coupled to an Autolab frequency response analyzer (FRA) with a PC-connected FRA2 module. To eliminate oxygen from the test solutions, argon bubbles were applied. The gas inlet was removed from the solution after 30 min of continuous bubbling and kept working over it throughout the run. The working electrode was then dipped in the test solution immediately.

S2.3. Electrochemical methods

The HER electrocatalytic activity of the prepared catalysts was assessed employing the linear sweep voltammetry (LSV) technique. LSV measurements were carried out at a sweep rate of 5.0 mVs^{-1} by polarizing the working electrode potential cathodically from the corrosion potential to a cathodic potential of -2 V vs. SCE.

S2.4. Catalyst stability and durability

The best catalyst reported here, namely GC- **Zn3** (0.8 mg cm⁻²)/GO, was assessed for its long-term stability and durability employing continuous overpotential cycling; the potential was linearly swept from the starting potential (E_{corr}) to the cathodic direction at a scan rate of 50 mV s⁻¹ till reaching an overpotential of -1.0 V vs. RHE, and then reversed with the same scanning rate up to the starting potential forming a complete cycle. The cycling process was repeated 10,000 times without removing the electrode from the solution and without delay in time.

The best electrocatalyst's stability was also evaluated using chronoamperometry measurements performed on the catalyst at a constant applied potential of -0.3 V vs. RHE for 24 h. Measurements were conducted in 0.1 M KOH at room temperature.

S2.5. Data reproducibility and statistics

By repeating each experiment at least three times, data reproducibility was assured. Each number in the electrochemical measurement tables is the arithmetical mean of the data obtained from at least three repeated independent experiments. Standard deviation was also estimated and evaluated.

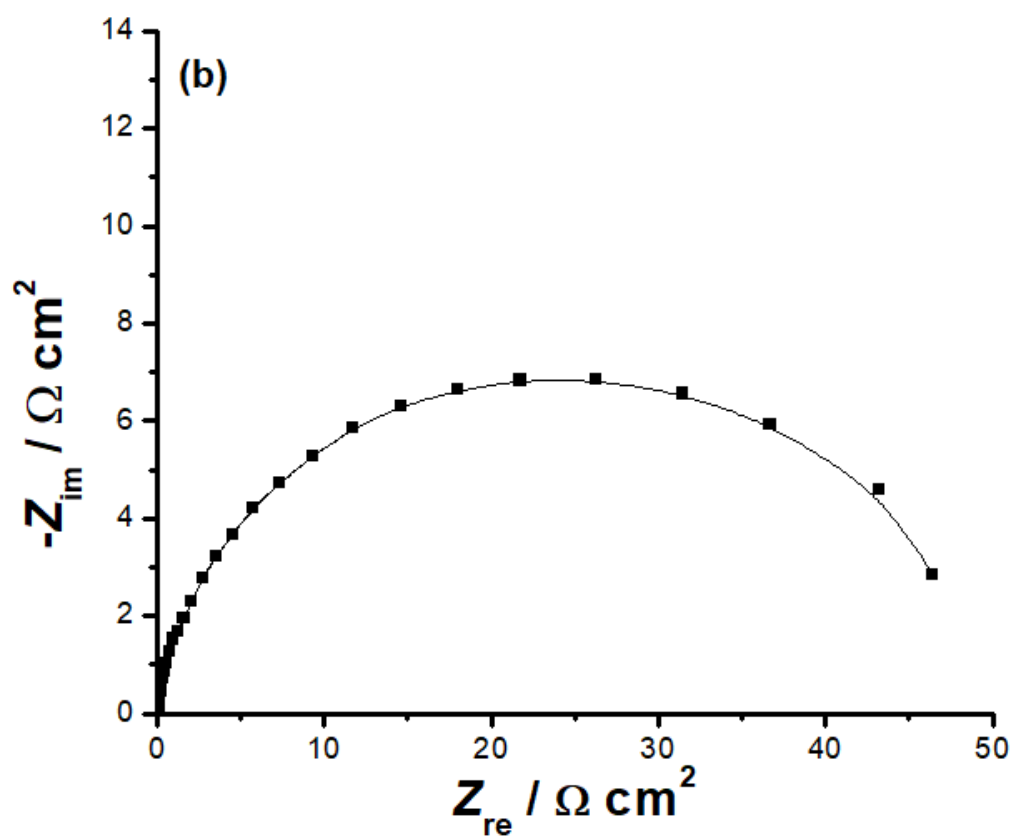
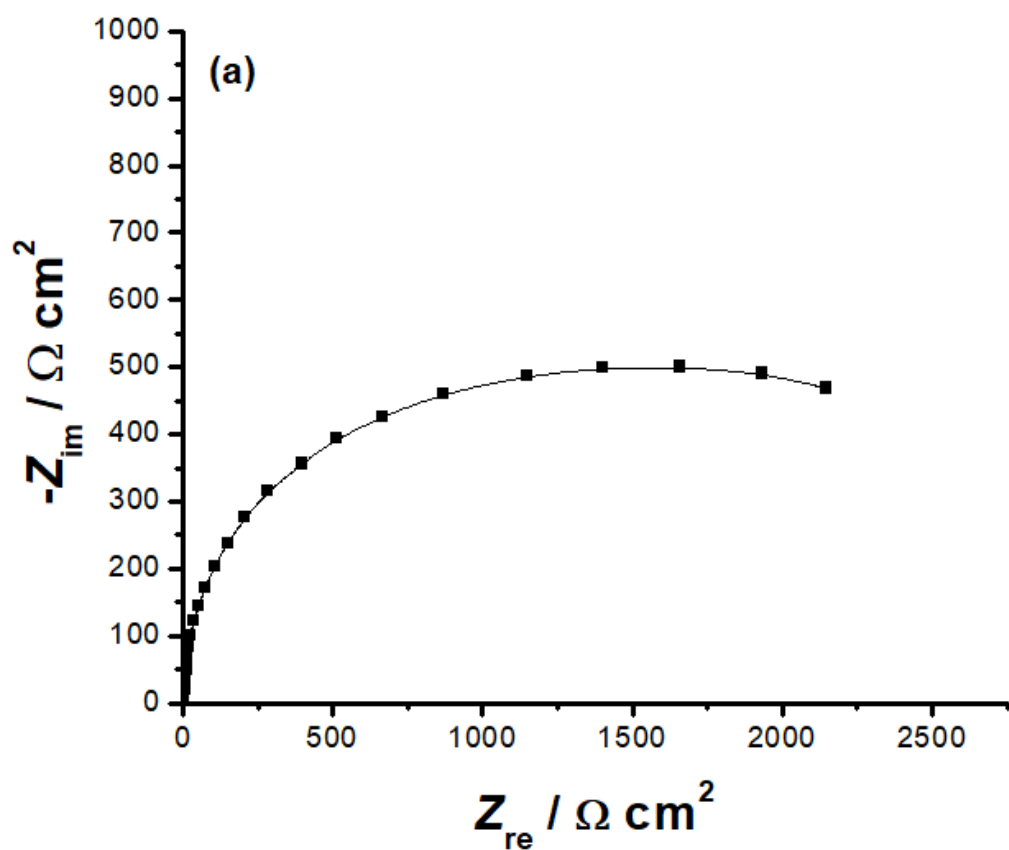


Figure S1. Complex-plane EIS plots for the bare GCE electrode (a) and Pt/C (b). Measurements were conducted in 0.1 M KOH at 500 mV at room temperature.

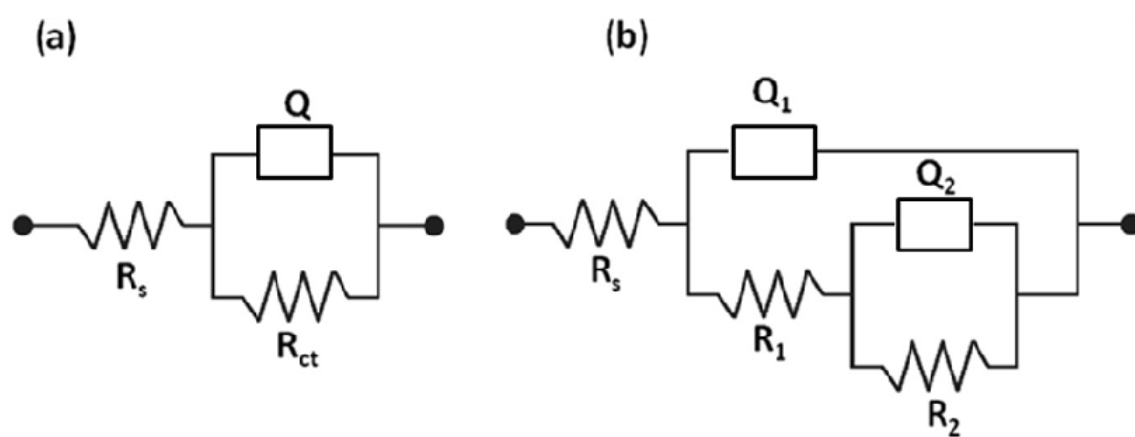


Figure S2: Equivalent circuits used to fit the experimental impedance data for the bare GC and Pt/C electrodes (a) and the investigated GC-loaded **Zn3** electrodes (b)

Table S2: Comparison of HER catalytic activity of our synthesized **Zn3** and **Zn3/GO** electrocatalysts with the highly efficient electrocatalysts reported in the literature.

| Sample | Electrolyte | Onset potential (V) | Potential @ 10 mA cm ⁻² (V) | Tafel slope (mV dec ⁻¹) | Ref. |
|--|---|---------------------|--|-------------------------------------|------------------|
| GC- Zn3 (0.8 mg cm ⁻²) | 0.1 M KOH | 0.102 | 0.205 | 155 | This work |
| GC- Zn3 (0.8 mg cm ⁻²)/GO | 0.1 M KOH | 0.025 | 0.122 | 118 | This work |
| GC- chlorobis(2-aminomethylbenzimidazole)zinc(II) perchlorate complex (loading density 0.8 mg cm ⁻²) | phosphate buffer aqueous solutions (pH 7) | 0.14 | 0.242 | 145 | [1] |
| N, S co-doped graphitic sheets with stereoscopic holes (SHG) | 0.1 M KOH | 0.23 | 0.31 | 112 | [2] |
| N-rich holey graphene monoliths (N-G) | 0.1 M KOH | 0.30 | 0.51 | 157 | [3] |
| N, P co-doped nanoporous graphene (N, P-G) | 0.1 M KOH | 0.35 | > 0.6 | --- | [4] |
| N, P Co-doped carbon networks (N, P-C) | 0.1 M KOH | 0.29 | 0.47 | --- | [5] |
| N, O, P tri-doped porous carbon (N, O, P-G) | 1.0 M KOH | 0.28 | 0.45 | 154 | [6] |
| g-C ₃ N ₄ @N-doped graphene (C ₃ N ₄ @N-G) | 0.1 M KOH | 0.35 | > 0.6 | --- | [7] |
| g-C ₃ N ₄ -S, Se co-doped graphene (C ₃ N ₄ @S,Se-G) | 0.1 M KOH | 0.45 | 1.1 | 93 | [8] |
| g-C ₃ N ₄ -N, P co-doped graphene (C ₃ N ₄ @N, P-G) | 0.1 M KOH | 0.45 | 0.58 | 129 | [9] |

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