Electronic Supplementary Information for

Bio-inspired Noble Metal-Free Nanomaterials Approaching Platinum Performances for H_2 Evolution and Uptake

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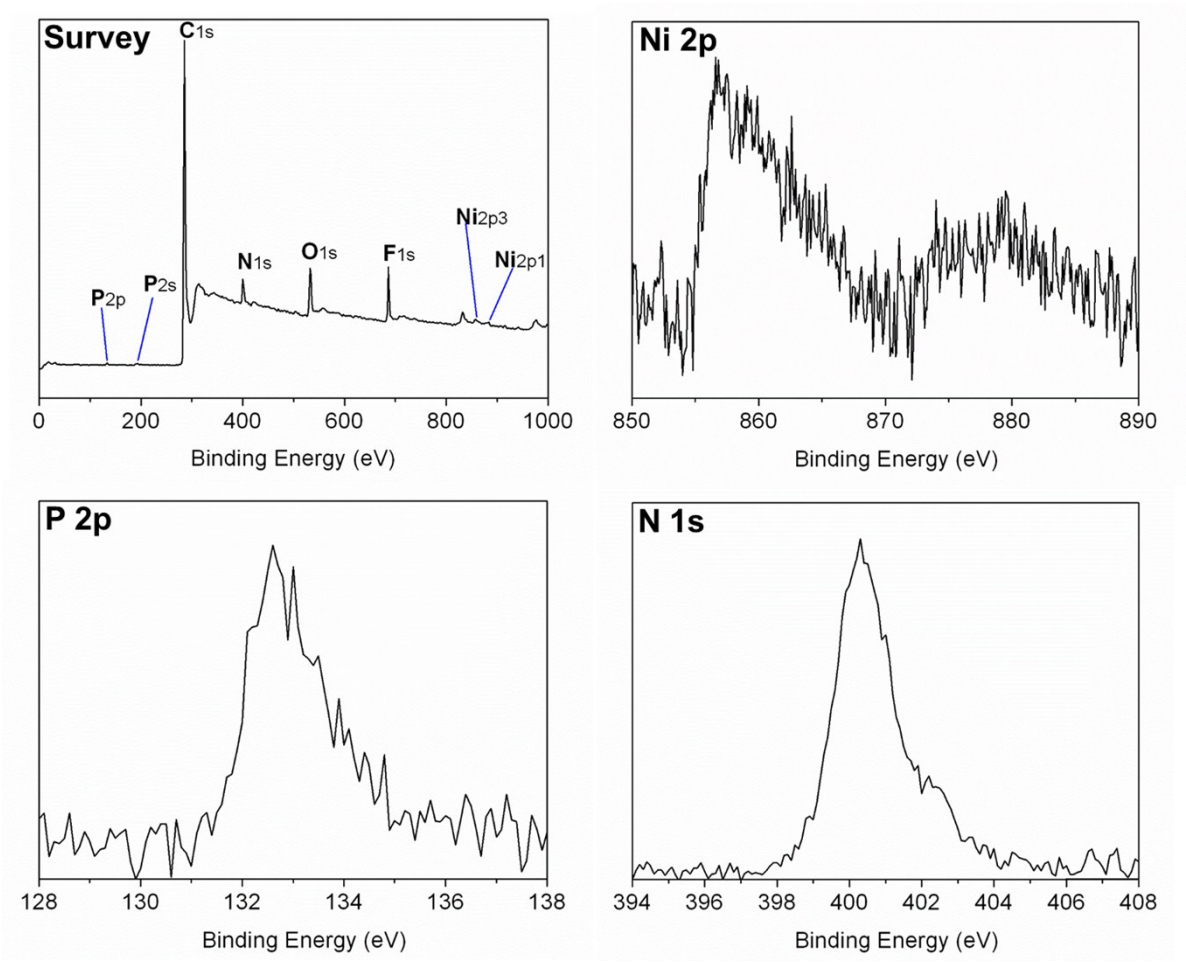

Figure S1: X-ray photoelectron spectra of NiP^{Cy}_2-functionalized MWCNT/GDL electrode.

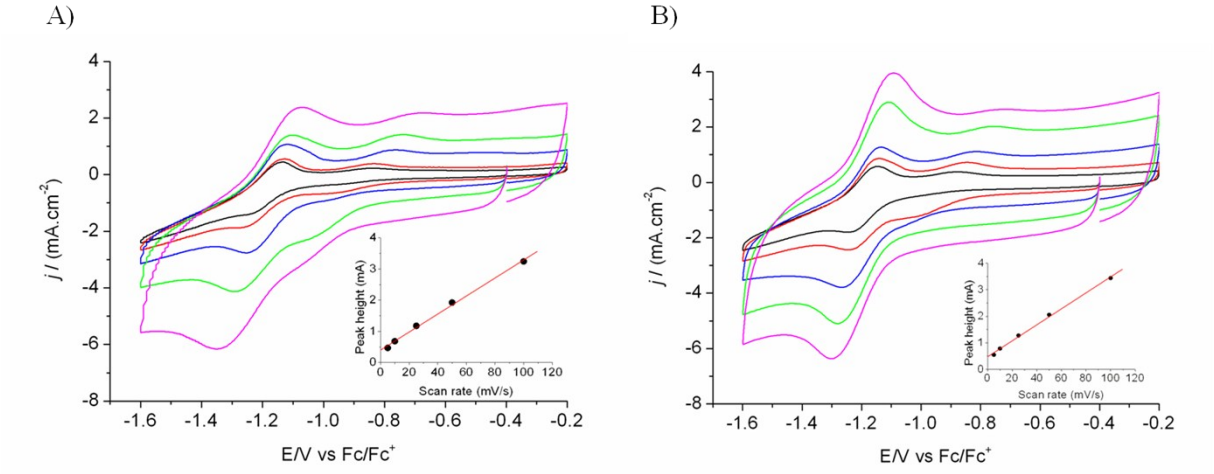

Figure S2: Cyclic voltammograms of NiP^{Cy}_2 (A) and NiP^{Ph}_2 (B) grafted on a MWCNT/GDL electrode in CH_3CN with 0.1M *n*-Bu_4BF_4 at different scan rates.

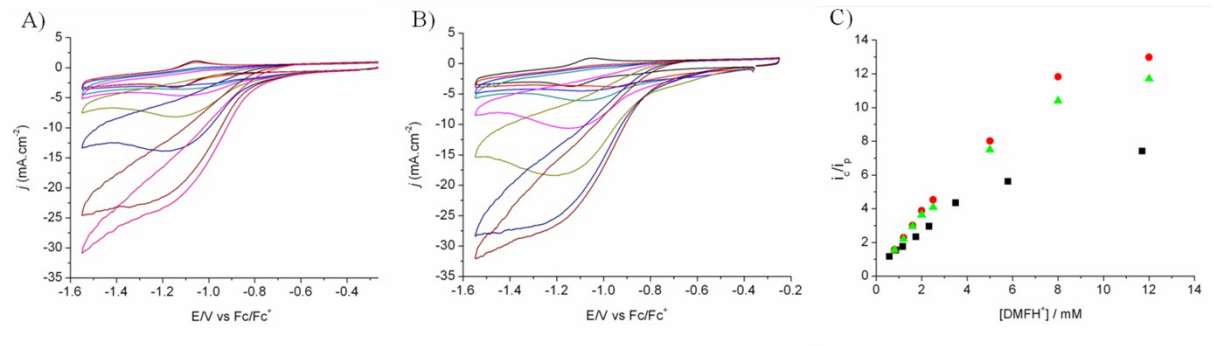

Figure S3: Electrocatalytic behavior of NiP^{Cy}_2 (A) and NiP^{Ph}_2 (B) grafted on a MWCNT/GDL electrode (1 cm^2) in CH_3CN with 0.2 M *n*-Bu_4NPF_6electrolyte at various concentrations of the acid 1:1 mol/mol [DMFH]OTf/DMF (0.8, 1.20, 1.6, 2.0, 2.5, 5.0, 8.0, and 12.0 mM) (50 mVs^{-1} scan rate). The appearance of an electrocatalytic wave at $E_{1/2}$ = –0.85 V versus Fc/Fc^+ (–0.32 V vs SHE) is assigned to hydrogen evolution. (C) comparison of i_c/i_p ratio (where i_c is the catalytic current and i_p is the peak current associated with the Ni(II/I) couple in the absence of acid) of NiP^{Cy}_2 (green) and NiP^{Ph}_2 (red) from (A) and (B) with the result (black) of classical $[Ni(P^{Ph}_2N^{R}_1)_2]^{2+}$ complex grafted on a MWCNT/GDL electrode (1 cm^2) [1].

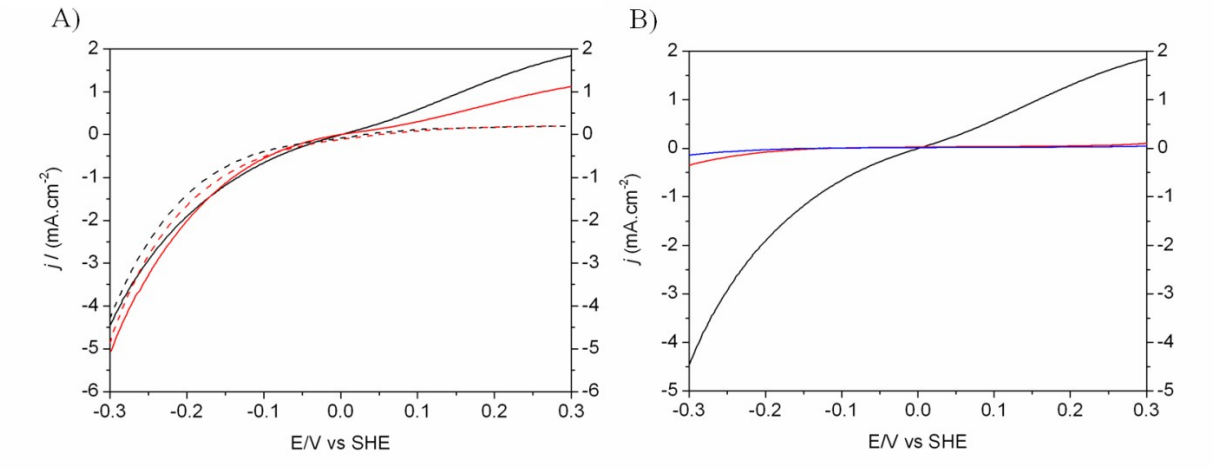

Figure S4: A) Comparison of the catalytic activity of NiP^{Cy}_2 (black) and NiP^{Ph}_2 (red) complexes synthesized from $Ni(CH_3CN)_6(BF_4)_2$ on 0.133 mg MWCNT/cm^2 GDL electrode under H_2 (solid trace) and N_2 (dashed trace); B) Comparison of the catalytic activity of NiP^{Cy}_2 grafted on MWCNT/GDL electrode (black) with pristine MWCNT/GDL (red) and P^{Cy}_2 grafted on MWCNT/GDL electrode (blue) in 0.5M H_2SO_4 under H_2. All electrodes contain the same amount of MWCNT (0.133 mg cm^{-2}). Data are not compensated for ohmic drop.

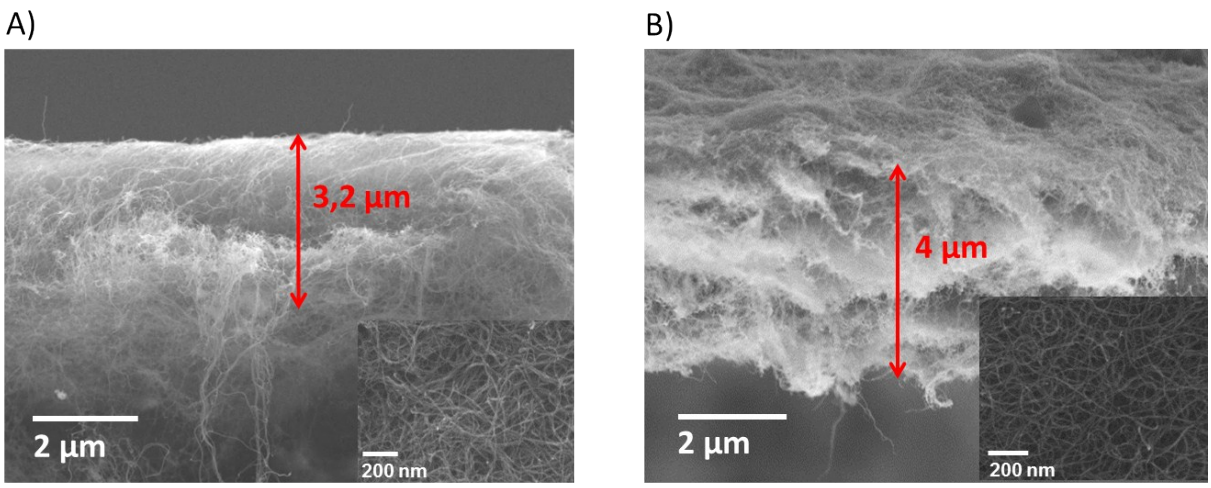

Figure S5: Cross section SEM images of 0.133 mg cm^{-2} MWCNT/GDL electrodes prepared by filtration (A) and drop-casting method (B). Insets show a top view with higher magnification.

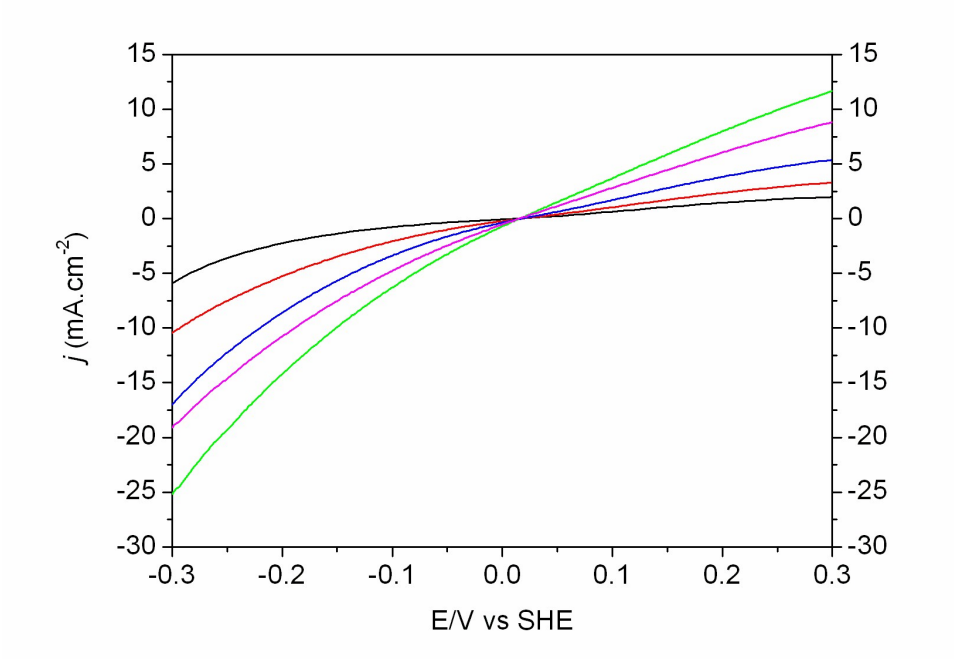

Figure S6: Comparison of the catalytic activity of NiP^{Cy}_2 grafted on different MWCNT/GDL electrodes: 0.133 mg MWCNT/cm^2 GDL by filtration (black), 0.133 mg MWCNT/cm^2 GDL by drop casting (red), (0.133 mg MWCNT and 0.067 mg carbon microfiber)/cm^{-2} GDL (blue), (0.133 mg MWCNT and 0.033 mg carbon microfiber)/cm^{-2} GDL (purple) and (0.267 mg MWCNT and 0.033 mg carbon microfiber)/cm^{-2} GDL (green). Data are not compensated for ohmic drop.

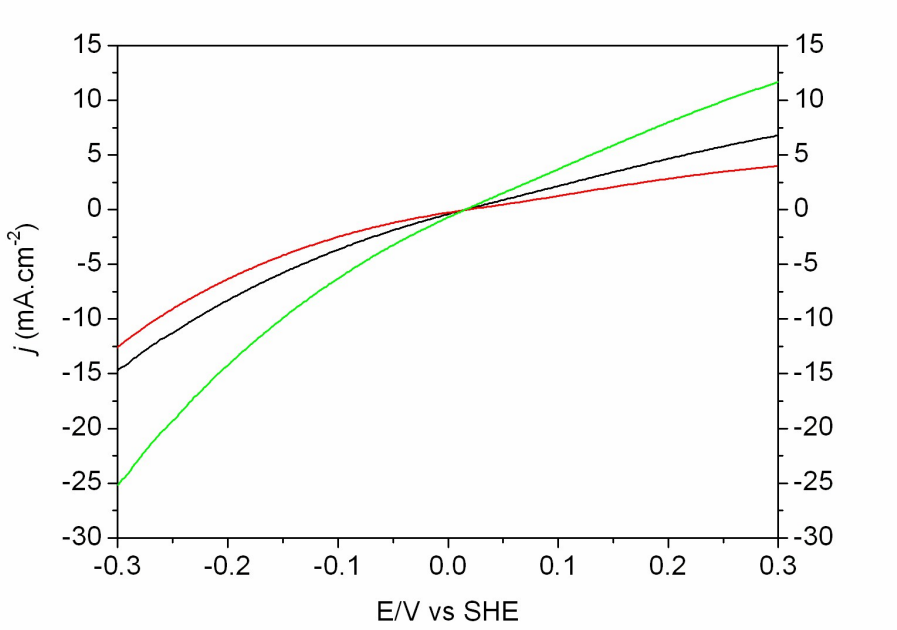

Figure S7: Comparison of the catalytic activity of NiP^{Cy}_2 grafted on different electrode: (0.267 mg MWCNT and 0.033 mg carbon microfiber)/cm^{-2} GDL (green), (0.267 mg MWCNT and 0.0166 mg carbon microfiber)/cm^{-2} GDL (black) and (0.267 mg MWCNT)/cm^{-2} GDL (red). Data are not compensated for ohmic drop.

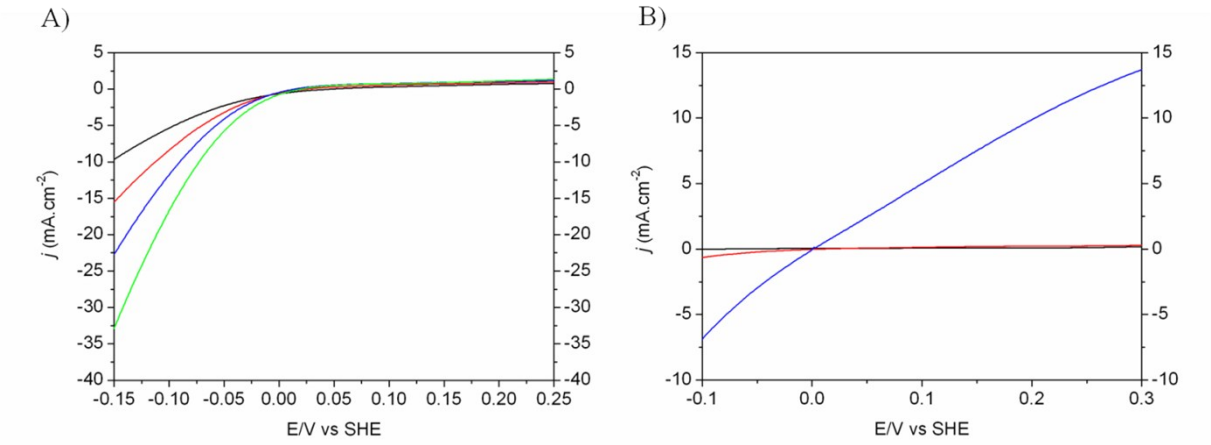

Figure S8: (A): Catalytic activity of NiP^{Cy}_2 grafted on a 0.267 mg cm^{-2} MWCNT + 0.033 mg cm^{-2} carbon microfiber GDL in the half-cell experiment at various temperatures under N_2: 25°C (black), 45°C (red), 65°C (blue) and 85°C (green). Potentials were referred to SHE, the potential of which was calculated at each temperature using the Nernst equation. (B): Comparison of the catalytic activity of (0.267 mg unfunctionalized MWCNTs and 0.033 mg carbon microfiber)/cm^{-2} GDL electrode at 25°C (black) and 85°C (red) with the corresponding electrode functionalized by NiP^{Cy}_2 at 25°C (blue). Data are not compensated for ohmic drop.

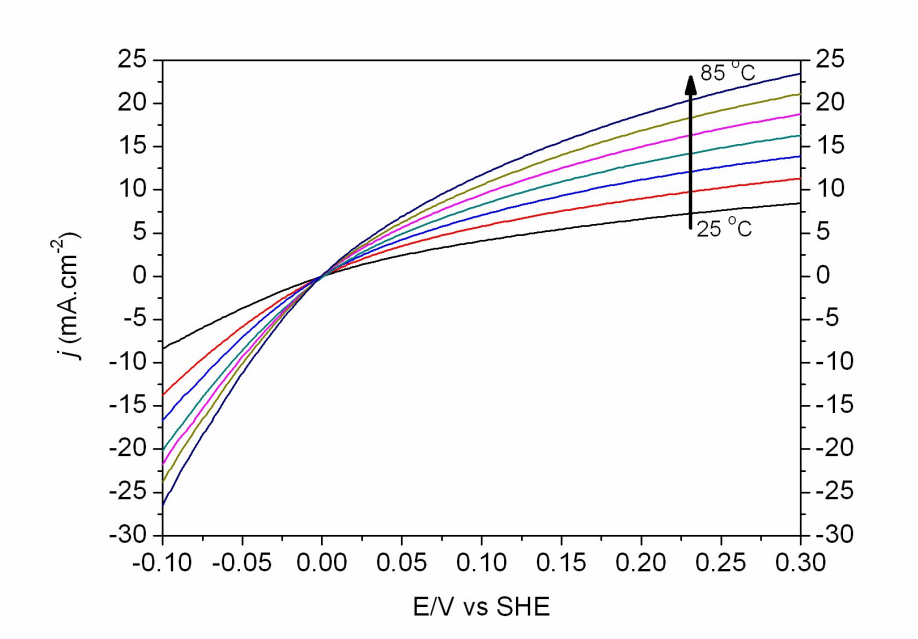

Figure S9: Catalytic activity of NiP^{Ph}_2 grafted on a 0.267 mg cm^{-2} MWCNT and 0.033 mg cm^{-2}carbon microfiber GDL in the half-cell experiment at various temperatures. Potentials were referred to SHE, which potential was calculated at each temperature using the Nernst equation. The calculated activation energies for hydrogen production and oxidation are 11.6 $kJ.mol^{-1}$ and 13.3 $kJ.mol^{-1}$, respectively. Data are not compensated for ohmic drop.

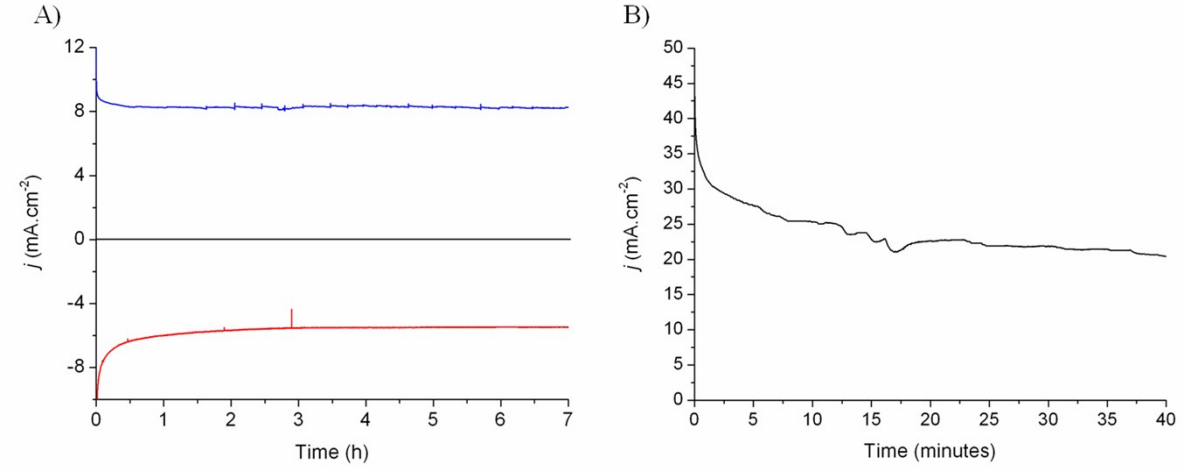

Figure S10: Long term stability of a (0.267 mg MWCNT and 0.033 mg carbon microfiber)/cm^{-2} GDL electrode grafted with NiP^{Cy}_2. (A): Hydrogen oxidation at +300 mV and hydrogen generation at –100 mV vs SHE at room temperature. (B): Hydrogen oxidation at +300 mV vs SHE at 85°C. Data are not compensated for ohmic drop.

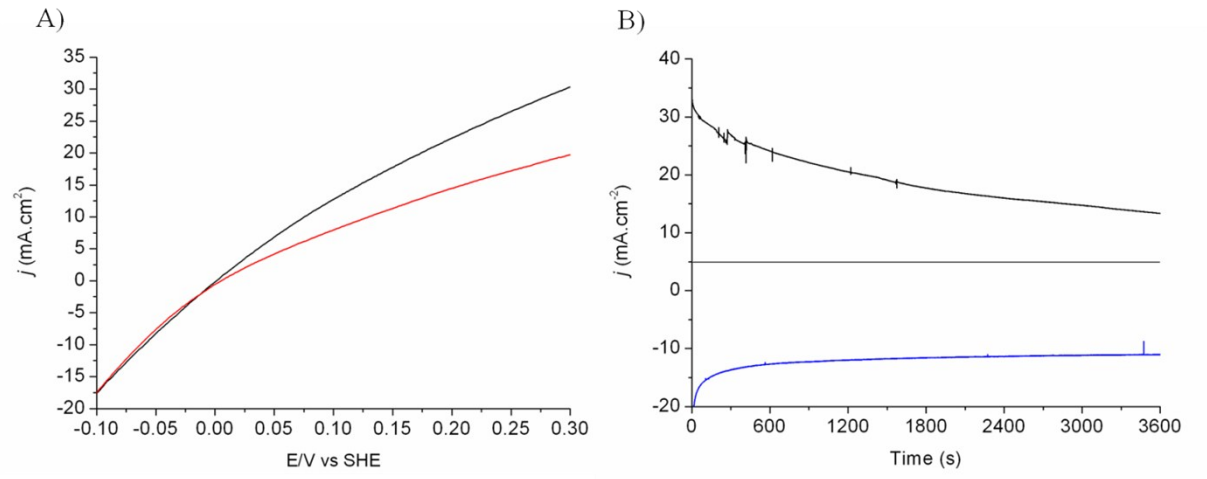

Figure S11: Catalytic activity at 55°C of a MWCNT/carbon microfiber GDL electrode grafted with NiP^{Cy}_2: (A): Half-cell CVs of the electrode at 55°C before (black) and after (red) 1 h electrolysis at +300 mV vs SHE at 55°C. (B): Current density at 55°C with a fresh electrode of hydrogen oxidation at +300 mV vs SHE (black) and hydrogen production at –100 mV vs SHE (blue). Data are not compensated for ohmic drop.

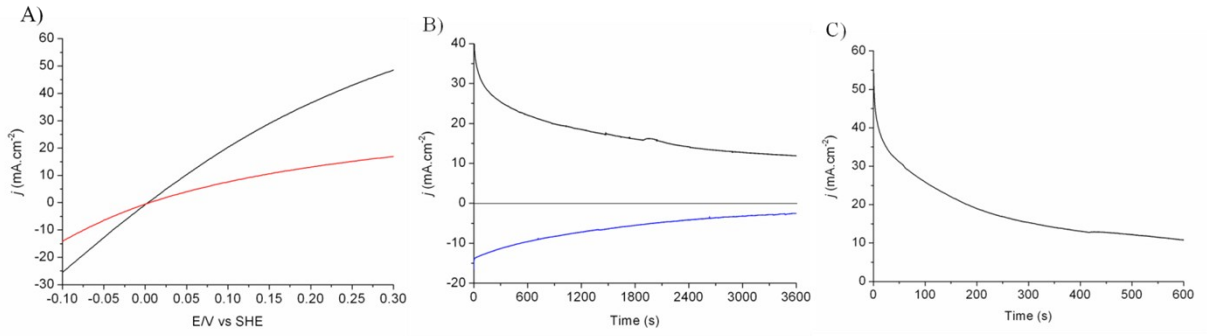

Figure S12: Catalytic activity for hydrogen oxidation at 55°C of a Pt/C electrode (0.05 $mg_{Pt}.cm^{-2}$): half-cell CVs of the electrode at 55°C before (black) and after (red) 1 h electrolysis H_2 oxidation at 300 mV vs SHE at 55°C (A), current density of hydrogen oxidation at +300 mV vs SHE (black) and generation at –100mV vs SHE (blue) at 55°C with a fresh electrode (B), and hydrogen oxidation at +300 mV vs SHE at 85°C. Data are not compensated for ohmic drop.

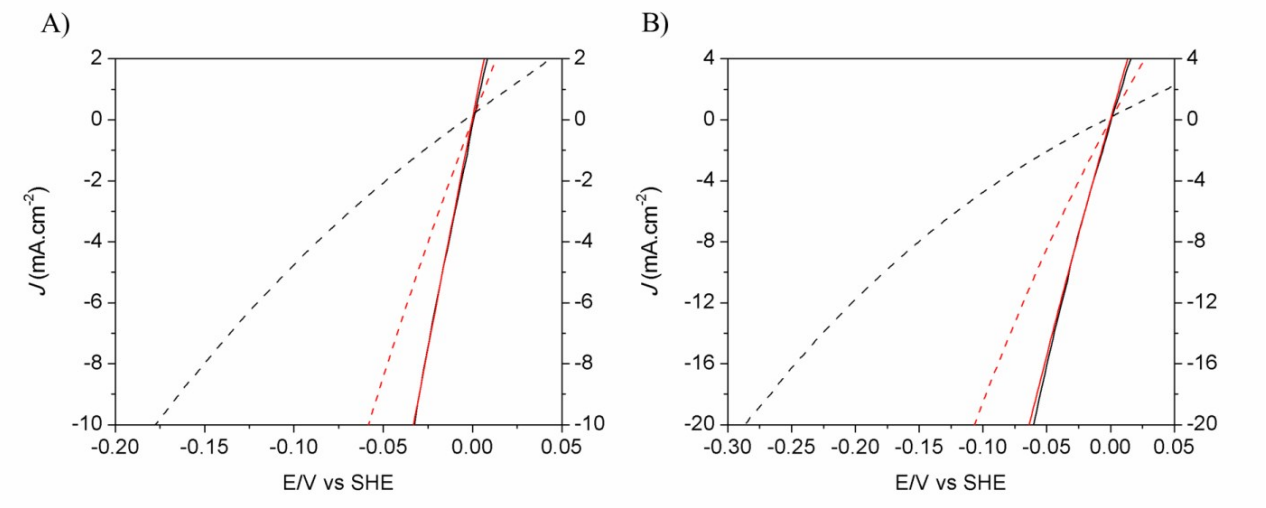

Figure S13: Comparison of the overvoltage required for 10 and 20 mA.cm^{-2} current density values for hydrogen production via linear sweep voltammetry on a Pt (red) and NiP^{Cy}_2-functionalized MWCNT+carbon fiber (black) electrode at 25°C (dashed trace) and 85°C (solid trace) in 0.5 M H_2SO_4. Data are not compensated for ohmic drop.

Figure S14: Comparison of the overvoltage required for 20 mA.cm^{-2} current density for hydrogen production via linear sweep voltammetry on a Pt (red) and NiP^{Cy}_2-functionalized MWCNT+carbon fiber (black) electrode at 25°C (dashed trace) and 85°C (solid trace) in 0.5 M H_2SO_4.

REFERENCES

1. A. Le Goff, V. Artero, B. Jousselme, P. D. Tran, N. Guillet, R. Metaye, A. Fihri, S. Palacin and M. Fontecave, *Science*, 2009, **326**, 1384-1387.