

Supporting Information

Mixed-Metal Hybrid Ultramicroporous Material (HUMs) to Graphene-supported Tetrataenite as highly active and durable NPG catalyst for OER

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Experimental Procedures:

Nickel hexafluorosilicate hexahydrate ($\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$), Nickel nitrate hexahydrate ($\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$), Ammonium hexafluorosilicate ($(\text{NH}_4)_2\text{SiF}_6$) and **pyrazine** was obtained from Sigma-Aldrich. Ferrous hexafluorosilicate hexahydrate ($\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$) was obtained from Alfa Chemsitry. **Graphene** was purchased from Alfa Aesar.

Preparation of $\{[\text{Ni}(\text{pyrazine})_2(\text{SiF}_6)]_n\}$ (SIFSIX-3-Ni). Nickel nitrate (0.870 g, 3 mmol), ammonium silicate (0.510 g, 3 mmol) and pyrazine (0.540 g, 6.75 mmol) were dissolved in 4 mL of deionised water and stirred for 24 h at room temperature to yield a polycrystalline **sql** precursor of **SIFSIX-3-Ni** (blue colour powder). The precursor was air dried and heated at 100 °C for 24 h to obtain the desired **SIFSIX-3-Ni** (1.06 g). Activation of **SIFSIX-3-Ni** was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 h (sample heated from RT to 100 °C with a ramp rate of 10 °C/min).

Preparation of $\{[\text{Ni}(\text{pyrazine})_2(\text{SiF}_6)]_n\cdot\text{graphene}\}$ (SIFSIX-3-Ni@G). Nickel nitrate (0.870 g, 3 mmol), ammonium silicate (0.510 g, 3 mmol), pyrazine (0.540 g, 6.75 mmol) and graphene (300 mg) were dissolved in 4 mL of deionised water and stirred for 24 h at room temperature to yield a dark black suspension. To the resulting suspension was added MeOH (10 mL) and the solid was then filtered under vacuum, washed with methanol and dried at 100°C for 1 day to yield the desired product **SIFSIX-3-Ni@G** (1.290 g). Activation of **SIFSIX-3-Ni@G** was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 h (sample heated from RT to 100 °C with a ramp rate of 10 °C/min).

Preparation of $\{[\text{Ni}_{0.5}\text{Fe}_{0.5}(\text{pyrazine})_2(\text{SiF}_6)]_n\}$ (SIFSIX-3-NiFe). Nickel hexafluorosilicate hexahydrate (924 mg, 3 mmol), Ferrous hexafluorosilicate hexahydrate (912 mg, 3 mmol), and pyrazine (1.04 g, 13 mmol) were dissolved in 6 mL of deionised water and stirred for 24 h at 80 °C to yield a dark brown suspension . To the resulting suspension was added MeOH (10 mL) and the solid was then filtered under vacuum, washed with methanol and dried at 100°C for 1 day to yield the desired product **SIFSIX-3-NiFe** (2.07 g). Activation of **SIFSIX-3-NiFe** was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 h (sample heated from RT to 100 °C with a ramp rate of 10 °C/min).

Preparation of $\{[\text{Ni}_{0.5}\text{Fe}_{0.5}(\text{pyrazine})_2(\text{SiF}_6)]_n\cdot\text{graphene}\}$ (SIFSIX-3-NiFe@G). Nickel hexafluorosilicate hexahydrate (924 mg, 3 mmol), Ferrous hexafluorosilicate hexahydrate (912 mg, 3 mmol), pyrazine (1.04 g, 13 mmol) and graphene (600 mg) were dissolved in 6 mL of deionised water and stirred for 24 h at 80 °C to yield a dark black suspension. To the resulting suspension was added MeOH (10 mL) and the solid was then filtered under vacuum, washed with methanol and dried at 100°C for 1 day to yield the desired product **SIFSIX-3-NiFe@G** (2.45 g). Activation of **SIFSIX-3-NiFe@G** was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 h (sample heated from RT to 100 °C with a ramp rate of 10 °C/min).

Preparation of pyrolysed samples. The synthesized HUMs and HUMs@G were placed in an unsealed quartz box with external dimensions of 100 x 36 x 20 mm. This box was placed into a tube furnace (Model “OTF-1200X-S-DVD” from MTI Corporation) and evacuated to approx. 500 mTorr before being flushed with argon for 5 mins. The argon pressure was then increased to 760 Torr. The box was heated to 800 °C at a ramp rate of 10 °C/min (at a constant pressure), held at that temperature for 2 hrs, before being allowed to cool naturally under argon to give the desired pyrolysed samples.

Powder X-ray Diffraction (PXRD). Diffractograms were recorded using a PANalytical Empyrean™ diffractometer equipped with a PIXcel^{3D} detector operating in scanning line detector mode with an active length of 4 utilizing 255 channels. The diffractometer is outfitted with an Empyrean Cu LFF (long fine-focus) HR (9430 033 7310x) tube operated at 40 kV and 40 mA and CuK α radiation ($\lambda\alpha = 1.540598 \text{ \AA}$) was used for diffraction experiments. Continuous scanning mode with the goniometer in the theta-theta orientation was used to collect the data. Incident beam optics included the Fixed Divergences slit with anti-scatter slit PreFIX module, with a 1/8° divergence slit and a 1/4° anti-scatter slit, as well as a 10 mm fixed incident beam mask and a Soller slit (0.04 rad). Divergent beam optics included a P7.5 anti-scatter slit, a Soller slit (0.04 rad), and a Ni- β filter. In a typical experiment, 20 mg of sample was dried, ground into a fine powder and was loaded on a zero background silicon disks. The data was collected from 5°- 40° (2 θ) with a step-size of 0.02626° and a scan time of 29 seconds per step. Crude data was analysed using the X'Pert HighScore Plus™ software V 4.1 (PANalytical, The Netherlands).

Infrared (IR) Spectra. Infrared spectra were obtained on a PerkinElmer Spectrum 100 FT-IR Spectrometer with a resolution setting of 2 and 16 scans per sample. Data was plotted as percent transmittance with a spacing of 1.929 cm⁻¹ and analyzed using the Spectrum V 6.3 software package.

Thermogravimetric Analysis (TGA). Thermograms were recorded under nitrogen using TGA instrument TA Q50 V20.13 Build 39. Platinum pans and a flow rate of 60 mL/min for the nitrogen gas were used for the experiments. The data was collected in the High Resolution Dynamic mode with a sensitivity of 1.0, a resolution of 4.0, and a temperature ramp of 20 °C/min up to 500 °C. The data was evaluated using the T.A. Universal Analysis suite for Windows XP/Vista Version 4.5A.

X-ray photoelectron spectroscopy (XPS). XPS was performed in a Kratos AXIS Ultra spectrometer using monochromatic Al K α radiation of energy 1486.6 eV. Survey and high-resolution spectra were acquired to determine elemental composition and investigate the chemistry of the surface coatings. Surface charge was efficiently neutralised by flooding the sample surface with low energy electrons. Binding energies were determined using C 1s peak at 284.8 eV as charge reference. For construction and fitting of synthetic peaks of high resolution spectra, a mixed Gaussian-Lorentzian function with a Shirley type background subtraction were used.

Electrochemical measurements. BioLogic SP-150 potentiostat was used in all the measurements. The measurements were conducted in polypropylene container with Pt wire as counter electrode and GCE modified by the material as the working electrode. About 2-3 mg of the solid, see **Table S4**, was dispersed in 500 μl of isopropanol with addition of 10 μl of nafion (10 wt% in isopropanol). The ink was sonicated briefly then applied as a drop-cast (60 μl) over GCE. A reference electrode (RE-61AP) Hg/HgO filled with 1M NaOH (E° vs. RHE = 118 mV at 25°C) from ALS instruments was utilized. For potential conversion from Hg/HgO in the alkaline KOH solution, the relationship $E(\text{RHE}) = E^\circ + (0.059 \cdot \text{pH}) + E_{\text{measured}}$ was used. Ohmic drop (iR) compensation was employed using the current interrupt (CI) method implemented on the EC-lab software of the potentiostat at 85% compensation level. Potassium Hydroxide, Extra Pure, SLR, Pellets, Fisher Chemical was utilized for preparation of 1 M KOH electrolyte solution.

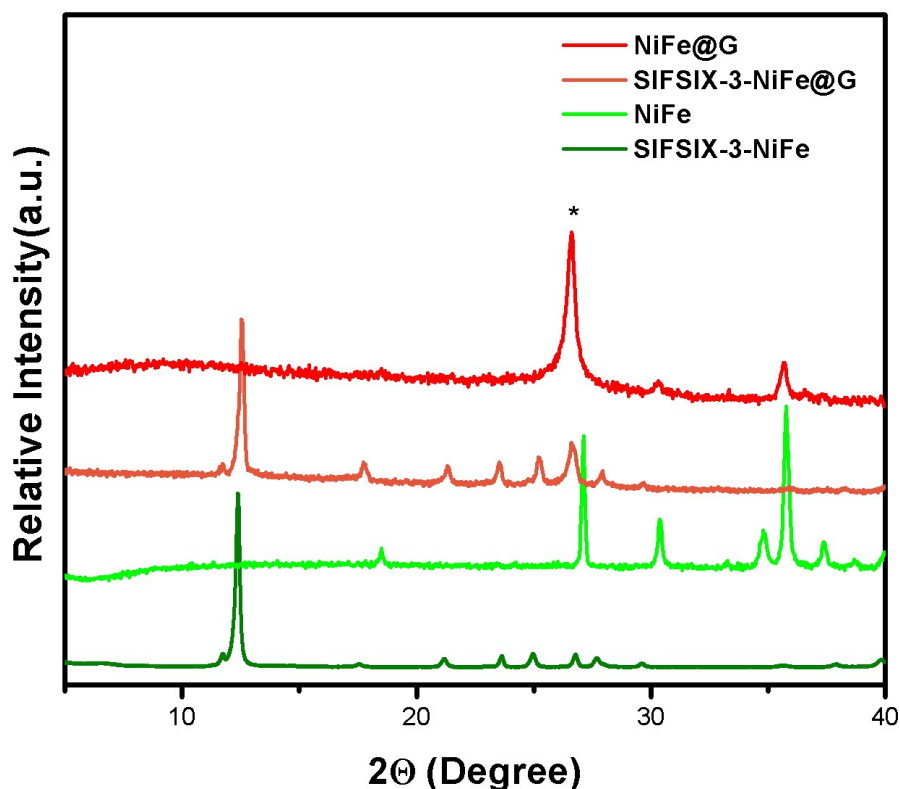


Figure S1. XRD patterns for SIFSIX-3-NiFe, SIFSIX-3-NiFe@G, NiFe and NiFe@G. The Graphitic peak is marked at 26.4°.

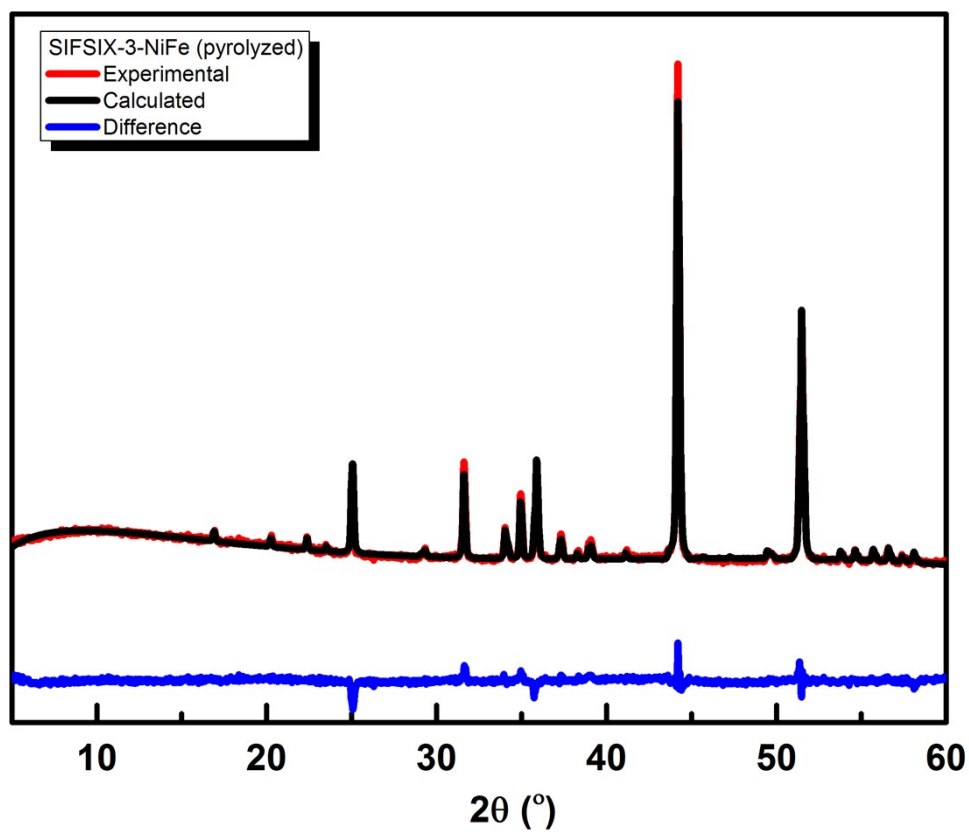


Figure S2. XRD pattern for **NiFe** (red) and the calculated pattern for the mixed phase of diiron silicate (Fayalite, $\text{Fe}_2\text{O}_4\text{Si}$) and Iron Nickel Silicon ($\text{Fe}_{1.5}\text{Ni}_{1.5}\text{Si}$) (black).

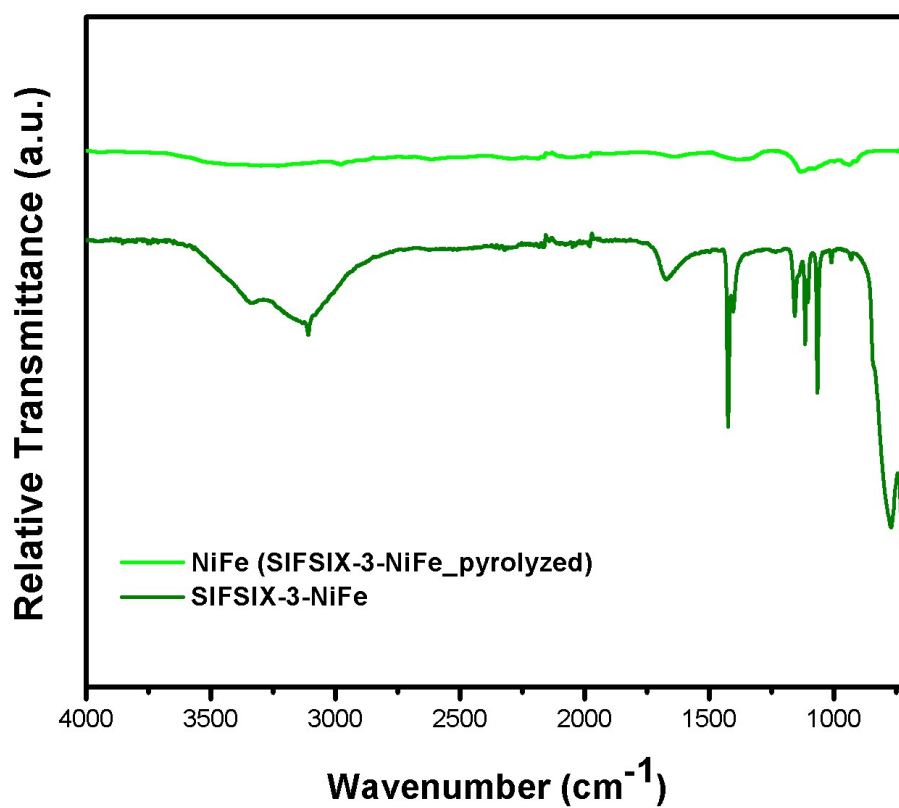


Figure S3. IR spectra for SIFSIX-3-NiFe and NiFe

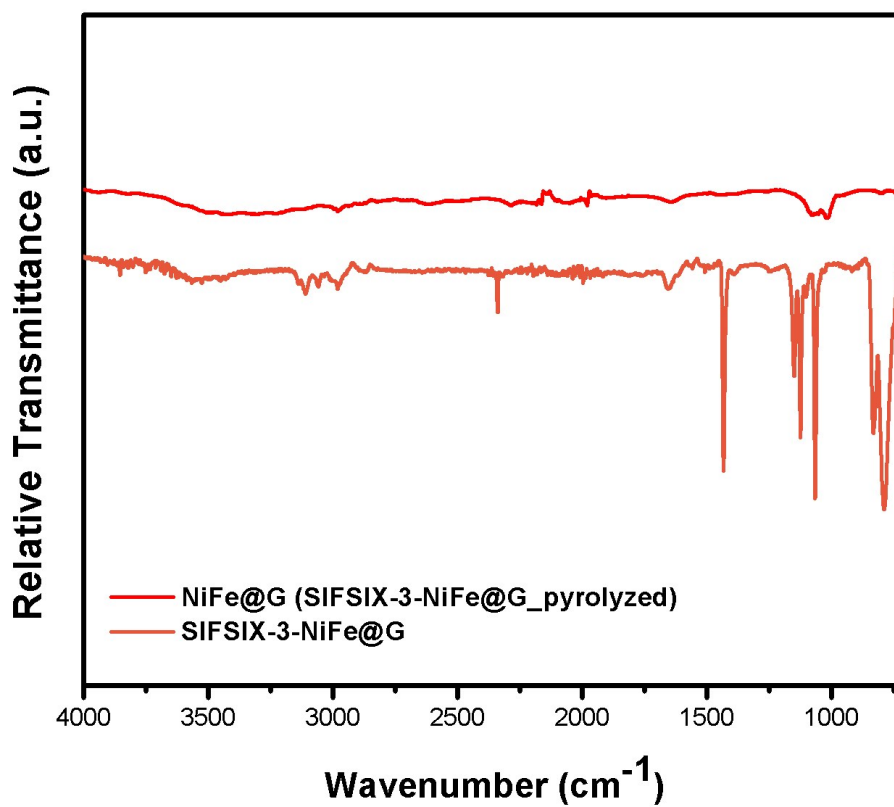


Figure S4. IR spectra for SIFSIX-3-NiFe@G and NiFe@G

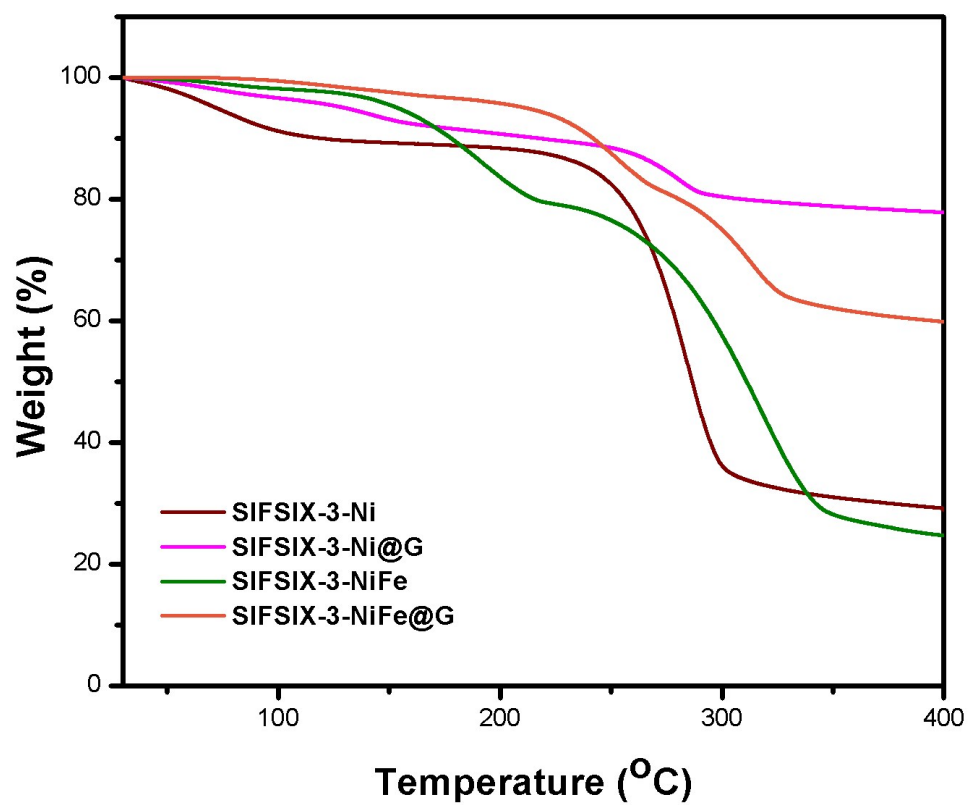


Figure S5. TGA curves for SIFSIX-3-Ni, SIFSIX-3-Ni@G, SIFSIX-3-NiFe and SIFSIX-3-NiFe@G

Peak fitting for SIFSIX-3-NiFe. It was performed in GSAS-II and tabulated in Table S1.^a A background was fitted using a Chebyshev function with five coefficients. Individual peaks were fitted and a unit cell was calculated in *P4/mmm*. Pawley refinement was used to extract peak intensities to a d_{\min} of 2.25 Å.

Table S1. Comparison of **SIFSIX-3-Ni** and **SIFSIX-3-Fe** with the solid solution **SIFSIX-3-NiFe**.

Compound	SIFSIX-3-Ni ^c	SIFSIX-3-NiFe	SIFSIX-3-Fe ^c
Space group	<i>P4/mmm</i>	<i>P4/mmm</i>	<i>P4/mmm</i>
a (Å)	7.001(<1)	7.1475(7)	7.183(1)
b (Å)	7.001(<1)	7.1475(7)	7.183(1)
c (Å)	7.498(<1)	7.5254(6)	7.584(1)
Volume (Å ³)	367.527	384.45(9)	391.306

Analysis of the pyrolysed SIFSIX-3-NiFe (NiFe) and SIFSIX-3-NiFe@G (NiFe@G). It was performed in HighScore Plus™ and tabulated in Table S2.^b Backgrounds were fitted with a polynomial function using six coefficients. The diffractograms were fitted using in automatic mode and the HighScore database was searched using both the peak and profile data to find structural content of the materials. An automatic Rietveld refinement command was used to determine the weight fraction of the underlying components of the mixture.

Table S2. Refinement values for **SIFSIX-3-NiFe**, **NiFe**, and **NiFe@G**.

Compound	SIFSIX-3-NiFe	NiFe	NiFe@G
Background Fitting	Chebyshev	Polynomial	Polynomial
Coefficients	29349.3906 254.1415 -2129.691 -3230.7642 5883.8798	8146.666 -1291.256 2337.475 -1642.072 -152.8447 -26266.08	6496.548 -1444.752 124.2932 96.96715 117.5349 28258.51
R_{exp}	0.056	1.111	1.092
R_p	0.0221	1.331	1.947
wR_p	0.0387	1.967	2.551
GOOF	6.95	1.771	2.335
R_{Bragg}	0.0464	2.83 (Fayalite) 1.51 (Iron Nickel Silicon)	1.310 (Tetrataenite) 0.180 (Graphite)

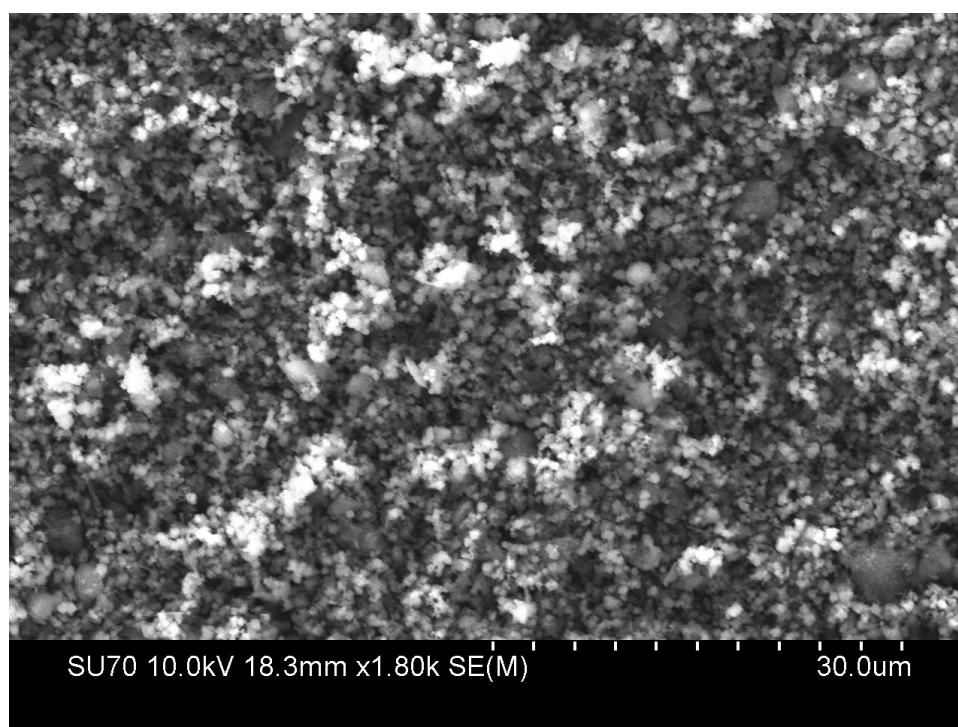


Figure S6. SEM image for **SIFSIX-3-Ni@G** showing the homogeneous deposition of HUMs atop G sheets.

Table S3. XPS elemental surface quantification of **NiFe@G**

	N	Si	C	O	F	Fe	Ni
Mass	1.1	1.3	81.9	6.4	3.0	3.9	2.4
Conc. %							
Atomic	1.0	0.6	89.7	5.2	2.1	0.9	0.5
Conc. %							

Table S4. Weights utilized to prepare ink for electrochemical characterization

Solid	Weight (mg)
NiFe@G	2.17
NiFe	3.21
Ni@G	2.37

References

- (a) Toby, B. H.; Von Dreele, R. B.; *J. Appl. Cryst.***2013**, 46, 544-549.

- (b) Degen, T.; Sadki, M.; Bron, E.; Koenig, U.; Nénert, G., *Powder Diffraction***2014**, 29, S13-S18.
- (c) Elsaidi, S. K.; Mohamed, M. H.; Simon, C. M.; Braun, E.; Pham, T.; Forrest, K. A.; Xu, W.; Banerjee, D.; Space, B.; Zaworotko, M. J.; Thallapally, P. K. *Chem. Sci.***2017**, 8, 2373.