Supporting Information

Pulsed electrodeposited, morphology controlled organic-inorganic nanohybrids as bifunctional electrocatalyst for urea oxidation

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Materials and methods

Materials

All reagents and chemicals were obtained commercially and used without further treatment. 3,4-Diaminobenzoic acid was purchased from Alfa Aser Pvt. Ltd. Amino acids and coupling reagents such as 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and Ni(NO₃)₂.6H₂O were purchased from SRL chemicals. Urea, hexane, ethyl acetate, dimethyl sulfoxide (DMSO) and *N*,*N*'-dimethylformamide (DMF) were purchased from Merck India Ltd. Thin-layer chromatography (TLC, silica gel 60 F_{254}) sheets were obtained from Merck KGaA. Carbon paper was purchased from Global Nanotech, Mumbai.

Characterization

¹H NMR and ¹³C NMR (400 MHz) spectra of organic compounds were recorded on a Bruker AV 400 MHz spectrometer at 300 K using tetramethylsilane as the internal standard. Compound concentrations were in the range of 5-10 mmol L⁻¹ in CDCl₃ and DMSO- d_6 . For SEM measurements, thin films were coated with copper. Then, the images were recorded on a field-gun scanning electron microscope (Jeol Scanning Microscope-JSM-7600F). XRD analysis was performed on Table Top D2-Phaser (Bruker). Transmission electron microscopy (TEM) study was performed on a JEM-2100F, JEOL system. X-ray Photoelectron Spectroscopy (XPS) analysis was performed on PHI 5000, VersaProbe III, Physical Electronics. Gas chromatography (GC) analysis was performed on GCMS-QP2010-SE, Shimadzu. The gaseous product was manually collected by air tight syringe (50 μ L) from a H-shaped electrolytic cell. The gas was manually injected to GC - thermal conductivity detector (TCD).

Synthetic procedure



Scheme S1. Synthetic scheme for liquid phase synthesis of dipeptide BSeFL.

Synthesis of benzo[2,1,3]selenadiazole-5-carboxylic acid (BSe): 1 g of 3,4-diamino benzoic acid (6.57 mmol) and 0.87 g of selenium dioxide (7.88 mmol) were refluxed in methanol (20 mL) and 1N HCl (10 mL) for 2 h at 80 °C. After completion of the reaction, the reaction mixture was cooled at room temperature and methanol was evaporated under reduced pressure. The product was precipitated and filtered with Milli-Q water. Final product **BSe** was obtained after precipitation. Yield = 88% (1.31 g, 5.79 mmol); ¹H NMR (400 MHz, DMSO-*d*6) δ 13.35 (s, 1H), 8.40-8.44 (d, 1H), 7.89-7.98 (m, 2H) ppm. ¹³C NMR (100 MHz, DMSO-*d*6) δ 167.29, 161.13, 159.60, 131.63, 128.28, 125.83, 123.57 ppm.

Synthesis of BSeF-OMe: In dry round bottom flask, 1.2 g of **BSe** (5.26 mmol) was dissolved in the minimum amount of DMF at cold condition. Neutralised phenylalanine methyl ester (1.88 g,

10.52 mmol) was added to the reaction mixture followed by addition of HOBt (0.85 g, 6.31 mmol) and coupling agent EDC (1.21 g, 6.31 mmol). The reaction mixture was allowed to stir at room temperature for 12 h. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was diluted with ethyl acetate and washed with 1N HCl (3×20 mL), saturated Na₂CO₃ solution (3×20 mL) and (3×20 mL) brine solution. The organic layer was separated and dried over anhydrous Na₂SO₄. Ethyl acetate was evaporated and the product was obtained. The product was further purified using silica gel flash column chromatography using hexane: ethyl acetate as solvent system. Yield = 81% (1.67 g, 4.26 mmol); ¹H NMR (400 MHz, CDCl₃) δ = 8.17 (s, 1H, BSe), 7.89-7.90 (m, 2H, BSe), 7.33-7.35 (m, 3H, Phe), 7.18-7.20 (d, *J* = 7 Hz, 2H, Phe), 6.80-6.82 (d, *J* = 7 Hz, 1H, NH), 5.16-5.17 (m, 1H, C^α H), 3.84 (s, 3H, -OCH₃), 3.27-3.40 (m, 2H, C^β H) ppm; ¹³C NMR (100 MHz, DMSO-*d*6): δ = 173.55, 166.18, 160.77, 159.67, 138.60, 134.54, 129.57, 128.72, 128.66, 128.19, 126.90, 125.78, 123.49, 122.85, 54.94, 36.83, 21.52 ppm

Synthesis of BSeF: A solution of BSeF-OMe (1.2 g, 3.08 mmol) in 30 mL distilled methanol was allowed to react with a solution of 2 mL (1N) NaOH solution. The reaction mixture was stirred for 3 h. The reaction progress was monitored by thin-layer chromatography. After the completion of the reaction, excess methanol was evaporated and diluted with 40 mL milli-Q water. Water mixture was washed with diethyl ether. The water mixture was acidified with 1N HCl in an ice bath. The product was extracted with ethyl acetate and dried over anhydrous Na₂SO₄. Ethyl acetate was evaporated under reduced pressure to obtain BSeF.

Yield = 83% (0.96 g, 2.55 mmol); ¹H NMR (400 MHz, DMSO-*d*6) δ = 12.95 (s, 1H, COOH), 9.17 (s, 1H, NH), 8.43 (s, 1H, BSe), 7.97 (s, 2H, BSe), 7.27-7.45 (m, 5H, Phe), 4.82 (m, 1H, C^{α} H), 3.23-3.35 (m, 2H, C^{β} H) ppm; ¹³C NMR (100 MHz, DMSO-*d*6): δ = 173.56, 166.21, 160.79, 159.68, 138.61, 134.55, 129.60, 128.74, 128.21, 126.92, 123.51, 122.87, 54.95, 36.84 ppm

Synthesis of BSeFL-OMe: In a dry round bottom flask, 0.8 g of BSeF (2.13 mmol) was dissolved in 5 mL DMF at cold condition. Neutralised leucine methyl ester (0.61 g, 4.26 mmol) was added to the reaction mixture followed by addition of HOBt (0.34 g, 2.55 mmol) and coupling agent EDC (0.49 g, 2.55 mmol). Reaction mixture was allowed to stir at room temperature for 12 h. The progress of the reaction was monitored by thin layer chromatography

(TLC). After completion of the reaction, the reaction mixture was diluted with ethyl acetate and washed with 1N HCl (3×20 mL), saturated Na₂CO₃ solution (3×20 mL) and (3×20 mL) brine solution. Organic layer was separated and dried over anhydrous Na₂SO₄. Ethyl acetate was evaporated and the product was obtained. The product was further purified using silica gel flash column chromatography using hexane: ethyl acetate solvent system.

Yield = 82% (0.88 g, 1.75 mmol): ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.95-8.97 (d, *J* = 8 Hz, 1H, -NH), 8.57- 8.59 (d, *J* = 8 Hz, 1H, -NH), 8.37 (s, 1H, BSe), 7.86-7.93 (dd, 2H, BSe), 7.42-7.46 (m, 2H, Phe), 7.31-7.35 (m, 2H, Phe), 7.21-7.24 (m, 1H, Phe), 4.84-4.89 (m, 1H, C^αH), 4.40-4.41 (m, 1H, C^αH), 3.69 (s, 3H, OCH₃), 3.03-3.24 (m, 2H, C^β H), 1.57-1.64 (m, 2H, C^β H), 1.69 (m, 1H, C^γ H), 0.87-0.99 (m, 6H, C^δ H) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ = 173.38, 172.06, 166.06, 160.74, 159.66, 138.79, 134.67, 129.67, 128.57, 128.29, 126.78, 123.39, 122.86, 55.21, 52.38, 50.97, 37.54, 24.75, 23.27, 21.85, 21.72 ppm.

Synthesis of BSeFL: 0.8 g of BSeFL-OMe (1.59 mmol) was dissolved in 20 mL distilled methanol. The reaction mixture was allowed to react with 1 mL of 1N solution of NaOH. The reaction mixture was stirred for 3 h. The reaction progress was monitored by thin layer chromatography. After the completion of the reaction, excess methanol was evaporated and diluted with 40 mL milli-Q water. The aqueous mixture was washed with diethyl ether. The aqueous layer was acidified with 1N HCl in an ice bath. The product was extracted with ethyl acetate and dried over anhydrous Na_2SO_4 . Ethyl acetate was evaporated under reduced pressure to obtain orange coloured BSeFL.

Yield = 83% (0.64 g, 1.31 mmol). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.54 (s, 1H, -COOH), 8.88-8.90 (d, *J* = 8 Hz, 1H, -NH), 8.37-8.39 (d, *J* = 8 Hz, 1H, -NH), 8.31 (s, 1H, BSe), 7.80-7.87 (m, 2H, BSe), 7.37-7.41 (m, 2H, Phe), 7.25-7.28 (m, 2H, Phe), 7.16-7.18 (m, 1H, Phe), 4.78-4.91 (m, 1H, C^{α}H), 4.26-4.32 (m, 1H, C^{α}H), 2.97-3.20 (m, 2H, C^{β} H), 1.70-1.73 (m, 1H, C^{γ} H), 1.53-1.62 (m, 2H, C^{β} H),0.82-0.93 (m, 6H, C^{δ} H) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ = 174.49, 171.90, 166.05, 160.74, 159.67, 138.88, 134.71, 129.68, 128.56, 128.31, 126.76, 123.38, 122.85, 79.68, 55.29, 50.91, 24.83, 23.38, 21.89, 14.58 ppm.



Figure S1. Calibration curve of Hg/HgO reference electrode at a scan rate of 1 mV s⁻¹ in hydrogen saturated 1M KOH solution (HOR : Hydrogen Oxidation Reaction).



Figure S2. Cyclic voltammetry curve of 1 mmol BSeFL and 50 mmol $Ni(NO_3)_2.6H_2O$ in 1:1 DMSO/deionized water solution with a scan rate of 10 mV s⁻¹.



Figure S3. SEM images of (a) bare carbon paper, (b) pulsed-electrodeposited BSeF/Ni(OH)₂ (- 1.4 V).



Figure S4. TEM-EDS analysis of pulsed-electrodeposited BSeF/Ni(OH)₂ (-1.0) nanohybrid.



Figure S5. High resolution XPS spectra of (a) N 1s and (b) Se 3d.

Table S1. The electrocatalytic performance of previously reported nickel and organic-inorganic

 nanohybrid based catalysts for OER and UOR performance

Sr. No.	Electrocatalyst	Overpotential (mV) / potential (V vs RHE) for OER @ mA cm ⁻²	Potential (V vs RHE) for UOR @ mA cm ⁻²	Ref.
1	BSeFL/Ni(OH) ₂ (-1.0 V)	180 mV @10 / 1.49 V	1.30 V @ 10 mA cm ⁻²	This Work
2	Ni-MOF	-	1.36 V @ 10 mA cm ⁻²	55
3	Ni ₃ N/NF	-	1.34 V @ 10 mA cm ⁻²	56
4	Ni ₃ N nanosheets	-	1.35 V @ 10 mA cm ⁻²	57
5	pa-NiFe LDH NS/NIF	233 mV @ 30 mA cm ⁻²	1.36 V @ 30 mA cm ⁻²	58
6	Ni(OH) ₂ -NMs	-	1.35 V Onset potential	59
7	1%Cu:α Ni(OH) ₂ /NF	-	1.40 V @ 100 mA cm ⁻²	60
8	Ni-Co ₉ S ₈ /CC 1:2	-	1.43 V @ 100 mA cm ⁻²	61

Table S2. Electrochemical analysis of organic-inorganic nanohybrids

Organic- inorganic Nanohybrid	Tafel Slope (mV dec ⁻¹)	R _{CT} (Ω)	Oxidation Peak Area × 10 ⁻⁴ (A V)	Number of Active Sites × 10 ¹⁸	TOF at 1.70 V VS RHE × 10 ⁻¹ (s ⁻¹)	<i>J</i> _θ (mA cm ⁻²)	ESCA (cm²)
BSeFL/Ni(OH) ₂ (-1.0 V)	167	18.4	7.055	2.177	0.88	0.35	0.50
BSeFL/Ni(OH) ₂ (-1.2 V)	195	22.3	16.8	5.19016E18	0.02436	0.28	0.53
BSeFL/Ni(OH) ₂ (-1.4 V)	322	56.4	18.3	5.65818E18	0.01572	0.11	0.65



Figure S6. (a) LSV curves of BSeFL/Ni(OH)₂ (-1.0 V) at different scan rates, (b) chronopotentiometry curve of BSeFL/Ni(OH)₂ (-1.0 V), (c) chronoamperometry curve of BSeFL/Ni(OH)₂ (-1.0 V) at different potentials, (d) CV curves of BSeFL/Ni(OH)₂ (-1.0 V), (e) BSeFL/Ni(OH)₂ (-1.2 V) and (f) BSeFL/Ni(OH)₂ (-1.4 V) at different san rates.



Figure S7. C_{dl} curves of organic-inorganic nanohybrids.



Figure S8. Gas chromatogram for OER process compared with oxygen. (The gaseous product was manually collected by air tight syringe (50 μ L) from a H-shaped electrolytic cell. The gas was manually injected for GC analysis).



Figure S9. (a) LSV curves of BSeFL/Ni(OH)₂ (-1.0 V) for UOR at different scan rates, (b) Linear relationship curve of current density BSeFL/Ni(OH)₂ (-1.0 V) with different scan rates for UOR. (c) EIS curves of BSeFL/Ni(OH)₂ (-1.0V) nanohybrids at 1.58 V (vs RHE) during OER and UOR, (d) chronoamperometry curve of BSeFL/Ni(OH)₂ (-1.0 V) at different potentials in urea containing 1 M KOH.



Figure S10. Gas chromatogram of UOR process compared with air and nitrogen. (The gaseous product was manually collected by air tight syringe (50 μ L) from a H-shaped electrolytic cell. The gas was manually injected for GC analysis).



Figure S11. High resolution XPS spectra of (a) C 1s and (b) O 1s.

¹H and ¹³C NMR spectroscopy analysis data:



Figure S12. ¹H NMR (DMSO-*d6*, 400 MHz) spectrum of BSe.



Figure S13. ¹³C NMR (DMSO-*d6*, 100 MHz) spectrum of BSe.



Figure S14. ¹H NMR (CDCl₃, 400 MHz) spectrum of BSeF-OMe.



Figure S15. ¹³C NMR (DMSO-*d*6, 100 MHz) spectrum of BSeF-OMe.



Figure S16. ¹H NMR (DMSO-*d*6, 400 MHz) spectrum of BSeF.



Figure S17. ¹³C NMR (DMSO-*d*6, 100 MHz) spectrum of BSeF.



Figure S18. ¹H NMR (DMSO-*d6*, 400 MHz) spectrum of BSeFL-OMe.



Figure S19. ¹³C NMR (DMSO-*d6*, 100 MHz) spectrum of BSeFL-OMe.



Figure S20. ¹H NMR (DMSO-*d6*, 400 MHz) spectrum of BSeFL.



Figure S21. ¹³C NMR (DMSO-*d6*, 100 MHz) spectrum of BSeFL.