**Supporting Information** 

# Electrodeposition of Binder Free Peptide/Co(OH)<sub>2</sub> Nanohybrid Electrodes for Solid State Symmetric Supercapacitor

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**Figure S8**. The photographs show LED lighted by BSeYY/Co(OH)<sub>2</sub>/CP symmetric solid state devices assembled in a series.



**Figure S9**. Nitrogen adsorption-desorption isotherm of (a) BSeYY and (b) BSeYY/Co(OH)<sub>2</sub> samples (the inset corresponds to BJH pore size distribution curve).

**Table S1.** Summary of the BET surface areas and pore structures of BSeYY andBSeYY/Co(OH)2

Sample	$S_{BET} (m^2 g^{-1})$	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore Diameter (nm)
BSeYY	3.77	0.009	3.80
BSeYY/Co(OH) <sub>2</sub>	6.70	0.082	3.79

**Table S2.** A comparison with recently developed cobalt hydroxides/oxides and organic inorganic

 hybrid electrode materials and electrochemical performances

S. No	Electrode materials	Specific capacitance	Current density	Electrolyte	Cycle number & % capacitance retention	Ref.
1	Co(OH) <sub>2</sub> rods	1116 F g <sup>-1</sup>	2 A g <sup>-1</sup>	1 M KOH		53
2	Co(OH) <sub>2</sub> /GNS	693.8 F g <sup>-1</sup>	2 A g <sup>-1</sup>	1 M KOH	3000 and 91.9%	58
3	Co(OH) <sub>2</sub> -rGO	734 F g <sup>-1</sup>	1 A g <sup>-1</sup>	2 M KOH	1000 and 95%	65
4	MOF-derived Co(OH) <sub>2</sub>	604.5 F g <sup>-1</sup>	0.1 A g <sup>-1</sup>	6М КОН	2000 and 70%	69
5	Flower-like Co(OH) <sub>2</sub>	429 F g <sup>-1</sup>	1 A g <sup>-1</sup>	2 M KOH		70
6	Co(OH) <sub>2</sub>	416 F g <sup>-1</sup>	1 A g <sup>-1</sup>	2 M KOH	500 and 93%	71
7	cobalt oxides/hydroxides	427 C g <sup>-1</sup>	1 A g <sup>-1</sup>	1 М КОН		72
8	BSeYY/Co(OH) <sub>2</sub> /CP	974.78 F g <sup>-1</sup>	1 A g <sup>-1</sup>	1 M KOH	3000 and 78.62%	This work



Scheme S1. Synthetic procedure of compound 5.

#### **Materials and Methods**

In this work, all the reagents were used without further purifications. L-Tyrosine (Y), 1hydroxybenzotriazole (HOBt), N,N'-dicyclohexylcarbodiimide (DCC), potassium hydroxide (KOH), hydrochloric acid (HCl), dimethyl sulphoxide (DMSO) and cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) were procured from SRL, India. 3,4-Diaminobenzoic acid and SeO<sub>2</sub> were purchased from Sigma-Aldrich, USA. Whatman filter paper was procured from Merck India Limited. CP substrate and Swagelok cell were purchased from Global Nanotech, Mumbai, India. Bruker AV 400 MHz NMR spectrometer was used to characterize peptide molecules (concentrations range of 5-10 mmol L<sup>-1</sup>) in CDCl<sub>3</sub> and DMSO-*d*6. Electrospray ionization mass spectrometry was performed using mass spectrometer (model: Bruker micrOTOF-Q II) by positive and negative modes. Fourier transform infrared spectroscopy was performed on KBr pellets on a FTIR spectrophotometer (model: Bruker Tensor 27) in the range of 500-4000 cm<sup>-1</sup>. The LabRAM HR Evolution, Horiba Scientific Raman spectrometer with a 633 nm He-Ne laser of 5 mW power at room temperature was used to record Raman spectra. X-ray diffraction (XRD) analysis of the synthesized BSeYY/Co(OH)<sub>2</sub>/CP nanohybrid was characterized by using a Bruker D<sub>2</sub> phaser X-ray diffractometer with Cu-K $\alpha$  irradiation ( $\lambda = 1.54$  Å). X-ray photoelectron spectroscopy (XPS) (model: AXIS Supra, Kratos Analytical) was used to study the compositions and oxidation states of the element of the electrodeposited materials. The elemental characterization and surface morphology of the BSeYY/Co(OH)<sub>2</sub>/CP nanohybrid were analyzed by Carl Zeiss JEOL FE-SEM together with Elemental mapping and EDS. The textural properties of the synthesized materials were characterized by Autosorb iQ3 (Quantachrome) gas sorption analyzer under N<sub>2</sub> adsorption at 77 K. Transmission electron microscope (TEM) was assessed to further analyze the microstructure of the synthesized BSeYY/Co(OH)<sub>2</sub>/CP nanohybrid using a JEM-2100F, JEOL system. Electronic balance was used to carry out the mass loading with weight difference method. The electrochemical measurements such as cyclic voltammetry (CV), cyclic stability, electrochemical impedance spectroscopy (EIS) and galvanostatic chargedischarge (GCD) test were conducted by Metrohm Autolab potentiostat (PGSTAT302N). The freshly prepared electrolyte solution was used during electrochemical analysis to sustain consistency.

#### Synthesis of organic compounds

Synthesis of benzo[2,1,3]selenadiazole-5-carboxylic acid (1): 3,4-Diaminobenzoic acid (3 g, 19.71 mmol) and selenium dioxide (4.37 g, 39.38 mmol) were refluxed in methanol (20 mL) and 1N HCl (10 mL) for 2 h at 80 °C. The reaction mixture was cooled at room temperature and methanol was evaporated at reduced pressure. The product was precipitated and filtered with ultrapure water. The obtained precipitate was dried in oven at 60 °C to yield 4.18 g (18.40 mmol, 93%) of **1** as a faint pink colored solid.<sup>1,2</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 8.38 (s, 1H, BSe), 7.94-7.86 (dd, 2H, J = 9.28, 9.20 Hz, BSe) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 167.29$ , 161.13, 159.58, 131.62, 128.29, 125.81, 123.61 ppm; MS (ESI): *m*/*z* calcd. for C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>O<sub>2</sub>Se: 228.9516 [M+H]<sup>+</sup>; found: 228.9370.

Synthesis of BSeY-OMe (2): 1 g (4.40 mmol) of 1 and HOBt (0.71 g, 5.28 mmol) was solubilized in 5 mL of DMF in a 100 mL round bottom flask. A neutralized solution of tyrosine methyl ester was extracted from its corresponding hydrochloride salt (2.04 g, 8.80 mmol) and concentrated by rotary evaporator to add the reaction mixture followed by coupling agent  $N_i N'$ dicyclohexylcarbodiimide (1.09 g, 5.28 mmol) at 0 °C and allowed to stir at room temperature for 12 h. After completion of the reaction, the reaction mixture was diluted with acetonitrile solvent and filtered by sintered glass funnel (Borosil G4) to remove the dicyclohexylurea (DCU). Then, the reaction mixture was concentrated by using rotary evaporator. The ethyl acetate was added to the reaction mixture and washed with 1N HCl, saturated Na<sub>2</sub>CO<sub>3</sub> solution and saturated brine solution. Solid brown colored compound of 2 was obtained after evaporating the solvent under reduced pressure. Compound 2 was purified using flash chromatography. Yield = 1.58 g, (3.90 mmol, 89%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.22$  (s, 1H, OH of Tyr), 9.13-9.12 (d, J =7.56 Hz, 1H, NH), 8.35 (s, 1H, BSe), 7.91-7.85 (dd, J = 9.52, 9.44 Hz, 2H, BSe), 7.13-7.11 (d, J = 7.96 Hz, 2H, Tyr), 6.68-6.66 (dd, J = 7.96 Hz, 2H, Tyr), 4.67-4.61 (m, 1H, C<sup> $\alpha$ </sup> H of Tyr), 3.66 (s, 3H, -OCH<sub>3</sub>), 3.10-2.99 (m, 2H,  $C^{\beta}$  H of Tyr) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ =172.60, 166.19, 160.75, 159.60, 156.43, 134.25, 130.49, 128.09, 128.02, 123.53, 122.93, 115.54, 55.31, 52.44, 36.01 ppm; MS (ESI): *m/z* calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>Se: 428.0125 [M+Na]<sup>+</sup>; found: 428.0179.

Synthesis of BSeY-OH (3): The solid compound 2 (0.7 g, 1.73 mmol) was dissolved in 30 mL distilled methanol and allowed to react with a solution of 3 mL (1N) NaOH solution. The reaction mixture was stirred. The hydrolysis progress was monitored by thin layer chromatography. After the completion of the reaction, the methanol was evaporated to dryness and diluted with 40 mL milli-Q water. Then, the water mixture was taken in a separating funnel and slowly washed with diethyl ether ( $2 \times 20$  mL). The aqueous layer was collected and cooled in an ice bath. Then, the cooled aqueous solution was acidified with 1N HCl. The pH of aqueous solution was adjusted to 2 and the product was extracted with ethyl acetate (3×30 mL). The ethyl acetate layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure to obtain a solid compound 3. Yield = 0.61 g (1.56 mmol, 91%); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 12.77 (s, 1H, -COOH), 9.19 (s, 1H, OH of Tyr), 8.99-8.97 (d, J = 7.84, 1H, -NH), 8.33 (s, 1H, BSe), 7.91-7.85 (dd, J = 9.76, 9.68, 2H, BSe), 7.14-7.12 (d, J = 7.76, 2H, Tyr), 6.67-6.65 (d, J = 7.76, 2H, Tyr), 7.67-6.65 (d, J = 7.76, 2H, Tyr), 7.67-6.65 (d, J = 7.76, 7.76, 7.76, 7.76-76, 7.76 (d, 7.80, 2H Tyr), 4.59 (s, 1H, C<sup>α</sup> H of Tyr), 3.13-2.95 (m, 2H, C<sup>β</sup> H of Tyr) ppm. <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ):  $\delta = 173.62, 166.14, 160.77, 159.67, 156.36, 134.57, 130.50, 128.58, 128.21, 100.50$ 123.51, 122.84, 115.52, 55.28, 36.05 ppm; MS (ESI): *m/z* calcd. for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub>Se: 389.9993 [M-H]<sup>-</sup>; found: 390.0138.

Synthesis of compound BSeYY-OMe (4): A solution of compound 3 (0.55 g, 1.40 mmol) and HOBt (0.230 g, 1.69 mmol) was stirred in DMF (2 mL). A neutralized solution of H<sub>2</sub>N-Tyr-OMe was extracted from its corresponding hydrochloride salt. It was concentrated for addition to the reaction mixture drop by drop followed by coupling agent *N*,*N*'-dicyclohexylcarbodiimide (0.35 g, 1.69 mmol) in ice cold condition and allowed to stir for 12 h. The TLC was used to confirm the product formation. The reaction mixture was diluted with acetonitrile solvent and, filtered it by sintered glass funnel to remove the DCU. The excess acetonitrile was evaporated by rotary evaporator. Then, the reaction mixture was diluted by the ethyl acetate. After that, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum by rotary evaporator to yield solid compound **4**. The flash chromatography was used to purification of compound **4** with ethyl acetate and hexane as eluent. Yield = 0.59 g (1.04 mmol, 74%): <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 9.19 (s, 1H, OH of Tyr), 9.15 (s, 1H, OH of Tyr), 8.84-8.82 (d, *J* = 8.08 Hz, 1H, -NH), 8.31 (s, 1H, BSe), 7.89-7.82 (dd, *J* = 9.16, 9.08 Hz,

2H, BSe), 7.16-7.14 (d, J = 7.60 Hz, 2H, Tyr), 7.03-7.02 (d, J = 7.60 Hz, 2H, Tyr), 6.65-6.63 (d, J = 7.60 Hz, 4H, Tyr), 4.72, (s, 1H, C<sup> $\alpha$ </sup> H of Tyr), 4.45-4.43 (d, J = 6.28 Hz, 1H, C<sup> $\alpha$ </sup>H of Tyr) 3.59 (s, 3H, OCH<sub>3</sub>), 3.02-2.83 (m, 4H, C<sup> $\beta$ </sup>H of Tyr) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta =$ 172.44, 172.01, 165.99, 160.75, 159.68, 156.53, 156.23, 134.73, 130.60, 130.54, 128.74, 128.34, 127.50, 123.38, 122.85, 115.57, 115.36, 55.54, 54.60, 52.30, 36.73, 36.40 ppm; MS (ESI); *m/z* calcd. for C<sub>26</sub>H<sub>24</sub>N<sub>4</sub>O<sub>6</sub>Se: 591.0759 [M+Na]<sup>+</sup>; found: 591.0871.

Synthesis of compound BSeYY (5): Compound 4 (0.40 g, 0.70 mmol) was dissolved in 30 mL distilled methanol. The solution was allowed to stirred for 5 h with adding 2 mL NaOH (1N) solution. The hydrolysis progress of the reaction was monitored by TLC. After completion the reaction, the methanol was evaporated by rotary evaporator. The residue was diluted with 40 mL milli-Q water and taken in a separating funnel. The aqueous layer was slowly washed with diethyl ether (2×20 mL). The aqueous layer was cooled in ice bath and adjusts the pH 2 by using 1N HCl. The aqueous reaction mixture was extracted with ethyl acetate (3×30 mL). The ethyl acetate layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure with rotary evaporator to yield a brownish solid compound 5. Yield = 0.34 g (0.61 mmol, 87%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.72 (s, 1H, -COOH), 9.24 (s, 1H, OH of Tyr), 9.20 (s, 1H, OH of Tyr), 8.88-8.86 (d, J = 8.52 Hz, 1H, -NH), 8.34 (s, 1H, BSe), 8.31-8.29 (d, J = 7.72 Hz, 1H, -NH), 7.93-7.85 (dd, J = 9.32, 9.24 Hz, 2H, BSe), 7.20-7.18 (d, J = 8.08 Hz, 2H, Tyr), 7.09-7.07  $(d, J = 7.92 \text{ Hz}, 2H, \text{Tyr}), 6.68-6.66 (d, J = 6.52 \text{ Hz}, 4H, \text{Tyr}), 4.76-4.72 (m, 1H, C^{\alpha} \text{ H of Tyr}),$ 4.46-4.41 (m, 1H, C<sup> $\alpha$ </sup>H of Tyr), 3.07-3.00 (m, 2H, C<sup> $\beta$ </sup>H of Tyr), 2.92-2.87 (m, 2H, C<sup> $\beta$ </sup>H of Tyr) ppm; <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ):  $\delta = 173.37$ , 171.85, 165.99, 160.73, 159.66, 156.43, 156.19, 134.74, 130.59, 128.77, 128.33, 127.89, 123.37, 122.82, 115.49, 115.36, 55.67, 54.41, 36.69, 36.37 ppm; MS (ESI); m/z calcd. for C<sub>26</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub>Se: 553.0626 [M-H]<sup>-</sup>; found: 553.0638.



Figure S10. <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) of 1.



Figure S11. <sup>13</sup>C NMR spectrum (100 MHz, DMSO-*d*<sub>6</sub>) of 1.



Figure S12. ESI-MS spectrum of 1.



Figure S13. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2.



**Figure S14**. <sup>13</sup>C NMR spectrum (100 MHz, DMSO-*d*<sub>6</sub>) of **2**.



Figure S15. ESI-MS spectrum of 2.



Figure S16. <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) of 3.



Figure S17. <sup>13</sup>C NMR spectrum (100 MHz, DMSO-*d*<sub>6</sub>) of **3**.



Figure S18. ESI-MS spectrum of 3.



Figure S19. <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) of 4.



Figure S20. <sup>13</sup>C NMR spectrum (100 MHz, DMSO-*d*<sub>6</sub>) of 4.



Figure S21. ESI-MS spectrum of 4.



Figure S22. <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) of 5.



Figure S23. <sup>13</sup>C NMR spectrum (100 MHz, DMSO-*d*<sub>6</sub>) of 5.



Figure S24. ESI-MS spectrum of 5.

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