Engineering of Benzoselenadiazole Based Organic-Inorganic Nanohybrids for Energy Storage and Energy Conversion

Ph.D. Thesis

by **DEVRAJ SINGH**



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Engineering of Benzoselenadiazole Based Organic-Inorganic Nanohybrids for Energy Storage and Energy Conversion

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Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by DEVRAJ SINGH



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INDIAN INSTITUTE OF TECHNOLOGY INDORE



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled Engineering of Benzoselenadiazole Based Organic-Inorganic Nanohybrids for Energy Storage and Energy Conversion in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from August-2017 to November-2022 under the supervision of Prof. APURBA K. DAS, Professor, Department of Chemistry, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Durray Singh

signature of the student with date (DEVRAJ SINGH)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge. Λ

Signature of Thesis Supervisor with date

(Prof. APURBA K. DAS)

DEVRAJ SINGH has successfully given his Ph.D. Oral Examination held on March 10, 2023.

10 Signature of Thesis Super (Prof. APURBA K. DAS)

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Date:

Devraj Singh

Dedicated to My Beloved

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LIST OF PUBLICATIONS

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literatures

LIST OF ABBREVIATIONS

DMF	-	Dimethyl Formamide
DCC	-	Dicyclehexylcarbodiimide
HOBt	-	1-Hydroxybenzyl Alcohol
HCl	-	Hydrochloric acid
MeOH	-	Methanol
Na ₂ CO ₃	-	Sodium Carbonate
NaCl	-	Sodium Chloride
TLC	-	Thin Layer Chromatography
EtOAc	-	Ethyl Acetate
DMSO	-	Dimethylsulfoxide
CDCl ₃	-	Chloroform-d
2D	-	Two-dimensional
3D	-	Three-dimensional
AC	-	Activated carbon
PVDF	-	Polyvinylidene fluoride
PVA	-	Polyvinyl alcohol
FTIR	-	Fourier-transform Infrared Spectroscopy
XRD	-	X-ray Diffraction
FE-SEM	-	Field-emission Scanning Electron Microscopy
TEM	-	Transmission Electron Microscopy
SAED	-	Selected Area Electron Diffraction
EDS	-	Energy Dispersive Spectroscopy
XPS	-	X-ray Photoelectron Microscopy
SCs	-	Supercapacitors
PVDF	-	Poly(vinylidenedifluoride)
PVA	-	Polyvinyl alcohol
DI	-	De-ionized
EDLCs	-	Electrical double-layer capacitors
CV	-	Cyclic voltammetry
GCD	-	Galvanostatic charge-discharge
ECSA	-	Electrochemical surface area
Cdl	-	Double layer capacitance
EIS	-	Electrochemical impedance spectroscopy
LSV	-	Linear sweep voltammetry
TOF	-	Turn over frequency
SSCs	-	Symmetric supercapacitors
ASCs	-	Asymmetric supercapacitors
OER	-	Oxygen evolution reaction
HER	-	Hydrogen evolution reaction

		OF SIMBOLS
Cs	-	Specific capacitance
π	-	Pi
σ	-	Sigma
m	-	Active mass
М	-	Molar
eV	-	Electron volt
μm	-	Micrometer
nm	-	Nanometer
Hz	-	Hertz
Ι	-	Current
Q	-	Charge
V	-	Voltage or Volt
E	-	Energy density
Р	-	Power density
А	-	Area of electrode
F	-	Farad
Ω	-	Ohm
W	-	Watt
h	-	Hour
k	-	Kilo
g	-	Gram
λ	-	Wavelength
d	-	Inter-atomic spacing
θ	-	Angle
t	-	Time
mV	-	Millivolt
mA	-	Milliampere
η	-	Overpotential
Ζ	-	Impedance
Z	-	Real part of the impedance
Z	-	Imaginary part of the impedance
Rs	-	Solution resistance
Rct	-	Charge transfer resistance

LIST OF SYMBOLS

GLOSSARY

Active material: The material in the electrodes of a cell that takes part in the electrochemical reactions of charge or discharge and electrocatalysis.

Aging: Permanent loss of capacity due to repeated use/passage of time.

Ambient temperature: The average temperature of the surroundings.

Ampere hour capacity: The quantity of electricity measured in ampere-hour which may be delivered by a cell under specified conditions.

Ampere-hour efficiency: The ratio of the output of a secondary cell measured in Ampere-hours to the input required to restore the initial state of charge under specified conditions.

Capacity: The total number of ampere-hours that can be withdrawn from a fully charged cell under specified conditions of discharge.

Capacity fade: Loss of capacity in a device with cycling.

Capacity retention: The fraction of its full capacity that is available under specified discharge conditions after a cell has been stored for a period of time.

Charge: The conversion of electrical energy from an external source (in the form of a current) into chemical energy within a cell or device.

Constant current charge: A method of charging the device using a current having little variation.

Constant voltage charge: A method of charging the cell or device by applying a fixed voltage and allowing variations in the current.

Current collector: An inert member of high electrical conductivity used to conduct current during charge/discharge and electrocatalysis.

Current density: The current per unit active area of the surface of an electrode. **Cutoff voltage:** The device voltage at which the discharge is terminated.

Cycle: The discharge and subsequent or preceding charge of a device such that it is restored to its original conditions.

Diffusion: The movement of ions under the influence of a concentration gradient.

Discharge: The conversion of chemical energy into electrical energy of a device and the subsequent withdrawal of that energy into a load.

Discharge rate: The rate usually expressed in amperes, at which electrical current is taken from the device.

Electrode: The site, area or location at which electrochemical processes take place.

Electrolyte: The medium which provides the ions/electrons transport mechanism.

Electron: A negatively charged particle that orbits the nucleus of an atom.

Energy: The output capability of a cell is usually expressed in watt-hours.

Energy density (Wh/kg): The amount of energy stored in a given system or region of space per unit volume.

Power density (W/kg): Power density is the amount of power (time rate of energy transfer) per unit volume.

Negative electrode: The electrode acts as an anode when a cell or device is discharging.

Positive electrode: The electrode acts as a cathode when a cell or device is discharging.

Separator: An ion-permeable, electronically non-conductive, spacer or material which prevents electronic contact between electrodes of opposite polarity in the same cell or device.

Watt hours: A common measurement of energy produced in a given time, arrived at by multiplying the voltage by the amp hours.

Overpotential: The difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis.

General Introduction

Chapter 1

1.1 Introduction

The climate change along with rapid energy consumption, scarcity of the fossil fuels and natural resources are becoming major threats to our planet accompanied by the destruction of ecosystems, habitats, extinction of wild life and deterioration of the environment. All these factors are encouraging modern society and researchers towards the development of renewable, efficient and sustainable resources using environmentally friendly technologies for efficient energy storage and conversion materials.^[1-11] As a consequence, energy is enormously being produced from natural resources such as water, wind and sunlight. Despite their widespread use, they have some limitations, such as the sun not shining at night, the wind not blowing when needed and so on. As a result, energy storage systems are becoming increasingly important in our daily lives. Several electrochemical energy conversion and storage systems such as fuel cells, batteries, supercapacitors and electrolyzers have been extensively investigated to achieve higher energy and efficiency.^[12-17] The performance of such devices have to be considerably improved to meet the basic necessities of human life including portable electronics, hybrid electric vehicles, large industrial equipment along with the proliferation of new materials and innovation of electrochemical interface at nanoscale. The traditional capacitors and batteries are frequently used. But, several drawbacks are accompanied with slow power delivery or uptake and reactivity of metal electrodes leading to dendrites formation, which can reduce the cycle life of capacitors. Since, a number of applications are needed to deliver faster and high energy systems. Electrochemical capacitors (ECs) or supercapacitors are fulfilling all the requirements. These are essential substitutes for energy storage systems that have the opportunity to fulfill rising energy demand and environmental concerns. The power devices or ECs can be fully charged/discharged in a matter of seconds. The urgent need for efficient energy storage devices as a consequence, ECs have a lower energy density than batteries, but they can supply or uptake more power in a shorter time. The ECs also called supercapacitors (SCs), golden capacitors or ultracapacitors. When high power uptake or delivery is necessary, supercapacitors can take the role of batteries. The SCs demonstrate excellent power density, long cycle life, quick charging, and safety over batteries. Now a days, the SCs are currently an emerging class of power sources that store the energy using either ion adsorption or fast surface redox reactions.^[18] Therefore, based on the accumulation of the charge, the SCs are separated into electrical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors. The EDLCs are composed of carbon-based materials and store the charge electrostatically or non-Faradaically. Therefore, there is no charge transfer between the electrode and the electrolyte, and there are no chemical or composition changes related to a non-Faradaic reaction. The charge can be stored in EDLCs using a variety of carbon materials including carbon nanotubes, carbon aerogels, and activated carbons.^[19,20] Additionally, a pseudocapacitors store charge faraday by passing electricity from electrode to electrolyte. This is

accomplished through electrosorption, oxidation-reduction, intercalation/deintercalation process, achieving higher capacitance properties and energy density than EDLCs.^[21] These are being developed for a wide range of applications including common electronic devices, medical utilities, transportation and defense-related systems. Power density (P) and energy density (E) are the two key factors that determine energy storage systems. Power density is the quantity of stored energy that can be supplied per unit volume, whereas energy density is the amount of energy stored per unit volume. Furthermore, electrochemical water splitting is receiving much attention to meet global energy demands and generate sustainable energy.^[22] The two half-reactions of the electrochemical water electrocatalysis process are the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). The OER is a four electron transfer reaction and requires 1.23 V theoretical overpotential, whereas HER is a two electron transfer process that requires 0.0 V overpotential.^[23] Therefore, the sluggish kinetics of the OER suppresses the water electrocatalysis process. So, highly efficient and active catalysts are required to accelerate the kinetics and reduce the overpotential of the OER reaction. The Ru and Ir based electrocatalysts are very active and exhibit low overpotential.^[24-27] But, their low abundance, high cost and instability during long-term electrocatalysis in the basic medium are restricted for large scale applications. Therefore, extensive research have been done to search for sustainable and non-precious metal materials.^[7,8,23,28-31] The electrocatalyst with weak bond strength of metal oxy hydroxide intermediate exhibits tremendous efficiency and kinetics during electrocatalysis.^[32,33] The electrode materials are the core constituent of the energy storage devices and electrolyzers. Therefore, several materials such as metal oxides, sulfides, nitrides and hydroxides have been used as electrode materials.^[34,35,36,37,38,39,40,41] Higher energy efficiency and energy storage densities require multifunctional novel electrode materials with high performance. Control over micro and nanoscale structures is important in electrochemical processes for efficient ion and electron movement at the electrode-electrolyte interface. The self-assembly of active electrode material into ordered architectures via van der Waals interactions, hydrogen bonding and electrostatic interactions provides ion transportation channels and active sites for electrochemical applications.^[27,42] Therefore, the organic-inorganic hybrid materials with non-precious metals are one of the most promising candidates for next-generation energy storage and energy conversion applications due to their exceptional intrinsic properties such as high specific surface area, electrical charge mobility, thermal conductivity, low cost and excellent electrochemical performance.^[23,43-45] The organicinorganic hybrid materials have received a lot of attention for their potential applications in energy storage and conversion devices due to their unique architecture and a variety of fascinating properties. The hybrid materials with ordered architecture is essential to enhance electrochemically active sites and facile intercalation/deintercalation of the ions.^[17,44-52] Organic-inorganic hybrid materials are composed of metal ions or metal ion clusters linked through
coordinative bonds or electrostatic interactions to organic ligands denoted as linkers. Ordinarily, aromatic polycarboxylates and organic multi-nitrogen compounds used as the organic linkers and these two types of compounds correspond to the two main coordination modes namely oxygen coordination and nitrogen coordination.^[10,46,53-56] The Organic-inorganic hybrids have the structural, electronic and chemical properties along with convenient production to validate the tremendous ongoing research initiatives that are anticipated to influence different commercial applications such as adsorption, sensing, solar cell, drug delivery, catalysis, energy storage and energy conversion.^[10,23,55,57-69] The use of organic-inorganic hybrids as electrode materials in energy storage and conversion is a rapidly growing field that offers the most promising, environmentally friendly and cost-effective solutions.^[10,55,56,63,65,66,70-72] Organic molecules having acid functional groups have drawn a lot of attention due to their capacity to combine with inorganic moieties to create organic-inorganic nanohvbrid materials.^[45,70,72-81] Organic-inorganic hybrid materials have been synthesized using many techniques, including hydrothermal, solvothermal, electrodeposition, chemical co-precipitation process, chemical bath deposition and atomic layer deposition.^[45,63,72,82-86] The electrodeposition approach allows for the cost-effective, straightforward, binder-free and in-situ controlled development of nanostructured metal hydroxide based material over a working electrode.⁸⁴ The electrodeposition method eliminates the need of expensive binders, reduces inactive surface area and extra contact resistance during electrochemical analysis.^[23,30,40,43,50,87-90]

1.2 Electrochemical methods to synthesize electrode materials

The electrochemical deposition method takes a short synthesis time and operates in mild conditions. In order to synthesize organic-inorganic nanohybrids electrochemically, an electrolytic solution containing inorganic and organic components as well as electrolytes is required. Cross-linking or coordination of organic and inorganic components in the presence of an electric field resulted in the formation of nanohybrid materials. A variety of redox mechanisms control the *in-situ* synthesis of organic-inorganic nanohybrids in an electrolytic solution containing precursors generated by an electric field. The electrochemical deposition method for nanohybrid synthesis can be divided into three categories depending on the type of precursors and the applied electric field: anodic electrodeposition, reductive electrodeposition, and electrophoretic deposition.^[91-94]

1.2.1 Anodic electrodeposition

Anodic electrodeposition is also an anodic dissolution in the linkers containing electrolytes near the electrode surface. The essential charge to oxidize the anode for the synthesis of organic-inorganic nanohybrid can be applied constant potential (potentiometric mode) or current (amperometric mode). In the anodic electrodeposition method, there is no need of metal salts. Therefore, when the anodic current or voltage applied then the metal substrate (anode) gets oxidized and dissolved in electrolyte solutions. The dissolved metal ions simultaneously interact with organic linkers near the electrode surface in the solution to form thin layer of organic-inorganic hybrid materials.^[93-96]

The anodic coordinated deposition method is schematically illustrated in **Figure 1.1**. In order to create the deposition bath, 4 g of chitosan (CS) powder were completely dissolved in 1 L of a 1% acetic acid solution. Then, 50, 100, 150, and 200 mL/L of the AgNPs-containing suspension were added to the newly created solution. 0.1 M NaOH was used to bring the pH of the created deposition bath down to 5.5 ± 0.1 . The solutions underwent a 10 min. ultrasonic treatment before to trials.



Figure 1.1 Schematic illustration of anodic CS-AgNP composite deposition using coordination with copper ions.

An Autolab 302N potentiostat/galvanostat was used to carry out the electrodeposition procedure. The following electrolyte was used to cathodically deposit the Cu pretreatment layer onto the steel surface: 40 g/L of CuSO₄ × 5H₂O, 100 g/L of H₂SO₄, and 3 mg/L of thiourea. Deposition was carried out for 25 s at a cathodic current density of 2 A/dm². The anode was made of a copper plate. The surface was then carefully cleaned with distilled water and allowed to air dry. Such a treatment allowed to exclude the influence of the pre-deposition bath's components on the characteristics of the CS coatings. The stability of Ag ions could be improved by adding a little amount of sulfuric acid, though. In a two-electrode arrangement, copper-coated steel served as the anode while Pt foil served as the cathode to deposit CS-based coatings. The deposition was carried out for 20 s at a current density of 2 A/dm². Initiation of the oxygen evolution with longer deposition, the hydrogel that forms may flake. After electrolysis, samples were taken out of the deposition bath, gently rinsed with deionized water, and allowed to air dry.^[95]

Tang *et al.* fabricated the ordered pattern of HKUST-1 on conductive ITO substrate. The HKUST-1 was synthesized on the ITO surface using two steps (**Figure 1.2**): The first step involves to synthesize thin layer of copper on ITO cathodically using a precursor solution containing 5 mmol L^{-1} CuSO₄ and 0.1 mol L^{-1} K₂SO₄ for 500 seconds. In the second step, HKUST-1 was synthesized by

anodically combining the Cu thin film with 25 mmol L^{-1} BTC (linker) and 50 mmol L^{-1} TBAP in a 3:1 v/v ethanol and water mixture (supporting electrolyte).^[97]



Figure 1.2 Schematic of an electrodeposited Cu film serving as the source for the quick synthesis of a HKUST-1 film on ITO.

Attfield *et al.* synthesized the zeolite imidazolate framework (ZIF-67) on Co electrode via anodic electrodeposition to utilize in energy storage application. The fixed potential was applied on the Co electrode in the electrolyte containing imidazolate linker and tributylmethylammonium methyl sulphate (TBMAMS) as shown in **Figure 1.3**.^[98]



Figure 1.3 The experimental setup used to create the ZIF coatings is depicted in this diagram.

Two Co or Zn electrodes are immersed in a tributylmethylammonium methyl sulphate (TBMAMS) electrolyte solution containing an imidazolate linker in an N,N-dimethylformamide (DMF):H₂O electrolyte solution. The ZIF coating on the anode is generated by applying heat while descrating the solution with N₂(g) and the 2.5 V applied potential difference.

1.2.2 Cathodic electrodeposition

Cathodic electrodeposition (CED) is also known as reductive electrodeposition. The negative current or potential is applied on the conductive substrate surface in an electrolyte solution containing inorganic and organic components. After applying potential, the pH near the working electrode increases due to the formation of the OH⁻ ions. Simultaneously, the deprotonation of the organic

component is started and deprotonated linkers combined with metal ions present in the electrolyte solution and organic-inorganic hybrid materials precipitated on the working electrode surface.^[89,99,100]

Mousavi *et al.* used a DMF-water mixture as a solvent. The organic linker is highly soluble in DMF and the water-based electrolyte ensures high electrical conductivity, produces OH- ions required for *in-situ* deprotonation of the organic linker and promotes the dissolution and ionic mobility of the metallic species. The optimal DMF:H₂O solvent ratio is 50:50 (v/v)% (**Figure 1.4**). When, the energy storage/conversion performance is taken into consideration, the pro-base (NO₃⁻) plays an important part in the electrodeposition process by making it easier for the BDC-NH₂ ligand to deprotonate in the bulk reaction medium. The addition of CTAB as a surfactant (at the optimal concentration of 0.09 M) helps to regulate ion transport in the reaction media, control the processes of nucleation and development and customize the size and shape of the resultant MOF.



Figure 1.4 The diagram of the reductive electrosynthesis of the Fe-Co-Ni trilayer MOF.

Another crucial variable that significantly influences the growth and orientation of the MOF throughout the electrosynthesis process is the applied reductive potential step. The driving force necessary to initiate and continue the electrosynthesis of the MOF is the reductive potential step that results in deprotonation of the linker and reduction of NO₃⁻ close to the surface of the working electrode. In order to get the required results in terms of structure, morphology, and performance, it is important to identify the proper reductive potential. The ideal potential is thought to be the reductive potential of -1.5 V vs. Ag/AgCl (KClO₄) reference electrode since it yields the best results. The following is a general description of the reductive electrodeposition mechanism:^[23]

$$NO_3^- + H_2 0 \rightleftharpoons NO_2^- + 20H^-$$
$$H_2BDC - NH_2 + 20H^- \rightleftharpoons (BDC - NH_2)^{2-} + 2H_2O^-$$

$$(BDC - NH_2)^{2-} + M^{2+} \rightleftharpoons [(BDC - NH_2)^{2-}M^{2+}] (i.e.MOF)$$

Dincă *et al.* reported a work to synthesize the MOF-5 organic-inorganic nanohybrid by potentiostatic reductive electrodeposition and proposed a mechanism for the fabrication of the hybrid materials. According to their study, the thin film on the FTO substrate after applying the -1.6 V constant potential for 15 min in the DMF/H₂O solution containing the $Zn(NO_3)_2$, 1,4-benzene dicarboxylic acid (H₂BDC) and tetrabutylammonium hexafluorophosphate [(NBu₄)PF₆] components, which acts as metals source, organic linkers and supporting electrolyte respectively.



Figure 1.5 Diagram showing the mechanism underlying the cathodic electrodeposition of MOFs.

The applied potential plays a vital role in the reduction of the NO_3^- to form NO_2^- ions and OH^- ions. Therefore, a rise in the local pH enhances the deprotonation of the linkers (H₂BDC) to interact with metal ions for the electrodeposition of the hybrid materials (Zn₄O(BDC)₃) as depicted in **Figure 1.5**.^[89]

Stupp *et al.* fabricated the organic-inorganic hybrid materials on stainless steel substrate by electrodeposition process using a precursor solution of pyrene butyric acid (PyBA) and Co(NO₃)₂ metal salts. They also synthesized the hybrid material using non-aromatic side chain organic molecule (decanoic acid) with Co(NO₃)₂ metal salts in water/dimethyl sulfoxide solution to investigate the effect of the organic molecule. The SEM analysis discloses the PyBA based hybrid material (Co(OH)₂/PyBA) exhibits perpendicular nanotubular morphology. Furthermore, TEM analysis reveals, the nanotubes constituted from the alternative rings of PyBA and Co(OH)₂ layers (**Figure 1.6**). Whereas, the

hybrid materials (Co(OH) $_2$ /DA) of decanoic acid and Co(OH) $_2$ exhibit flat film morphology.



Figure 1.6 Characterization of the layered hybrid nanostructure morphology (a) $Co(OH)_2/PyBA$ nanotubes growing perpendicular to the substrate in a cross-sectional SEM picture. (b) $Co(OH)_2/PyBA$ nanotubes are depicted in bright-field TEM images (left and top right) and a high-angle annular dark field STEM picture (bottom right). (c) Diagram showing the layering inside a nanotube made of PyBA bilayers and inorganic $Co(OH)_2$ tubes and (d) SEM image of a flat $Co(OH)_2/DA$ film developed on a substrate.

Furthermore, electrochemical measurements revealed that the $Co(OH)_2/PyBA$ hybrid material had better electrochemical performance and stability than the $Co(OH)_2/DA$ nanohybrid materials owing to the easy and non-covalent interactions as well as the well-integrated PyBA and $Co(OH)_2$ bilayers.^[101]

Das *et al.* synthesized the *in-situ* crosslinked organic-inorganic nanohybrids (**Figure 1.7**) directly on the conductive surface of the carbon paper via potentiastatic electrodeposition method. Which were utilized in electrochemical water splitting.^[102]



Figure 1.7 Diagram illustrating the electrochemical deposition of organicinorganic nanohybrids utilizing peptides on a carbon paper electrode.

1.2.3 Electrophoretic deposition

Electrophoretic deposition (EPD) is extensively used technique to allow the fabrication of the thin films of inorganic nanoparticles or macromolecular organic components by the influence of an electric field. The deposition can be performed on flat, cylindrical and any substrate shape. The EPD technique provides a short processing time, cost-effectiveness, ease of control of the thickness and morphology of the deposited layer with a simple change in deposition time and potential.



Figure 1.8 Schematic diagram of the electrophoretic deposition (EPD) process of the hybrid MoS₂/PANI electrode.

Depending on the surface charge associated with the particle, EPD drives through two steps cathodic and anodic electrophoretic deposition. The motion of the positively charged particles towards the negatively charged electrode is called cathodic deposition. Conversely, the mobility of the negatively charged ions or particles in the direction of the positive electrode is called anodic EPD. Numerous materials such as oxides, hydroxides, borides, carbides, nitrides, carbonates, metals, alloys, and polymers can be fabricated with EPD.^[92,103-107] This method is more appropriate to fabricate inexpensive, less time consuming synthesis, electric conductive, magnetic, ferroelectric and other functional properties materials.^[103,104,108] Hupp *et al.* have synthesized the four types of MOFs HKUST-1, Al(1,4-benzenedicarboxylate)(C₈H₅AlO₅, Al-MIL-53), UiO-66 and Zr₆(OH)₁₆[1,3,6,8-tetrakis(benzoate)pyrene]₂(C₈₈H₄₄O₃₂-Zr₆, NU-1000) with using EPD by applying 90 V constant DC voltage in toluene precursor suspensions via fluorine doped tin oxide (FTO).^[109] Nam *et al.* exploited the electrophoretic technique to fabricate a binder-free $MoS_2/PANI$ hybrid electrode. The homogeneous colloidal solution of the synthesized 1D polyaniline (PANI) and 2D MoS_2 fabrication $MoS_2/PANI$ was obtained by dispersing in acetonitrile (ACN) solvent. The 32 V DC voltage was applied for 20 min. on conducting stainless steel substrated against the graphite electrode in the precursor solution to fabricate the $MoS_2/PANI$ nanohybrid electrode. **Figure 1.8** shows the porous $MoS_2/PANI$ structure that was generated by a synergistic nanohybrid interface between layered MoS_2 and PANI nanowires.^[110]

1.3 Principles and mechanism of energy storage in supercapacitors

Different types of capacitors have recently become available for energy storage. Each capacitor has unique properties and uses from high voltage power factor (supercapacitors) adjustment to minor trimming applications in electronics (normal capacitors). Research on supercapacitors has risen in recent years to fulfil the demand for uses that need characteristics like increased specific energy, improved cycle life and reliability. When confronted with electrochemical behaviour, supercapacitors have a battery-like configuration. The bi-electrode configuration of a supercapacitor is separated by an electrolyte-immersed separator. The main parts of the supercapacitor device assembly are two electrodes, electrolyte solution, separator, and current collector.^[111]

Supercapacitors exploit the processes of charging and discharging at the electrode-electrolyte interface to store energy. Supercapacitors store energy in the same way that a traditional capacitor does, but they are better suited for quick energy release and storage.

Two mechanisms serve as the foundation for the governing principles of energy storage:

- The adsorption of Coulombian charge near to the electrode-electrolyte interface is the cause of the EDL capacitance.
- Pseudocapacitance caused by quick redox reactions that are associated with their respective potential.
- While, the storing principle of the hybrid supercapacitor is a combination of both types.

1.4 Electrochemical assessment for energy storage and conversion

The cyclic voltammetry (CV), galvanostatic charge discharge (GCD), electrochemical impedance (EIS), linear sweep voltammetry (LSV) and chronopotentiometry measurements were assessed for electrochemical profiling. These analysis techniques are elaborated in the following sections.

1.4.1 Cyclic voltammetry

CV is a frequently used potentiodynamic technique to estimate the qualitative and quantitive parameters of the electrode materials. CV analysis helps to

determine the electrochemical kinetics, electrochemical surface area (ECSA), reversibility of the reactions, reaction mechanism, electrocatalytic processes and redox properties. The CV analysis is generally carried out with using three electrodes (reference electrode, counter electrode and working electrode) system. CV is recorded by scanning the potentials back and forth within the specific upper and lower limits.

1.4.2 Galvanostatic charge/discharge assessment (GCD)

GCD is one of the best technique for evaluating the specific capacitance of the electrode materials in one particular potential window with a controlled current density. The discharging curve is used to estimate the specific capacitance. Moreover, this measurement is very useful to evaluate the stability of the materials with the assessment of the several charging/discharging cycles at fixed potential windows and constant current density.

The electrochemical profile assessment includes the calculation of specific capacitance (F g^{-1}), energy density (W h k g^{-1}) and power density (W k g^{-1}) corresponding to specific current density (A g^{-1}). These factors determine the electrochemical performance of an electrode material in any supercapacitor assembly. An electrode substance can inherit a certain amount of energy according to the relationship stated in the equation:^[72,112]

$$Cs = \frac{I \times \Delta t}{m \times \Delta V}$$

Where ΔV denotes the potential drop, I (A) represents the constant current, Δt (s) represents the discharging time on GCD and m (mg) exhibits the mass of active material on the electrode.

The following equations can be used to estimate the energy and power density of the asymmetric supercapacitor (ASC) device:^[72,113-115]

$$E = \frac{Cs \times \Delta V^2}{2 \times 3.6} (Wh/kg)$$
$$P = \frac{3600 \times E}{\Delta t} (W/kg)$$

The following formulas are used to estimate the specific capacitance (Cs) value, energy density (E) and power density (P) of the symmetric supercapacitor device:^[116-118]

$$Cs = \frac{2(I.\Delta t)}{m.\Delta V} (F g^{-1})$$
$$E = \frac{Cs \times \Delta V^2}{8 \times 3.6} (Wh kg^{-1})$$
$$P = \frac{3600 \times E}{\Delta t} (W kg^{-1})$$

Here, Cs denotes the specific capacitance of the device (F/g), I (A) represents discharge current, Δt represents the discharge time (s), m (g) stands for the active material mass on one electrode and ΔV (V) represents operating potential window

after internal resistance drop, E stands for the energy density (Wh/kg) and P represents the power density (W/kg).

1.4.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements are used to calculate the impedance of electrode materials. EIS analysis is typically carried out in the frequency range of 0.01 Hz to 100 kHz, with amplitudes ranging from 5 mV to 10 mV. The Nyquist plot is frequently used to calculate solution resistance, charge transfer resistance and other values.

1.4.4 Linear sweep voltammetry (LSV)

LSV is the electrochemical analysis to examine the efficiency, overpotential and kinetics (Tafel slope) of the electrocatalysis. It is uni-directional from the initial point to the end point. It is often used to determine the current response of the working electrode, which is generated due to the oxidation or reduction of the active materials during linear scanning of potential between a working electrode and a reference electrode.

1.5 Characteristic features of the supercapacitors device

The energy storage device must be manufactured for practical use as shown in **Figure 1.9**.



Figure 1.9 Schematic illustration for supercapacitor device.

The active material electrode, electrolyte, separator and sealants make up the supercapacitor device. All of these features contribute to increase the capacity and performance of the device. As a result, these critical characteristics are briefly discussed in the following section:

1.5.1 Electrolyte materials

The electrolyte is the most important constituent of the cell, which contains salt in an aqueous and non-aqueous medium to conduct ions and charge on both electrodes of the cell or device. Researchers have developed and employed a variety of electrolytes including organic electrolytes, aqueous electrolytes, ionic liquids and solid state polymer electrolytes. The H₂SO₄, KOH, Na₂SO₄, Li₂SO₄, pyrrolidinium dicyanamide, PVA/H₃PO₄ and PVA/KOH electrolytes are frequently used for supercapacitors. Based on the solvent nature, the electrolytes are divided into aqueous and non-aqueous electrolytes. The conducting salts dissolved in the organic solvents are called the organic electrolyte. The organic electrolytes procure a wider potential window to enhance the capacitive performance. But, organic electrolytes exhibit some drawbacks like high cost, lower specific capacitance, inflammability, volatility, toxicity and inferior conductivity. In contrast, aqueous electrolytes are considered much attention due to their high ionic concentration, lower resistance and uplift ionic conductivity. The three categories of aqueous electrolytes are acidic, neutral and basic electrolyte. Thus, the most widely used electrolytes are H_2SO_4 , Na_2SO_4 , and KOH because of their abundant availability and low price. The smaller potential window is still a problem for the aqueous electrolytes despite their improved specific capacitance. Therefore, solid polymer electrolyte-based supercapacitors have attracted significant attention due to their higher ionic conductivity, high thermal, chemical and electrochemical stability. Additionally, solid polymer electrolyte both ionic conducting electrode acts as media and separator.^[21,111,119,120]

1.5.2 Separator

The separator is the sandwich material between the two electrodes. It prevents the cell from short circuit, allows ions to pass through and performs vital cell-sustaining functions. The inferior quality separators play an important role to sustain the overall cell performance and reduce additional resistance. Therefore, the selection of a separator is an important task to enhance the ionic conductivity, which affects the energy and power density of the device.^[21] The separators must satisfy the criteria as follows:

• Non-conductive separators are required.

• Separator should have minimum ionic resistance with optimum porosity.

• They should possess high mechanical and chemical stability to counter the volume change of the cell.

• Separators should possess the ease of high electrolyte uptake to provide sufficient ions to the electrode.

1.5.3 Current collectors

Current collectors aid in the improvement of electrolyte/active materials contact. Fast current transmission between the electrode and current source as well as between the electrode and an external medium is made possible by the current collector.



Figure 1.10 Substrate materials for building self-supported electrodes for electrochemical energy conversion and storage.

Active materials coated on current collectors facilitate electrolyte contact, lower interfacial resistance and enhance electrochemical performance. Nickel mesh, nickel foam, carbon paper, carbon cloth, graphene sheet, graphene and stainless steel have been used as current collectors in recent years and their images depicted in **Figure 1.10**.^[21,120-122]

1.5.4 Sealants

Sealants play a supporting role in the supercapacitor assembly and restrict from performance degradation. Sealant serves as a protective shield against external pollutants like air, water, chemicals and more.^[123] These pollutants may result in electrode surface oxidation and electrolyte degeneration. As a result, proper supercapacitor device sealing is essential to avoid contamination and shunt resistance. Inadequate sealing can result in shunt resistance between the cells connected to the assembly. This shunt current causes a reduction in charging efficiency, as well as self-discharging and short circuiting.^[124]

1.6 Material requirements and their characterizations

The effectiveness of energy storage and catalytic activity are significantly influenced by the electrode material. And it has received a lot of interest among the researchers. It is clear that enhancing electrochemical performance, such as high specific capacitance, low overpotential, good rate capability, and long-term stability, requires control of the architecture and interface properties of electrode materials. Fortunately, nanotechnology has widened the scope of materials science and engineering, and it is becoming more crucial in the advancement and development of materials to address the issues. An electrode material with a large surface area and high electric conductivity is expected to emerge to allow the easy ion penetration, efficient electrode/electrolyte interaction and fast intercalation/deintercalation of electrolyte ions during energy storage and conversion performances. Innovative materials design techniques have been used to examine a number of materials including carbonaceous materials, metal complexes and conducting polymers. The Engineered nanostructures provide enough electroactive sites and improve ion and electron transport kinetics. Figure 1.11 depicts the general characterization techniques, controllable architectures and properties of organic-inorganic hybrid materials.



Figure 1.11 The schematic image depicts the definition, characterizations, controllable architectures and properties of organic-inorganic hybrid materials.

Moreover, **Figure 1.12** represents the synthesis processes, structure, materials properties and application of organic-inorganic compounds in various processes and fields.

Chapter 1



Figure 1.12 The image depicts the synthesis processes, structure, materials properties and applications of organic-inorganic compounds.

Several organic-inorganic hybrid materials have been utilized in energy storage applications. Wang et al. assembled a device (Figure 1.13) to illuminate an LED using hydrogel made of Fmoc-EF-NH₂ and thin layer of TiO₂. The dissolution of peptide electrode in electrolyte was prevented by the thin film coating of TiO₂.^[83]



Figure 1.13 (a) The image of the peptide-coated electrode (top) and the image of the fabricated symmetrical double-layer capacitor (bottom). (b) HRTEM image of a peptide fiber with a thin TiO_2 layer on it. (c) Peptide electrode cyclic voltammograms at various scan rates. (d) Cyclic voltammograms for peptide fiber coated with a thin layer of TiO_2 at various scan rates. (e) Galvanostatic charge/discharge analysis of peptide fiber with a thin TiO_2 coating at various current densities. (f) The cyclic stability of the peptide@TiO_2 electrode devices (pink line) and the areal capacitances computed from the CV curves at various scan rates (deep green line). The inset image displays peptide@TiO_2 capacitor devices connected in series lighting an LED.

Cheng *et al.* synthesized the nickel terephthalate (Ni-Tp) based organic-inorganic hybrid material directly on nickel foam using a hydrothermal synthesis process. The SEM images displayed in **Figure 1.14 (a-c)** that the NF is fully coated with uniform and aggregated rectangular crystals.



Figure 1.14 SEM pictures of the prepared samples on Ni foam. (a-c) Ni-Tp and (d-f) Ni-Tp/PANI.

Furthermore, as shown in **Figure 1.14** (**d-f**), the surface of the hydrothermally synthesized Ni-Tp electrode was completely covered with PANI after electrodeposition to form Ni-Tp/PANI electrode. The Ni-Tp/PANI electrode exhibited excellent cycling stability and a specific capacitance of 938.845 F g⁻¹ at 1.818 A g⁻¹ current density. Moreover, the areal specific capacitance of the Ni-Tp/PANI electrode (10.327 F cm⁻²) is nearly twice that of the Ni-Tp electrode (5.353 F cm⁻²) as shown in **Figure 1.15**. As a result, electrochemically deposited PANI electrodes perform better electrochemically in terms of capacitance.^[125]



Figure 1.15 Electrochemical behaviour of Ni-Tp and Ni-Tp/PANI electrodes compared using (a) CV curves at a 5 mV s⁻¹ scan rate, (b) GCD curves at a 20 mA cm⁻² current density, (c) EIS Nyquist plots and (d) coulombic efficiency at a 50 mA cm⁻² current density.

Stupp *et al.* reported the cobalt hydroxide based organic-inorganic hybrid material that was made using the electrochemical deposition approach.



Figure 1.16 Electrochemical assessment of hybrid films. (a) Galvanostatic charge/discharge charcaterisation for a tubular $Co(OH)_2/PyBA$ film at various current densities. (b) Specific capacity and capacitance values for the charge/discharge curves in (c) Cyclic voltammograms in 1M KOH at a scan rate of 10 mV of a flat $Co(OH)_2/PyBA$ film and a nanotubular $Co(OH)_2/PyBA$ film. Comparing the estimated specific charge capacity from CV of a nanotubular film on a flat film. (d) 1M KOH (e) 0.1M TBAP/acetonitrile. (f) CV in 1M KOH for

b-value estimation of nanotubular and flat films. (g) Nyquist impedance plot of nanotubular and flat films in 1 M KOH.

Their team tested the effects of organic moiety on electrochemical performance by replacing the intercalated decanoic acid (DA) molecules in a Co(OH)₂/DA flat film with pyrene butyric acid (PyBA) to form nanotubular Co(OH)₂/PyBA for comparison as depicted in **Figure 1.16**. The flat film has a low specific capacity of 14.0 mA h g⁻¹ compared to 40.6 mA h g⁻¹ for nanotubular films at 10 A g⁻¹ current density. Furthermore, the capacity of the nanotubular film decreased to 18.5 mA h g⁻¹ after 10000 cycles. As a result of the charging and discharging, they noticed changes in surface area and morphology. Moreover, the flat film retains only 1.5 mA h g⁻¹ capacity after 10000 cycles. As a result, Co(OH)₂/DA flat films have a lower specific capacity than nanotubular films, indicating that film morphology is the most important factor in electrochemical performance.

1.7 Energy conversion application

The extensive demands of energy and environmental concerns have promoted researchers to look for highly efficient, clean and renewable energy sources. Electrocatalytic water splitting has received much attention for generating sustainable energy sources.^[126-129] However, water splitting is a challenging task due to the inherent stability of the water molecules. The oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode are both involved in the electrochemical water splitting process. However, OER is a sluggish kinetics reaction and needs a higher overpotential (more than 1.23 V) due to the transport of the four protons and four electrons to generate one molecule of oxygen from two molecules of water.^[127-131] Therefore, highly active and efficient electrocatalysts are required to facilitate electrocatalysis. The catalyst of precious metal contents and oxides exhibits tremendous catalytic activity, but their low abundance and high cost restrict commercial applications. Thus, alternative electrocatalysts with low cost, highly active, stable and low overpotential are required to compete with precious metalbased catalysts. Therefore, 3d transition metal based oxides, hydroxides, sulphides and organic-inorganic hybrid materials are taking much interest to develop highly efficient electrocatalytic materials.^[132,133,134] Moreover, significant efferts have been directed to synthesize efficient electrocatalyst to tune the binding strength of the intermediate with active sites and facilitate ions and electrons transport. Markovic *et al.*, explains the trends of electrocatalytic activity of 3d transition metal ions are in the order of Ni > Co > Fe > Mn for HER (bifunctional) and OER (monofunctional) in an alkaline medium. This is inversely related to the strength of the intermediate bond. Moreover, the presence of greater number of the d-electrons in the 3d orbitals of nickel promote the electron-electron repulsion as well as electron-lone pairs (2p of oxygen atoms) repulsion. Therefore, various type repulsion decrease the bond strength of the metal(oxy)hydroxide intermediate, which enhance the OER activity.^[32,33]

Therefore recent design and synthesis of the electrocatalysts based on 3dtransition metals are exploring for future perspectives due to their low cost and high abundance. Moreover, the multi-metallic materials possess good electrochemical activity than monometallic materials due to synergistic effect between the metals, which lead to enhance the active sites and conductivity.^[23,56,129,135-141]



Figure 1.17 (a) ECD method of Fe/Ni-BTC MOF thin films. (b) Design and fabrication of Fe/Ni-BTC MOFs. (c) Optical image, (d) scanning electron microscopy (SEM) image and (e) SEM image of Fe/Ni-BTC@NF at high magnification.

On the other hand, the organic-inorganic catalyst with monometallic and bimetallic transition metal ions are taking enormous attention due the exposer of more electrochemically active sites, facile transport of the ions and enhance electrical conductivity.^[23,49,56,76,126,131,134,138,142-144] Wang *et al.* fabricated the ECD Ni-BTC@NF, ECD Co-BTC@NF and ECD Fe/Ni-BTC@NF highly active organic-inorganic material via cathodic electrodeposition (CED) method (**Figure 1.17**) without using binder on nickel foam (NF) substrate with applying -1.5 V potential for 30 s. Among them, the ECD Fe/Ni-BTC@NF exhibits superior OER performance with 270 mV overpotential at 10 mA cm⁻² and Tafel slope 47 mV dec⁻¹ as depicted in **Figure 1.18**.^[145]



Figure 1.18 (a) ECD Ni-BTC@NF, ECD Fe-BTC@NF, ECD Fe/Ni@NF, ECD Fe/Ni-BTC@NF and NF LSV curves recorded at 2 mV s⁻¹. (b) ECD Ni-BTC@NF, ECD Fe-BTC@NF, ECD Fe/Ni@NF, and ECD Fe/Ni-BTC tafel graphs measured at 1 mV s⁻¹. (c) Comparison of ECD Ni-BTC, ECD Fe-BTC, ECD Fe/Ni, ECD Fe/Ni-BTC, bulk Ni-Fe oxides, and porous Ni-Fe oxides.

The long-term stability test is a good criteria for determining the robustness and catalytic stability in practical applications. As a result, there are two common methods for estimating long-term catalytic performance. Setting a current density of 10 mA cm⁻² or higher for an extended period of time is one method. Another method for evaluating stability is to use CV or LSV experimental techniques to evaluate long-term cycling performance.

The total electrode activity is usually determined by using a linear sweep voltammetry measurement (LSV). The reference electrode was calibrated to the RHE scale for electrocatalysis in all measurements using the following equation:^[76] $E_{RHE} = E_{Ag/AgCl} + 0.197 + (0.0591 \times pH)$ V. All the tests were carried out at room temperature. The extra potential needed for the electrochemical reaction over and above its reversible potential is known as the overpotential (η) at a specific current density. Intrinsic reaction activation barriers, in addition to other resistances like solution and contact resistance, are the main causes of the overpotential.

 $\eta_{\text{HER}} = E_{\text{RHE}} - 0 (V)$

 $\eta_{OER} = E_{RHE} - 1.23 (V)$

The Tafel diagram illustrates the relationship between the overpotential (η) and the current density and is obtained from LSV findings (*j*). Tafel equation: $\eta = a + blog(j)$, where b is the Tafel slope. The Tafel slope value is frequently used to

assess the catalytic activity of the catalyst toward the OER and also offers crucial details about the reaction mechanism. A low Tafel slope is a necessary characteristic of an OER electrocatalyst. ECSA = C_{dl}/Cs formula. Where, Cs is the specific capacitance of real surface area.^[23,146] Whereas, C_{dl} is the double layer capacitance and estimated from a fitted straight line slope between current density and scan rates.

Water electrolysis includes deceptively simple reactions, but there are numerous theoretical and technological issues that must be resolved immediately. Electrocatalytic water splitting is the process by which electrical energy is transformed into renewable energy in the presence of a catalyst. Which consists of two half reactions called the cathodic HER and the anodic OER as shown in Figure 1.19a. Figure 1.19b depicts the water splitting reactions in acidic and alkaline media. The HER is a typical two-electron transfer reaction that includes intermediate adsorption and desorption steps. As illustrated in Figure 1.19c and **1.19d**, there are two widely accepted mechanisms that relate to the HER in both acidic and alkaline electrolytes, respectively. The intermediate H^{*} participates in the production of hydrogen regardless of whether the process uses the Volmer-Heyrovsky or Volmer-Tafel mechanism, which makes the hydrogen adsorption free energy (ΔGH^*) into the primary criterion for hydrogen evolution activity. Additionally, the ΔGH^* of the ideal catalyst should be close to 0. The HER in an alkaline electrolyte is noticeably different from that in an acid electrolyte Due to the absence of the H^+ proton. The dissociation of the H_2O molecule adsorbed on the surface via the Volmer reaction. Whereas, the combination of H^* and a hydrogen through the Heyrovsky step or Tafel step to produce a hydrogen molecule. Actually, compared to those in acid solution, the activity and exchange current density of the catalyst are much lower in the alkaline electrolyte. This is mostly because the succeeding reaction needs excessive dissociation of water molecules in the Volmer step, which determines the rate of the HER in an alkaline electrolyte. Moreover, the OER is extensively used in a variety of clean and green energy storage and conversion technologies, including metal-air batteries, electrolytic water, photoelectric electrolytic water, and CO₂ reduction. However, the energy conversion efficiency is reduced due to the slow kinetic reaction rate and high reaction overpotential due to the involvement of the four electron processes. There are two widely accepted OER mechanisms: the conventional adsorbate evolution mechanism (AEM) and the lattice oxygenmediated mechanism (LOM) respectively. As seen in Figure 1.19e and 1.19f, the OER is a four-electron transfer process with a number of intermediates (M-OH, M-O, and M-OOH) generating an oxygen molecule. In acidic aqueous solution, first, the active sites interact with water molecules to generate M-OH intermediates. Next, MOH interacts with oxygen to form MO. There are two different ways to generate oxygen in an acidic aqueous solution: One is that the immediate release of oxygen atoms from two MO intermediates, and the other is that MO combines with water molecules to produce the MOOH intermediate, which is then used to liberate O₂ atoms. The MOOH intermediate has not formed in the OER, as illustrated in **Figure 1.19e**. But, the O-O bond has been formed through two nearby oxo species making the LOM substantially distinct from the AEM.^[71,147]



Figure. 1.19 (a) Scheme of a typical water electrolysis system. (b) Watersplitting semi-reaction under acidic and alkaline conditions. Schematic representation of the mechanism of the hydrogen evolution reaction under (c) acidic and (d) alkaline conditions, where M stands for the active sites on the electrode surface. (e) The adsorbate evolution mechanism (AEM) of OER processes in acidic (blue lines) and alkaline (orange lines) electrolytes. The purple lines denote the reaction of MOOH intermediates to generate oxygen, and the green lines the reaction of two M-O intermediates to produce an oxygen molecule. Here, M stands for the active sites on the electrode surface. (f) The elementary steps of the AEM mechanism under acidic and alkaline conditions.

The continuous progress and advancement in the field of energy conversion and storage are offering ample opportunities to design and synthesize the efficient electrode materials with using scalable techniques. Therefore, different metal oxides, sulfides, hydroxides and organic-inorganic hybrids have been synthesized and utilized. More importantly, organic-inorganic hybrid materials based on mixed metal ions are gaining a lot of attention because of the metal-metal synergistic effect and the ease of interaction and coordination with the organic moiety, which makes it very active for electrochemical energy conversion and storage applications.

1.8 Summery and objectives of the thesis

The introduction stated that the organic-inorganic hybrid materials exhibit synergistic characteristics and multifunctional activities. The unique nanoscale architectures of the organic-inorganic hybrid materials enable them to provide more electrochemically active sites for energy storage and conversion applications. The following are the goals of our thesis work;

- Synthesis of amino acid functionalized organic molecules using liquid phase synthesis method and characterized by various spectroscopic techniques.
- The fabrication of organic-inorganic nanohybrid electrode materials using different electrochemical methods.
- The analysis of the organic-inorganic hybrid materials with using advanced characterization techniques to estimate the chemical and physical properties.
- Further, the estimation of the electrochemical energy storage and conversion performance of the synthesized organic-inorganic hybrid materials with using different electrochemical techniques.
- The fabrication of the device to explore the practical applicability of the synthesized hybrid materials.

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Electrodeposited stable binder-free organic-Ni(OH)₂ flexible nanohybrid electrodes for high performance supercapacitors

2.1 Introduction

Researchers have shown great interest in the development of new electrode materials for energy storage.^[1-7] Li-ion battery, rechargeable alkaline batteries, fuel cells and supercapacitors (SCs) have been studied as potential energy storage devices.^[8-12] SCs show reversible and fast surface or near-surface redox reactions on electrodes for charge storage with high power density, specific capacitance and cyclic stability. Researchers have developed various electrode materials in order to enhance the charge storage capacity of SCs and their commercial use. Among the reported materials, RuO₂ shows high specific capacitance and excellent electrochemical properties. However, less abundance and expensive ruthenium have impeded for commercial use.^[13,14] On the other hand, relatively abundant and cheap transition metal oxides and hydroxides like NiO,^[15] TiO₂,^[16] CuO,^[17] MnO₂,^[18] Ni(OH)₂^[19] and Co(OH)₂^[20,21] have gained attention due to their potential electrochemical properties. The use of nickel hydroxide has gained much attention due to their eco-friendly compatibility, cheap and abundant resources.^[19,22] Nickel hydroxide based materials have been explored as an active material for various applications including electrocatalytic and photocatalytic energy conversion. Ni(OH)2 with petal-like morphology has shown high electrocatalytic activity for the oxygen evolution reaction at lower overpotential.^[22,23] In present, organic materials and organic-inorganic hybrid materials have been explored as potential candidates for energy storage. The organic-inorganic hybrid compounds imply inexpensive, environmentally friendly features and specially the acid functional groups present in organic moieties can act as a nucleation site for inorganic materials.^[24] The structural and functional flexibility of organic molecules with reversible redox properties of metal ions display useful electrochemical properties for energy storage applications. Peptides can be used as an electrode material due to their covalent bond formation using acid functionalities on the working electrode and their performance can be improved via TiO₂ coating.^[16] The fabricated peptide@TiO₂ based SC device showed an outstanding mass-specific capacitance of 125 F g⁻¹ at 0.1 A g⁻¹ current density in 1M aqueous H₃PO₄ electrolyte.^[16] Naphthoquinone and RuO₂ based hybrid material with graphene hydrogel was fabricated for asymmetric SCs applications. The naphthoquinone and RuO₂ based hybrid material shows significant specific capacitance of 450.8 F g⁻¹ in 1M H₂SO₄ electrolyte.^[25] Various methods such as hydrothermal,^[25,26] electrodeposition,^[21] chemical bath deposition^[27] and atomic layer deposition^[16] have been developed to synthesize organic-inorganic hybrid materials. Liu et al reported the synthesis of nickel based pillared organic-inorganic hybrid material using solvothermal method, which showed specific capacitance of 552 F g⁻¹ at 1 A g⁻¹.^[28] One-pot hydrothermal growth of nickel terephthalate on Ni foam followed by electrodeposition of PANI nanofibers showed higher capacitance with high cycling stability.^[29] The presence of nickel and organic moieties in organicinorganic nanohybrids provides structural stability during fast faradic reactions which enhances energy storage performance. Stupp *et al* reported nanotubes of cobalt hydroxide based organic-inorganic hybrid material, which was fabricated through the potentiostatic electrochemical deposition method.^[21] The nanotubular morphology provides high accessible surface area for electrochemical redox activity. The electrodeposition method facilitates inexpensive, easy, binder-free and in situ controlled growth of nanostructured metal hydroxide based material over working electrode. The binder-free method allows not using expensive binders and minimizes inactive surface area and extra contact resistance during electrochemical analysis.^[21,30,31]

In the present work, the potentiostatic electrodeposition method was used for *in situ* synthesis of organic-inorganic nanohybrid material directly on flexible NF substrate. The NF substrate is widely used as supporting substrate for active materials in SCs due to their three dimensional network with large surface area, high porosity and superior electrical conductivity.^[32,33] Benzoselenadiazole protected dipeptides containing with different amino acid sequences were employed as organic moieties. Aromatic diphenylalanine containing BSeFF and aliphatic dileucine containing BSeLL were explored to study the effect of peptide chains on organic-inorganic nanohybrids with their electrochemical properties.

2.2 Materials and Experimental Methods

2.2.1 Materials

Chemicals such as, L-phenylalanine (F), L-leucine (L), *N*,*N*'dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) and nickel nitrate hexahydrate were purchased from SRL chemicals, India. 3,4-Diamino benzoic acid and selenium dioxide were purchased from Sigma-Aldrich, U.S.A. Hydrochloric acid and dimethyl sulphoxide (DMSO) were purchased from SRL chemicals, India. All chemicals were used without further purification. Solvents were purchased from Merck India Limited and used after proper drying and distillation. NF substrate was purchased from J. K. Impex, Mumbai, India.

2.2.2 Instrumentation

All NMR spectra were recorded on Bruker AV 400 MHz spectrometer. The compound concentrations were in the range of 5-10 mmol L⁻¹ in (CD₃)₂SO and CDCl₃. Mass spectra were recorded on Bruker micro TOF-Q II mass spectrometer by positive and negative mode electrospray ionization. The peptide/Ni(OH)₂ nanostructured hybrid materials were characterized by Fouriertransform infrared (FTIR) spectroscopy performed on KBr pellets on a Bruker Tensor 27 FTIR spectrophotometer. The compositions and oxidation states of the element in the synthesized materials were studied using X-ray photoelectron spectroscopy (XPS) using a Model/Supplier: PHI 5000 Versa Probe II, FEI Inc..The surface morphology and elemental characterization of the peptide/nickel hydroxide thin film were conducted by Karl Zeiss JEOL FE-SEM together with EDS and Elemental mapping. Transmission electron microscope (TEM) was employed to further analyse the microstructure of the prepared peptide/Ni(OH)₂ thin film using a FEI Technai 20 U Twin Transmission Electron Microscope. The mass loading was carried out with weight difference method using electronic balance. All the electrochemical measurements such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and cyclic stability test were assessed by Metrohm Autolab potentiostat (PGSTAT302N) in 1M aqueous KOH solution. The solution was prepared freshly before each experiment to sustain consistency.

2.2.3 Synthesis of organic component

BSe N-protected phenylalanine compound **1** was synthesized using solution phase peptide synthesis. The synthesized compound **1** and all intermediates was well characterized by Mass, ¹H NMR spectroscopy and ¹³C NMR spectroscopy.



Scheme 2.1. Synthetic procedure of 1.

2.2.4 Synthesis of organic compounds

2.2.4.1 Synthesis of benzo[2,1,3]selenadiazole-5-carboxylic acid (6): An amount of 3,4-diamino benzoic acid (3g, 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 Milli-Q water. The obtained precipitate was dried in oven at 60 °C to yield 4.18 g (18.40 mmol, 93%) of **6** as a faint pink colored solid.^[34] ¹H NMR (400 MHz, DMSO-*d*₆): δ = 13.43 (s, 1H, -COOH), 8.46 (s, 1H, BSe), 8.03-7.96 (dd, 2H, *J* = 9.32, 9.24 Hz, BSe) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 167.34, 161.21, 159.65, 131.69, 128.34, 125.88, 123.74 ppm; MS (ESI): *m/z* calcd. for C₇H₃N₂O₂Se: 226.9360 [M-H]⁻; found: 226.9418.



Figure 2.1. ESI-MS spectrum of 6.



Figure 2.2. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of 6.



Figure 2.3. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of **6**.

2.2.4.2 Synthesis of BSeF-OMe (7): A solution of 2 g (8.80 mmol) 6 and HOBt (1.43 g, 10.58 mmol) was stirred in 5 mL of DMF in a 100 mL round bottom flask. A neutralized solution of phenyl alanine methyl ester was extracted from its corresponding hydrochloride salt (3.79 g, 17.57 mmol) and concentrated to add to the reaction mixture followed by coupling agent N,N'dicyclohexylcarbodiimide (2.18 g, 10.56 mmol) at 0 °C and allowed to stir at room temperature for 12 h. The progress of the reaction was monitored by thin layer chromatography (TLC). After the reaction, the reaction mixture was diluted with ethyl acetate and washed with 1N HCl (3×30 mL), saturated Na₂CO₃ solution (3×30 mL) and brine solution. Solid light yellowish colored compound of 7 was obtained after evaporating the solvent under reduced pressure. Compound 7 was purified using flash chromatography. Yield = 2.97 g, (7.64 mmol, 87%); ¹H NMR (400 MHz, CDCl₃): $\delta = 8.13$ (s, 1H, BSe), 7.89-7.83 (dd, J = 9.36, 9.28 Hz, 2H, BSe), 7.31-7.26 (m, 3H, Ph), 7.16, 7.14 (dd, J = 8 Hz 2H, Ph), 6.76, 6.74 (d, J = 7.88, 1H, NH), 5.15-5.10 (m, 1H, C^{α} H of Phe), 3.80 (s, 3H, -OCH₃), 3.33-3.27 (m, 2H, C^{β} H of Phe) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.11, 161.15, 156.40, 155.04, 130.88, 130.21, 124.57, 124.03, 123.03,$ 122.65, 119.04, 117.34, 49.00, 47.87, 33.11 ppm; MS (ESI): m/z calcd. for C₁₇H₁₅N₃O₃SeNa: 412.0176 [M+Na]⁺; found: 412.0282.



Figure 2.4. ESI-MS spectrum of 7.



Figure 2.5. ¹H NMR spectrum (400 MHz, CDCl₃) of 7.



Figure 2.6. ¹³C NMR spectrum (100 MHz, CDCl₃) of 7.

2.2.4.3 Synthesis of BSeF (8): A solution of **7** (1.18 g, 3.03 mmol) in 40 mL distilled methanol was allowed to react with a solution of 4 mL (1N) NaOH solution. The reaction mixture was stirred for 4 h. The hydrolysis progress was monitored by thin layer chromatography. After the completion of the reaction, excess methanol was evaporated to dryness and diluted with 50 mL milli-Q water. Then, the water mixture was taken in a separating funnel and slowly washed with diethyl ether (2×20 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 Na₂SO₄ and evaporated under reduced pressure to obtain a solid compound

8.Yield = 1.05 g (2.80 mmol, 92%); ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.82 (s, 1H, -COOH), 9.08, 9.06 (d, *J* = 8.04, 1H, -NH), 8.34 (s, 1H, BSe), 7.93-7.86 (dd, *J* = 9.28, 9.24, 2H, BSe), 7.38-7.19 (m, 5H, Ph), 4.73-4.67 (m, 1H, C^α H of Phe), 3.25-3.13 (m, 2H, C^β H of Phe) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 173.48, 166.14, 160.76, 159.65, 138.59, 134.50, 129.57, 128.73, 128.16, 126.92, 123.53, 122.83, 54.89, 36.78 ppm; MS (ESI): *m*/*z* calcd. for C₁₆H₁₂N₃O₃Se: 374.0044 [M-H]⁻; found: 374.0175.



Figure 2.7. ESI-MS spectrum of 8.



Figure 2.8. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **8**.



Figure 2.9. ¹³C NMR spectrum (100 MHz, DMSO- d_6) of 8.

2.2.4.4 Synthesis of compound BSeFF-OMe (9): A solution of compound 8 (0.60g, 1.60 mmol) and HOBt (0.260g, 1.92 mmol) was stirred in DMF (2 mL). A neutralized solution of H₂N-Phe-OMe was extracted from its corresponding hydrochloride salt. It was concentrated for addition to the reaction mixture followed by coupling agent N,N'-dicyclohexylcarbodiimide (0.40 g, 1.94 mmol) at 0 °C and allowed to stir at room temperature for 12 h. After the reaction, the reaction mixture was diluted with ethyl acetate and the organic layer was washed with 1N HCl (3×30 mL), saturated Na₂CO₃ (3×30 mL) and again with brine. The organic layer was dried over Na₂SO₄ and evaporated under vacuum by rotary evaporator to yield solid compound 9. The purification of compound 9 was performed by flash chromatography on silica gel (100-200 mesh) with ethyl acetate and hexane as eluent. Yield = 0.74g (1.40 mmol, 86%): ¹H NMR (400 MHz, DMSO- d_6): $\delta = 8.92$, 8.90 (d, J = 8.32 Hz, 1H, -NH), 8.62, 8.60 (d, J =7.12 Hz, 1H, -NH), 8.32 (s, 1H, BSe), 7.90-7.83 (dd, J = 9.32, 9.20 Hz, 2H, BSe), 7.40-7.18 (m, 10H, aromatic Hs of Phe), 4.84, 4.82 (d, J = 7.52, 1H, C^{α}H of Phe), 4.60-4.55 (m, 1H, C^aH of Phe) 3.62 (s, 3H, OCH₃), 3.16-2.97 (m, 4H, $C^{\beta}H$ of Phe) ppm; ¹³C NMR (100 MHz, DMSO- d_{δ}): $\delta = 172.29, 171.92, 165.98,$ 160.74, 159.65, 138.70, 137.56, 134.62, 129.65, 129.61, 128.75, 128.55, 128.30, 127.06, 126.76, 123.36, 122.87, 55.13, 54.26, 52.37, 37.47, 37.05 ppm; MS (ESI); m/z calcd. for C₂₆H₂₄N₄O₄SeNa: 559.0860 [M+Na]⁺; found: 559.0660.



Figure 2.10. ESI-MS spectrum of 9.



Figure 2.11. ¹H NMR spectrum (400 MHz, DMSO- d_6) of 9.



Figure 2.12. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of 9.

2.2.4.5 Synthesis of compound BSeFF (1): Compound 9 (0.70 g, 1.31 mmol) was dissolved in 30 mL distilled methanol. After that, the solution was allowed to react with 1N solution of NaOH (3 mL). The progress of the reaction was monitored by TLC. The reaction mixture was stirred for 5 h. Then, the methanol was removed by rotary evaporator. The residue was diluted with 50 mL milli-Q water. The aqueous layer was taken in a separating funnel and slowly washed with diethyl ether (2×20 mL). The pH of the cooled aqueous layer was adjusted to 2 by using 1N HCl and extracted with ethyl acetate (3×30 mL). The ethyl acetate layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure with rotary evaporator to yield a light yellowish solid compound $\mathbf{1}$.^[35] Yield = 0.54 g (1.03 mmol, 79%). ¹H NMR (400 MHz, DMSO- d_6) δ = 12.86 (s, 1H, -COOH), 8.92, 8.90 (d, J = 8.52 Hz, 1H, -NH), 8.41, 8.39 (d, J = 7.68 Hz, 1H, -NH), 8.31 (s, 1H, BSe), 7.90-7.82 (dd, J = 9.36, 9.28 Hz, 2H, BSe), 7.39-7.18 (m, 10H, Phe-Phe), 4.84-4.79 (m, 1H, C^αH of Phe), 4.54-4.49 (m, 1H, C^αH of Phe), 3.17-3.13 (m, 2H, C^{β} H of Phe), 3.02-2.98 (m, 2H, C^{β} H of Phe) ppm; ¹³C NMR (100 MHz, DMSO- d_6): $\delta = 173.38$, 173.24, 171.74, 171.54, 165.97, 160.73, 159.64, 138.79, 137.97, 137.92, 134.64, 129.80, 129.68, 129.65, 128.67, 128.55, 128.30, 126.92, 126.74, 123.36, 122.84, 55.23, 54.11, 37.44, 37.10 ppm; MS (ESI); m/z calcd. for C₂₅H₂₁N₄O₄Se: 521.0728 [M-H]⁻; found: 521.1046.



Figure 2.13. ESI-MS spectrum of 1.



Figure 2.14. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **1**.



Figure 2.15. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of 1.



Scheme 2.2. Synthetic procedure of 2.

The above-mentioned procedures (Scheme 2.1) were used to synthesize compounds **10**, **11**, **12** and **2** (Scheme 2.2). Compounds **10** and **12** were purified by flash chromatography.

2.2.4.6. BSeL-OMe (10): Yield = 1.32 g, (3.72 mmol, 85%); ¹H NMR (400 MHz, CDCl₃): $\delta = 8.17$ (s, 1H, BSe), 7.85-7.79 (dd, J = 9.44, 9.32 Hz, 2H, BSe), 6.70, 6.68 (d, J = 7.92, *1H*, NH), 4.85-4.80 (m, 1H, C^{\alpha} H of Leu), 3.73(s, 3H, - OCH₃), 1.74-1.71(m, 2H, C^{\beta} H of Leu), 1.67-1.1.65 (m, 1H, C^{\gar} H of Leu), 0.96-0.92 (m, 6H, C^{\delta} H of Leu) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 173.56$, 166.19, 161.11, 159.79, 134.99, 127.89, 123.68, 122.08, 52.57, 51.44, 41.76, 25.09, 22.86, 22.07 ppm; MS (ESI): m/z calcd. for C₁₄H₁₇N₃O₃SeNa: 378.0333 [M+Na]⁺; found: 378.0336.



Figure 2.16. ESI-MS spectrum of 10.



Figure 2.17. ¹H NMR spectrum (400 MHz, CDCl₃) of 10.



Figure 2.18. ¹³C NMR spectrum (100 MHz, CDCl₃) of 10.

2.2.4.7. BSeL-OH (**11**): Yield = 0.59 g, (1.73 mmol, 88%); ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.68 (s, 1H, -COOH), 8.97, 8.95 (d, *J* = 7.76, *1H*, NH), 8.47 (s, 1H, BSe), 8.01-7.93 (dd, *J* = 9.36, 9.32 Hz,2H, BSe), 4.55-4.50 (m, 1H, C^α H of Leu), 1.84-1.77 (m, 2H, C^β H of Leu), 1.69-1.66 (m, 1H, C^γ H of Leu), 0.99-0.93 (dd, *J* = 6.28, 6.28Hz, 6H, C^δ H of Leu) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 174.48, 166.23, 160.77, 159.69, 134.51, 128.29, 123.45, 122.91, 51.59, 25.04, 23.42, 21.63 ppm; MS (ESI): m/z calcd. for C₁₃H₁₄N₃O₃Se: 340.0200 [M-H]⁻; found: 340.0536.



Figure 2.19. ESI-MS spectrum of 11.



Figure 2.20. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of 11.



Figure 2.21. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of 11.

2.2.4.8. BSeLL-OMe (12): Yield = 0.44 gm (0.94 mmol, 64%): ¹H NMR (400 MHz, CDCl₃): δ = 8.18 (s, 1H, BSe), 7.82 (s, 1H, BSe), 7.19 (s, 1H, BSe), 6.85, 6.83 (d, *J* = 8.16 Hz, 1H, -NH), 6.39, 6.37 (d, *J* = 8.12 Hz, 1H, -NH), 4.70-4.64 (m, 1H, C^{α} H of Leu), 4.58-4.54 (m, 1H, C^{α} H of Leu), 3.69 (s, 3H, -OCH₃), 1.88-1.84 (m, 2H, C^{β} H of Leu), 1.63-1.60 (m, 2H, C^{β} H of Leu), 1.26-1.22 (m, 1H, C^{γ} H of Leu), 1.04-1.01 (m, 1H, C^{γ} H of Leu), 0.95-0.84 (m, 12H, C^{δ} H of Leu) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 173.10, 171.65, 166.38, 161.12, 159.83, 156.74, 127.78, 123.70, 122.28, 52.40, 52.28, 50.93, 49.19, 33.96, 25.63, 24.95, 22.92, 22.77, 22.31, 21.87 ppm; MS (ESI); *m*/*z* calcd. for C₂₀H₂₉N₄O₄Se: 469.1354 [M+H]⁺; found: 469.1354.



Figure 2.22. ESI-MS spectrum of BSeLL-OMe 12.



Figure 2.23. ¹H NMR spectrum (400 MHz, CDCl₃) of 12.



Figure 2.24. ¹³C NMR spectrum (100 MHz, CDCl₃) of 12.

2.2.4.9. Synthesis of BSeLL (2): Yield = 0.28 gm (0.62 mmol, 82%): ¹H NMR (400 MHz, DMSO- d_{δ}): δ = 12.49 (s, 1H, -COOH), 8.79, 8.77 (d, *J* = 8.20 Hz, 1H, -NH), 8.46 (s, 1H, BSe), 8.21, 8.19 (d, *J* = 7.84 Hz, 1H, -NH) 7.98-7.90 (dd, *J* = 9.36, 9.32 Hz, 2H, BSe), 4.65-4.59 (m, 1H, C^{\alpha} H of Leu), 4.30-4.25 (m, 1H, C^{\alpha} H of Leu), 1.75-1.71 (m, 4H, C^{\beta} H of Leu), 1.62-1.58 (m, 2H, C^{\geta} H of Leu), 0.97-0.86 (m, 12H, C^{\deta} H of Leu) ppm; ¹³C NMR (100 MHz, DMSO- d_{δ}): δ = 174.46, 172.58, 166.04, 160.79, 159.75, 134.81, 128.50, 123.36, 122.96, 52.30, 50.71, 24.91, 24.76, 23.65, 23.38, 21.94, 21.84 ppm; HRMS (ESI); *m*/*z* calcd. for C₁₉H₂₅N₄O₄Se: 453.1014 [M-H]⁻; found: 453.1192.



Figure 2.25. ESI-MS spectrum of 2.



Figure 2.26. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **2**.



Figure 2.27. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of **2**.

2.3 Results and discussion

2.3.1 Electrode fabrication

The NF substrate $(1 \text{ cm} \times 2 \text{ cm})$ was treated with 1N HCl solution for 10 min and further washed with ultrapure water and ethanol and dried in the oven at 60 °C for 6 h. For the potentiostatic electrodeposition on NF substrate, the solution of Ni(NO₃)₂.6H₂O and organic peptide surfactant (1 or 2) in water/dimethyl sulphoxide (DMSO) (1:1) V/V were used. Here, DMSO was used as organic co-solvent due to the solubilization of peptide moiety as well as its miscible behavior in water.^[21] The conventional electrodeposition set-up consists of three electrodes. The NF was used as working electrode, Pt wire as counter electrode and Ag/AgCl as reference electrode. The organic-inorganic hybrid material was grown on flexible NF substrate through a electrodeposition for 10-60 min by applying -0.9 V constant current and the temperature of the solution was maintained at 60 °C by water bath with continuous magnetic stirring.^[36,37] After the electrodeposition, the deposited thin film surface was washed with ultrapure water, ethanol and dried at 60 °C for 6h.

The specific capacitance (Cs) of active material was calculated on the basis of charge/discharge data and the equation is as follows:^[38-40]

$$Cs = \frac{I \times \Delta t}{m \times \Delta v}$$

Where Δv represents the potential drop, I (A) denote constant current, Δt (s) is the discharge time on GCD and m (mg) is the mass of active material.

2.3.2 Hybrid material characterization

Benzoselenadiazole protected N-capped dipeptides with aromatic (BSeFF, F = phenylalanine) and non-aromatic amino acids (BSeLL, L = leucine) were synthesized using solution phase peptide synthesis and well characterized by ¹H NMR, ¹³C NMR and mass spectrometry. The organic-inorganic hybrid materials were grown by potentiostatic electrodeposition at a constant potential of - 0.9 V vs Ag/AgCl over NF substrate (**Figure 2.28**). The layer formed over the flexible NF substrate indicates the deposition of peptide/Ni(OH)₂ based nanohybrid material. The electrochemical conversion of dipeptide and Ni(NO₃)₂ to peptide/Ni(OH)₂ can be expressed as follows.^[37,41]

 $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$ (1)



Figure 2.28. Schematic representation of the electrochemical synthesis of organic-inorganic nanohybrids. Peptides BSeFF and BSeLL were used as organic compounds.

On applied potential, the nitrate ions reduced on the cathodic surface to form NO_2^- and OH⁻. The formation of OH⁻ at cathode increases the local pH near the electrode, resulting in the deposition of nanohybrid peptide/Ni(OH)₂ over the flexible NF substrate. Structurally, BSeFF and BSeLL peptides are made up by three elementary units *i.e.* N-capped heterocyclic aromatic ring, dipeptide backbone with different amino acid sequence and a carboxylic acid functional group. In peptide molecules, the polar moieties such as carboxylate anions could facilitate the interaction with Ni²⁺ ions.^[42-44] The aromatic rings in peptide molecules could form attractive intermolecular interactions such as π - π stacking interactions providing structural stability to the hybrid nanoscale architecture of the thin films.^[43-47] The amide functional groups over peptide backbone induce the formation of peptide self-assembly through intermolecular hydrogen bonding interactions. The carboxylate groups of peptides interact with Ni(OH)₂ to form peptide/Ni(OH)₂ based organic-inorganic nanohybrids.^[42,45,48]

The FT-IR spectroscopy (**Figure 2.29**) was used to analyse the characteristic absorption of the functional groups present in BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ hybrid materials. A broad and strong vibration band ranging from 3200 cm^{-1} to 3500 cm^{-1} observed due to -OH stretching confirms the

existence of hydroxyl groups in BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrids (**Figure 2.29**).^[27]



Figure 2.29. FTIR spectra of (a) BSeFF and BSeFF/Ni(OH)₂ and (b) BSeLL and BSeLL/Ni(OH)₂.

The typical bands between 3000 cm⁻¹ to 2800 cm⁻¹ are observed due to the stretching vibration of the C-H bond.^[49] The bands between 1600-1700 cm⁻¹ correspond to amide carboxyl stretching (amide I) and aromatic C=C stretching vibrations. The peaks in between 1400-1550 cm⁻¹ are observed due to the amide N-H bending (amide II) and aromatic ring vibrations of peptide groups present in both BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ hybrid materials.^[50-54] Besides, the bands in between 1020-1170 cm⁻¹ are observed due to the presence of in-plane vibration of C-H band and C-N stretching vibration of amide groups of peptides present in BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrids (**Figure 2.29**) respectively.^[50] A vibration mode assigned at ~672 cm⁻¹ is observed due to to δ-Ni-O-H stretching band in between 3000-3100 cm⁻¹ (-OH stretching vibration) and 1700-1720 cm⁻¹ (C=O stretching frequencies) disappeared due to metal-carboxylate interactions between metal ions and carboxylate group of peptide moiety (**Figure 2.29**) respectively.^[41,45,48]

XPS analysis was conducted to investigate the surface characteristics and chemical compositions present in organic-inorganic nanohybrids. The XPS survey scans containing nanohybrid material provide the surface based elemental composition of the prepared peptide/Ni(OH)₂ (**Figure 2.30** and **2.31**). The XPS spectra of BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ show Ni 2p, C 1s, N 1s, O 1s and Se 3d peaks indicating the presence of Ni, C, N, O and Se elements. **Figure**

2.30b shows Ni 2p peaks, which is splitted into four peaks. Two major peaks of Ni $2p_{1/2}$ and Ni $2p_{3/2}$ are observed at 873.6 and 855.9 eV respectively. The energy separation between Ni $2p_{1/2}$ and Ni $2p_{3/2}$ is 17.6 eV, which indicates the presence of Ni in +2 oxidation state in the organic-inorganic nanohybrid. In addition, two satellite peaks at 879.5 (Ni $2p_{1/2}$) and 861.4 eV (Ni $2p_{3/2}$) are also observed in the Ni 2p spectrum.^[29,56,57]



Figure 2.30. (a) XPS survey spectrum for BSeFF/Ni(OH)₂. (b) High resolution XPS spectra of Ni 2p, (c) O 1s, (d) N 1s, (e) C 1s and (f) Se 3d for BSeFF/Ni(OH)₂ nanohybrid.



Figure 2.31. (a) XPS survey spectrum for BSeLL/Ni(OH)₂. High resolution XPS spectra of (b) Ni 2p, (c) O 1s, (d) N 1s, (e) C 1s and (f) Se 3d for BSeLL/Ni(OH)₂ hybrid.

The fitted O 1s (**Figure 2.30c**) core level spectrum of BSeFF/Ni(OH)₂ exhibits three peaks at 530.6, 531.2 and 532.6 eV binding energies, which are assigned to oxygen-metal bond, hydroxyl groups (O-H) and carboxylate groups (O-C=O).^[26,29,58] The carbon bound nitrogen components were confirmed by high-resolution N 1s spectrum (**Figure 2.30d**). The fitted peaks for N 1s at 398.9 and 400.3 eV are assigned to C=N bonding (BSe) and amide groups in peptide moiety. The peak at 406.8 eV is the N 1s satellite feature.^[50,59,60] **Figure 2.30e** exhibits the peaks at 284.2, 284.6, 285.47 and 288.4 eV which can be observed due to carbon components of C-C, aromatic rings, C-N and carboxylate/N-C=O

groups respectively.^[26,29,50,53,61] All of the above-stated results support the successful electrochemical deposition of peptide/Ni(OH)₂ nanohybrids.

2.3.3 Morphological Analysis

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) experiments were performed to investigate the morphological alterations and formation process of the BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂. The morphological investigation of the synthesized BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrids was examined by SEM, which shows that the different peptide sequences have significant effect on the morphology of nanohybrids. As shown in **Figure 2.32a** and **2.32c**, the samples show flower-like and microsphere-like structures. Several sheets assembled like petals to form flower-like morphology (**Figure 2.32a**). The colonial or net-like growth of the sheets produces flowers like structure with compact constructions.



Figure 2.32. Structural evolution of synthsized peptide/Ni(OH)₂ thin film with changing peptide moiety. SEM (a, b) and TEM (c, d) images of BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrids respectively. EDS spectra (e, f) of BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrids respectively.

Nanosheet based ordered flower-like structures (Figure 2.32a) have high electrocative surface which plays an active role to reduce the interface contact resistance between electrode surface and electrolyte solution. SEM image (Figure 2.32a) clearly shows the flower-like structures of the electrodeposited BSeFF/Ni(OH)₂.^[62-64] TEM analysis was also performed to reveal the insights of the flower-like and microsphere-like texture of organic-inorganic nanohybrids. Figure 2.32b and Figure 2.32d show TEM images of the BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrids respectively. TEM image shows enlarged view of flower-like morphology of BSeFF/Ni(OH)₂. However, Figure 2.32d shows the microsphere-like structure of BSeLL/Ni(OH)₂. Morphological characterization of organic-inorganic nanohybrids suggests nucleation based growth mechanism during electrochemical deposition process. Structurally BSeFF contains aromatic phenylalanine residues in peptide sequence while BSeLL contains aliphatic leucine residues. Aromatic residues present in peptide backbone provide π - π stacking interaction for the formation of flower-like morphology. However, BSeLL/Ni(OH)₂ shows microsphere like morphology which was composed of tightly concentrated sheets. Furthermore, the chemical composition of the flowerlike and microsphere-like BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ was analysed by elemental mapping and EDS analysis. The EDS spectra (Figure 2.32e and Figure 2.32f) show Ni, C, N, O and Se peaks. Further chemical composition of peptide/Ni(OH)₂ was analysed by elemental mapping. The elemental mapping images show the presence of Ni, O, N, C and Se elements in Figure 2.33 and 2.34, which confirmed the fabrication of flower and microsphere-like BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ hybrids. The prepared peptide/Ni(OH)₂ nanohybrids can potentially exhibit excellent performance in supercapacitor applications.



Figure 2.33. Elemental mapping of BSeFF/Ni(OH)₂.



Figure 2.34. Elemental mapping of BSeLL/Ni(OH)₂.

2.3.4 Electrochemical characterization of $BSeFF/Ni(OH)_2$ and $BSeLL/Ni(OH)_2$

The electrochemical analysis was performed to investigate the morphological effects of BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrids and their applicability for electrochemical energy storage application. CV analysis was perforamed to understand the redox behaviour of the nanohybrids. **Figure 2.35a** shows the cyclic voltammograms of the BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ electrodes in 1M KOH solution at 6 mVs⁻¹ scan rate over the potential range of 0.0 to 0.55 V (vs Hg/HgO). **Figure 2.35b** and **Figure 2.36a** show the CV curves of the flower-like BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrids at different

scan rates ranging from 2-10 mV s⁻¹ respectively. All CV curves show a pair of oxidation and reduction peaks. The peak appeared at ~0.46V is attributed to the oxidation of Ni(OH)₂ to NiOOH, however, another peak appeared at ~0.20V corressponds to the reduction process. The redox nature of CV curves suggests that the specific capacitance of nanohybrids is majorly governed by the Faradic reactions. Among these electrodeposited electrodes, BSeFF/Ni(OH)₂ possesses larger enclosed area than BSeLL/Ni(OH)₂. The difference in surface area is seen in **Figure 2.35a**, which might be attributed to the better electrolyte accessibility, higher diffusion rates and exposure of more electrochemically active sites for the intercalation of ions.^[58] Based on the surface redox reactions, the corresponding electrochemical reaction is expressed as follows.^[39,40,57]

$$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e^-$$
(3)

The energy storage performance of nanohybrids was analysed by GCD to calculate the specific capacitance of the electrodeposited BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ over the potential range of 0 to 0.55 V.



Figure 2.35. Electrochemical characterization of peptide/Ni(OH)₂ in 1M KOH: (a) Cyclic voltammograms of BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrid

thin films at 6 mV s⁻¹. (b) CV curves for flower like BSeFF/Ni(OH)₂ at 2, 4, 6, 8 and 10 mV s⁻¹ scan rate. (c) GCD curves at a current density of 2 A g⁻¹. (d) GCD profiles of flower-like BSeFF/Ni(OH)₂ at various current densities. (e) Nyquist impedance plot of flower-like BSeFF/Ni(OH)₂ at 0.05 V amplitude. (f) Cyclic stability test of flower-like BSeFF/Ni(OH)₂ at constant current density 10 A g⁻¹.

Figure 2.35c presents the GCD curve of BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ at current density of 2 A g⁻¹. BSeFF/Ni(OH)₂ thin film containing flower-like structures shows much higher specific capacitance of ~1250 F g⁻¹ at a current density of 2 A g⁻¹. However, BSeLL/Ni(OH)₂ shows specific capacitance of 689 F g⁻¹ at 2 A g⁻¹. The higher specific capacitance of BSeFF/Ni(OH)₂ nanohybrid is attributed to its unique flower-like structure. **Figure 2.35d** and **2.36b** represent the GCD curves of BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ at different current densities from 2 to 10 A g⁻¹. The specific capacitance of BSeFF/Ni(OH)₂ at different current densities of 2, 4, 6, 8, and 10 A g⁻¹ is observed as 1250, 1025, 924, 854 and 260 F g⁻¹ respectively. Similarly, the specific capacitance of BSeLL/Ni(OH)₂ is observed as 689, 627, 582, 537 and 494 F g⁻¹ at current densities of 2, 4, 6, 8 and 10 A g⁻¹ respectively.



Figure 2.36. Electrochemical characterization of BSeLL/Ni(OH)₂ in 1M KOH: (a) CV curves for microsphere like BSeLL/Ni(OH)₂ at 2, 4, 6, 8 and 10 mVs⁻¹ scan rate. (b) GCD profiles of microsphere like BSeLL/Ni(OH)₂ at various

current densities 2, 4, 6, 8 and 10 Ag^{-1} . (c) Nyquist impedance plot of microsphere like BSeLL/Ni(OH)₂ at 0.05 V amplitude. (f) Cyclic stability test of microsphere like BSeLL/Ni(OH)₂ at constant current density 10 A g^{-1} .

In particular, the BSeFF/Ni(OH)₂ exhibits excellent capacitance performance due to flower-like structure, which provides more electrochemically active sites for the intercalation of the electrolyte. The specific capacitance is decreased with increment in current density whereas the area of CV curves is increased with increase in scan rates owing to their poor conduction of ions at the electrode surface.⁶⁵ BSeFF/Ni(OH)₂ shows high specific capacitance retention of ~72% (**Figure 2.35f**) than BSeLL/Ni(OH)₂ (~41%) after 1000 cycles (**Figure 2.36d**) at a current density of 10 A g⁻¹. Among both prepared electrodes, BSeFF/Ni(OH)₂ electrode possesses excellent electrochemical performance than BSeLL/Ni(OH)₂ which is observed due to the exposure of more electrochemically active sites for intercalation/deintercalation of ions. **Table 2.1** lists the difference in electrochemical performance between BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂.

Table 2.1. The list of difference in electrochemical performance between

 the flower-like BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂.

Electrode	Electrolyte	Current	Specific	Capacitance
Material		density	capacitance	retention after
		(Ag ⁻¹)	(Fg ⁻¹)	1000 cycles
BSeFF/Ni(OH) ₂	1M KOH	2	1250	72%
BSeLL/Ni(OH) ₂	1M KOH	2	689	41%

The electrochemical properties of the peptide/Ni(OH)₂ hybrid thin films were further investigated with electrochemical impedance spectroscopy (EIS). The impedance spectra of BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ thin films were recorded in the frequency range of $10^5 - 0.01$ Hz at 0.05 V amplitude.^[66] Nyquist plots of the electrodes show the frequency response of the electrode/electrolyte system in **Figure 2.35e** and **Figure 2.36c**.^[67] It is known that intersection of the semicircle on real component axis (Re(Z)) at higher frequency corresponds to solution resistance (R_s) of the electrode. However, diameter of the semicircle shows the charge transfer resistance at electrode and electrolyte interface.^[38,63] Nyquist plot of BSeFF/Ni(OH)₂ (**Figure 2.35e**) shows R_s values of 1.53 Ω which is close to R_s value of BSeLL/Ni(OH)₂ (1.63 Ω). However, BSeFF/Ni(OH)₂ exhibits lower intrinsic charge transfer resistance of 418.13 Ω than R_{ct} of BSeLL/Ni(OH)₂, which indicates high conductivity and improved capacitive behaviour of BSeFF/Ni(OH)₂ nanohybrids in KOH solution.^[38,63] The straight line in the lower frequency regions corresponds to the diffusive resistance known as Warburg line which is the result of ion diffusion on electrode-electrolyte interface.

2.4 Conclusion

The flower and microsphere-like peptide/Ni(OH)₂ nanohybrids have been successfully grown on NF substrate via one step electrodeposition method. Peptide/Ni(OH)₂ sample exhibited excellent electrochemical energy storage performance at higher current densities with high cyclic stability. The specific capacitance of BSeFF/Ni(OH)₂ (72%) and BSeLL/Ni(OH)₂ (41%) nanohybrids retained even after 1000 cycles. Among developed nanohybrids, BSeFF/Ni(OH)₂ showed maximum specific capacitance of 1250 F g⁻¹ while BSeLL/Ni(OH)₂ showed specific capacitance of 689 F g⁻¹ at current density of 2 A g⁻¹ The synthesized flower and microsphere-like peptide/Ni(OH)₂ nanohybrids exhibited excellent electrochemical performance in 1M KOH electrolyte. The high capacitance and long cyclic stability can be easily altered by changing the structural configuration of organic moiety of the studied organic-inorganic nanohybrids, which provides contribution in the development of high performance electrode material for energy storage applications.

2.5 References

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ElectrodepositionofBinderFreePeptide/Co(OH)2NanohybridElectrodesforSolid State Symmetric Supercapacitor

Chapter 3

3.1 Introduction

Bioinspired hybrid nanomaterials have been explored in the area of sustainable energy storage considering their promising properties such as, eco-friendly behavior, flexible nature, low-cost, high energy storage capacity and cyclic stability.^[1-8] Several electrode materials such as carbon materials,^[9] oxides,^[10-13] hydroxides^[14] and conducting polymers^[15] have been explored to fabricate energy storage devices. Cobalt hydroxide based hybrid materials have paramount importance, which provide sustainable energy path for the generation of clean, cost effective and renewable energy storage properties.^[16-20] Currently, researchers are engaged on the development of organic-inorganic nanohybrid materials.^[7,10,21-24] Organic molecules with acid functionalities have drawn considerable attention due to their binding with inorganic moieties which form organic-inorganic nanohybrid materials.^[16,20,25-29] Therefore, structurally flexible and environmentally compatible self-assembling peptides with metal interacting functional groups have been used for the construction of nanohvbrid materials.^[2,11,30] In addition, the reported self-assembling peptides like diphenylalanine and aromatic derivatives have been exhibited immense mechanical, electrochemical and optical properties.^[8,14,19,31] Rosenman et al have modified carbon electrode with bioinspired diphenylalanine based peptide nanotubes for supercapacitor applications.^[1] Furthermore, Wang et al have fabricated a device to light-up a LED by using Fmoc-EF-NH₂ based hydrogel and thin layer of TiO_2 . The peptide was deposited with thin layer of TiO_2 by atomic layer deposition to restrict the electrolyte dissolution of peptide electrode.^[2] Organic-inorganic nanohybrid materials have been explored in the production of energy storage and conversion devices in recent years. Because of its extended cycle life, light weight, high charge/discharge rate, and safe and eco-friendly nature, supercapacitors (SCs) have been appraised as the most encouraging electrode materials.^[11] The electrochemical charge storage mechanism in SCs mainly governed by the properties of electrode material. On the electrodeelectrolyte interface, the charge storage process primarily involves the creation of an electric double layer or quick Faradic redox processes.

Carbon-based substrates including carbon fiber paper and carbon cloth have been used as conductive electrodes to boost the electrochemical performance. The 3D carbon substrates have been widely used for SCs applications due to their efficient electrode-electrolyte contacts.^[14,32-34] Carbon materials fulfill all the requirements for energy storage applications due to their light weight, high conductivity and electrochemical stability.^[4,16,35-39] Furthermore, the electrolytes play a major role on the electrochemical charge storage performance. The charge storing surface redox process and insertion and de-insertion of electrolytic ions have vital importance over charge storing capacity and retention. Hence along with the pseudocapacitive redox properties of electrode material, the ionic conductivity as well as mobility of electrolytes has more importance to improve charge storing efficiency. Here, attention was paid on the effect of electrolytic anions using two different electrolytes i.e. LiOH and KOH.^[40,41] An aromatic

amino acid based nanohybrid material has shown excellent electrochemical performance. For the exploration and advancement of these type of nanohybrid materials, we have synthesized benzo[2,1,3]selenadiazole (BSe) protected dityrosine peptide (BSeYY) by simple liquid phase synthesis method. BSeYY and cobalt nitrate hexahydrate (Co(NO₃)₂.6H₂O) have been used for the fabrication of BSeYY/Co(OH)₂/CP based nanohybrid using one step electrodeposition method.^[22,42-46] The electrochemical performances of hybrid electrode have been analyzed in alkaline electrolytes and efficient charge storage performance have been observed in 1M KOH compared to 1M LiOH electrolyte solution. For the practical application, a symmetric supercapacitor device has been assembled by using two BSeYY/Co(OH)₂/CP nanohybrid electrodes. The nanohybrid electrodes have been emerged in polyvinyl alcohol/potassium hydroxide (PVA/KOH) gel and integrated together by using Whatman filter paper as a separator for the construction of solid state symmetric device.^[47,48]

3.2 Materials and Experimental Methods

3.2.1 Materials and Methods

In this work, all the reagents were used without further purifications. L-Tyrosine (Y), 1-hydroxybenzotriazole (HOBt), N,N'-dicyclohexylcarbodiimide (DCC), potassium hydroxide (KOH), hydrochloric acid (HCl), dimethyl sulphoxide (DMSO) and cobalt nitrate hexahydrate (Co(NO₃)₂.6H₂O) were procured from SRL, India. 3,4-Diaminobenzoic acid and SeO₂ 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^{-1}) in CDCl₃ and DMSO-d₆. 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⁻¹. 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)₂/CP nanohybrid was characterized by using a Bruker D_2 phaser X-ray diffractometer with Cu-K α 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)₂/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 N₂ adsorption at 77 K. Transmission electron microscope (TEM) was assessed to further analyze the microstructure of the synthesized BSeYY/Co(OH)₂/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 charge-discharge (GCD) test were conducted by Metrohm Autolab potentiostat (PGSTAT302N). The freshly prepared electrolyte solution was used during electrochemical analysis to sustain consistency.

3.2.2 Synthesis of organic component

BSe N-protected tyrosine compound **3** was synthesized using solution phase peptide synthesis. The synthesized compound **3** and all intermediates was well characterized by Mass, ¹H NMR spectroscopy and ¹³C NMR spectroscopy.



Scheme 3.1. Synthetic procedure of compound 3.

3.2.3. Synthesis of compound 3

3.2.3.1. Synthesis of benzo[2,1,3]selenadiazole-5-carboxylic acid (6): 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 **6** as a faint pink colored solid.^[30,49] ¹H NMR (400 MHz, DMSO-*d*₆): 8.38 (s, 1H, BSe), 7.94-7.86 (dd, 2H, *J* = 9.28, 9.20 Hz, BSe) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 167.29, 161.13, 159.58, 131.62, 128.29, 125.81, 123.61 ppm; MS (ESI): *m*/*z* calcd. for C₇H₅N₂O₂Se: 228.9516 [M+H]⁺; found: 228.9370.



Figure 3.1 ¹H NMR spectrum (400 MHz, DMSO- d_6) of 6.



Figure 3.2 13 C NMR spectrum (100 MHz, DMSO- d_6) of 6.





3.2.3.2. Synthesis of BSeY-OMe (13): 1 g (4.40 mmol) of **6** 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 N.N'agent 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 Na₂CO₃ solution and saturated brine solution. Solid brown colored compound of 13 was obtained after evaporating the solvent under reduced pressure. Compound 13 was purified using flash chromatography. Yield = 1.58 g, (3.90 mmol, 89%); ¹H NMR (400 MHz, DMSO- d_6): $\delta = 9.22$ (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^{α} H of Tyr), 3.66 (s, 3H, -OCH₃), 3.10-2.99 (m, 2H, C^β H of Tyr) ppm; ¹³C NMR (100 MHz, DMSO- d_6): $\delta = 172.60, 166.19, 160.75, 159.60, 156.43, 134.25,$ 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 C₁₇H₁₅N₃O₄SeNa: 428.0125 [M+Na]⁺; found: 428.0179.



Figure 3.4. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **13**.



Figure 3.5. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of **13**.

Chapter 3



Figure 3.6. ESI-MS spectrum of 13.

3.2.3.3. Synthesis of BSeY-OH (14): The solid compound 13 (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 (2×20 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 Na₂SO₄ and evaporated under reduced pressure to obtain a solid compound 14. Yield = 0.61 g (1.56 mmol, 91%); ¹H 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 = 7.80, 2H Tyr), 4.59 (s, 1H, C^{α} H of Tyr), 3.13-2.95 (m, 2H, C^{β} H of Tyr) ppm. ¹³C NMR (100 MHz, DMSO- d_6): δ = 173.62, 166.14, 160.77, 159.67, 156.36, 134.57, 130.50, 128.58, 128.21, 123.51, 122.84, 115.52, 55.28, 36.05 ppm; MS (ESI): m/z calcd. for C₁₆H₁₃N₃O₄Se: 389.9993 [M-H]⁻; found: 390.0138.



Figure 3.7. ¹H NMR spectrum (400 MHz, DMSO- d_6) of 14.



Figure 3.8. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of 14.



Figure 3.9. ESI-MS spectrum of 14.

3.2.3.4. Synthesis of compound BSeYY-OMe (15): A solution of compound 14 (0.55 g, 1.40 mmol) and HOBt (0.230 g, 1.69 mmol) was stirred in DMF (2 mL). A neutralized solution of H₂N-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 washed with 1N HCl (3×30 mL), saturated Na₂CO₃ (3×30 mL) and again with brine. The organic layer was dried over Na₂SO₄ and evaporated under vacuum by rotary evaporator to yield solid compound 15. The flash chromatography was used to purification of compound 15 with ethyl acetate and hexane as eluent. Yield = 0.59 g (1.04 mmol, 74%): ¹H NMR (400 MHz, DMSO- d_6): $\delta = 9.19$ (s, 1H, OH of Tyr), 9.15 (s, 1H, OH of Tyr), 8.84-8.82 (d, J = 8.08 Hz, 1H, -NH), 8.47-8.45 (d, J = 6.76Hz, 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^{α} H of Tyr), 4.45-4.43 (d, J = 6.28 Hz, 1H, C^aH of Tyr) 3.59 (s, 3H, OCH₃), 3.02-2.83 (m, 4H, C^βH of Tyr) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 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 C₂₆H₂₄N₄O₆SeNa: 591.0759 [M+Na]⁺; found: 591.0871.



Figure 3.10. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **15**.



Figure 3.11. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of 15.



Figure 3.12. ESI-MS spectrum of 15.

3.2.3.5. Synthesis of compound BSeYY (3): Compound 15 (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 $(2 \times 20 \text{ mL})$. 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 $(3 \times 30 \text{ mL})$. The ethyl acetate layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure with rotary evaporator to yield a brownish solid compound 3. Yield = 0.34 g (0.61 mmol, 87%). ¹H NMR (400 MHz, DMSO- d_6) $\delta = 12.72$ (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 Hz, 2H, Tyr), 6.68-6.66 (d, J = 6.52 Hz, 4H, Tyr), 4.76-4.72 (m, 1H, C^{α} H of Tyr), 4.46-4.41 (m, 1H, C^{α}H of Tyr), 3.07-3.00 (m, 2H, C^βH of Tyr), 2.92-2.87 (m, 2H, C^βH of Tyr) ppm; ¹³C 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 C₂₆H₂₂N₄O₆Se: 553.0626 [M-H]⁻; found: 553.0638.



Figure 3.13. ¹H NMR spectrum (400 MHz, DMSO- d_6) of 3.



Figure 3.14. ¹³C NMR spectrum (100 MHz, DMSO- d_6) of 3.



Figure 3.15. ESI-MS spectrum of 3.

3.3 Results and discussion

3.3.1 Synthesis and characterization of organic-inorganic nanohybrids

In-situ electrodeposition technique was used for the fabrication of nanohybrid electrodes (**Scheme 3.2**). In this process, $Co(NO_3)_2.6H_2O$ (0.08 mol) and a synthesized BSe protected dipeptide (BSeYY) (1 mmol) were mixed in water/dimethyl sulphoxide (DMSO) (1:1) solution. Before the electrodeposition of nanohybrid material, a piece of CP substrate was cleaned with 1N HCl, Milli-Q water and ethanol for 10 min and dried at 50 °C for 6 h. The potentiostat was used for the electrodeposition with conventional three electrode cell configuration. The Pt wire (counter), Ag/AgCl (reference) and pretreated CP (working electrode, 1 cm \times 2 cm) were used in electrodeposition. The electrodeposition was conducted at constant negative potential -0.9 V for 20 min

at the water bath at a temperature of 65 °C. Finally, the resulted thin film was washed with milli-Q water (3 times), ethanol (3 times) and dried at 60 °C overnight prior to use for electrochemical analysis. The active mass loading on substrate was calculated gravimetrically by measuring the weight difference of CP before and after deposition. The active material mass loading on the carbon paper substrate was 1.1 mg. The BSeYY/Co(OH)₂/CP nanohybrid was formed due to the electrochemical reactions and deposition.^[22,30,42] The reactions have been proposed as follows;



Scheme 3.2. A representation for nanohybrid electrode fabrication using electrodeposition technique.

FTIR spectroscopy was carried out to analyze the changes of the functional groups present in BSeYY after the synthesis of nanohybrid. **Figure 3.16a** shows the characteristic absorption peaks in the region of 3200-3600 cm⁻¹ due to stretching vibration of O-H bonds.^[50,51] The peak at 1640 cm⁻¹ is assigned to the C=O stretching vibration present in BSeYY/Co(OH)₂/CP nanohybrid.^[51] The FTIR spectrum of BSeYY/Co(OH)₂/CP exhibits the peaks at 600-650 cm⁻¹ due to the bending of Co-OH.^[52] It is noteworthy that the peak of carboxylic acid group at 1715 cm⁻¹ is disappeared in hybrid material due to the interaction between metal and carboxylate ions.^[53]

Raman analysis was conducted to identify the chemical compositional feature of the BSeYY/Co(OH)₂/CP nanohybrid. The prominent Raman bands appear in the Raman spectrum of nanohybrid (**Figure 3.16b**). The BSeYY/Co(OH)₂/CP shows a band at 197 cm⁻¹ corresponding to F₂g mode. The O-Co-O bending band appears at 482 cm⁻¹.^[54] The band at 522 cm⁻¹ is ascribed to CoO (A_g) symmetric stretching mode.^[54] The band at 482 cm⁻¹ is ascribed to E_g mode. A band at 620 cm⁻¹ is attributed to F₂g mode and 690 cm⁻¹ is ascribed to more polarized A_{1g} (CoO) symmetric stretching mode.^[14,54-56]



Figure 3.16. (a) FTIR spectra of the peptide BSeYY and BSeYY/Co(OH)₂/CP nanohybrid. (b) Raman spectrum of deposited BSeYY/Co(OH)₂ nanohybrid on CP.

The XPS survey was conducted to characterize the chemical composition and electronic state of the hybrid material. The XPS survey profile (**Figure 3.17a**) unveils the presence of Co, O, N, C and Se elements which are more consistent with the EDX analysis.^[18] The high resolution XPS spectrum of the cobalt shows (**Figure 3.17b**) two high intensity peaks located at around 781.1 and 796.6 eV due to Co $2p_{3/2}$ and $2p_{1/2}$ spin-orbit separation respectively. The spin-orbit energy separation between two major peaks is observed at the binding energy of 15.5 eV.



Figure 3.17. (a) XPS survey spectrum of BSeYY/Co(OH)₂/CP nanohybrid. Core level analysis of (b) Co 2p, (c) C1s and (d) O1s.



Figure 3.18. High resolution XPS spectra of (a) N 1s and (b) Se 3d for BSeYY/Co(OH)₂/CP nanohybrid.

The low intensity and broad peaks appeared at 786.3 and 802.8 eV correlating with the satellite peaks of Co $2p_{3/2}$ and $2p_{1/2}$ respectively, which confirm the divalent state of cobalt ions.^[52,57,58] The core level C 1s spectrum (**Figure 3.17c**) consists of four fitted peaks including C=C (284.6 eV), C-C (285.2 eV), C-OH/C-N (286.0 eV), and C=O (288.5 eV).^[25,57,59] The core level O 1s spectrum is shown in **Figure 3.17d**. The well fitted peaks at the binding energies of 531.3 and 532.8 eV are originated from O-H of Co-OH and O-C=O respectively.^[25] The high resolution N 1s spectrum (**Figure 3.18a**) mainly displays two prominent fitted peaks, which are assigned to C=N (398.2 eV) and C-N (400.2 eV). The **Figure 3.18b** shows a peak for Se 3d at the binding energy of 58 eV. The XPS results confirm the formation of BSeYY/Co(OH)₂ based hybrid material.

FE-SEM study was conducted to examine the surface morphology of the nanohybrid materials. **Figure 3.21a** shows that the petal-like sheets are interconnected and interlaced to constitute open framework-like structures. The electrodeposited nanohybrids show uniform flower-like surface morphology which help to enhance the contact with electrolytic ions during the electrochemical measurements.



Figure 3.19. EDS analysis of BSeYY/Co(OH)₂/CP nanohybrid.

The energy dispersive X-ray (EDX) spectroscopy (**Figure 3.19**) and elemental mapping analysis (**Figure 3.20**) were conducted to elucidate the chemical composition and elemental distribution of the compound respectively. The EDX and elemental mapping analysis suggest that the nanohybrid material is composed of Co, C, N, O and Se elements. It is observed that all elements are distributed uniformly.



Figure 3.20. Elemental mapping and corresponding SEM image of BSeYY/Co(OH)₂/CP nanohybrid.

The petal-like sheets of BSeYY/Co(OH)₂/CP nanohybrid stack to each other to form flower-like structures which was further confirmed by the TEM morphological characterization (**Figure 3.21b**). The average width of the nanosheets is 2.6 nm. The hierarchical morphology could not only beneficial to easy transport of the electrolyte ions but also promotes fast charge transport for Faradic reactions on electrochemical interface. This type of morphology facilitates the energy storage behavior.^[59,60]



Figure 3.21. (a) SEM and (b) TEM images of BSeYY/Co(OH)₂/CP nanohybrid at different resolutions.

Figure 3.22 shows X-ray diffraction (XRD) profile of the hybrid material. The absence of additional peaks in electrodeposited BSeYY/Co(OH)₂/CP nanohybrid as compared to bare CP is ascribed to the amorphous nature of the nanohybrid.^[61-63]



Figure 3.22. XRD pattern of electrodeposited BSeYY/Co(OH)₂/CP nanohybrid and bare carbon paper (CP).

The selected area electron diffraction (SAED) pattern (**Figure 3.23**) confirms the amorphous nature of the hybrid nanomaterial.^[28,64]



Figure 3.23. Selected area electron diffraction of the electrodeposited hybrid material.

The expensive binder-free method does not minimize the inactive surface area but also reduces the extra contact resistance during the electrochemical analysis. In this work, In-situ potentiostatic electrodeposition method was used to synthesize binder-free BSeYY/Co(OH)₂/CP nanohybrid. In electrodeposition process, the NO₃⁻ gets reduced in the solution to generate NO₂⁻ and OH⁻ on applied potential. The Co²⁺ ions react with carboxylate ions of dipeptides and OH⁻ ions on the electrode surface using Coulombic attractions resulting in the formation of sheet-like nanostructure over CP surface. Structurally, the peptide molecule (BSeYY) is constituted with N-capped benzoselenadiazole ring, peptide backbone and a carboxylic acid group. Carboxylate anions of peptide molecules facilitate the interaction with Co²⁺ ions. However, the aromatic rings and amide groups in the peptides could induce the attractive hydrogen bonding and π - π stacking interactions which provide the structural stability to the nanohybrid. It enhances the structural stability of the nanohybrid during fast Faradic reaction and improves the electrochemical active sites. The sheet-like nanostructures crosslink with each other for the construction of flower like morphology.

The nitrogen adsorption/desorption measurements were conducted to investigate specific surface area and porous structure of the prepared materials (**Figure 3.24**). The obtained surface area and pore size characteristics are summarized in **Table 3.1**. Based on the IUPAC classification, the obtained isotherm is classified as Type 4 isotherms with slit-like mesoporous structures.^[65] The specific surface area of BSeYY and BSeYY/Co(OH)₂ are calculated as 3.775 m² g⁻¹ and 6.699 m² g⁻¹ respectively using standard multipoint Brunauer-Emmett-Teller (BET) method.



Figure 3.24. Nitrogen adsorption-desorption isotherm of (a) BSeYY and (b) $BSeYY/Co(OH)_2$ samples (the inset corresponds to BJH pore size distribution curve).

Table 3.1. Summary of the BET surface areas and pore structures of BSeYY and BSeYY/Co(OH)₂.

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

Moreover, the BSeYY/Co(OH)₂ and BSeYY exhibit ~0.082 cm³ g⁻¹ and ~0.009 cm³ g⁻¹ pore volume according to the Barrett-Joyner-Halenda (BJH) pore size distribution at the desorption branch respectively. The BSeYY/Co(OH)₂ nanohybrid exhibit narrow pore-size distribution with a peak pore size of ~3.79 nm, which is shown in insets **Figure 3.24b**. All the results suggest that the BSeYY/Co(OH)₂ composite has excellent textural properties for the efficient charge storage process by providing more number of electrochemical active sites.^[65-69]

3.3.2 Electrochemical performance of the hybrid material.

Electrochemical surface area (ECSA) determines the surface area of electrode material in electrolytic solution, which is as an effective way for the estimation of active surface area. The electrochemical double layer capacitance (C_{dl}) of nanohybrid in non-Faradic regions was used to estimate the ECSA of electrodeposited BSeYY/Co(OH)₂ nanohybrid. The C_{dl} (**Figure 3.25b**) of the BSeYY/Co(OH)₂ nanohybrid was calculated using capacitive current densities vs scan rates (**Figure 3.25a**). The ECSA of nanohybrid was calculated using equation (5);

$$ECSA = C_{dl}/C_s \tag{5}$$

where, Cs is specific electrochemical double layer capacitance of flat surface with 1 cm² of real surface area. Here, Cs is 0.04 mF cm⁻² for flat surface.^[63] A straight line slope representing the C_{dl} of nanohybrid was obtained by varying current densities in relation to scan rates (**Figure 3.25b**). The C_{dl} of the BSeYY/Co(OH)₂ nanohybrid is 0.329 mF cm⁻² with an ECSA of 8.22 cm². The

high capacitive behavior of nanohybrids can be ascribed to their large active surface area.



Figure 3.25. (a) CV diagrams of BSeYY/Co(OH)₂/CP within the range of 0.49-0.6 V at scan rates of 5, 10, 15, 20, 25, 30, 40, 50 and 60 mV s⁻¹ respectively. (b) Linear relationship between current density (corresponding to 0.59 V) and scan rate.

The electrochemical performances of the fabricated BSeYY/Co(OH)₂/CP electrode were evaluated to determine the redox and capacitive behavior in 1M KOH and LiOH electrolytes using three electrode system. Cyclic voltammetry (CV) was conducted in the range of the potential window -0.15 to 0.45 V in 1M KOH solution (**Figure 3.26a**) and 1M LiOH solution (**Figure 3.28a**) at different scan rates. The possible chemical reaction is mentioned as follows considering the surface redox peaks.

 $Co(OH)_2 + OH^- \rightleftharpoons CoOOH + H_2O + e^-$ (3)

The anodic and cathodic redox peaks appear due to the intercalation and deintercalation of the ions.^[70] The high symmetric reversibility of the redox peaks exhibit the Faradic behavior of the BSeYY/Co(OH)₂/CP nanohybrid. The galvanostatic charge-discharge (GCD) of BSeYY/Co(OH)₂/CP electrode was examined in 1M KOH (**Figure 3.26b**) and 1M LiOH (**Figure 3.28b**) electrolytes to know the capacitive properties at various current densities. The following equation is used to evaluate the specific capacitance (Cs) of the three electrode setup:⁹

$$Cs = \frac{I \times \Delta t}{m \times \Delta V} (F g^{-1})$$
(4)

where ΔV (V) denotes the discharge potential window excluding IR drop, I (A) represents discharge current, Δt (s) is the discharge time and m (g) is the mass of active material.

The Cs of the BSeYY/Co(OH)₂/CP electrode at 1, 2, 3, 5, 7, 10 and 15 A g⁻¹ in 1M KOH (**Figure 3.26b**) and 1M LiOH (**Figure 3.28b**) electrolytes are calculated as 974.78, 914.12, 887.51, 862.57, 844.05, 835.42, 756.85 F g⁻¹ and 441.23, 436.31, 431.50, 421.53, 410.94, 398.71, 364.43 F g⁻¹ respectively. The transport properties of charge carriers within the electrode were evaluated using electrochemical impedance spectroscopy (EIS). EIS analysis was carried out in 1M KOH over the frequency range from 100 kHz to 0.1 Hz shown in **Figure**

3.26c. The EIS spectrum of BSeYY/Co(OH)₂/CP nanohybrid consist of a linear line at lower frequency range and semicircle at higher frequency range. The solution resistance (R_s) can be aroused due to the electrode/ electrolyte interface resistance, the electrolyte resistance and the electrode contact resistance. The diameter of semicircle at higher frequency level is generated due to the participation of OH⁻ ions in Faradic redox reaction on the electrodes indicating the charge transfer resistance (R_{cl}). Warburg resistance, which appears owing to OH⁻ ion diffusion and transport in the electrolyte, is attributed to the straight line at post-semicircle in the low frequency area. The BSeYY/Co(OH)₂/CP nanohybrid electrode shows vertical line at lower frequency region corresponding to ideal capacitive behaviors.^[71,72,73] The GCD cycling performance (Figure 3.26d) of BSeYY/Co(OH)2/CP hybrid electrode is obtained with 78.62% capacitance retention after 3000 cycles at 18 A g⁻¹ in 1M KOH electrolyte solution. Figure 3.27a represents the comparative CV analysis of the BSeYY/Co(OH)₂/CP hybrid electrode and bare CP electrode in 1M KOH and 1M LiOH electrolytes. It is noteworthy that hysteresis area of BSeYY/Co(OH)₂/CP in 1M KOH is higher as compared in 1M LiOH electrolyte and bare CP electrode in 1M KOH electrolyte. The GCD (Figure 3.27b) of BSeYY/Co(OH)₂/CP and bare CP was performed in 1M KOH and 1M LiOH electrolytes. BSeYY/Co(OH)₂/CP electrode exhibits enhanced performance in 1M KOH than 1M LiOH at a constant current density of 1 A g⁻¹, whereas bare CP shows negligible capacitive properties in 1M KOH electrolyte. The larger hysteresis area and enhanced capacitive properties of BSeYY/Co(OH)₂/CP electrode in 1M KOH than 1M LiOH are attributed to the better access and intercalation/deintercalation of the electrolytic ions.^[40,66] The fitted EIS spectrum of the BSeYY/Co(OH)₂/CP in 1M LiOH is shown in Figure 3.27c. The calculated R_s values for the BSeYY/Co(OH)₂/CP electrode are 1.56 Ω and 1.78 Ω in 1M KOH (Figure 3.26c) and 1M LiOH (Figure 3.27c) electrolytes respectively. The values of R_{ct} in 1M KOH and LiOH are 2.20 Ω and 7.01 Ω respectively. The lower value of R_{ct} in 1M KOH electrolyte suggests that the transfer and mobility of electrolytic ions are favorable in 1M KOH than 1M LiOH electrolyte due to the smaller size of hydrated sphere of ions.^[40,72,73] Figure 3.27d displays the Cs vs current density plot of BSeYY/Co(OH)₂/CP electrode performed in 1M KOH and LiOH electrolytes. The Cs of the hybrid electrode decrease with the increase in current densities due to the minimum time to respond for the active material and less utilization of the electrochemically active sites. The capacitive ability of BSeYY/Co(OH)₂/CP in 1M KOH electrolyte is higher than the 1M LiOH electrolyte at 1 A g⁻¹. The hydrated ionic radius of the Li⁺ ions is larger than hydrated K⁺ ions (rLi⁺(H₂O)^{δ -}) rK⁺(H₂O)^{δ -}) which creates hindrance in ionic mobility and intercalation/deintercalation of the ions during electrochemical performances.^[40,41,66] Therefore, BSeYY/Co(OH)₂/CP hybrid electrode exhibits largest Cs and low solution and charge transfer resistance in 1M KOH as compared to 1M LiOH. The BSeYY/Co(OH)₂/CP hybrid electrode exhibits higher electrochemical performance as compared to recently developed

cobalt hydroxide and organic-inorganic hybrid based electrodes. The electrochemical activity of cobalt based nanomaterials and hybrids has been compared with BSeYY/Co(OH)₂ nanohybrids in **Table 3.2**.^[54,59,71,74-77]



Figure 3.26. (a) CV curves of BSeYY/Co(OH)₂/CP in 1M KOH at different scan rates. (b) GCD curves of BSeYY/Co(OH)₂/CP at 1, 2, 3, 5 and 7 A g^{-1} current densities. (c) EIS Nyquist plot in the range of 0.1-10⁵ Hz. (d) Cyclic stability curve of BSeYY/Co(OH)₂/CP electrode at 18 A g^{-1} .



Figure 3.27. (a) CV curves of BSeYY/Co(OH)₂/CP nanohybrid and bare electrodes at 50 mV s⁻¹ in 1M KOH and LiOH electrolytes. (b) GCD profiles of BSeYY/Co(OH)₂/CP and bare electrode at 1 A g⁻¹ in 1M KOH and LiOH electrolytes. (c) EIS Nyquist plot in the range of $0.1-10^5$ Hz and their circuit fit in 1M LiOH electrolyte. (d) Cs vs current density plots of BSeYY/Co(OH)₂/CP compared in 1M KOH and LiOH electrolytes.



Figure 3.28. Electrochemical analysis of BSeYY/Co(OH)₂/CP electrode in 1M LiOH aqueous electrolyte. (a) CV curves at 5, 10, 20, 30, 40 and 50 mV s⁻¹ scan rates. (b) GCD curves of BSeYY/Co(OH)₂/CP electrode at various current densities.

Table 3.2. 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 &%capacitanceretention	Ref.
1	Co(OH) ₂ rods	1116 F g ⁻¹	2 A g ⁻¹	1 M KOH		53
2	Co(OH) ₂ / GNS	693.8 F g ⁻¹	2 A g ⁻¹	1 M KOH	3000 and 91.9%	58
3	Co(OH)2- rGO	734 F g ⁻¹	1 A g ⁻¹	2 M KOH	1000 and 95%	65
4	MOF- derived Co(OH) ₂	604.5 F g ⁻¹	0.1 A g ⁻¹	6M KOH	2000 and 70%	69
5	Flower- like Co(OH) ₂	429 F g ⁻¹	1 A g ⁻¹	2 M KOH		70
6	Co(OH) ₂	416 F g ⁻¹	1 A g ⁻¹	2 M KOH	500 and 93%	71
7	cobalt	427 C g ⁻¹	1 A g ⁻¹	1 M KOH		72

	oxides/hy droxides					
8	BSeYY/ Co(OH) ₂ / CP	974.78 F g ⁻¹	1 A g ⁻¹	1 М КОН	3000 and 77.62%	This work

A gel was prepared by the addition of 2 g polyvinyl alcohol (PVA) and 1.2 g KOH in 20 mL deionized water. The mixture was heated and stirred at 80 °C till the solution became transparent. The fabricated two electrodes were dipped in PVA/KOH gel for 3-4 min. To assemble symmetric solid state device, two BSeYY/Co(OH)₂/CP electrodes were separated using Whatman filter paper (**Scheme 3.3**) and placed in a Swagelok cell for electrochemical characterization.^[12]



Scheme 3.3. A representation for the construction of solid-state symmetric supercapacitor device.

3.3.3. Electrochemical analysis of the assembled device.

The electrochemical analysis of the assembled device was assessed using the combination of CV, GCD and EIS techniques. Figure 3.29a shows the CV curves for the assembled device at different scan rates (from 10 to 150 mV s⁻¹) within the potential window of 0.0 to 1.6 V. The cyclic voltammograms exhibit a nearly symmetric redox peaks at scan rate of 150 mV s⁻¹, which is an indicative of excellent contact with the electrolytic ions and high electric conductivity. The current response of the CV increases with increase in scan rate and vice-versa. CV voltammograms of different potential window 1.0 to 1.6 V at 50 mVs⁻¹ scan rate are shown in Figure 3.29b. GCD (Figure 3.29c) measurements were performed at various current densities which exhibit good capacitive performance for the assembled device. The Figure 3.29d shows GCD profiles at different potential window ranging from 1.0 to 1.55 V at 1 A g⁻¹. These results indicate that the capacitance of the device decreases with the decrease in potential window. The Cs versus current densities are plotted based on the equations 7 and 8 (Figure 6e). The values of power density (P) and energy density (E) are important criteria for the assessment of constructed symmetric supercapacitor device. The Cs (F g⁻¹), P (W kg⁻¹) and E (Wh kg⁻¹) of the symmetric solid state device were estimated using following equations:^[9,78]

$$Cs = \frac{2I \times \Delta t}{m \times \Delta V} (F g^{-1})$$
(6)

$$E = \frac{1}{8 \times 3.6} Cs \times \Delta V^2 (Wh \ kg^{-1})$$
(7)

$$P = \frac{3.6 \times E}{\Delta t} \times 1000 \ (W \ \text{kg}^{-1})$$
 (8)

Here, I (A) stands for discharge current, Δt stands for discharge time (s), m (g) is active material mass on one electrode and ΔV (V) is the potential window after ohmic drop.

The symmetric device shows a maximum energy density of 16.35 Wh kg⁻¹ at 0.5 A g⁻¹ and higher power density of 617.37 W kg⁻¹ at 2 A g⁻¹. The cycling durability of the device was tested via GCD at a current density of 2 A g⁻¹. The capacitor device exhibits 81.04% retention of their initial capacitance after 5000 cycles (**Figure 3.29f**). For the practical applications, the symmetric solid-state device was constructed to light up a LED (**Scheme 3.2**). Two assembled devices were arranged in a series for light up a LED (**Figure 3.30**) for few seconds. The device works in the range of 2.8-3.2 V.^[2,79,80]



Figure 3.29. (a) CV of the BSeYY/Co(OH)₂/CP based symmetric supercapacitor obtained at various scan rates within potential window of 0.0 to 1.6 V. (b) CV curves for BSeYY/Co(OH)₂/CP measured in different potential window at 50 mV s⁻¹ scan rate. (c) GCD profiles of symmetric SCs device at different current densities. (d) GCD profiles of symmetric SCs device with upper voltage limit values ranging from 1.0 to 1.55 V at fixed current density of 1 A g⁻¹. (e) Cs vs

current density plot of symmetric capacitor device at various current densities. (f) Cyclic stability of symmetric SCs device at constant current density 2 A g^{-1} for 5000 cycles.



Figure 3.30. The photographs show LED lighted by BSeYY/Co(OH)₂/CP symmetric solid state devices assembled in a series.

3.4 CONCLUSION

In summary, a dipeptide based nanohybrid material was synthesized using electrodeposition process on carbon paper without any binder. The electrochemical analyses were performed to know the redox and capacitive behavior of the synthesized hybrid material in 1M KOH and 1M LiOH aqueous electrolytes. The prepared BSeYY/Co(OH)₂/CP nanohybrid achieved an outstanding capacitance of 974.78 F g⁻¹ at 1 A g⁻¹ current density and 78.62% capacitance retention after 3000 cycles at 18 A g⁻¹. The fabricated all solid-state symmetric SCs device with PVA/KOH electrolyte exhibited maximum energy density of 16.35 Wh kg⁻¹ at 0.5 A g⁻¹ and highest power density of 617.37 W kg⁻¹ at 2 A g⁻¹ with excellent cyclic stability (81.04%) even at 5000 cycles. The lightening of the LED was demonstrated the excellent findings of peptide-based hybrid material. These findings indicate that the peptide-based supercapacitor device offers uppermost importance for the ever-growing green and implantable energy storage applications.

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In Situ Fabricated Small Organic Molecule-Anchored Bimetallic Hydroxide-based Nanohybrids for Symmetric Supercapacitor

Chapter 4

4.1 Introduction

The researchers are engaged to develop sustainable and effective energy storage materials and technologies due to the rising demand of energy and the quick depletion of natural resources. Therefore, several electrochemical energy storage systems including fuel cells, batteries, supercapacitors and electrolyzers have been thoroughly studied to produce and store more energy.^[1-12] The electrochemical capacitors (ECs) or supercapacitors meet all requirements by virtue of their rendering high power density, rapid charge-discharge process and long term performance. The primary component of electrochemical devices are the electrode materials. Therefore, the control over micro and nanoscale architectures and the optimized concentration of the materials are important in electrochemical processes for efficient ion and electron transportation at the electrode-electrolyte interface, which improves the electrochemically active sites and facilitates the intercalation/deintercalation of the ions.[13-15] Therefore, solgel, atomic layer deposition, hydrothermal, solvothermal, electrodeposition methods have been used to synthesize efficient materials including metal oxides, sulphides, nitrides, hydroxides, conducting polymers and organic-inorganic hybrid materials.^[3,6,8,16-25] However, the electrodeposition method enables lowcost, simple handling, binder free, controlled growth and uniform distribution to exploit the high surface area and exposes more electrochemically active sites for smooth electrolyte ions diffusion and transport of electrons during electrochemical measurements to achieve high energy storage property.^[26] Moreover, sustainable bio-derived nanomaterials have attracted enormous attention due to their eco-friendly, easy to handle, light weight, renewable and highly stable properties.^[27-29] The fabrication of nanohybrid materials with distinct characteristics and functions could be achieved by the cross-linking of organic and inorganic components. The aromatic rings and heteroatoms in the organic molecules can enhance the intermolecular interactions through π - π stacking, hydrogen bonding and Van der Waals interactions, which stabilize the nanoscale architecture of the nanohybrids through the self-assembly process. Moreover, the use of non-precious metals with organic moiety to fabricate organic-inorganic hybrid electrode materials with distinctive architectures is one of the most promising, economical and environmentally friendly solutions in the field of energy storage and conversion.^[7,8,12,18,30-34] The asymmetric supercapacitors exhibit better energy density than simple supercapacitors. However, balancing the charges between the cathode and anode involves a number of complex steps. Therefore, symmetric supercapacitors have benefited in this regard due to both electrodes are made of the same materials. In order to maintain the high energy density of the device, it is necessary to employ the right electrode and electrolyte while making symmetric supercapacitors.^[35,36] Therefore, the organic molecules with acid functionalities have drawn a lot of attention due to their ability to bind with inorganic moieties to form organicinorganic nanohybrid materials for electrochemical applications.^[30,37-41] Herein, we synthesized several nanohybrid electrodes by varying the metal salt

concentrations via one pot galvanostatic electrodeposition method at room temperature without any binders to achieve the best electrochemical properties of synthesized nanohybrids. Among all the fabricated electrodes, the 2:2 hybrid electrode exhibits better electrochemical properties due to the facile synergistic characteristics and functionalities between organic and inorganic components, which provide more electrochemically active sites. Moreover, all solid-state symmetric devices (SSC) have been constructed by assembling two pieces of the electrodeposited electrodes. The fabricated SSC device yields an energy density 18.27 Wh/kg at a power density of 571.97 W/kg. In addition, the device retained 85.25% of its initial capacitance at 7 A g⁻¹ after 5000 cycles.

4.2 Materials and Experimental Methods

4.2.1 Materials

Selenium dioxide and 3,4-diaminobenzoic acid were purchased from Alfa Aesar Pvt. Ltd. and L-tyrosine (Y), L-tryptophan (W), N,N'-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) were purchased from SRL chemicals, India. All chemicals were used without further purification. The solvents ethanol, dimethyl sulfoxide (DMSO), hexane, ethyl acetate and N,N'-dimethylformamide (DMF) were purchased from Merck India Ltd. The solvents were dried and distilled before used. The pre-coated silica gel thin layer chromatography (Kieselgel 60 F₂₅₄) plates were purchased from Merck K GaA. Ni(NO₃)₂.6H₂O and Co(NO₃)₂.6H₂O were purchased from SRL chemicals. Carbon paper (CP) was obtained from Global Nanotech, Mumbai, India.

4.2.2 Methods

The Flash Chromatography (TELEDYNE ISCO. USA: model: CombiFlash®Rf+) using silica gel (100-200 mesh) column was used to purify the compound and their intermediates. The ethyl acetate/hexane solvents were used as eluent. The NMR analysis was performed on Bruker AV 400 MHz spectrometer in $CDCl_3$ and $DMSO-d_6$ and the concentration of the compound was in the range of 5-10 mmol L^{-1} . The positive and negative mode electrospray ionization mass spectrometry was recorded on a Bruker micrOTOF-Q II mass spectrometer. The characteristic absorption of the functional group present in the compound was carried out on a Bruker Tensor 27 FTIR spectrophotometer by using KBr pellets. X-ray diffraction (XRD) analysis of the materials was characterized by using a Bruker D₂ phaser X-ray diffractometer with Cu-Ka irradiation ($\lambda = 1.54$ A°). The Raman spectra were performed at room temperature on Raman spectrometer (LabRAM HR Evolution, Horiba Scientific) with a 633 nm He-Ne laser of 5 mW power. The compositions and oxidation states of the element in the synthesized materials were studied using X-ray photoelectron spectroscopy (XPS) using a PHI 5000, VersaProbe III, Physical Electronics. The Karl Zeiss JEOL FE-SEM was used to characterize the morphology, EDS and elemental mapping of synthesized hybrid materials. The morphology was further characterized by transmission electron microscope using a JEM-2100F, JEOL system. The BET of the synthesized materials was characterized by Autosorb iQ3 (Quantachrome) gas sorption analyzer under N2 adsorption at 77 K. Metrohm Autolab potentiostat (PGSTAT302N) was used to perform all the electrochemical measurements.

4.2.3 Synthesis of organic component



Scheme 4.1. Synthetic procedure of compound 4.

4.2.4 Synthesis of compound 4

4.2.4.1 Synthesis of benzo[2,1,3]selenadiazole-5-carboxylic acid (6): 3,4-Diaminobenzoic acid (1 g, 6.57 mmol) and selenium dioxide (1.46 g, 13.15 mmol) were refluxed in methanol (15 mL) and 1N HCl (10 mL) for 2 h at 80 °C. The reaction mixture was cooled at room temperature and methanol was evaporated by a rotary evaporator. The precipitate of the product was filtered by sintered glass funnel (Borosil G4) with Milli-Q water. The faint pink colored solid precipitate was dried in oven at 60 °C to yield 1.37 g (6.01 mmol, 91%) of **6**. $^{[42,43]}$ ¹H NMR (400 MHz, DMSO- d_6): δ 8.43 (s, 1H, BSe), 8.00-7.91 (dd, 2H, J = 9.32, 9.28 Hz, BSe); ¹³C NMR (100 MHz, DMSO- d_6): δ 167.33, 161.17, 159.63, 131.66, 128.33, 125.86, 123.62; MS (ESI): *m/z* calcd. for C₇H₄N₂O₂Se: 226.9360 [M-H]⁻; found: 226.9512.



Figure 4.1. ESI-MS spectrum of 6.



Figure 4.2. ¹H NMR spectrum (400 MHz, DMSO- d_6) of BSe-OH (6).



Figure 4.3. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of BSe-OH (6).

4.2.4.2 Synthesis of BSeY-OMe (13): A solution of 1 g 6 (4.40 mmol) and HOBt (714.1 mg, 5.28 mmol) was solubilized and stirred in 4 mL of DMF in a 100 mL round bottom flask. In the reaction mixture a neutralized solution of Ltyrosine methyl ester was extracted from its corresponding hydrochloride salt (2.04 g, 8.80 mmol) and added after concentrated by a rotary evaporator. The coupling agent N,N'-dicyclohexylcarbodiimide was added (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 to remove the dicyclohexylurea (DCU). Then, the filtrate of the reaction mixture was concentrated by using rotary evaporator. The concentrated reaction mixture was diluted with ethyl acetate and washed with 1N HCl (3×30 mL), saturated Na₂CO₃ solution (3×30 mL) and saturated brine solution (2 \times 30 mL). The extracted ethyl acetate layer was dried over Na₂SO₄. Solid brown colored compound of 13 was obtained after evaporating the solvent under reduced pressure. Compound 13 was purified by using flash chromatography. Yield = 1.56 g, (3.90 mmol, 87%); ¹H NMR (400 MHz,

DMSO-*d*₆): δ 9.42 (s, 1H, OH of Tyr), 9.32, 9.30 (d, *J* = 7.72, 1H, NH), 8.52 (s, 1H, BSe), 8.09-8.03 (dd, *J* = 9.52, 9.24 Hz, 2H, BSe), 7.31,7.29 (d, *J* = 8.32 Hz, 2H, Tyr), 6.86, 6.84 (dd, *J* = 8.32 Hz 2H, Tyr), 4.85-4.79 (m, 1H, C^a H of Tyr), 3.84 (s, 3H, -OCH₃), 3.30-3.16 (m, 2H, C^β H of Tyr); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 172.77, 166.39, 160.92, 159.77, 156.59, 134.43, 130.66, 128.27, 128.19, 123.71, 123.09, 115.72, 55.48, 52.62, 36.18; MS (ESI): m/z calcd. for C₁₇H₁₅N₃O₄SeNa: 428.0125 [M+Na]⁺; found: 428.0109.







Figure 4.5. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of BSe-Y-OMe (**13**).



Figure 4.6. ¹³C NMR spectrum (100 MHz, DMSO- d_6) of BSe-Y-OMe (13).

4.2.4.3 Synthesis of BSeY-OH (14): 0.8 g (1.98 mmol) of the solid compound 13 was dissolved in 40 mL distilled methanol. The reaction mixture was allowed to react with a solution of 5 mL (0.5 N) NaOH solution. The reaction mixture was stirred and the progress of the hydrolysis was monitored by thin layer chromatography. After the completion of the reaction, the excess methanol was evaporated with a rotary evaporator till dryness and diluted with 30 mL milli-Q water. Then, the aqueous mixture was taken in a separating funnel and slowly washed with diethyl ether (2×20 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 the 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_2SO_4 and evaporated by a rotary evaporator to obtain a solid compound 14. Yield = 0.67 g (1.71 mmol, 87%); ¹H NMR (400 MHz, DMSO d_6): $\delta = 9.40$ (s, 1H, OH of Tyr), 9.18, 9.16 (d, J = 8.04, 1H, -NH), 8.51 (s, 1H, BSe), 8.09-8.03 (dd, J = 9.4, 9.24, 2H, BSe), 7.33, 7.30 (d, J = 8.12, 2H, Tyr), 6.86, 6.83 (d, J = 8.12, 2H Tyr), 4.80-4.74 (m, 1H, C^{α} H of Tyr), 3.32-3.13 (m, 2H, C^{β} H of Tyr). ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 173.76, 166.32, 160.90, 159.80, 156.48, 134.71, 130.64, 128.71, 128.35, 123.66, 122.97, 115.66, 55.42, 36.18; MS (ESI): m/z calcd. for C₁₆H₁₂N₃O₄Se: 389.9993 [M-H]⁻; found: 390.0381.

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Figure 4.9. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of BSe-Y-OH (**14**).

4.2.4.4 Synthesis of compound BSeYW-OMe (16): The compound 14 (0.40 g. 1.02 mmol) and HOBt (0.166 g, 1.23 mmol) were stirred in DMF (3 mL) at ice cold condition. A neutralized solution of L-tryptophan methyl ester was extracted from its corresponding hydrochloride salt. It was concentrated at reduced pressure for addition to the reaction mixture drop by drop followed by coupling agent N,N'-dicyclohexylcarbodiimide (0.254 g, 1.23 mmol) in ice cold condition and allowed to stir for 12 h at room temperature. After completion of the reaction, the reaction mixture was diluted with acetonitrile solvent and filtered it by sintered glass funnel (Borosil-G4) to remove the DCU. The excess acetonitrile was evaporated at reduced pressure. Then, the reaction mixture was diluted by ethyl acetate. After that, the organic layer was washed with HCl (1N, 3×30 mL), saturated Na₂CO₃ (3×30 mL) and again with brine (2×30 mL). The organic layer was dried over Na₂SO₄ and evaporated under reduced pressure to yield a solid compound 16. The flash chromatography was used to purification of compound 16 with ethyl acetate and hexane as eluent. Yield = 0.49 g (0.83 mmol, 80%): ¹H NMR (400 MHz, DMSO-d₆): δ 10.97 (s, 1H, NH of Trp), 9.23 (s, 1H, OH of Tyr), 8.91, 8.89 (d, J = 8.4 Hz, 1H, -NH), 8.64, 8.62 (d, J = 7.24 Hz, 1H, -NH), 8.37 (s, 1H, BSe), 7.95-7.89 (dd, J = 9.44, 9.32 Hz, 2H, BSe), 7.59, 7.57 (d, J =7.6 Hz, 1H, Tyr), 7.41, 7.39 (d, J = 7.96 Hz, 1H, Tyr), 7.29-7.03 (m, 5H, Indole side chain of Trp), 6.72, 6.70 (d, J = 8.24 Hz, 2H, Tyr), 4.85-4.64 (m, 2H, C^{α}H of Tyr and Trp), 3.65 (s, 3H, OCH₃), 3.32-2.89 (m, 4H, $C^{\beta}H$ of Tyr and Trp); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 172.73, 172.16, 166.08, 160.78, 159.71, 156.25, 136.59, 134.77, 130.64, 128.78, 128.38, 127.59, 124.26, 123.38, 122.89, 121.50, 118.97, 118.49, 115.39, 111.95, 109.78, 55.66, 53.75, 52.38, 36.86, 27.47; MS (ESI); m/z calcd. for C₂₈H₂₅N₅O₅SeNa: 614.0919 [M+Na]⁺; found: 614.0702.



Figure 4.10. ESI-MS spectrum of BSe-YW-OMe (16).



Figure 4.11. ¹H NMR spectrum (400 MHz, DMSO- d_6) of BSe-YW-OMe (16).



Figure 4.12. ¹³C NMR spectrum (100 MHz, DMSO- d_6) of BSe-YW-OMe (16).

4.2.4.5 Synthesis of compound BSeYW (4): Compound 16 (0.3 g, 0.51 mmol) was dissolved in 25 mL distilled methanol. The solution was allowed to stir with adding 4 mL NaOH (0.5 N) solution. The progress of the reaction was monitored by TLC. After the completion of the reaction, the methanol was evaporated at reduced pressure. The residue mixture was diluted with 30 mL milli-Q water and taken in a separating funnel. The aqueous mixture was slowly washed with diethyl ether (2×20 mL). The pH of the aqueous layer was adjusted 2 in cold conditions with using HCl (1N). The product was extracted with ethyl acetate (3×30 mL). The ethyl acetate layer was dried over anhydrous Na₂SO₄ and evaporated by a rotary evaporator to yield a yellowish solid compound 4. Yield =0.25 g (0.43 mmol, 86%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.89 (s, 1H, NH of Trp), 9.18 (s, 1H, OH of Tyr), 8.84, 8.83 (d, J = 8.25 Hz, 1H, -NH), 8.42, 8.40 (d, J = 6.65 Hz, 1H, -NH), 8.30 (s, 1H, BSe), 7.88-7.82 (dd, J = 9.30, 9.15 Hz, 2H, BSe), 7.58, 7.56 (d, J = 7.40 Hz, 1H, Tyr), 7.35, 7.33 (d, J = 7.80 Hz, 1H, Tyr), 7.23-6.97 (m, 5H, Indole side chain of Trp), 6.66,6.64 (d, J = 7.40 Hz, 2H, Tyr), 4.76-4.56 (m, 2H, C^{α}H of Tyr and Trp), 3.28-2.86 (m, 4H, C^{β}H of Tyr and

Trp); ¹³C NMR (100 MHz, DMSO- d_6): $\delta = 173.74$, 172.00, 166.04, 160.72, 159.66, 156.18, 136.53, 134.76, 130.60, 128.83, 128.34, 127.70, 124.12, 123.34, 122.82, 121.40, 118.88, 118.65, 115.34, 111.84, 110.15, 55.72, 53.52, 36.82, 27.45; MS (ESI); m/z calcd. for C₂₇H₂₂N₅O₅Se: 576.0786 [M-H]⁻; found: 576.0536.



Figure 4.13. ESI-MS spectrum of BSe-YW-OH (4).



Figure 4.14. ¹H NMR spectrum (500 MHz, DMSO-*d*₆) of BSe-YW-OH (4).



Figure 4.15. ¹³C NMR spectrum (125 MHz, DMSO-*d*₆) of BSe-YW-OH (4).

4.3 Results and discussion

4.3.1 Procedure Through Electrodeposition: A new chemical formulated small organic molecule BSeYW and the inorganic compounds Ni(NO₃)₂.6H₂O and $Co(NO_3)_2.6H_2O$ were used as precursor materials for electrodeposition. The benzo[2,1,3]selenadiazole-capped tyrosine-tryptophan (BSeYW) based organic molecule was synthesized by the solution phase synthetic method and well characterized by NMR and mass spectrometry. A pretreated carbon paper (CP) was used as a working electrode, which served as the backbone and current collector. The treatment of the working electrode was carried out by 1N HCl, Milli-O water and ethanol with the assistance of ultrasonic washing. The threeelectrode system with CP (working electrode), platinum wire (counter electrode) and Ag/AgCl (reference electrode) was used for the electrodeposition process. The inorganic compounds (40 mM overall) and small organic molecule (2 mM) were dissolved in 50 mL solvent (1:1 dimethyl sulphoxide and milli-Q water) for the fabrication of electrodes. Several electrodes were electro-synthesized with a constant concentration of the BSeYW (2 mM) and varying the concentrations of $Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ metal salts as 40:0 (4:0), 0:40 (0:4), 30:10 (3:1), 20:20 (2:2) and 10:30 (1:3) by galvanostatic deposition with applying constant current -1 mA/cm² for 480 seconds (Scheme 4.2). In the electrodeposition process, the nitrate ions of the metal salts are reduced, which increases the electrolyte pH and subsequently deprotonates the carboxylic acid groups of organic molecule molecules by applying the current. Therefore, metal ions bind with carboxylate groups to form nanohybrids which subsequently deposit on the electrode substrate. The synthesized BSeYW/NCDH hybrid electrodes were washed several times with Milli-Q water and ethyl alcohol to avoid surface salt impurities. Then, the electrode was properly vacuum dried and used for electrochemical analysis.



Scheme 4.2. Schematic diagram of the fabrication of BSeYW/NCDH nanohybrid

The changes in vibrations of functional groups of BSeYW/NCDH nanohybrids were analyzed by FTIR analysis (Figure 4.16). The stretching peak of -O-H functional groups is assigned in the range 3300-3500 cm⁻¹. Furthermore, the peak at 1721 cm⁻¹ is assigned in the BSeYW spectrum due to the stretching mode of C=O in the carboxylic acid group. However, this peak is disappeared in all nanohybrid spectra due to the interactions of the metal-carboxylate ions. Moreover, the prominent bands at 1642 and 1565 cm⁻¹ are attributed to amide C=O stretching and –N-H bending of the nanohybrids respectively. The nanohybrids exhibit the vibrational mode of M-OH (M=Ni and Co) in between 600-700 cm^{-1.[44-47]}



Figure 4.16. FTIR spectra of (i) BSeYW and BSeYW/NCDH nanohybrids with various Ni/Co ratios of (ii) 4:0 (iii) 0:4 (iv) 3:1, (v) 2:2 and (vi) 1:3 materials. Figure 4.17 represents the XRD diffraction patterns of the synthesized BSeYW/NCDH nanohybrids. No additional peak is observed except the peaks of carbon paper in X-ray diffraction patterns due to the amorphous nature of the synthesized materials.^[48-50]



Figure 4.17. XRD patterns of (i) bare CP and electrodeposited BSeYW/NCDH nanohybrids with various Ni/Co ratios of (ii) 4:0, (iii) 0:4, (iv) 3:1, (v) 2:2 and (vi) 1:3.

The chemical compositional feature of BSeYW/NCDH was identified by Raman spectroscopy (Figure 4.18). The nanohybrids show several peaks at 206, 466, 573, 618 and 663 cm⁻¹ indicative of Ni(OH)₂ and Co(OH)₂ phase. The band appeared at 206 cm⁻¹ is assigned to F_{2g} mode. The broad band at 466 cm⁻¹ is ascribed to a Ni-OH/Co-OH symmetric mode. Similarly, the band located at 573 cm⁻¹ indicates the asymmetric bending of the M-O bond. The band is appeared at 618 cm⁻¹ due to F_{2g} mode. The Raman band at 663 cm⁻¹ is the indicative of A_{1g} symmetric mode of the cobalt hydroxide phase.^[50-57]



Figure 4.18. Raman spectra of BSeYW/NCDH nanohybrids with various bending and stretching mode peaks in different Ni/Co ratios of 4:0, 0:4, 3:1, 2:2 and 1:3.

The SEM characterization of the synthesized nanohybrids with different Ni-Co ratio was conducted to analyze the morphology of the nanohybrids. The surface of the CP is uniformly covered with various ratios of Ni-Co based nanohybrids as shown in Figure 4.19. The architecture of the 2:2 (Figure 4.20a) BSeYW/NCDH is formed with aggregated crosslinked network like architectures on the CP with an average width of 20 nm. It is noteworthy that the numerous crosslinked network-like architectures are more convenient for facile transport, intercalation/deintercalation, the lowering of the electrode/electrolyte interface contact resistance and enhance the electrochemically active sites to boost the contact between electrode and electrolyte ions during the electrochemical performances for the effective utilization of the active materials.



Figure 4.19. SEM images of (a) bare CP and BSeYW/NCDH nanohybrids with different Ni-Co ratios of (b) 4:0 (c) 0:4 (d) 3:1 (e) 2:2 and (f) 1:3.



Figure 4.20. (a) Crosslinked network-like SEM image of BSeYW/NCDH(2:2) nanohybrid. (b) TEM image and inset of SAED pattern of BSeYW/NCDH(2:2) nanohybrid with crosslinked architecture and amorphous nature. (c) High resolution TEM image of BSeYW/NCDH(2:2) nanohybrid.

TEM image of BSeYW/NCDH(2:2) nanohybrid (Figure 4.20b) further discloses the nanosheets stacking each other to generate network like structures and 2 nm is the measured average width of the nanosheets. The interconnected network like morphology would be highly desirable and convenient for facile ion diffusion and fast electron transport during electrochemical measurements.^[58] Furthermore, the halo diffused and broad ring is observed in a selected area electron diffraction (SAED) pattern (inset of Figure 4.20b), which indicates the amorphous properties of the hybrid materials.^[48,49] Additionally, the high resolution TEM image (Figure 4.20c) does not exhibit the characteristic lattice fringes due to the amorphous nature of the 2:2 nanohybrid material.^[49]

The EDX was performed to elucidate the chemical composition of the nanohybrids as shown in Figure 4.21 for various nanohybrids. The BSeYW/NCDH is composed of Ni, Co, O, N, C and Se elements.



Figure 4.21. EDS analysis of BSeYW/NCDH nanohybrids with various Ni/Co ratios of (a) 4:0 (b) 0:4 (c) 3:1 (d) 2:2 and (e) 1:3.

Moreover, elemental mapping analysis proves the composition of hybrid materials as well as the uniform distribution of elements on the surface of the CP substrate. It clearly indicates that all elements are uniformly distributed on the CP substrates as depicted in Figures 4.22, 4.23, 4.24, 4.25 and 4.26 for 4:0, 0:4, 3:1, 2:2 and 1:3 nanohybrids, respectively.



Figure 4.22. Elemental mapping and corresponding SEM image of BSeYW/NCDH(4:0) nanohybrid.

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Figure 4.23. Elemental mapping and corresponding SEM image of BSeYW/NCDH(0:4) nanohybrid.



Figure 4.24. Elemental mapping and corresponding SEM image of BSeYW/NCDH(3:1) nanohybrid.



Figure 4.25. Elemental mapping and corresponding SEM image of BSeYW/NCDH(2:2) nanohybrid.



Figure 4.26. Elemental mapping and corresponding SEM image of BSeYW/NCDH(1:3) nanohybrid.

XPS was performed to investigate the elemental compositions and binding energy of the elements present in the nanohybrids. The XPS survey spectrum (Figure 4.27a) of BSeYW/NCDH(2:2) nanohybrid reveals the presence of Ni, Co, C, O, N and Se elements. Figure 4.27b represents the core-level spectrum of Ni 2p, which demonstrates the intense peaks of Ni $2p_{1/2}$ and Ni $2p_{3/2}$ at the binding energies of 873.8 and 856.3 eV, respectively. Furthermore, the 17.5 eV spin-energy separation between Ni $2p_{1/2}$ and Ni $2p_{3/2}$ peaks demonstrates the existence of Ni²⁺ in BSeYW/NCDH(2:2). Moreover, Ni 2p spectrum is associated with two satellite peaks positioned at 879.6 and 861.7 eV for Ni $2p_{1/2}$ and Ni 2p_{3/2} respectively.^[47,59] In the case of the core level spectrum of Co 2p (Figure 4.27c), a couple of main peaks are present at 797.5 and 781.6 eV and two satellite peaks are located at 803.7 and 785.3 for Co 2p_{1/2} and Co 2p_{3/2} signals, respectively. The spin-orbit splitting value between the main peaks of Co $2p_{1/2}$ and Co $2p_{3/2}$ is determined as 15.9 eV, which confirms the characteristics of Co^{2+.[47,59]} According to previously published research works and our findings, the transition metal switches to a higher binding energy when it binds with the carboxylate group of the organic moiety (M-O) than the M-O bond of M(OH)₂ materials. It is thought that the carboxylate group of organic moiety performs better electron acceptor from the transition metal center. As a result, the M-O bond of organic and inorganic materials has a higher binding energy than the M-O bond between M(OH)₂ containing materials.^[40,60-62] The high resolution spectrum of C 1s (Figure 4.27d) represents the binding energies of bonding interactions. The peaks are assigned at 284.7, 285, 286 and 288.2 eV, which can be attributed to C=C (sp²C), C-C (sp³C), C-O/C-N and O-C=O bonding interactions, respectively.^[59,63,64] The core-level spectrum of O 1s is displayed in Figure 4.27e. The two fitted peaks are assigned at 531.4 and 532.8 eV for the C=O/M-OH (M=Ni or Co) and C-O bonding interactions, respectively.^[47,63] Furthermore, the N 1s signals in the N 1s high resolution spectrum (Figure 4.27f) are centered at 398.2, 399.7 and 400.2 for C=N (benzoselenadiazole bonding interaction), amide C-N and N-H interactions, respectively.^[45,65,66] The Se 3d



spectrum (Figure 4.28) shows the peak at 61.6 eV for the N-Se-N bonding interaction.

Figure 4.27. XPS spectra of BSeYW/NCDH(2:2). (a) XPS full scan survey spectrum. (b-f) Core-level spectra of (b) Ni 2p, (c) Co 2p, (d) C 1s, (e) O 1s and (f) N 1s.



Figure 4.28. High resolution XPS spectra of Se 3d for BSeYW/NCDH(2:2) nanohybrid.

The surface area and porous structure of the BSeYW/NCDH nanohybrids were investigated using N₂ adsorption-desorption isotherms depicted in Figure 4.29. The obtained isotherms correspond to typical IV-type hysteresis with the slit-like pores in the nanosheets. The BSeYW/NCDH (2:2) has a maximum specific surface area of 24.28 m² g⁻¹ and pore volume of 0.035 cm³ g⁻¹ compared to other nanohybrids (Table 4.1).



Figure 4.29. Nitrogen adsorption-desorption isotherm of (a) 4:0 (b) 0:4 (c) 3:1 (d) 2:2 and (e) 1:3 BSeYW/NCDH nanohybrid samples (the inset corresponds to BJH pore size distribution curve).

The insets of Barrett-Joyner-Halenda (BJH) curves (Figure 4.29) clearly validate the mesoporous feature of the samples with an average diameter ranging from 3 to 5 nm within the nanosheets. The enhanced surface area and suitable pore size structure can efficiently facilitate the interfacial active sites during electrochemical performances. Furthermore, excellent textural properties could enhance the electrode/electrolyte interfaces with higher order electrolytic ions migration within the pores, which play a vital role in enhancing supercapacitive performance.^[67,68]

Samples (BSeYW-NCDHs)	S _{BET} (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Pore Diameter (nm)	
4:0	11.783	0.015	3.387	
0:4	4.590	0.008	3.795	
3:1	16.036	0.019	3.791	
2:2	24.278	0.035	3.394	
1:3	10.908	0.018	3.386	

Table 4.1. Summaries of the BET surface areas and pore structures of various

 BSeYW/NCDH nanohybrids

The density of catalytically active sites is measured by ECSA to reflect the intrinsic electrochemical activity. The electric double layer capacitance (C_{dl}) is determined from current density vs voltage curves in a non-faradaic area (Figure 4.30), which is proportional to the ECSA. ECSA reveals the principal surface active area, which is a useful method for the estimation of the electrochemically active surface area. The following equation was used to compute the ECSA of the nanohybrid.

$$ECSA = \frac{C_{dl}}{C_s}$$

Where, Cs (0.04 mF cm⁻²) represent the specific electrochemical double-layer capacitance of the flat surface with an actual surface area of 1 cm².^[69] The C_{dl} of the nanohybrid was derived as a straight line slope (Figure 4.31) by current densities vs scan rates. The BSeYW/NCDH (2:2) nanohybrid exhibits higher C_{dl} = 0.303 mF cm⁻² with an ECSA of 7.57 cm² than other nanohybrids as shown in Table 4.2.



Figure 4.30. CV curves of (a) 4:0, (b) 0:4, (c) 3:1, (d) 2:2 and (e) 1:3 nanohybrid electrodes at different scan rates from 10-30 mV s⁻¹ in a potential window ranging from 0.1 to 0.2 V vs Hg/HgO in 1 M KOH electrolyte.



Figure 4.31. Linear relationship between current density and scan rate of (a) 4:0, (b) 0:4, (c) 3:1, (d) 2:2 and (e) 1:3 nanohybrid electrodes at a potential of 0.19 V.

Materials (BSeYW/NCDH)	4:0	0:4	3:1	2:2	1:3
C_{dl} (mF cm ⁻²)	0.139	0.092	0.175	0.303	0.110
ECSA (cm ²)	3.47	2.30	4.37	7.57	2.75

Table 4.2. Cdl and ECSA results of various BSeYW/NCDH nanohybrids

The electrochemical performance of two (full-cell) and three electrodes (halfcell) cell configurations were employed with Metrohm Autolab potentiostat (PGSTAT302N). The GCD, CV and electrochemical impedance spectroscopy (EIS) were investigated to evaluate electrochemical performance in 1M KOH electrolyte with three electrode system. The specific capacitance values of the electrodes were computed from the GCD curves *via* the formula: $Cs = I.\Delta t/m.\Delta V$, where, Cs represents the specific capacitance in F g^{-1} , Δt (s) is the discharge time, I is the current value in ampere (A), ΔV (V) is the potential window and m (g) represents the total active mass (subtracting the weight of CP). Figure 4.32a represents the comparative study of CV at 10 mV s⁻¹ with 4:0, 0:4, 3:1, 2:2 and 1:3 composition of BSeYW/NCDH nanohybrid electrodes in the potential window range of 0.0-0.55 V. The CV profile of 2:2 hybrid electrode exhibits a larger hysteresis loop area and peak current compared to 4:0, 0:4, 3:1 and 1:3 electrodes due to its greater exposure of electrochemically active sites, surface area and higher charge storage nature. The higher current response of 2:2 enables due to the well aligned small sheets are directly attached to the 3D substrate, which exposes the higher electrochemically active sites for the better accessibility of the aqueous electrolytic ions during electrochemical performances.

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Figure 4.32. Comparative electrochemical analysis of BSeYW/NCDH nanohybrid electrodes with Nickel-Cobalt ratio of 4:0, 0:4, 3:1, 2:2 and 1:3 in 1M KOH electrolyte. (a) CV curves detected at 10 mV s⁻¹ in the 0.0-0.55 V potential window. (b) GCD measured at 2 A g⁻¹ current density for all the hybrid electrodes. (c) EIS analysis of the organic molecule based nanohybrid electrodes obtained with various BSeYW/NCDH nanohybrid electrodes. (d) Specific capacitance vs current density plot of nanohybrid electrodes as obtained from the GCD.

Furthermore, the CV curves of the 4:0, 0:4, 3:1, 2:2 and 1:3 nanohybrids were investigated at different scan rates of 1, 3, 5, 7 and 10 mV s⁻¹ (Figure 4.33). The distinguishable oxidation and reduction (redox) peaks of the entire hybrid electrodes are increasing in opposite directions with the increase in scan rates. It suggests that the charge diffusion polarizations as well as the increase in Ohmic resistance within the electrode enhance the redox current shift with the increase in scan rates. Furthermore, fast intercalation/deintercalation of the electrolytic ions could be responsible for the shifting in redox peaks with the increase in scan rates. ^[47,56,58]



Figure 4.33. CV curves at 1, 3, 5, 7 and 10 mV s⁻¹ scan rates of BSeYW/NCDH nanohybrid electrodes under the various Ni-Co ratio with (a) 4:0 (b) 0:4 (c) 3:1 (d) 2:2 and (e) 1:3.

The galvanostatic charge-discharge (GCD) was performed to understand the capacitive properties of these electrodes at 2 A g⁻¹ (Figure 4.32b). It is observed that BSeYW/NCDH(2:2) electrode exhibits superior capacitive properties of 1734 F g⁻¹ than BSeYW/NCDH hybrid electrodes with the ratio of 4:0 (848 F g⁻¹ ¹), 0:4 (421 F g⁻¹), 3:1 (1195 F g⁻¹) and 1:3 (676 F g⁻¹) at 2 A g⁻¹ current density in 1M KOH. The specific capacitances of the BSeYW/NCDH(2:2) hybrid electrode are estimated as 1734, 1604, 1549, 1484 and 1394 F g⁻¹ at 2, 5, 7, 10 and 15 A g⁻¹ respectively. Furthermore, the GCD analysis of different BSeYW/NCDH nanohybrids 4:0, 0:4, 3:1, 2:2 and 1:3 are depicted in Figure 4.34 (a), (b), (c), (d) and (e) at various current densities respectively. It is noted that the small ultrathin sheets are stacked to each other to form network-like morphology of BSeYW/NCDH(2:2). The well-integrated ultrathin sheets of BSeYW/NCDH(2:2) nanohybrid electrode and perfect synergistic effect between multi-metal hydroxides phase and organic moiety make the unique composites. So, the BSeYW/NCDH(2:2) composite shows superior electrochemical performances due to good electrical conductivity, the facile transportation and diffusion of the ions at the electrode/electrolyte interface. In addition, networklike morphology provides the large number of electrochemically active sites and low internal resistance to enhance the specific capacity.^[56]



Figure 4.34. GCD curves at 2, 5, 7, 10 and 15 A g^{-1} current densities under the various Ni-Co ratio nanohybrid electrodes with (a) 4:0 (b) 0:4 (c) 3:1 (d) 2:2 and (e) 1:3.

The EIS was used to elucidate the electrochemical kinetics of the electrodes and explore the electrochemical performance. Figure 4.32c represents the plots of Z' and Z'' parts of the impedance of BSeYW/NCDH hybrid electrodes. All the Nyquist plots reveal semicircle curves on the real axis at the higher frequency region and linear shapes at the lower frequency region. The solution resistance (R_s) is the collective behaviors of the ionic resistance of the electrolyte, the internal resistance of the active materials and the contact resistance between the interface of active materials and the current collector.



Figure 4.35. Electrochemical impedance spectroscopy circuit fit of BSeYW/NCDH nanohybrid materials: (a) 4:0 (b) 0:4 (c) 3:1 (d) 2:2 and (e) 1:3. Furthermore, the cyclic performance of the BSeYW/NCDH(2:2) nanohybrid electrode was estimated by galvanostatic charge-discharge analysis at 25 A g^{-1} (Figure 4.36). The electrode exhibits excellent GCD capacitance retention of 86.18% after 3000 cycles.

The diameter of the partial semicircle on the real axis is generated due to charge transfer resistance (R_{ct}) at the electrode/electrolyte interface. The straight line at the low frequency region corresponds to the Warburg element (W_o), which is generated due to the ion diffusion into the surface of the electrode.^[56,58,70] The comparative EIS analysis and electrochemical circuit fit (Figure 4.35) results exhibit the low R_s (1.54 Ω) and R_{ct} (3.05 Ω) of the 2:2 nanohybrid as compared to 4:0, 0:4, 3:1 and 1:3 BSeYW/NCDH nanohybrids owing to its superior electrochemical performances. The specific capacitance at various current densities of different BSeYW/NCDH (4:0, 0:4, 3:1, 2:2 and 1:3) nanohybrids are depicted in Figure 4.32d. Moreover, Table 4.3 exhibits the summary of the electrochemical performances of the BSeYW/NCDH nanohybrids.



Figure 4.36. Cyclic performance of BSeYW/NCDH(2:2) hybrid electrode at 25 A g⁻¹.

Table 4.3: The summary of the electrochemical performances of theBSeYW/NCDH nanohybrids.

Materials	Current	Specific	Solution	Charge transfer	ECSA
	density	capacitance	resistance	resistance (Rct)	(cm ²)
	(A g ⁻¹)	(F g ⁻¹)	(Ω)	(Ω)	
4:0	2	848	3.42	8.77	3.47
0:4	2	421	4.72	15.7	2.30
3:1	2	1195	2.58	8.63	4.37
2:2	2	1734	1.54	3.05	7.57
1:3	2	676	3.88	16.6	2.75

For the practical application of the nanohybrids, the solid-state symmetric supercapacitor device was assembled using BSeYW/NCDH(2:2) nanohybrid electrodes. 20 mL of ultrapure water mixed with 1 g KOH and 2 g PVA was sonicated to prepare PVA/KOH gel. After that, the solution was stirred at 85 °C in an oil bath until clarification of the solution. Here, the binder free

BSeYW/NCDH(2:2) nanohybrid electrode was used for assembling a symmetric supercapacitor device. The hybrid electrodes were utilized as a positive electrode as well as a negative electrode and a piece of cellulose paper was used as a separator. During the construction of the SSCs, the surfaces of the electrodes were coated with the gel electrolyte. After evaporation of the water at room temperature, two identical electrodes were sandwiched face to face with cellulosic paper. The entire device was placed in a Swagelok cell.^[58] The electrochemical measurements of the fabricated SSCs were evaluated by CV, GCD and cyclic stability test. The following formulas were used to estimate the Cs value, energy density (E) and power density (P) of the SSCs:^[27,71,72]



Figure 4.37. The solid state electrochemical characterization of the BSeYW/NCDH(2:2) nanohybrid electrode device. (a) CV results of the device detected at various scan rates. (b) CV curves of the device performed at different voltage windows. (c) GCD results of the device at different current densities. (d) GCD cyclic performance for 5000 cycles at 7 A g^{-1} . (e) Specific capacitance and current density plot of SSC device. (f) Ragone plot of the SSCs.

$$Cs = \frac{2(I.\Delta t)}{m.\Delta V} (F g^{-1})$$
$$E = \frac{Cs \times \Delta V^2}{8 \times 3.6} (Wh kg^{-1})$$
$$P = \frac{3600 \times E}{\Delta t} (W kg^{-1})$$

Here, I (A) is the discharge current, Δt represents the discharge time (s), m (g) stands for the active material mass on one electrode and ΔV (V) represents the operating potential window after resistance drop.

Figure 4.37a represents the CV curves of the SSC device in the potential window of 0 to 1.6 V from 20 to 200 mV s⁻¹ scan rates. Interestingly, the CV curves exhibit significant distortion with the increase in scan rates due to the charge diffusion polarization within the SSCs. Moreover, CV voltammograms of SSCs at various potential windows 1.0 to 1.6 V at 100 mV s⁻¹ scan rate are depicted in Figure 4.37b. The GCD measurements were performed at 1.5, 2, 3, 4, 5 and 6 A g⁻¹ current densities (Figure 4.37c) and their corresponding specific capacitances were calculated as 226.19, 220.52, 204.31, 194.60, 183.89 and 175.52 F g⁻¹, respectively. In addition, to validate the longer cyclic stability, the GCD cycles of the SSC devices were performed at 7 A g⁻¹ for 5000 cycles. The SSC devices show 85.25% capacitance retention (Figure 4.37d).

The current density and specific capacitance are plotted based on GCD analysis at various current densities (Figure 4.37e). The essential parameters E and P are estimated to evaluate the performance of the SSC devices. The Ragone plot (Figure 4.37f) displays the relationship between E and P for the BSeYW/NCDH(2:2) based SSC devices. The electrochemical performance of BSeYW/NCDH(2:2) nanohybrid is considerably better than previously reported materials (Table 4.4).^[27,68,70-80]

Materials	Specific	Energy density	Power density	Ref.
	Capacitance	$(W h kg^{-1})$	(W kg ⁻¹)	
	$(F g^{-1})$	_		
SLSAC-5	330	18.6	199.2	27
4M-P@NiCo	7 F cm ⁻²	18.1	750	66
LDH//AC				
A-LAC2	317.5	6.7	3486	69
AAWHC	374	11.46		70
Ni/Co-ZIF-67	696	7	100.4	71
Ni/Zn-BDC-MOF	1198	28	748.9	72
Mn/Mo-MOF	1162	31	388.3	73
NiCo-MOF	1315	36.98	801.5	74
CoNi-MOF	1235.9	21.9	348.9	75
HC/N/KOH	492	12	1008	76

Table 4.4: Comparative study of the previously reported materials for supercapacitor applications

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C/KOH-700	348	8.3	1105	77
CGS-700	268	9.0	51.9	78
BSeYW/NCDH(2:2)	1734.32	18.27	571.97	This work

In addition, the SSC device can efficiently light-up a light-emitting diode (LED) for few minutes (Figure 4.38) as well as spinning of a small fan (insets of Figure 4.37d and 4.37e).



Figure 4.38. The photographs show LED lighted by BSeYW/NCDH(2:2) symmetric solid state devices assembled in a series.

4.4 Conclusion

We optimized the successful synthesis of BSeYW/NCDH nanohybrids with various ratios of metal ions *via* in situ one step galvanostatic electrodeposition. The well aligned uniform nanosheet-like networks of BSeYW/NCDH(2:2) were synthesized on conductive CP for utilization in symmetric supercapacitor applications. Moreover, the BSeYW/NCDH(2:2) nanohybrid electrodes attributed the outstanding electrochemical performances. The excellent electrochemical performances were achieved due to the well-defined nanosheet arrays with 3D conductive scaffold of CP substrate as well as binder-free synthesis, which could allow efficient ion diffusion and small intrinsic resistance of the electrode to reduce the energy dissipation. For practical utilization, the assembled SSC device with BSeYW/NCDH(2:2) electrodes delivered excellent energy density, power density and capacitance retention. Moreover, the assembled device can light-up a LED for few minutes as well as the spinning of a small fan. These electrochemical findings demonstrate its promising application for portable energy storage systems.

4.5 References

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MultifunctionalBenzoselenadiazole-cappedOrganicMolecule-basedNanohybridforEfficientAsymmetricSupercapacitorandOxygen Evolution Reaction

Chapter 5

5.1 Introduction

The sustainable energy and a clean environment are important to all aspects of human development at present time. The ever-growing need for energy and the increase in environmental challenges have stimulated to develop the greener, inexpensive and scalable technology for energy storage and conversion applications.^[1-4] The advancement of energy storage and conversion devices have emerged to explore the earth-abundant and efficient materials.^[4-14] SCs are also known as ultracapacitors, which have taken a lot of attention because of their various benefits and potential for future applications in power storage devices. SCs are expected to be broadly used in a variety of applications including portable electronics, biomedical devices, space systems, electric vehicles, power back-up, hybrid electric vehicles and high power applications.^[10,15-17] Moreover, water splitting is a facile way to generate clean, sustainable and eco-friendly energy. Now a days, electrochemical water splitting is taking much attention to produce high purity of O_2 and H_2 . The oxygen evolution reaction (OER) takes place at the anode, while the hydrogen evolution reaction occurs at the cathode during electrochemical water splitting. This process converts the renewable energy into chemical energy. However, OER is a sluggish kinetics reaction due to the 4 electrons transfer reaction and requires more threshold potential (1.23 V) than HER (0.0 V).^[8,17-21] Although, the more efficient, cheap, abundant and robust electrocatalyst requires to accelerate the OER activity and decrease the energy loss in water electrolysis. In general, low abundance Ru and Ir based electrocatalysts exhibit efficient electrocatalysis, but high cost restricts them for commercial use. So, the researchers are taking attention towards the use of 3d transition metal-based compounds.^[6,19,22-26] The materials with enormous abundance, low cost and competitive electrochemical properties with novel transition metals need to develop for the enhancement of electrocatalytic activities and cost effectiveness.^[25,27,28] Therefore, the monometallic and bimetallic oxides, sulphides and hydroxides have been employed as electrocatalysts and energy storage materials.^[22,23,29-35] However, bimetallic systems with organic moiety have attracted lots of interest owing to their facile synergistic effect between bimetallic system with organic moiety, reversible redox reactions, environmental friendliness and relatively low fabrication cost for commercial applications. Organic-inorganic nanohybrids represent a new class of material, which offers exciting opportunities for the development of a new class of electronically, optically and electrochemically active materials.^[31,36-42] Organic-inorganic nanohybrids have been synthesized using a variety of methods including hydrothermal method,^[43,44] solution phase method,^[45] atomic layer deposition^[46] and electrochemical deposition for energy conversion and storage applications.^[47,48] The electrochemical deposition is a viable approach to fabricate ordered morphology, low cost, no need of temperature and binder-free synthesis among various synthetic methods. In addition, nickel foam (NF) is significantly used as current collector due to its high conductivity, flexible behavior and three-dimensional (3D) nature.^[43] The 3D nature of NF would efficiently reduce the ion diffusion paths, which significantly helps in electrodeelectrolyte contacts and easily provides electroactive sites of electrode materials for energy storage and energy conversion.^[14,16,49] Here, a heterocyclic moiety benzoselenadiazole protected organic molecule BSeFY was used to synthesize organic-inorganic nanohybrids due to its various physical and chemical properties. The negatively charged carboxylate groups, amide bond and aromatic side chain play fundamental role in binding with inorganic metal ions through electrostatic and non-covalent interactions. We fabricated the organic-inorganic nanohybrid electrodes with the monometallic and bimetallic system by galvanostatic electrodeposition process (applying -1 mA/cm² current density) to identify the best combination of the metal ions with organic template for the exploration in electrochemical area. The fabricated BSeFY/NCDH electrodes 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 exhibit good electrochemical properties but bimetallic 20:20 nanohybrid demonstrate superior electrochemical performance in both energy storage and conversion application. Therefore, the 20:20 nanohybrid provides favorable synergistic effect between metal ions and organic template enhances Faradaic redox properties due to the plentiful valence transition and offers adequate electrochemically active sites for smooth diffusion of the ions and transports the electrons to attain superior supercapacitive and OER performances.

5.2 Materials and Methods

5.2.1 Materials

The chemicals and materials were obtained commercially and used without further purification. Selenium dioxide and 3,4-diaminobenzoic acid were purchased form Alfa Aeser Pvt. Ltd. and L-phenylalanine (F), L-tyrosine (Y), N,N'-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) were purchased from SRL chemicals, India. All the solvents such as dimethyl sulfoxide (DMSO), hydrochloric acid, hexane, ethyl acetate and N,N'-dimethylformamide (DMF) were purchased from Merck India Ltd. All the solvents were proper dried and distilled from standard procedures prior to use. The pre-coated silica gel thin layer chromatography (Kieselgel 60 F₂₅₄) plates were purchase from SRL chemicals. Nickel foam (NF) was purchased from Global Nanotech, Mumbai, India.

5.2.2 Methods

The purification of peptides and their intermediates were done by Flash Chromatography (TELEDYNE ISCO, USA; model: CombiFlash®Rf+) using silica gel (100-200 mesh) column with ethyl acetate/hexane eluent. NMR spectroscopy was recorded on Bruker AV 400 MHz spectrometer in DMSO- d_6 and CDCl₃ solvents. The positive and negative mode electrospray ionization mass spectrometry was performed on Bruker microTOF-Q II mass spectrometer. FTIR spectroscopy was performed on KBr pellets on a Bruker Tensor 27 FTIR

spectrophotometer. The compositions and oxidation states of the element in the synthesized materials were studied using X-ray photoelectron spectroscopy (XPS) using a Model/Supplier: PHI 5000 Versaprobe-II, FEI Inc. SEM, EDS and elemental mapping were performed by Karl Zeiss JEOL FE-SEM. Transmission electron microscope (TEM) was assessed to further analyse the morphology of the synthesized BSeFY/Co(OH)₂/NF nanohybrid material using a FEI Technai 20 U Twin Transmission Electron Microscope. All the electrochemical measurements such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and cyclic stability performance were conducted by Metrohm Autolab potentiostat (PGSTAT302N) in 1M aqueous KOH solution. The electrolyte solution was prepared freshly before each experiment to sustain consistency.



Scheme 5.1. Synthetic scheme for solution phase preparation of BSeFY dipeptide molecules.

5.2.3 Synthesis of compound 5

5.2.3.1 Synthesis of benzo[2,1,3]selenadiazole-5-carboxylic acid (6): The mixture of 3,4-diaminobenzoic acid (1 g, 6.57 mmol) and selenium dioxide (1.46 g, 13.15 mmol) were refluxed in methanol (20 mL) and 1N HCl (15 mL) for 2 h at 80 °C. The reaction mixture was cooled at room temperature and methanol was evaporated by rotary evaporator. The precipitate of the product was filtered by sintered glass funnel (Borosil G4) and washed with Milli-Q water. The faint pink colored solid precipitate was obtained and dried it in oven at 60 °C to yield 1.385 g (6.1 mmol, 92%) of **6**.^[50] ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.41 (s, 1H, BSe), 7.98-7.89 (dd, 2H, *J* = 9.36, 8.80 Hz, BSe); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 167.32, 161.15, 159.61, 131.64, 128.31, 125.83, 123.60; MS (ESI): *m/z* calcd. for C₇H₄N₂O₂Se: 226.9360 [M-H]⁻; found: 226.9566.

Chapter 5





Figure 5.3. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of **6**.

5.2.3.2. Synthesis of BSeF-OMe (7): A solution of **6** (1 g, 4.40 mmol) and HOBt (711 g, 5.28 mmol) was stirred in 5 mL of dry DMF in a 100 mL round bottom flask. A neutralized solution of phenylalanine methyl ester was extracted from its corresponding hydrochloride salt (1.89 g, 8.76 mmol) and concentrated to add in the reaction mixture followed by coupling agent N,N'-dicyclohexylcarbodiimide (1.08 g, 5.28 mmol) at 0 °C and allowed to stir at room temperature for 12 h. The

progress of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the reaction mixture was diluted with ethyl acetate and washed with 1N HCl (3×30 mL), saturated Na₂CO₃ solution (3×30 mL) and brine solution. Solid light yellowish colored compound of **7** was obtained after evaporating the solvent under reduced pressure. Compound **7** was purified using flash chromatography. Yield = 1.51 g, (3.88 mmol, 88%); ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (s, 1H, BSe), 7.82-7.76 (dd, *J* = 9.44, 9.32 Hz, 2H, BSe), 7.26-7.08 (m, 5H, Ph), 6.71, 6.69 (d, *J* = 7.16, 1H, NH), 5.08-5.04 (m, 1H, C^{\alpha} H of Phe), 3.74 (s, 3H, -OCH₃), 3.26-3.16 (m, 2H, C^{\beta} H of Phe) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 171.88, 165.92, 135.64, 134.95, 129.32, 128.78, 127.79, 127.40, 123.79, 122.09, 53.75, 52.63, 37.86 ppm; MS (ESI): m/z calcd. for C₁₇H₁₅N₃O₃SeNa: 412.0176 [M+Na]⁺; found: 412.0182.



Figure 5.5. ¹H NMR spectrum (400 MHz, CDCl₃) of 7.



Figure 5.6. ¹³C NMR spectrum (100 MHz, CDCl₃) of 7.

5.2.3.3. Synthesis of BSeF-OH (8): The compound of 7 (0.7 g, 1.80 mmol) was taken in round bottom flask with 40 mL distilled methanol and allowed to react with a solution of 4 mL (1N) NaOH solution. The reaction mixture was stirred for 4-5 h. The hydrolysis progress was monitored by thin layer chromatography. After the completion of the reaction, excess methanol was evaporated to dryness with rotary evaporator and diluted with 40 mL milli-Q water. Then, the water mixture was taken in a separating funnel and slowly washed with diethyl ether (2×20 mL). The aqueous layer was collected and cooled in an ice bath. Then, the cooled aqueous solution was acidified with 1N HCl and adjusted to pH 2. The product was extracted with ethyl acetate (3×30 mL). The ethyl acetate layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to obtain a solid compound 8. Yield = 0.602 g (1.6 mmol, 89%); ¹H NMR (400 MHz, DMSO- d_6): $\delta = 12.87$ (s, 1H, -COOH), 9.10, 9.08 (d, J = 8.08, 1H, -NH), 8.35 (s, 1H, BSe), 7.94-7.87 (dd, J = 9.48, 9.28, 2H, BSe), 7.39-7.20 (m, 5H, Ph), 4.75-4.69 (m, 1H, C^{α} H of Phe), 3.17-3.11 (m, 2H, C^{β} H of Phe) ppm. ¹³C NMR (100 MHz, DMSO- d_6): $\delta = 173.48$, 166.16, 160.75, 159.64, 138.57, 134.49, 129.56, 128.72, 128.16, 126.91, 123.52, 122.82, 54.89, 36.77 ppm; MS (ESI): m/z calcd. for C₁₆H₁₃N₃O₃Se: 374.0044 [M-H]⁻; found: 374.0368.



Figure 5.7. ESI-MS spectrum of 8.



Figure 5.9. ¹³C NMR spectrum (100 MHz, DMSO- d_6) of 8.

5.2.3.4. Synthesis of compound BSeFY-OMe (17): A solution of compound 8 (0.2 g, 0.534 mmol) and HOBt (0.866 g, 0.64 mmol) was stirred in DMF (2 mL). A neutralized solution of H₂N-Tyr-OMe was extracted from its corresponding hydrochloride salt (0.248 g, 1.07 mmol). It was concentrated for addition to the reaction mixture followed by coupling agent *N*,*N*'-dicyclohexylcarbodiimide (0.132 g, 0.64 mmol) at 0 °C. The reaction mixture was allowed to stir at room temperature for 12 h. After the reaction, the reaction mixture was diluted with ethyl acetate and the organic layer was washed with 1N HCl (3×30 mL), saturated Na₂CO₃ (3×30 mL) and brine solution. The organic layer was dried over Na₂SO₄ and evaporated under vacuum by rotary evaporator to yield solid compound **17**. The purification of compound **17** was performed by flash chromatography on silica gel (100-200 mesh) with ethyl acetate and hexane as eluent. Yield = 0.229 g (0.415 mmol, 77%): ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.32 (s, 1H, -OH of Tyr), 8.97, 8.95 (d, *J* = 8.44 Hz, 1H, -NH), 8.59, 8.57 (d, *J* = 7.32 Hz, 1H, -NH), 8.36 (s, 1H, BSe), 7.94-7.86 (dd, *J* = 9.32, 9.28 Hz, 2H,

BSe), 7.44-7.22 (m, 5H, aromatic Hs of Phe), 7.10,7.08 (d, J = 8.08 Hz, 2H, Hs of Tyr), 6.72, 6.69 (d, J = 8.08 Hz, 2H, Hs of Tyr), 4.90-4.49 (m, 1H, C^αH of Phe and Tyr) 3.66 (s, 3H, OCH₃), 3.18-2.96 (m, 4H, C^βH of Phe and Tyr) ppm; ¹³C NMR (100 MHz, DMSO- d_6): $\delta = 172.44$, 171.92, 166.09, 160.75, 159.66, 156.53, 138.68, 134.66, 130.56, 129.68, 128.59, 128.31, 127.51, 126.81, 123.40, 122.85, 115.60, 55.18, 54.64, 52.35, 37.47, 36.38 ppm; MS (ESI); *m*/*z* calcd. for C₂₆H₂₄N₄O₄SeNa: 575.0810 [M+Na]⁺; found: 575.0814.



Figure 5.11. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **17**.



Figure 5.12. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of **17**.

5.2.3.5. Synthesis of compound BSeFY-OH (5): Compound 17 (0.17 g, 0.308 mmol) was dissolved in 30 mL distilled methanol. After that, the solution was allowed to react with 1N solution of NaOH (3 mL). The progress of the reaction was monitored by TLC. The reaction mixture was stirred for 5 h. Then, the methanol was removed by rotary evaporator. The residue was diluted with 50 mL milli-Q water. The aqueous layer was taken in a separating funnel and slowly washed with diethyl ether (2×20 mL). The pH of the cooled aqueous layer was adjusted to 2 by using 1N HCl and extracted with ethyl acetate (3×30 mL). The ethyl acetate layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure with rotary evaporator to yield a light yellowish solid compound 5. Yield = 0.137 g (0.254 mmol, 82%). ¹H NMR (400 MHz, DMSO d_{6}) $\delta = 12.77$ (s, 1H, -COOH), 9.16 (s, 1H, -OH of Tyr), 8.84, 8.82 (d, J = 8.64Hz, 1H, -NH), 8.47, 8.45 (d, J = 8.36 Hz, 1H, -NH), 8.30 (s, 1H, BSe), 7.88-7.80 (dd, J = 9.40, 9.36 Hz, 2H, BSe), 7.38-7.14 (m, 5H, aromatic Hs of Phe), 7.05,7.03 (d, J = 8.24 Hz, 2H, Hs of Tyr), 6.62, 6.60 (d, J = 8.16 Hz, 2H, Hs of Tyr), 4.83-4.39 (m, 1H, C^{α}H of Phe and Tyr), 3.02-2.76 (m, 4H, C^{β}H of Phe and Tyr) ppm; ¹³C NMR (125 MHz, DMSO- d_6): $\delta = 173.32$, 171.66, 165.99, 160.72, 159.64, 156.43, 138.78, 134.66, 130.57, 129.64, 128.52, 128.28, 127.86, 126.71, 123.34, 122.80, 115.48, 55.23, 54.40, 37.42, 36.38 ppm; MS (ESI); m/z calcd. for C₂₅H₂₂N₄O₄Se: 537.0677 [M-H]⁻; found: 537.0708.



Figure 5.13. ESI-MS spectrum of 5.



Figure 5.14. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **5**.



Figure 5.15. ¹³C NMR spectrum (125 MHz, DMSO-*d*₆) of 5.

5.3 Results and Discussion

A heterocyclic aromatic benzoselenadiazole-capped⁵⁰ organic molecule BSeFY and metal salts in water/dimethyl sulphoxide (DMSO) (1:1) V/V were used as precursors for electrochemical galvanostatic electrodeposition. We used different concentrations of Ni(NO₃)₂.6H₂O and Co(NO₃)₂.6H₂O metal salts in mmol/L ratios of 0:40, 40:0, 20:20, 10:30 and 30:10 with a constant concentration of organic material (2 mM) for the synthesis of organic-inorganic nanohybrids and termed as 0:40, 40:0, 20:20, 10:30 and 30:10 respectively. We also fabricated the NCDH-20:20 electrode without organic material using the same parameters and conditions for comparative studies. The electrodeposition (ED) was performed with three electrodes assemblies NF, platinum wire and Ag/AgCl (working electrode), platinum wire (counter electrode) and Ag/AgCl (reference electrode). Prior to its use as a growth process, the NF (1cm × 1cm) was cleaned with HCl (1N), ultrapure water and ethanol consequently with ultrasonication to avoid surface impurities. The galvanostatic electrodeposition was performed to synthesize the organic-inorganic nanohybrids on NF substrate by applying a constant -1 mA/cm² current density for 600 seconds at room temperature. The formation of hybrid material can be seen in the black layer formed over the flexible NF substrate. We used NF as the substrate for the growth of nanohybrids due to its high conductivity, 3D nature, large surface area and good mechanical properties. After applying the current, the pH of the precursor electrolyte was enhanced near the working electrode due to the reduction of the NO₃⁻ ions to NO₂⁻ and simultaneously the formation of the hydroxyl ions. The acid groups of the small organic molecules deprotonate due to the enhancement of the precursor pH and form carboxylate anions. As a result, the deprotonated small organic molecules interact with metal ions to form BSeFY/NCDH organic-inorganic nanohybrids. Moreover, non-covalent interactions such as π - π stacking and hydrogen bonding facilitate the intermolecular interaction during the fabrication of the nanohybrids.^[31,51,52] The chemical reactions occurred during the electrodeposition process are discussed in Scheme 5.2.

Scheme 5.2: Schematic depiction for the formation of organic-inorganic nanohybrids



The changes in vibrations of functional groups of BSeFY/NCDH nanohybrids were analyzed by FTIR analysis (Figure 5.16). The stretching peak of -O-H functional groups appeared 3300-3500 cm⁻¹. Furthermore, the peak at 1719 cm⁻¹ is assigned in the BSeFY spectrum due to the stretching mode of C=O in the carboxylic acid group. However, this peak is disappeared in all nanohybrid spectra due to the metal-carboxylate ions interactions. Moreover, the prominent bands at 1636 and 1567 cm⁻¹ are attributed to amide C=O stretching and –N-H bending of the amide functional group present in nanohybrids, respectively. The nanohybrids exhibit the vibrational mode of M-OH (M=Ni and Co) in between 600-700 cm^{-1.[53-58]}



Figure 5.16. FTIR spectra of 0:40, 40:0, and 20:20 nanohybrids.

The X-ray photoelectron spectroscopy (XPS) is a quantitative procedure to detect the oxidation states and chemical composition of the nanohybrids. The composition of the BSeFY/NCDH(20:20) nanohybrid was detected by the XPS survey (Figure 5.17a) and Ni, Co, O, N, C and Se elements present in the XPS spectra.



Figure 5.17. (a) XPS survey spectrum for BSeFY/NCDH (20:20) nanohybrid. The high resolution XPS spectra of 20:20 nanohybrid in the (b) Ni 2p, (c) Co 2p and (d) C 1s areas.

Furthermore, the core level spectrum of Ni 2p (Figure 5.17b) shows two intense peaks at 872.8 (Ni $2p_{1/2}$) and 855.3 (Ni $2p_{3/2}$) eV due to the spin-orbital energy change (17.5 eV) and corresponding satellite peaks at 878.7 and 860.8 eV,

respectively.^[53,57,59,60] Similarly, the core level spectrum of Co 2p (Figure 5.18c) exhibits two peaks at 796.3 and 780.8 eV and two low intensity satellite peaks at 801.6 and 784.8 eV for Co $2p_{1/2}$ and Co $2p_{3/2}$, respectively. The difference in spin energy between Co $2p_{1/2}$ and Co $2p_{3/2}$ is observed as 15.5 eV. The satellite peaks are associated to the existence of divalent species in nanohybrids.^[57,59-61]



Figure 5.18. Core level XPS spectra of (a) O 1s, (b) Se 3d and (c) N 1S.

Moreover, Figure 5.17d corresponds to the C 1s high resolution spectrum, which is associated with 284.4, 285.5 and 287.6 eV binding energy due to the presence of C=C, C-C/C-N and O-C=O bonding interactions, respectively.^[43,59,60,62,63] The core-level spectrum of O 1s is displayed in Figure 5.18a. The two fitted peaks are assigned at 530.9 and 532.5 eV for the -O-H and O-C=O groups respectively.^[43,62] The peak at 55.8 eV binding energy in Se 3d enlarged spectrum (Figure 5.18b) appears for the N-Se-N bonding interaction. Furthermore, the N 1s core level spectrum (Figure 5.18c) is attributed to the fitted peaks at 399.1 and 400.2 eV for C=N and C-N groups, respectively.^[55,64,65]

Figure 5.19 represents the XRD diffraction patterns of the synthesized BSeFY/NCDH nanohybrids. No additional peak is observed except the peaks of nickel foam in X-ray diffraction patterns due to the amorphous nature of the synthesized nanohybrids.^[66,67]

	— After OER 20:20	(v)	
Intensity (a.u.	20:20	(iv)	
	<u> </u>	(iii)	
	0:40	(ii)	
	—— NF	(i)	
	20 40 20 (I	⁶⁰ Degree)	80

Figure 5.19. XRD patterns of (i) bare NF and nanohybrids of (ii) 0:40, (iii) 40:0, (iv) 20:20 and (v) after OER 20:20.

Figure 5.20 demonstrates the high-magnification SEM images of as-synthesized NCDH-20:20 (a), 0:40 (b), 40:0 (c), 30:10 (d), 10:30 (e) and 20:20 (f) materials, which disclose the comprehensive morphological information. The uniform network-like morphology is gained from NCDH-20:20, 0:40, 40:0, 30:10, 10:30 and 20:20 materials, which exhibit the crosslinked thick sheets and interconnected granular sheet architecture. Moreover, the architecture of the 20:20 sample looks like small petal-like sheets staked to each other and exhibits network-like morphology. The thin network like architecture of 20:20 provides more open spaces and electrochemically active sites, which enhance the rate of redox reaction, increase the rapid transport of ions and electrons, reduce the transport pathway leading to improved storage capacity and electrocatalytic performances. The TEM measurement (Figure 5.20g) was performed to further characterize the morphology of the 20:20 nanohybrid. The TEM image further reveals the presence of petal-like sheets, which are stacked to each other. The formation of the interconnected network-like architecture of 20:20 nanohybrid is more suitable for electrochemical measurement due to the exposure of the more electrochemically active spaces. The selected area electron diffraction (SAED) pattern (inset of Figure 5.20g) exhibits a halo diffused ring due to the amorphous nature of the nanohybrid material. Moreover, the HR-TEM image (Figure 5.20h) reveals that the synthesized nanohybrid material is amorphous in nature due to the absence of distinctive lattice fringes.^[66]



Figure 5.20. The magnified SEM images of (a) NCDH-20:20, (b) 0:40, (c) 40:0, (d) 30:10, (e) 10:30 and (f) 20:20 materials. TEM (g) and HR-TEM (h) image of synthesized 20:20 nanohybrid.

Furthermore, EDS was performed to detect the elemental composition of the nanohybrids. Figure 5.21 exhibits the peaks due to the presence of Ni, Co, O, N, C and Se elements in the nanohybrids.



Figure 5.21. EDS study of (a) 0:40, (b) 40:0, (c) 20:20, (d) 10:30 and (e) 30:10 nanohybrids.

Furthermore, elemental mapping was studied to identify the distribution of the elements present in nanohybrids. The Figures 5.22, 5.23, 5.24, 5.25 and 5.26 disclose the uniform distribution of elements present in 0:40, 40:0, 20:20, 10:30 and 30:10 nanohybrids, respectively.



Figure 5.22. Elemental mapping study of 0:40 nanohybrid.

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Figure 5.23. Elemental mapping study of 40:0 nanohybrid.



Figure 5.24. Elemental mapping study of 20:20 nanohybrid.



Figure 5.25. Elemental mapping study of 10:30 nanohybrid.



Figure 5.26. Elemental mapping study of 30:10 nanohybrid.

5.3.1 Electrochemical Measurements

The electrochemical measurements of the BSeFY/NCDH were investigated in 1M KOH electrolyte with three electrode setup. The electrodeposited material on NF, Ag/AgCl and platinum wire were used as working electrode, reference electrode and counter electrode, respectively. An electrochemical workstation Metrohm Autolab potentiostat (PGSTAT302N) was utilized to perform all electrochemical measurements.

The following formula was used to estimate the specific capacitance (Cs).^[61]

$$Cs = \frac{I \times \Delta t}{m \times \Delta V}$$
(S1)

Here ΔV denotes the potential window, I (A) represents constant current, Δt (s) exhibits the discharge time of GCD and m (mg) represents the active mass.

The 20:20 and AC electrodes were used as the positive and negative electrodes to assemble the asymmetric supercapacitor device. The following equation was used to get the optimal mass ratio between the positive electrode and the negative electrode:^[68]

$$\frac{m_+}{m_-} = \frac{C_- \Delta V_-}{C_+ \Delta V_+} \tag{S2}$$

Where, m_+ and m_- are the mass of positive and negative electrode materials, respectively, C_+ and C_- are the specific capacitance of the positive and negative electrodes, respectively and ΔV_+ and ΔV_- are the potential window of the positive and negative electrodes respectively.

The energy and power density of the asymmetric supercapacitor (ASC) device can be estimated using following equations:^[33,69,70]

$$E = \frac{Cs \times \Delta V^2}{2 \times 3.6} (Wh/kg)$$
(S3)
$$P = \frac{3600 \times E}{\Delta t} (W/kg)$$
(S4)

Where E represents the energy density (Wh/kg), Cs denotes for the specific capacitance of the device (F/g), ΔV represents the operating potential window (V), P denotes the power density (W/kg) and Δt represents discharge time (s).

The electrocatalytic oxygen evolution reaction was carried out in 1M KOH electrolyte at room temperature. All the potential were calibrated to the RHE scale based on the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + (0.0591 \times pH) V$.

All Nyquist plots were obtained with the frequency range of 100000 to 0.1 Hz at 0.41 V.

The following equation can be used to determine the turn over frequency (TOF) of catalysts:^[62,71]

$$FOF = \frac{JA}{4Fm}$$
(S5)

Where J is the current density (A cm⁻²) at an obtained overpotential, A refers to geometric area of the electrode (cm²), 4 possesses the 4 electrons involved in the oxidation and reduction reactions of O_2 , F is the Faraday constant (96,485 C mol⁻¹) and m stands for number of moles of the active sites (mol).

$$Slope = \frac{n^2 F^2 A \Gamma_0}{4 R T}$$
(S6)

The CV curves of the catalysts at various scan rates were used to estimate slopes (peak current vs scan rate plot). The obtained slope is used to determine the m (which is equivalent to A Γ_0). A is the geometric surface area (cm²), Γ_0 is the surface concentration of active sites (mol cm⁻²), R is the ideal gas constant (J mol⁻¹ K⁻¹), and T is the absolute temperature (K).

Furthermore, exchange current density (J_0) is another important factor for assessing catalytic efficiency, which can be calculated as follows.:^[72]

$$J_0 = \frac{RT}{\mathrm{nF}R_{ct}} \tag{S7}$$

where, R stands for gas mole constant (8.314 J mol⁻¹K⁻¹), T represents the temperature (298 K), n stands for the electron transfer number, F is Faraday's constant (96485 C mol⁻¹) and Rct represents the charge transfer resistance.

The cyclic voltammetry (CV) was investigated in the potential window of 0.0-0.55 V to reveal the redox properties of the BSeFY/NCDH electrodes. The Figure 5.27a shows the comparative study of the CV at 50 mV/s of the 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 electrodes. CV curves clearly indicate that the BSeFY/NCDH(20:20) hybrid electrode exhibits a higher hysteresis area than other electrodes suggesting the unique structural design and greater electrochemical activity. Moreover, Figure 5.28 exhibits the CV studies of 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 hybrid electrodes at 10, 15, 20, 30, 40 and 50 mV/s scan rates. The BSeFY/NCDH hybrids assign a pair redox peak, which originates mainly from the Faradaic reactions due to the generation of the metal oxyhydroxide in the alkaline electrolyte during electrochemical measurements. The following reactions explain the formation of metal oxy species with OH⁻ ions and the generation of redox peaks:^[60]

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$$
$$Co(OH)_2 + OH^- \leftrightarrow CoOOH + H_2O + e^-$$

Figure 5.27b (comparative study at 2 A/g) and Figure 5.29 (at various current densities) exhibit the galvanostatic charge-discharge (GCD) analysis to measure the Cs (Equation S1) of the 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 electrodes. It is observed from GCD analysis (Figure 5.27b) that the specific capacitance of the 20:20 nanohybrid (1338.46 F/g) is higher than the 0:40

(661.36 F/g), 40:0 (845.17 F/g), 10:30 (817.30 F/g), 30:10 (1145.83 F/g) and NCDH-20:20 (808.33 F/g) electrode materials at the current density of 2 A/g. The highest specific capacitance of the 20:20 hybrid electrode reveals that the ordered nanoarchitecture of hybrid and synergistic effect between bimetallic ions make it more facile to enhance the specific capacitance as well as favorable intercalation/deintercalation of the ions. The GCD performance of nanohybrids (Figure 5.29) at different current densities exhibits the decrease in the charging-discharging time due to the diffusion of the electrolyte ions on the outer surface of the electrode materials instead of overall active materials.



Figure 5.27. Comparative electrochemical analysis of 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 electrodes in 1M KOH electrolyte. (a) CV curves measured at 50 mV/s in the 0.0-0.55 V voltage window. (b) GCD performed at 2 A/g current density for all the hybrid electrodes. (c) Nyquist plots of nanohybrids in the frequency range of 0.1 to 10^5 Hz. (d) Cyclic stability analysis of 20:20 for 2500 cycles at 20 A/g current density.

The electrochemical impedance spectroscopy (EIS) was carried out between 100000 to 0.1 Hz frequency to examine the electrical conductivity, internal resistance and diffusion resistance. Figure 5.27c exhibits the Nyquist plots for 0:40, 40:0, 20:20, 10:30, 30:10 BSeFY/NCDH nanohybrid electrodes and NCDH-20:20 electrode and the plots exhibit semicircle in high frequency region. The semicircle radius of 20:20 is smaller than the 0:40, 40:0, 10:30, 30:10 and NCDH-20:20 electrode materials revealing the lower charge transfer resistance (Rct), which indicates the higher electrical conductivity of the nanohybrid electrodes. The Rct values of the 0:40, 40:0, 20:20, 10:30, 30:10 nanohybrid electrodes and NCDH-20:20 electrode were estimated from the circuit fit of EIS (Figure 5.30) and corresponding values are 4.64 Ω , 589 m Ω , 384 m Ω , 4 Ω , 446 m Ω and 3.84 Ω electrode respectively. The straight line in low frequency region

indicates Warburg impedance, which denotes the ionic diffusion resistance.^[61] Furthermore, the long-term stability of 20:20 nanohybrid was investigated with GCD at 20 A/g current density and the 20:20 nanohybrid retains 80.74% capacitance after 2500 cycles (Figure 5.27d). It is clearly observed from the electrochemical results that the facile synergistic effect between bimetallic ions as well as organic moiety makes BSeFY/NCDH (20:20) nanohybrid as a most promising material to enhance the redox activity, promotes better binding of hydroxide ions in electrolyte towards active sites and reduce Rct. The electrochemical results suggest that BSeFY/NCDH (20:20) exhibits excellent electrochemical properties due to the nanoarchitecture of the 20:20 hybrid, which allows smooth electrolyte penetration as well as ion transport and reduces the electrons and ions diffusion pathway. Moreover, the nanohybrid offers high conductivity, faster kinetics and provides higher electrochemically active sites.



Figure 5.28. CV measurements of BSeFY/NCDH (a) 0:40, (b) 40:0, (c) 20:20, (d) 10:30, (e) 30:10 and (f) NCDH-20:20 electrodes at scan rates of 10, 15, 20, 30, 40 and 50 mV/s.



Figure 5.29. GCD analysis of (a) 0:40, (b) 40:0, (c) 20:20, (d) 10:30, (e) 30:10 and (f) NCDH-20:20 electrodes at current densities of 2, 5, 8, 10, 12 and 15 F/g.



Figure 5.30. EIS circuit fit of (a) 0:40, (b) 40:0, (c) 20:20, (d) 10:30, (e) 30:10 and (f) NCDH-20:20 electrodes.

Table 5.1 exhibit the all electrochemical results of the synthesized materials.

Materials	Cs at	Cs at	Rs	Rct				
	2 A/g	5 A/g	8 A/g	10 A/g	12 A/g	15 A/g	(Ω)	(Ω)
0:40	661.36	652.48	643.11	640.33	632.47	636.16	1.96	4.64
40:0	845.17	825.93	813.11	769.45	754.73	730.98	1.50	589
20:20	1338.46	1319.45	1181.44	1104.83	1024.21	902.7	1.34	384
10:30	817.30	780.35	688.59	657.59	616.21	600.41	1.66	4.00
30:10	1145.83	1135.42	1116.67	1083.33	1075	1000	1.33	446
NCDH-	808.33	791.66	783.33	770.83	725	656.25	1.80	3.84
20:20								

Table 5.1. Electrochemical performance of synthesized materials with three

 electrode system in 1M KOH electrolyte

5.3.2 Electrochemical measurements of the activated carbon electrode (AC):

The activated carbon, carbon black and polymer binder were used to make the negative electrode on NF. The slurry was prepared using activated carbon, carbon black and polyvinylidene fluoride (PVDF) in the ratio of 80:15:5 and mixed well with a few drops of N-methyl-2-pyrrolidine solvent to get a homogeneous slurry using a pestle and mortar.^[73] The slurry was applied on the NF uniformly and kept for dry at 80 °C for 4 h. After that, the slurry pasted NF was pressed with compressing machine to get AC/NF negative electrode. The electrochemical measurements of the prepared AC/NF electrode were conducted in 1M KOH electrolyte using three electrode assemblies. The obtained quasirectangular CV curves at various scan rates (Figure 5.31a) without any redox peaks suggest the electric double-layer capacitance nature of the electrode materials. There is no obvious distortion appeared when the scan rates are increased from 20 to 100 mV/s in the potential window of -1 to 0.0 V, indicating that the electrode has good ion diffusion. Figure 5.31b depicts the GCD curves for various current densities ranging from 1 to 10 A/g. GCD reversibility is indicated by the symmetric triangular profile. Figure 5.31c represents the CV measurement of the activated carbon (AC) electrode and 20:20 hybrid electrode at 50 mV/s.

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Figure 5.31. Electrochemical measurements of AC electrode: (a) CV curves at various scan rates and (b) GCD measurement at different current densities (c) CV of (i) AC electrode and (ii) 20:20 nanohybrid electrode at 50 mV/s in combined graph.

The CV of the AC electrode was investigated in the potential window of 0.0 to -1.0 V, which shows non-faradaic CV. Moreover, CV analysis of the 20:20 nanohybrid electrode exhibits the Faradaic redox CV in the voltage window of 0.0-0.55 V. The CV results suggest that the high voltage window of the SC device can be achieved by combining the positive and negative electrode materials potential window. All of these findings indicate that the AC electrode exhibits good electrochemical properties, making it a good candidate for use in supercapacitor devices. The charge stored and mass loading ratio on positive (20:20) and negative (AC) electrodes of the asymmetric device was balanced by equation S2.^[68,73]

For the practical application, the asymmetric supercapacitor (ASC) device was assembled with the BSeFY/NCDH(20:20), AC, PVA/KOH and cellulosic paper which acts as a positive electrode, negative electrode, gel electrolyte and separator, respectively. The electrodes were soaked in the electrolyte for 1 h prior to assembly for the device. The separator (cellulosic paper) was used to restrict any short-circuit. The ASC device (BSeFY/NCDH(20:20)//AC) was electrochemically characterized and the results are displayed in Figure 5.32. Figure 5.32a exhibits the CV analysis in the potential window of 0.0-1.6 V at various scan rates. The CV analysis reveals that the current response increases with the increase in scan rates and vice-versa. Furthermore, Figure 5.32b displays the CV profiles at various potential windows at the constant scan rate 200 mV/s.

The specific capacitances of the device at various current densities were estimated from GCD performance (Figure 5.32c). Thus, the ASC device shows the specific capacitance of 106.25, 101.25, 90.62, 83.12 and 75.10 F/g at the current densities of 1, 2, 5, 7 and 10 A/g. The GCD measurement (Figure 5.32d) represents that the specific capacitance decreases as the potential window shrink. The ASCs device's Ragone plot is depicted in Figure 5.32e with the comparative study of previously reported literatures. The energy density (E) and power density (P) are well known benchmark criteria for assessing the efficiency of the device and calculated from the equations S3 and S4 respectively.



Figure 5.32. The electrochemical characterization of the BSeFY/NCDH(20:20)//AC asymmetric device. (a) CV results of the device detected at various scan rates. (b) CV curves of the device performed at various potential windows. (c) GCD results of the ASC device at various current densities. (d) GCD performances at various voltage windows. (e) Ragone plot of the ASCs. (f) Long-term stability test for 5000 GCD cycles at 7 A/g current density and inset of Figure represents the lightening of red LED and spinning of a small fan.

The ASC device achieves maximum energy density of 35.48 W h/kg at 751.36 W/kg power density. Moreover, the ASC device could remain 17.91 W h/kg energy density at 5373.79 W/kg power density. In addition, Figure 5.32e also demonstrates that the fabricated device exhibits good energy density and power density as compared with previously published asymmetric supercapacitors.^[74-81] The long-term performance of the ASC device was investigated by repeating the 5000 GCD cycles within the potential window of 0.0 to 1.6 V at a current density of 7 A/g. The assembled ASC device retained 91.24% capacitance of its initial capacitance. Furthermore, the inset of Figure 5.32f shows that the ASC device is capable of efficiently lighting a red LED (2V) and running a small fan. Moreover, Figure 5.33 shows that the ASC device can light-up a red LED for few minutes. Therefore, the obtained promising consequences indicate (Table 5.2) that the BSeFY/NCDH(20:20)//AC based ASC device have great potentials for energy storage applications.

Current density	Specific capacitance	Energy density	Power density
(A / g)	(F / g)	(Wh kg ⁻¹)	(W kg ⁻¹)
1	106.25	35.48	751.36
2	101.25	32.53	1445.89
5	90.62	26.07	3236.4
7	83.12	22.02	4173.27
10	75.10	17.91	5373.79

 Table 5.2. Electrochemical results of the fabricated BSeFY/NCDH(20:20)//AC device



Figure 5.33. The pictures show LED lighted by BSeFY/NCDH(20:20)//AC two asymmetric devices connected in a series.

5.3.3 Electrochemical surface area (ECSA) measurements: The CV (Figure 5.34) was carried out in the non-Faradaic potential region to obtain double-layer capacitance (C_{dl}) value by the fitted linear relationship of the graph between current vs scan rates.



Figure 5.34. CV measurements at 10, 15, 20, 25, 30, 35 and 40 mV/s scan rate of (a) 0:40, (b) 40:0, (c) 20:20, (d) 10:30, (e) 30:10 and (d) NCDH-20:20 electrodes.



Figure 5.35. C_{dl} curves of (a) 0:40, (b) 40:0, (c) 20:20 (d) 10:30, (e) 30:10 and (f) NCDH-20:20 electrode materials.

The value of C_{dl} (Figure 5.35) was utilized to estimate the electrochemical surface area (ECSA) of the nanohybrids by using ECSA = C_{dl}/Cs formula. Cs is the areal capacitance of nickel foam and the value is 1.7 mF/cm².^[71] C_{dl} represents the double layer capacitance and it is estimated from the fitted straight line slope. The C_{dl} of the 20:20 (0.286 mF/cm²) is obtained higher than the 0:40 (0.074 mF/cm²), 40:0 (0.178 mF/cm²), 10:30 (0.148 mF/cm²), 30:10 (0.268 mF/cm²) and NCDH-20:20 (0.123 mF/cm²). Therefore, the 20:20 hybrid is attributed more ECSA (0.168 cm²) as compared to 0:40 (0.043 cm²), 40:0 (0.0104 cm²), 10:30 (0.087 cm²), 30:10 (0.157 cm²) and NCDH-20:20 (0.072 cm²). The larger electrochemical active surface area of 20:20 can afford more accessible electrochemically active sites, smooth intercalation/deintercalation of ions and rapid transport of electrons to enhance the OER activity. Additionally, The TOF was estimated (equation S5) to know the improved catalytic activity of the catalysts. The slope was calculated using the CV curves (Figure 5.36) of the catalysts at varied scan rates (peak current vs scan rate plot). In order to calculate

the m (which is comparable to A Γ_0), the obtained slope is used (equation S6). Therefore, the 20:20 nanohybrid possesses the highest TOF 0.091 s⁻¹ at an overpotential of 212 mV. These findings (Table 5.3) show that superior OER performance of the 20:20 nanohybrid catalyst can be attributed to its high ECSA and TOF and the facile synergistic interactions between its metal active sites.



Figure 5.36. CV curves of (a) 0:40, (b) 40:0, (c) 20:20 (d) 10:30, (e) 30:10 and (f) NCDH-20:20 electrode materials in 1 M KOH. Insets of Figure (a) 0:40, (b) 40:0, (c) 20:20 (d) 10:30, (e) 30:10 and (f) NCDH-20:20 show the linear relationship of the oxidation peak current vs. scan rates.

5.3.4 Exchange current density (J_{θ}) :

Furthermore, exchange current density (J_0) is another important factor for assessing catalytic efficiency and calculated by equation S7 using Rct values.^[72] The J_0 of 20:20 (3.84 mA/cm²) is higher than those of 40:0 (1.24 mA/cm²), 0:40 (0.57 mA/cm²), 10:30 (1.04 mA/cm²), 30:10 (1.6 mA/cm²) and NCDH-20:20 (0.98 mA/cm²). A direct relationship exists between the catalytic active area and the exchange current density. The greater J_0 of 20:20 indicates the greater the specific active sites of the materials, which is more favourable to increasing catalytic efficiency. As a result, the prepared 20:20 exhibits significant OER catalytic efficiency due to its higher value of exchange current density.

Materials	Overpotential	Tafel	Rct	TOF	J_{0}	C _{dl}	ECSA
	$(J = 10 \text{ mA/cm}^2)$	slope	(Ω)	(s ⁻¹)	(mA/cm ²)	(mF/cm ²)	(cm ²)
		mV/dec					
0:40	212	118	11.1	0.068	0.578	0.074	0.043
40:0	151	96	5.16	0.082	1.244	0.178	0.104
20:20	141	87	1.67	0.091	3.844	0.286	0.168
10:30	170	108	6.16	0.077	1.042	0.148	0.087
30:10	146	91	3.98	0.085	1.612	0.268	0.157
NCDH-	187	112	6.52	0.074	0.984	0.123	0.072
20:20							

Table 5.3. Electrocatalytic performance of all synthesized materials

5.3.5 Electrochemical oxygen evolution performance: OER The electrocatalytic activity of BSeFY/NCDH was examined in 1M KOH using three-electrode setup. The reversible hydrogen electrode scale was used to calibrate all potentials for linear sweep voltammetry (LSV) curves. For comparison, 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 were tested under same conditions. The 20:20 nanohybrid is highly active material for OER having low overpotential of 141 mV at the current density 10 mA/cm² than 0:40 (212 mV) and 40:0 (151 mV), 10:30 (170 mV), 30:10 (146 mV) and NCDH-20:20 (187 mV) without iR compensation. The Tafel plots (Figure 5.37b) were obtained from LSV curves using the Tafel equation: $\eta = a + b \log j$, where j represents current density, b denotes for Tafel slope, and a exhibits the intercept relative to the exchange current density.



Figure 5.37. (a) LSV measurement of 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 materials at 2 mV/s scan rate in 1M KOH electrolyte for OER without iR compensation. (b) Tafel plots of corresponding 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 electrodes. (c) Nyquist plots and Bode plots

(insets) of 0:40, 40:0, 20:20,10:30, 30:10 and NCDH-20:20 electrode materials at 0.41 V in between 10^{-1} to 10^{5} Hz. (d) Chronopotentiometry stability test at 10 mA/cm² current density. (e) Multistep chronopotentiometry in between 5-50 mA/cm² current density. (f) LSV curves of 20:20 nanohybrid before and after electrocatalytic performance.

The obtained Tafel values of 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 are 118, 96, 87, 103, 91 and 112 mV/dec, respectively. The lower Tafel slope value of the 20:20 hybrid suggests that the rapid catalytic kinetics towards the OER activity than 0:40, 40:0, 10:30, 30:10 and NCDH-20:20 electrocatalysts. The EIS measurement was used to elucidate the internal resistance of the materials. Figure 5.37c exhibits the EIS Nyquist plots and Bode plots (insets of Figure 5.37c) of 0:40, 40:0, 20:20, 10:30, 30:10and NCDH-20:20 electrode materials in the range of 0.1Hz to 100 MHz at 0.41V. The Nyquist plot of 20:20 nanohybrid shows a lower semicircle radius than the 0:40, 40:0, 10:30, 30:10 and NCDH-20:20 electrodes, which suggests the facile intercalation/deintercalation of ions, high conductivity and more efficient for electrocatalytic performances. The values of charge transfer resistance (Rct) for 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 electrodes are 11.10 Ω , 5.16 Ω , 1.67 Ω , 6.16 Ω , 3.98 Ω and 6.52 Ω respectively. Furthermore, The Bode plot offers a deeper understanding of the gain and phase characteristics of the catalyst for various frequencies. The insets of Figure 5.37c exhibits the phase angle values of 44.3°, 29.6°, 20.9°, 35.6°, 26.2° and 37.8° for 0:40, 40:0, 20:20, 10:30, 30:10 and NCDH-20:20 materials respectively. The low phase angle value of 20:20 nanohybrid exhibits better OER than other electrocatalysts.^[82] Moreover, chronopotentiometry activity measurement (Figure 5.37d) exhibits the slight loss in the efficiency after continuous 20 h electrolysis of 20:20 nanohybrid electrode. The long-term stability result suggests that the catalyst is highly robust and durable for electrolysis measurements. Furthermore, multistep chronopotentiometry measurement was performed in the current density range 4 to 40 mA/cm² with increase in 4 mA/cm² current density for each step (Figure 5.37e). All steps reveal that the applied potential rapidly levels off and remains constant in the next 400 s. The similar results of multistep chronopotentiometry indicate rapid electron transportation, high conductivity and electrochemical robustness of the 20:20 hybrid material even at high current densities. Figure 5.37f represents the LSV analysis before and after electrochemical performance at 2 mV/s scan rate of 20:20 nanohybrid. The LSV measurement exhibits 161 mV overpotential at 10 mA/cm² current density even after long-term performance. It is observed from the electrocatalytic performances (Table 5.3) that the 20:20 exhibit significant performance than 0:40, 40:0, 10:30, 30:10 and NCDH-20:20 due to the facile electrode/electrolyte interactions, smooth ion transport and presence of more electrochemically active sites. Moreover, 20:20 hybrid material (Table 5.4) demonstrating good electrocatalytic performances compared to previously reported non-noble metal based electrocatalysts. [39,41,87-96]

Figure 5.38a and b show the SEM images of 20:20 nanohybrid material and the inset of Figure 5.38a exhibits smooth surface of the bare NF. The SEM characterization reveals that the material is uniformly intact on the NF substrate even after electrocatalytic performance. Furthermore, XPS analysis was used to evaluate the change in the chemical composition after the electrochemical analysis. Figure 5.39a reveals that Ni, Co, O, N, C and Se elements are present after electrocatalytic performances. Moreover, M-O and C-O-M bonding interactions can be seen in the high-resolution XPS spectrum of C 1s (Figure 5.38e) and O 1s (Figure 5.39b) after electrocatalytic analysis. In addition, changes in the high-resolution Ni 2p, Co 2p spectrum and C 1s XPS spectrum were observed. The characteristic peaks of Ni 2p1/2, Ni 2p3/2 and their corresponding satellite peaks appear at different binding energies in the Ni 2p high resolution spectrum (Figure 5.38c) and an additional NiO peak appears at 853.7 eV. Moreover, the core level spectrum (Figure 5.38d) of Co 2p exhibits Co 2p_{1/2}, Co 2p_{3/2} and their corresponding satellite peaks at different binding energies with an additional CoO peak appearing at 779.7 eV.[83-85] The highresolution C 1s XPS spectrum (Figure 5.38e) supports the formation-deformation of active sites at the electrocatalytic interface by showing characteristic C-C, C-N, C-O=O, and C=C bonding interactions with an additional peak of the -COOH group at 289 eV after the electrocatalytic process.^[85,86] The additional peaks appear in high resolution spectra of various elements due to the continuous formation and deformation of active sites during the electrocatalytic process, which results in a localized compositional change on the electrode surface.



Figure 5.38. (a) FE-SEM image of 20:20 electrode before electrocatalytic stability performance (b) FE-SEM image of 20:20 electrode after electrocatalytic stability test. The high resolution XPS spectra of 20:20 nanohybrid for (c) Ni 2p, (d) Co 2p and (e) C 1s elements.

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Figure 5.39. XPS characterization of 20:20 nanohybrid after electrocatalytic performances. (a) Full survey XPS spectrum of 20:20 nanohybrid and core level spectrum of (b) O 1s (c) N 1s and (d) Se 3d.

Table 5.4. Comparison of the electrocatalytic OER activity of the 20:20 catalyst with other previously reported literatures.

Materials	Current	Overpotential	Tafel slope	Ref.
	density	(mV)	(mV/dec)	
	(mA/cm ²)			
Ni-Fe/oA-POM/CPE	10	330	113	87
NiCo ₂ O ₃ @OMC	10	281	96.8	88
NiCoEDA	10	330	99.2	41
CoFe LDH	10	218	59.9	89
Ni ₂ CoFe _{0.5} -LDH/NF	10	240	65	90
NiFe-LDH/RGO-3	30	273	49	91
MPN@Fe ₃ O ₄	10	260	33.6	39
Ni-Fe _{0.52}	10	344	97	92
Ni-ZIF/Ni-B	10	234	57	93
Co-NCNTFs NF	10	230	94	94
NiFe(dobpdc)	10	207	36	95
Ni ₁₁ (HPO ₃) ₈ (OH) ₆	10	231	91	96
BSeFY-NCDH(20:20)	10	141	87	This
				work
5.4 Conclusion

In conclusion, we have designed and prepared BSeFY/NCDH nanohybrid electrodes using a facile galvanostatic electrodeposition process at room temperature without using any binder and additives. The 20:20 nanohybrid demonstrated higher specific capacitance 1338.46 F/g at 2 A/g current density and the nanohybrid electrode kept 80.74% of its initial capacitance even after 2500 GCD repetition at 20 A/g current density. Furthermore, the asymmetric device assembled with BSeFY/NCDH(20:20) and AC electrodes exhibited the highest energy density of 35.48 Wh/kg. The device retained its initial capacitance of 91.24% after 5000 GCD cyclic stability test at 7 A/g current density. Furthermore, the nanohybrids were highly active towards OER performance and showed low overpotential. However, the 20:20 nanohybrid demonstrated low Tafel slope 87 mV/dec and 141 mV overpotential at the current density 10 mA/cm^2 . Moreover, long-term chronopotentiometry at 10 mA/cm² and multistep chronopotentiometry at different current densities results suggested that the 20:20 nanohybrid is highly robust and durable. Therefore, the unique nanoarchitecture and composition of the 20:20 nanohybrid electrode make it highly active material for energy storage and energy conversion applications.

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Conclusion and future outlook

Chapter 6

6.1 Introduction

The organic-inorganic hybrid materials are one of the most promising materials in the field of energy storage and conversion. The linkers bind to the metal ions via hydrogen bonding, non-covalent and coordinative interactions to form organic-inorganic nanohybrids. It is important to find out the easy approach to control the nanoarchitecture, binder-free and scalable technique for the enhancement of the electrochemically active sites and activity. The electrochemical deposition method is one of the simple ways to achieve high electrochemical performance. The electro-synthesized materials could be used in energy storage and conversion applications.

6.2 Brief outcome of thesis work

Chapter 1 describes organic-inorganic nanohybrids as a new class of functional material with their use in electrochemical energy storage and energy conversion applications. We provided a summary of electrochemical deposition techniques for the synthesis of organic-inorganic nanohybrids and applied in the field of energy storage and conversion.

Chapter 2 depicted the synthesis of the benzo[2,1,3]selenadiazole (BSe) capped dipeptide of phenylalanine (BSeFF) and leucine (BSeLL) for the fabrication of the BSeFF/Ni(OH)₂ and BSeLL/Ni(OH)₂ nanohybrids respectively on nickel foam via one step *in-situ* potentiostatic electrodeposition technique with identical metal system and parameters to elucidate the effect on morphology and electrochemical performances. Organic components (benzoselenadizole functionalized amino acids with free -COOH) and inorganic salt cross-linked with applying negative potential in the electrolytic solution. More importantly, these organic-inorganic nanohybrids possess desirable characteristics such as chemical and physical stability, nanoscale morphology, structural flexibility and good electrochemical performances. The binder-free organic-inorganic nanohybrid electrodes were used to achieve electrochemical energy storage.

In chapter 3, we synthesized the BSeYY/Co(OH)₂/CP electrode materials by potentiostatic electrodeposition method using benzo[2,1,3]selenadiazole-5-carbonyl-protected BSeYY (BSe = benzo[2,1,3]selenadiazole; Y = tyrosine) dipeptide molecule. The fabricated electrode material was utilized to estimate the effect of various electrolytes during electrochemical performances and fabricated

a symmetric supercapacitor device for practical application to light-up a LED. The energy storage parameters such as specific capacitance, energy density and power density were used to estimate the energy storage performances.

In the chapter 4, Several bioinspired organic-inorganic nanohybrid electrodes were synthesized via one step galvanostatic electrodeposition process at room temperature and optimizes the best combination of the metal salts with organic moiety to achieve the excellent capacitive properties. Moreover, two serially attached symmetric full-cell devices efficiently light up a LED and spinning of a small fan. Bioinspired nanohybrids offer as promising electrode materials for energy storage applications.

Chapter 5 depicted the development of the organic-inorganic hybrid materials for multifunctional asymmetric supercapacitor and oxygen evolution reactions. We synthesized the organic-inorganic nanohybrids (BSeFY/NCDH) directly on nickel foam (NF) substrate by *in situ* galvanostatic electrodeposition using monometallic and bimetallic compositions of nickel, cobalt metal salt and organic molecule to examine the effect of all nanohybrids on electrochemical properties. Moreover, we fabricated an asymmetric device for practical application (light up a LED and run a small fan). Furthermore, the designed and fabricated materials are highly efficient towards the oxygen evolution reaction (OER). This study emphasizes the potential of electrodeposited organic-inorganic nanohybrid materials as multifunctional electrode materials without binders for electrochemical energy storage and energy conversion applications.

6.3 Future Outlook

Electrochemical energy storage and conversion could be extremely essential in the future due to the increasing challenges relating to energy resources. This research could be continued to develop organic-inorganic nanohybrids for the use in real-world electrochemical energy storage and energy conversion applications. Additionally, the industrial production of the necessary fuels and chemicals heavily depends on fossil fuel resources. However, fossil resources suffer greatly from their erratic availability and environmental pollution. One of the most fascinating solutions to the challenging energy demands of the world is the direct conversion (and storage) of energy into chemical bonds. For instance, one can envisage the synthesis of alternative chemical fuels using either solar energy (photocatalysis), electrochemical energy (electrocatalysis) and both (photoelectrocatalysis) to produce fuels such as hydrogen (by water splitting) and carbohydrate feedstock molecules (by CO_2 reduction). The engineered organicinorganic nanohybrids are anticipated to be used as an active catalyst in bioelectrocatalysis to mimic enzymatic processes as well as various organic transformations using organic electrosynthesis. The developed organic-inorganic nanohybrids can be utilized as an active catalyst for the electrochemical conversion of H_2O , CO_2 and N_2 to value-added chemicals and products like hydrogen, oxygen, methane, ethanol and ammonia. Moreover, organic-inorganic hybrid materials can be used for effective electrochemical energy storage such as batteries, supercapacitors and micro-supercapacitor devices.