# Fabrication of Nanostructured Electrodes for Biosensing and Energy Applications using Ni-Co Functional Inks

*A Thesis submitted by*
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# 8
# Summary and Future Outlook

In the summary, this thesis is focused on the large-scale development of Ni-Co based electrodes from solution processable inks. These electrodes are characterized using various techniques and used in energy and biosensing application. The summary of this thesis work is explained in brief with the upcoming sections.

## 8.1 Summary

**Chapter 1** emphasizes on the nanomaterials, different methods and synthesis process for large-scale fabrication. Further, the importance of solution processed method for fabrication of electrodes in energy and biosensing.

The **chapter 2** gives brief introduction to various characterization techniques utilized to characterized the nanomaterials formed in details.

**In chapter 3**, Ni nanostructures have been used as mediators and have proven to be highly efficient as an electrocatalyst for glucose sensors. In this context, Ni alkanethiolate complex ink are used as a redox-active electrode material and coated them on a transparent Au mesh network for a transparent and highly efficient sensor. The different chain length Ni alkanethiolate complex inks were subjected to 50 cycles in the alkaline medium that gave rise to Ni redox-active centers ($Ni(OH)_2$) with sharp anodic and cathodic peaks. Among Ni alkylthiolates, Ni-BT with the shortest carbon chain (C4) was found to be most efficient in retaining sharp oxidation at the low potential value and high current density. Electrochemical properties of Ni-BT were studied towards glucose oxidation on different electrode surfaces such as Au thin film, Au mesh, and FTO for understanding the glucose response in a better way. Interestingly, glucose oxidation takes place most efficiently on the Au mesh network as compared to Au film and FTO substrates. The $Ni(SC_4H_9)_2$/Au mesh exhibited two linear ranges of detection from 0.5 - 2 mM and 2 - 11 mM with the sensitivity value of 675.97 $\mu A.mM^{-1}cm^{-2}$ and Limit of Detection (LOD) of 2.2 μM along with excellent selectivity and reproducibility. The present study demonstrates that Ni butanethiolate on Au mesh acts as a promising functional and transparent electrode material with a possibility of large-scale production for practical glucose detection.

**In Chapter 4**, Ni butanethiolate (Ni-BT) Ni-BT and cobalt hexadecyl thiolate (Co-HDT) for the large-scale fabrication of electrodes has been explored. Electrocatalytic materials have gained importance for developing efficient energy technologies such as water splitting and fuel cells. The scalability and stability of electrocatalysts are some of the biggest challenges for their practical applicability. In this context, NiO and $Co_3O_4$ nanoparticles conformally coated on a lightweight, 3D, and highly conducting carbon cloth is fabricated using an easily synthesized Ni-BT and Co-HDT complex as ink, respectively**.** This method is beneficial for large-scale production as the complex can be synthesized in large quantities and coated on 3D substrates by a simple dip-coating method (Figure 1.6). The optimum loading of the catalyst is achieved through a Layer-by-layer (LbL) assembly of Ni-BT and Co-HDT complex inks via repeated dip-coating of carbon cloth electrodes in the solution. The $Co_3O_4$/CC undergoes electrochemical oxidation and converts to CoOOH as active species, and acts as a highly efficient electrocatalyst with optimized loading. The $Co_3O_4$-16/CC with sixteen times and NiO-24/CC with twenty-four times dip-coating exhibited remarkable stability with lower overpotentials at 10 $mA/cm^2$ and Tafel slope. The high catalytic activity towards oxygen evolution reaction (OER) in 1 M KOH due to the LbL coating is better than conventional $Co_3O_4$ and NiO. The values obtained are

comparable to $IrO_2$ and $RuO_2$ electrocatalyst, with a future possibility of commercial-scale production at a lower cost.

**In chapter 5**, the large-scale Ni-Co oxide electrocatalyst as active electrode material are synthesized with reasonable control over catalytic active surface sites for oxygen evolution reaction (OER). In this chapter, we have reported an industrially scalable, dip-coating method of Co and Ni thiolate hybrid inks on 3D substrates followed by solventless thermolysis to form 2D nanoplates of Ni-Co oxide (NCO) with spinel structure and superparamagnetic nature (Figure 1.7). The NCO electrocatalyst exhibits excellent OER performance in alkaline media with low overpotential values of 310 mV and long-term stability. XPS studies reveal that $Ni^{3+}$ and $Co^{3+}$ species on the surface of NCO-20 nanoplates enhance the OER activity. The superparamagnetic NCO with 20% Ni shows enhancement in OER with the external magnetic field due to the polarization of electron spin. Thus, NCO-20 electrocatalyst is of high technological potential in terms of performance and possible commercialization with scalable production.

**In chapter 6**, we have synthesized ultra-thin $Co_3O_4$, NiO, and $NiCo_2O_4$ nanostructures supported on a carbon cloth following thermal reduction of self-assembled metal alkane thiolates. These act as a sensing platform for testing the simultaneous electrochemical detection of dopamine (DA) and uric acid (UA), which are important biological molecules in physiological and pathological tests. The morphology and elemental states are studied by transmission electron microscopy (TEM), energy dispersive X-ray (EDX) elemental mapping, electron diffraction (ED), and high-resolution X-ray photoelectron spectroscopy (XPS). The ultrathin 2D nanoplates of $NiCo_2O_4$ formed in this study exhibit high electrochemical activity compared to pristine NiO and $Co_3O_4$. The electrochemical characterization studies indicate $NiCo_2O_4$/CC electrodes possess a high potential for simultaneous detection of the oxidation of DA and UA with a separation of peak potential of ~140 mV with high sensitivity and excellent selectivity. A biosensor possessing a wide working range of 0.001-1000 μM with detection limits of 0.7 and 0.6 nM for DA and UA, practically achievable limit of quantification in nM range, with excellent anti-interference from biologically relevant species is realized in this study.

**In chapter 7**, the conversion of waste polymer into useful carbon using Ni-BT as a catalyst was studied. A unique approach is developed for obtaining graphitic carbon from waste polystyrene as a raw carbon source. The conversion process is catalyzed using Ni-butanethiolate ink in ultra-low quantities under optimized temperature (800 °C) in the presence of 5% hydrogen in nitrogen. Interestingly, macroporous sugar cubes are used as a soft template to hold the polystyrene and catalyst together during decomposition, eliminating the need for a high-pressure source to retain the carbon for graphitization at high temperatures. An additional step of hydrogen annealing for pyrolyzed carbon nullifies the surface effects and improves the graphitization, reduces the point defects, enhances the crystallinity of carbon and electrical conductivity specifically required for Electric Double Layer Capacitors (EDLC). The SPC8H-based graphitic carbon electrode exhibits perfect rectangular CV characteristics with asymmetric triangular charge-discharge curve and the specific capacitance of ~158 F/g at 1 A/g. The two-electrode EDLC device demonstrated excellent cyclic stability with capacitance retention of ~ 90% even after 10,000 cycles. This study reveals that the trashed polystyrene waste could be transformed into highly crystalline, graphitic carbon electrodes for energy storage devices.

### 8.2 Closing Remarks

The increasing population of the world has led to energy demands and consciousness towards healthcare. Therefore, people have been depending on energy and biosensing for a healthy and comfortable lifestyle. In this thesis work, we have tried to explore possible of fabricating large-scale Ni-Co electrodes using solution processable inks. This method does not need any

additives or binders because the carbon formed after annealing the thiolates, acts as a binder, which ultimately increases the intrinsic conductivity.
The fabricated electrodes show a significant increase in the performance towards biosensing, OER and supercapacitors.

The future scope of the thesis work can be laid down as follows:

- The Ni and Co alkyl thiolates based inks can be used as a platform on any metallic mesh for biosensing and point of care devices. The advancements in the Ni-BT based transparent glucose sensor can enable in the manufacturing of contact lens that can used for glucose detection using tears.

- The Ni- Co based thiolate inks can be used for obtaining different morphologies and nanostructures when subjected to different gas environment and annealing temperature. The properties can be tuned to obtain catalytically rich facets for exploring the application in energy, environment and healthcare.

- The Ni-Co based thiolate inks can enable the fabrication of electrodes that can be used for gradient patterning, which can open up the possibility for multiplex sensing of biomaterials owing to the tuned composition and morphology.

- The Ni-Co based electrodes can be used for environmental pollution detection and possibly heavy metal ion detection.

- The $NiCo_2O_4$ nanoplates formed in this study can be used for application in electronic devices and gas sensing.

- The quality and SSA of the graphitic carbon can be further improved which can be used in the application of die adsorption, odor trapping, gas ($CO_2$ and $CH_4$) adsorption and catalytic convertor in combination of the various Ni-Co oxides.