Fluorinated Nanomaterials for Energy and Sensing Applications

A Thesis submitted by

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Doctor of Philosophy

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Summary and Future Outlook

In summary, the thesis involves the development of novel fluorination processes for inorganic nanomaterials using stable, non-hazardous, commercially available electrophilic fluorinating source Selectfluor™, (F-TEDA). Different nanomaterials have then been tested as active material in a wide field of research involving energy and sensing applications. The thesis work is summarized in the upcoming section.

8.1 SUMMARY

Chapter 1 gives an overview of the importance of inorganic fluorinated materials for energy and sensing applications. A detailed literature survey of the synthesis and the application of fluorinated nanomaterials in energy and sensing devices is also discussed.

In Chapter 2, the characterization techniques and the electrode fabrication used in the thesis are detailed. A brief introduction to the electrochemical methods and techniques is also presented.

Chapter 3 focuses on the fluorination of nanocarbon performed via the solution-processable method for enhanced supercapacitor applications. The fluorinated nanocarbon electrodes in a two-electrode supercapacitor device exhibit one order higher specific capacitance with negligible capacitance loss over 5,000 cycles resulting in enhanced supercapacitive performance. The methodology developed in the study is extendable to various types of carbon for the fabrication of electrodes with high electrochemical performance.

In chapter 4, F-TEDA is tested as an additive in organic electrolyte $TBABF_4$. Mixed electrolyte exhibit improved electrolytic properties with moisture sensitivity. Under the ambient condition, the device with mixture electrolyte shows a relative increase by 102% and 172.7% in specific capacitance and energy density compared to $TBABF_4$. This study explores the strength of fluorine-containing electrolytes in energy storage devices for enhanced performance.

In chapter 5, F-TEDA is established as a humidity sensor with a sensitivity value of ~10^6 (10%–95%), and was found to be highly selective and specific to humidity with a fast response and recovery time (4 ms and 40 ms, respectively). The high sensitivity of the humidity sensor is due to the synergistic effect of the intrinsic structure of the F-TEDA molecule and the conventional Grotthuss mechanism. The fabricated humidity sensor is successfully tested as breath-rate monitoring and touch-free skin moisture sensing device.

In Chapter 6, fluorinated Fe_2O_3 dendritic nanostructures are synthesized by hydrothermal method using Selectfluor as novel fluorinating agent. Interestingly, the fluorination exhibited a transition from antiferromagnetic to ferromagnetic nature with one order increase in saturation magnetisation and it is attributed to uncompensated surface spins of Fluorine atoms. Moreover, a 300% increase in photoelectrochemical performance of Fe_2O_3 in comparison to the pristine counterpart is observed due to a reduction in recombination losses upon fluorination.

In Chapter 7, a surface fluorination of SnO_2 film by solution-processed method using Selectfluor™ as a fluorinating agent is proposed. The fluorine content is optimised to be < 1% resulting in a significant decrease in the oxygen defects, increase in conductivity and reduction in persistent photoconductivity accompanied by a faster decay of the photogenerated charge carriers. The transparent F-SnO_2 film is integrated with a transparent heater as an areal display sensor for VOCs and optimized to efficiently work at low temperatures of 150 °C. The F-SnO_2 based sensor works efficiently towards a variety of polar and non-polar VOCs (amines, alcohols, carbonyls, alkanes, halo-alkanes and esters) and response is easily differentiable with the sensitivity in order with the electron donating tendency of the functional group present with triethylamine showing the highest response amongst the analyzed VOCs.

8.2 Future Scope of the Work

Energy and sensing are the most important research sectors as the comfortable existence of the human generation is highly dependent on these fields. In the thesis, fluorination as a step towards tailoring the properties of various nanomaterials for enhanced properties in energy and sensing applications is successfully undertaken in this thesis. The easy to handle fluorination approach and the significant improvements observed in the performance of supercapacitors, photoelectrochemical cells, humidity sensors, and VOC sensors are indeed noteworthy.

The future prospects of the thesis works are as follows:

- Fluorinated SnO_2 films developed in the study exhibit a lower concentration of oxygen defects and higher conductivity. These form essential characteristics to be tested as an efficient transport layer with reduced trap states in photoelectrochemical cells and perovskite solar cells.
- The fluorinated nanocarbon synthesized in the study can be explored in a variety of sensing applications, including biosensing, metal ion detection, and VOC/gas sensing.
- The concept of fluorination developed in the study can be extended to other nanomaterials like metal oxides, sulfides, and their two-dimensional counterparts. Further, the control over fluorination for tuning oxygen defects can also be explored.
- The humidity sensor developed in the study can be commercialized (both as technical and day to day apparatus) by extensive baseline and temperature calibrations using advanced electronics for smart living.
- Fluorinated materials are known to exhibit biological and antimicrobial activities, and hence the fluorination techniques developed in the thesis can be explored in various biological applications.

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