Abstract

The emergence of novel nanomaterials has led to significant advancement in various devices such as solar cells, supercapacitors, batteries, and sensors, to name a few. The surface effects in nanomaterials are crucial in determining their active role in these devices. The chemical, electrical, mechanical, thermal, optical, and catalytic properties of the nanomaterials can be tuned by functionalization and doping for achieving the best performance for any device application. The work presented in this thesis is focused on developing various fluorine functionalized nanomaterials for application in energy production, storage, and chemical sensors.

Fluorination of nanocarbon and metal oxide nanoparticles is performed by developing a simple recipe involving a commercially available electrophilic fluorinating agent, Selectfluor™, as a direct source of fluorine in solution. The innovative method allows fluorinating nanomaterials without posing any major safety issues as it is usually known with other fluorine precursors such as HF. Fluorination of carbon nanomaterials and metal oxides resulted in a significant enhancement in their physical, chemical, and electrochemical properties that has been applied in supercapacitors, photoelectrochemical cells, humidity sensors, gas, and VOC sensors. As an example, pristine α-Fe_2O_3 became ferromagnetic on fluorination due to an increase in uncompensated surface spins. It also exhibited enhancement in photocurrent density in photoelectrochemical cells as a result of preferential growth of α-Fe_2O_3 along (110) direction resulting in an improved charge transfer efficiency and reduced recombination losses. In another study, fluorinated nanocarbon exhibited remarkable improvement in electrical conductivity and wettability, resulting in enhanced electrochemical energy storage performance. Fluorination of carbon material led to the formation of semi-ionic C-F (F=8.02 at%) that resulted in high specific capacitance for fluorinated nanocarbon due to induced surface polarization.

As the structure of Selectfluor™ (F-TEDA) resembled conventional electrolytes, it is utilized as an additive in organic electrolytes for realizing an ultrafast electric double layer supercapacitor. The ionic conductivity of the mixture electrolyte is found to be 5.10 mS/cm, which increased on exposure to humid conditions resulting in superior electrochemical behavior in terms of high rate capability and capacitance retention in supercapacitor. The device assembled in ambient condition despite a decrease in operating voltage window exhibits a remarkable increase in specific capacitance by 102%. The interesting aspect of moisture sensitivity of F-TEDA is further exploited for the fabrication of an extremely stable, high sensitive, and exceptionally selective humidity sensor operating in a wide range of humid conditions (10% -95% RH). The as-fabricated humidity sensor displayed a sensitivity of six orders of magnitude. The sensor didn't respond upon exposure to various volatile organic compounds and reactive gases, except for humidity. The humidity sensor also worked as a healthcare device for breath rate monitoring and touch-free examination of skin moisture.

In another work, a solution-processed method for fluorination of SnO_2 films is developed, and fluorine doping is optimized to be < 1% that resulted in a significant increase in conductivity and reduction in persistent photoconductivity. A combination of these modified properties, together with the intrinsic sensing ability of SnO_2, is exploited in designing a transparent display sensor for ppm level detection of VOCs at an operating temperature of merely 150 °C. A sensor-reset method is devised while shortening the UV exposure time, enabling complete sensor recovery at low operating temperatures. The sensor is tested towards a variety of polar and non-polar VOCs exhibiting an easily differentiable response with the sensitivity falling in-line with the electron-donating tendency of the analyte. Importantly, the sensor is designed in the form of a portable and wearable display with a UV-pulse-based regeneration mechanism for instant use, as in the case of sequential events, a sensor in a ready-to-use form could be an urgent necessity.