Development of Carbon Based Nanomaterials and Their Applications

ABSTRACT

Carbon based nanomaterials such as carbon nanotubes (CNTs), graphene, carbon black (CB) and carbon dots (CDs) are one of the most widely researched topics due to their outstanding electrical, mechanical and optical properties. Much attention is focused on finding ways to incorporate them in devices or systems so as to extract better performance. For instance, one-dimensional CNTs with a high aspect ratio cylindrical structure and exceptional electrical conductivity are ideal for detecting volatile organic compounds (VOCs) like methanol. When added in small amounts as filler in polyaniline nanotube (PAniNT) based nanocomposite, it makes the material sensitive to small fluctuations in its conductivity on exposure to methanol vapors. Meanwhile, an important feature observed with entry into the nano-regime is the manifold increase in surface area of the material. This is a very useful property when dealing with electrode/electrolyte interfacial systems. In this thesis, we have exploited this property for creating electrode materials comprising CB/PAniNT nanocomposite, and PAniNT and silver nanorod (AgNR) functionalized reduced graphene oxide (rGO) aerogels to use them as counter electrode in dye sensitized solar cell (DSSC) and flexible asymmetric supercapacitor respectively. As the newest member on the block, CDs are a class of carbon nanoparticles with unique fluorescent properties. They show both up-conversion and down-conversion properties that are applied for sensitizing TiO_2 nanoparticles to visible light and act as a catalyst in methanol oxidation reaction (MOR) as well as a photo-anode in DSSC. Finally, considering the ability of 2,4,6-trinitrophenol (TNP) to quench the fluorescence of CDs in its vicinity, the CDs are also applied as sensing element for TNP detection. Chapter-wise summary of this doctoral thesis is given below.

Chapter 1: General Introduction.

This chapterpresents the general idea behind the motivation for the present research work. Starting with a brief historical background about the evolution of carbon based materials throughout the ages, the chapter especially emphasizes on the carbon nanomaterial family, an area of intense research jump-started by the discovery of fullerenes in 1985. Different synthetic allotropes of the carbon nanomaterial family are introduced in chronological order, along with their properties and methods of production. These include fullerenes, CNTs, graphene and CDs. Amorphous forms of carbon like CB are also described in this chapter. Next, different types of nanocomposites incorporating carbon nanomaterials are described. These nanocomposites primarily include polymer (PAniNT), metal (AgNR) or metal oxide (TiO_2). Finally, the suitability of these carbon based nanomaterials for different areas of application are reviewed,

including gas sensor, fluorescence based sensor, DSSC, supercapacitor and anode in direct methanol fuel cell (DMFC).

Chapter 2: A Room Temperature Methanol Vapor Sensor Based on Highly Conducting Carboxylated Multi-walled Carbon Nanotube/Polyaniline Nanotube Nanocomposite.

The toxicity and health hazards associated with VOCs necessitate the need for their monitoring. In this chapter, a novel carboxylated multi-walled CNT/PAniNT (c-MWCNT/PAniNT) nanocomposite is reported as a potential room temperature methanol vapor sensing element. The nanocomposite is prepared by *in situ* chemical oxidation polymerization of aniline in the presence of c-MWCNT. c-MWCNT/PAniNT nanocomposite with 6 wt% c-MWCNT shows significantly higher electrical conductivity compared to that of pristine PAniNT. This material is subsequently tested as a methanol sensing element using a simple two probe configuration. When exposed to methanol vapor, PAniNT forms hydrogen bonds with the methanol molecules, leading to a change in its resistance. This change is then correlated with the response of the sensing element. The presence of c-MWCNT in the nanocomposite leads to its exceptional sensitivity towards methanol as compared to pure PAniNT. The proposed concept of hydrogen bonding and the diminished sensitivity of the nanocomposite towards higher alcohols are theoretically verified by density functional theory studies.

Chapter 3:A Low Cost Carbon Black/Polyaniline Nanotube Nanocomposite as Efficient Electro-catalyst for Triiodide Reduction in Dye Sensitized Solar Cells.

The cost of Pt counter electrode accounts for over 40% of the total cost of a DSSC, thus replacing it with a cheaper material can significantly reduce the overall cost of the device.To this end, a novel cost-effective mesoporous CB/PAniNT nanocomposite is prepared as a potential counter electrode material. The nanocomposite is synthesized by *in situ* chemical oxidation polymerization of aniline in the presence of CB. Cyclic voltammetry (CV) is used to study the electro-catalytic activity of the CB/PAniNT nanocomposite towards reduction of triiodide ions to iodide ions. Current density-voltage (*J-V*) measurements and electrochemical impedance spectroscopy (EIS) analysis show that incorporation of an optimum amount of CB (0.75 wt%) results in an augmented active catalytic surface area and enhanced charge transfer from the counter electrode to the electrolyte. These factors contribute towards achieving a high performance DSSC with a conversion efficiency of 6.62% in liquid electrolyte and 4.82% in poly(methyl methacrylate) based polymer gel electrolyte under irradiation of simulated sunlight when the counter electrode layer is 10.58 μm thick.

Chapter 4: Flexible Asymmetric Supercapacitor Based on Functionalized Reduced Graphene Oxide Aerogels with Wide Working Potential Window.

Flexible energy storage devices are the need of the hour with the advent of flexible electronics. So far, flexible supercapacitors based on graphene analogues usually have low operating potential windows. To this end, two dissimilar electrode materials with complementary potential ranges are employed to obtain an optimum cell voltage of 1.8 V. Low temperature organic sol-gel method is used to prepare two different type of functionalized rGO aerogel: AgNR functionalized rGO aerogel acts as the negative electrode (with electrochemical double layer capacitive behavior) while PAniNT functionalized rGO aerogel acts as the positive electrode (with pseudo-capacitive behavior). Both the materials comprehensively exploit their unique properties to produce a device that has both high energy and high power densities. The assembled asymmetric supercapacitor gives a high energy density of 52.85 W h kg^{-1} and power density of 31.5 kW kg^{-1} with excellent cycling stability. The device also performs extraordinarily well under different bending conditions suggesting its potential to meet the requirements for flexible electronics.

Chapter 5:Hydro/solvothermalSynthesis of Carbon Dots for Different Applications.

Part (a): Hydrothermally Synthesized Carbon Dots as Sensitizer for TiO_2 Supported Pt Photo-electrocatalyst for Broadening the Sunlight Response Region in Methanol Oxidation Reaction.

TiO_2 is an eminent photo-catalyst for methanol oxidation reaction (MOR). However, its modification is necessitated by a narrow light response region and swift recombination of electrons and holes. Incorporating CDs with TiO_2 can broaden the light response range, while a composite of TiO_2 with Pt can significantly enhance the catalytic performance and also suppress the electron-hole recombination process. In the first part of this chapter, we report the structural, optical and electrochemical evaluation of a new photo-electrocatalyst - platinized TiO_2 sensitized by CDs - through a series of systematic studies. Reasonably, by combining both photo-catalytic and electro-catalytic mechanisms, the ternary nanocomposite catalyst ($Pt/CD/TiO_2$) under irradiation shows better performance in the MOR in terms of the forward peak current density value of 2.5 mA cm^{-2}, which exceeds that obtained without illumination by 24%. The performance enhancement can be attributed to the unique up-conversion property of CDs that allows the utilization of the visible solar range, which is otherwise restricted in case only TiO_2 is present.

Part (b): Solvothermally Synthesized Green Emitting Carbon Dots as Co-sensitizer in Dye Sensitized Solar Cell.

The emissions of CDs can be tuned by manipulating the reaction conditions of their formation. In the second part of this chapter, we present a facile solvothermal route for producing CDs by employing *N*,*N*-dimethylformamide (DMF) as the solvent medium. Using a commonly reported green carbon source, citric acid, along with ethylene diamine we were able to obtain green emitting CDs simply by using DMF, serving the dual purpose of a solvent and a nitrogen source. The optical analysis of the CDs suggests an extensive overlap between their emission spectrum and the absorption spectrum of N719 dye used as sensitizer in dye sensitized solar cell (DSSC), giving rise to the possibility of energy transfer from the CDs to N719 dye upon simulated solar light irradiation. CDs can additionally harness the unused higher energy blue light, causing better charge extraction by the device. Following this hypothesis, a solar cell was designed using both CDs and N719 dye as co-sensitizers. The device gave a photo-conversion efficiency of 6.9%, which is 9.8% higher than that obtained with only N719 dye sensitized device (6.28%).

Part (c): Solvothermally Synthesized Blue Emitting Carbon Dots as Fluorescence Sensor For 2,4,6-Trinitrophenol Detection in Organic Medium.

In the third part of this chapter, we report a facile solvothermal route for producing CDs by employing gallic acid for the first time as the carbon source in DMF medium to produce hydrophobic blue emitting CDs. The CDs produced by this method are easily dispersed in DMF, and allows for their application as sensor for detecting 2,4,6-trinitrophenol (TNP) in an organic medium. Their emission spectrum places them in a suitable position to act as a sensing element for TNP detection in organic medium (DMF) by way of inner filter effect. The blue emission of B-CDs is quenched in the vicinity of TNP in less than 1 min with a limit of detection of 0.75 μM. The sensor is quite stable giving consistent results upto a period of 2 hours, and is also selective towards TNP when compared to other nitrophenol analogues.

Chapter 6: Conclusion and Future Scope

The chapter-wise concluding remarks and future scope of this research work are summarized in this last chapter. Our studies reveal that c-MWCNT/PAniNT nanocomposite is highly conducting which could be used as a methanol vapor sensor. Meanwhile, CB/PAniNT, AgNR/rGO aerogel and PAniNT/rGO aerogel are highly porous and high surface area materials suitable for fabricating electrodes for DSSC and asymmetric supercapacitor. The most recently discovered CDs, with their exceptional optical properties, are likely to have a huge impact in the fields of catalysis support, co-sensitizer in DSSC and TNP sensor.