DEVELOPMENT OF HIGHLY STABLE AND REUSABLE FUNCTIONAL NANOMATERIALS FOR SENSOR, CATALYSIS AND SUPERCAPACITOR APPLICATIONS

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DEVELOPMENT OF HIGHLY STABLE AND REUSABLE FUNCTIONAL NANOMATERIALS FOR SENSOR, CATALYSIS AND SUPERCAPACITOR APPLICATIONS

Metal and metal-oxide nanoparticles exhibit their intrinsic electronic properties and high surface-to-volume ratios and can be exploited for a number of applications like sensors, catalysis, solar cells, batteries, energy conversion and storage, drug delivery, bio imaging and light emitting diodes. However homogeneous nanocatalysts possess some drawbacks such as long reaction time, easy aggregation or precipitation, easy loss of photocatalytic activity, lower supercapacitor activity, poor sensitivity, selectivity, reduction/oxidation in catalytic activities, difficulty in product separation and catalysts recycling. For this reason, it is highly desirable to design functional hybrid nanomaterials leading to the development of numerous useful materials for environmental remediation.

The environment has been severely polluted by toxic heavy metals and organic pollutants along with the rapid increase in greenhouse gas emissions. Hence it is important for the detection of organic compounds, toxic metals and biological fluids which should be applied in forensic investigation and medical diagnosis. The most sustainable option for the degradation of environmental pollutants is photocatalysis, because it is simple, clean and environmentally benign. These techniques should be efficient enough to remove the organic pollutants rapidly. Also design and development of highly performing new electrode materials are essential to boost up the practicality of supercapacitors in various energy storage devices.

Functional nanomaterials for sensing, photocatalytic, and supercapacitor applications in relation to the determination of various environmental and biological molecules, decontamination of environmental pollutants and high performance energy storage devices, reveals that the materials on hand are not sufficient and still there should be continuous progress towards sustainable materials chemistry. Hence an attempt has been made herein to synthesize functional nanomaterials with potential sensing, photocatalytic and supercapacitor applications.

The thesis consists of five chapters.

Chapter 1

Introduction

A brief introduction to the nanomaterials, metal and metal oxide nanoparticles, functional nanomaterials for the applications in sensors, photocatalytic conversions and energy storage devices has been given along with relevant literature in Chapter I. Objectives and scope of the research work are presented in this chapter.

The main objectives of the present work are:

- Synthesis/fabrication of functional nanomaterials with unique properties such as high surface area, improved reactivity, high porosity, good conductivity, high instinct redox properties and good environmental stability

- Thorough characterization of synthesized nanomaterials by various instrumental techniques including, UV-Vis, UV-DRS, FT-IR, XRD, FE-SEM, Mapping analysis, HR-TEM, SAED, EDAX, Raman and TGA

- Applications of the synthesized/fabricated nanomaterials for

- ✓ Trace level detection of environmental and biological contaminants electrochemically
- ✓ Photocatalytic decontamination of organic pollutants under visible light irradiation
- ✓ Electrode materials for high performance supercapacitors

Chapter 2

This chapter describes the design and development of functional nanomaterials for the applications in the detection of biological and environmental disease causing analytes. This chapter is subdivided into four sections comprising the applications of functional nanomaterials for sensing four different analytes.

2.1 A new analytical device incorporating a nitrogen doped lanthanum metal oxide with reduced graphene oxide sheets for paracetamol sensing

This section reports the novel N-CeO_2 nanoparticles decorated on reduced graphene oxide (N-CeO_2@rGO) composite by sonochemical method. The characterization of as prepared nanocomposite was intensely performed by UV–Vis, FT-IR, EDX, FE-SEM, HR-TEM, XRD, and TGA analysis. The synthesized nanomaterial was further investigated for its selective and sensitive sensing of paracetamol (PM) based on a N-CeO_2@rGO modified glassy carbon electrode. A distinct and improved reversible redox peak of PM is obtained at N-CeO_2@rGO nanocomposite compared to the electrodes modified with N-CeO_2 and rGO. It displays a very good performance with a wide linear range of 0.05–0.600 µM, a very low detection limit of 0.0098 µM (S/N=3), a high sensitivity of 268 $\mu A \mu M^{-1}$ cm^{-2} and short response time (< 3 s). Also, the fabricated sensor shows a good sensibleness for the detection of PM in various tablet samples.

2.2 New electrochemical sensor based on silver-doped iron oxide nanocomposite coupled with polyaniline and its sensing application for picomolar-level detection of uric acid in human blood and urine samples

This section reports a simple and very sensitive electrochemical sensor for the detection of uric acid (UA) based on polyaniline (PANI) merged into a silver doped iron oxide (Ag−Fe_2O_3) nanocomposite-modified glassy carbon electrode. The synthesized ternary composite material (Ag−Fe_2O_3@PANI) was characterized by UV−visible spectroscopy, Fourier transform infrared spectroscopy, energy-dispersive X-ray, High-resolution transmission electron microscopy, X-ray diffraction, and thermo gravimetric analysis analyses. The nanocomposite-modified electrode shows an exceptional electrocatalytic activity and reversibility toward the oxidation of UA in a 0.1 M phosphate buffer (pH 7.0) compared to those of PANI and Ag−Fe_2O_3. The detection limit is found to be 102 pM with a linear dynamic range of 0.001− 0.900 μM. The fabricated UA sensor also exhibits good selectivity, reproducibility and long-time stability. The limit of detection and linear range attained for the synthesized composite are much greater compared to those of any other composite materials reported in the literature. The proposed method has been successfully applied for the selective detection of UA in various real samples such as human serum and urine with good recoveries. This platform that assimilates such electrocatalytic ternary nanocomposite with high performance can be widely employed for fabricating diverse sensors.

2.3 Picomolar-level electrochemical detection of thiocyanate in the saliva samples of smokers and non-smokers of tobacco using carbon dots doped Fe_3O_4 nanocomposite embedded on g-C_3N_4 nanosheets

Thiocyanate (SCN^-) is a metabolite of cyanide detoxification with equivalent toxicity. The SCN^-, even in trace concentration affects the health adversely. Notwithstanding various methods have been used for SCN^- analysis, a fast and simple electrochemical process has been hardly ever tried. This section describes a novel material, carbon dots doped Fe_3O_4 embedded on g-C_3N_4 nanosheets (CDs/Fe_3O_4@g-C_3N_4) which has been synthesized for the electrochemical detection of SCN^- level in the saliva samples of smokers and nonsmokers of tobacco. The synthesized material was characterized by FT-IR, HR-TEM, TGA, UV-Vis and XRD analysis. The linearity range exhibited by this sensor is wide (0.001-0.900 mM) and the detection limit is in picomolar. The proposed system can be very well applied for the construction of sensing devices for clinical diagnosis and environmental monitoring.

2.4 A glassy carbon electrode modified with a copper tungstate and polyaniline nanocomposite for voltammetric determination of quercetin

This section describes a binary nanocomposite of type copper tungstate and polyaniline ($CuWO_4$@PANI) which was obtained by single step polymerization on the surface of a glassy carbon electrode (GCE). The resulting electrode is shown to be a viable tool for voltammetric sensing of quercetin (Qn) in blood, urine and certain food samples. The nanocomposite was characterized by UV-Visible absorption spectroscopy, Fourier-transform infrared spectroscopy, thermogravimetric analysis, X-ray diffraction and high resolution transmission electron microscopy. Differential pulse voltammetry was applied to quantify Qn, typically at the relatively low working potential of 0.15 V (vs. Ag/AgCl). The modified GCE has a wide analytical range (0.001–0.500 μM) and a low detection limit (1.2 nM). The sensor is reproducible, selective and stable, which makes it suitable for the determination of Qn in real samples without complicated sample pretreatment.

Chapter 3

Chapter 3 deals with the photocatalytic decontamination of organic pollutants using novel functional nanomaterials, which is divided into two sections with varied photocatalytic applications.

3.1 Efficacious separation of electron–hole pairs in CeO_2-Al_2O_3 nanoparticles embedded GO heterojunction for robust visible-light driven dye degradation

Herein a facile and one pot synthesis of ternary CeO_2-Al_2O_3@GO nanocomposite via wet chemical method has been reported. The structural and morphological characteristics of the synthesized nanocomposite was investigated using UV–DRS, FT-IR, XRD, FE-SEM, HR-TEM, EDX and TGA analysis. The CeO_2- Al_2O_3@GO composite was tested for its ability to photocatalytically degrade Rhodamine B (RhB) under visible light illumination. The influence of various operational parameters such as pH, catalyst dosage and initial dye concentration on the photo degradation was investigated in detail. The synthesized CeO_2-Al_2O_3@GO composite shows greater photocatalytic degradation of RhB (99.0%) under visible light irradiation than the raw CeO_2, Al_2O_3 and GO catalysts and any other reported nanocomposite materials. The recyclability results also demonstrate the excellent stability and reusability of the CeO_2-Al_2O_3@GO nanocomposite. This work will be beneficial in the field of industrial and engineering applications in the degradation of organic pollutants. Also, a study of this kind will definitely stimulate many researches in the recently emerging field of solar-driven water splitting.

3.2 Effectual light-harvesting and electron-hole separation for enhanced photocatalytic decontamination of endocrine disruptor using Cu_2O/BiOI nanocomposite

Any body system controlled by hormones (or endocrine) can be spoilt by hormone disruptors. Bisphenol A (BPA) is a notorious endocrine disruptor, found in the inside coating of infant formula cans, plastic food containers and plastic bottles. This hazardous BPA causes breast malignancy, thyroid tumor and prostate cancer. More importantly it induces hormonal imbalance resulting in sexual growth problems such as male-feminization and female-masculinization. Hence, its destruction from food, water and environment is very much required. Amongst the techniques employed for the degradation of perilous pollutant such as BAP, an effective technique is photocatalysis, in which the key issue is the development of materials with high photocatalytic efficiency. The fast recombination of light-produced electron-hole pairs, trivial surface area and deprived visible light utilization are the major negatives associated with any photocatalyst. These issues have been overcome here with the aid of one-step assembled oxygen vacancy-rich semiconductor, dicopper oxide doped iodo(oxo)bismuthine (Cu_2O/BiOI). The as-prepared nanocomposite behaves in an outstanding way for the photocatalytic destruction of BPA (99.9%) under visible light irradiation. A suitable reaction mechanism has been recommended for the photocatalysis. This work, by and large, kindles new visions for achieving high-performance photocatalysis which will be very much useful for environmental remediation.

Chapter 4

Chapter 4 deals with the supercapacitor applications of fabricated functional nanomaterials, which is again divided into two sections with two different supercapacitor applications.

4.1 Ultrasound-assisted fabrication of a new nanocomposite electrode of samaria and borazon for high performance supercapacitors

The fabrication of hetero structured materials with supercapacitor applications for industrial use remains a key challenge. This work reports a new supercapacitor material with high capacitance, comprising samaria and borazon (O_3Sm_2/BN) synthesized ultrasonically (40±3kHz, 200W). The successful synthesis, probable interfaces between O_3Sm_2 and BN and thermal stability of the nanocomposite were studied by UV–Vis. and FT-IR spectroscopies, X-ray diffraction (XRD) and thermo gravimetric analyses (TGA). The morphology of nanocomposite was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Elemental mapping analysis and energy dispersive X-ray analysis (EDAX) confirmed the elements present in the material. This supercapacitor material shows a maximum discharge capacitance of $414Fg^{-1}$ at $0.25Ag^{-1}$ and an exceptional retention of specific capacitance (92.5%) in 5000 cycles. Such nanocomposite with better specific capacitance and charge/discharge rates makes it a right candidate as next generation supercapacitor, which certainly finds applications in various unconventional energy storage devices.

4.2 A new high-power supercapacitor electrode of advantageously united ferrous tungstate and functionalized multi-walled carbon nanotubes

The disadvantages that prevent supercapacitors from swapping batteries in most of the applications are linear discharge voltage, low specific energy and high cost. Herein a new nanocomposite electrode has been developed by strategically combining the electrical double layer capacitance behavior of multi-walled carbon nanotubes and pseudo-capacitance behavior of ferrous tungstate (FeO_4W/f-MWCNTs) hydrothermally for high performance supercapacitors. The as-synthesized supercapacitor electrode exhibits specific capacitance as high as 875 Fg^{-1}. The cycle tests done electrochemically on the electrode show capacitance retention of 93.80% in 5000 cycles of charging/discharging at 0.5 Ag^{-1} current density. A high power density of 238 W/Kg is obtained at an energy density of 1.35 Wh/Kg. Such discovery of novel supercapacitor electrode will certainly pave way for the design and development of advanced nanocomposite electrodes for energy storage applications with substantial charge time, specific power, cycle life and safety. Analytical techniques such as UV–Vis and FT-IR measurements confirmed the presence of individual elements/functionalities in the composite, while TGA of the nanocomposite revealed better thermal stability as compared to individual counterparts. The crystallinity of the composite was ascertained by XRD. The inter planner spacing (d_{hkl}) in the nanomaterial was measured from HR-TEM and SAED. EDAX was used for elemental analysis.

Chapter 5

Summary and Conclusion

Overall summary and conclusion are presented in the last chapter. This research work provides an account for the synthesis of N-CeO_2@rGO, Ag−Fe_2O_3@PANI, CDs/Fe_3O_4@g-C_3N_4, $CuWO_4$@PANI, CeO_2-Al_2O_3@GO, Cu_2O/BiOI, O_3Sm_2/BN and FeO_4W/f-MWCNTs nanocomposites, characterization and their most promising applications in sensors, photocatalysis and supercapacitor. It is very much understood that the synthesized nanocomposites in this research work can be in fact used as a potential tool to detect various analytes, degrade hazardous pollutants and create new electrode materials for energy storage devices. It is hopeful that the implementation of these approaches on a large scale and their commercial applications in the field of sensor, photocatalytic and supercapacitor will undoubtedly take place in the future.