GRAPHENE AND MoS_2 BASED NANO FUNCTIONAL MATERIALS FOR ELECTROCHEMICAL SENSING/STORAGE APPLICATIONS

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ABSTRACT

Electrochemistry, the chapter of chemistry that deals with the relations between electrical and chemical phenomena, has an ever increasing impact in everybody's daily life. Out of the myriad applications of electrochemistry, considerable attention has been devoted to the fields of electrochemical (EC) sensing and energy storage in recent decades. The emergence of nanotechnology as an indispensable tool for great advancement in science and technology has generated great capability of controlling materials at the nanometer scale and has enabled exciting opportunities to design materials with desirable electronic, ionic, photonic, and mechanical properties. This development has also contributed to develop and fabricate new structures and devices for EC sensing and energy storage applications in the recent years. In this scenario, this thesis work aims to address the challenges in the fields of EC sensing and storage by the rational design of nanofunctional materials, using 2D materials such as graphene (Gr) and Molybdenum disulphide (MoS_2).

The on-site monitoring of various analyte species in the diversity of fields by EC sensor requires considerable improvements in sensitivity, selectivity, and accuracy along with its inherently fast, accurate, compact, portable and cost-effective properties. Herein, we are trying to meet the aforementioned needs by developing various nanofunctional materials based on Gr and MoS_2. The various steps involved in the study are: the preparation of different types of Gr and MoS_2 based materials, their characterization, development of modified electrodes using the prepared materials, study of their EC sensing properties and finally examining the reasons/mechanisms behind the effective sensing behaviors.

A gold nanoparticle functionalized Gr (Au-Gr) is synthesized using a green synthetic strategy which exhibits excellent non-enzymatic sensing properties towards the detection of biomolecules glucose and ascorbic acid (AA). The limit of detection (LOD) values obtained were as low as 10 and 40 nM respectively for glucose and AA. The principal reason behind the remarkable electrocatalytic behavior is assigned to the synergistic effect of better conductivity properties of the atomically thin Gr sheets due to the cyclodextrin (CD) molecules and the catalytic properties of Au NPs (This work was published in *RSC Advances, 2015*). Mechanical pulverization of graphite for an optimized duration leads to highly solvent dispersible and high surface area Gr nanosheets called pulverized graphite (pGr) which displays highly sensitive and selective EC sensing towards dopamine (DA) with nanomolar detection capability and enables the simultaneous sensing of DA, AA and uric acid (UA). The sensor was found to be effective for real blood sample analysis also. The mechanism of sensing is explained on the basis of the unique aromatic basal plane structure of pGr with fewer oxidation sites and the edges rich with functional groups and/or defects (This work was published in *Sensors and Actuators, 2018*).

Further, this thesis tries to scrutinize the use of MoS_2/Gr based nanofunctional materials as EC sensing platforms for the effective environmental monitoring also. A solvent exfoliated MoS_2 prepared by a simple ultrasonication procedure has been subjugated for the parts per quadrillion (ppq) levels EC detection of mercury (II) ions (Hg^{2+}) exploiting the affinity of S^{2-} towards Hg^{2+}. The sensor assures its excellence towards Hg^{2+}detection in real sea water and tap water samples as well. Further it was found that the spontaneous redox reactions resulting from the affinity between the S^{2-} groups of MoS_2 and Hg^{2+} play the dominant role in achieving the unusual EC sensing realization (This work was published in *Journal of Materials Chemistry A, 2018*). A novel and simple hydrothermal method was utilized to prepare Nitrogen-doped graphene quantum dots (N-GQD) from polyaniline (PANI) and its EC sensing behavior was examined by taking nitrocompounds as analytes. The N-GQD exhibits ultra trace detection (0.2 ppb) of 2, 4, 6- trinitrophenol (TNP) and provides effective differentiation of various nitroaromatics. The unparalleled EC behavior of N-GQD is allocated to the richly N-doped aromatic structure of the N-GQD resulting from PANI, which can possibly promote closer molecular interactions with nitroaromatic compounds along with the enhanced conductivity and improved electron transfer ability owing to the *insitu* N-doping (This work was published in *ACS Sustainable Chemistry and Engineering, 2019*).

The final part of this thesis tries to explore the energy storage possibilities of Gr based nanofunctional composites contributing ideas to improve the capacity and cycle life of Si based anode materials in lithium ion batteries (LIBs). A novel and simple core-shell strategy for the preparation of a Si-Gr based composite, named as Si-nanographene oxide (Si-nGO) as an anode in LIB, results in an incomparable stability and remarkable storage capacity. The exceptional EC properties of the Si-nGO anode are attributed to the core-shell structure which limits the volume expansion of the Si NPs in all the directions, minimizing its volume expansion and the improved flexibility & conductivity offered by the thin nGO sheet matrix (This work was published in *Chemistry Select, 2018*).

In conclusion, this thesis presents an understanding of, how the logical designing of nanofunctional materials can meet the needs and conquer the challenges in the EC sensing of various analytes and the energy storage in LIBs.