GRAPHENE QUANTUM DOT AND METAL NANOCLUSTER-BASED NANO FUNCTIONAL MATERIALS FOR ELECTROCHEMICAL SENSING APPLICATIONS

A Thesis submitted
in partial fulfillment for the Degree of

Doctor of Philosophy

by

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February, 2023

ABSTRACT

Electrochemistry, the chapter of chemistry that deals with the relations between electrical and chemical phenomena, have an ever-increasing impact on everybody's daily life. Out of the myriad applications of electrochemistry, considerable attention has been devoted to the fields of electrochemical (EC) sensing 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 developing and fabricating new structures and devices for EC sensing applications in recent years. In this scenario, this thesis work aims to address the challenges in the fields of EC sensing by the rational design of nano-functional materials using graphene quantum dots (GQD) and metal nanoclusters (MNC).

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 nano-functional materials based on GQD and MNC. The various steps involved in the study are preparing different types of GQD and MNC-based materials, their characterization, developing modified electrodes using the prepared materials, studying their EC sensing properties, and examining the reasons/mechanisms behind the effective sensing behaviors.

The sensing capability of nitrogen-doped graphene quantum dots (N-GQDs) was explored for the first time towards hazardous heavy metal ions and found to be selectively detecting cadmium ions (Cd(II)). Cd(II) is one of the hazardous heavy metal ions in the World Health Organization's list of 10 chemicals of major public concern. The aromatic N-GQDs, synthesized through a hydrothermal route using a single precursor polyaniline, exhibited a 25-fold increase in the current response compared to that of a glassy carbon electrode (GCE). The LOD value of 1.0×10^{-5} ppb, i.e. in parts per trillion by N-GQDs is the lowest value ever reported, which is 3-4 magnitudes lower than the previously reported values. The effective N-doping, which is attributed to the synthesis procedure, seems to play a crucial role in the sensing performance of N-GQDs, which spontaneously reduces Cd(II), mostly through the N-sites (This work was published in *RSC New Journal of Chemistry, 2020*). A white emissive sulfur co-doped nitrogen-graphene quantum dots (S,N-GQDs) was synthesized from polyaniline using sulfuric acid as an acid catalyst and S-doping agent. The S,N-GQDs, for the first time, exhibited simultaneous sensing towards three of the top ten toxic metal ions: Cd(II), Pb(II), and Hg(II), with highly sharp peaks and adequate peak-to-peak separation. The limit of detection values of Cd(II), Pb(II), and Hg(II) on S,N-GQD were 1, 10, and 1 pM and is the lowest reported hitherto for the simultaneous sensing of the metal ions. The enhanced sensitivity and the simultaneous sensing capability of S, N-GQD is assigned to the co-doping with S, which enabled the sensing of Pb(II) and Hg(II) through the M(II)-S interactions and the enhanced electronic properties, respectively (This work is published in *ACS, Applied Nano Materials*).

Further, a highly stable copper (Cu) nanocluster (NC), which exhibited stability for more than one year, was synthesized using N-GQD as reducing and capping agents and smaller glutathione molecules as additional capping agents. The synthesized NC, CuNC@N-GQDs, successfully sensed three neurofunctional molecules, dopamine (DA), serotonin (SER), and nicotine (NIC), which are functionally correlated to each other, simultaneously with well-defined peaks and good peak-to-peak separation. The limits of detection obtained were 0.001, 1.00, and 0.01 nM for DA, SER, and NIC, respectively. The higher sensitivity and the simultaneous sensing are indicative of the synergistic effect of CuNCs and N-GQDs in the CuNC@N-GQDs (This work was published in *RSC Journal of Materials Chemistry B, 2022*). An ultra-stable gold-copper nanocluster on nitrogen-doped graphene quantum dot (AuCuNC@N-GQD), with a stability of more than one year, was achieved through a galvanic exchange process. The AuCuNC@N-GQD displayed intense solid- and solution-state near-infrared (NIR) emission. The NC exhibited selective and enhanced glycine (GLY) sensing through a (non-enzymatic) EC strategy. The detection limit obtained for GLY was 10 nM, which is the lowest in the detection limits reported hitherto. The enhanced and selective sensing of AuCuNC@N-GQD towards GLY is assigned to the preferential Au-GLY interaction and the improvement in the electronic and conductivity characteristics of the NC (This work is under review in *ACS, Applied Nano Materials*). The EC sensing capability of AuCuNC@N-GQD was further extended towards heavy metal ions and observed a highly selective sensing property towards Pb(II) with almost nil current response for all other interfering metal ions studied. Pb(II) is included in the top ten list of chemicals of major public health concern by the World Health Organization, and its prevalent usage in batteries and other industries makes the detection of Pb(II) in environmental samples decidedly significant. The LOD value obtained was 1 pM, the lowest reported hitherto for Pb(II) by any other material. The selective interaction between Au(I) and Pb(II) is attributed to the selective sensing of Pb(II) by AuCuNC@N-GQD. (Manuscript under preparation)

In conclusion, this thesis presents an understanding of, how the logical designing of nano-functional materials can meet the needs and conquer the challenges in the EC sensing of various analytes.