Graphene and Molybdenum disulphide Based Nano-Structures for Toxic Metal ion Removal from Water and Electrochemical Sensing Applications

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by

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ABSTRACT

Material science has always played a vital role in the evolution of provisions for humans. The emergence of nanoscience has made considerable improvements in materials applications. Amongst the nanomaterial's, layered nanomaterials have gained a significant role since their discovery, and huge activity has been generated in most areas of science due to their remarkable unique electrical, thermal, catalytic, optical, and mechanical properties. Particularly, graphene (Gr), the thinnest known and the strongest ever measured material in the universe, has emerged as a rapidly rising star in material science. Likewise, molybdenum disulfide (MoS_2), a graphite analogue, has attracted the research community due to its intriguing electrical and optical properties in the nanoscale. Of the various exceptionally unique properties of Gr and MoS_2, many properties favour adsorption studies and electrochemical (EC) sensing applications, including their possible higher specific surface area, chemical, and electrochemical inertness, good conductivity, etc., structural flexibility, catalytic activity, and biocompatibility. Here, we discuss the environmental and EC sensing applications through the nanostructures synthesized using Gr and MoS_2.

Faced with more stringent environmental regulations, heavy metals are now the priority pollutants of surface and ground waters. Water contamination with these compounds is becoming one of the most severe environmental problems because of the toxic nature of the heavy metal ions, even at low trace levels. Hence, removing heavy metal ions from wastewater is of prime importance for a clean environment and human health. Different reported methods were devoted to heavy metal ions removal from various wastewater sources, such as adsorption-, membrane-, chemical-, electric-, and photocatalytic-based treatments. Among them, adsorption-based methods are meticulous because of their simplicity, speed, low cost, frugal setup, convenience, and versatility offered by the flexibility in choosing different materials. Here in, we are trying to develop different Gr and MoS_2 based adsorbent materials to remove toxic metal ions with high removal efficiency and thereby decrease the concentration of metal ions to the acceptable level (ppb) in the water suggested by the U.S Environmental Protection Agency (US-EPA).

A MoS_2-hollow nano roses (MoS_2-HNR) is synthesized using a simple hydrothermal method by using precursors: sodium molybdate and thioacetamide. Further, the ability of the MoS_2-HNR for the simultaneous removal of the toxic metal ions: Hg (II), Pb (II), and Ag (I) from water with very high efficiency was successfully demonstrated. A single treatment of contaminated real water samples with MoS_2-HNR can rapidly (in ~ 5 - 30 minutes) decrease the concentration of Hg (II), Pb (II), and Ag (I) simultaneously from 10,000 ppb to 1.43, 11.62 and 1.01 ppb, respectively, the levels less than the safe limits suggested by the U.S EPA with an efficiency of ≥ 99 % at a V/m ratio of 10000, in real water samples. A possible mechanism for the high-efficiency removal and the order of adsorption Hg (II) >Ag (I) >Pb (II) is explained based on the affinity between S^{2-} and metal ions and the electrochemistry factor (This work was published in Applied Materials Today, Elsevier, 2020). Further, we synthesized a Gr-MoS_2 nanocomposite starting from graphene oxide (GO) and precursors of MoS_2 by a facile hydrothermal reaction and obtained partially reduced GO nanosheets decorated with MoS_2 (prGO-MoS_2), and systematically studied its adsorption properties towards various toxic metal ions. Interestingly, the prGO-MoS_2 was unlike our previous MoS_2-HNR and exhibited different adsorption properties with higher selectivity towards Pb (II) and ultra-fast removal from contaminated water with very high efficiency, as high as ≥ 99.99 %. The adsorption was ultra-fast that it took ≤ 3 minutes to reach the safe level or lower (from 10,000 to 0.86 ppb) as specified by US-EPA at a V/m ratio of 1.42 ml/mg. The higher efficiency was attributed to the presence of prGO and the structure of prGO-MoS_2 formed (This work is accepted in Advance Sustainable Systems, Wiley).

Further, sensing/detecting the concentration of metal ions in water samples after treatment is an essential part of the treatment process and is similarly significant in monitoring environmental water samples' concentration. Though many different types of quantitative analysis, EC sensors represent the most rapidly growing class of chemical sensors because of their sensitivity, selectivity, accuracy, and inherently fast, accurate, compact, portable, and cost-effective properties. The on-site monitoring of various analyte species in the diversity of fields by EC sensor requires considerable improvements in the properties mentioned above. Thus, in the second part of the thesis, we are trying to meet the aforementioned needs by developing various nanomaterials based on Gr and MoS_2. As we observed an EC mechanism in the prGO-MoS_2 nanocomposite towards Pb (II), the EC sensing of different metal ions was attempted. The developed prGO-MoS_2 exhibited a 200- and 100-fold increase in peak current for Pb (II) and Cd (II), respectively, on prGO-MoS_2/glassy carbon electrode (prGO-

MoS_2/GCE) compared to that of GCE and the limit of detection (LOD) was the lowest reported so far and was in pM/nM levels as 0.1 pM and 0.1 nM for Pb (II) and Cd (II), respectively, (Manuscript is under preparation). Further, we report, a graphene-molybdenum disulphide (pGr-MoS_2) nanocomposite synthesized from pulverized graphite and the precursors of MoS_2 which demonstrated a remarkable selectivity towards DA by exhibiting current response only for DA in the presence of possibly interfering biomolecules such as AA, UA, Folic acid (FA), glucose (GC), nicotine (NC), caffeine (CA), acetylcholine (AC), Histidine (HS), Hydroquinone (HQ), and H_2O_2, various metal ions and even in the presence of neurotransmitters with highly similar structure and an aromatic ring such as Serotonin (ST), Epinephrine (EP), and Norepinephrine (NP). To our surprise, none of the tested biomolecules exhibited a current response on pGr-MoS_2, except DA. A possible mechanism for the selectivity offered by pGr-MoS_2 to DA was proposed and discussed with evidence. Further, the sensing performance was successfully extended to real blood samples spiked with DA (This work was published in Sensors and Actuators, Elsevier, 2021). Since the synthesized material pGr-MoS_2 exhibits high selectivity towards DA, which has an aromatic structure, this thesis further tries to scrutinize pGr-MoS_2/GCE-based material as an EC sensing platform for the effective environmental monitoring. Here, pGr-MoS_2 was utilized for the simultaneous EC sensing of dihydroxy benzene isomers: hydroquinone (HQ), catechol (CA), and resorcinol (RE). The developed material shows three well-distinguished oxidation peaks for the three DHBIs with high current intensity values with the lowest LOD, such as 0.1 pM, 1 pM, and 10 nM (S/N=3) for HQ, CA, and RE. The pGr- MoS_2/GCE exhibits no interference from other interfering molecules and metal ions studied. Then, the pGr-MoS_2/GCE was successfully applied to determine DHBIs in the real aquatic environmental samples. (This work is under review in Analyst, RSC)

In conclusion, this thesis presents an understanding of how the logical designing of Gr and MoS_2 based materials can meet the needs and conquer the challenges in the environmental and EC sensing applications.