CHEMICAL SENSING APPLICATIONS OF LUMINESCENT MoS_2 AND WS_2 BASED 2D MATERIALS

A thesis submitted

in partial fulfillment for the Degree of

Doctor of Philosophy

By

NEEMA. P. M

SC15D006

Department of Chemistry

INDIAN INSTITUTE OF SPACE SCIENCE AND TECHNOLOGY

THIRUVANANTHAPURAM

JUNE 2020

ABSTRACT

The enduring interest in miniaturizing silicon-based electronics coalesce with the discovery of graphene has driven the focus of the scientific community toward atomically thin two-dimensional (2D) semiconductors. A total of more than forty layered materials have been isolated with unique and intriguing properties. The emergence of photoluminescence (PL) from nearly atomically thin semiconducting layered materials opened a new way for optoelectronic and chemical sensor applications. MoS_2 and WS_2 are two of the typical transition metal dichalcogenides (TMDs) that gain earnest attention in this regard. Although there was a substantial number of applications, where these nanomaterials have scrutinized, there is still room for exploration in terms of understanding the fundamentals, their intriguing physical and chemical nature, and fabrication of these materials in accordance with the current needs.

We have synthesized a range of nanomaterials based on MoS_2 and WS_2 via an environmentally benign hydrothermal route. A comprehensive morphological and photophysical characterizations of these materials have been performed and demonstrated their chemical sensor applications for the detection of biological, environmental and industrially relevant analyte molecules. The studies conducted using various nanomaterials given in this Thesis is briefed below.

Dopamine is a neurotransmitter in our body and the numerous in-depth study of dopamine and its oxidative pathways exhibited its role in diseases such as Parkinson's, Huntington's and Alzheimer's. Though several strategies are available for the detection of dopamine, a handy tool for its detection without being interfered with molecules such as ascorbic acid, uric acid, etc. are highly appealing. The high quenching efficiency of dopamine and its oxidized products towards the PL emission of an alkaline solution of MoS_2 quantum dots dispersed over nanosheets (MoS_2 QDNS), has been explored and a selective sensor for dopamine has been devised. The Förster resonance energy transfer (FRET), along with the inner filter effect (IFE) play a major role in the quenching and a satisfactory dynamic range of 2.5 nm to 10.4 μM with a calculated limit of detection of 0.9 nM.

Though the optical and electronic properties of MoS_2 has been studied in detail, the chemistry of MoS_2 nanomaterials towards different pH is still blurry and an attempt towards understanding the mechanism of difference in PL emission towards different pH of the solution has been carried out meticulously. It has been observed that, by changing the pH of the MoS_2 QDNS solution from highly alkaline to extremely acidic, the PL emission intensity is found to be plummeted, with the change in color of the solution from light yellow to deep yellow. The emergence of new peaks in the

absorption spectra attests to the formation of new compounds in the solution upon the addition of mineral acids such as H_2SO_4, HCl, etc. for altering the pH. The etching of edge S and subsequent formation of smaller molecules such as NaHS are surmised to be the reasons for color change as well as quenching of fluorescence emission. In the presence of the strong oxidizing agent, H_2O_2, the color of the solution is found to be faded away. From XPS and Raman analysis, it has been hypothesized that the oxidation of NaHS to its colorless $NaSO_4$ is the reason behind this observation, and as the energy transfer pathway established between sensor solution and NaHS has been shut away, the PL emission is found to be recovered. Hence we drafted an indirect turn-on sensing of glucose using acidified MoS_2 QDNS (MoS_2 $QDNS_{ac}$), by incorporating it with glucose oxidize (GOx) enzyme. In the presence of ambient oxygen, GOx can oxidize glucose into gluconic acid and H_2O_2, so an indirect quantitative determination of glucose can be achieved. A satisfactory linear range of 2-90 µM was obtained for glucose sensing with a limit of detection of 0.6 µM. A real sample detection of glucose content in the blood sample of a diabetic patient is accomplished with excellent recovery values.

Apart from MoS_2, we have synthesized nanomaterials of another TMDs material; WS_2 materials with luminescence and utilized them as chemical sensors. Förster resonance energy transfer, together with electron transfer, made WS_2 quantum dots a selective turn-off sensor for the detection of trinitrophenol (TNP); a highly explosive nitroaromatic compound. The sensor operates within a dynamic range of 0.5 to 94.5 µM concentration of TNP, which follows the Stern-Volmer equation. The high selectivity of the sensor towards TNP against chemically similar molecules such as dinitrophenol, dinitrotoluene, etc. was achieved because of the existence of FRET as a major quenching mechanism, against commonly observed electron transfer mechanism.

A turn-on sensor for basic amino acids was designed using highly photoluminescent WS_2 nanosheets obtained by the hydrothermal reaction route. The PL emission of nanosheets (λ_{max}= 452 nm upon λ_{ex} 360 nm), were found to be quenched initially upon the addition of $AgNO_3$. The quenching is followed by a color change of the solution from slightly yellow to turn deep yellow with the advent of a distinct absorption peak near to 400 nm. This inferred the formation of Ag NPs, upon the addition of $AgNO_3$ into a solution of WS_2 NS and was confirmed by TEM analysis. The quenching of PL emission is attributed to the FRET mechanism. The negatively charged Ag NPs were selectively aggregated by using three basic amino acids viz, lysine, histidine and arginine, which can shut the FRET pathway and thus the recovery of PL emission of WS_2 nanosheets. The aggregation of Ag NPs occurs in a sensor solution of pH below the isoelectric points of each amino acids help to discriminate

them. The analytical parameters, dynamic range and limit of detection have been evaluated for the sensor system. Various spectroscopic analyses unraveled the mechanism of the quenching and subsequent recovery.

We demonstrated a simple strategy for the synthesis of luminescent MoS_2 and WS_2 nanomaterials and the utilization of the material for the detection of useful molecules. The fundamental understanding of the materials, mechanism of sensor action and demonstration of real sample analysis would help to extend the use of such materials in chemical sensor technologies.