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Enhancement in the Selectivity and Sensitivity of Ni and Pd Functionalized MoS_2 Toxic Gas Sensors

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Atmospheric pollution is one of the major aspects of concern which led to the research of sensors for the detection of toxic gases. The supreme surface-to-volume ratio makes two-dimensional MoS_2 a promising material to be used as an electronic sensor. Here, we demonstrate the fabrication of a high-performance gas sensor based on atomic-layered MoS_2 nanoflakes synthesized by a facile hydrothermal process. Structural and morphological studies confirmed the formation of few-layered phase pure hexagonal MoS_2 nanoflakes. The results demonstrate that the Pd-MoS_2 layers exhibited a very high relative response to NO gas (700%) at 2 ppm concentration with a minimum NO detection limit of 0.1 ppm and Ni-MoS_2 demonstrated a relative response of 80% towards H_2S gas with a limit of detection of 0.3 ppm with good repeatability and selectivity, owing to the increased adsorption energy of NO on Pd-MoS_2 and H_2S on Ni-MoS_2 through the formation of $PdNO_x$ and NiS_2 complexes respectively. The improved sensing performance of this MoS_2-based sensor also suggests the great potential and possibility of MoS_2 related 2D materials and its combinations for the development of futuristic highly sensitive nanosized gas sensors suitable for anti-pollution automotive system and as volatile biomarkers.

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In the present scenario, detection and monitoring of toxic gases leading to tremendous deterioration of atmospheric environment as a result of industrial and automobile exhausts, increased population, combustion of fossil fuels, excessive use of chemicals in scientific, industrial and agricultural fields, explosives are of great demand for environmental and national security and for a sustainable biosphere. Researchers have studied on a variety of materials such as organic materials (polymers, porphyrins)[1,2] metal-oxides,[3] carbon nanotubes,[4] graphene and based-oxides[5,6] for the sensing of toxic gases such as NH_3, NO_2, NO, SO_2, CO, CO_2, organic vapors etc. NO, being one of the common and toxic air pollutants from automobile exhausts, combustion of fossil fuels, home heaters, furnace exhausts, arc welding, electroplating and power plants. On reaction with chemicals produced from sunlight, NO forms nitric acid which is a major constituent of acid rain and it also leads to the formation of ozone, smog etc. When inhaled by human beings, NO causes severe damage to human respiratory organs and nerves. Apart from this, NO is an abundant and signaling molecule produced in human body having many pathophysiological roles and is detected in the exhaled breaths of humans. The variations in the NO exhalation profile are a significant tool for understanding the normal and diseased functioning of lung and serves as a biomarker for lung diseases and pulmonary inflammations such as bronchial asthma.[7,8] Similarly, H_2S is also identified as an endogenous mediator in human body. Morselli-Labate et al.[9] demonstrated the presence of higher levels of H_2S and NO in the exhaled breaths of chronic pancreatitis.

Currently, owing to the unique physical, chemical, optical and electrical properties, two-dimensional (2D) layered nanomaterials show intriguing prospects for sensor application. Inspired by the enhanced performance of graphene and graphene-based nanomaterials for gas sensing applications because of their high sensitivity, large specific surface area, fast electron transport kinetics and strong surface activities led to increased research efforts on other graphene analogues for efficient and enhanced gas sensing. Also, the main drawbacks of metal oxide-based sensors such as the requirement of high operating temperatures, the easiness to get poisoned under sulfur atmosphere, long recovery periods, limited maximum sensitivity etc. stimulated an extensive research for highly sensitive and portable sensors that require low operating temperatures. Two-dimensional (2D) layered material, MoS_2 have aroused great research interest as a promising gas sensing material due to their high surface-to-volume ratio, high surface activities and sensitivities, fast response time and good stability.[10–13] Especially, the semiconducting nature of MoS_2 with suitable and tunable band gap energies has made it more desirable than graphene-based gas sensors.[14–17]

The direct band gap of MoS_2 is being considerably exploited and extensive theoretical and experimental research investigations are performed on the fabrication of MoS_2 nanodevices. Apart from these, the high surface-to-area ratio of 2D MoS_2 provides new avenues making MoS_2 and its various combinations as excellent sensing materials to various analytes such as NH_3, NO_2, H_2S, NO, humidity, SO_2, H_2 etc. and has been demonstrated by several research groups.[18–24] Yue et al. investigated the adsorption of a wide range of gas molecules such as H_2, O_2, H_2O, NH_3, NO, NO_2 and CO on monolayer MoS_2 using first-principles calculations. They also studied the effect of charge transfer mechanism between the adsorbed molecule and MoS_2 on the application of an external electric field.[25] In order to completely actualize the gas sensing capability of MoS_2, Zhao and co-workers demonstrated the adsorption of various gas molecules including CO, CO_2, NH_3, NO, NO_2, CH_4, H_2O, N_2, O_2 and SO_2 employing the first-principles calculations. It was found that the binding of NO, NO_2 and SO_2 with MoS_2 is the strongest among the other gas molecules.[19] In another report Li et al. fabricated MoS_2 FET devices consisting of single and multilayer MoS_2 films to detect the adsorption of NO and it was found that the multilayer films exhibited high sensitivity to NO with a detection limit of 0.8 ppm.[26] Apart from these, several research works were also performed on MoS_2-based bio and DNA sensors,[27–29] that find potential application as cancer biomarkers.[30,31]

Being a widely studied material for gas sensing applications, ZnO possess large specific surface area, high carrier mobility, non-toxicity, good electrochemical stability etc.[31] Also our earlier report on MoS_2-ZnO has already demonstrated its bio-activity presenting as an effective agent for anti-angiogenesis and anti-cancer theranostics.[32] Moreover, several reports suggest the capability of Pd and Ni to adsorb certain molecules and form complexes leading to improved selectivity. Based on first principle calculations Wei et al.[33] have reported the interaction of H_2S and SO_2 molecule with Ni-MoS_2 surface by strong adsorption energy and has been proposed as a novel gas adsorbent to be used in SF_6-insulated equipment. Reports also suggests the ability of Pd to form complexes such as the

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