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Hierarchical Ultrathin Nanosheet of $Ni(OH)_2$/rGO Composite Chemically Deposited on Ni Foam for NO_x Gas Sensors

P. E. Lokhande,[1, 2, 3,*] Vishal Kadam,[2] Chaitali Jagtap,[2] U. S. Chavan,[3] Udayabhaskar Rednam[4] and H. M. Pathan[2]

Abstract

Hierarchical nanoflower-like Nickel hydroxide/reduced graphene oxide ($Ni(OH)_2$/rGO) was synthesized through the chemical deposition method on Ni foam. The nanoflower-like structure was obtained which comprises ultrathin nanosheets or nano pedals containing porous nanostructure. Further, the addition of rGO enhances the electrical conductivity of synthesized material which is exhaustively exploited during the proton transfer process. The $Ni(OH)_2$/rGO nanocomposite exhibited excellent NO_x gas sensing performance, such as high response time and sensitivity.

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1. Introduction

Economic growth and continuous industrial development consume fissile fuel as the main source of energy, other than this automobile sector use majorly organic fuel like diesel or petrol.[1] The consumption of such fossil fuel generates exhaust pollutant gases such as NO_x, H_2S, NH_3, Cl_2, *etc*. in the atmosphere.[2] Among these gases, NO_x is the most noxious, poisonous, and abundant air pollutant, which is the main content of producing acid rain, the responsible factor to form photochemical smog and O_3 consumption in the atmosphere.[3,4] Further, NO_x gases badly affect human health such as nose and throat discomfort, eye irritation, transient cough, *etc*.[1] In that context, detecting such hazardous gas at ppm level has become important research to protect human health and the environment. The development of portable gas sensors has received much attention over the last two decades for the detection of harmful and toxic gas.[1]

Metal oxide like Zinc Oxide (ZnO),[5] Tin Oxide (SnO_2),[6] Titanium Oxide (TiO_2),[7] Tungsten Oxide (WO_3)[8] and Chromium Oxide (Cr_2O_3)[9] generating considerable interest towards detection of NOx gas. Though these materials render high and rapid response but such devices work at elevated temperatures or require doping of noble metals. In addition to this, the expensive price of such materials restricts their utilization in the development of efficient sensor materials. Hence, great efforts have been taken to develop NO_x sensors that can operate at room temperature with excellent performance at a lower cost.[4] Researchers addressed this problem by using $In(OH)_3$, $Ni(OH)_2$, and conductive polymers as NO_x gas sensors, which can operate at room temperature. Xu *et al.* synthesized non-single crystal cubic $In(OH)_3$ with porous structure through the hydrothermal method.[4] Such porous $In(OH)_3$ was investigated for the gas sensor at room temperature and found great reliability and high sensitivity. Wang *et al*. prepared 3-dimensional (3D) flowerlike α-$Ni(OH)_2$ via a one-step method, which is composed of a thin nanosheet and contains ultrafine nanoparticles.[10] The research work focused on the relation between porosity and diffusion that is adsorption/desorption of NO_x on the surface of α-$Ni(OH)_2$ and the effect of chemical composition on proton transportation between adjacent NiOH layers. The gas sensing results obtained at room temperature for α-$Ni(OH)_2$ not only display excellent gas sensing properties but also good repeatability and longer service life. The performance of metal oxide material is further enhanced by preparing a composite with a carbon-based material such as graphene, carbon black, *etc*., and selecting the proper substrate material. Yang *et al*. developed a composite to room temperature gas sensor based on α-$Ni(OH)_2$ TNS/rGO composite material.[3] As compared

[1] *Department of Mechanical Engineering, Sinhgad Institute of Technology, Lonavala- India-410401.*
[2] *Advanced Physics Laboratory, Department of Physics, Savitribai Pule Pune University, Pune- India 411007.*
[3] *Depearment of Mechanical Engineering, Vishwakarma Institute of Technology, Pune, India 411037.*
[4] *Instituto de Investigaciónes Científicas Y Tecnológicas (IDICTEC), Vicerrectoría de Investigación Y Postgrado, Universidad de Atacama, Avenida Copayapu, 485 Copiapó, Chile.*
**Email:* prasadlokhande2007@gmail.com (P. E. Lokhande)

to bare α-$Ni(OH)_2$, the composite of $Ni(OH)_2$ with carbon-based materials demonstrated excellent NO_x gas sensing performance with a low detection limit of 970 ppb and with high response and fast response at room temperature.

In this report, we the first time developed an electrode for a gas sensing device working at room temperature by direct chemical deposition of $Ni(OH)_2$/rGO on a conductive Ni foam substrate. The synergetic effect of rGO and $Ni(OH)_2$ enhances the electric conductivity and specific surface area. The prepared composite material delivered excellent gas sensing performance for NO_x gas.

2. Experimental

The graphene oxide was synthesized from graphite powder by using the modified hummer method. The composite Ni(OH)2/rGO was prepared through the chemical deposition method proceeds as follows:[11] 1M $Ni(NO_3)_2.6H_2O$ as a source of nickel was dissolved in 40 ml deionized water under continuous magnetic stirring followed by the addition of precipitation agent 2 M HMT in this solution and stirred for 10 min. Another solution of 10 mg rGO in 10 mL water was prepared through ultrasonication. After that nickel salt solution was added to the rGO solution under magnetic stirring for 30min. The cleaned Ni foam (3 × 2 cm) was inserted into the above solution. The beaker of this solution was covered with aluminum foil and kept in an electric oven for 4 hrs at 90 °C. After that $Ni(OH)_2$/rGO deposited pieces of nickel foam washed with ethanol and DI water twice. Finally, pieces of Ni foam dried overnight in an electric oven at 60 °C.

The $Ni(OH)_2$/rGO deposited on Ni foam was used as an electrode for gas sensing detection and electrode spacing was 20 µm. The sensor was installed in a gas chamber with having inlet and outlet. The test was performed at room temperature. Before the test started chamber was flushed with fresh air to remove contaminants in a gas chamber. The NO_x gas was inserted into the chamber in a specific amount by using the syringe. As gas comes in contact with the electrode, the change in resistance was automatically recorded in homemade automatic resistance apparatus. The further gas chamber was purged with air to recover the sensor resistance. The sensitivity for the sensor is defined using the following equation:

$$\frac{R_N - R_0}{R_0} \quad (1)$$

where R_N is the resistance in NO_x gas and R_0 is the sensor resistance in the air. The response time is defined as after the test gas is inserted, the time required for variation in resistance to reach 85% of the equilibrium value.

3. Result and discussion

To investigate the crystallographic structure and composition of prepared $Ni(OH)_2$/rGO composite, the X-ray diffraction (XRD) technique was adopted and the obtained results have been demonstrated in Fig. 1. The diffraction peaks at 2θ = 26°, 34° and 61° indexed to the plane (002), (101) and (110), respectively. The broad and weak diffraction peak at 2θ = 26° demonstrates the presence of graphene oxide while the other two high-intensity peaks arise due to the $Ni(OH)_2$. The XRD pattern indicates that the formation of α-$Ni(OH)_2$ hexagonal structure is well grown on an exfoliated graphene sheet. The remaining three high-intensity peaks were generated due to the substrate material Ni foam.

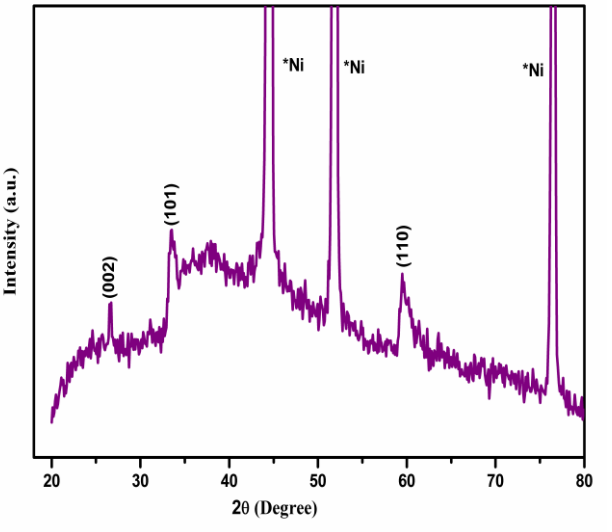

Fig. 1 XRD patterns of $Ni(OH)_2$/rGO nanosheets deposited on nickel foam

The morphology of the prepared composite material was investigated by using scanning electron microscopy (SEM)

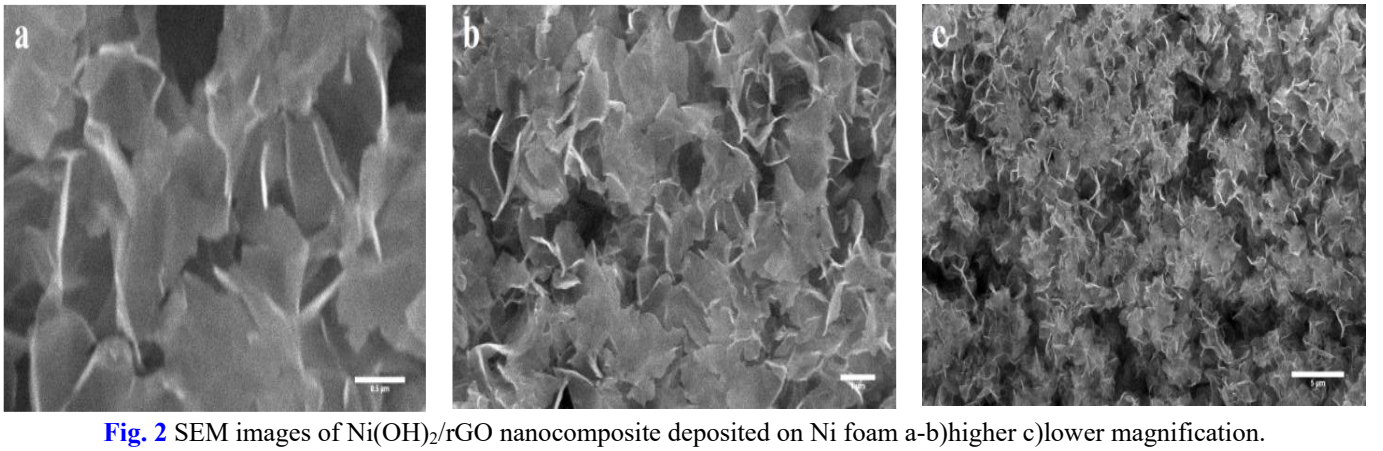

Fig. 2 SEM images of $Ni(OH)_2$/rGO nanocomposite deposited on Ni foam a-b)higher c)lower magnification.

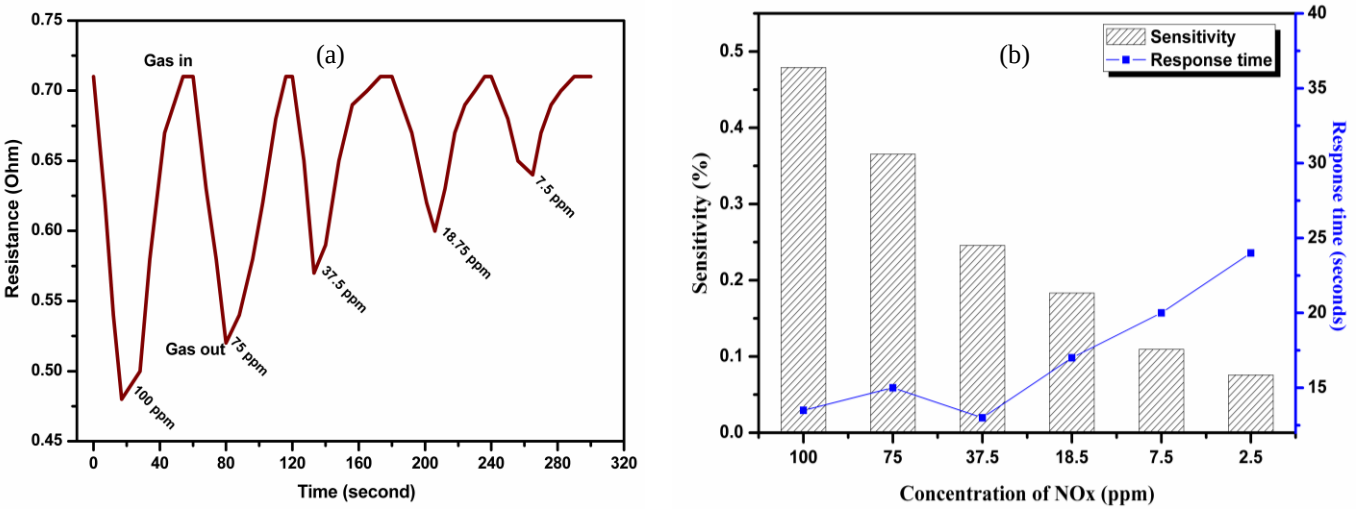

Fig. 3 a) Dynamic response–recovery curves b) sensitivity and response time curves of the $Ni(OH)_2$/rGO sensor to 100 ppm–7.5 ppm NO_x at room temperature in air.

techniques. As shown in Fig. 2, SEM images of $Ni(OH)_2$/rGO composite at various magnifications. The morphology of prepared material consists of ultrathin nanosheets connected to each other, forming a nanoflower-like structure of α-$Ni(OH)_2$ uniformly loaded on rGO. The nanosheets connected to each other increase porosity and enhance gas adsorption, dispersion, and desorption channels. The average thickness of nanosheets is 40 to 50 nm. The electrochemical performance of $Ni(OH)_2$/rGO composite mainly depends on the charge transfer capability of this material. Gas sensors are working on the principle of variation in the conductance of sensing material when they are exposed to a certain gas atmosphere.

The interface of $Ni(OH)_2$/rGO will generate *p-p* heterojunctions. The $Ni(OH)_2$ is the p-type semiconductor having band gap energy ranges from 3.04 to 3.06 eV. Due to the major proportion being $Ni(OH)_2$ in composite, hence it may presence of *p*-$Ni(OH)_2$/*p*-rGO heterojunctions, and it was responsible for generating depletion region, decreasing conduction and thus sensitivity increment.[12] The prepared sample of $Ni(OH)_2$/rGO has great significance as a gas sensor; therefore gas sensing performance of this sample was investigated to NO_x at room temperature. In Fig. 3, a few cycles of the gas response of an α-$Ni(OH)_2$/rGO composite deposited on Ni foam during the cyclic exposure of NO_x gas concentration ranging from 100 to 7.5 ppm. Fig. 3a demonstrates the response-recovery curve for the prepared sample of $Ni(OH)_2$/rGO has great significance as a gas sensor; therefore, the gas sensing performance of these samples was investigated to NO_x at room temperature. Fig. 3a demonstrates the response-recovery cyclic curves of a sensor as a varying concentration of NO_x. Once NO_x was introduced into a gas chamber, the resistance of $Ni(OH)_2$/rGO composite declined rapidly and reaches the minimum value within a short time. The relation between sensitivity and response time at different NO_x concentrations is displayed in Fig. 3b. When exposed NO_x is 100 ppm, the response time calculated is 7 s while the highest sensitivity reaches 48%. The response of $Ni(OH)_2$/rGO composite was observed at 8, 11, 18, 25, 37, and 48% for NO_x concentrations of 7.5, 18.75, 37.5, 75, and 100 ppm. As the concentration of NO_x decreases sensitivity goes on decreasing. The lower concentration of NO_x covers a lower surface area of the electrode and hence less interaction between deposited composite material and gas molecule.[2]

The probable mechanism has been proposed for change in resistance. When the composite material is exposed to the NO_x gas, the ultrathin nanosheets of $Ni(OH)_2$ act as the reaction center where it catalytically reacts with NO_x gas molecules. The adsorption of NO_2 and NO on the surface of composite material leads to the formation of NO_2^- and NO^- and this process traps electrons from the conduction band or donor level of the sample, resulting in the increase of hole density. Finally, the results of the process are a rapid decrease in resistance. The gas-sensing reactions are given below:

$$O_2 + e\text{-} \rightarrow O^{2-} (2O^-) \quad (2)$$

$$NO_x + e \rightarrow NO_x^- \quad (3)$$

$$NO_x + O^{2-} + 2e \rightarrow NO_{x+1}^- + O^- \quad (4)$$

The superior gas sensing property of $Ni(OH)_2$/rGO composite is due to complementary and synergetic effects between both and also the synergism of the higher conductivity of the composite.

4. Conclusions

In the summary, the nanostructured $Ni(OH)_2$/rGO composite was successfully deposited on Ni foam by a chemical deposition method for gas sensor application. Synthesized ultrathin nanosheets of $Ni(OH)_2$ on the rGO sheet showed an excellent sensing property to NO_x with the highest sensitivity of 48% at 100 ppm NO_x concentration and a response time of that 7 seconds. Therefore, prepared composite material exhibits excellent sensitivity and fast response, which opens a new window to develop an advanced portable electronic device to detect hazardous gases.

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Conflict of Interest
There is no conflict of interest.

Supporting Information
Not applicable.

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