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Research Article

Quantitative Detection of Ammonia Gas Via V_2O_5 Metal-Oxide Based Sensor Combining with Regression Model

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Abstract

In this proposed work, nanoparticles of vanadium pentoxide (V2O5) and vanadium pentoxide with rGO have been fruitfully synthesized through a suitable hydrothermal method at a constant temperature (180○C).As synthesized V2O5 nano particles were characterized, and fabricated as a gas sensor by coating the synthesized material on ITO glass substrate. The NH3gas sensing properties of the fabricated sensors were carried out. Structural investigation of the same showed that V2O5 nanoparticles formed have orthorhombic crystal phase and the size of the nanorods was found to be 90 nm. The gas sensor studies revealed a higher sensing response at 2500C and demonstrated excellent gas sensing properties toward 1-3.2 ppm NH3 gas. It also exhibited a good selectivity, sensitivity and stability, with rapid response/recovery time, and a linear relationship between the response and the target gas concentration. In particular, the sensing performance of the V2O5 gas sensor was trained through MATLAB for regression analysis, which suggests the permissible R2 value of 0.88 of a prompt gas sensing response.

Keywords: Gas Sensors; Nano Materials; Gas Chamber

Introduction

Nanomaterials in the recent days have invaded into every walk of life. Almost all the bulk materials have been minimized to the nano level for exploring their unique properties and behavior in the extreme environments. Semiconducting materials, some of the metal oxides, polymers, etc., have been investigated for various applications from a small sensor to large super capacitors [1]. Semiconductors which have been synthesized as nanomaterial based sensor have the limitations of selectivity and sensitivity. Also since the metal oxides are cheaper and easily available, they are preferred for semiconductors in gas sensing applications. Some of the conductometric sensors are usually based on metal oxide semiconductors [2]. Among the various metal oxides, vanadium pentoxide is a promising material in terms of cost and availability [3]. Vanadium pentoxide is the most stable and widely available compound and hence it finds wide applications in the areas of energy storage as cathode/anode material, catalysis, sensing of various harmful gases, supercapacitor, redox batteries etc. They possess exceptional electrical and conducting property, which makes them suitable for gas sensing applications. Being a transition metal, it has $3d^3\ 4s^2$ electrons in the outer shell with 2^+, 3^+, 4^+ and 5^+ oxidation states. This makes it a complex and an interesting material. Vanadium pentoxide can be synthesized in various ways like physical route, wet chemical route, solvothermal method, hydrothermal method, thermal evaporation, pulsed layer deposition, etc. A number of nanostructures synthesized with Vanadium pentoxide has been reported like nanoflowers, nanobelts, nanorods, nanowires, etc.

During the past decade, efforts are being made to increase the sensitivity and reduce the response and recovery time of these vanadium pentoxide based ammonia gas sensors. There are several study reported with focus on the miniaturization, doping with other materials for improved conductivity, addition of catalysts, which can aid the adsorption of gas molecules at room temperature, overall reduction of power dissipated by providing micropores for the sensors after fabrication. Although Vanadium pentoxide gas sensors have been reported with good sensitivity, selectivity and fast recovery time, the higher temperatures pose a problem for the shelf life of the sensor. Also, the physical experimentation with ammonia gas would pose hazards to the lay person involved with the testing of such type of sensors. In such a scenario, simulation of the experimental set up and prediction are given utmost importance [4]. Machine Learning (ML) is applied globally in real time applications and predictions. The essence of using such algorithms is that all the points set are situated in a low-dimensional compound and they can be trained for further analysis and investigations especially in the tiny world. In these considerations, ML can help bridge the gap between theoretical and experimental design with respect to synthesis, characterization and modelling [5]. The gas sensing system is one of the applications which aims to sense the target gas based on the previously collected large data and gives an alert in anonymous conditions [6]. The main aim of machine learning is to predict the missing data or forecast the variance of output with reference to the input material used [7]. Thus in a nano world, various parameters are considered for performing the analysis and implement them practically. The working of the gas sensing system can be modelled and simulated by many other ways like modelica, e-sim, comsol [8], ANN and machine learning methods. The first three methods are traditional methods with non-scalable and changing environmental conditions. Machine learning method can be done under two categories- supervised and unsupervised. Supervised method is more vigorous and can be used for applications like gas sensors.

In this paper, we present the synthesis and fabrication of Vanadium pentoxide with rGO for sensing ammonia gas. This sensor dataset consists of many types of atmosphere properties like temperature, concentration, pollutant gas, time, voltage, resistance, current, etc. These data sets are collected by thin film sensors, which are fabricated using spin coater and tested in the lab under real time environment.

Experimental setup

Preparation of V_2O_5 and V_2O_5-rGO nanoparticles

Preparation of V_2O_5 and V_2O_5-rGO Nanoparticle has been synthesized by hydrothermal synthesis using ammonium metavanadate as starting materials at 1800C in a muffle furnace. The main reason for employing hydrothermal synthesis is that the product formed have metastable phase and have unique condensed phase [9]. The stoichiometric ratios of the precursor solution was taken with varying concentration of V_2O_5 and V_2O_5 with rGO. The solution was stirred on a magnetic stirrer for 1 hour at room temperature until the solution becomes homogeneous. After 1 hour, the whole homogeneous mixture was transferred into a Teflon lined stainless steel autoclave and heated in muffle furnace at 1800C for 2h. After cooling, resultant products were separated by centrifuge and washed several times with DI water and enthanol to remove impurities.

Instrumentation and characterization

The prepared vanadium pentoxide nano powders have been characterized by standard spectroscopic techniques such as UV-vis spectrometer (Agilent technology Cary Eclipse), X-Ray diffractometer with Rigaku Smart Lab and finally FESEM to observe the morphology and size of the prepared samples.

Material fabrication and sensor testing

Prepared samples of V_2O_5 and V_2O_{5-}rGO nanoparticles were dried in vacuum at room temperature for 24 hours. Vanadium pentoxide thin films were deposited onto ITO substrate for electrical characterization and sensor measurements by means of spin coating.

The building method of the gas sensor is as under

- The as-organized gas sensing material was mixed with ethanol at a weight ratio of 5:1 and this solution was ultrasonically perturbed for 15-20min until a consistent slurry was formed.

- The slurry was coated on ITO substrate and later Ag electrodes were marked for electrical measurements using 2 probe measurement system.

Figure 1 demonstrates the circuit used to measure the gas sensor, Rf is a load resistor connected in series with the gas sensor and Rs denotes the resistance of the sensor.

In the testing process a suitable bias voltage (Vworking = 1V) was applied. The sensor response was measured by monitoring the current (Ioutput) through RF. The sensitivity(S) of the sensor is defined as S=Ra/Rg for reducing gases and S=Rg/Ra for oxidized gases, where Rg and Ra are the resistance of the sensor measured in the target gas and in air respectively. The sensor was thus fabricated and was setup in the testing chamber connected to the gas sensing and measurement unit (Keithley). The temperature and humidity of the chamber was maintained at 250Cand 50% respectively. The concentrations of NH3 testing gas mixed with air were controlled via mass flow controllers.

The sensor response for every 10 minute pulses of NH_3 in concentrations ranging from 3.1 ppm to 0.5ppm was observed. Carrier gas of 20% O_2 in presence of NH_3 was passed through the chamber and temperature was increased [10]. Optimization of concentration of the gas and temperature was done by trial and error and suitable operating point for sensing NH3 gas was found to be 2 ppm and 2500C. The gas sensor setup is shown in figure 1.

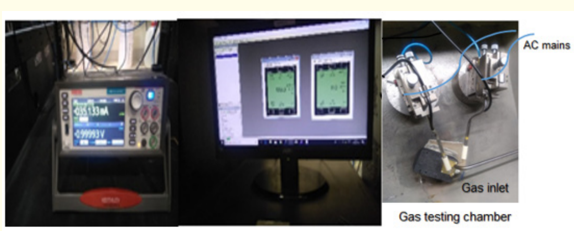

Figure 1: Gas sensor setup for testing of NH_3 gas.

Results and Discussions

XRD analysis

XRD studies were performedto determine the crystal structure of the synthesized nanoparticle. The XRD patterns in figure 2 shows sharp peaks for (2 0 0), (0 0 1), (1 0 1), (1 1 0), (4 0 0), (01 1), (3 10) and (0 0 2) diffraction planes, which are in agreement with rhombohedral structure (JCPDS card no: 09-0387) of the V_2O_5 phase. The V_2O_5 shows several reflections corresponding to the (200), (001), (101), (110) and (310) planes of V_2O_5 with orthorhombic structure (JCPDS no. 41-1426). No impurities were found in this sample. The V_2O_5-rGO composite present the characteristic peaks of V_2O_5 phase, exhibit a (001) reflection peak of graphene at 26°, which suggests that presence of graphene sheets in the composite.

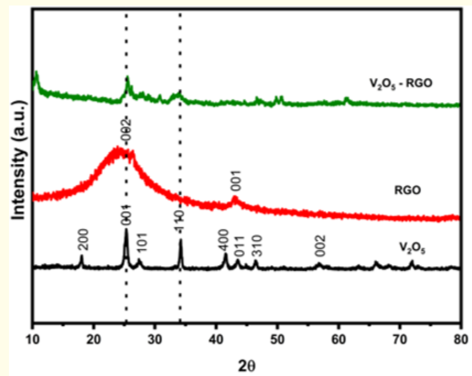

Figure 2: XRDpattern of a) V_2O_5, b) rGO c) V_2O_5-rGO nanocomposite.

SEM analysis

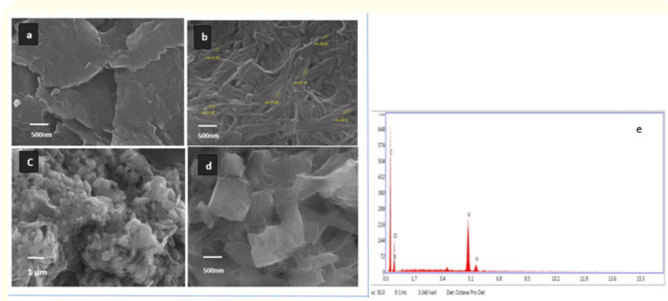

Figure 3: (a) SEM image of rGO, (b) SEM image of vanadium pentoxide (c-d) SEM image of vanadium pentoxide with rGO nanocomposites (e) EDS of vanadium pentoxide with rGO nanocomposites.

Figure 3 presents morphology of both V_2O_5 and V_2O_5-rGO nanocomposites samples. Figure 3a represents 1 D nano structure of rGO nanosheets, figure 3b represents nanostructure of bare vanadium pentoxide and figure 3c-drepresents the combined nanostructure of V_2O_5 with rGO in the ratio 3:1 for low magnification and higher magnification. Figure 3e represents EDS studies which showed the presence of Graphene Oxide and Vanadium Pentoxide. From the figure 3a it is observed that rGO samples showed sheet like morphology. Figure 3b shows that V_2O_5 nanoparticles with 1D rod like morphology. Figure 3c-d presents morphology of V_2O_5-rGO compound where it is observed that V_2O_5 nanoparticles homogeneously wrapped with rGO sheets.

Electrical properties

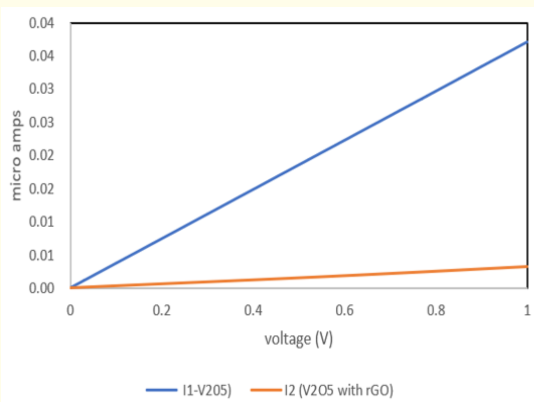

Figure 4: I-V characteristics of V_2O_5 and V_2O_5 with rGO.

The I-V characteristics of V_2O_5 and V_2O_5-rGO composite is shown in figure 4. The resistivity of the samples are 2.5MΩ and 312.5kΩ respectively. The I-V characteristics shows that the material is suitable to operate as a gas sensor.

Gas sensing characteristics

The response of the sensor to NH_3 gas is shown in figure 5 a. The response of the material to ammonia gas was thus found. After several trials, the optimum temperature of the vanadium pentoxide and vanadiaum pentoxide-rGO nanocomposite was found to be 250^0C. In the majority of the thin films, resistivity decreased each time the gas was injected. This is one indication that the thin film is possibly behaving as a p type semiconductor. Also at temperatures above 200^0C, the resistivity thin films increased rapidly, indicating the transition of metal to insulator. Figure 5 b shows the response of the gas sensor for varying temperatures starting from 75^0C to 350^0C. The vanadium pentoxide-rGO nanocomposite showed a slight increase in the resistivity at a temperature of 250^0C. This indicates that the material behaves as a n type semiconductor. Also, the gas detection limit of the thin films is 2ppm.

Regression analysis

In general, regression analysis is done for analysing two or more variables. Regression includes dependent variables and other variables which gives the analysis and behaviour of the parameters within the environment [11]. Other than the regression analysis, support vector machine (SVM) is also used in the gas sensor analysis for variants of gases and their concentration. During the last decade, studies are being carried out in the direction of optimising the gas sensor towards sensitivity, selectivity, correlation between different gas sensors, and other infinite characteristics. All the analysis pertaining to classification and regression are reported in some of the papers, but liner regression for one type of gas sensing and optimisation is not reported.

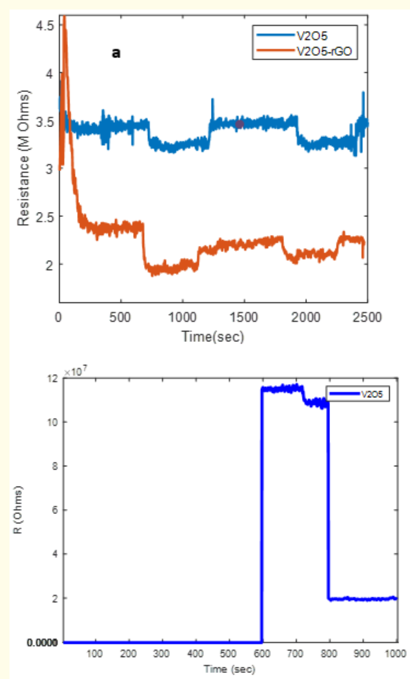

Figure 5: a) Response of R Vs T for nanostructures of V_2O_5 and V_2O_5 -rGO composite. b) Response of the sensor for 2 ppm ammonia gas for varying temperatures.

The behaviour of V_2O_5 gas sensors towards different levels of ammonia were further investigated [12]. The concentration of Ammonia gas was varied from 3.1ppm to 0.5 ppm. Figure 6 shows the gas sensor response for various samples. Linear regression model of Machine learning techniques were applied to the sensor data to correctly assess the overall sensor performance of the materials. A high level of accuracy was achieved in determining the class of gas observed. Besides the results, figure 6 (a) demonstrated linearity between the temperature and resistance for the correlation.

Where y is the temperature and x is the resistance; the regression coefficient is 0.8836 [13].

The Receiver Operating Characteristic (ROC) curve associates the probability of temperature and the Probability of resistance variation. For a given detection threshold, the pair (T, R_{GO}) defines performance. This pair can be considered as coordinates of a point in R^2 (square integrable space of real numbers) with axes representing T and R_{GO}. Let us consider that axes takes values in the range [−∞; +∞], these points belong to a curve called Receiver Operating Characteristic (ROC) which is a parametric curve with the parameter [14]. The ROC curve plotted on Figure 6 corresponding to normal distributions. The "best" curve in Figure 6 is from 250 inputs. As the number of input variables decreases, the curves get "worse," which is an indication of loss of discrimination capability as variables are discarded from the original input set. Furthermore, a parametric representation for the curves is more natural since ROC curves need not be functions. In this figure polynomials series upto 4 has been considered to ROC data with the end-point constraint. Polynomial representations provide us a way of computing derivatives at various locations of the ROC curve, which are necessary in order to find the optimal operating points. The sensor was optimized at 250⁰C for ammonia concentration of 2 ppm. These data were validated, supervised and trained for regression model and the R^2 value was found to be 0.88. This value denotes the closeness of the data to the predicted model.

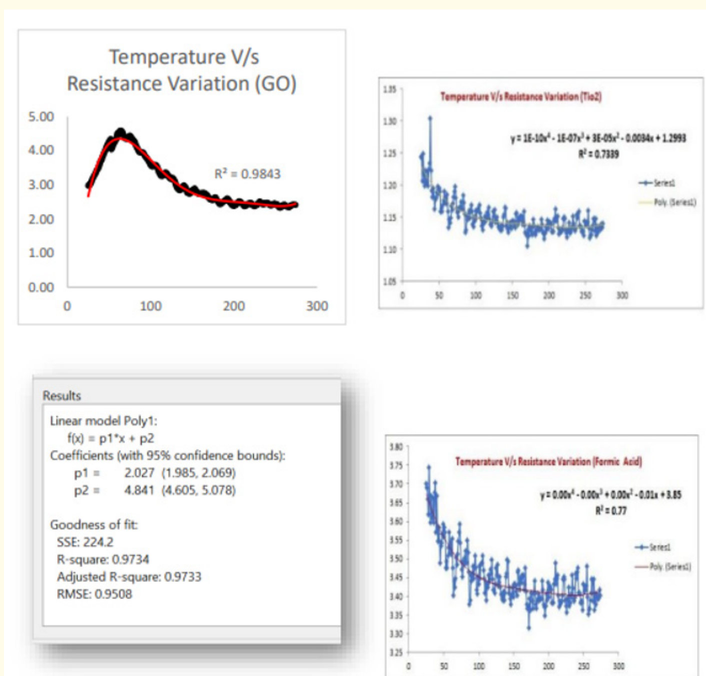

Figure 6: Gas sensing properties of the V_2O_5 nanostructures gas sensors for different concentrations of NH3 gas: (a) Resistance variation of V_2O_5 nanostructures with rGO, (b) Resistance variation of V_2O_5 nanostructures (c) linear regression colinear graph (e) coefficients with 95% bounds.

Conclusions and Predictions

V_2O_5 nanostructures sensing material was synthesized and an NH_3 sensor was fabricated. The gas sensing performance of both V_2O_5 and V_2O_5-rGO were studied. The results were that the characterization displayed the different nanostructures under varying environments. The fitting quality might be improved when this kind of multiple regression is considered. The inclusion of additional variables would be more beneficial in calculating the R^2 value. Regression models proved to be more effective in the selection of signals from sensors for training. To sum up the entire activity, the regression analysis showed that the raw signals have to be attuned to obtain outputs matched with reference devices. It can be used for the modification of calibration equation for data validation and data processing.

About the Authors

Vinutha Srikanth is working as Assistant professor in the department of Electronics and communication engineering at RVITM, Bangalore. She has more than 20 years academic experience with 3 years research experience. She is working in the area of nano gas sensor and energy storage. She had been selected for Indian National Users Program (INUP) at IISc, Bangalore. Field of interest includes Analog Electronics, Power Electronics, Basic Electrical Engineering, Design thinking and Electronic Devices

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