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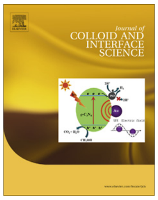

# Superior selectivity and enhanced response characteristics of palladium sensitized vanadium pentoxide nanorods for detection of nitrogen dioxide gas

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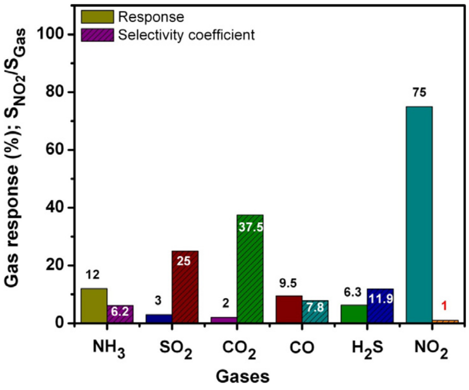
## GRAPHICAL ABSTRACT



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## ABSTRACT

Vanadium pentoxide ($V_2O_5$) nanorods have been deposited onto the glass substrates by spraying 75 ml of 30 mM vanadium trichloride ($VCl_3$) solution at optimized substrate temperature of 400 °C. The XRD study confirms the formation of orthorhombic crystal structure of $V_2O_5$ nanorods. The FE-SEM micrograph shows the nanorods-like morphology of $V_2O_5$. The presence of palladium (Pd) in the Pd-sensitized $V_2O_5$ nanorods is confirmed using EDAX study. The gas sensing measurements show that the Pd-sensitized $V_2O_5$ sensing material is an outstanding candidate for nitrogen dioxide ($NO_2$) gas detection. Obtained results demonstrate that the Pd-sensitized $V_2O_5$ nanorods show the superior selectivity for $NO_2$ gas in comparison with other gases such as $NH_3$, $H_2S$, CO, $CO_2$ and $SO_2$ at an operating temperature of 200 °C. It shows the 75% response for 100 ppm $NO_2$ gas concentration with response and recovery times of 22 s and 126 s, respectively. Finally, the gas sensing mechanism based on chemisorption process is proposed to illustrate how Pd nanoparticles affect the gas sensing characteristics (response and response-recovery times).

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## 1. Introduction

Recently, the increasing industrial processes involve the use and manufacture of highly dangerous substances with the escape of hazardous gases which create a potential hazardous effect on the industrial plant, health of its employees and people living nearby [1]. The problem of environmental pollution due to emissions of especially nitrogen oxides ($NO_x$) by various combustion processes remains serious because it is the source of acid rain, photochemical smog and global warming. The $NO_x$ group contains highly reactive gases such as nitric oxide (NO) and $NO_2$ which causes the serious damage of lung tissues and respiratory diseases such as emphysema and bronchitis [2]. Therefore, different government agencies all over the world have regulated and limited the concentration of $NO_x$ emissions in air by imposing legal controls on the emissions from automotive and industrial plants [3]. To detect hazardous gases causing the bad effects on human health, the gas sensors are very important for monitoring the gases present in the environment. The use of gas sensors alarms us to prevent the accidents due to gas leakages, thereby saving lives and equipments. Hence, there is a great need of developing the simple, low cost and reliable gas sensors [4]. The detection and monitoring of hazardous gases below the lower explosive limit (LEL) is important in different fields such as industrial emission control, vehicle emission control, household security and environmental monitoring [5]. The advantages of nanostructured metal oxide semiconductor (MOS) thin films for their use in gas sensor application involve the high surface area to volume ratio, short response-recovery times, smaller size, smaller amount of sensing material with high sensitivity, low cost, on-line operation and high compatibility with microelectronic processing [6,7].

Recently, considerable efforts have been concentrated on improving the sensor response and selectivity. The higher response usually enhances the detection limit while a better selectivity enables the response of gas sensor to a certain target gas among the mixture of gases. An effective method for developing an enhanced gas sensor with excellent performance is to introduce the noble metal nanoparticles into the sensor support materials [8]. The sensitization of MOS with noble metal nanoparticles increases the sensitivity, stability and lower operating temperature of the sensor with less power consumption [7]. Pd is used as a star catalyst for a series of chemical reactions. The Pd nanoparticles increase the response of MOS in two possible sensitization mechanisms: an electronic (work function) sensitization mechanism and a chemical (catalytic) sensitization mechanism. In electronic sensitization mechanism, gas molecules do not interact directly with the MOS surface but the gas adsorption occurs on Pd metal nanoparticles. When gas molecules are chemisorbed on the Pd nanoparticles, their electronic density and oxidation state changes which affect on their work function. These facts modify the electron exchange properties between the Pd nanoparticles and the MOS surface and hence, the electronic conductivity in the MOS changes. Thus, in electronic sensitization mechanism, the sensitization is promoted by direct exchange of electrons between the MOS and the Pd nanoparticles [9]. In chemical sensitization mechanism, gas molecules chemisorbed on the surface of Pd nanoparticles get dissociated into separate atomic species. These dissociated species spill-over on the MOS surface and changes the conductivity of MOS. The adsorbed species act as donors or acceptors to induce depletion layer and react with the lattice atoms to alter the stoichiometry of the film. Thus, the chemical sensitization mechanism is mediated by a spill-over process of gas molecules from the surface of Pd nanoparticles to the surface of MOS [10].

In the present work, $V_2O_5$ nanorods have been successfully deposited onto the glass substrates using chemical spray pyrolysis (CSP) deposition method at optimized substrate temperature of 400 °C. The structural and surface morphological characterization of these nanorods is studied using X-ray diffraction (XRD) and field emission-scanning electron microscopy (FE-SEM), respectively. The chemical dip and dry method is used for Pd-sensitization on the spray deposited $V_2O_5$ nanorods. Finally, effect of Pd-sensitization on the gas sensing properties of $V_2O_5$ nanorods is studied at different operating temperatures and $NO_2$ gas concentrations. The present sensor exhibits significantly the high selectivity towards $NO_2$ gas in comparison to other gases including $NH_3$, $H_2S$, CO, $CO_2$ and $SO_2$.

## 2. Experimental details

The 75 ml of 30 mM $VCl_3$ solution was prepared by dissolving 0.32 g of $VCl_3$ powder in double distilled water (DDW) and then sprayed onto the glass substrate at optimized substrate temperature of 400 °C. The optimized spray parameters such as spray nozzle to glass substrate distance of 27.5 cm and solution spray rate of 1.5 ml/min with air as carrier gas were kept constant during the deposition process. The mechanism of $V_2O_5$ nanorods formation using CSP deposition method is reported in our previous report [11]. The palladium chloride ($PdCl_2$) powder procured from S. D. Fine Chemicals Limited, Mumbai was used for preparation 10 mM $PdCl_2$ solution by dissolving it in cold 20 ml DDW. For Pd-sensitization on the $V_2O_5$ nanorods, the chemical dip and dry deposition method was used. In this method, $V_2O_5$ nanorods were dipped into the 10 mM $PdCl_2$ solution for 2 min. and then dried at room temperature. The Pd-sensitization on the $V_2O_5$ nanorods was done for 10 and 20 dipping cycles of deposition. Finally, the Pd-sensitized $V_2O_5$ nanorods were annealed at 200 °C for two hrs to remove the chloride from the deposits. However, the better response was observed for Pd-sensitized $V_2O_5$ nanorods of 10 dipping cycles, so the results of the same have been discussed here.

The $V_2O_5$ film thickness measurement was carried out using Ambios, XP-I stylus surface profiler, USA. The structural characterization of spray deposited $V_2O_5$ nanorods was carried out using X-ray diffractometer (Bruker, D2 phaser, USA) with Cu $K_\alpha$ radiation of wavelength 1.5406 Å. The surface morphology of $V_2O_5$ material was carried using FE-SEM (Tescan, Mira-3, Brno-Czech Republic). The surface compositional analysis of Pd-sensitized $V_2O_5$ nanorods was studied using FE-SEM equipped with an energy dispersive X-ray analysis (EDAX). The Pd-sensitized $V_2O_5$ nanorods were used for gas sensing measurements with silver paste as electrodes. The gas response of Pd-sensitized $V_2O_5$ nanorods for oxidizing gases ($NO_2$, $SO_2$ and $CO_2$) and reducing gases ($H_2S$, CO and $NH_3$) was calculated using the formula:

$$\text{For oxidizing gas, } S(\%) = \frac{|R_g - R_a|}{R_a} \times 100\% \qquad (1)$$

$$\text{For reducing gas, } S(\%) = \frac{|R_a - R_g|}{R_g} \times 100\% \qquad (2)$$

where $R_a$ and $R_g$ are the resistances of Pd-sensitized $V_2O_5$ nanorods in presence of air and target gases, respectively. To evaluate the selectivity of Pd-sensitized $V_2O_5$ nanorods, the gas responses were tested towards 100 ppm concentration of various gases such as $NH_3$, $H_2S$, CO, $CO_2$, $SO_2$ and $NO_2$ at an operating temperature of 200 °C. The selectivity coefficient (K) of the sensor was then calculated using the formula:

$$K = \left|\frac{S_t}{S_i}\right| \qquad (3)$$

where $S_t$ and $S_i$ are the sensor responses towards target and interfering gases, respectively. The effect of Pd-sensitization on gas sensing properties of $V_2O_5$ nanorods was studied at different