Improvement in NO$_2$ Gas Sensing Properties of Semiconductor-Type Sensors by Loading Pt into BiVO$_4$ Nanocomposites at Room Temperature

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Abstract: In the present study, we report the first attempt to prepare a conducive environment for Pt/BiVO$_4$ nanocomposite material reusability for the promotion of sustainable development. Here, the Pt/BiVO$_4$ nanocomposite was prepared using a hydrothermal method with various weight percentages of platinum for use in NO$_2$ gas sensors. The surface morphologies and structure of the Pt/BiVO$_4$ nanocomposite were characterized by scanning electron microscope (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). The results showed that Pt added to BiVO$_4$ with 3 wt.% Pt/BiVO$_4$ was best at a concentration of 100 ppm NO$_2$, with a response at 167.7, and a response/recovery time of 12/35 s, respectively. The Pt/BiVO$_4$ nanocomposite-based gas sensor exhibits promising nitrogen dioxide gas-sensing characteristics, such as fast response, highly selective detection, and extremely short response/recovery time. Additionally, the mechanisms of gas sensing in Pt/BiVO$_4$ nanocomposites were explored in this paper.

Keywords: NO$_2$; gas sensors; Pt/BiVO$_4$; nanocomposite

1. Introduction

Nitrogen dioxide (NO$_2$) emissions are largely the result of fossil fuel combustion in automobiles and electrical power plants [1,2]. NO$_2$ exposure at concentrations as low as a few ppb can be dangerous to human health and higher concentrations have been linked to smog and acid rain [3,4]. In the current study, we developed a highly sensitive NO$_2$ sensor capable of detection at extremely low concentrations at room temperature [5–7]. One common approach to NO$_2$ detection involves nanostructures of bismuth vanadate (BiVO$_4$). Beyond NO$_2$ detection [8–10], BiVO$_4$ has been used in a wide variety of applications, such as formaldehyde degradation [11,12], H$_2$S production [13,14], hydrogen production [15,16], CO$_2$ capture [17,18], and other fields [19–21]. Table 1 lists a variety of NO$_2$ sensors based on Pt or BiVO$_4$. BiVO$_4$ is inexpensive, highly responsive to visible light, stable, non-toxic, and environmentally benign with a narrow bandgap of $E_g$ = 2.4 eV [22]. However, the low charge transfer rate of BiVO$_4$ impedes efforts to enhance photocatalytic activity [23].

To improve charge transfer, various methods have been planned, including doping with various metals [24,25], the surface deposition of noble metals [26–28], and the formation of compound semiconductors [29,30]. The use of dopants has been shown to introduce
electronic barriers, which capture photogenerated electrons and transfer them to other materials to prevent electron-hole recombination.

In this study, we developed a novel Pt/BiVO₄ composite designed specifically for the sensing of NO₂ at room temperature.

**Table 1.** Comparison of the NO₂-sensing performance of different contents of Pt/BiVO₄ nanocomposites.

| Sensing Material | Response Time (T₉₀, s) | Recovery Time (Tᵣ₉₀, s) | Response (100 ppm) | Pt Crystalline Size (by XRD) (nm), hkl, 111 | Bi Crystalline Size BiVO₄ (by XRD) (nm), hkl | Linearity (R²) |
|------------------|------------------------|-------------------------|-------------------|---------------------------------------------|---------------------------------------------|----------------|
| BiVO₄            | 72                     | 44                      | 91.3              | -                                           | 24.8                                        | 0.983          |
| 0.5 wt.% Pt/BiVO₄| 79                     | 24                      | 99.2              | 10.1                                        | 24.2                                        | 0.950          |
| 1 wt.% Pt/BiVO₄  | 64                     | 51                      | 143.5             | 10.6                                        | 25.2                                        | 0.982          |
| 3 wt.% Pt/BiVO₄  | 12                     | 35                      | 167.7             | 12.1                                        | 25.5                                        | 0.992          |
| 5 wt.% Pt/BiVO₄  | 95                     | 102                     | 173.9             | 12.9                                        | 25.8                                        | 0.980          |
| 10 wt.% Pt/BiVO₄ | 43                     | 67                      | 181.4             | 16.3                                        | 24.6                                        | 0.928          |

2. Materials and Methods

2.1. Materials

(Bi(NO₃)₃·5H₂O), (NH₄VO₃), ethanol (C₂H₅OH), nitric acid (HNO₃) ammonium hydroxide (NH₄OH), sodium borohydride (NaBH₄), ethylenediaminetetraacetic acid (EDTA), silver(I) nitrate (AgNO₃) and dihydrogen hexachloroplatinate (VI) hexahydrate (H₂PtCl₆·6H₂O) were purchased from Sigma-Aldrich Co., Inc. (St. Louis, MO, USA). Distilled H₂O obtained using the distillation water system provided by the Millipore Corporation (Millipore Corp. Molsheim, France) was used.

2.2. Preparation of Bismuth Vanadate

Briefly, a few mmol of Bismuth nitrate (4 g) was added to 6.8 mmol of EDTA (2 g) in acidic medium (0.3 M), whereupon gradual heating to 85 °C was performed for the mixture to procure a colourless solution (named Solution A). A total of 8.5 mmol (1 g) of NH₄VO₃ was then dissolved in 50 mL of H₂O at 60 °C under vigorous stirring for the generation of a yellow solution (named Solution B). The above two solutions mentioned (i.e., Solution A + Solution B) were then further processed with mixing at 50 °C for 1 hour with controlled stirring, after which, the resulting mixture was controlled with pH adjustment to 3.0 by the addition of salt (1 M). The prepared mixed product was poured into the autoclave (Dogger, New Taipei City, Taiwan) made of stainless steel with Teflon lining and further covered with sealant, then kept for heating, which was maintained at 180 °C for 6 h. After cooling of the autoclave, the resultant product was withdrawn via centrifugation, before undergoing multiple washings using ultrapure water and ethanol, followed by drying in an oven at 80 °C overnight and calcination at 450 °C for 4 h to complete the synthesis of BiVO₄ [11].

2.3. Synthesis Method for Pt/BiVO₄ Nanocomposite

Distilled water containing a pre-calculated quantity of H₂PtCl₆·6H₂O was added to the as-prepared product of BiVO₄, which was dispersed in 100 mL and further maintained for 1 h at a continuous stirring rate. The precursor suspension was produced as the product was extracted for centrifugation, washed three times using DI water, and then three times again using alcohol. The precipitate obtained was prepared by drying at 80 °C for more than 6 h. Pt/BiVO₄ preparation was done with Pt at various weight concentrations labelled as follows: 0, 0.5, 1, 3, 5, or 10 wt.% Pt/BiVO₄.
2.4. Characterization

The proposed Pt/BiVO$_4$ nanocomposite was determined using a transmission electron microscope for morphology and structure with an energy-dispersive X-ray spectroscopy (TEM/EDS; JEM-2100F), and a field emission scanning electron microscope (FESEM; JEOL JSM-7500F) operated at 30 kV. Pt/BiVO$_4$ was characterized to understand its crystal structure using a Shimadzu X-ray diffractometer at 1.5405 Å at 40 kV and 30 mA, supported by a vertical goniometer in the range of 10° to 80° (2theta) at a scan speed of 2°/min.

2.5. Sensor Fabrication and Measurements

The designed sensors were prepared by a dipping and coating procedure (Binder: PVA) on an alumina-based solid substrate (10 × 5 mm$^2$; and fab of chip-based sensor; rotational speed, 1000 rpm) in the prepared material, to fabricate an electrode with a comb-like structure. The chips were subsequently pretreated to 80°C over a period of 0.5 h and then calcined at a temperature of 400°C for 2 h.

Figure 1 presents a schematic diagram showing the experimental setup used to measure the electrical response of the sensors [3]. A homemade arrangement for the sensor in the glass chamber was designed with a dynamic flow rate system to evaluate gas sensing performance. The target gas was injected into the chamber at the desired concentrations with a design including a mass controller arrangement for controlling the flow rate (1, 10, 30, 50, 70, or 100 ppm NO$_2$) via a hole in the cover of the chamber. A simple circuit was utilized to understand signals coming from the head of the sensor, which is further showcased by resistance values; later on, collection of data for evaluation and processing was done with a PC. All resistance measurements were averaged from multiple measurements obtained using a Jiehan5000 data acquisition system with the input voltage from a power supply (Vs) set at 4.0 V. $S = \frac{R_g}{R_a}$—which is the ratio that is used for the calculation of the response from the sensor [31], where $R_a$ indicates the resistance in the presence of air and $R_g$ indicates the resistance in the presence of NO$_2$ gas in the provided system. The times required for a 90% variation in resistance upon exposure to NO$_2$ or air are described as the response and recovery times. Selectivity toward NO$_2$ was assessed by exposing the sensor individually, including carbon monoxide, nitric oxide, methane (concentrations equal to 100 ppm), and further recording the characteristics of the response with corresponding values. Long-term stability was assessed by repeating the sensing measurements on multiple consecutive days.

Figure 1. Diagrammatic representation of the experimental setup.
3. Results and Discussion
3.1. Structure Property

Figure 2 shows XRD measurements, indicating the phases and structure of pure BiVO$_4$ and various Pt/BiVO$_4$ nanocomposites. The samples exhibited characteristic peaks corresponding to a structure of BiVO$_4$ (JCPDS 14-0688) with a monoclinic arrangement, as follows: 18.6° (110), 19.0° (011), 29.3° (121), 30.5° (040), 34.5° (200), 35.2° (002), 39.5° (211), 43.2° (051), 46.0° (042), 47.6° (240), 50.3° (202), 53.6° (161), 57.9° (321), and 59.3° (132) [19]. Peaks at 39.8° (111) and 46.0° (200) correspond to face-centred cubic Pt (JCPDS card: No. 04-0802) [32]. No other impurity peak was detected, indicating that the prepared samples were of high purity. Moreover, with increases in the amounts of deposited Pt, the diffraction peaks of Pt (111) were gradually intensified. Using Scherrer’s equation, the mean Pt (111), BiVO$_4$ (051) and (161) crystalline sizes were estimated and listed in Table 1. Table 1 reveals that the crystalline sizes of Pt wt.% loading at 0.5%, 1%, 3%, 5% and 10% were 10.1 nm, 10.6 nm, 12.1 nm, 12.9 nm and 16.3 nm, respectively. The BiVO$_4$ (051) and (161) crystalline sizes were 24.2–25.8 nm and 25.8–28.2 nm, respectively. This shows that the Pt (111) crystalline size was increased by enlarging the amount of Pt loading. However, the BiVO$_4$ crystal size did not change greatly with the addition of platinum. These results indicate that the sensing material was a simple mixture.

![Figure 2](image-url)

Figure 2. XRD patterns of different contents for Pt/BiVO$_4$ nanocomposites.

The morphology and microstructure of the BiVO$_4$ and Pt/BiVO$_4$ were characterized by FESEM and TEM evaluation of the nanocomposite structures. As shown in Figure 3a, SEM images revealed an arrangement comprising a large number of irregularly stacked BiVO$_4$ structures with an average diameter of 0.7–2.5 µm. Figure 3b shows the Pt/BiVO$_4$ nanocomposite containing Pt particles, with uneven diameters on the BiVO$_4$ sample. As shown in Figure 3c, TEM micrographs revealed d-spacing in the prescribed range of 0.227 and 0.196 nm, respectively corresponding to the original Pt-based (111) and (200) lattice plane [32]. As shown in Figure 3d, the EDS spectra confirmed the presence of Pt, V, Bi, Cu and O. The presence of strong signals from Cu can be ascribed to the Cu grid. Taken together, these confirm the formation of fully developed nanocomposites with a pure phase structure.
Figure 3. (a) FESEM images of BiVO$_4$ (b) Pt/BiVO$_4$; (c) TEM images of Pt/BiVO$_4$ (d) EDS spectrum of 3wt.% Pt/BiVO$_4$ nanocomposites.

3.2. Gas-Sensing Performance of Pt/BiVO$_4$

Figure 4a illustrates fluctuations in the response of sensors comprising (0, 0.5, 1, 3, 5 and 10) wt.% Pt/BiVO$_4$ nanocomposites following exposure to NO$_2$ gas at concentrations of 1–100 ppm at 25 °C. The increased response at all gas concentrations is indicative of typical n-type semiconductor behavior. The unloaded BiVO$_4$ materials exhibited a strong response (91.3) when exposed to high concentrations of NO$_2$ gas (100 ppm). Loading samples with a high concentration of Pt (10 wt.% Pt) increased the response strength substantially to 181.4. Table 1 lists the response times, recovery times, sensor responses, and base linearity results. The response and recovery times of sensors based on Pt/BiVO$_4$ nanocomposites were shorter than those of Pt/BiVO$_4$ nanocomposites. The 3 wt.% Pt/BiVO$_4$ nanocomposites achieved a T$_{90}$ of only 12 s and a T$_{90}$ of 35 s. As shown in Figure 4b, this sample also presented the highest linearity ($R^2 = 0.992$) and sensor response ($S = 167.7$).

Figure 4. (a) Discrepancies in response relative to variations in 1–100 ppm NO$_2$ for varying Pt/BiVO$_4$ nanocomposites contents. (b) Response of the 3wt.% Pt/BiVO$_4$ sensor to 1–100 ppm NO$_2$ at room temperature.
Note that the response and recovery times of samples with high Pt concentrations (5 wt.% and 10 wt.%) were slower than those of the 3 wt.% Pt/BiVO₄ nanocomposite. These results are similar to those reported in [31,33], indicating that at higher Pt concentrations, the formation of Pt aggregates tends to hinder the response and recovery of Pt/BiVO₄ nanocomposites. Overall, the 3 wt.% Pt/BiVO₄ sensor presented the best NO₂ sensing performance and was therefore selected as the gas sensor material for all subsequent experiments.

Response and recovery times are important parameters in sensor characterization and should be as short as possible. Figure 5a presents typical dynamic response curves as a function of the weight ratios of Pt/BiVO₄ when exposed to NO₂ at a concentration of 100 ppm at room temperature. Figure 5b presents the dynamic sensing curve of the Pt/BiVO₄ sensor when exposed to NO₂ gas at various concentrations (1–100 ppm). Table 1 lists sensing properties, sensor response times, recovery times, and linearity (R²). The dramatic response of the sensors upon exposure to NO₂ is typical of n-type semiconductors.

Figure 5. (a) The response for varying Pt/BiVO₄ nanocomposites contents of 100 ppm nitrogen dioxide at room temperature; (b) Curves for responses of the 3wt.% Pt/BiVO₄ in the range of 1–100 ppm nitrogen dioxide at room temperature; (c) Three-cycle repeated response curves of the 3wt.% Pt/BiVO₄ to 100 ppm nitrogen dioxide at room temperature.
We can see in Figure 5a that the strength of the responses increased with low NO\textsubscript{2} concentrations (1–100 ppm), as shown in Figure 5b. As shown in Figure 5c, the results from the proposed sensor maintained high reproducibility throughout the test cycle, thereby demonstrating that the Pt/BiVO\textsubscript{4} sensor could reliably be at this particular concentration level to monitor the concentration of NO\textsubscript{2}.

Gas sensors are utilized and mostly evaluated with a range of selectivity, which is an important parameter. Figure 6 illustrates the responses of 3 wt.% Pt/BiVO\textsubscript{4} nanocomposites to NO\textsubscript{2}, CO, NO, and CH\textsubscript{4} (100 ppm) at room temperature. Under these conditions, the response to NO\textsubscript{2} was 167.7, whereas the responses provided by the other selected gases were all lower, at a value of 30—thereby confirming the extraordinary selectivity demonstrated in 3 wt.% Pt/BiVO\textsubscript{4} nanocomposites to NO\textsubscript{2}.

![Figure 6. Selectivity test of the 3wt.% Pt/BiVO\textsubscript{4} nanocomposites to 100 ppm of various gases at room temperature.](image)

As shown in Figure 7, we did not observe a significant decrease in the response of the 3 wt.% Pt/BiVO\textsubscript{4} nanocomposite despite continuous exposure to NO\textsubscript{2} (10 ppm) for a period of 10 days, thereby demonstrating the stability of the sensors.

![Figure 7. Stability of 3 wt.% Pt/BiVO\textsubscript{4} nanocomposites to 10 ppm NO\textsubscript{2} operating at room temperature.](image)
3.3. Underlying Sensing Mechanism

This study demonstrated that the addition of Pb to BiVO\textsubscript{4} notably enhanced the response characteristics of the sensors. We assume that these effects are described by the provided reaction mechanism (1)-(4) \cite{9,26,31,34,35}:

\begin{align*}
O_2(gas) + e^- &\rightarrow O_2^- (ads) \quad (1) \\
NO_2(gas) &\rightarrow NO_2(ads) \quad (2) \\
NO_2(ads) + O^- (ads) &\rightarrow NO(gas) + O_2^- (ads) \quad (3) \\
NO_2(gas) + O_2^- (ads) + 2e^- &\rightarrow NO_2^- (gas) + 2O^- (ads) \quad (4)
\end{align*}

The enhancement mechanism was projected and illustrated in Figure 8. The Pt-based BiVO\textsubscript{4} nanocomposite exhibited typical n-type semiconductor behaviour \cite{9,36}. When exposed to air, the active sites on the BiVO\textsubscript{4} started adsorbing the oxygen molecules, which in turn gave free electrons from the BiVO\textsubscript{4} material for the process of chemisorbed behaviour of oxygen ions (O\textsubscript{2}\textsuperscript{-}) at RT (Equation (1)). The subsequent adsorption of NO\textsubscript{2} molecules at available adsorption sites on the BVO\textsubscript{4} surface enables the direct extraction of the surface electrons of the prepared sensor, producing a breaking of bond in the form of NO—the result of which leaves free oxygen ions (O\textsubscript{2}\textsuperscript{-}) (Equations (2) and (3)) \cite{37}. Catalysis of platinum can help in the enhancement of responsiveness of materials used for sensors to the various provided gases, due to a phenomenon referred to as the spillover effect \cite{38,39}. The activity of Pt in this catalysis can help in accelerating the adsorption behaviour of molecular level oxygen; the adding of Pt dopants has a significant effect on surface area, which can lead to further chemisorbed oxygen species spillover, which increases the number of active sites on the BiVO\textsubscript{4} \cite{11,26,33,40}. This increases the number of electrons that are captured, and in so doing enhances the response of the sensor. As shown in Equation (4), the availability of additional oxygen molecules for reactions with incoming NO\textsubscript{2} gas molecules increases the number of interactions between gas molecules in nitrous oxide and the sensing layer. The surface modification of BiVO\textsubscript{4} with platinum also increases the number of dissociated NO\textsubscript{2} molecules migrating to the surface of BiVO\textsubscript{4}, thereby increasing responsivity to NO\textsubscript{2} gas. For comparison, the various NO\textsubscript{2} sensors based on Pt or BiVO\textsubscript{4} are listed in Table 2.

![Figure 8. Schematic diagram of NO\textsubscript{2} gas sensing mechanism for Pt/BiVO\textsubscript{4} nanocomposite.](image-url)
Table 2. Comparison of working temperature and various NO$_2$ sensors based on Pt or BiVO$_4$ nanocomposites.

| Sensing Material | Response (Rg/Ra or Ra/Rg) | NO$_2$ (ppm) | Temperature ($^\circ$C) | References |
|------------------|---------------------------|--------------|------------------------|------------|
| Pt-SnO$_2$       | 1.3                       | 30           | 50                     | [41]       |
| $\alpha$-Fe$_2$O$_3$/BiVO$_4$ | 7.8                       | 2            | 110                    | [10]       |
| BiVO$_4$/Cu$_2$O | 4.2                       | 4            | 60                     | [34]       |
| BiVO$_4$/Cu$_2$O/rGO | 8.1                       | 1            | 60                     | [9]        |
| rGO-NiO-BiVO$_4$ | 8.1                       | 2            | 60                     | [7]        |
| Pt/WO$_3$        | 11.24                     | 1            | 150                    | [35]       |
| Pt/BiVO$_4$      | 167.7                     | 100          | 25                     | This work  |

4. Conclusions

In this study, a Pt/BiVO$_4$ nanocomposite was prepared using a hydrothermal method with various weight percentages of platinum for use in NO$_2$ gas sensors. The structure and morphology of samples were characterized by XRD, TEM, FESEM, and EDX. The experiment results demonstrated that the addition of Pt to BiVO$_4$ at a concentration of 3 wt.% can greatly enhance the responsivity of Pt/BiVO$_4$ nanocomposite sensors to NO$_2$ at relatively low concentrations (100 ppm) as follows: sensor response (167.7), response time (12 s), and recovery time (35 s). The proposed Pt/BiVO$_4$ nanocomposite-based gas sensor exhibited promising nitrogen dioxide gas-sensing characteristics, including high sensitivity, high selectivity, and extremely short response/recovery times.

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