Full Paper

Graphene/nano-sized Imprinted Polymer/poly(methyl methacrylate) Nanocomposite as a New Gas Sensor for the Determination of Nitrobenzene Vapors

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Abstract- A new nitrobenzene vapor chemiresistor sensor was introduced based on a nanocomposite of graphene/imprinted polymer nanoparticles/poly (methyl methacrylate). The nano-sized molecularly imprinted polymers (nano-MIP) holding the cavities compatible with nitrobenzene molecules were synthesized utilizing methacrylic acid and vinyl benzene as the functional monomers and Divinylbenzene as the cross-linker. The copolymerization reaction was fulfilled in acetonitrile via precipitation method. The nano-MIP particles were mixed with graphene to produce a chemiresistor gas sensor. The addition of poly(methyl methacrylate) in the nanocomposite resulted in better physical durability, enhanced selectivity and higher resistance against humidity effect. The response of MIP based sensor was considerably higher than that of the NIP based gas sensor. The response of the gas sensor was reversible and a relative standard error equal to 3.1% was calculated for 4 relations in the determinations. The sensor showed linear response in the concentration range of 0.10–55.0 ppm. The detection limit was calculated to be 0.04 parts per million (S/N).

1. INTRODUCTION

Graphene is considered as two dimensional carbon material with a one-atom-thick planar sheet of sp^2 bonded carbon atoms that are densely packed in a honeycomb crystal lattice

[1,2]. One of the most intriguing and fascinating field for the application of this material is sensor field [3,4]. Graphene has practically been applied for the fabrication of several sensors for detection of some environmental gases like H_2, NH_3, CH_4 [5], NO_2 [6], CO_2 [7], organic vapors [8,9] and formaldehyde [10]. However, the selectivity of graphene for the majority of the above mentioned gases is not sufficient.

The polymer films are the best chemical interfaces to detect organic vapors because of their high sensitivity, fast vapor diffusion, reversible response and good ability to work at room temperature. In general, the selectivity of these coatings is not sufficient for selective detection of a single component with a single sensor. To perform a selective analysis of target organic gas in the presence of interference agents, it is necessary to use an array of several gas sensors with different polymers possessing partial selectivity to various gaseous components [11–21].

Molecularly imprinted polymers (MIPs), on the other hand, are a class of cross-linked polymer that can bind certain target compound with high specificity [22–26]. Unlike the common polymers, the selectivity of MIP to the target molecule is not only due to the solvating parameters of the vapors but also to the shape and size of the template molecule. This makes the MIP to distinguish a target molecule from the structurally similar one. The molecular imprinting technique has been used to create sensors with a predetermined selectivity for molecules in the gas phase [27, 28]. MIPs have been used to monitor terpenes [29], formaldehyde [30], 2-methylisoborneol [31], explosive vapor [32] and toluene [33].

Nitrobenzene has been widely used in the industries for the production of aniline, aniline dyes, explosives, pesticides and drugs, and also as a solvent in products like paints, shoes and floor metal polishes [34]. As a toxic and suspected carcinogenic compound, nitrobenzene released to the environment poses a great threat to human health. Even at low concentrations, it may present high risks to the environment [35]. Interest in nitrobenzene determination in environmental samples has fueled the development of several analytical methods for their quantification, including those based on high-performance liquid chromatography [36], gas chromatography [37,38] and voltammetry [39,40]. Piezoelectric sensor [41,42] and poly(4-vinylpyridine)-based chemiresistor [43] have already been reported for gas phase detection of nitrobenzene. However, low selectivity is the main drawback of these sensors.

Previously we reported a grahene/graphite/MIP composite as an efficient nitrobenzene vapor sensor [44]. However, the presence of graphite together with graphene was shown to be necessary to observe the recognition capability of the MIP particles in the sensing film. In this work, the coupling of graphene material with the nano-sized imprinted polymer was investigated to examine the feasibility to achieve high sensitive and selective gas sensor. It was observed that decreasing of the MIP size led to observation of the MIP recognition capability in the sensing film without requirement to introduce graphite together with graphene in the sensing film.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Methacrylic acid (MAA), 4-vinylpyridine (VB), divinylbenzene (DVB), ethylene glycol dimethacrylate (EGDMA), 2,2-azobisisobutyronitrile (AIBN) and poly(methyl methacrylate) (PMMA) were obtained from Sigma–Aldrich (Munich, Germany). Graphite powder was purchased from Fluka (Buchs, Switzerland). Other chemicals were of analytical grade and were purchased from Merck (Darmstadt, Germany).

2.2. Synthesis of graphene

Graphene was prepared using modified Hummers and Offeman method [39]. In a typical procedure, graphite (5 g), $NaNO_3$ (5 g) and 200 mL of H_2SO_4 were stirred together in an ice bath. $KMnO_4$ (15 g) was then slowly added while stirring. The mixture was then transferred to a 35 °C water bath and stirred for about 0.5 h, forming a paste. Subsequently, 200 mL deionized water was added gradually. After 15 min, the mixture was further treated with 1 L deionized water and 50 mL 30% H_2O_2 solution. The solution was then filtered and washed with deionized water until the pH became about 7 and dried at 70 °C under vacuum. The obtained material (graphene oxide) was loaded in a 250 mL round-bottom flask and water (100 mL) was then added, yielding an inhomogeneous yellow-brown dispersion. This dispersion was then sonicated for 30 min. Hydrazine hydrate (2.0 mL, 32.1 mmol) was then added and the solution was heated in an oil bath at 100 °C under a water-cooled condenser for 24 h, over which the reduced graphene oxide gradually precipitated out as a black solid. This product was isolated by filtration, washed copiously with water and methanol, and dried under a continuous airflow through the solid product cake.

2.3. Preparation of molecularly imprinted polymer

In order to prepare imprinted polymer, methacrylic acid (as the first functional monomer, 2 mmol), vinyl benzene (as the second functional monomer, 2 mmol) and nitrobenzene (as the template, 2 mmol) were transferred into a vessel, containing 75 mL of acetonitrile. Then, 2.5 mmol of divinylbenzene (as cross-linking agent) and 0.03 g of 2,2-azobisisobutyronitrile (as radical initiator) were added to the mixture. The solution was then purged with N_2 gas for 15 min, followed by heating at 60 °C for 10 h in a water bath. The obtained polymer was dried overnight at 80 °C under reduced pressure to remove the template molecule. The non-imprinted polymer (NIP) was also synthesized according to above mentioned method except that the template (nitrobenzene) was absent in the polymerization. The obtained polymer powder was suspended in acetone and the supernatant portion was collected after about 10 min. This was done three times sequentially and the finally obtained polymer powder was dried and conserved for the next uses.

2.4. Preparation of sensor device

Substrate for the chemiresistor was prepared by depositing platinum electrodes on a silicon wafer using a custom-designed mask. Each chip had 8 pairs of electrodes that acted as the conductive electrodes of the chemiresistor. The line widths of the platinum electrodes were about 0.4 mm, and the spacing between electrodes was about 0.2 mm. In order to prepare resistive ink, a known mass of PMMA (4 mg) was dissolved in tetrahydrofuran by sonication. Once the polymer was fully dissolved, determined amounts of graphene (6 mg) and MIP (9 mg) were added to the solution and sonicated further for 6 h to promote uniform dispersion. Small amount of the obtained mixture was placed directly above the electrodes by using a micropipette.

The prepared sensor was set in a thermostated (25 °C) special measuring barrel. The barrel inside atmosphere was purged with dry nitrogen gas before any experiment In order to generate nitrobenzene vapor a small volume (microliter) of the nitrobenzene liquid (or solution containing a determined amount of nitrobenzene, dissolved in dichloromethane) was placed in a small plate (fixed inside the barrel and heated by passing electrical current through a small heater attached beneath the plate). This was done via a syringe needle, present inside the barrel. A fan was set inside the barrel and used to circulate the barrel inside the atmosphere. The concentration of the nitrobenzene was calculated according to the volume of the evaporated vapor, the concentration of nitrobenzene in the solution (in the case of injection of nitrobenzene solution instead of nitrobenzene liquid) and total volume of the chamber, assuming the total pressure was kept constant at 1 atm and 25 °C. Therefore, different concentrations of nitrobenzene were obtained by controlling the amount of liquid dropped on the plate. When the nitrobenzene solution (in dichloromethane) was utilized for vapor generation in place of liquid nitrobenzene, the responses obtained for every nitrobenzene concentration was normalized regarding the relevant blank solution response, obtained by injection of the same amount of liquid without nitrobenzene (pure dichloromethane). After every measurement, the sensor environment (barrel inside) was cleaned by purging dry N_2 gas into the barrel. In order to test the effect of humidity on the sensor response characteristic the wet nitrogen gas was passed through the sensor chamber, previously filled with dry nitrogen, while the relative humidity (RH) inside the barrel was monitored via a humidity meter device, fitted inside the barrel. As soon as a desired RH was recorded; the N_2 gas flow was stopped and both valves were closed. The resistance response of the sensor was measured by an LCR-meter (LCR-821, Instek) device connected to a computer. In order to evaluate the response behavior of the sensor as a function of time or other parameters, relative resistance change percent was calculated according to the following equation:

$$Response = R - R_0 / R_0 \qquad (1)$$

Where R and R_0 are sensor resistance after exposure to a given vapor concentration and its base resistance (Ω), respectively.

3. RESULTS AND DISCUSSION

3.1. Nanocomposite sensor and the sensing mechanism

Figure 1 represents scanning electron microscopy image of the nanocomposite, used for the sensing of nitrobenzene vapors. As can be seen all components of the as mentioned nanocomposite are tightly attached together. This nanocomposite comprises three main components of graphene sheets, nano-sized nitrobenzene-imprinted polymer and poly(methyl methacrylate). Graphene provide a conducting material within the composite and the imprinted polymer functions as the recognition element of the sensing device. The presence of the third member of the nanocomposite, namely, poly (methyl metacrylate), acts either as the composite components binder and the agent resistive to the negative effect of the environment humidity on the sensor performance. This is because of the highly hydrophobic nature of this polymer which repulse the water molecules from the sensing surface.
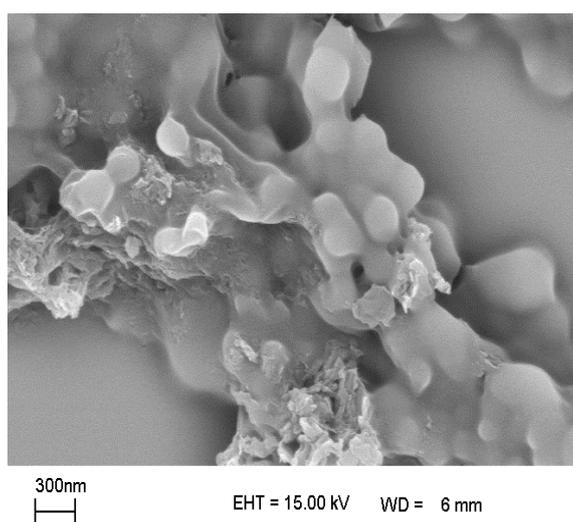

Fig. 1. Scanning electron microscopy image of the sensing nanocomposite

The principal of conventional polymer–carbon black composite chemiresistors [33,34] can be relatively expanded to rationalize the working mechanism of the MIP based sensor, aimed to be constructed. The interaction between the MIP and the nitrobenzene (NB) can be described by the following equilibrium.

$$NB + MIP \quad \underset{K2}{\overset{K1}{\rightleftharpoons}} \quad NB\text{-}MIP \tag{2}$$

Herein, K_1 and K_2 are adsorption and desorption rate constants, respectively. According to Eq. (2), exposure of the sensing composite of the sensor to the NB gas results in diffusion of the gas into the recognition cavities of the MIP, designed specifically for the analyte gas. Subsequently, this leads to swell of the MIP particles, situated among the graphene material, enhancing the distances among them and thus increasing the electrical resistance of the sensor. Moreover, depletion of NB gas from the sensor environment leads to removal of the template molecules from the recognition cavities of the MIP particles of the sensor surface, increasing the conductance of sensing nanocomposite.

3.2. Response characteristics of the sensing nanocomposite

Figure 2 displays the resistance responses obtained for the different sensing nanocomposites. It can be seen that the sensors sensitivities obey the order of: MIP/G-PMMA>NIP/G-PMMA>G-PMMA. It can be seen that the MIP based composite response to nitrobenzene is significantly higher than both NIP based and cross-linked polymer free nanocomposites. This means that the swelling of the polymer is the dominant mechanism in the creation of nanocomposite signal to nitrobenzene.
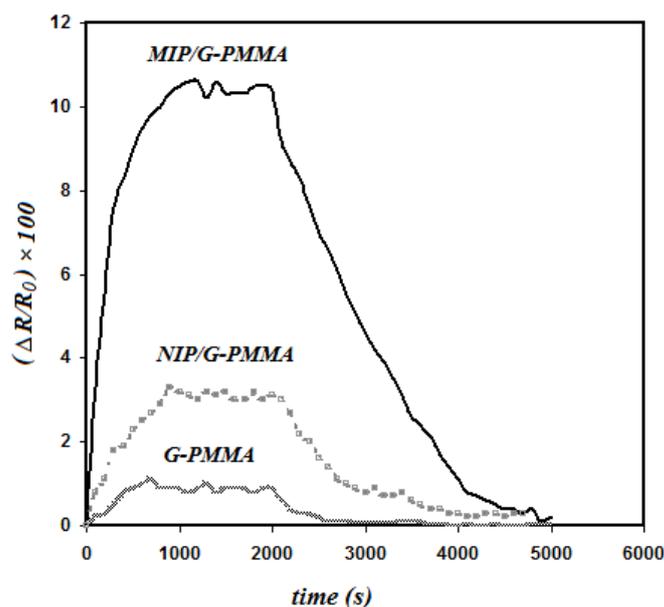

Fig. 2. Resistive responses of the sensor to the fixed concentration of nitrobenzene vapor

3.3. Evaluation of the sensor response characteristics and its selectivity

Figure 3 represents the response behavior of the optimized sensor, after four successive injection and then cleaning steps in four incremental concentrations. It can be seen that after every injection step the sensor response increases sharply and then reaches to a steady state. By starting a cleaning step the sensor response starts to decrease. These observations suggest

that the MIP-based sensing film has a reversible adsorption/desorption characteristic for the nitrobenzene vapor, verifying Eq. (2). Furthermore, the depicted results in the described figure indicate that the sensor response magnitude depends on the nitrobenzene concentration, injected in the sensing environment.
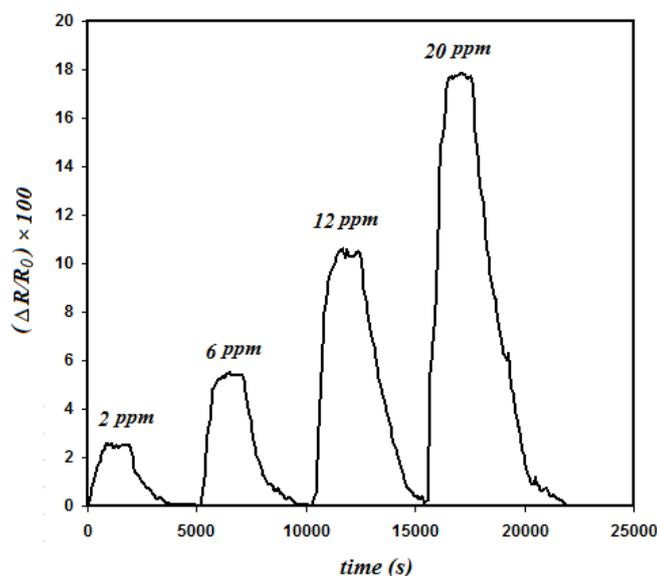

Fig. 3. responses of the MIP/G-PMMA sensing device to various concentrations of nitrobenzene

3.4. Analytical characteristics of the sensor

The developed sensor was used to prepare a calibration curve. Correlation between the sensor response and nitrobenzene concentration is illustrated in Figure 4 (I). According to this figure, the relationship between nitrobenzene concentration and sensor response is linear in the concentration range of 0.1–55 ppm. The detection limit of the sensor was found to be 0.04 ppm (S/N=3, T=25.0±0.2 °C, relative humidity <50%).

Relative standard deviation of 4 separate determinations of 2 ppm of nitrobenzene (in a day) with the sensor was found to be 3.1%. Furthermore, relative standard deviation of the determination of a fixed concentration of nitrobenzene with five different sensors was calculated to be equal to 4.2%. This suggested an acceptable reproducibility of the fabrication of the proposed gas sensor. It must be noted that in order to obtain the response data for the calculation of standard errors the sensor(s) was allowed to fully return to baseline during cleaning, after exposure to the vapor. The signal of the sensor for a given concentration did not differ significantly (confidence level=95%) within 6 months, indicating good durability of the developed sensor. It must be mentioned that in order to obtain all of the above described data, the sensor response was permitted to reach the baseline before the next experiment. Since the sensor cleaning time was longer in the case of higher nitrobenzene

concentration, the time of sensor testing experiment was longer when testing higher concentrations of nitrobenzene.

In order to evaluate the selectivity of the optimized sensor, it was exposed to different vapors. The results of these experiments are shown in Figure 4 (II). As can be seen, the sensor shows high selectivity to nitrobenzene; because, its response to nitrobenzene is much higher than the other tested vapors, possessing the same concentrations. According to the depicted results, nitrobenzene similar vapors like toluene, benzene, aniline and phenol create very small signals on the developed sensor, compared with nitrobenzene.
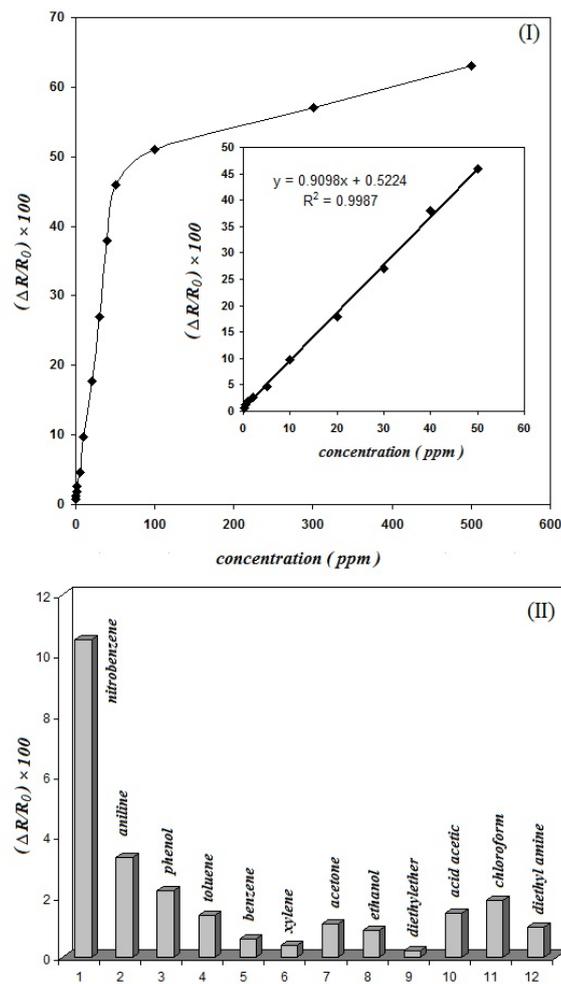

Fig. 4. Calibration curve obtained for the developed NB gas sensor (I); the linear section of the calibration curve; selectivity of the developed gas sensor (II)

4. CONCLUSION

A new chemiresistor sensor based on graphene/nano-MIP nanocomposite was introduced to sense nitrobenzene vapor. The response of the sensor to NB vapor was demonstrated to be

reversible. The sensor was selective to nitrobenzene, especially compared to structurally similar vapors.

Acknowledgement

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