

Palladium/Polymer Nanocomposite Based Chemiresistive SO₂ Sensor

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ABSTRACT

We report a highly sensitive palladium/polymer nanocomposite based SO₂ gas sensor. The palladium/polycarbonate (Pd/PC) nanocomposite was synthesized by utilizing two different techniques. The *ex-situ* method involved the homogenous mixing of pre-synthesized Pd nanoparticles with the PC matrix. The *in-situ* method on the other hand involved the synthesis of Pd nanoparticles in the presence of PC matrix. The semi-conducting behavior of the *in situ* Pd/PC nanocomposites and the chemical affinity of Pd nanoparticles towards the Lewis acid gases were efficiently employed to develop the SO₂ sensor. A chemiresistive technique was used in the detection of the SO₂ gas molecules in which the change in the electrical resistance of the nanocomposite associated with the adsorption of SO₂ molecules by the nanocomposite was measured.

Keywords: palladium, polycarbonate nanocomposites, chemiresistive sensor, sulfur dioxide, electrical conductivity.

1. INTRODUCTION

Sulfur dioxide (SO₂) is one of the six common air pollutants that is released into the atmosphere which causes a wide variety of health and environmental impacts like respiratory effects, visibility impairments, acid rains, etc., because of the way it reacts with other substances in the air [1-3]. Therefore, it is useful to measure the emission of this gas into the atmosphere by various sources.

Developing a lower ppm level sensitive, reliable, low cost, solid state fluid sensor in a portable format has always been a challenge. Using metal nanoparticles to solve the above problem constitutes an important research area in the field of nanotechnology. Volkening et al. [4] reported the H₂ sensing capability of nanocrystalline Pd particles. However, utilizing the metal nanoparticles alone had some limitations in the sensor application domain due to handling constraints and easily oxidizable nature of the metal oxide nanoparticles [5]. As an alternative metal-polymer nanocomposites have been utilized for the same purpose. For example, Methanol sensing by palladium/polyaniline (Pd/PANI) nanocomposites was reported by Athawale et al. [6]. These nanocomposites have demonstrated tunable optical, thermal and electrical properties that are utilized as

the parameters used for sensing [4-6]. From the earlier work [7-10], it can be inferred that the morphology of the nanoparticles depend on several factors such as the molecular weight of the protecting agent; metal salt; protecting agent ratio; functional groups in the protecting agents; temperature of the reaction; reducing agent; reduction rate and the mode of synthesis.

In this study, we report the varied electrical behavior during chemiresistive detection of SO₂ utilizing the Pd/PC nanocomposite synthesized by two different methods: the *ex-situ* and *in-situ* methods with different Pd content.

2. CHEMIRESENSITIVE SO₂ SENSOR

The principle of operation of the chemiresistive sensor is based on the measurement of resistance change associated with the adsorption/reaction of gaseous analyte by/with the nanomaterial matrix [11,12]. The prototype gas sensor functions based on the chemiresistive principle, where variations in the resistance of the SO₂ gas sensitive Pd/PC nanocomposite is observed and measured due to selective reaction between the nanocomposite and the SO₂ gas molecules that in turn decreases the number of free electrons resulting in a concentration dependant resistance increase.

This chemiresistive SO₂ sensor consists of a two main components: the Pd/PC nanocomposite film that functions as the active sensing element and the electrical circuitry supporting the nanocomposite film. Each component is discussed in turn.

2.1. Pd/PC Nanocomposites

In the *ex situ* method, C₁₂H₂₅SH-protected Pd nanoparticles were prepared using the Brust method [13]. The Pd nanoparticles were then homogeneously mixed with a solution of 40 mg of PC in 20 ml of CH₂Cl₂ (1.6 μM) followed by film casting at room temperature. In the case of the *in situ* method, PC (40 mg) was dissolved in CH₂Cl₂ (20 ml) (1.6 μM). 15 mg of PdCl₂ was first dissolved in 2ml of conc. HCl so as to form a complex [PdCl₄]²⁻, and was further dissolved in 48 ml water to form a 1mM solution. This biphasic mixture was stirred continuously using a magnetic stirrer for 30 minutes. A freshly prepared solution of NaBH₄ in 20 ml water (0.1M) was added drop-wise to

the mixture. The color of the reaction mixture changed rapidly from golden yellow to black, indicating the formation of Pd nanoparticles. After stirring for 3 hours, the organic phase was separated, washed with water and was directly cast into film at room temperature. Soon after the reduction nearly all of the reduced Pd nanoparticles get transferred from the aqueous phase to the organic phase. The *ex situ* nanocomposite yielded a dispersed mixture in contrast to the *in situ* nanocomposite which produced an agglomerated mixture. (Figure 1)

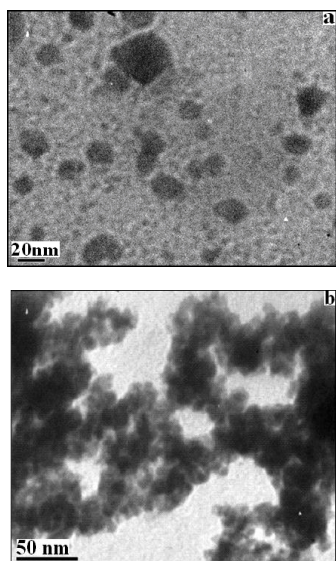


Figure 1. TEM image of the *ex situ* and *in situ* Pd/PC nanocomposites showing (a) Dispersed Pd nanoparticles, and (b) Agglomerated Pd nanoparticles, respectively.

The *in situ* and *ex situ* two nanocomposites were packaged on to a miniature base platform. The base platform comprised of a metallic interdigitated microelectrode structure (Figure 2). Coating the interdigitated electrode (IDE) with the nanocomposite resulted in an active sensing area that was investigated for its sensitivity and selectivity for SO₂ detection. 1wt. % of carbon nanoparticles (CNPs) was added into these nanoparticles in order to improve their electrical conductivity.

2.2. Electrical Circuitry

When the Pd/PC nanocomposite was exposed to SO₂ gas, it was observed that the SO₂ gas molecules resulted in a change in the nanocomposite's electrical resistance. In order to measure this change in electrical resistance in a continuous manner, we employed a Wheatstone's bridge circuit, which detected the change in resistance between the balanced and imbalanced condition. The amount of imbalance observed in the Wheatstone bridge was observed to be a function of the concentration of SO₂. The measurand obtained was an output voltage proportional to the change

in the electrical resistance of the nanocomposite (Figure 2). In the entire circuit, the IDE pattern functions as an electrical resistor whose resistance changed following reaction between the Pd/PC nanocomposite and the SO₂ gas molecules.

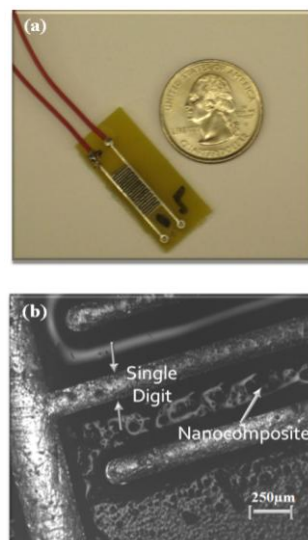


Figure 2 (a) The optical micrograph of the chemiresistive sensor chip with the interdigitated electrodes coated with polymer nanocomposite. Each sensor array comprised of 20 digits. Each digit is ~200μm in width and 2mm in length with 300μm spacing. (b) The optical micrograph of the chemiresistive sensor covered with the Pd/PC nanocomposite forming a homogenous layer on the surface.

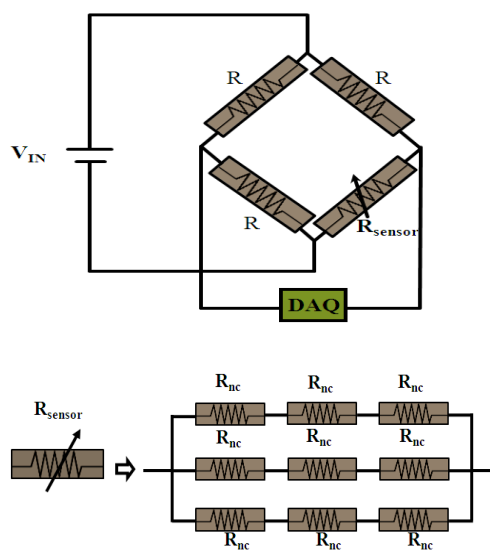


Figure 3. The equivalent circuit of the entire experimental setup and equivalent resistance of the nanocomposite are shown. The resistor R_{sensor} in the Wheatstone bridge circuit is the resultant resistance of the nanocomposite.

3. RESULTS AND DISCUSSION

3.1. Morphology of Pd/PC nanocomposites

The TEM image of the *ex situ* nanocomposite with 2 vol.% Pd, revealed dispersed Pd nanoparticles of ~15 nm embedded in PC matrix (Figure 1a). Based on earlier reports on the synthesis and morphology of n-alkanethiol-protected Pd nanoparticles, the presence of dodecanethiol on the surface of the Pd nanoparticles in the present study is likely to ensure the separation of the nanoparticles even after mixing with PC. Although an identical metal salt: thiol ratio and reducing agent were used in the present study, an increase in the size of the nanoparticles was found than the prior work by Brust et al.[13]. This may be due to the absence of the surfactant, in the reaction mixture which helps in phase transfer of reduced Pd nanoparticles. The effect of increased temperature of the reaction mixture from ice-cold condition in the earlier studies in comparison to the reaction room temperature may have also contributed to the increased size of the nanoparticles.

In contrast to the above system, the *in situ* nanocomposites of Pd nanoparticles (2 vol.% on a stoichiometric basis) in PC showed significant agglomeration (Figure 1b). Similar observations on agglomeration were reported by Chen et al using Pd/mercapto-poly(ethylene glycol) [7], and Chatterjee et al with Au/poly(dimethylamino ethyl methacrylate-methyl methacrylate) copolymers [8]. Wang et al have suggested that in order to obtain discrete nanoparticles, the rate of adsorption of organic ligands on the surface of nanoparticles should equal the rate of nanocluster formation [14]. Accordingly, organic ligands with lower molecular weight have generally been found to be more effective in limiting the nanoparticles size. In addition, the nature of interactions between the polymer and the surface of the nanoparticles may also play a role in determining the morphology of the resulting nanocomposites. The following sections examine the consequences of the differences in morphology on the resulting electrical properties and the SO₂ sensing capabilities of these nanocomposites.

3.2. Electrical Properties

PC is electrically insulating in nature with a volume resistivity of about $2 \times 10^{14} \Omega\text{-m}$. No significant difference was observed for the *ex situ* nanocomposites (with 2 vol. % Pd (on a stoichiometric basis)) with resistivity of $7.2 \times 10^{13} \Omega\text{-m}$. However, the *in situ* nanocomposite films having 2 vol. % Pd (on a stoichiometric basis) showed a linear increase in the current with the voltage indicating a constant resistance of about 440 Ω and thus a resistivity of $2.1 \times 10^5 \Omega\text{-m}$.

Similar results were observed by Athawale et al [5] on Pd/polyaniline nanocomposites and by Rao et al [15] on Pd/polypyrrole nanocomposites. However, these results

involved conducting polymers for electrical conductivity studies on nanocomposites. In the present study an electrically insulating polymer (PC) was used instead of a conducting polymer. The reasons for the differences in electrical conductivity between the *in situ* and *ex situ* are not known although there may be a link between the differences in microstructure as seen in Fig 1.

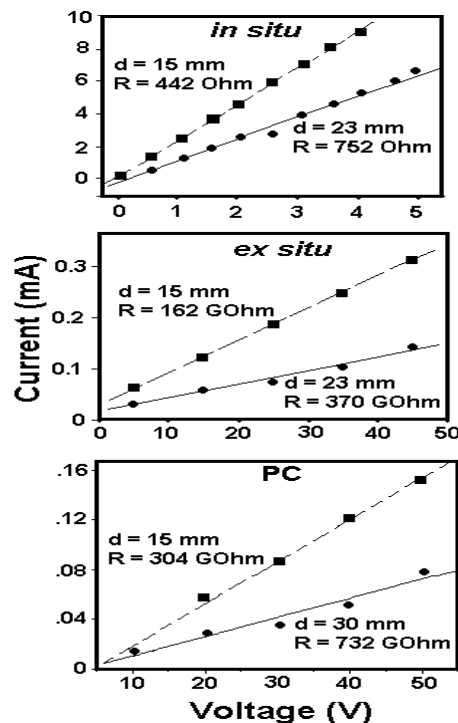


Figure 4. Electrical properties of 2 vol. % Pd/PC nanocomposites compared that of PC.

3.3. Sensitivity towards SO₂

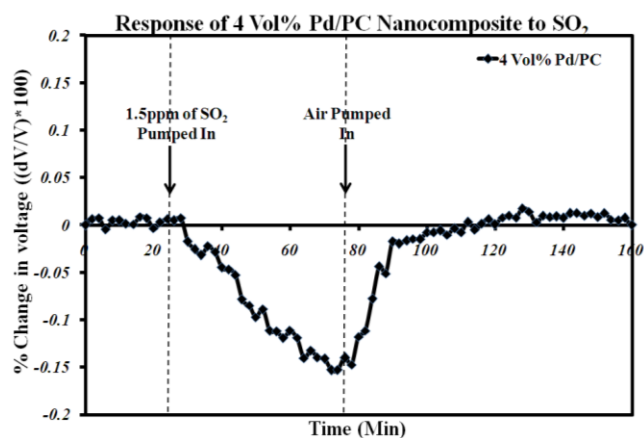


Figure 5. The electrical response of 4 vol. % *in situ* Pd/PC nanocomposite film with 1 wt. % CNPs following exposure to SO₂.

The influence of SO₂ exposure on the Pd/PC nanocomposite was monitored by measuring the change in

voltage as a function of time (Figure 5). We observed that there was a change in the electrical conductivity of the Pd/PC *in situ* nanocomposite when it was exposed to SO₂. This change in electrical conductivity was due to the adsorption of SO₂ molecules by the Pd/PC nanocomposite. However, this change in electrical resistance due to the adsorption of the SO₂ gas molecules was not observed in the case of *ex situ* Pd/PC nanocomposite.

In summary, the variations in synthetic procedure affects the morphology and electrical properties of Pd/PC nanocomposites. These differences can be used for designing chemiresistive sensors with tailored performance for detecting chemical species.

4. REFERENCES

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