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Understanding the response of nanostructured polyaniline gas sensors

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ABSTRACT

Polyaniline/Ag nanocomposite gas sensors have been fabricated with a single-step technique. The current response of the sensors to triethylamine and toluene was monitored and analyzed. The time dependence of the response to the two gases of the sensors was found to be exponential and was fit to chemisorption and diffusion models. The equilibrium absorption amounts from the chemisorption model were found to obey a Langmuir isotherm. The results of the diffusion model to the data were consistent with a dual sorption process, i.e., diffusive and non-diffusive adsorption sites. The estimated diffusion coefficients were found to increase with the concentration of diluent, probably due to the swelling of the polymer by the organic vapors. Our results suggest that both models can be employed to mathematically fit the sensor response.

1. Introduction

Gas sensors, sometimes denoted as electronic noses, have been widely studied ever since the design of a gas sensor was reported by Seiyama et al. in 1962 [1]. Chemical methods for determining unknown species, such as gas chromatography/mass spectrometry (GC/MS), are time-consuming, expensive, and require trained personnel. There is a need to develop miniature devices for rapid and inexpensive analysis of volatile compounds. Significant research has been focused on conducting polymer-based gas sensors [2]. Polyaniline is a promising candidate for gas sensing applications because of its relatively easy synthesis, low cost, high sensitivity, and fast response [3,4]. In particular, nanostructured polyaniline-based gas sensors have shown excellent performance because of their large surface areas and high porosity of nanostructured polyaniline [5–10]. Most methods of making polyaniline are multi-step and a facile one-step environmental-friendly method may overcome its poor processability. Our group has reported a novel method to synthesize polyaniline nanofibers and nanocomposites based on either gamma or ultra-violet radiation [11–13]. This technique can be utilized to fabricate nanostructured polyaniline-based electrochemical gas sensors in a single step. This type of sensor has shown a fast response to various organic vapors [9,10].

Although considerable research has been carried out in the development of novel conducting-polymer sensors, some basic problems still remain, especially with respect to nanostructured conducting-polymer sensors. The modeling of time-dependent sensor response is particularly relevant for understanding the sensing kinetics. The gas sensor response is basically controlled by two factors. One is the transport process of gas molecules to or into the sensor film. The other is the interaction of the sensing material and gas molecules, i.e., a physical interaction or chemical reaction. A few models have been proposed for bulk-conducting-polymer-based gas sensors [14–17].

Previous work from our group has shown how these sensitive materials can be made in a single step. It was found that the incorporation of nanometals into the composite enhanced the sensitivity of the sensors [9]. The incorporation of Ag, in particular, gave faster and more sensitive responses to triethylamine than other metals because of the affinity of amines for Ag. We also showed that this enhancement was primarily due to the charge transfer to the Ag and that the sensor response of our polyaniline materials to triethylamine can be fit with an exponential decay as a function of time and gas concentration [9]. This paper reports the response of one-step polyaniline/Ag based sensors and interprets the response in terms of chemisorption and diffusion.

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The chemisorption model is based on the de-doping (or swelling) of the conducting polymer when a guest molecule is adsorbed at or near the surface of that polymer. For nanostructures with high surface areas, such as in our PANI nanocomposites, this model embodies importance of the capture of the guest molecule by the polymer at active sites. It would be consistent with the limiting response factor being adsorption at the interface. The diffusion model is based on the penetration of the polymer by the guest molecules. It assumes that the guest molecules go quickly to the surface, but the limiting step for sensing is diffusion into the polymer. We find that both of these models fit the responses of the nanostructured polyaniline based gas sensors to organic vapors, probably because both fitting methods are consistent with exponential decay functions. The chemisorption model was found to fit a Langmuir isotherm, while the diffusion model was consistent with a dual sorption mechanism.

2. Experimental

2.1. Synthesis of polyaniline/Ag nanocomposites

To produce nanocomposites for the sensors, 0.1 M aniline (93 mg), 0.01 M $AgNO_3$ (17 mg) and 0.1 M nitric acid were first dissolved in 10 mL distilled water. The aniline began to polymerize after the addition of 0.05 M ammonium persulfate (114 mg). After vigorous shaking, the solution was immediately irradiated with a low-pressure Hg–UV light source (Model: PASCO Scientific OS-9286A) [10].

2.2. Fabrication of polyaniline/Ag nanocomposite sensors

Sensors were fabricated by placing a 10 μL drop of premixed precursor solution on the active area of an interdigitated microelectrode array. The precursor solution had the same composition as described above. The drop was then illuminated with the UV lamp. After the reaction (approximately 30 min), the polyaniline thin films were washed with distilled water and dried at room temperature before being used for measurements [10].

2.3. Characterization

The morphology of the polyaniline/Ag nanocomposites was characterized using a Hitachi S-4700 scanning electron microscope (SEM) operated at accelerating voltages of 5 kV and a JEOL JEM-2100 transmission electron microscope (TEM). The changes in electrical current for polyaniline/Ag based thin film sensors were measured at room temperature as a function of time and exposure to organic vapors. The real-time current changes were monitored using a Keithley 4200 semiconductor analyzer operated at 0.1 V. To test the sensors, nitrogen gas was used as both the carrier and diluting gas. The carrier gas was passed through the neat liquids in a gas bubbler. The resulting gas mixtures were then diluted with additional diluting gas that was then directed to the sensor, which was kept at room temperature. The relative concentration (or volume fraction, measured in ppm) of gases in the carrier gas, c, was determined using:

$$c = \frac{M/\rho}{(M/\rho) + L_1 + L_2} \qquad (1)$$

where M is the weight loss rate of the liquid sample (in g/min), ρ is the density of the vapor (in g/L), L_1 is the nitrogen carrier gas flow rate (in L/min), and L_2 is the nitrogen diluting gas flow rate (in L/min). The flow rate of the nitrogen diluting gas was 1.5 L/min, and the total gas pressure was about 15 psi.

The mathematical fitting of experimental data was performed in Excel or Mathematica using least-squares method. The best fit was achieved when the sum of the squares of the residuals was minimized. The standard deviation (SD) of the residuals, the square root of the sum of the squares of the residuals divided by $n-1$ (n is the number of data points) was used to estimate the uncertainty of the fit. The uncertainty in the fitting parameters was estimated by varying each fitting parameter independently from the best-fit value until the SD increased to 1.96 × SD, which corresponds to a 95% confidence interval [18,19].

3. Theory

3.1. Chemisorption model

This model is based on that originally developed for chemisorption, which states that the rate of adsorption is affected by the evaporation and condensation processes [20–23]. The application of the model to our systems was based on the following assumptions [17,24]:

(1) The conductivity of the polyaniline is proportional to the number of conduction sites (dopant sites), N, which are uniformly distributed on the polymer surface. These sites can adsorb species that affect the conductivity.
(2) All dopant sites are equivalent and the probability of a gas molecule adsorbing on any site is the same. Each site can only adsorb one molecule.

The adsorption process is described by the following equation:

$$\mathrm{A} + (\text{dopant site}) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (\mathrm{A}) \qquad (2)$$

where A is the adsorbate, (A) is the adsorbate at an occupied site, k_1 is the adsorption rate constant and k_{-1} is the desorption rate constant. The net adsorption rate (rate of adsorption minus the rate of desorption), R, equals

$$R = \frac{d\theta}{dt} = k_1 c f(\theta) - k_{-1}\theta \qquad (3)$$

where θ is the fractional amount of surface coverage, c is the vapor concentration, and $f(\theta)$ is a surface coverage function. In this case $f(\theta)$ is given by $M_0 - \theta$, where M_0 is the fractional coverage of the surface for the maximum adsorption of a monolayer. This definition of M_0 accounts for the possibility that not all of the surface is accessible to the absorbant. The absorptions are normalized to their monolayer amounts and θ ranges from 0 to M_0. Assuming that k_1, k_{-1}, and c are independent of θ, integrating Eq. (3) gives, for the boundary condition $\theta = 0$ at $t = 0$:

$$\theta_{\text{abs}}(t) = \frac{M_0 k_1 c}{k_1 c + k_{-1}}(1 - e^{-(k_1 c + k_{-1})t}) \qquad (4)$$

Eq. (4) describes the approach to equilibrium absorption, starting from when no initial analyte is present and the amount adsorbed is referred to as θ_{abs}. Similarly, the approach toward complete desorption, given by $\theta_{\text{des}}(t)$, when the material begins saturated with analyte and then is exposed to an atmosphere with no analyte, can be similarly derived as:

$$\theta_{\text{des}}(t) = M_0(1 - e^{-k_{-1}t}) \qquad (5)$$

3.2. Langmuir adsorption isotherm

Langmuir, in 1918, suggested that the adsorption process is controlled by the rates of evaporation and condensation. At