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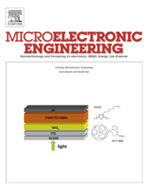

Influence of humidity on kinetics of xylene adsorption onto ball-type hexanuclear metallophthalocyanine thin film

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ABSTRACT

The effects of relative humidity on baseline conductivity, xylene sensitivity and adsorption kinetics of xylene vapor on hexylthiometallophthalocyanines substituted ball-type hexanuclear metallophthalocyanine thin film have been studied. The first results showed that the presence of humidity, acting as interference gas, modifies both the baseline conductivity and sensitivity of the film toward xylene vapor. Three kinetic models, the first-order equation, the Elovich model and the Ritchie's equation were selected to follow the adsorption process. The rate constants, equilibrium capacities and related correlation coefficients for each kinetic model were calculated and discussed. The first-order equation was the best of the various kinetic models studied to describe the adsorption kinetic of xylene on Pc film in humid conditions, as evidenced by the highest correlation coefficients. On the other hand, it was observed that Elovich equation generates a straight line that best fit to the data of adsorption of xylene on Pc film in dry atmosphere.

1. Introduction

Among the various volatile organic compounds (VOCs) xylene is common species of indoor air pollutants. Inhaling excessive xylene can cause huge damage to human being and induce horrible diseases such as colon cancer, rectal cancer, and lung cancer [1]. Because of this, the development of very sensitive and selective sensors for detection of xylene is a vital issue to monitor the level of xylene inside buildings and houses. In order to detect xylene selectively and sensitively, various methods such as gas chromatography technique [2], optical waveguide technique [3], chemical sensors [4] and magnetoelastic sensors [5] have been employed. Among which chemical sensors are possible candidates as xylene sensors because they have the advantages of a simple structure, small size and low-cost in addition to relatively high response to various gases [6,7]. The materials developed for xylene sensors so far include ZnO nanoparticles and Co–ZnO composite nanofibers [8,9], poly(4-vinylbenzyl chloride) (PVBC) and poly(4-vinylbenzyl chloride-co-methyl methacrylate) (P(VBCco-MMA)) [10], and α-Fe_2O_3 nanostructures [11]. However, this type of sensing device has met with little success since the sensor has a relatively slow response and high operating temperatures ($T > 150\,°C$). The associated power consumption of devices based on these compounds could limit portable gas sensing applications. Further improvement or a novel design is needed to increase the response to xylene. An alternative approach is to exploit thin films of organic materials.

The applications of phthalocyanines (Pcs) and their peripherally substituted derivatives in gas sensor devices has gained considerable interest in recent years. These compounds offer a large variation of molecular properties, which can be tuned by introducing various chemical moieties. The response of thin film of Pc compounds toward strong electron donor or electron acceptor compound such as, NH_3 [12], NO_x [13,14], SO_2 [15], CO_2 [16], VOC vapors [17] and halogens [18] have been evaluated by monitoring the changes in spectroscopic or electrical properties of the films. Unlike some other phthalocyanines, the xylene sensing properties, kinetics of xylene adsorption on ball-type hexanuclear metallophthalocyanine thin film and the effect of the relative humidity (RH) on the adsorption kinetics have not been widely studied.

The aim of the present work is to clarify the effect of humidity on the xylene sensing performance of ball-type hexanuclear metallophthalocyanine thin film. This study also highlights the kinetics of xylene adsorption and the effect of humidity on it. Kinetic models evaluated include the Elovich equation, Ritchie's equation and the first-order equation.

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2. Experimental

The synthesis details of the novel ball-type hexanuclear metallophthalocyanine bridged by calix[4]arenes substituted with four hexylthiometallophthalocyanines through nitro coupling shown in Fig. 1, was reported elsewhere [19]. For gas sensing measurements, substrates were 10 × 10 mm^2 glass slides with photolithographically-patterned gold interdigitated electrodes (IDEs) with 50 μm electrode spacing. Gold was selected as the electrode material, since it is well-known that it forms ohmic contact to the phthalocyanine thin film of ball-type 25′,27′-tetrakis-bis(2′,10′,16′,24′-phthalocyaninatodizinc(II))-dioxy-(5′-tetrakisazo 2′,3′,9′,10′,16′,17′ hexylthiophthalocyaninyltetrazinc (II))-11′,17′,23′-tris-tert-butylcalix[4]arene (**5**) was chosen as chemically sensitive layer. The 100 nm thick sensing film of **5** was deposited on IDEs by the spin coating method using a spinner (Speciality Coatings Systems Inc., Model P6700 Series). The elipsometric technique was used to measure the thickness of the Pc film. Because of the good solubility of the compound **5**, chloroform ($CHCl_3$) was used as the solvent. For the spin coating, spreading solutions were prepared by dissolving the Pc in extra pure grade $CHCl_3$ at concentrations of 5×10^{-2} M. Twenty microlitres of such solutions were added with a glass pipette onto the IDEs held on a spinner. The substrate was spun at 2500 rpm for 75 s and then the films were dried at 80 °C under vacuum for 2 h to ensure removal of the residual solvent in the film. During deposition, substrates were kept at ambient temperature. To test the response of the film to the xylene vapors, the variation of the sensor current was measured as the concentration of the xylene vapors in the nitrogen carrier gas was increased from 1% to 5% at room temperature. During the sensing experiment the level of the relative humidity (RH) was negligibly small.

The gas sensing properties of the coating material were tested in a cylindrical chamber of Teflon, 8 cm long and 4 cm diameter, through which a gas could be passed. The variation of the sensor currents were measured by applying a constant dc bias of 1 V and monitoring the current using Keithley model 6517A electrometer. The first stage is to flush a reference gas N_2 through the sensor to obtain a baseline. After MPc sensor in the chamber was stable, it was exposed to five different concentrations of the target gases. A typical experiment consisted of exposure to test gases and subsequent purging with dry nitrogen. The flow rate of the N_2 gas was adjusted as 100 standard cubic centimeter (sccm) during the xylene exposure and purging experiments. For humidity measurements, the N_2 gas was divided into dry gas and wet gas, which was prepared by bubbling the N_2 gas through deionized water. The relative humidity inside the measurement chamber was varied between 0% and 80% RH and controlled with a commercially available humidity meter. Gas sensing data was recorded using an IEEE 488 data acquisition system incorporated into a personnel computer.

3. Results and discussion

3.1. Effect of humidity on xylene sensing

To see the effect of the xylene vapors on the electrical conductivity of the compound, response curves were recorded for different concentration (100 ppm, 500 ppm, 1000 ppm, 5000 ppm, and 10,000 ppm) of xylene vapors (Fig. 2). As can be seen clearly from the Fig. 2, the compound does not show a satisfactory response to the low concentrations of xylene vapor. For this reason, high concentrations of xylene vapor has been chosen to study kinetics of adsorption and the effect of relative humidity on it.

The variation in room temperature sensor current as a function of test duration for various concentrations of xylene vapor in the condition of different RH is presented in Fig. 3. It is clear from the Fig. 3 that not only the baseline current (before doping with xylene vapor) but also the sensor sensitivity (*S*) show a strong dependence on relative humidity. A considerable increase in baseline current in humid atmosphere, compared to dry atmosphere, is clear.

This behavior can be explained by the adsorption of water molecules on the film surface. The adsorbed water molecules may have

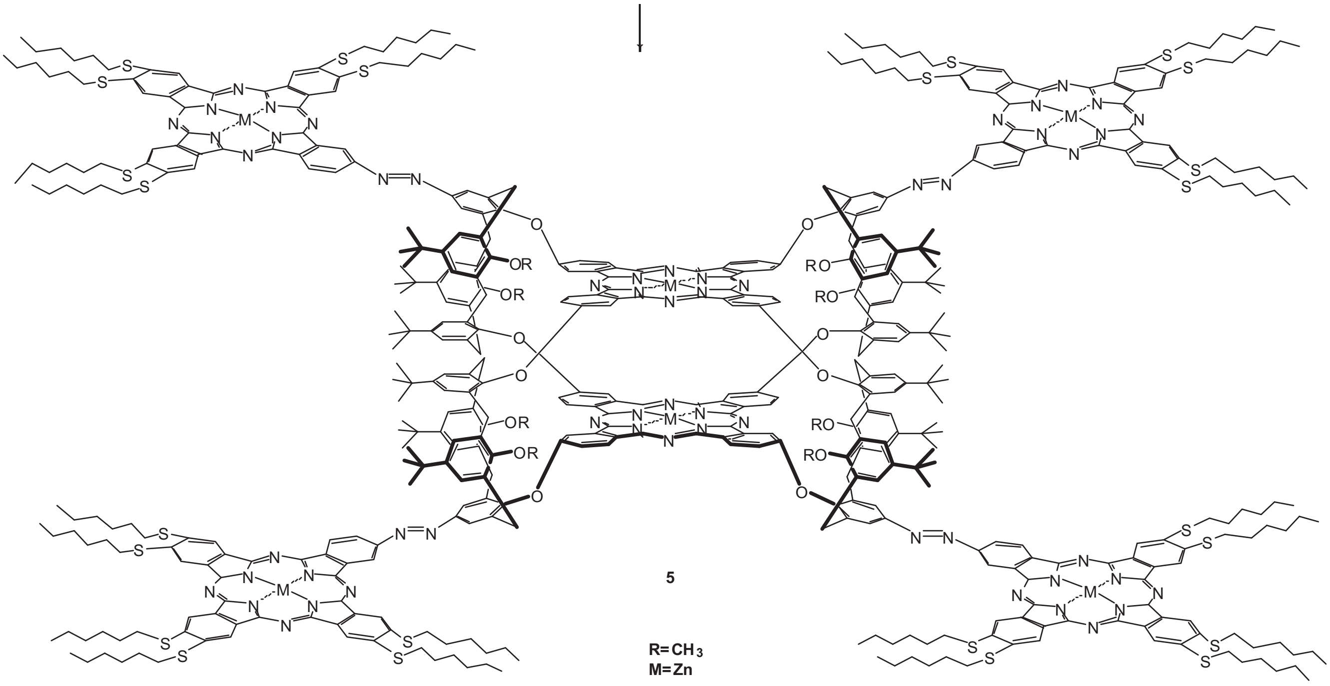

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Fig. 1. Structural formula for 25′,27′-tetrakis-bis(2′,10′,16′,24′-phthalocyaninatodizinc(II))-dioxy-(5′-tetrakisazo-2′,3′,9′,10′,16′,17′ hexylthiophthalocyaninyltetrazinc (II))-11′,17′,23′-tris-tert-butylcalix[4]arene.