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A guest/host composite of $Fe(NO_3)_3$/nanoporous polytriphenylamine assembly for humidity sensor

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ABSTRACT

A nanoporous organic polymer based on triphenylamine was synthesized, and the structure and morphology of the resultant polytriphenylamine (PTPA) were described by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N_2 adsorption/desorption analysis. PTPA was acted as the host to load the guest $Fe(NO_3)_3$ for preparing humidity sensitive composites. Compared with pure PTPA sensor, $Fe(NO_3)_3$/PTPA sensors showed improved humidity sensitive properties, especially the 20 wt% $Fe(NO_3)_3$/PTPA sensor. The impedance of the 20 wt% $Fe(NO_3)_3$/PTPA sensor changed four orders of magnitude over the whole humidity range, with a good linearity, litter hysteresis, rapid response and good long-time stability. The complex impedance plots and direct current (DC) reverse polarity method were used to research the mechanism of the optimized sensor.

1. Introduction

Humidity sensors play an important role in many areas of daily life, such as meteorological forecast, food storage, plant cultivation, medical care, drug manufacturing, etc. [1–5]. The basic work principle of humidity sensors base on some physical quantities such as current, impedance, capacitance or volume of the sensing material changed at various relative humidities (RH). Hence, the performance of a humidity sensor mainly depends on the sensitive materials. Recently, researches on humidity sensitive materials have focused on organic polymers [6–8], ceramic semiconductors [9–11] and hybrid composites [12–14]. In particular, polymeric humidity sensors are attractive because of their advantages of low cost, easy fabrication and high sensitivity [15,16]. But the main defect of polymeric humidity sensors is that the dissolution of hydrophilic polymers under high humidity environment restricts their stability.

Recently, porous polymers have attracted an increased research interest owing to their potential to merge the properties of both porous materials and polymers [17]. Their unique properties of large surface area, good chemical tunability, easy processability make them attractive media for applications in gas storage and separation [18,19], sensors [20,21], light-emitting organics [22,23] and heterogeneous catalysis [24,25]. The abundant pores in the polymers not only can physically encapsulate and immobilize moisture-sensitive materials, but also make water molecules or other ions transport freely in the polymers. Moreover, the crosslinked structure of porous polymers ensures their insolubility in water to enhance the stability under high humidity atmospheres. Hence, the porous polymer as a host to load a moisture-responsive guest is a potential class of materials for fabricating humidity sensors.

In this paper, the porous polymer based on triphenylamine is used as a host to load ferric nitrate ($Fe(NO_3)_3$) to fabricate humidity sensors. The function of the porous polymer is providing porous crosslinked skeleton for loading moisture-sensitive materials. $Fe(NO_3)_3$ has been chosen as the dopant for its excellent humidity sensitive properties [26]. The sensing properties of the humidity sensors can be controllable by changing loading contents of $Fe(NO_3)_3$ in porous polymers, and appropriate loading content of $Fe(NO_3)_3$ in porous polymers shows the best humidity sensing properties. In addition, the mechanism about the influence of $Fe(NO_3)_3$ in porous polymers is discussed via complex impedance plot and direct current (DC) reverse polarity method.

2. Experimental

2.1. Materials

Triphenylamine (TPA) was purchased from Chengdu Gracia Chemical Reagent Co., Ltd., China. Iron chloride ($FeCl_3$) and ferric

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nitrate ($Fe(NO_3)_3$) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Chloroform was obtained from Xilong Chemical Reagent Co., Ltd., China. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

2.2. Synthesis of the porous polymer poly(triphenylamine) (PTPA)

Porous PTPA was synthesized by oxidation polymerization of TPA. $FeCl_3$ (3.24 g, 20 mmol) was dissolved in chloroform (20 mL), then TPA (1.22 g, 5 mmol) was added to the solution and the mixtures were stirred for 4 hours at room temperature. The product was washed with methanol and chloroform to remove the unreacted monomer and catalyst residues. Further purification was carried out by Soxhlet extraction with methanol and chloroform for 24 h respectively. The obtained product was dried under vacuum at 60 °C for 24 h.

2.3. Characterizations

Fourier transform infrared spectrum (FTIR) was recorded with Perkin-Elmer spectrometer, using KBr pellets as substrate. Nitrogen isotherms were obtained at 77 K on a Micromeritics Tri-star3000 analyzer. Samples were pretreated by degassing for 12 h at 150 °C. The morphologies of the films were performed on a JEOL JSM-6700F scanning electron microscopy (SEM). The microstructures of the films were checked using a Hitachi H-800 transmission electron microscopy (TEM), with an accelerating voltage of 200 kV.

2.4. Fabrication and measurement of humidity sensors

The humidity sensing materials were prepared by mixing PTPA and $Fe(NO_3)_3$ aqueous solution with certain ratio to form pastes, then the pastes were spin-coated onto ceramic substrates (6 mm × 3 mm, 0.5 mm in thick) with five pairs of Ag–Pd interdigitated electrodes (electrodes width and distance: 0.15 mm) to form sensing films with the thickness of 0.12 mm, and then the films were dried at 60 °C for 5 h. Finally, the humidity sensors were obtained after aging at 95% relative humidity (RH) with a voltage of 1 V AC, 100 Hz for 24 h.

The characteristic curves of humidity sensitivity were measured on a ZL-5 model LCR analyzer (Shanghai, China). The voltage applied in our studies was AC 1 V, and the frequency varied from 20 Hz to 100 kHz. The measuring temperature was controlled at 25 °C by air-conditioner. The atmosphere of humidities were produced by different saturated salt solutions in their equilibrium states including LiCl for 11% RH, $MgCl_2$ for 33% RH, $Mg(NO_3)_2$ for 54% RH, NaCl for 75% RH, KCl for 85% RH and KNO_3 for 95% RH at 25 °C.

3. Results and discussions

3.1. Characterizations of PTPA

The FTIR spectrum of PTPA is shown in Fig. 1. The peaks at 3407 and 2363 cm^{-1} stand for the stretching of H_2O and CO_2 in the atmosphere. The absorption peaks at 3027, 2923, 1250, 1180 and 816 cm^{-1} come from the stretching of C—H in the benzene ring. The absorption peak at 1599 and 1500 cm^{-1} are assigned to the stretching of the aromatic C=C. The absorption peaks at 1379 and 1090 cm^{-1} are assigned to the stretching of C—N. The results confirm the successful preparation of PTPA.

For the sake of observing the morphology of PTPA films, SEM and TEM images of PTPA films were shown in Fig. 2a and b, respectively. As can be seen in Fig. 2a, the obtained polymers consisted of nanoparticles and the accumulation of these nanoparticles formed some pores. TEM image affirmed that there were abundant pores existed in PTPA films as shown in Fig. 2b.

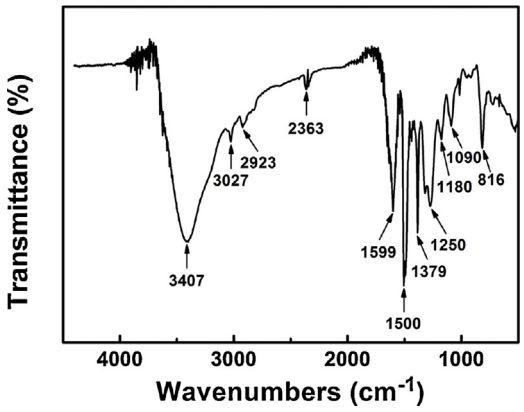

Fig. 1. The FTIR spectrum of PTPA.

In order to investigate the porosity of PTPA sample, N_2 sorption isotherms of PTPA were measured at the relative pressure range of 0–1 as shown in Fig. 3a. The Brunauer–Emmett–Teller (BET) surface area and pore volume were calculated to be 815 m^2/g and 0.66 cm^3/g, respectively. The adsorption isotherm of PTPA sample indicated a steep nitrogen gas uptake at low relative pressure ($P/P_0 < 0.001$), which reflected abundant micropores existed in PTPA sample [27]. Meanwhile, the sorption isotherms of PTPA showed a slight hysteresis loop at medium and high pressure region implying a spot of mesopore structure [27]. The pore size distribution profile of PTPA also confirmed the presence of such heterogeneous porous structure, which showed two main kinds of pore sizes (0.84 and 2.17 nm) in Fig. 3b.

3.2. Humidity sensitive properties

Initially, the pure PTPA sensor was fabricated and measured under different RH at 1 V AC, 100 Hz as shown in Fig. 4 (black line). As can be seen, the pure PTPA sensor showed almost no response at low RH and little response at high RH. The component of polymer is responsible for PTPA sensor without intensive response, because there are no hydrophilic groups in the polymer PTPA to interact with water molecules. Afterwards, humidity sensors based on PTPA loading different contents of $Fe(NO_3)_3$ were fabricated and also measured under different RH at 1 V AC, 100 Hz. $Fe(NO_3)_3$, which is provided with hygroscopy, is able to attract more water molecules and ionize to Fe^{3+} participating in electrical conduction together with H^+ ionized by H_2O. Hence, the impedances of sensors gradually decreased with the increase of loading content of $Fe(NO_3)_3$ as shown in Fig. 4. When the content of $Fe(NO_3)_3$ was under 15 wt%, the impedance at 33% RH changed little compared with that of 11% RH, which indicated that the composites were less sensitive to humidity. When the content of $Fe(NO_3)_3$ was above 20 wt%, the adsorption of water molecules in composites was saturated at high RH leading to a little change of impedance from 85% to 95% RH. And the sensor based on 20 wt% $Fe(NO_3)_3$/PTPA showed the best linearity and sensitivity. It was sensitive in whole humidity range and the impedance changed four orders of magnitude from 11% to 95% RH. Hence the 20 wt% $Fe(NO_3)_3$/PTPA sensor was selected for further research.

The measuring frequency plays an important role in the humidity sensitive properties of the 20 wt% $Fe(NO_3)_3$/PTPA sensor, thus the impedance as a function of RH at different frequencies were measured to determine the optimum frequency. As can be seen from Fig. 5, the impedance decreased remarkably with raising frequency at low RH, and the difference of impedance