Sensors and Actuators B 269 (2018) 110–117

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Electrical and humidity-sensing properties of flexible metal-organic framework M050(Mg) and KOH/M050 and AuNPs/M050 composites films

Pi-Guey Su*, Xin-Han Lee

Department of Chemistry, Chinese Culture University, Taipei 111, Taiwan

ARTICLE INFO

Article history:
Received 1 December 2017
Received in revised form 2 April 2018
Accepted 1 May 2018
Available online 1 May 2018

Keywords:
Flexible humidity sensor
MOF
Composite
Sensing properties
Complex impedance spectra

ABSTRACT

A commercial metal-organic framework (MOF) of Basosiv M050 and its composite materials potassium hydroxide/M050 (KOH/M050) and Au nanoparticles/M050 (AuNPs/M050) were coated on a polyethylene terephthalate (PET) substrate to form novel flexible impedance-type humidity sensors. The electrical properties of M050 to which were added various amounts of KOH or AuNPs were studied in detail as functions of relative humidity (RH). The contributions of the KOH or the AuNPs to the humidity-sensing (linearity and sensitivity) properties and flexibility were thus elucidated. The M050 and composites of KOH/M050 and AuNPs/M050 films that were coated on PET substrates were analyzed using scanning electron microscopy (SEM), atomic force microscopy (AFM), UV–vis spectroscopy and infrared spectrometry. The sensor that was made of KOH/M050 film with 0.05 M added KOH exhibited high flexibility, the highest sensitivity, acceptable linearity, a short response time, a low temperature coefficient and long-term stability. The humidity-sensing mechanism of the KOH/M050 film was explained using complex impedance spectra.

1. Introduction

Flexible humidity sensors are widely integrated into smart textiles, radio frequency identification (RFID) tags and the Internet of Things (IoT) to improve quality of life and industrial processes; because they are flexible, light, soft and transparent. Many polymers-based materials have been coated on flexible substrates to fabricate flexible humidity sensors [1–13]. Flexible capacitive-type humidity sensors were fabricated by using hydrophobic polymers-based materials [1–3]. Additionally, flexible impedance-type humidity sensors were produced by using hydrophilic polymers-based with —COOH, —NH_2 and —OH functional groups and their composite materials [4–13]. Many challenges should be considered to develop flexible humidity sensors including manufacture processes, the stability of their mechanical, flexibility, electrical and humidity-sensing properties under repeated bending.

Metal-organic frameworks (MOFs) are mesoporous crystalline materials, which comprise metal ions connecting to organic ligands in a networked structure [14]. Recently, MOFs have attracted substantial interest for use in chemical sensors owing to their ultrahigh surface areas, uniform pore size, flexible structure, and high thermal and mechanical stabilities. Such sensors include the volatile organic compounds (VOCs)-based gas sensor [15,16], the alcohol-based gas sensor [17], NH_3-based gas sensor [18] and humidity sensors [19–22]. Notably, the MOFs coatings on the substrates in the cited studies were deposited on rigid substrates, such as ceramics or SiO_2/Si. However, it is difficult to integrate rigid sensor devices on flexible electronics because rigid substrates do not allow any flexibility. To the best of our knowledge, the fabrication of flexible humidity sensors that are based on MOFs and their composite materials has not been reported. The commercial MOF (Basosiv M050; magnesium formate) [23] was chose in this work because that the Mg-based MOF exhibited water stable in a high-humidity environment [24]. Alkali salts (such as LiOH and KOH) and noble nanometals (such as Pt, Pd and Au) are used as additives for improving sensing properties of sensors because they had many chemisorption sites for gas vapors owing to their small size and high local charges [25–27]. Therefore, composite materials of potassium hydroxide/M050 (KOH/M050) and Au nanoparticles/M050 (AuNPs/M050) were prepared in this study. M050 and composite materials of KOH/M050 and AuNPs/M050 were drop-coated on a polyethylene terephthalate (PET) substrate to form flexible impedance-type humidity sensors.

* Corresponding author.
E-mail address: spg@faculty.pccu.edu.tw (P.-G. Su).

https://doi.org/10.1016/j.snb.2018.05.002
0925-4005/

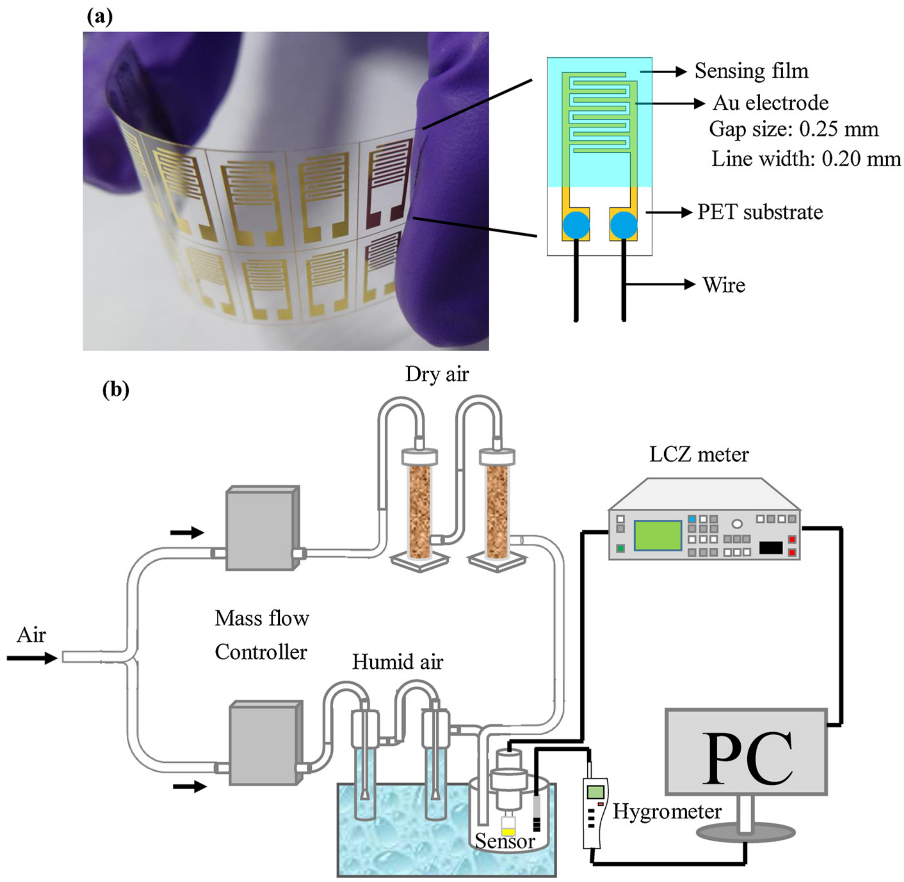

Fig. 1. (a) Photograph of flexible humidity sensors on a PET substrate and structure of a humidity sensor, (b) Schematic structure of the impedance measurement of flexible humidity sensors and the humidity atmosphere controller.

2. Experimental

2.1. Materials and preparation of flexible impedance-type humidity sensors

The Mg-based MOF (magnesium formate, Sigma Aldrich, trademark M050) directly used without any further purification. AuNPs were obtained using the method in the literature [28]. The AuNPs colloidal particles were prepared by adding 38.8 mM sodium citrate (Shimakyu's Pure. Chemicals, Lancashire, United Kingdom, 99%) to boiling aqueous 1.0 mM tetrachloroauic acid ($HAuCl_4$, Alfa Aesar, Osaka, Japan, 99%). Then, the solution was boiled for 15 min with vigorous stirring, and finally allowed to cool to room temperature to produce 0.9 mM AuNPs colloidal solution.

Fig. 1(a) schematically plots the pattern of the flexible impedance-type humidity sensor. Firstly, sputtering Cr (thickness 50 nm) and then Au (thickness 250 nm) on a flexible substrate (polyethylene terephthalate; PET) in the temperature range of 120 ~ 160 °C formed the interdigited Au electrodes (gap 0.25 mm). The substrates were firstly treated with an H_2O_2/H_2SO_4 mixture (1:2, 15 mL), washed in de-ionized water (DIW) and then cleaned in acetone solution for 3 min.

M050 precursor solution was prepared by adding 100 mg of M050 powder to 1 mL ethanol and stirring vigorously. Precursor solutions of KOH/M050 and AuNPs/M050 composite materials were prepared by mixing KOH and AuNPs in various ratios with the as-prepared M050 precursor solution. Table 1 presents the various compositions examined. The as-prepared M050 and composite solutions were coated onto as-prepared PET substrate, and allowed to dry at 60 °C. Therefore, a flexible impedance-type humidity sensor was obtained.

Table 1
Compositions of M050 and its composites-based films used to prepare flexible impedance-type humidity sensors.

Sensor number	MOF (mg)	KOH (M)	AuNPs (mg)
1	100	0	0
2	100	0.005	0
3	100	0.05	0
4	100	0	60
5	100	0	180
6	100	0	540

2.2. Instruments and characterizations

UV–vis spectroscopy (Agilent 8453, Santa Clara, USA) was used to characterize the formation of M050, AuNPs, and AuNPs/M050 composite. An infrared spectrometry (Nicolet 380, Wilmington, USA) was used to obtain the IR spectra of the samples. The surface microstructure of the films that were coated on a PET substrate was investigated using a scanning electron microscope (SEM, Ibaraki, Japan) and an atomic force microscope (AFM, Ben-Yuan, CSPM 4000, Baijing, China) in tapping mode. Fig. 1(b) shows the humidity-sensing measurement system. A divided flow humidity generator was used to produce the testing humidity, as same as previously reported [29]. The required humidity (RH values) was adjusted according to readings from a standard humidity hygrometer (accuracy of ±0.1% RH, Rotronic, Bassersdorf, Switzerland)