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Metal organic frameworks enhanced graphene oxide electrode for humidity sensor

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Abstract. Copper benzene-1,3,5-tricarboxylate (Cu-BTC), a typical metal organic framework, is deposited on the graphene oxide (GO) film to prepare a resistance humidity sensor (Cu-BTC/GO) for improving humidity sensing. The characteristics of Cu-BTC, GO and Cu-BTC/GO were measured by scanning electron microscopy (SEM), X-ray diffraction (XRD), nitrogen isotherm adsorption and electrochemical impedance spectroscopy (EIS). The humidity sensing properties of the Cu-BTC/GO were investigated in detail. The obtained Cu-BTC/GO demonstrates good sensitivity and repeatability over 11%-85% relative humidity (RH) measurements. The Cu-BTC/GO coated device shows high normalized response (S) value (6200%), which is much higher than that of pure GO coated device. Sensing mechanism of Cu-BTC/GO is discussed based on different RH and the results indicate that moderate amounts of Cu-BTC deposition can enhance sensing abilities of GO. High specific surface area and interfacial conductivity are crucial factors to fabricate humidity sensors with high performance.

1. Introduction

Humidity sensors have attracted considerable attention because of their wide applications in many fields, such as industry, agriculture, medicine, meteorology, environment monitoring, home appliance and so on. Recently, some researches also find that relative humidity (RH) level can affect photochemical reaction speed of O₃ and NO₂ in the air [1]. Therefore, humidity is an important factor for the air quality evaluation. Various transduction techniques are used to develop humidity sensors, such as capacitance [2], resistance [3], surface acoustic wave (SAW) [4], quartz crystal microbalance [5] and optical fiber [6]. Among these, resistive humidity sensors are gaining much more attention because they have the features of small form factor, easy to fabricate and able to be integrated with circuits [3].

During the past decade, various materials have been adapted to the sensing layers of humidity sensors (*e.g.*, graphenes [3], carbon nanotubes [7], metal oxides [8], polymers [9], metal-organic frameworks (MOFs) [10] and composites [11]), which are expected to improve the performance by virtue of their intrinsic properties, porous morphology, and large surface-to-volume ratio. Among these sensing materials, graphene, a two-dimensional monolayer of sp²-bonded carbon atoms exhibiting exceptional mechanical thermal and electrical properties, holds great potential for ultra sensitive detection. Graphene oxide (GO) is a graphene derivative covered by oxygen-containing



functional groups. The hydroxyl and the epoxy groups decorated on the basal plane and carboxyl groups at the edges according to the Klinowski model of GO [12]. These oxygen-containing functional groups are highly hydrophilic and reactive, therefore, GO-based materials are considered to be good candidates for fabricating efficient humidity sensors. A. De Luca et al. used GO to produce a sensor for the humidity monitoring in indoor environment, which shows a strong response in humidity due to high proton conduction and fairly high specific area [3]. A flexible humidity sensor made by D. Zhang et al. [13] exhibits excellent sensing behaviour to humidity, fast response to recover time and good repeatability by using reduced GO/polymer nanocomposite film as the sensing materials. Although there have a few successful cases, the application of graphene-based electronic sensors is still in its infancy.

In a humidity sensor, high surface-to-volume ratio of the sensitive material is the most important part to get good signals. GO has high surface area, but it's easy to aggregate and lost its advantages. MOFs are kinds of porous crystal materials which have high porosity because of their unique structures. Furthermore, MOFs can be modified easily through changing their surface functional groups [14-16]. Among thousands of MOFs, copper benzene-1,3,5-tricarboxylate noted as Cu-BTC ($[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]$) coating is a promising candidate because of its high porosity and sensitivity to water. The framework of Cu-BTC composed of dimeric cupric tetra-carboxylate units [16]. Each metal completes its pseudo octahedral coordination sphere with an axial aqua ligand opposite to the Cu-Cu vector [17]. Therefore, Cu-BTC has high porosity and huge gas storage potential due to its unique structure. Li's group [16] proves that the composite of Cu-BTC@GO can remain its structure and porosity and its Brunauer-Emmett-Teller (BET) surface area is $1205 \text{ m}^2/\text{g}$. Küsgens [18] et al. demonstrate that the water stability of Cu-BTC is sufficient for molecular recognition if the framework is not directly exposed to liquid water. Experiments proves that even though Cu-BTC is unstable in liquid water, it is a promising material for applications in removal of trace water or molecular sensing.

Herein, a novel type of resistance humidity sensor with high conductivity and large porosity was prepared by depositing GO and Cu-BTC layer on Ag inter-digital electrodes. The Cu-BTC/GO humidity sensor shows significant enhancement of sensing performance with the humidity ranging from 11% to 85% RH, indicating that MOFs have great potential application in humidity sensor. In addition, the sensing mechanism has also been discussed.

2. Materials and methods

All the chemicals were bought from Sigma-Aldrich and used without further purification. The Cu-BTC powder was synthesized according to a previous method [19]. Copper nitrate tri-hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 1 mmol) and 1,3,5-benzenetricarboxylic acid (H_3BTC , 0.67 mmol) were added in an autoclave with DMF (12 mL), ethanol (12 mL) and DI water (8 mL). The mixture was stirred for 15 min and the autoclave was placed in an oven at 80°C for 24 h. The product was isolated by filtration and rinsed with 10 mL of ethanol for three times, and then immersed in methanol for 3 days, during which the activation solvent was decanted and replaced freshly everyday. After that, the sample was dried at 200°C in vacuum to yield Cu-BTC. The final powder was dispersed in ethanol to form 50 mg/mL Cu-BTC ethanol solution for further use.

GO was prepared by a modified Hemmer method [20]. Firstly, flake graphite powder (1 g) and concentrated sulfuric acid (23 mL) were added into a 500 mL of glass bottle, which was stirred at room temperature for 24 h. Secondly, the mixture was heated up to 40°C , NaNO_3 (0.1 g) and KMnO_4 (3 g) were added with stirring for 30 min. Then 5 mL of deionized water was added slowly and stirred for 5 min for two times. Next, 40 mL of water was added and stirred for 15 min. Subsequently, 140 mL of water and 10 mL of H_2O_2 (30%) was added with continuous stirring for 5 min. Finally, the bright yellow reaction system was centrifugal separated at 8000 rpm, then the precipitation was ultrasonic washed with HCl (5%). The collected supernatant was washed with ethanol for several times. The obtained product was mixed to form 1 mg/mL GO ethanol solution for further use.

The humidity sensor was fabricated on a glass substrate through microfabrication technology, including spin coating of photoresist, exposure, development, and lift-off technique. Then, Ag

interdigitated electrode (IDE, ~120 nm thick) was fabricated on the glass substrate. The width and gap of IDE finger was both 0.5 mm. After that, the sensing film was formed by dropping the GO ethanol solution (0.1 mg/cm²) and the Cu-BTC ethanol solution (1 mg/cm²) successively on the interdigital part to cover it entirely. At last, the sensing layers were dried at 50 °C for 6 h.

The crystal structure for Cu-BTC is investigated by X-ray powder diffraction (XRD) using a LabX XRD-6000 with Cu K radiation (1.54 Å), operating at 40 kV and 35 mA. The morphologies of GO and Cu-BTC were examined using field emission scanning electron microscopy (SEM, JEOL S4800, Japan) operating at an accelerating voltage of 15 kV. N₂ adsorption isotherms of GO and Cu-BTC were carried out at -196 °C and 1 atm. The electrochemical impedance spectroscopy (EIS) were also measured by CHI660D using three electrode system. The testing frequency range is 1 Hz to 100000 Hz, and the electrolyte is 0.01 M K₃Fe(CN)₆ in 0.1 M KCl.

The humidity sensing measurement was carried out by exposing the prepared sensor to different relative humidity levels, and the humidity environment was provided by different saturated aqueous solutions in closed vessels. In this work, five saturated aqueous solutions of LiCl, MgCl₂, Mg(NO₃)₂, NaCl and KCl were adopted at room temperature to yield approximately 11%, 33%, 54%, 75% and 85% RH levels, respectively. The resistance of the Cu-BTC/GO film was measured by Agilent B2902A. The Fig. of merit used for the evaluation of sensor performance is the normalized response(S), determined by $S = (R_{RH} - R_{11})/R_{11} \times 100\%$, where R_{RH} and R_{11} are the electrical resistance of the sensor in the given RH and 11% RH, respectively [11].

3. Results and discussion

3.1. Material characterization

Figure 1 shows the X-ray pattern of pure GO, Cu-BTC and Cu-BTC/GO. The sample of Cu-BTC is powder, while the other two samples are prepared by dropping the materials dispersed in ethanol on substrates, so the intensity of XRD for Cu-BTC is much stronger than those of the other two samples. For comparison purposes, the intensity of XRD for Cu-BTC has been deduced to 1/100. It can be found that the powder sample shows the typical patterns of Cu-BTC [17, 24]. The appearance of sharp peaks in XRD patterns is a testimony of good degree of crystallinity in synthesized products. The main peak of GO usually located in the range of 8 to 11° [20]. According to Bragg's law, the major peak of GO in this work is at $2\theta = 8.59^\circ$, which reveals that there has a distance between the carbon layers of 10.3 Å. The peak indicating GO becomes $2\theta = 10.17^\circ$ (8.8 Å) due to the deposition of Cu-BTC on GO. Other X-ray diffraction patterns of the Cu-BTC/GO contain both of the characteristic peaks of Cu-BTC and GO.

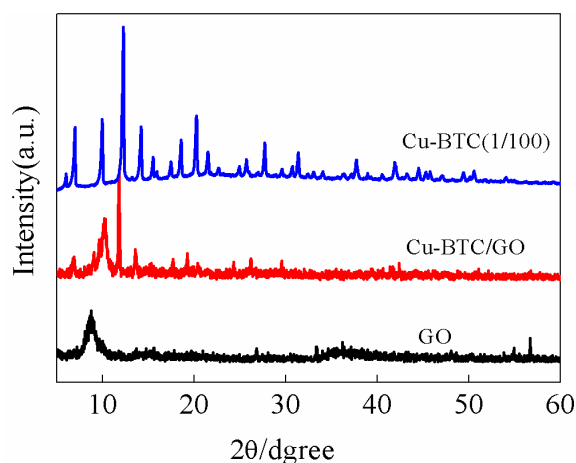


Figure 1. X-ray diffraction for Cu-BTC, Cu-BTC/GO and GO.

The morphological structures and size distribution histograms of Cu-BTC, GO, and Cu-BTC/GO are displayed in Figure 2. It can be observed that the typical shape of Cu-BTC is octahedron and the

size of Cu-BTC is about 2-10 μm . Figure 2(b) shows that GO has several thin layers folded together. After dropping GO and Cu-BTC ethanol solutions on the Ag IDE, the surface of GO is covered by Cu-BTC crystal practically (figure 2c and d). The average diameter of the Cu-BTC/GO is 3-10 μm , and MOFs and GO maintain their original structures.

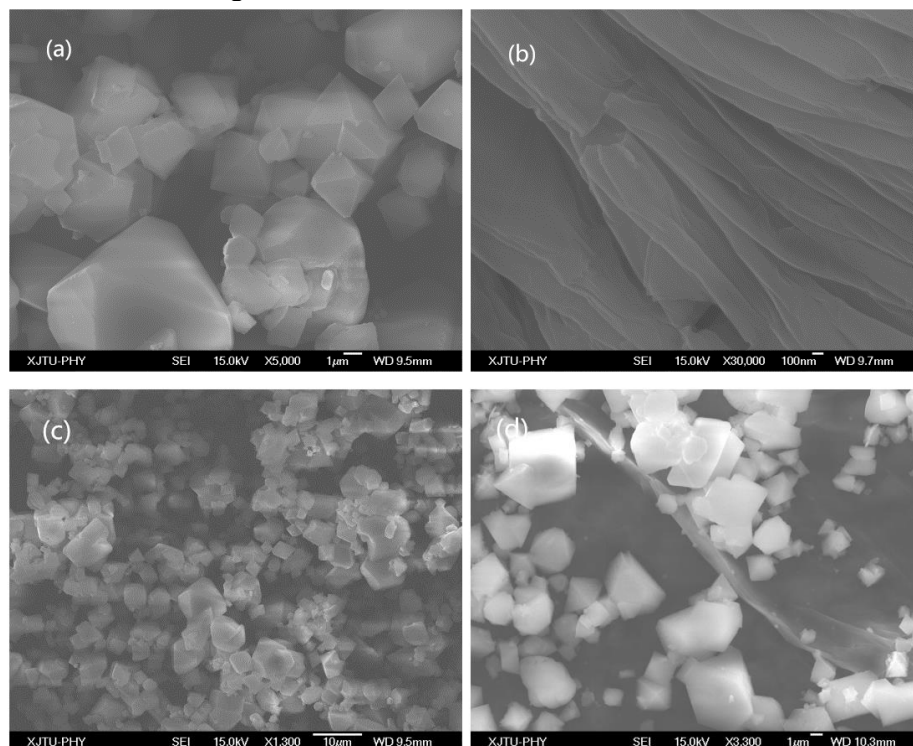


Figure 2. The SEM images of Cu-BTC(a), GO(b) and Cu-BTC/GO with different magnification(c and d).

The nitrogen adsorption isotherm of Cu-BTC and GO were investigated. (Figure 3). As expected, GO has no much nitrogen adsorption. [19] According to the standard Brunauer Emmett Teller (BET) method, the specific surface area of Cu-BTC is calculated to be 1272 m^2/g . It is hard to directly detect the N_2 adsorption isotherm for the Cu-BTC/GO on the Ag IDE, we assume that the BET surface area of Cu-BTC/GO might be similar with that of pure Cu-BTC. Because there is only physical attachment and the proportion of the two raw materials is 10:1 (Cu-BTC:GO=10:1).

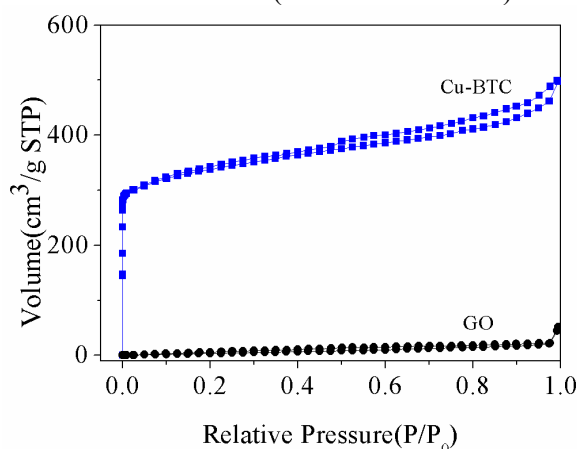


Figure 3. The N_2 adsorption isotherms of Cu-BTC and GO.

The electrochemical impedance spectroscopy (EIS) of Cu-BTC, GO and Cu-BTC/GO were measured and presented in Figure 4. It is clear that the impedance of Cu-BTC is much larger than

those of GO and Cu-BTC/GO. The semicircle is invisible. The resistant of the testing materials are extremely high, but they are unimpeded for ion and electron in the electrolyte. The straight line might stem from the ionic and/or electrolytic conductivity [23]. The impedance of Cu-BTC/GO and GO are almost the same, suggesting that coating Cu-BTC layer on the GO could not change the behaviour of conductivity of GO.

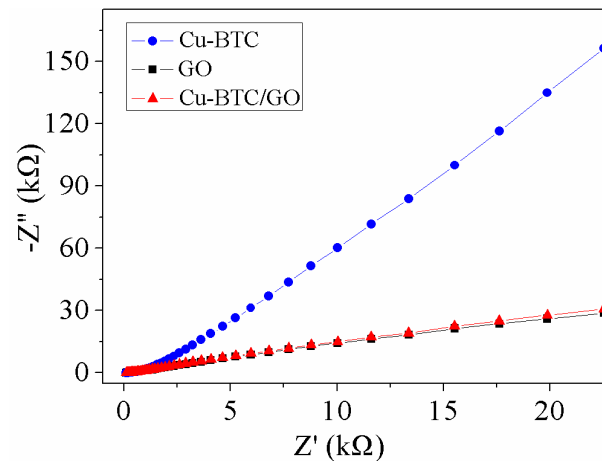


Figure 4. The electrochemical impedance spectroscopy (EIS) plots of GO, Cu-BTC and Cu-BTC/GO.

3.2. Response property of the sensors

The loading amount of the sensing materials can greatly affect the humidity sensing signal. Excessive amount of GO might reduce the adhesive force to the substrate and lead to the layer exfoliate from the substrate, while too much Cu-BTC may enhance the resistance and result no effective signal. According to the experimental results, the optimized amount ratio for GO: Cu-BTC = 0.1:1 mg/cm² is chosen in this paper.

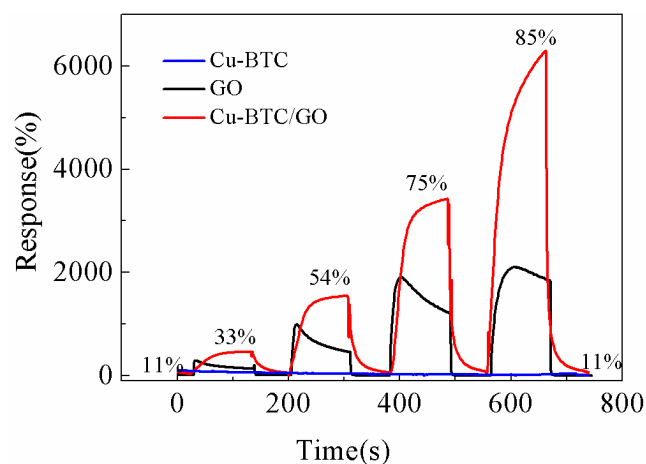


Figure 5. The humidity sensitive performance of GO, Cu-BTC and Cu-BTC/GO.

Figure 5 shows the response of the sensors exposing to different relative humidity levels. For comparison, Cu-BTC, GO and Cu-BTC/GO are deposited on the electrodes separately. Each exposure/recovery cycle was carried out by an exposure interval of 100 s followed by a recovery interval of 100 s at 11% RH. The Cu-BTC device has almost no peak and shows very weak response compared with GO and Cu-BTC/GO. The sensitive peak significantly increases with the rising of RH

in the range of 11% -85% for both GO and Cu-BTC/GO. The sensitive peak of the Cu-BTC/GO coated device can reach up to 6200%, which is much higher than that of GO device (2100%).

We know that GO has good electrical conductivity, but pure Cu-BTC shows very low electrical conductivity (10^{-6} S/m) [14]. It could combine the merits of Cu-BTC and GO when depositing appropriate amount of Cu-BTC/GO. Cu-BTC not only has high surface-to-volume ratios, but also possesses a large density of Cu-Cu unsaturated sites [21], which make Cu-BTC facilitate water molecule to be captured from external environment. Meanwhile, hydrophilic functional groups decorated on the basal planes and the edges of GO can also absorb water molecules. Based on this, the humidity sensing mechanism for the Cu-BTC/GO can be explained (Figure 6).

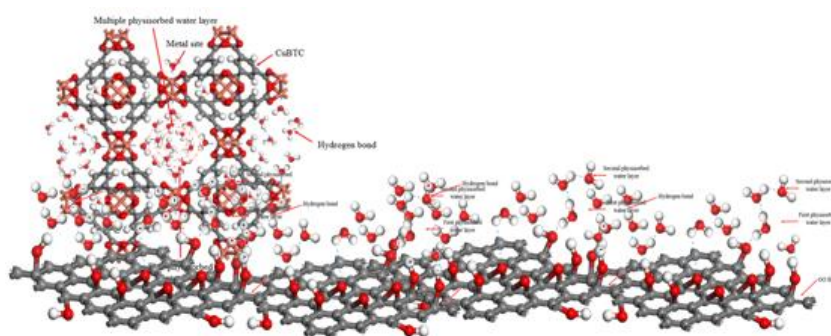


Figure 6. The mechanism for Cu-BTC improving the moisture sensitivity of GO.

At low RH, only a few water molecules are absorbed on the sensing materials. Water molecules can be quickly absorbed on the hydrophilic groups of the exposed GO. Although the ionize protons are restricted by discontinuous mobile layers, they contribute to the leak conduction due to the proton hopping between the adjacent water molecules [23]. Meanwhile, water molecules can also be absorbed on Cu-Cu unsaturated sites of Cu-BTC, which is a slower process associating with diffusion. The accumulated water molecules in the MOFs pore can provide a proton conducting channel to gain higher response current. Therefore, the sensing ability of water vapour can be ascribed to the coordination between the oxygen groups in GO and Cu^{2+} metal centre in Cu-BTC.

As the RH increases, the water molecules are absorbed in the pores of framework and the surface of the GO by the multilayer physical adsorption. At the second physical absorption layer, water molecules are absorbed through hydrogen bonds. Then the hydroxyl groups on the surface will be combined with water molecules, and protons can be transferred from hydroxyl group to water molecules to come into hydronium ions (H_3O^+). The hydronium ions are the main charge carriers and conductivity is generated by a Grotthuss chain reaction [25], which can cause an increase of the leak conduction. Thereafter, the water molecules become mobile and progressively more identical to those in the bulk liquid.

At higher RH, the physical absorbed water layers gradually exhibit liquid-like behaviour, which is beneficial for the hydrolysis of the functional groups (carboxyl, sulphonic and/or hydroxyl) on GO sheets. These ions will contribute to the ionic conductivity [10, 23] and the physical absorbed water can penetrate into the interlayer of GO films [3]. In addition, there is another ionic conductivity channel formed by absorbing a large amount of water molecules in Cu-BTC porous crystals, which greatly increases the response signals.

The repeatability of Cu-BTC/GO humidity sensor was measured for five exposure/recovery cycles repeatedly for 54%, 75% and 85% RH (Figure 7). The ratio of maximum deviation to full-scale measurement is under the same conditions, and the repeatable error is less than 1.3%. The results demonstrated that the adsorption of water molecules in the Cu-BTC and on the GO are both physical adsorption, and the Cu-BTC has enough stability for enhancing humidity sensing.

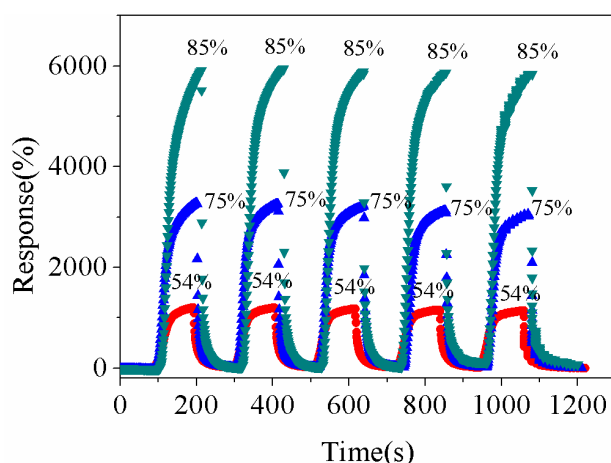


Figure 7. The humidity sensitive repeatability of Cu-BTC/GO sensor at different humidity.

4. Conclusions

In this work, a Cu-BTC/GO resistance humidity sensor has been fabricated by depositing GO and Cu-BTC crystal on silver interdigitated electrodes. The Cu-BTC/GO coated device shows high normalized response (S) value (6200%) and good repeatability for humidity sensing. This can be explained by rich oxygen groups on the GO and high density of Cu²⁺ metal centre in the Cu-BTC. The satisfactory capability of Cu-BTC/GO suggests the potential practical application of preparing better humidity sensor or other gas sensors using MOF.

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