Nanocomposites of Carbon Nanotube (CNTs)/CuO with High Sensitivity to Organic Volatiles at Room Temperature

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Abstract

In order to enhance the sensitivity of carbon nanotube based chemical sensors at room temperature operation, CNTs/CuO nanocomposite was prepared under hydrothermal reaction condition. The resulted-product was characterized with TEM (transmission electron microscopy), XRD (X-ray diffraction) and so on. A chemical prototype sensor was constructed based on CNTs/CuO nanocomposite and an interdigital electrode on flexible polymer substrate. The gas-sensing behavior of the sensor to some typical organic volatiles was investigated at room temperature operation. The results indicated that the carbon nanotube was dispersed well in CuO matrix, the CuO was uniformly coated on the surface of carbon nanotube, and the tubular structure of carbon nanotube was clearly observed. From morphology of TEM images, it can also be observed that a good interfacial adhesion between CNT and CuO matrix was formed, which maybe due to the results of strong interaction between CNTs with carboxyl groups and CuO containing some hydroxy groups. The CNTs/CuO nanocomposite showed dramatically enhanced sensitivity to some typical organic volatiles. This study would provide a simple, low-cost and general approach to functionalize the carbon nanotube. It is also in favor of developing chemical sensors with high sensitivity or catalysts with high activity to organic volatiles at low temperature.

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1. Introduction

Recent years, there has been still received great consideration in the research and development of carbon nanotubes (CNTs) and its composites due to their unique physical and chemical properties [1-10], which is not only widely used in catalysts [11], nanoelectronic devices [12-15], solar cells [16], displays [14], hydrogen storage materials [17], supercapacitors, but also has potential applications in sensors [18, 19].

As a chemical sensor, gas-sensing at low temperature is of special interest because of low-energy consumption. However, most currently available sensors, except a few types of polymer-based sensors, operate at elevated temperatures. To improve its sensitivity, many approaches have been described. For example, Penza and co-workers [20] enhanced the sensitivity in gas chemiresistors based on carbon nanotube surface functionalized with noble metal Au and Pt nanoclusters. Maeng and co-workers [21] had developed highly sensitive NO$_2$ sensor array based on undecorated single-walled carbon nanotube monolayer junctions, etc.

To functionalize and widen their applications of CNTs, many methods have been reported, including modification or filling with noble metal, metal oxides or organic functional modifiers, and great progresses were obtained. Such as Yang and co-workers [22] carried out controllable deposition of Ag nanoparticles on carbon nanotubes as a catalyst for hydrazine oxidation. Other metal nanoparticle or nanowires [23-25] were also used to be filled or activated carbon nanotube. Xu and co-workers [26] studied covalent binding of nanoparticles onto carbon nanotubes using a facile strategy. Li and co-workers [27] prepared nanocomposites of metals, metal oxides, and carbon nanotubes via self-assembly approach. Zhang and co-workers [28] anchored zinc oxide quantum dots on functionalized multi-walled carbon nanotubes by covalent coupling. Peng and co-workers [29,30] prepared carbon nanotubes/iron oxides composites as adsorbent for removal of Pb(II) and Cu(II) from water. Wang and co-workers [31] carried out controlled modification of multiwalled carbon nanotubes with ZnO nanostructures. Hang and co-workers [32] utilizing Fe$_2$O$_3$-filled carbon nanotubes as a negative electrode for battery. Capobianchi and co-workers [33] investigated controlled filling and external cleaning of multi-wall carbon nanotubes using a wet chemical method. There are many references on filling of carbon nanotubes with metal oxides or other functional materials [34-36]. Reddy and co-workers [37] studied conducting polymer functionalized multi-walled carbon nanotubes with noble metal nanoparticles, including its synthesis, morphological characteristics and electrical properties. Wang and co-workers [38] synthesized carbon nanotube/cobalt oxide core-shell one-dimensional nanocomposite, and examined applications as an anode material for lithium-ion batteries. Cava and co-workers [39] prepared iron- and iron oxide-filled multi-walled carbon nanotubes, and investigated their electrical properties and memory devices. Lee and co-workers [40] prepared nickel oxide/carbon nanotubes nanocomposite for electrochemical capacitance.

In the aspect of functionalized carbon nanotube for applications of chemical sensors and biosensors, Yogeswaran and co-workers [41] prepared nanocomposite of functionalized multiwall carbon nanotubes with nafion, nano platinum, and nano gold to construct biosensor for simultaneous determination of ascorbic acid, epinephrine, and uric acid. Espinosa and co-workers [42] developed hybrid metal oxide (SnO$_2$, WO$_3$ or TiO$_2$) and multiwall carbon nanotube films for low temperature gas sensing for detecting NO$_2$. Hieu and co-workers [43] studied gas-sensing properties of tin oxide doped with metal oxides and carbon nanotubes to ethanol and liquid petroleum gas. Penza and co-workers [44] carried out functional characterization of carbon nanotube-networked films functionalized with various loading of Au nanoclusters for gas sensing applications, including responses to oxidizing NO$_2$ gas and reducing gases (NH$_3$, CO, N$_2$O, H$_2$S, SO$_2$). The results indicated that negligible response has been found for CNTs and Au-modified CNTs sensors exposed to CO, N$_2$O, SO$_2$. In contrast, significantly enhanced gas response of NO$_2$, H$_2$S and NH$_3$, up to sub-ppm level, has been measured for Au-functionalized CNTs-chemiresistors.
Bittencourt and co-workers [45] prepared WO₃ films modified with functionalized multi-wall carbon nanotubes, and studied its morphological, compositional and gas response. Penza and co-workers [46] developed Pt- and Pd-nanoclusters functionalized carbon nanotubes networked films for sub-ppm gas sensors. Ionescu and co-workers [47] studied novel hybrid materials for gas sensing applications made of metal-decorated MWCNTs dispersed on nano-particle metal oxides, and so on.

Among many metal oxides, copper oxide (CuO) is a typical functional material, which has been extensively investigated for use in semiconductors, catalysts, gas sensors, lithium ion electrode materials and many other areas [48-54]. Chen and co-workers [55] constructed CuO nanowire array sensors. Hoa and co-workers [56] synthesized porous CuO nanowires and studied its application to hydrogen detection. Due to good charge transporting properties and conductivity of carbon nanotube, and excellent absorption properties to organic volatiles of CuO [57], it is expected that CNT/CuO nanocomposite would have some outstanding properties or lowering the operating temperature of CuO based gas sensor. Therefore, Reddy and co-workers [58] prepared multi-walled carbon nanotubes coated with cuprous oxide nanoparticles by a new one-step synthesis method. Venkatachalam and co-workers [59] obtained in-situ formation of sandwiched structures of nanotube/CuxOy/Cu composites for lithium battery applications. Zheng and co-workers [60] carried out introducing dual functional CNT networks into CuO nanomicrospheres toward superior electrode materials for lithium-ion batteries. In this paper, we prepared the carbon nanotube/CuO nanocomposite by wet chemical approach and examined the gas sensing behaviors to several typical gases and organic vapors, and excellent results were obtained.

2. Experimental

2.1 Materials

Multiwalled carbon nanotube (MWCNT), copper sulfate pentahydrate (CuSO₄.5H₂O) (Analytical Reagent, i.e. AR), hexamethylenetetramine (AR), dry sulfuric acid (AR), nitric acid (AR), hydrochloric acid (AR), ammonia (AR), formaldehyde (AR), toluene (AR) and chloroform (AR) were used which were all commercially available. Deionized filtered water was used in this study.

2.2 Treatment of carbon nanotube (CNTs)

A 2-6 g portion of as-received nanotubes was added to 1000 mL of a mixture of dry sulfuric acid/ nitric acid (3:1 ratio by volume). The mixture was sonicated in a bath for 0.5-1 h at ambient temperature. After waiting for 96-120 h, the mixture was diluted with distilled water, followed by filtering, and washed with an excess of water until no residual acid was present. The resulted product was dried at room temperature for several days.

2.3 Carbon nanotube coated with CuO

A 0.3 g carbon nanotube with carboxyl group was added to 70 mL water, a certain amount of CuSO₄.5H₂O (0.2g) were added to form a homogeneous solution, placed at room temperature for more than 48 h, then was transferred into a 100 mL Teflon-lined stainless steel autoclave, a certain amount of hexamethylenetetramine (0.3 g) was added, sealed and maintained at 120 °C for 10-18 h. After the reaction was completed, the resulted solid product was filtered, washed with distilled water repeatedly to remove any possible remnant in the final products, and finally dried at room temperature. The resulted-products of carbon nanotube functionalized with CuO were obtained.
2.4 Morphology observations with TEM

The transmission electron microscopy (TEM) observation was performed with a JEM-1400 under an acceleration voltage of 160 kV.

2.5 XRD characterization

X-ray diffraction (XRD) patterns were recorded using a XRD-6100X diffraction device, with rotating anode of X-ray generator working at 40 kV, 300 mA, and Cu Ka monochromatic radiation.

2.6 Construction of prototype sensors

Modified carbon nanotube was dispersed in filtered deionized water, and then casted on the interdigital electrodes on flexible polymer substrate (as shown in Fig. 1).

![CNTs/CuO nanocomposite](image)

Fig. 1. The structure of the sensor in the experiments.

2.7 Characterization of the gas-response of the sensors (Sensor’s Gas-Sensitivity)

The method to characterize the sensor’s sensitivity to vapors is seen also in the references [61]. A 1 V DC voltage was applied and the DC current was measured in the airproof test chamber (about 1 L) with LK2000A Electrochemical Work Station from LANLIKE Chemistry and Electron High Technology Co., LTD (China). The programmed constant-voltage method was applied. The device was put into the test chamber, which can be vacuumed or filled up with high purity N₂ by operating a three-way valve. The DC current under N₂ atmosphere was continuously monitored in an adjustable time interval and recorded in an IBM PC compatible computer. After the test chamber was flushed with high-purity N₂ repeatedly until the current slowly reached a steady value and kept stable, a certain amount of ammonia vapor or other gases (certain amount of saturated vapors) was injected into the test chamber with a syringe. The
gas-sensitivity (R) of the film is defined as the ratio of $I_{\text{gas}}/I_{\text{N}_2}$ or $I_{\text{N}_2}/I_{\text{gas}}$, where $I_{\text{gas}}$ and $I_{\text{N}_2}$ represent the current of the sensor on exposure to the measured gas and N$_2$, respectively.

3. Results and discussion

A typical TEM image of carbon nanotube modified with CuO is shown in Fig. 2. The whole morphology is shown in Fig. 2 (a). The typical local morphology is shown in Fig. 2 (b).

![Fig. 2. TEM of carbon nanotube coated with CuO.](image)

As shown in Fig. 2, the carbon nanotube was dispersed in CuO matrix, the CuO was uniformly coated on the surface of carbon nanotube, and the tubular structure of carbon nanotube is clearly observed. From local morphology of TEM, it can be observed good interfacial adhesion between CNT and CuO matrix, which is probably due to the results of strong interaction between CNTs with carboxyl groups and CuO containing some hydroxy groups. XRD pattern of carbon nanotube modified with CuO under hydrothermal condition is shown in Fig. 3.

![Fig. 3. XRD of carbon nanotube coated with CuO.](image)
Figure 3 shows that there are some strong peaks of 2θ at 35.4, 46.37, 48.88, 51.22, 56.7, 58.77 degree, which belongs to monoclinic lattice of CuO.

We all know that the ammonia gas is a typical toxic gas in many chemical factories. The leakage of small amount of ammonia gas would strongly affect the health of employees and environment of inhabitance. Therefore, effects of CuO modification on the gas-sensitivity of carbon nanotube were examined. The comparative experimental results of gas-sensitivity between carbon nanotube and carbon nanotube coated with CuO to ammonia gas at similar conditions were carried out. The results are shown in Fig. 4.

Fig. 4. Comparative results of gas-sensitivity between carbon nanotube (CNTs) and carbon nanotube coated with CuO to 30 mL saturated ammonia vapor diluted in a 1000 mL chamber with N₂ at similar conditions.

Fig. 5. Comparative results of gas-sensitivity between carbon nanotube and carbon nanotube coated with CuO to 30 mL saturated toluene vapor diluted in a 1000 mL chamber with N₂ at similar conditions.

Fig. 6. Comparative results of gas-sensitivity between carbon nanotube and carbon nanotube coated with CuO to 30 mL saturated formaldehyde vapor diluted in a 1000 mL chamber with N₂ at similar conditions.

Fig. 7. Comparative results of gas-sensitivity between carbon nanotube and carbon nanotube coated with CuO to 30 mL saturated chloroform vapor diluted in a 1000 mL chamber with N₂ at similar conditions.

Figure 4 shows that the sensitivity of carbon nanotube coated with CuO to ammonia gas is much higher than that of carbon nanotube at similar conditions. It is not only dramatically increasing the response rate (for carbon nanotube, the response time is about 90 s; whereas, for carbon nanotube coated with CuO,
the response is about 40-50 s.), but also enhancing the sensitivity value at great extent. This main reason is possibly due to the results of CuO been one of the good catalysts for oxidation of organic compounds, which favors the adsorption to ammonia molecule [57], and led to greatly increasing the sensitivity. Not only to increase the gas-sensitivity value, but also to enhance the response speed dramatically.

At present, pollution in China is currently considered to be a serious issue, especially, organic solvent is one of the main pollution sources. Specially, during recent several decades, the coating and adhesive have been gained widely applications in decoration industry. Therefore, toluene, formaldehyde vapor and other some common organic volatiles have become strong impact to environment of inhabitance in China.

The comparative response behaviors of the sensor based on CNT/CuO nanocomposite and CNT to toluene, formaldehyde, and other organic vapors were carried out. The typical comparative results are shown in Fig. 5-7. As shown in Fig. 5-7, there is little response to toluene vapor, formaldehyde vapor, chloroform vapor, etc., for carbon nanotube based sensor. However, for the sensor fabricated with carbon nanotube coated with CuO, the gas-sensitivities to toluene vapor, formaldehyde vapor, chloroform vapor, etc. were increased clearly. The main reason is possibly that CuO is one of the good catalysts, which favors the adsorption or oxidation to organic vapor molecule, and greatly increase the sensitivity.

The effects of vapor concentration on the sensitivity of the CNT/CuO nanoposite sensor are also examined. The typical curves of sensitivity to various vapors as function of the concentration are shown in Fig.8-10. From Fig. 8-10, we can see that the sensitivity of sensor is strongly depending on the vapor concentration.

Fig. 8. Effect of concentration of the ammonia gas on the sensor response.

Fig. 9. Effect of concentration of the formaldehyde vapor on the sensor response.

Fig. 10. Effect of concentration of the chloroform vapor on the sensor response.
Besides, we also examined the gas-sensing behaviors of CNTs based composites modified with other metal oxides and graphene oxide/CuO nanocomposites, and some obtained good results, in which, some nanocomposites showed excellent sensitivity and selectivity to particular organic vapors. Herein, the improvements of other nanocomposites to organic vapors were not intended to be introduced in this paper, which will be published in another paper.

4. Conclusions

In summary, CuO was uniformly coated on the surface of carbon nanotube under hydrothermal reaction condition. The CNT/CuO nanocomposite shows remarkably enhanced the sensitivity to some poisonous gases. It would provide a simple, low-cost and general approach to functionalize the carbon nanotube. It is also in favor of developing chemical sensor with high sensitivity at low temperature operation, flexible nanoelectronic devices or catalysts with high activity to organic volatiles at low temperature.

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