Research Article

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Silver-loaded carbon nanofibers for ammonia sensing

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Abstract: Carbon nanofibers (CNFs) were prepared by electrospinning, and silver (Ag) ions were grown on the surface of the CNFs by *in situ* solution synthesis. The structure and morphology of obtained Ag-doped CNFs (Ag-CNFs) were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The gas sensibility of the composite fiber was investigated by ammonia (NH₃) obtained by natural volatilization from 1 to 4 mL of NH₃ solution at room temperature. It was found that the fibers exhibited a sensitive current corresponding to different NH₃ concentrations and a greater response at high concentrations. The sensing mechanism was discussed, and the good absorptivity was demonstrated. The results show that Ag-CNF is a promising material for the detection of toxic NH₃.

Keywords: electrospinning, carbon nanofibers, sensors

1 Introduction

In recent years, many studies have focused on the development of low-cost, flexible, multi-application, and lightweight sensors with stable operation, high sensitivity, fast response, and low operating temperature. At present, displacement sensors (1–3), strain sensors (4,5),

humidity sensor (6,7), pressure sensors (8,9), temperature sensors (10,11), and gas sensors (12,13) have been widely explored. Electrospinning is a low-cost, simple, highly efficient, and promising method for the preparation of one-dimensional (1D) micro-/nanofibers (14,15). It can be used to prepare polymer, organic, inorganic and multi-component composite nanofibers, having been widely used in nanoelectronics, nanosensors, drug release, and catalysts (16–21). Compared to thin-film sensors, fiber-based sensors produced by electrospinning have higher sensitivity and faster response time (22–25), having been used to detect multiple chemicals, including NH₃, NO₂, CO, N₂H₄, formaldehyde, ethanol, and other organic gases (26–30).

Nowadays, metal oxide semiconductors and solid electrolytes sensors occupy most of the markets for gas sensors (31,32). However, both of them need to work at higher temperatures (hundreds to more than 1,000°C), consume large power, and have low sensitivity, poor anti-interference ability, and inconvenient use. With the development of nanotechnology, a large number of research reports on carbon-based gas sensors have been published in recent years, which show good analytical sensitivity at room temperature (33,34), such as carbon nanotubes (CNTs), graphene, graphene oxide and activated carbon (35–39). 1D CNFs have high surface adsorption capacity, good electrical conductivity, electronic ballistic transmission characteristics, and other excellent properties, becoming one of the ideal materials for the fabrication of nanoscale gas sensors with high sensitivity, fast response, small size, and low energy consumption (40–42). Among the many CNFs, the CNFs prepared based on the polyacrylonitrile (PAN) are the most common ones with high tensile strength (43–45), low production cost, and suitable for large-scale production.

Ammonia is a common irritating gas. It is widely used in chemical and agricultural fields and has corrosive and irritating effects on human skin and mucous membranes. This study found that carbon materials have good response characteristics to NH₃. Silver and its compounds are one of the most important antibacterial materials. They have high bactericidal

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Table 1: Applications of Ag-loaded nanomaterials

Materials	Function	Ref.
Ag-CNT	Gas sensor for NH_3 and CO_2 ; improved field emission properties	(44,45)
Ag/ZnO	IOT and field electron emission application	(46)
Al/Ag-CNF	Gas sensors for C_2H_2	(47)
Ag-TiO ₂	Visible light photocatalysis	(48)
Ag/SnO ₂	Sensor for H_2O_2	(49)
Ag-Pt/pCNFs	Detect DA	(50)
Ag-TiO ₂ -CNT	Light photocatalysis	(51)
PANI/Ag/CNF	Solid flexible aerogel supercapacitor	(52)

activity and biocompatibility and have antibacterial effects against bacteria, fungi, and even viruses. Many studies have modified nanomaterials based on this property of Ag, such as Ag-CNT, Ag/ZNO, and so on, see Table 1 for details (46–54). This study describes an antibacterial NH_3 sensor based on the CNFs. Ag-CNFs were prepared by electrospinning and impregnation. We measured and analyzed the response characteristics to NH_3 by focusing on the change in resistance of Ag-CNFs and found that it exhibits good NH_3 sensing performance in 1–4 mL of NH_3 solution. Ag-CNFs can be used as an NH_3 gas sensor at room temperature that is inexpensive to produce, flexible, sensitive, and antibacterial.

2 Experimental section and characterization

2.1 Materials

Silver nitrate (AgNO_3 , $\geq 99.8\%$), 2,2-dimethylolbutanoic acid (DMBA), *N,N*-dimethylformamide (DMF), and NH_3 solution (25–28%) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. The PAN (MW = 1,50,000) was purchased from Sigma-Aldrich, USA.

2.2 Preparation of pure PAN fibers by electrospinning

The PAN–DMF solution having a polymer mass ratio of 12% was prepared by stirring at room temperature for 4 h by a magnetic stirrer. Self-assembled equipment was

used for electrospinning, including a high-voltage power supply, propulsion pumps, and aluminum foil as the receiver. The spinning solution was placed in a plastic syringe and mounted on a propulsion pump. The aluminum foil was placed perpendicular to the horizontal plane and connected to the ground. The volume feed rate, applied voltage, and tip-to-collector distance were 1 mL/h, 15 kV, and 10 cm, respectively. The spinning temperature was 20°C and the humidity was 50%.

2.3 Preparation of Ag-CNFs

The pure PAN fiber obtained by electrospinning was subjected to a two-stage heating process. First, the pre-oxidation process was carried out by heating at 260°C for 140 min and the heating rate was 2°C/min. Then, the temperature was raised to 900°C for 120 min at a rate of 5°C/min in an argon atmosphere. Finally, natural cooling is performed to obtain CNFs. Since the Ag nanostructure has antibacterial properties, it is compounded onto the CNF to protect it (55,56). AgNO_3 (10 mM) was mixed with 20 mL water to soak the CNFs for 3 h. CNFs were taken out and washed with DMBA until no bubbles generated. Then, it was dried at 60°C for 4 h to obtain Ag-CNFs.

2.4 Sensor assembly

A simple gas sensor was assembled by sandwiching Ag-CNFs between two copper electrodes (copper sheets), and the size of the composite was $20 \times 60 \times 2 \text{ mm}^3$. Two copper wires were fixed to the copper electrodes by soldering. Copper wire was used to connect an electrical performance measurement system that responds to changes in current in an NH_3 environment.

2.5 Characterization

The samples were characterized by XRD at room temperature. Scanning electron microscopy (SEM, JSM-6390) was used to observe the surface morphology of pure PAN fibers, CNFs and Ag-CNFs. Electrical properties were tested by a Keithley 6487 high resistance meter system (Washington, USA) at room temperature.

2.6 Simulation by COMSOL Multiphysics

COMSOL Multiphysics has been increasingly used in the process of simulating gas sensing mechanism. And in this article, COMSOL is applied to demonstrate the distribution of NH_3 in Ag-CNFs. The model of transport of diluted species has been used and the boundary concentration of NH_3 around Ag-CNFs has been set as 0.5 mol/m^3 to make simulation results more obvious. The temperature has been set as 20°C and the porosity of Ag-CNFs is 0.1.

3 Results and discussion

3.1 XRD

X-ray diffraction is a powerful tool for characterizing the structure of materials. The diffraction peaks of the nanofibers are indexed by standard cards of C and Ag (PDF No. 80-0017 and 87-0717). A comparison of the XRD patterns of the CNFs and Ag-CNFs with the standard map is shown in Figure 1. It can be seen that the diffraction peaks appear in the spectra of both samples, indicating a good crystallinity. The main peak of the CNFs is at 44° , corresponding to the (111) plane of C. The main peak of Ag-CNFs at 44° corresponds to the (200) crystalline plane of Ag and the (111) plane of C, and the second-largest peak at 38° corresponds to the (111) plane of Ag. This confirms that the Ag-ions are effectively modified on the surface of the CNFs.

3.2 SEM

Figure 2a shows the morphology of the as-spun pure PAN nanofibers prepared by electrospinning with a smooth surface and uniform diameter. Its average diameter is $320 \pm 24.67 \text{ nm}$. To avoid fiber melting or fusion, we oxidized PAN nanofibers at 260°C to convert C–C and $\text{C}\equiv\text{N}$ to $\text{C}=\text{C}$ and $\text{C}=\text{N}$ bonds (57,58), followed by carbonization at 900°C . After carbonization, a significant color change from white to black was observed, and the morphology of the obtained CNFs is shown in Figure 2b. It can be seen that CNFs have uniform diameter distribution, have no significant change in appearance, and maintain fibrous morphology, which is related to the entanglement network and flexibility of pure PAN fibers. The average diameter of the CNFs is $301 \pm 26.20 \text{ nm}$. It is reduced by $\sim 20 \text{ nm}$ than pure PAN fiber, derived from the volatilization of DMF as a

Figure 1: XRD patterns of CNFs and Ag-CNFs.

solvent and the disappearance of O and H components in PAN. The SEM image in Figure 2b shows that the nanofibers are slightly curved. This is because the defects in the PAN fiber itself will be inherited in the CNF fiber (59). In the figure, it can be observed that the PAN fiber precursors have a certain phenomenon of adhesion and merging due to problems such as residual solvent during the spinning process. Manocha *et al.* tested the shrinkage of PAN fibers when heated at $200\text{--}1,000^\circ\text{C}$. The shrinkage of fibers happened in three temperature sections $200\text{--}350^\circ\text{C}$, $600\text{--}800^\circ\text{C}$, and $800\text{--}1,000^\circ\text{C}$ and was mainly concentrated in the first two stages. Under the combined effect of shrinkage stress and defects, the fibers become bent (60). Ag-CNFs were obtained by Ag-ion modification of CNFs with AgNO_3 solution, and its morphology is as shown in Figure 2c. It can be seen that there are micron-/nanoscale Ag particles on the surface of the fiber, which proves the feasibility of the inorganic salt impregnating the surface of the nanofiber to form a nanostructure (61).

3.3 NH_3 sensing measurement

We tested the NH_3 sensing performance of Ag-CNFs at room temperature. The Ag-CNF sensor was placed in a sealed container and the concentration of NH_3 was controlled by the natural evaporation of the NH_3 solution. The voltage across the sensor was 0.2 V . The structure of test device is shown in Figure 3. The electrical properties of the sensor were measured at different NH_3 concentrations. Figure 4 shows the electrical response of Ag-CNFs to 1, 2, 3, and 4 mL of the NH_3 solution, in a closed container, the density of 1–4 mL of NH_3 after volatilization is 0.0754, 0.1508, 0.2262, and 0.3016 mol/m^3 , indicating

Figure 2: (a) SEM images and diameter distribution histogram of pure PAN fibers, (b) CNFs, and (c) Ag-CNFs.

the effect of NH_3 on electrical transport behavior. It can be seen that a high concentration of NH_3 results in a bigger current, meaning that the resistance of the sensor decreases and the conductivity is improved. A sensor exposed to a higher concentration of NH_3 solution exhibits a larger current change, that is, as the gas concentration increases, the sensor response becomes larger. In addition, the sensor current remains stable at the same NH_3 concentration, indicating that Ag-CNFs have good NH_3 sensing properties.

This is due to the adsorption of NH_3 by Ag-CNFs, as shown in Figure 4. Ag-CNFs is exposed to NH_3 (Figure 5a). The NH_3 molecule adheres to the pores on the surface of the sample that is not electrically conductive compared with the state after adsorption, increasing the cross section of the conductive path, as shown in Figure 5b. The resistance of Ag-CNFs adsorbed with NH_3 decreased and the current increased. When the surface adsorption reaches saturation, NH_3 molecules begin to diffuse from the surface to the inside. When the adsorption process is completed, the conductive regions of the Ag-CNFs are stabilized and the current is constant (Figure 5c). The higher the concentration of NH_3 , the larger the corresponding current change, indicating its better adsorption performance.

Figure 3: Schematic diagram of the device for Ag-CNF testing NH_3 concentration, the voltage applied during the test is 0.2 V.

When the Ag-CNFs are in the NH_3 environment, the NH_3 concentration on the surface will increase rapidly. As the time in the NH_3 environment increases, the internal NH_3 concentration will gradually increase until it reaches saturation. The equation of gas diffusion in this simulation can be described by:

$$D_{e,i} = \frac{\varepsilon_p}{\tau_{F,i}} D_{F,i} \quad (1)$$

where $D_{e,i}$ is gas diffusion coefficient in Ag-CNFs, ε_p is porosity of Ag-CNFs, $\tau_{F,i}$ is effective diffusivity constant, and $D_{F,i}$ is gas diffusion coefficient in free air. The effective diffusion coefficient model can be described by Millington–Quirk model or Freundlich equation:

$$\tau_{F,i} = \varepsilon_p^{-\frac{1}{3}} \quad (2)$$

$$k_{P,i,F} = K_{F,i} N_{P,i} \frac{C_{F,i}^{N_{F,i}-1}}{C_{\text{ref},i}^{N_{F,i}}} \quad (3)$$

Figure 4: Sensing properties of Ag-CNFs for NH_3 at different NH_3 contents. After adding NH_3 water, it was allowed to stand for 10 min, and the power-on test time was 1 min.

Figure 5: Process of adsorption of NH_3 by Ag-CNFs. (a) Ag-CNFs in NH_3 atmosphere. (b) Ag-CNFs begin to adsorb NH_3 and surface seepage occurs. (c) Surface adsorption is saturated and begins to diffuse internally.

where $k_{P,i,F}$ is adsorbate constant of NH_3 , $N_{P,i}$ is adsorbent constant of Ag-CNFs, $K_{F,i}$ is Freundlich constant, $N_{F,i}$ is Freundlich exponent, and $C_{\text{ref},i}$ is reference concentration. In fact, Millington–Quirk model describes better in this case, because Freundlich equation focuses too much on the surface state. And, the simulation result is shown in Figure 6. This figure demonstrated the adsorption of NH_3 molecules on Ag-CNF by different colors and inward diffusion. As previously imagined, NH_3 adsorption mainly happened on the surface, and after a certain period of diffusion, NH_3 would appear in deeper parts, but with much lower concentration. It showed that diffusion on fibers with smaller diameters will reach equilibrium faster, which has a quicker response at low NH_3 concentration. In case of this report, this means that in a given period, the NH_3 concentration will be reflected more obviously by the change of resistance and this explains the high sensitivity of the sensor.

Ag-CNF-based sensors can be used not only for toxic gas alarm systems, but also for characterizing food

spoilage. When animals, plants, and foods prepared by them are decomposed by enzymes produced by micro-organisms, abnormal odors may occur. If the protein is decomposed, it will produce harmful gases such as NH_3 and H_2S . Human senses may be more difficult to capture trace amounts of gas from food spoilage in a timely manner. By putting Ag-CNFs sensors together with food, we can get information on food spoilage in a sensitive and timely manner, avoiding food poisoning caused by consumption.

Gas sensors involve physical and chemical adsorption and other reasons. The chemical gas sensor itself requires a long time of adsorption and desorption processes, so the repeatability problem of the gas sensor has always been a problem in the field. When the gas is to be measured, there are differences in the same concentration response multiple times in a short time, but after a longer time interval and calibration, better repeatability can be obtained (62,63). With further research on the sensor, optimizing the conditions of electrospinning PAN, and to get finer fibers, continuous operation of the gas sensor reliability will be improved due to the larger specific surface area.

Figure 6: Distribution of the NH_3 concentration in the Ag-CNFs surface simulated by COMSOL.

4 Conclusions

In summary, Ag-CNFs were successfully prepared by electrospinning and *in situ* solution polymerization, prepared into an NH_3 sensor at room temperature. The surface of the CNFs was modified with Ag nanoparticles having antibacterial properties to protect the fibers. It can be used to detect NH_3 naturally evolved from 1 to 4 mL of NH_3 solution in a closed vessel and has a high response at higher NH_3 concentrations. This work can provide a viable way to create a low-cost, high-sensitivity, stable, detectable NH_3 concentration sensor for use in toxic gas alarm systems and characterize food spoilage.

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