NOVEL GAS SENSITIVITY OF ELECTROSPUN CARBON NANO-FIBERS BY DEVELOPED PRE STRUCTURE AND INDUCED FUNCTIONAL GROUP

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Introduction

The detection of NO and CO gases has recently become a critical issue since they are some of the most common air pollutants. Many types of NO and CO sensors have been investigated, using materials such as metal oxide semiconductors (MOS) and carbon nanotubes (CNTs)[1]. MOS sensors often operate at temperatures between hundreds to more than 1000 ℃, whereas CNT-based sensors show good analytical sensitivity at room temperature. The ability of CNT sensors to operate in low-temperature regimes is an advantage. While CNT-based materials have been widely used for gas sensing for the reasons mentioned above and high responsibility, but the sensitivity of gas sensing is limited by the low specific surface area of active sites for gas adsorption[2,3].

In this study, carbon based materials were used to fabricate a gas sensor matrix by electrospinning and heat treatment. To improve the sensitivity of the sensor, a porous structure was developed, and functional groups were induced using chemical activation and fluorination. The resulting material effectively transferred the resistive response from the surface of the gas sensor to the electrode due to the carbon blacks embedded inside the fibers.

Experimental

The polymer solution (PAN/DMF, 10 wt%, 30 g) was prepared at 393 K and stirred for 3 h. CB additives (1.5 g) were mixed into the prepared polymer solution and sonicated to disperse the CBs. The two resulting polymer solutions (with/without CB additives) were ejected from a syringe tip onto a collector using an electrospinning apparatus. The electrospinning process was carried out under the following conditions: 1 ml/h polymer solution feed rate, 15 kV supplied voltage, 10-cm tip to collector distance and 100-rpm collector rotation. The stabilization of the electrospun materials was carried out in air by heating up to 523 K at a heating rate of 1 K·min^{-1}, and finally, samples were treated at 523 K for 5 h. Carbonization of the stabilized electrospun materials was carried out under an argon atmosphere with the following conditions: 10-K/min heating rate, 1373-K reaction temperature, 1-h holding time and a 100-ml/h argon feed rate.

KOH solutions (4, 6 and 8 M) were prepared as chemical activation agents. The sample was placed on an alumina boat in a steel pipe at a ratio of 15 ml/g (KOH solution/sample) to carry out the chemical activation. Activation was conducted at 1023 K for 1 h in an argon atmosphere. The heating rate was 5 K/min, and the feed rate of the argon gas was 40 ml/min. After chemical activation, the resulting samples were washed with distilled water several times to remove residual potassium and were then dried at 383 K overnight.

The samples were pre-treated at 473 K for 3 h under vacuum to remove water and impurities. Fluorination was carried out at 323 K and 0.02 MPa for 10 min by directly introducing the fluorine gas onto the samples in the reactor. These fluorinated samples are labeled FCCF, FCACF-4, FCACF-6 and FCACF-8.[4]

Nitrogen adsorption was carried out at 77 K using a Brunauer-Emmett-Teller (BET) apparatus (Micromeritics ASAP 2020) to investigate the specific surface area, total pore volume, pore size distribution and micropore fraction.

The electrical resistance was measured using a programmable electrometer (Keithley 6514) to evaluate the gas-sensing properties of the prepared sample.

Results and Discussion

The nitrogen isotherms of the fluorinated samples were presented in Fig. 1 to investigate the effect of the activation condition on the pore structure. The non-activated sample FCCF did not show any change in the adsorption of nitrogen, indicating a non-porous material. However, in the case of the activated samples (FCACF-4, FCACF-6 and FCACF-8), a more significant increase was apparent as they were treated by higher concentrations of the KOH solution.
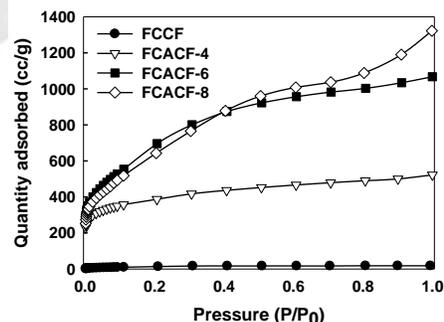

Fig. 1 Nitrogen isotherms of the fluorinated samples.

The specific surface area (SSA) was increased by KOH activation to over 2200 m^2/g in the case of FCACF-6 and FCACF-8. The SSA of FCACF-6 was higher than for FCACF-8, even though more chemical agent was used for FCACF-8. However, the micropore volume fraction of FCACF-6 was 53.4%, and that of FCACF-8 was 38.7%.

The resistive response was presented against the time of exposure to CO gas in Fig. 2. Development of a porous structure enhanced the CO gas sensing ability up to around 5% as shown in FCACF-6 and FCACF-8. This result implies that the porous structure generated by chemical activation

effectively improved the gas adsorption sites. In the case of the FCACF-4 sample, the electrical resistance decreased significantly to around 3% compared with time zero within 3 min (see arrow 1), and after that there was no significant change. For the FCACF-6 and FCACF-8 samples, however, the change in resistance was observed by two areas with steep and slow decreases with inflection points marked by arrows 2 and 3, respectively.

The effects of fluorination were also investigated by comparing the CACF-4 and FCACF-4 samples. Although the SSA and total pore volume were decreased by fluorination, the sensitivity was higher for the fluorinated sample (FCACF-4). This result can be explained by the effects of the functional groups induced during fluorination, which guide the gas capture to pores of samples.
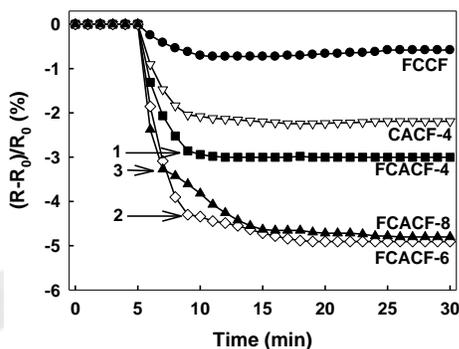

Fig. 2 Resistive response over time for CO gas sensing.

Fig. 3 presents the resistive response against exposure time to NO gas. The resistive response followed a similar trend to the CO gas. The effects of the porous structure and the fluorination treatment noted for CO were confirmed for NO, but the sensitivity to NO was more than twice as high. This result indicates that the electron hopping effect is stronger with the NO gas than the CO gas.
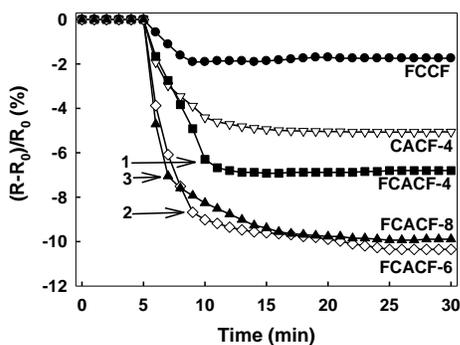

Fig. 3 Resistive response over time for NO gas sensing.

This reaction is available due to the electronic structures of the NO and CO gases, as shown in Fig. 4. After activation process, the activated carbons did not show the semiconductor's characteristics and then the change of electrical resistance depended on the adsorbed gas molecules in pores. During stabilization of electrical resistivity, the

electrical resistivity might increase by N_2 adsorption on activated carbon. But after inducing easily electron polarized gas molecules such as CO and NO, the electrical resistance would reduced by electron hopping effects[6].
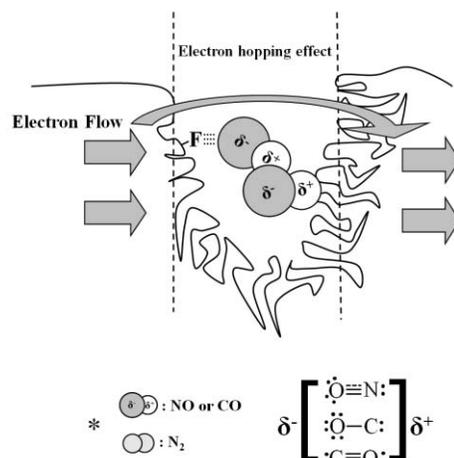

Fig. 4 Suggested mechanism of gas sensing.

Conclusions

This paper reports the development of electrospun CFs with high electrical conductivity, a porous structure and functional groups to improve the sensitivity of the gas sensor. CB additives increase the electrical conductivity, KOH chemical activation resulted in a porous structure, and fluorination treatment was used to modify the surface of the activated sample. The mechanism of enhanced gas sensing was suggested as a microporous structure leading to a rapid resistance response and induced functional groups improving the sensitivity of gas sensing by attracting the target gases to the carbon surface of pores. This resistive response was transferred effectively by the electrically conductive network constructed by the CB additives. Eventually, the sensing ability for the NO and CO gases was significantly improved based on the effects of chemical activation, CB additives, and fluorination treatments.

References

[1] Liu CY, Chen CF, Leu JP, Lu CC, Liao KH. Fabrication and carbon monoxide sensing characteristics of mesostructured carbon gas sensors. Sensor Actuator B Chem 2009;143(1):12-16.
[2] Park YH, Song HK, Lee CS. Fabrication and its characteristics of metal-loaded TiO2/SnO2 thick-film gas sensor for detecting dichloromethane. J Ind Eng Chem 2008;14(6):818-823.
[3] Suehiro J, Zhou G, Imakiire H, Ding W, Hara M. Controlled fabrication of carbon nanotube NO2 gas sensor using dielectrophoretic impedance measurement. Sensor Actuator B Chem 2005;108(1-2):398-403.
[4] Lee YS. Syntheses and properties of fluorinated carbon materials. J Fluor Chem 2007;128(4):392-403.
[5] Kauffman DR, Star A, Carbon nanotube gas and vapor sensors. Angew Chem Int Ed 2008;47:6550-6570.
[6] Chiu HS, Lin PI, Wu HC, Hsieh WH, Chen CD, Chen YT. Electron hopping conduction in highly disordered carbon coils. Carbon 2009;47:1761-1769.