ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

The Synergistic Effect of Fluorination and Embedded SnO_2 on the NO Gas Sensing of Expanded graphite

Min Il Kim[1,2], Sangmin Lee[2], Young-Seak Lee[2,*]

1 Convergence Materials & Parts Technology Research Center, Gumi Electronics & Information Technology Research Institute, Gumi 39171, Republic of Korea; 2 Department of Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon 34134, Republic of Korea

**Corresponding author: youngslee@cnu.ac.kr*

Highlights

- To obtain high-performance NO gas sensor, expanded graphite was modified by SnO_2 and fluorine functional groups.
- The high sensitivity to NO gas on expanded graphite was attributed to a synergistic effect of the introduced SnO_2 and fluorine functional groups
- The SnO_2 induces adsorption of NO gas and the fluorine functional groups were transferred electron from expanded graphite surface to the NO gas adsorbed on SnO_2.

1. Introduction

Expanded graphite (EG) is a layered structure material whose expansion is due to the intercalation of compounds into graphite. The expansion between the carbon layers enables the easy insertion of atoms or molecules into the carbon-carbon layers. EG has multiple pores and functional groups, which facilitate physical and chemical adsorption between the EG and transition-metal solutions. The functional groups on EG anchor the metal ion and benefit the dispersion. The adsorption of NO gas with the SnO_2 was appeared by the oxygen defects [1]. Moreover, NO molecules cannot be trapped efficiently on the SnO_2 surface unless the SnO_2 surface has been modified. Direct fluorination is a method of surface modification of metal oxides using F_2 gas. Direct fluorination proceeds spontaneously at room temperature, and its reaction time is short. Additionally, fluorination is a dry technology and can be used irrespective of the polymer's shape.

In this paper, to fabricate a high-performance NO-gas-sensing electrode, EG was modified by being doped with SnO_2 and fluorine functional groups. We carried out the fluorination at various temperatures to study the effect of fluorination on the surface of EG/SnO_2. The effects of the fluorination and SnO_2 doping on the gas-sensing properties of EG were also investigated, and the results indicate that the gas sensors exhibit a high sensitivity that is caused by a synergistic effect between the introduced SnO_2 and fluorine functional groups.

2. Methods

To obtain EG, expandable graphite (grade 1721, Asbury Carbons) was treated by microwave irradiation (700 W) for 10 s. EG (0.5 g) and an aqueous solution of $SnCl_2$ (98%, Sigma-Aldrich) (60 mmol) were mixed by ultrasonication for 30 min and stirred at 80 °C for 16 h, so that SnO_2 was introduced into the EG (EG/SnO_2). The EG and EG/SnO_2 were treated by thermal fluorination. The thermal fluorination was carried out at room temperature (30 °C), 200 and 400 °C for 10 min at 1 bar of fluorine gas (99.0%). After fluorination, the fluorinated samples were degassed to remove unreacted gases. The thermally fluorinated samples were named FEG/SnO_2-RT (fluorinated EG/SnO_2 at room temperature), FEG/SnO_2-200 (fluorinated EG/SnO_2 at 200 °C) and FEG/SnO_2-400 (fluorinated EG/SnO_2 at 400 °C) according to their thermal fluorination conditions. The properties of samples was analyzed by XPS, NO gas sensing.

3. Results and discussion

The Sn^{2+} (from $SnCl_2$) introduced into the EG formed a crystalline SnO_2 phase. During the ultrasonication and stirring of the EG and $SnCl_2$ solution, the oxygen functional groups in EG oxidized the Sn^{2+} to SnO_2 [2].

The introduced SnO_2 was observed as clusters on the EG surface. The size of the SnO_2 clusters decreased with increasing fluorination temperature. To investigate the Sn distribution on the surface of the EG, elemental mapping images of the EG/SnO_2 were obtained by energy-dispersive X-ray spectroscopy. The Sn-mapping images confirm that the Sn almost covered the EG surface. On the basis of these results, we concluded that the fluorination method decreased the size of the SnO_2 clusters on EG and did not change the EG morphology. The chemical bonds of the fluorinated EG/SnO_2 surface were analyzed by XPS. In the case of EG/SnO_2, the number of C-O bonds increased and new C=O (286.9 eV) bonds appeared with the introduction of SnO_2. New components, including C-F semi-covalent (287.8 eV), C-F covalent (289.0 eV), and CF_2 (291.1 eV) bonds, appeared after the fluorination of EG/SnO_2. The number of C-F covalent and CF_2 bonds in the samples increased with increasing fluorination temperature. However, no peak associated with C-F bonds appeared in the spectrum of the FEG/SnO_2-RT sample.

The NO gas sensitivity of the samples, as measured by changes in their electrical resistance, is presented in Fig. 1 (a). The EG exhibits characteristics typical of a p-type semiconductor, which is attributed to electron transport from the EG surface to the NO gas (oxidizing gas), resulting in a reduced electrical resistance. The EG exhibited 0.8% NO gas sensitivity, consistent with the typical characteristics of a p-type semiconductor. The EG/SnO_2 (1.0%) and FEG/SnO_2-RT (0.7%) samples exhibited NO gas sensitivities similar to that of EG. The FEG/SnO_2-400 sample showed an approximately 5-fold higher NO gas sensitivity than the EG/SnO_2 did, exhibiting a 5.2% change in NO gas sensitivity. The high NO gas sensitivity of FEG/SnO_2-400 is attributed to the synergistic effect of the introduced SnO_2 and the fluorine functional groups (Fig. 1 (b)). The introduced SnO_2 on FEG/SnO_2-400 induces adsorption of the NO gas [1]. The introduced fluorine functional groups on the EG surface transferred electrons from the EG surface to the NO gas adsorbed onto the SnO_2. Therefore, the NO-gas-sensing efficiency of the FEG/SnO_2-400 sample is the highest among the investigated samples. In the cases of EG/SnO_2 and FEG/SnO_2-RT, which do not have fluorine functional groups on the EG, the electrons cannot transfer from the EG surface to the NO gas adsorbed onto the SnO_2 because of the absence of the fluorine functional groups.

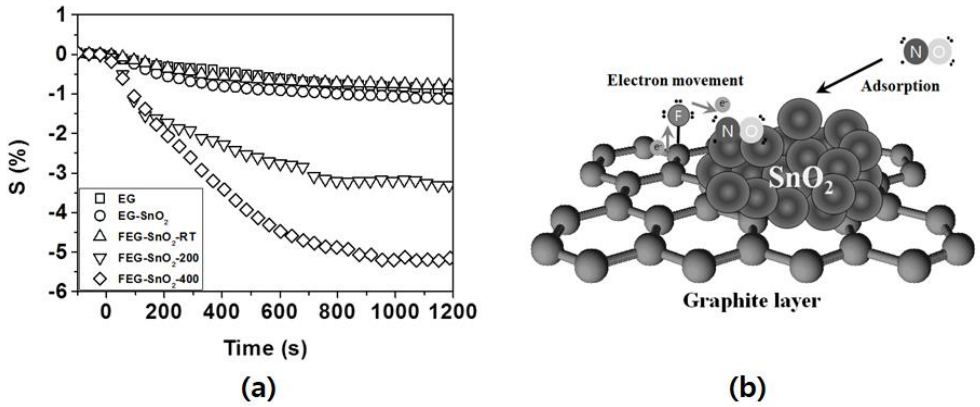

Figure 1. NO gas sensing properties of samples (a) and the suggested mechanism of NO gas sensing (b).

4. Conclusions

The fluorinated SnO_2/EG that was treated at 400 °C showed an approximately 5-fold higher NO gas sensitivity than the EG alone, exhibiting a 5.2% change in electrical resistance. The high sensitivity to NO gas was attributed to a synergistic effect of the introduced SnO_2 and fluorine functional groups.

References

[1] Y. Yan, L. Ben, Y. Zhan, X. Huang, Electrochim. Acta 187 (2016) 186-192.
[2] Y. Huang, X. Lin, Q. Pan, Q. Li, X. Zhang, Z. Yan, X. Wu, Z. He, H. Wang, Electrochim. Acta 193 (2016) 253-260.

Keywords
NO gas sensing; fluorination; fluorine functional groups; Tin oxide; expanded graphite