

Improvement of gas sensing properties of carbon nanofibers based on polyacrylonitrile and pitch by steam activation

Jeongsik Kim¹, Hyung-II Kim^{1,*} and Jumi Yun²

¹Department of Industrial Chemistry, Chungnam National University, Daejeon 34134, Korea

²Hanwha Chemical Research and Development Center, Daejeon 34128, Korea

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*Corresponding Author

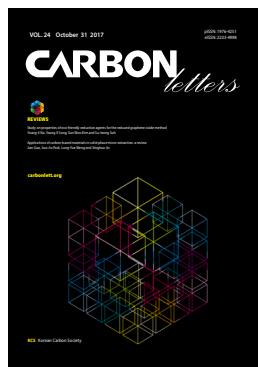
E-mail: hikim@cnu.ac.kr

Tel: +82-42-821-6694

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Abstract

Polyacrylonitrile/pitch nanofibers were prepared by electrospinning as a precursor for a gas sensor material. Pitch nanofibers were properly fabricated by incorporating polyacrylonitrile as an electrospinning supplement component. Polyacrylonitrile/pitch nanofibers were activated with steam at various temperatures followed by subsequent carbonization to make carbon nanofibers with a highly conductive graphitic structure. Steam activation was effective in facilitating gas adsorption onto the carbon nanofibers due to the increased surface area. The carbon nanofibers activated at 800°C had a larger surface area and a lower micro pore fraction resulting in a higher variation in electrical resistance for improved CO gas sensing properties.

Key words: carbon nanofibers, pitch, electrospinning, CO sensing, activation

1. Introduction

Due to the severity of air pollution in recent years, industries are interested in more sensitive detection of discharged gases into the atmosphere. Air pollution gases include CO, NO_x, and SO₂ [1]. These gases have the most critical effect on the human respiratory system and cause acid rain and smog in the atmosphere. Among the air pollution gases, CO gas is very dangerous because it is colorless and odorless making it difficult to detect by humans. A CO gas content of about 0.1% in the air leads to the death of humans. CO is generated mostly from incinerators, power plants, and automobiles [2,3]. There is much CO included in exhaust gas especially in the case of incomplete combustion resulting in a high mortality rate. The development of a sensitive sensor for detecting CO gas during the various situations involved in the combustion process is essential for saving lives.

The majority of gas sensing materials are mostly metal oxide semiconductors, liquid electrolytes, and solid electrolytes. According to the recent development of nanotechnology in materials, carbon nanofibers (CNFs) have been utilized as sensing materials [4-6]. Gas sensors based on metal oxide semiconductors and solid electrolytes need a high operating temperature. A high operating temperature is a fatal drawback in gas sensing because of the risk of explosion in detecting a gas at high concentration. On the other hand, gas sensors using CNFs have good gas sensitivity even at room temperature [7-9]. One-dimensional CNFs are suitable for gas sensors because of their high surface-to-volume ratio and good thermal and chemical stability. Among the many methods of manufacturing CNFs, the electrospinning method is especially easy, simple and inexpensive [10,11].

The activation is divided into chemical activation and physical activation. Chemical activation is more feasible for developing micro pores than physical activation, but it has a high cost and environmental problems based on the use of chemical agents. Thus, it is challenging to develop physical activation conditions that include a micro pore structure which has the advantages of low cost and being an environmentally friendly

procedure [12-14]. Physical activation in the preparation of gas sensors can generate micro pores in CNFs leading to a larger surface area for efficient absorption of gas molecules. A fiber shape with one-dimensional characteristics shows a directional morphology. It has excellent electrical characteristics compared to a particle shape [5]. The gas sensing mechanism of activated CNFs is based on the sensitive variation in the electrical conductivity caused by the gas adsorption onto the CNFs. Pitch is one of the raw materials used to produce CNFs. The pitch prepared from coal or petroleum residue has hydrocarbons of various molecular weights and heat stability as well as a low cost. Pitch has excellent electrical conductivity because of the graphitic structure [15,16].

In this study, electrospun CNFs were prepared and then used as materials for a CO gas sensor. Precursors of CNFs were prepared using a mixed solution of polyacrylonitrile (PAN) and pitch. The pitch nanofibers were prepared successfully using electrospinning with the proper composition of pitch and PAN. The pitch nanofibers were further treated by carbonization and activation processes to improve both the electrical conductivity and gas sensitivity. The prepared electrospun and steam-activated CNFs were evaluated as CO gas sensing materials by measuring the variation in the electrical resistance upon adsorption of CO gas.

2. Experimental

2.1. PAN/pitch nanofiber preparation

Pitch was dissolved in *N,N*-dimethylformamide (DMF; Aldrich, USA) at 70°C for 12 h. DMF-soluble pitch was eliminated from the pitch solution through filtration. DMF-insoluble pitch was separated and then dissolved in a mixed solvent of DMF (5 g) and tetrahydrofuran (THF; Aldrich, 5 g) at 60°C. PAN (Mw=150,000, Aldrich) was dissolved in DMF at 60°C for 12 h. The weight ratio of the PAN and pitch was varied as follows: 1:2.8, 1:3.3, 1:3.75, and 1:4.5. When the pitch content was higher than 4.5 times the PAN content, the fiber shape could not be obtained by electrospinning. The spinning solution was prepared by mixing both the pitch and PAN solutions in an appropriate composition. PAN/pitch nanofibers were prepared by the electrospinning method using the spinning solution. Electrospinning was carried out with a tip having a diameter of 0.84 mm, a supply power of 25 kV, and a flow rate of 1.0 mL/h. The distance between the tip and collector was maintained as 18 cm. The manufactured PAN/pitch nanofibers were named as NFs-2.8, NFs-3.3, NFs-3.75, and NFs-4.5, respectively, depending on the weight ratios of the PAN and pitch.

2.2. Thermal treatment and steam activation

A prior oxidation process is necessary for the stabilization of the PAN/pitch nanofibers during the fabrication process of the CNFs. Carbonization without oxidation leads to the collapse of the fiber form. Oxidation was carried out for about 4 h by heating up to 225°C with a heating rate of 1°C/min., and the subsequent carbonization was carried out for about 1 h by heating up

to 900°C with a heating rate of 10°C/min. The electrical conductivity of the CNFs fabricated by the carbonization was measured with the four-point probe method. CNFs with the highest electrical conductivity were prepared by further treatment with steam activation which is an eco-friendly activation method. Steam activation was carried out at various temperatures of 600, 700, and 800°C, respectively, with a steam feed rate of 50 mL/h. The manufactured CNFs were named CNFs-2.8, CNFs-3.3, CNFs-3.75, and CNFs-4.5, respectively, according to the weight ratio of the PAN and pitch in their PAN/pitch nanofibers.

2.3. Characterizations of the carbon nanofibers

The morphology of the CNFs was studied using a cold type field-emission scanning electron microscope (FESEM; Hitachi, Japan). The surface area of the activated CNFs was measured by Brunauer-Emmett-Teller (BET) method by degassing and subsequently introducing nitrogen into the measuring equipment. The electrical resistance of the activated CNFs was measured with an electrometer to evaluate the properties of the gas sensor. The CNFs were ground by a mixer and attached onto a polyimide film. Then, it was connected by two Pt electrodes in a stainless steel chamber with a volume of 2000 cm³. The electrical resistance was monitored with a programmable electrometer (Keithley 6514). After sealing and degassing the chamber, N₂ gas was injected into the chamber; after which, the initial electrical resistance was measured. CO gas with a concentration of 100 ppm was injected into the chamber at a feeding rate of 500 sccm. Then, the change in electrical resistance was measured. The variation in electrical resistance is expressed as the difference between the initial electrical resistance and the electrical resistance after the adsorption of CO gas.

3. Results and Discussion

3.1. Surface characterization of the PAN/pitch nanofibers

The surface morphology of the electrospun PAN/pitch nanofibers was studied by FESEM. Fig. 1 shows the rugged surface of the PAN/pitch nanofibers with entangled structures on the rough surface. As the pitch content was increased in the nanofibers, more entangled structures were formed on the nanofibers. The diameter of the PAN/pitch nanofibers ranged from 200 to 400 nm. The electrospinning of PAN alone produced nanofibers with a smoother surface texture and a less entangled fiber shape. As the pitch content was increased, surface texture of the nanofiber became rougher. However, a particle shape was produced instead of a fiber shape by electrospinning when using more than 4.5 times the content of pitch compared to that of PAN. Fig. 2 shows the SEM images of various CNFs after oxidation and carbonization of the electrospun PAN/pitch nanofibers. Both the diameter and length of the CNFs decreased after oxidation and carbonization because a denser structure was formed in the nanofibers by the elements removed at the high temperature during the carbonization process.

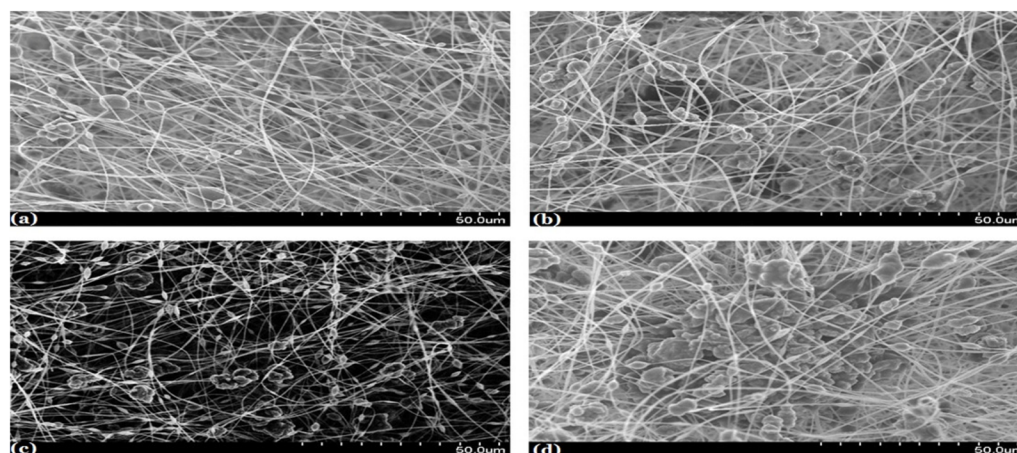


Fig. 1. Field-emission scanning electron microscope micrographs of the nanofibers (a) NFs-2.8, (b) NFs-3.3, (c) NFs-3.75, and (d) NFs-4.5 samples.

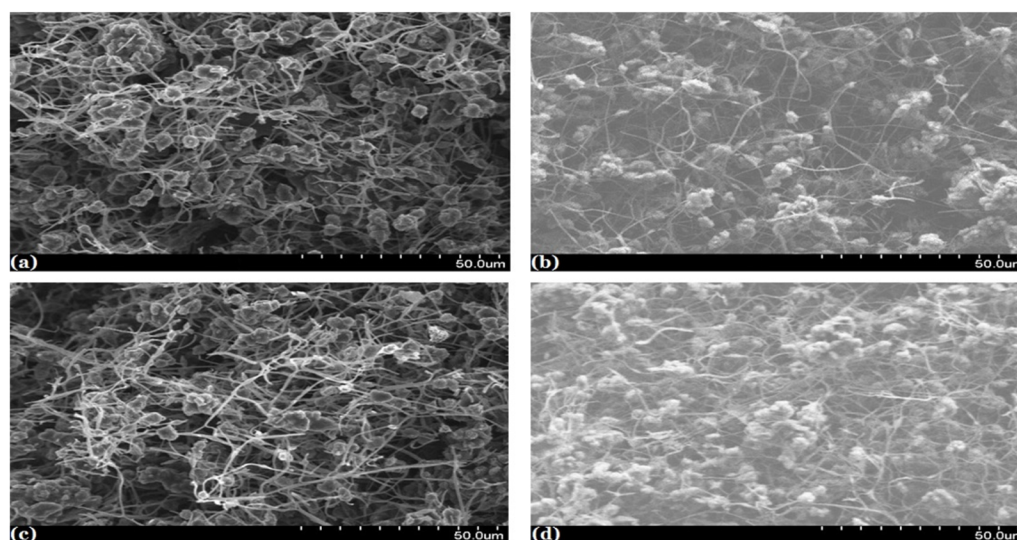


Fig. 2. Field-emission scanning electron microscope micrographs of the carbon nanofibers (a) CNFs-2.8, (b) CNFs-3.3, (c) CNFs-3.75, and (d) CNFs-4.5 samples.

3.2. Effect of the pitch content on the electrical properties of the carbon nanofibers

The electrical conductivity of various CNFs is presented in Table 1. A higher pitch content in the CNFs effectively increased the electrical conductivity of the CNFs. The graphitic structure of the pitch consists of a layered structure of graphene sheets. Each graphene sheet with sp^2 hybrid carbon bonds is beneficial for the transportation of electrons resulting in a higher electrical conductivity [17]. Therefore, the pitch has a better electrical conductivity than that of the PAN after the carbonization process. For this reason, when a higher pitch content was used in the CNFs, a higher electrical conductivity was obtained. Impurities and other components in the polymer are removed during carbonization at high temperature [18]. Carbonization changes both non-graphitic PAN and pitch to a graphitic structure which is favorable for

a higher electrical conductivity. A highly conductive material is especially important in gas sensing because it enables the rapid detection of a change in electrical resistance caused by gas adsorption.

Table 1. Electrical conductivity of the various CNFs

| CNFs | Electrical conductivity ($S\ cm^{-1}$) |
|-----------|--|
| CNFs-2.8 | 2.72 |
| CNFs-3.3 | 2.91 |
| CNFs-3.75 | 3.31 |
| CNFs-4.5 | 3.47 |

CNFs, carbon nanofibers.

Table 2. Surface area and micro pore fraction of CNFs-4.5 activated with steam at various temperatures

| Activation temperature (°C) | BET surface area (m ² g ⁻¹) | Micro pore fraction (%) |
|-----------------------------|--|-------------------------|
| 600 | 590 | 81 |
| 700 | 774 | 76 |
| 800 | 936 | 55 |

CNFs, carbon nanofibers; BET, Brunauer-Emmett-Teller.

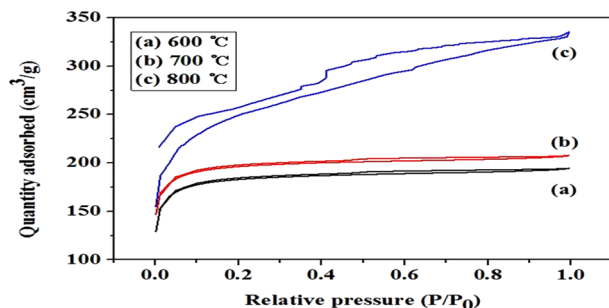


Fig. 3. Nitrogen adsorption behavior of CNFs-4.5 activated with steam at various temperatures.

3.3. Pore structure of the carbon nanofibers

NFs-4.5, which was the raw nanofibers used for the preparation of the CNFs with the highest electrical conductivity among the various prepared nanofibers, was activated with steam at 600, 700, and 800°C, respectively. The surface area of CNFs-4.5, which was activated with steam at various temperatures followed by carbonization, was measured by the BET method shown in Table 2. The micro pore fraction in CNFs-4.5 decreased as the steam activation temperature was increased. Facilitated merging of micro pores into meso- and macropores with a large pore size at a higher temperature was responsible for the decreased micro pore fraction. On the other hand, the BET surface area of CNFs-4.5 increased at the higher activation temperature due to the contribution of the meso- and macropore structure formation. The nitrogen adsorption behavior of CNFs-4.5, which was activated with steam at various temperatures, is shown in Fig. 3.

3.4. CO gas sensing characteristics of the carbon nanofibers

The variation in electrical resistance was measured for CNFs-4.5, which was activated with steam at various temperatures, through the injection of CO gas shown in Fig. 4. Because an inert gas such as N₂ is adsorbed, it interferes with the movement of the electrons. Therefore, the electrical resistance is increased. Because N₂ gas has a stable electron configuration, the activated carbon fibers have an insulator effect. When polarized gases such as CO gas and NO gas are adsorbed onto the pores, the adsorbed gases accelerate the movement of electrons and reduce the electrical resistance. This phenomenon is called the electrohopping effect [3]. The variation in electrical resistance (S) was

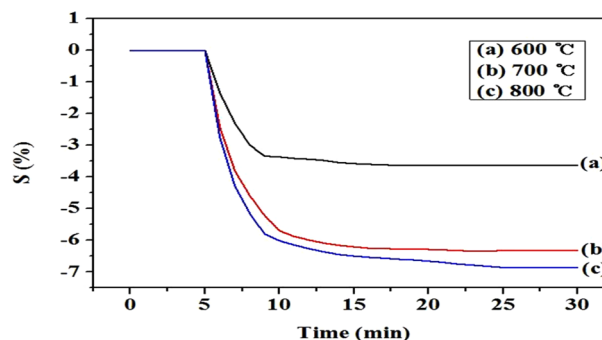


Fig. 4. Variation in electrical resistance of CNFs-4.5 over time for CO gas detection.

obtained with the following equation:

$$S = [(R_1 - R_0)/R_0] \times 100$$

, where R_1 is the electrical resistance measured after the CO adsorption, and R_0 is the initial electrical resistance before the CO adsorption. CNFs-4.5 had a higher variation in electrical resistance upon exposure to CO gas as the steam activation temperature was increased due to both the availability of a higher surface area to facilitate the adsorption of CO gas and a higher electrical conductivity.

The electrical resistance of the CNFs was reduced by the adsorbed CO gas molecules. Carbon material is known to work as a p-type semiconductor based on the exchange between the carbon materials and the adsorbed gas molecules. Some graphitic structures of carbon materials are destroyed to create various meso-, macro-, and micropores in the CNFs [3]. The carbon material loses its inherent semiconductor properties due to the activation process. Therefore, the electrical resistance of an activated carbon material is affected predominantly by the relation between the carbon material and the adsorbed gas molecules in the pores of the CNFs. The adsorbed gas molecules on the CNFs transfer the electrons. This phenomenon is referred to as electron hopping. Due to electron hopping, the electrical resistance of the activated CNFs decreased as the CO molecules were adsorbed onto the surface of the CNFs. Therefore, the electrical resistance of the CNFs became smaller as the CO molecules were adsorbed onto the CNFs resulting in the negative values for the variation in electrical resistance shown in Fig. 4.

A gas sensor using a metal oxide is capable of adsorption and desorption at a high temperature. On the other hand, a gas sensor using activated carbon can adsorb and desorb gas molecules based on physical adsorption [3]. Thus, it is necessary to study the cycle performance of a gas sensor to ensure that it feasibly works under a vacuum or heat treatment at a relatively low temperature [3,19].

4. Conclusions

PAN/pitch nanofibers were prepared with the electrospinning method using various compositions of PAN and pitch. CNFs were prepared from the PAN/pitch nanofibers with steam activa-

tion at various temperatures and with subsequent carbonization. As the pitch contents increased, the CNFs showed a non-uniform surface texture with a number of particle shapes in the fibers. The CNFs with the higher pitch contents showed a higher electrical conductivity. Steam activation of the PAN/pitch nanofibers formed pores of various sizes resulting in the facilitated adsorption of CO gas onto the CNFs. As the steam activation temperature was increased, the surface area of the CNFs increased, and the micro pore fraction decreased. CNFs-4.5 activated at 800°C had the highest variation in electrical resistance upon exposure to CO gas resulting in excellent CO gas sensing characteristics.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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References

- [1] Son MW, Choi JB, Hwang HI, Yoo KS. Fabrication and characteristics of NO_x gas sensors using WO₃ and In₂O₃ thick films to monitor air pollution. *J Sens Sci Technol*, **18**, 263 (2009). <https://doi.org/10.5369/JSST.2009.18.4.263>.
- [2] Kim MJ, Lee YJ, An HJ, Lee SH. Fabrication and evaluation of the SnO₂ based gas sensor for CO and NO_x detection. *Trans Korean Soc Automot Eng*, **23**, 515 (2015). <https://doi.org/10.7467/KSAE.2015.23.5.515>.
- [3] Im JS, Kang SC, Lee SH, Lee YS. Improved gas sensing of electrospun carbon fibers based on pore structure, conductivity and surface modification. *Carbon*, **48**, 2573 (2010). <https://doi.org/10.1016/j.carbon.2010.03.045>.
- [4] Zeng J, Hu M, Wang W, Chen H, Qin Y. NO₂-sensing properties of porous WO₃ gas sensor based on anodized sputtered tungsten thin film. *Sens Actuators B Chem*, **161**, 447 (2012). <https://doi.org/10.1016/j.snb.2011.10.059>.
- [5] Kadir RA, Li Z, Sadek AZ, Rani RA, Zoofakar AS, Field MR, Ou JZ, Chrimes AF, Kalantar-zadeh K. Electrospun granular hollow SnO₂ nanofibers hydrogen gas sensors operating at low temperatures. *J Phys Chem C*, **118**, 3129 (2014). <https://doi.org/10.1021/jp411552z>.
- [6] Durrer L, Helbling T, Zenger C, Jungen A, Stampfer C, Hierold C. SWNT growth by CVD on Ferritin-based iron catalyst nanoparticles towards CNT sensors. *Sens Actuators B Chem*, **132**, 485 (2008). <https://doi.org/10.1016/j.snb.2007.11.007>.
- [7] Sharma HJ, Sonwane ND, Kondawar SB. Electrospun SnO₂/polyaniline composite nanofibers based low temperature hydrogen gas sensor. *Fiber and Polym*, **16**, 1527 (2015).
- [8] Sayago I, Santos H, Horrillo MC, Aleixandre M, Fernández MJ, Terrado E, Tacchini I, Aroz R, Maser WK, Benito AM, Martínez MT, Gutiérrez J, Muñoz E. Carbon nanotube networks as gas sensors for NO₂ detection. *Talanta*, **77**, 758 (2008). <https://doi.org/10.1016/j.talanta.2008.07.025>.
- [9] Lee JH. Gas sensors using hierarchical and hollow oxide nanostructures: overview. *Sens Actuators B Chem*, **140**, 319 (2009). <https://doi.org/10.1016/j.snb.2009.04.026>.
- [10] Machado FM, Fagan SB, da Silva IZ, de Andrade MJ. Carbon Nano-adsorbents. In: Bergmann CP, Machado FM, eds. *Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications*, Springer, New York, 11 (2015).
- [11] Varghese SS, Varghese SH, Swaminathan S, Singh KK, Mittal V. Two-dimensional materials for sensing: graphene and beyond. *Electronics*, **4**, 651 (2015). <https://doi.org/10.3390/electronics4030651>.
- [12] Lozano-Castelló D, Lillo-Ródenas MA, Cazorla-Amorós D, Linares-Solano A. Preparation of activated carbons from Spanish anthracite: I. activation by KOH. *Carbon*, **39**, 741 (2001). [https://doi.org/10.1016/S0008-6223\(00\)00185-8](https://doi.org/10.1016/S0008-6223(00)00185-8).
- [13] Hui TS, Zaini MAA. Potassium hydroxide activation of activated carbon: a commentary. *Carbon Lett*, **16**, 275 (2015). <https://doi.org/10.5714/CL.2015.16.4.275>.
- [14] Maciá-Agulló JA, Moore BC, Cazorla-Amorós D, Linares-Solano A. Activation of coal tar pitch carbon fibres: physical activation vs. chemical activation. *Carbon*, **42**, 1367 (2004). <https://doi.org/10.1016/j.carbon.2004.01.013>.
- [15] Choi YO, Yang KS. Preparation of carbon fiber from heavy oil residue through bromination. *Fibers Polym*, **2**, 178 (2001).
- [16] Park SH, Kim C, Yang KS. Preparation of carbonized fiber web from electrospinning of isotropic pitch. *Synth Met*, **143**, 175 (2004). <https://doi.org/10.1016/j.synthmet.2003.11.006>.
- [17] Cooper DR, D'Anjou B, Ghattamaneni N, Harack B, Hilke M, Horth A, Majlis N, Massicotte M, Vandsburger L, Whiteway E, Yu V. Experimental review of graphene. *ISRN Condens Matter Phys*, **2012**, 501686 (2012). <https://doi.org/10.5402/2012/501686>.
- [18] Saha B, Schatz GC. Carbonization in polyacrylonitrile (PAN) based carbon fibers studied by ReaxFF molecular dynamics simulations. *J Phys Chem B*, **116**, 4684 (2012). <https://doi.org/10.1021/jp300581b>.
- [19] Liobet E. Gas sensors using carbon nanomaterials: a review. *Sens Actuators B Chem*, **179**, 32, (2013). <https://doi.org/10.1016/j.snb.2012.11.014>.