

Conducting Graphite/Cellulose Composite Film as a Candidate for Chemical Vapor-Sensing Material

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A type of conductive graphite/cellulose composite film used for chemical vapor-sensing material was prepared at room temperature in the ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIm]Cl). Graphite was pretreated with both oxidation and reduction processes. Due to the use of N,N-carbonyldiimidazole (CDI), as a covalent cross-linking agent in [BMIm]Cl, there were limited chemical bonds between the graphite and cellulose. The composite film was analyzed using Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). When these conducting films were exposed to certain organic vapors, their electrical resistances quickly changed, showing gas sensitivity. The percolation threshold of the conducting film was about 5 wt%. The gas-sensing behavior of these films in solvent were the opposite of those gas-sensing materials based on a non-polar polymer matrix. A typical negative vapor coefficient (NVC) was observed when the film was placed in polar organic solvents such as methanol, ethanol, and acetone.

Keywords: Graphite/cellulose composite; Gas-sensing material; Negative vapor coefficient

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INTRODUCTION

Vapor-sensing materials are receiving more and more attention from many scholars (Jin *et al.* 2004; Hong *et al.* 2012; Wang *et al.* 2011). Compared with organic and inorganic vapor-sensing materials, organic/inorganic (O/L) composites have better film forming properties, uniformity, gas-sensitivity, and selectivity (Song *et al.* 2012). Of all the inorganic conducting fillers such as carbon black (CB), graphite powder, and carbon nanotubes (CN), filled polymer composite is one of the most common O/L composites and has been studied as both a positive temperature coefficient (PTC) material and a gas-sensing material (Bin *et al.* 2002). In principle, the working mechanism of the electrical response of composites to vapors is similar to that of the PTC effect. That is to say, the variation in the composites' conductivity is a result of the change in conducting filler arrangement.

Some of the polymer matrix/conductive particles composites exhibited a remarkable sensitivity to organic vapors similar to the PTC effect, which is known as the negative vapor coefficient (NVC) effect (Chen *et al.* 2000, 2004). In our previous work, polystyrene/CB composites prepared by *in-situ* polymerization showed high sensitivity to some organic vapors with weak polarity, such as tetrahydrofuran, cyclohexane, chloroform, and acetone. However, polystyrene/CB composites showed almost no sensitivity to polar vapors; when exposed to vapors such as methanol and ethanol, their

resistance remained unchanged (Li *et al.* 2003a,b, 2005). This may be because the solubility parameters of weak-polarity vapors are similar to those of the polystyrene matrix, which induced a better compatibility between the substrate and vapors and was more conducive to producing an NVC effect.

As the most naturally abundant biopolymer, cellulose has many advantages compared with synthetic polymer materials including biocompatibility, easy modification, eco-friendliness, and low price (Kim *et al.* 2002, 2006). Cellulose and its derivatives have been used for coatings, laminates, optical films, and pharmaceuticals (Klemm *et al.* 2005).

Recently, it has been reported that cellulose/conductive particles composites can be used as a smart material in many fields, such as gas detection (Sungryul *et al.* 2010), humidity and temperature sensors (Suresha *et al.* 2011), electric actuators (Sungryul *et al.* 2009), and supercapacitors (Weng *et al.* 2011). Sungryul reported the multi-walled carbon nanotubes-cellulose (M/C) paper as a chemical vapor sensor. The M/C paper showed a reversible and rapid response to some polarity vapors with the following rank: methanol < ethanol < 1-propanol < 1-butanol (Sungryul *et al.* 2010).

Graphite, as a conductive particle, has natural electrical, mechanical, and thermal properties (Lin 2009), and it is relatively cheap and easy to obtain. Herein, we have developed a pretreated graphite/cellulose composite film as a flexible electrode sensitive to some polarity vapors. The graphite particles were treated first by oxidation and reduction reactions and then grafted onto the surface of the cellulose with N, N-carbonyldiimidazole (CDI) as a covalent cross-linking agent in [BMIm]Cl. The conductive composite film based on cellulose was obtained after washing away the residual ionic liquid with deionized water.

EXPERIMENTAL

Materials and Fabrication Process

The graphite/cellulose composite fabrication process is illustrated in Fig. 1.

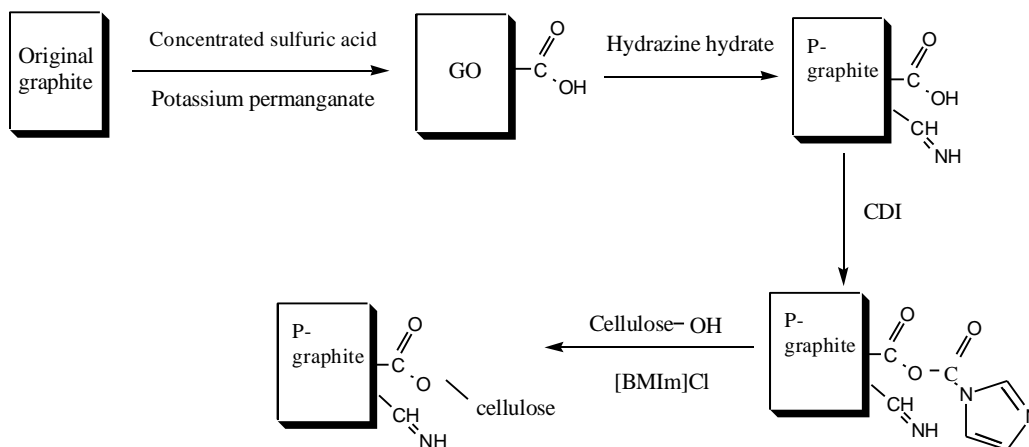


Fig. 1. Graphite/cellulose composite fabrication process

Cotton cellulose, which was purchased from Xuzhou Health Material Co. Ltd of China, was dried in an oven at 50 °C for 24 h before use. Its degree of polymerization (DP) is 4050, as measured by Ubbelodh viscometer in cuprammonium hydroxide solution. The cellulose was dissolved in [BMIm]Cl (purchased from Lanzhou Physical and Chemical Research Institution of China) with a mass ratio of 1/50 by heating at 100 °C under mechanical stirring. Then the cellulose and ionic liquid can form the homogeneous solution which is conducive to reaction between cellulose and graphite.

First, graphite oxide (GO) was prepared by the oxidation of graphite (325-mesh, purchased from Tianjin Fuyu Fine Chemical Co. Ltd of China) by sulfuric acid (90%, AR, came from Guangzhou Chemical Reagent factory of China) and potassium permanganate (AR, came from Guangzhou Chemical Reagent factory of China). Then, the GO was reduced in hydrazine hydrate (AR, came from Tianjin Fuyu Fine Chemical Co. Ltd of China), and the resulting pretreated graphite was obtained after it was filtered and washed with deionized (DI) water until neutral.

The pretreated graphite (2 mg) was dispersed in [BMIm]Cl (1 g) in an ultrasonic bath for 20 min; then, N,N-carbonyldiimidazole (CDI, 400 mg, obtained from Adamas Reagent Co. Ltd.) was added to react at 60 °C for 14 h. After that, the reaction solution containing imidazolide-graphite was mixed with a cellulose/[BMIm]Cl solution at 60 °C for 10 h. Finally, the covalently grafted cellulose with graphite was obtained.

The final ionic liquid solution containing cellulose/graphite was spin-coated onto a homemade glass electrode (Li *et al.* 2003a), then washed with [BMIm]Cl, ethanol and DI water in a sequence and dried in a vacuum for 12 h before use.

Methanol(AR) and actone(AR) came from Guangzhou Chemical Reagent factory of China, ethanol (AR) and chloroform (AR) were obtained from Tianjin Fuyu Fine Chemical Engineering Co. Ltd of China, benzene(AR) and phenixin(AR) came from Jiangsu Qiangsheng Functional Chemical Co. Ltd of China. The six reagents were the tested solvents of the vapor-sensing performance test.

Characterization

The different statuses of carboxyl on graphite were investigated using an FT-IR spectrometer (Thermo Nicolet, USA). The three-dimensional structure of the pretreated graphite was shown by AFM (Veeco Nanoscope IIIa, USA). Infra-red absorption spectra were taken using an FT-IR vacuum spectrometer (Thermo Nicolet, USA) to investigate the presence of covalent bonds between graphite and cellulose. A Raman spectrometer (LanRAM Aramis, France) was used to characterize the structure of the film. X-ray diffraction patterns were acquired to investigate changes in the crystalline region with a D8ADVANCE (BRUKER/AXS Instruments, Germany). The voltage and current of the X-ray source were 40 kV and 40 mA, respectively. The scanning range of the Bragg angle (2θ) was from 5° to 45° under the scanning rate of 0.015°/s.

Vapor-Sensing Performance Test

The glass electrode was prepared at a size of 20 mm (length) × 10 mm (width). The electric resistance measurements, the investigation of its vapor-sensing performance and detecting device were all performed in accordance with our previous work (Li *et al.* 2003b). The electrical response of the composites to organic solvent vapors was measured by hanging the electrode coated with composites film in a glass conical flask containing pure solvent (methanol, ethanol, acetone, chloroform, benzene, and phenixin)

at the bottom. The distance between the composites and solvent surface was 3 to 4 cm. Direct current electric resistance was recorded with a digital multimeter (Victor VC9808). The corresponding responsivity is characterized by the ratio of the transient resistance to the initial resistance in air.

RESULTS AND DISCUSSION

Characterization of the Pretreated Graphite

Figure 2 shows the FT-IR spectra of graphite (a), GO (b), and pretreated graphite (c). The absorption peak in line (b) at 1712 cm^{-1} corresponds to the carboxyl on the surface of the graphite oxide. There still is a much weaker carboxyl absorption peak at 1715 cm^{-1} in line (c), which means that the majority of carboxyl had been reduced by hydrazine hydrate. The absorption peak in line (c) at 1450 cm^{-1} is the infrared characteristic absorption peak of the $-\text{CH}=\text{NH}$, which indicated that the graphite was partly reduced.

The adsorption peak at 3200 cm^{-1} is the stretching vibration absorption peak of the $-\text{OH}$ which was from the water molecule. It might be due to the hygroscopicity of the original graphite, GO, and pretreated graphite.

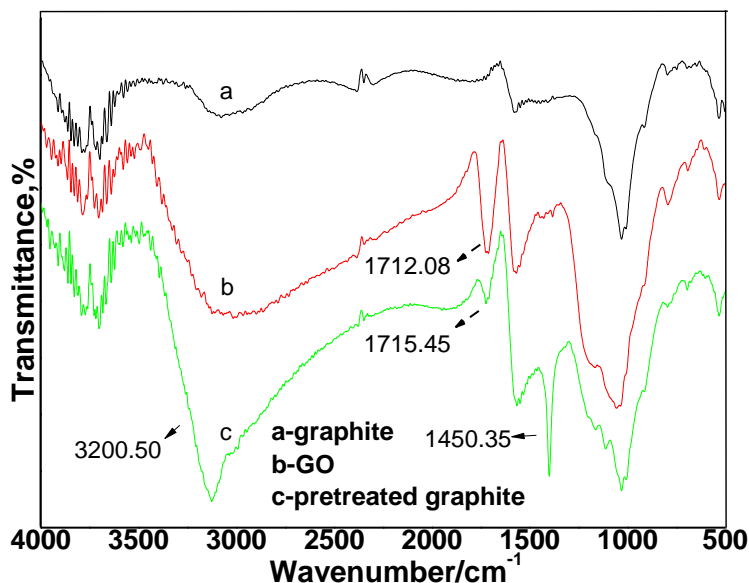


Fig. 2. FT-IR spectra of graphite (a), GO (b), and pretreated graphite (c)

Figure 3 shows the size of the pretreated graphite. It is apparent that the length and the height of this composite is about $10\text{ }\mu\text{m}$ and 9 nm , respectively, so we consider that its size belongs to the nanoscale. Moreover, the graphite can form a hierarchical structure by redox reaction. The graphite/cellulose composite might have a relatively low percolation threshold (Jing *et al.* 2000).

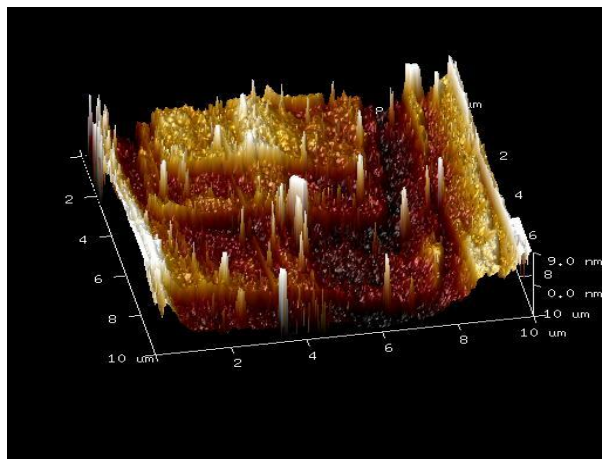


Fig. 3. The three-dimensional structure of pretreated graphite

Characterization of the Pretreated Graphite/Cellulose Composite

Graphite-imidazolide is obtained by the reaction of pretreated graphite with CDI. It produced a few of chemical bonds between the graphite and cellulose when graphite-imidazolide reacts with cellulose in ionic liquid.

Figure 4 shows the FT-IR spectra of the cellulose/graphite physically blend composite film (a) and graphite/cellulose composite film (b). The new ester absorption peak that appears at 1757 cm^{-1} clearly indicates the presence of covalent bonds between graphite and cellulose. Because a small amount of cellulose was grafted onto the surface of the graphite, the absorption peak of the ester bond presents weak intensity.

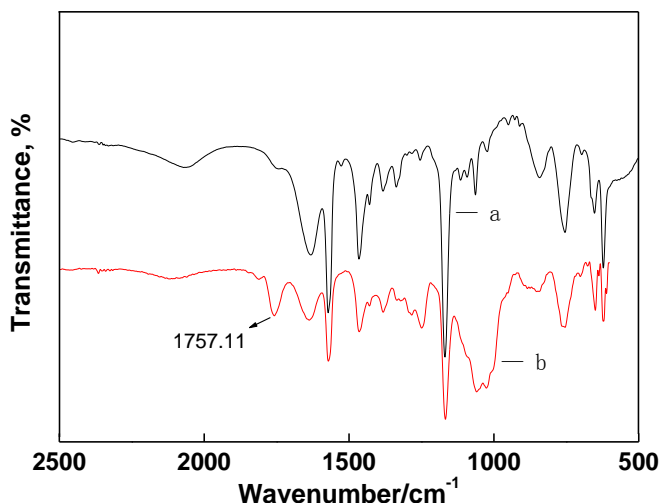


Fig. 4. FT-IR spectra of cellulose/graphite physically blend film (a) and graphite/cellulose film (b)

Figure 5 shows the Raman spectra of pretreated graphite (a), cellulose/graphite physically blend film (b), and graphite/cellulose composite film (c). The spectrum of pretreated graphite (a) displays two intense bands at 1329 and 1551 cm^{-1} . The D-band corresponds to the breathing mode of k-point phonons of A_{1g} symmetry, while the G-

band corresponds to the first-order scattering of the E_{2g} phonon of sp^2 carbons. Both bands are attributable to the graphene structure according to the literature (Staito *et al.* 2011). The D-band and G-band were also observed in lines (b) and (c), while their breadth decreased, which might due to the fact that the surface of the graphite was covered by cellulose molecules. Comparing lines (b) and (c), one can see that most of their peaks are parallel, and further changes are observed for the tangential displacement mode (TDM) of G-band compared with line (a), the TDM of G-band in line (b) exhibits a definite upward shift of 2 cm^{-1} and even further upshift of 39 cm^{-1} in line (c). This phenomenon led to the suggestion that most of the graphite and cellulose were physically blended in the graphite/cellulose composite film (Chambers *et al.* 2003). Combined with the results discussed in Figs. 2 and 3, it appears that only a limited amount of cellulose was grafted onto the surface of the graphite because achieving a solid phase grafting reaction between cellulose and graphite is very difficult.

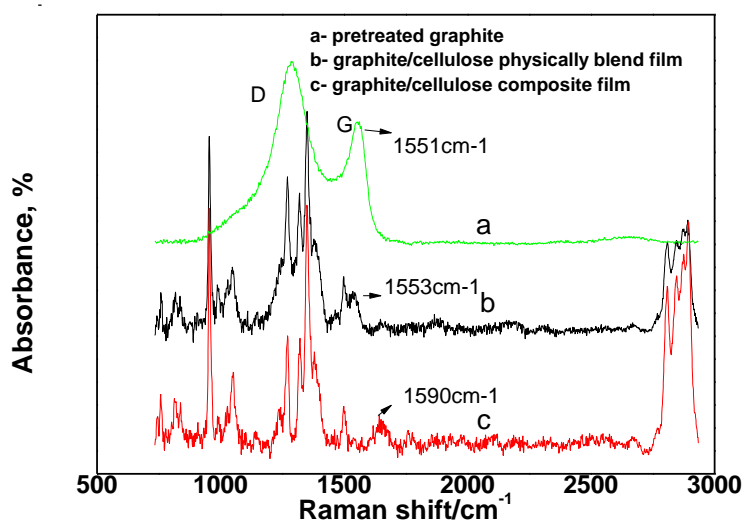


Fig. 5. Raman spectra of pretreated graphite (a), cellulose/graphite physically blend film (b), and graphite/cellulose film (c)

Figure 6 shows the XRD profiles of pretreated graphite/cellulose composite (A, graphite: 5 wt %), regenerated cellulose from [BMIm]Cl (B), and original cellulose (a). Original cellulose has three reflection peaks at 15.2° , 16.7° , and 23.1° , which indicates the cellulose I structure (Wu *et al.* 2009). Regenerated cellulose exhibited a diffuse XRD profile because of the increase of amorphous regions during dissolution. The pretreated graphite/cellulose composite film showed a similar XRD profile to regenerated cellulose. The crystallinity of the film can be evaluated by calculating the crystallinity index (CI) with the following formula (Marson and Seoud 1999)

$$CI \text{ (crystallinity index)} = 1 - I_{\min}/I_{\max} \quad (1)$$

where I_{\min} is the minimum intensity between $2\theta = 18$ and 19° and I_{\max} is the maximum intensity between $2\theta = 18$ and 19° .

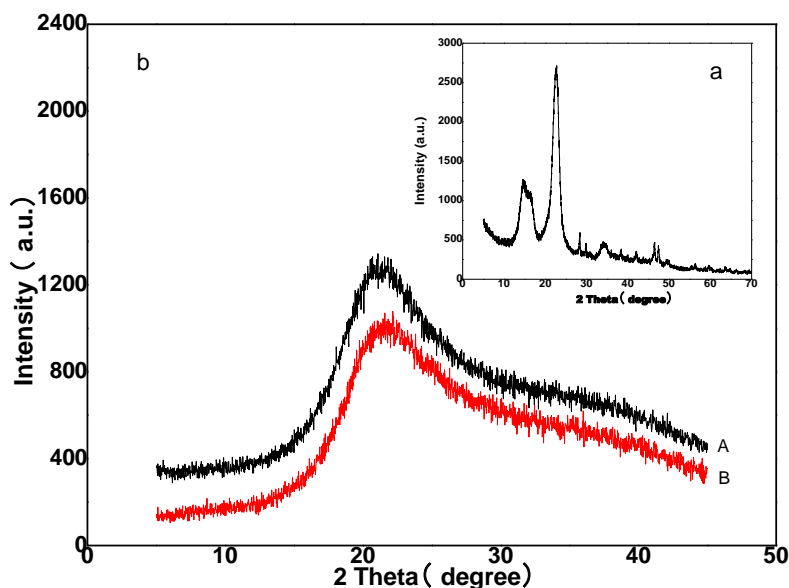


Fig. 6. XRD profiles of pretreated graphite/cellulose composite (A, graphite: 5wt %), regenerated cellulose from [BMIm]Cl (B), and original cellulose (a)

The CIs of pretreated graphite/cellulose and regenerated cellulose calculated using Eq. 1 are 0.32 and 0.46, respectively. The decline in the CI of pretreated graphite/cellulose may be interpreted as a result of the destructive effects of graphite on the crystalline regions of cellulose.

Vapor-sensing Performance of Composite Film

Conductive filler content has a significant impact on the performance of polymer-based PTC material. This phenomenon was reported by Mark *et al.* (1996). Figure 7 shows the electrical resistance variation of pretreated graphite/cellulose composite as a function of graphite content.

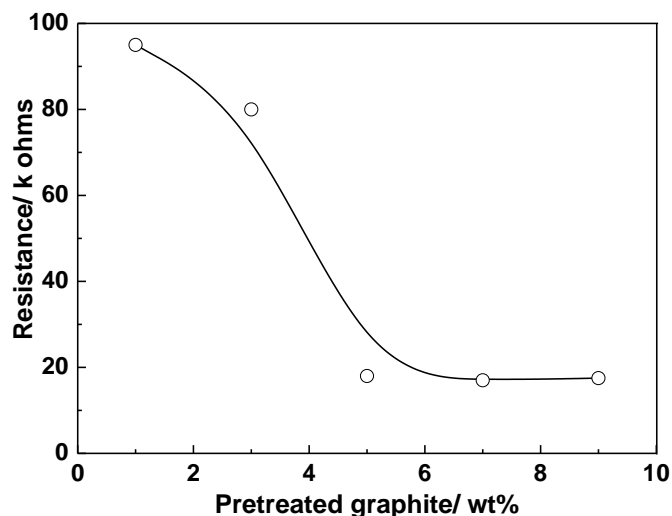


Fig. 7. Resistance of pretreated graphite/cellulose composite as a function of graphite content

It can be seen that the resistance of the composite decreased sharply with an increase in graphite when graphite content was less than about 5 wt%. However, it became smooth when the content exceeded 5 wt%. That is to say, the percolation threshold of the composite was about 5 wt%. In most cases, when the content of conductive filler is near the percolation value, the composite may show the best gas-sensing properties. Therefore, in the absence of special instructions, the graphite content of composite used for gas-sensing performance test is controlled at 5 wt% in this paper.

Unlike polymer material, the cellulose matrix of a composite could not be dissolved or swollen when the pretreated graphite/cellulose film was placed into saturated polar organic vapors; however, the vapors may destroy the hydrogen bonds between cellulose molecules, which causes aggregation of the graphite. This phenomenon is similar to the NVC effect. Beyond that, rearranging parts of the graphite to form the new conductive channels in the film improve electron pathways in the film. Therefore, the resistance of composite film reduces sharply in some polar organic vapors such as methanol, ethanol, and acetone. However, for non-polar or low-polarity organic vapors such as chloroform, benzene, and carbon tetrachloride, the composite shows hardly any sensitivity (Fig. 8).

Interestingly, when the composite film is transferred from the organic steam atmosphere into the air, its resistance can quickly return to the initial value. This is probably because the hydrogen bonds between graphite particles and cellulose are formed again after desorption of the organic steam from the composite, which impedes the restrictions of graphite particles to forming a conductive channel.

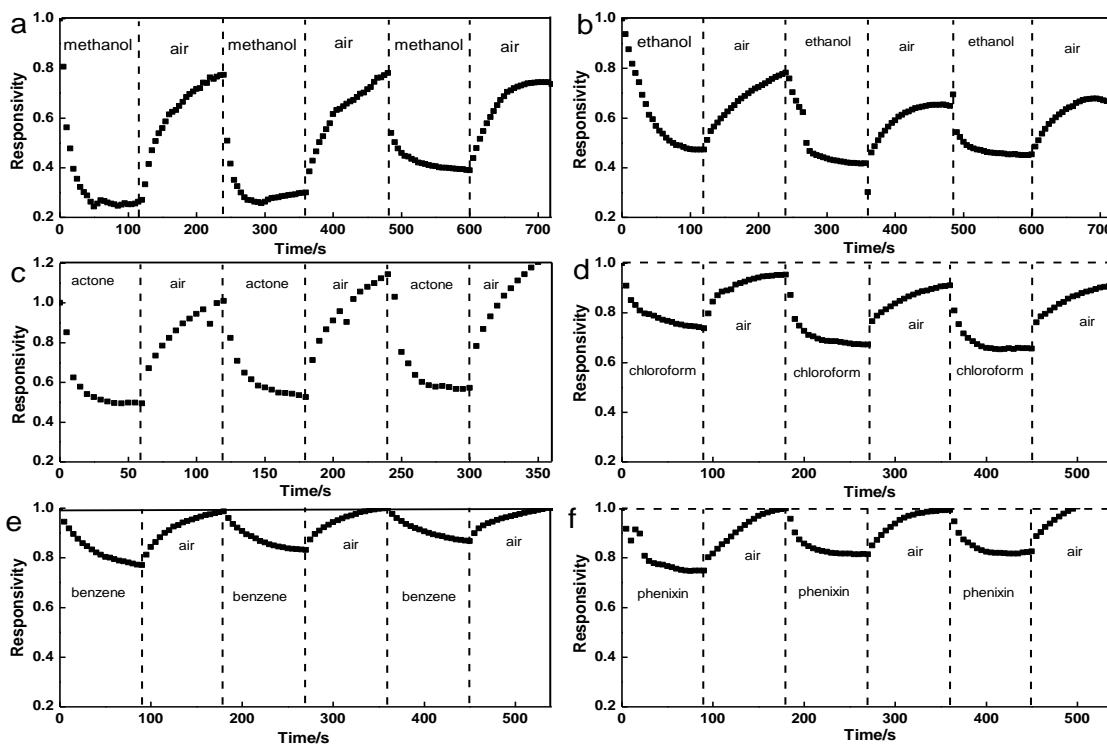


Fig. 8. Responsiveness and stability of pretreated graphite/cellulose film to organic vapors at 30 °C

Figure 8 also shows that the composite has a good repeatability in organic vapors. It indicates that the composite film prepared by pretreated graphite/cellulose is very stable, which means that it has a practical performance and is suitable to use as a gas-sensing electrode. The results are very similar to those found in our previous research (Liu *et al.* 2014).

The polarity data of the six types of organic vapors used in this work are shown in Table 1. It can be seen that the polarity of methanol is the strongest and that of carbon tetrachloride is the weakest.

Table 1. Comparison of the Polarity of Six Solvents

Vapors	Methanol	Ethanol	Acetone	Chloroform	Benzene	Phenixin
Polarity	6.6	6.0	5.4	4.4	3.0	1.6

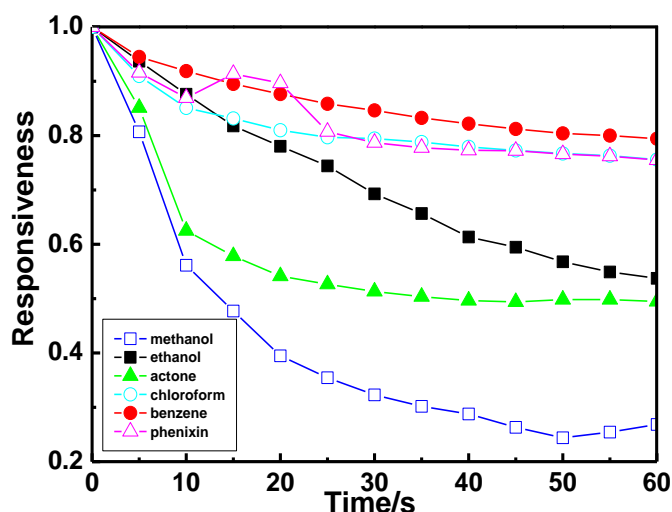


Fig. 9. Time-dependence of responsiveness of pretreated graphite/cellulose film to organic vapors at 30 °C

Figure 9 shows the different response capabilities of pretreated graphite/cellulose film in six organic vapors from 0 s to 60 s. As can be seen in Fig. 9, the composite electrode for methanol steam was the most sensitive, and for carbon tetrachloride it was the least sensitive. The result is substantially the same as the solvent polarity sequence shown in Table 1. This is because the polar polymer in the process of dissolving and swelling in the solvent must follow similar principles concerning polarity. As a consequence, the swelling effect of cellulose caused by methanol was the most significant in six types of organic vapors. Therefore, vapors with high polarity can make the film show more sensitivity. However, the sensitivity of the composite electrode to acetone was slightly stronger than its sensitivity to alcohol, presenting an opposing trend, mostly because the saturated vapor pressure of acetone is higher than that of ethanol at the same temperature (Chen *et al.* 2005); therefore, there would be more acetone molecules than alcohol under the same conditions.

CONCLUSIONS

1. New types of sensing materials based on cellulose matrix and pretreated graphite fillers were prepared successfully by dissolving cotton in [BMIm]Cl. The percolation threshold of the composite was about 5 wt%, and the crystallinity indices of the composite and regenerated cellulose were 0.32 and 0.46, respectively.
2. The composite electrode had a better sensitivity and repeatability for polar organic vapors such as methanol, ethanol, and acetone, and showed only slight sensitivity for non-polar vapors.
3. The sensing behaviors of pretreated graphite/cellulose composites in polar organic vapors are opposite to those sensing materials based on a non-polar polymer matrix, and more similar to another type of NVC effect.

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REFERENCES CITED

- Bin, Y., Xu, C., Zhu, D., and Matsuo, M. (2002). "Electrical properties of polyethylene and carbon black particle blends prepared by gelatin/crystallization from solution," *Carbon* 40(2), 195.
- Chambers, G., Carroll, C., Farrell, G. F., Dalton, A. B., Mcnamara, M., Panhuis, M., Byrne, H. J. (2003). "Characterization of the interaction of Gamma cyclodextrin with single-walled carbon nanotubes," *Nano Lett.* 3(6), 843-846.
- Chen, J., and Tsubokawa, N. (2000). "Electric properties of conducting composite from poly(ethylene oxide) and poly(ethylene oxide)-grafted carbon black in solvent vapor," *Polym. J.* 32(9), 729-736.
- Chen, S. Hu, J., and Zhang, M. Q. (2004). "Gas sensitivity of carbon black/waterborne polyurethane composites," *Carbon* 42(3), 645-651.
- Chen, S. G., Hu, J. W., Zhang, M. Q., and Rong, M. Z. (2005). "Effect of temperature and vapor pressure on the gas sensing behavior of carbon black filled polyurethane composites," *Sensor. Actuat. B* 105(2), 187-193.
- Hong, L. J. (2012). "Preparation of polypyrrole and its nanocomposites and investigations on their humidity and gas sensing properties," Dissertation, Hangzhou, Zhejiang Univ.
- Jin, G., Norrish, J., Too, C., and Wallace, G. (2004). "Polypyrrole filament sensors for gases and vapors," *Curr. Appl. Phys.* 4(2-4), 366-369.
- Jing, X. L., Zhao W. B., and Lan L. W. (2000). "The effect of particle size on electric conducting percolation threshold in polymer/conducting particle composites," *J. Mater. Sci. Lett.* 19, 377-379.

- Klemm, D., Heublein, B., Flank, H. P., and Bohn, A. (2005). "Cellulose: Fascinating biopolymer and sustainable raw material," *Chem. Int. Ed.* 44(36), 3358-3393.
- Kim, J., and Seo, Y. B. (2002). "Electro-active paper actuators," *Smart Mater.* 11(3), 355-360.
- Kim, J., Yun, S., and Ounaies, Z. (2006). "Discovery of cellulose as a smart material," *Macromolecules* 39(12), 4202-4206.
- Li, J. R., Xu, J. R., Zhang, M. Q., and Min, Z. R. (2003a). "Carbon black/polystyrene composites as candidates for gas sensing materials," *Carbon* 41(12), 2353-2360.
- Li, J. R., Xu, J. R., Zhang, M. Q., and Rong, M. N. (2003b). "Electrical response to organic vapor of conductive composites from amorphous polymer/carbon black prepared by polymerization filling," *Macromol. Mater. Eng.* 288(2), 103-107.
- Li, J. R., Xu, J. R., Zhang, M. Q., Rong, M. Z., and Zhang, Q. (2005). "The role of crystalline phase in triblock copolymer PS-PEG-PS based gas sensing materials," *Polymer* 46(24), 11051-1159.
- Lin, W. (2009). "Study on novel modified graphite/epoxy resin conductive adhesives," Dissertation, Harbin, Northeast Forestry University.
- Liu, K. H., Li, J. R., He, B. H., and Liang, M. L. (2014). "Preparation and gas-sensing properties of MWCNTs/cellulose-chitosan conducting composite," *Acta Materialiae Compositae Sinica* 31(4), 752-757.
- Marson, G. A., and Seoud, O. A. (1999). "Cellulose dissolution in lithium chloride/N,N-dimethylacetamide solvent system: Relevance of kinetics of decrystallization to cellulose derivatization under homogeneous solution conditions," *J. Polym. Sci. A* 37(19), 3738-3744.
- Song, X., Yan, C. Y., Zhang, Y., Jiang, W., and Xie, H. (2012). "Research progress and prospect of gas sensitive materials," *Mater. Rev.* 26(6), 36-39.
- Staito, R., Hofmann, M., Dresselhaus, G., Jorio, A., Dresselhaus, M. S. (2011). "Raman spectroscopy of graphene and carbon nanotubes," *Advan. Physics* 60, 413-550.
- Sungryul, Y., and Jaehwan, K. (2009). "Covalently bonded multi-walled carbon nanotubes-cellulose electro-active actuator," *Sensor. Actuat. A* 154(1), 73-78.
- Sungryul, Y., and Jaehwan, K. (2010). "Multi-walled carbon nanotubes-cellulose paper for a chemical vapor sensor," *Sensor. Actuat. B* 150(1), 308-313.
- Suresha, K. M., Sungryul, Y., and Jaehwan, K. (2011). "Flexible humidity and temperature sensor based on cellulose-polypyrrole nanocomposite," *Sensor. Actuat. A* 165(2), 194-199.
- Wang, Z. M., Tang, X. C., Xiao, Y. H., Yu, X. J., Zhang, L., Jia, D. A., and Chen, G. C. (2011). "Polypyrrole coated carbon nanotubes: Preparation, characterization, and gas-sensing properties," *J. Inorg. Mater.* 26(9), 962-968.
- Weng, Z., Su, Y., Wang, D. W., Li, F., Du, J. And Cheng, H. M. (2011). "Graphene-cellulose paper flexible supercapacitors," *Adv. Energy Mater.* 1(5), 917-922.
- Wu, R. L., Wang, X. L., Wang, Y. Z., Bian, X. C., and Li, F. (2009). "Cellulose/soy protein isolate blend films prepared via room-temperature ionic liquid," *Ind. Eng. Chem. Res.* 48(15), 7132-7136.

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