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Chemical-vapor-sensitive materials based on a multiwalled carbon nanotube/hydroxyl propyl methylcellulose/cellulose composite

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ABSTRACT: A type of chemical vapor-sensing material made from multiwalled carbon nanotubes/hydroxyl propyl methyl cellulose/cellulose composite films were prepared in the room-temperature ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIm]Cl). A typical negative vapor coefficient was observed when the film was placed in polar organic solvents, such as methanol and ethanol. The sensitivity of the film to vapors increased significantly with increasing temperature. Interestingly, the resistance of the films increased almost linearly with decreasing vacuum, and the changes in resistance with the vacuum show good repeatability. The surface morphology, thermostability, and stress–strain properties of the composite films were analyzed with scanning electron microscopy, thermogravimetric analysis, and an electrical universal testing machine, respectively. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41639.

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INTRODUCTION

Conductive composites consisting of inorganic conductive fillers and synthetic polymer matrices have been used as sensitive materials in many fields.[1–6] Nowadays, conducting composites based on biological resources, such as natural polymers, are being given more and more attention.[7,8]

Cellulose is one of the most naturally abundant biopolymers, and its derivatives have been used for coatings, laminates, optical films, and pharmaceuticals.[9] Cellulose/conductive particles film have played a significant role in gas detection,[10] humidity, temperature sensors,[11] electric actuators,[12] and supercapacitors.[13] What is more, cellulose has been rediscovered as a smart material; it has advantages in terms of biocompatibility, easy modification, ecofriendliness, and low price.[14,15] Yun *et al.*[12] prepared a kind of cellulose/conductive particle material, a multiwalled carbon nanotube (MWCNT)–cellulose paper, as a chemical vapor sensor.

Carbon nanotubes (CNTs) have unique electronic, mechanical, and thermal properties.[16] Because of possible improvement in the electrical characteristics of polymers via the homogeneous distribution of CNTs, many researchers have investigated various methods for preparing CNTs/polymer composites.[17,18] CNTs in composites act as a conducting network, and they can aggregate or disperse with changes in cellulose; as a result, the composites can be sensitive to their surroundings, such as vapors, humidity, and temperature.[2]

In this study, we developed a conducting composite film based on cellulose and CNTs as a candidate for chemical vapor sensors with ionic liquid as the blending solvent. The hydroxypropyl methylcellulose (HPMC), as an auxiliary material which had good compatibility with cellulose, was added to improve the strength properties of the composite film because of its good film-forming and mechanical properties.[19]

The resulting MWCNTs/HPMC/cellulose conducting composite films showed a reversible and fast response to some polarity vapors. Furthermore, the composite films exhibited extensive sensitivity to the surrounding vacuums, and this phenomenon has not been reported in other literature.

EXPERIMENTAL

MWCNTs were treated by nitric acid (87%, CP) and then filtered with deionized water until its pH value reached 7. The resulting MWCNTs (1 mg) were dispersed in [BMIm]Cl (1 g) in an ultrasonic bath for 20 min. The cotton cellulose with a degree of polymerization of 4050 was dissolved in [BMIm]Cl at 100°C with mechanical stirring for 10 min. Then, HPMC (3 mg) was added to the mixed solution, and we continued to stir it for a further 50 min. The proportion of the HPMC, cotton cellulose, and [BMIM]Cl was 3:40:1000. The weight

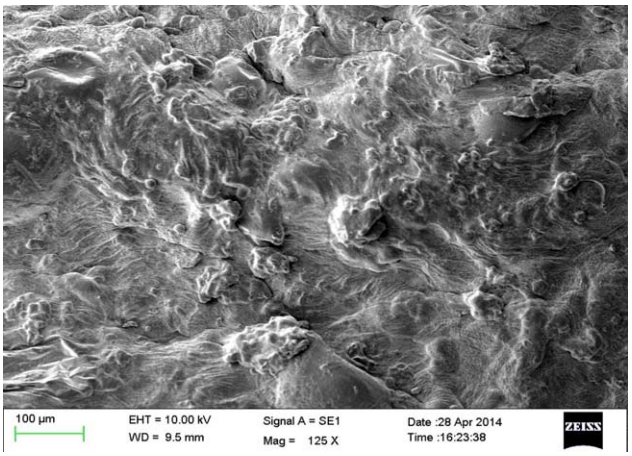

Figure 1. SEM image of a cellulose/MWCNT/HPMC composite film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

percentages of the MWCNTs were 0.1, 3.5, 7.0, 14.0, and 28.0 wt %, respectively. The final solution was spin-coated on a glass electrode and washed with ethanol and deionized water in a sequence. The size of the resulting composite film was about 20 mm (length) ×10 mm (width) × 1 mm (thickness).

The surface morphology of the MWCNTs/HPMC/cellulose composite film was observed with a scanning electron microscope (EVO, Germany) at an acceleration voltage of 10 kV. The thermostability of the film was investigated by thermogravimetric analysis (Q-500). The mechanical properties of the films were investigated by an electrical universal testing machine (Instron 5565). The chemical vapor-sensing performance was done according to our previous work.[20] We measured the electrical response of the composites to organic solvent vapors by hanging the electrode coated with composites film in a glass conical flask

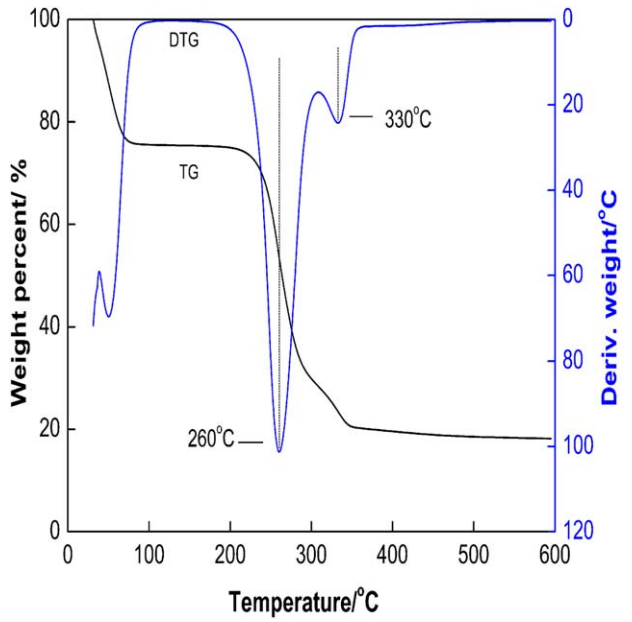

Figure 2. TG and derivative thermogravimetry (DTG) curves of the MWCNT/HPMC/cellulose composite films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

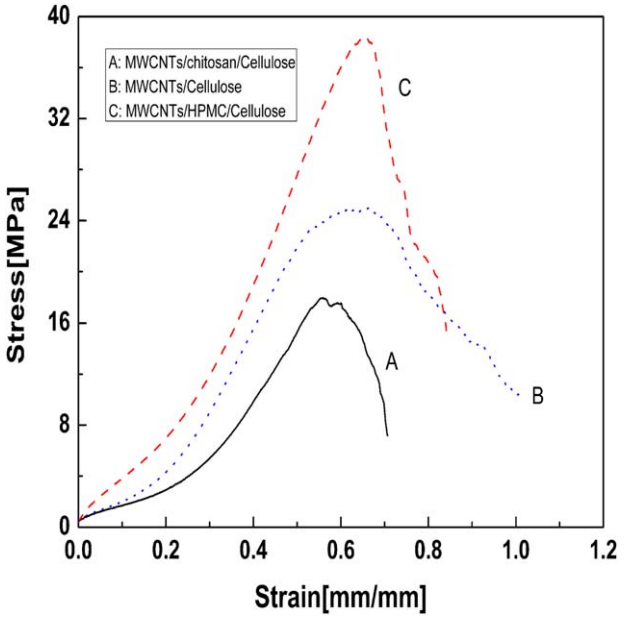

Figure 3. Stress–strain curves of three kinds of composite films: (A) MWCNT/cellulose, (B) MWCNT/chitosan/cellulose, and (C) MWCNT/HPMC/cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containing pure solvent (methanol, ethanol, acetone, or chloroform) at the bottom. The distance between the composites and solvent surface was 3–4 cm. Direct-current electric resistance was recorded by a digital multimeter (Victor VC9808). The corresponding responsivity was characterized by the ratio of the transient resistance to the initial resistance in air.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) images of the composite films made from cotton cellulose, MWCNTs, and HPMC in the ionic liquid [BMIm]Cl are shown in Figure 1. Many conductive pathways were formed by MWCNTs. Furthermore, the surface of the composite film was rough; this was beneficial for the adsorption and desorption of chemical vapors.[21]

Figure 2 shows the thermogravimetry (TG) curves of the MWCNTs/HPMC/cellulose composite films. Most of moistures containing in composite film are removed at about 100°C. The thermal weight loss peaks at 260 and 330°C represent the thermal decomposition and carbonization temperature of cellulose and HPMC, respectively. The MWCNTs/HPMC/cellulose films showed a degree of thermal stability from 100 to about 230°C.

In our previous research,[22] a kind of chemical vapor-sensing composite film made from MWCNTs/chitosan/cellulose was prepared. The film showed good response to alcohol vapors, but its mechanical strength was poor. In this study, to improve the mechanical properties of the composite films, the chitosan was replaced by HPMC, a kind of cellulose ether, which has a good compatibility with cellulose and better film-forming characterisitics.[19]

Figure 3 shows the stress–strain curves of three kinds of composite films tested under the same conditions. According to the

Table I. Young's Modulus Values of Three Kinds of Cellulose Composite Films

	Young's modulus (MPa)
MWCNT/chitosan/cellulose	28.84 ± 2.03
MWCNT/cellulose	43.98 ± 2.54
MWCNT/HPMC/cellulose	58.93 ± 2.78

Hooke's law, the Young's modulus values of the three films were calculated and are presented in Table I.

It was clear that the Young's modulus of the cellulose/MWCNTs/HPMC composite film was the highest of the three films. That is, the addition of HMPC greatly improved the mechanical properties of the composite films.

The conductive filler content had a significant impact on the performance of the polymer-based sensor material.[23] Figure 4 shows the electrical resistance variation of the MWCNTs/HPMC/cellulose composite film as a function of the MWCNT contents. As shown, the resistance of the composite decreased sharply with increasing MWCNTs when the MWCNT content was less than about 7 wt %. However, it became smooth when the content exceeded 7 wt %. That is, the percolation threshold of the composite was about 7 wt %. In most cases, when the content of the conductive filler was near the percolation value, the composite showed the best gas-sensing properties. Therefore, the MWCNT content of the composites used for the gas-sensing performance test was controlled at 7 wt % in this study.

Figure 5 shows the sensitivity and reusability of the MWCNTs/HPMC/cellulose composite films to the saturated organic vapors at 30°C. Because of the absorption and desorption of the organic vapors, the resistance of the film changed rapidly in vapors and air. The cellulose matrix of the composite could not be dissolved or swollen when the cellulose/MWCNTs/HPMC composite film was placed into saturated polar organic vapors; however, the vapors may have destroyed the hydrogen bonds between the cellulose fibers and MWCNTs. This caused the aggregation of the MWCNTs. Therefore, the resistance of the composite film decreased sharply in some polar organic vapors, such as methanol and ethanol. This phenomenon was similar to the negative vapor coefficient effect. When the composite film was transferred from the organic vapors into the air, its resistance could quickly return to the initial value. This was probably because the hydrogen bonds between the cellulose fibers and MWCNTs were formed again after the desorption of the organic vapors from the composite; this impeded the MWCNTs from forming a conductive channel. Clearly, the sensitivity and reusability of the MWCNTs/HPMC/cellulose composite films to methanol vapor were the best because they had the strongest polarity in the four vapors.

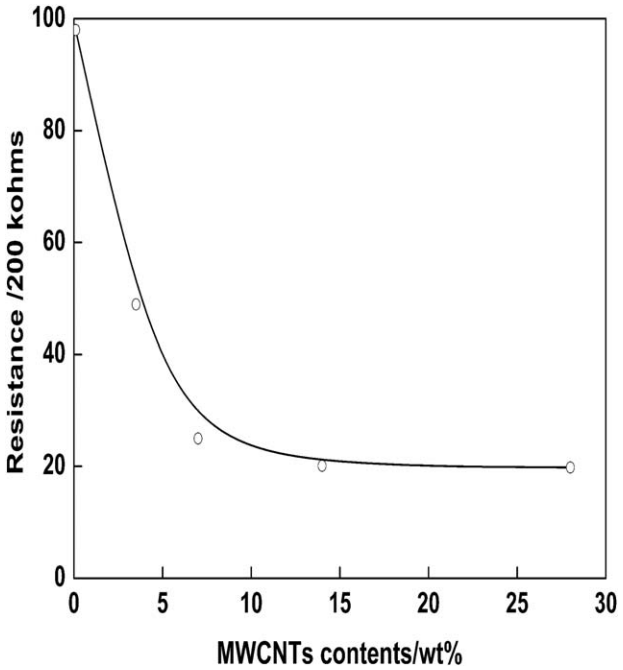

Figure 4. Resistance of the cellulose/MWCNT/HPMC composite films as a function of the MWCNT content.

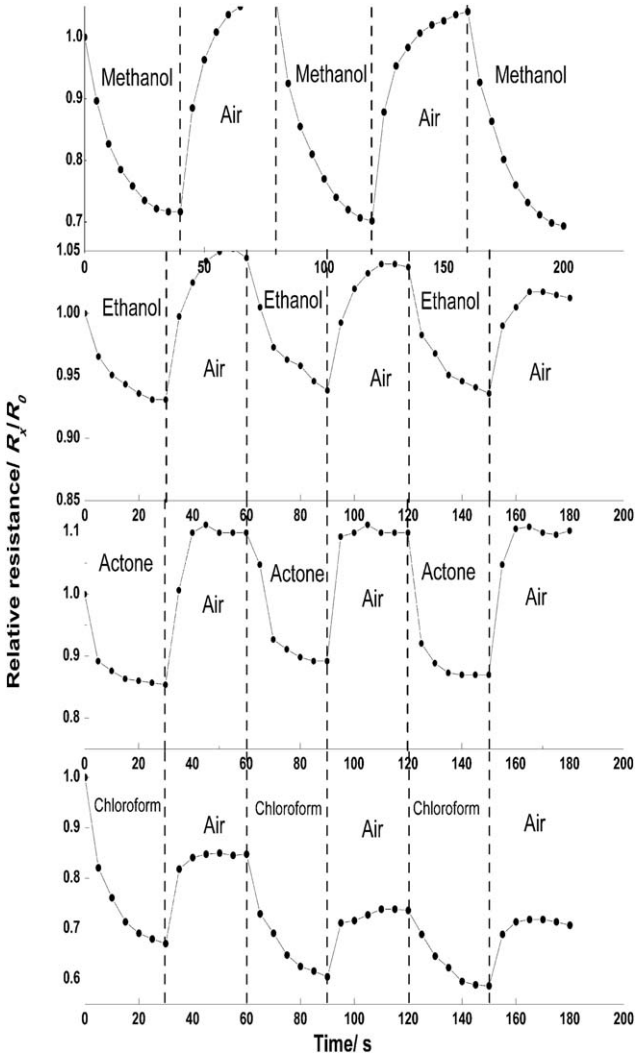

Figure 5. Sensitivity and reusability of the MWCNT/HPMC/cellulose composite films to saturated organic vapors at 30°C. R_0 = initial resistance; R_x = instant resistance.

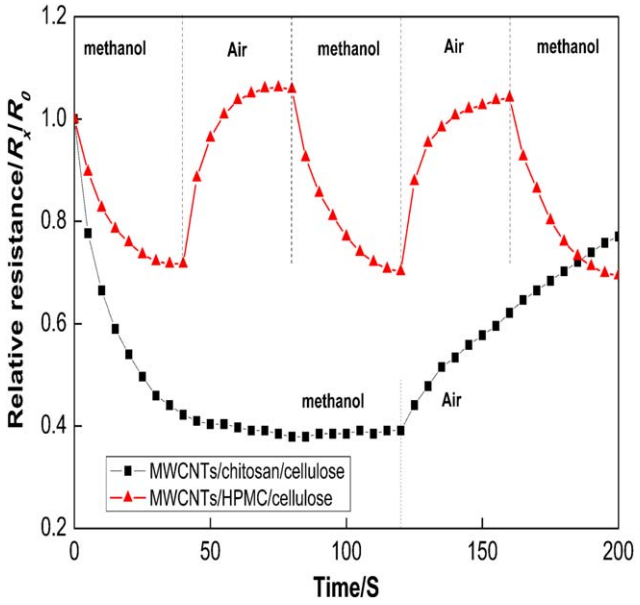

Figure 6. Sensitivity of two kinds of composite films to methanol vapor at 30°C. R_0 = initial resistance; R_x = instant resistance. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 shows the different response behaviors of the MWCNTs/HPMC/cellulose and MWCNTs/chitosan/cellulose composite films to methanol at 30°C. Although the composite film added chitosan showed better sensitivity to methanol vapor, the composite film with added HPMC exhibited more excellent reusability.

Because the temperature was a key factor in the sensitivity of gas-sensing materials, the sensitivities of the composite films

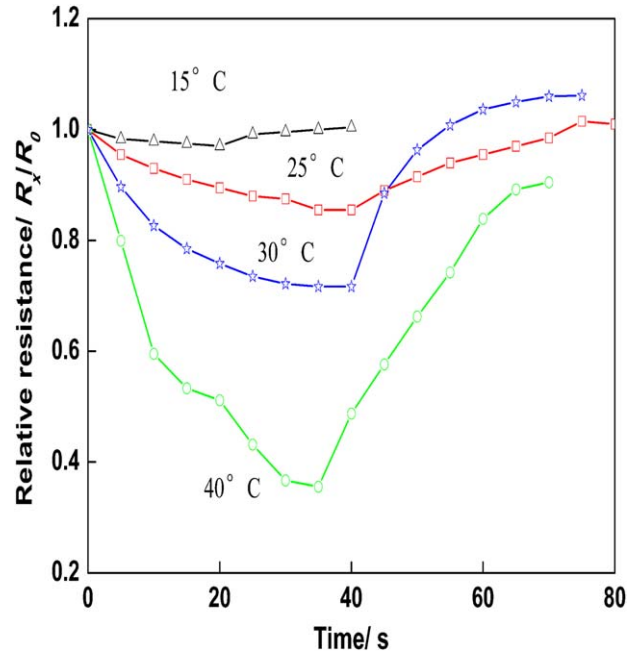

Figure 7. Effects of the temperature on the sensitivity of the MWCNT/HPMC/cellulose composite films to methanol. R_0 = initial resistance; R_x = instant resistance. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

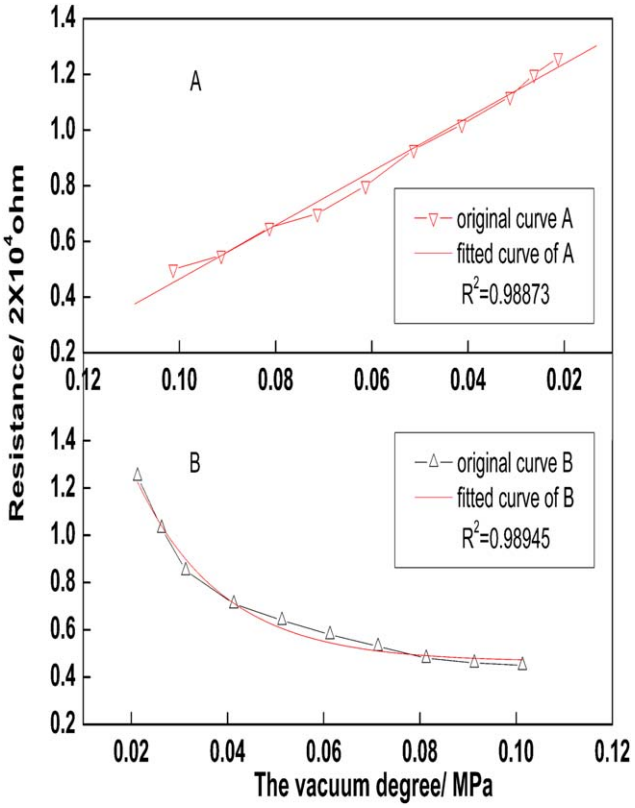

Figure 8. Resistance changes of the MWCNT/HPMC/cellulose composite films with a vacuum: (A) vacuum down and (B) vacuum up. R^2 = fit error. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were tested at 15, 25, 30, and 40°C, respectively. Figure 7 shows the temperature dependence of the sensitivity of the MWCNTs/HPMC/cellulose composite films on methanol. The composite film hardly exhibited any response to methanol at 15°C, whereas the sensitivity of the film increased gradually when the temperature was increased from 25 to 40°C. These phenomena not only indicated that the vapor pressure had an important influence on the response behavior of the film, but it also demonstrated that the vapor sensitivity was a function of the absorption thermodynamics of both the MWCNTs fillers and the cellulose matrix.[6]

In this study, we also found a very interesting phenomenon, namely, that when the MWCNTs/HPMC/cellulose films were placed in a closed container, their resistance increased almost linearly with decreasing vacuum degree in the container, just as shown in Figure 8. Furthermore, the changes in the resistance with the vacuum indicated a very good repeatability (as shown in Figure 9). When the vacuum was back to the normal, the resistance was restored to the initial value quickly. This phenomenon maybe valuable in some fields, and it has not been reported in the literature. We are doing further study to reveal the nature of the results.

The most possible explanations of this phenomenon are as follows. When the vacuum was reduced, the water molecules in the air rapidly decreased, so the water molecules contained in

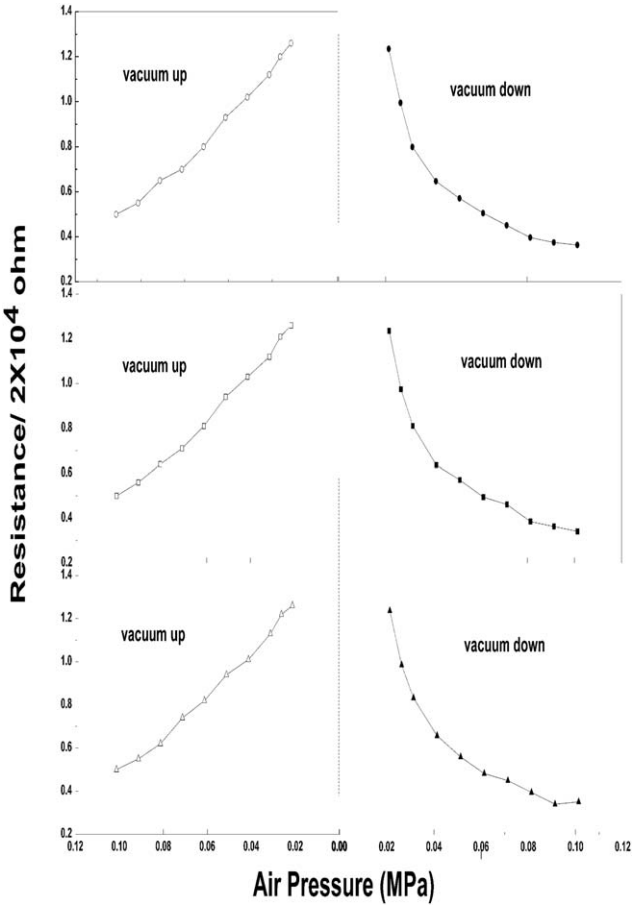

Figure 9. Repeatability of the resistance–vacuum dependence.

the composite film were gradually discharged, and the material resistance increased subsequently because of the damage to the hydrogen bonds between the cellulose fibers. This resulted in a re-aggregation of the MWCNTs. When the vacuum was gradually restored, the water molecules in the air around the film gradually increased. The cellulose film absorbed the water again, and so the resistance returned to its initial state because of the re-formation of hydrogen bonds between the cellulose fibers. This blocked the channels of the conductive MWCNTs. The differences in the two processes may have been caused by the different desorptions and adsorption rates of the water molecules in the cellulose composite films.

CONCLUSIONS

MWCNTs/HPMC/cellulose conducting films for chemical vapor-sensing were fabricated successfully in [BMIm]Cl system. The films showed reversible and response to some polarity vapors, such as methanol, ethanol, acetone and etc. Comparing to the chitosan, the HPMC could improve the mechanical properties and enhance the repeatability. Sensitivity of the composite film on the steam has strong temperature dependence. Furthermore, the resistance of composite film increased almost linearly with when he vacuum decreased, and it was restored to its initial value quickly in the form of exponential mode when the vacuum was back to normal. The responsive behavior to the changes in the vacuum exhibited good repeatability.

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