JOURNAL OF Applied Polymer SCIENCE

Humidity Switching Properties of Sensors Based on Multiwalled Carbon Nanotubes/Polyvinyl Alcohol Composite Films

Teng Fei, Kai Jiang, Fan Jiang, Ren Mu, Tong Zhang
State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, People's Republic of China
Correspondence to: T. Zhang (E-mail: zhangtong@jlu.edu.cn)

ABSTRACT: Multiwalled carbon nanotubes (CNTs) were used as the conductive filler of composites for switching type humidity sensor. The CNTs were oxidized by mixed acids ($H_2SO_4 : HNO_3$) at a mild temperature to modify carboxylic acid (COOH) groups on the surface of the nanotubes. The dispersibility of acid treated CNTs (CNTs-COOH) in water is much improved, which is beneficial for dispersing CNTs in the polyvinyl alcohol (PVA) matrix without external additives. The obtained CNTs-COOH/PVA sensors show nonlinear response to relative humidity (RH), that is, switching properties. The resistances of the sensors remain constant before 80% relative humidity (RH) and then increase sharply with RH, indicating excellent switching characteristic of the sensors. The 10 wt % CNTs-COOH/PVA sensor shows a sensitivity ($\Delta R/Ro$) of 32.3 at 100% RH. The humidity switching properties of CNTs-COOH/PVA are much better than that of pristine CNTs/PVA. The improvements are attributed to the improved balance between the dispersibility of CNTs-COOH and electrical conductivity of the composite films. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39726.

KEYWORDS: swelling; nanotubes; graphene and fullerenes; sensors and actuators

Received 7 May 2013; accepted 2 July 2013
DOI: 10.1002/app.39726

INTRODUCTION

Humidity measurement is essential in many applications, such as environmental monitoring, electrical devices and wireless sensor networks, and humidity sensors have attracted the attention of many groups.[1,2] The polymeric humidity sensors can be normally classified as resistive-type and capacitive-type. The capacitive-type humidity sensors need less power and have much better linearity. However, resistive measurements are much simpler and more straightforward than capacitive measurements.[3] Different kinds of materials have been used as humidity sensing materials, such as organic polymers,[1,2] ceramics,[4,5] and composite materials.[6–9]

Most of above works focused on humidity sensitive materials with a wide sensing range, usually showed linear working curves from low to high RH. However, few researches on the switch-type humidity sensors, for which there is almost no response before certain humidity and the sensitivity increases sharply above the humidity point. The switch-type humidity sensors could be used to monitor and control different humid atmospheres in many fields, such as storage, plant growing, and electronic product manufacturing, etc. The core of a switch-type sensor is sensitive composite film composed of the conductive filler and a polymer matrix with swelling-shrinkage properties. Most of previous works on switch-type sensors utilized carbon black (CB) particles as the conductive filler.[10–12] For example, Chen et al. researched the humidity sensor formed of CB/hydroxyethyl cellulose (HEC) film with nonlinear humidity characteristic.[10] Barkauskas et al. researched the interaction between polyvinyl alcohol (PVA) and CB surface and determined the size of clusters formed in the PVA matrix.[13] The humidity switching characteristic and stability of switch-type sensors under high humidity are not ideal and require further research to improve the sensing performance.

The carbon nanotubes (CNTs) are attractive in chemical sensors because their electrical properties are extremely sensitive to charge transfer and chemical doping effects by various molecules.[14] CNTs were first found to be sensitive to NH_3 and NO_2 at room temperature by Kong et al.,[15] and applications for organic vapors sensing have also been reported.[16] Then the application of CNTs in humidity sensors was developed.[17–21] Both pure CNTs and CNTs-based composites have been used for humidity sensing. Bradley et al. developed CNTs based field-effect transistors for humidity sensing.[22] Jiang et al. researched the humidity sensitivity of arrayed multiwalled carbon nanotubes (MWCNTs) grown on arrayed nanoporous silicon pillars.[23] Su et al. fabricated a low humidity sensor based on a quartz crystal microbalance coated with MWCNTs/Nafion composites.[24] Zhang et al. researched the humidity sensitive properties of poly(*m*-aminobenzene sulfonic acid) functionalized

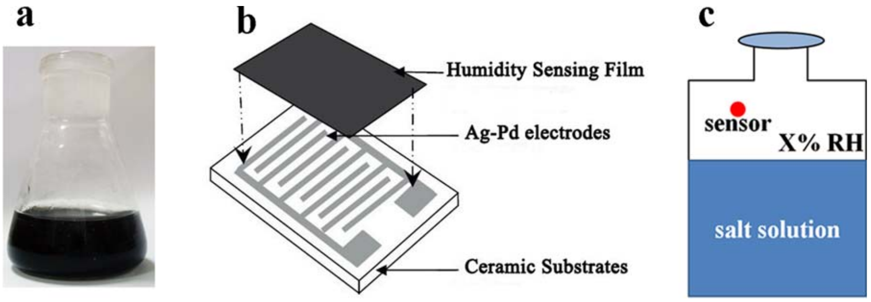

Figure 1. (a) The photograph of 10 wt % CNTs/PVA composite suspension. (b) A schematic diagram of the humidity sensor and (c) the schematic image of the equipment for measurement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

single-walled carbon nanotubes (SWCNTs).[25] Yoo et al. reported a resistive-type humidity sensor based on plasma-treated MWCNTs/polyimide composite films.[26] In general, the CNTs based composites are more sensitive for humidity sensing compared with pure CNTs. However, the application of CNTs-based composites in switch-type humidity sensor has not been reported so far.

As a special nanomaterial, CNTs may be the ideal candidate for conductive of switch-type sensor by enhancing the mechanical properties and conductivity of CNT/polymer composites.[27,28] To employ CNTs as reinforcements, physical and chemical methods have been developed to disperse CNTs in matrices.[29–31] The surface functionalizations of CNTs are effective, and the most facile method is oxidation with the acid.[32] The acid treatment could improve the stability of CNTs in polar solvents and the interfacial bonding properties between CNTs and the polymer matrices.

In this work, MWCNTs are used as conductive filler after treating with mixed acids ($H_2SO_4 : HNO_3$) at a mild temperature to balance the dispersibility and conductive ability of CNTs. MWCNTs rather than SWCNTs were chosen as the conductive filler because MWCNTs are easier to be dispersed in polymer matrices compared with SWCNTs, which is very important for switching type humidity sensor, and MWCNTs are much cheaper than SWCNTs.[33] The humidity switching properties of acid treated CNTs (CNTs-COOH)/PVA composites were researched, which are much better than that of pristine CNTs/PVA.

MATERIAL AND METHODS

Preparation and Characterization of Sensing Materials

MWCNTs produced by chemical vapor deposition (CVD) from Nanjing XFNANO Materials Tech were used in our experiments. The CNTs were 10–20 nm in diameter and 10–30 μm in length with a purity of 95%. To functionalize the CNTs and remove residual catalysts and amorphous carbon particles in the meantime, the raw CNTs were undergone an oxidation treatment in a mixture of 95% sulfuric acid and 65% nitric acid with a ratio of 3 : 1 at 70°C for 1 h. The acid treatment can greatly enhance the dispersibility of CNTs in water by introducing hydrophilic carboxylic functional groups to the sidewalls and ends of CNTs. PVA with a degree of polymerization of 1750 and an alcoholysis degree higher than 98% was from Sinopharm chemical reagent limited corporation. It is not soluble in water at room temperature, which is beneficial for the stability of the sensor at high RH. And it could dissolve well in hot water, which is favorable for the preparation of composite films by a solution process.

Sensor Preparation

The sensitive films were prepared by a simple solution process. In a typical procedure, PVA and CNTs (10 wt %) were added into the conical flasks, and then distilled water was added. The mixtures were heated to 75°C to reduce the time required to fully dissolve the polymer (PVA concentration 100 mg mL^{-1}) and stayed for 2 h with stirring to form a stable composite suspension, as shown in Figure 1(a). After cooling to room temperature, the suspension was casted onto clean ceramic substrates (10 mm × 8 mm × 0.8 mm) with a thickness of about 30 μm, where an interdigitated array of Ag-Pd electrodes had been previously screen-printed, as shown in Figure 1(b). The sensing film thickness is an important parameter for the development of sensors. The thickness was controlled by fixing the suspension capacity with 0.1 mL for every device. The ceramic substrate was then heated at 100°C for 2 h to obtain the humidity sensor. The thermal treatment is beneficial for stabilizing the sensitive film.

Measurements

The UV–visible absorption spectra were recorded on a UV-3100 spectrophotometer. Transmission electron microscopy (TEM) images were recorded on a Hitachi H-800 electron microscope with an accelerating voltage of 200 kV at the relative humidity (RH) of about 30%. Thermal gravimetric analysis (TGA) was undertaken on a Perkin–Elmer thermal analysis system at a heating rate of 10°C min^{-1} and a nitrogen flow rate of 80 mL min^{-1}. The humidity switching properties of the sensors were investigated by recording the electrical response of the sensors at 1 V DC under different humidities at room temperature. The atmosphere of humidities are produced by different saturated salt solutions in their equilibrium states including LiCl for 11% RH, $MgCl_2$ for 33% RH, $Mg(NO_3)_2$ for 54% RH, NaCl for 75% RH, KCl for 85% RH, KNO_3 for 95% RH, and H_2O for 100% RH. The uncertainty of the RH values is about ±1%. Every sensor was exposed to all the saturated salt solution-air atmospheres sequentially for resistance measurement in different humid atmospheres, which is in a closed system as shown in Figure 1(c).

RESULTS AND DISCUSSIONS

Characterization

To produce a well-dispersed CNTs suspension, surface chemical treatment of CNTs is necessary. By oxidation with H_2SO_4-HNO_3

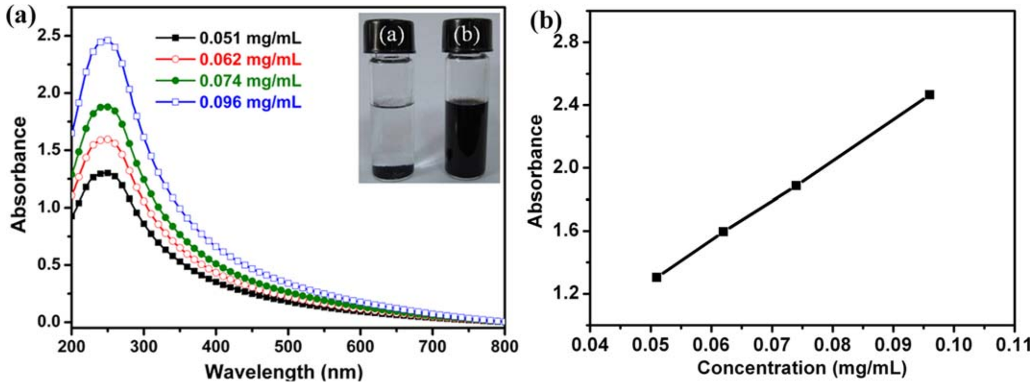

Figure 2. (a) UV–visible absorption spectra of CNTs-COOH in aqueous solutions with different concentrations and (b) the absorbance intensity at 246 nm to the CNTs-COOH concentration. Inset of (a) shows the photographs of solutions of (a) pristine and (b) acid treated CNTs with a concentration of ~1 mg mL^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixture, the CNTs surface was functionalized with a certain amount of COOH groups. The hydrophilic COOH groups render the CNTs disperse well in water to form a suspension. The absorption spectroscopy was used to evaluate the dispersion efficiency of CNTs-COOH in the suspension. The suspension was diluted before measurement, and the absorption spectra of CNTs-COOH in aqueous solutions with different concentrations are shown in Figure 2. The absorption peaks at 246 nm [Figure 2(a)] and the absorbance enhances with the content of soluble CNTs-COOH.[34] It is worthy to note that the absorption intensity is proportional to the CNTs-COOH concentration [Figure 2(b)], indicating pretty good dispersibility of CNTs-COOH in water. As shown in inset of Figure 2(a), the additive-free CNTs could be dispersed uniformly in deionized water with a concentration of ~1 mg mL^{-1}, while the pristine CNTs could not disperse in water at all. It is observed that the CNTs-COOH aqueous solution is stable at room temperature for more than 180 days. So CNTs-COOH could be dispersed in the matrix by a solution process, which is much easier than mechanical dispersion[31] or melt mixing.[35]

The content of COOH groups in the oxidized CNTs was investigated using TGA. As shown in Figure 3, the thermal degradation of CNTs-COOH is a multistage process. The weight loss below 150°C is attributed to the weight loss of the adsorbed water. The decomposition stage in the range of 150–350°C is attributed to the decarboxylation of the COOH groups present on the CNTs walls.[36,37] A weight loss of ~5.7% was detected for the acid-treated CNTs. Then there is a rapid weight loss of 13% in the range of 350–600°C, and at the end point the amount of the CNTs residue is about 76 wt %. Except the introduction of COOH groups, the oxidative treatment also removed amorphous carbon and metal oxide impurities in the pristine CNTs and made the CNTs shorten and own more ends open.[38] The open ends and polar groups on the surface could enhance the water molecules adsorption ability of CNTs, which is beneficial for humidity sensing.

Humidity Switching Properties

For the matrix PVA dissolve well in hot water and CNTs-COOH could disperse well in water, CNTs-COOH/PVA composite films were prepared by an easy solution process with water as the solvent. Sensors based on composites formed of different contents of CNTs-COOH and PVA were fabricated and their humidity switching properties were researched. The resistances of the sensors to RH are shown in Figure 4. It is obvious that the resistances of sensors change little before 80% RH, while there is a sharp resistance increase at about 80% RH when the films swell abruptly. And it is worthy to note that the shape of the sorption isotherm of the water-PVA system shows the same abrupt change at high humidities.[39] Resistances of the sensors with more than 8 wt % content of CNTs-COOH are about 6 kΩ at 11% RH, and decrease with the increase of CNTs-COOH content. The resistance increases to about 60 kΩ for 5 wt % CNTs-COOH/PVA, indicating the percolation threshold of the CNTs-COOH/PVA composite films is between 5 and 8 wt %. The value of percolation threshold is bigger than previous reports on MWCNTs (about 1–3 wt %),[40] which is attributed to the different types of the used CNTs and the structural damage of CNTs-COOH in the oxidation process.

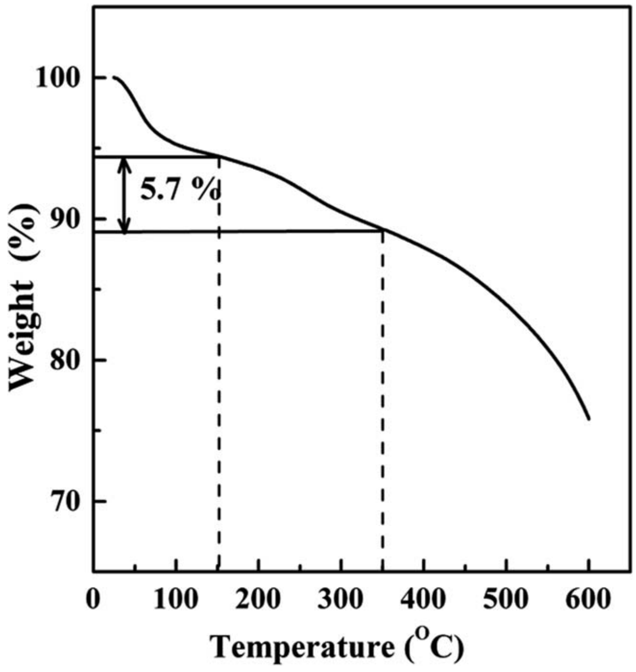

Figure 3. TGA curve of the resultant CNTs-COOH.

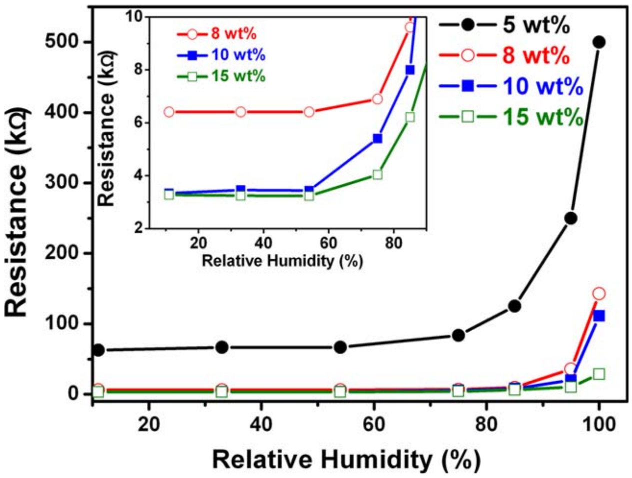

Figure 4. The resistances of CNTs-COOH/PVA films with different CNTs-COOH contents to RH. Inset shows the amplified curves of sensors with 8, 10, and 15 wt % CNTs-COOH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

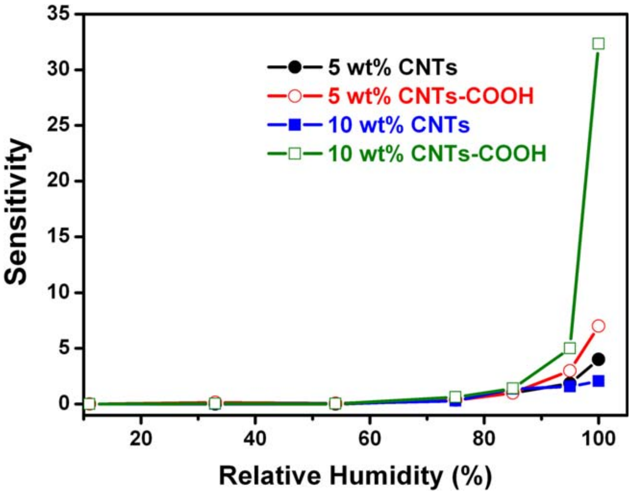

Figure 6. The sensitivities of 5 wt %, 10 wt % pristine CNTs/PVA and 5 wt %, 10 wt % CNTs-COOH/PVA sensors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The sensitivities (S) of the composite films to RH can be determined from the equation

$$S=(R_{\mathrm{RH}}-R_0)/R_0 \tag{1}$$

where R_0 is the initial resistance at 11% RH, and R_{RH} is the steady state resistance under certain humidity. According to the equation (1), the sensitivities of the sensors based on different CNTs-COOH contents in PVA are calculated and shown in Figure 5. As can be seen, the sensors show obvious switching characteristic, which is very beneficial for use in on-off switching system. The sensitivity is 7.0, 21.3, 32.3, and 7.7 at 100% RH for 5, 8, 10, and 15 wt % CNTs-COOH/PVA sensors, respectively. The 10 wt % CNTs-COOH/PVA sensor shows the highest sensitivity, demonstrating the conductive networks of CNTs-COOH have the greatest change when the film swells. The switching characteristic and sensitivities at high RH of the obtained sensors are much improved compared with the reported switch-type sensors with CB as the conductive filler,[10,12] while the preparation process of sensing film was much simplified. It is necessary to note that the 10 wt % CNT-COOH/PVA sensor exhibits the highest response, for which the filler loading is a little higher than the percolation threshold. As can be seen in Figure 4, the resistance of 8 wt % CNT-COOH/PVA and 10 wt % CNT-COOH/PVA sensors at 11% RH is 6.4 and 3.3 kΩ, respectively. The resistance increases greatly after the swelling of the matrix, and although the value of resistance change from 11% RH to high RH of 10 wt % CNT-COOH/PVA sensor is much lower than that of 8 wt % CNT-COOH/PVA sensor, the sensitivity of 10 wt % CNT-COOH/PVA sensor is higher because the calculation method is based on the ratio of resistances at high RH to that of 11% RH.

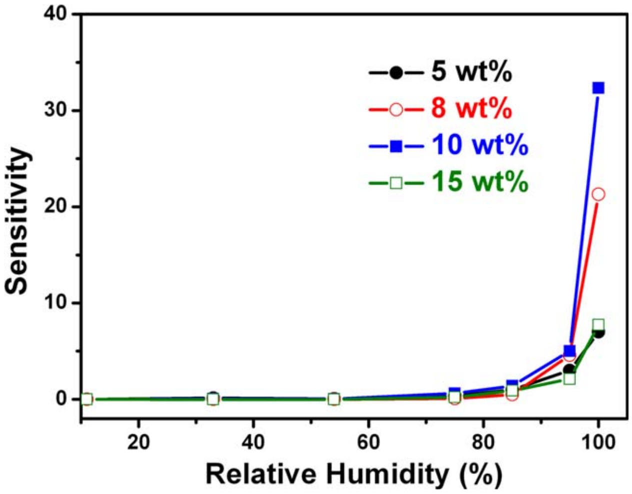

Figure 5. The sensitivities of CNTs-COOH/PVA sensors with different CNTs-COOH contents to RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sensors based on pristine CNTs were also fabricated by the same process with that of CNTs-COOH and their humidity sensing properties were researched. Figure 6 shows the sensitivities of 5 wt %, 10 wt % CNTs/PVA, and 5 wt %, 10 wt % CNTs-COOH/PVA sensors. It could be seen that with the same content of conducting filler, the two sensors show much different sensing performances. The sensitivity is only 4.0 and 2.1 at 100% RH for 5 wt % and 10 wt % CNTs/PVA sensors, respectively, which are much lower than CNTs-COOH/PVA sensors, although 5 or 10 wt % may not be the optimum content for CNTs/PVA film. It is also worthy to note that the sensitivity of 10 wt % CNTs-COOH/PVA sensor is much higher than 5 wt % CNTs-COOH/PVA sensor, while the character is opposite for CNTs-based sensors. The higher optimum content of CNTs-COOH is attributed to its better dispersibility and lower conductivity than pristine CNTs.

The dispersion state of conducting filler in the matrix is key for the enhancement of the composite film, especially for the system with switching characteristic. The TEM micrographs of 1 wt % CNTs/PVA and 1 wt % CNTs-COOH/PVA films are shown in Figure 7. It is observed that CNTs are dispersed into PVA and

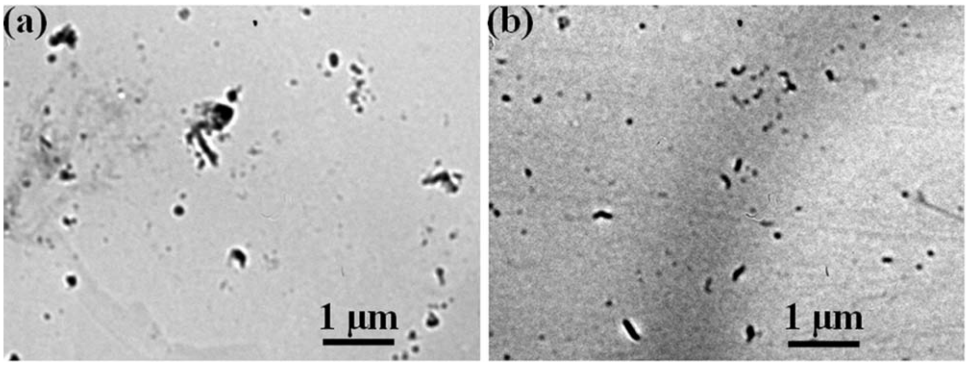

Figure 7. TEM micrographs of (a) 1 wt % pristine CNTs/PVA and (b) 1 wt % CNTs-COOH/PVA films.

form conductive networks in the composite films. There is obvious aggregation of CNTs in PVA as shown in Figure 7(a), while the dispersion of CNTs-COOH in PVA is more uniform as shown in Figure 7(b). It is necessary to note that the weight percent of CNTs in the composite films for TEM was much smaller than the practical sensing films to obtain clearer TEM characterization. For practical sensors with higher CNTs contents in the films, the difference between the dispersion states of the films would be much greater. The improved dispersion of CNTs-COOH is attributed to their enhanced dispersibility and interfacial bonding with PVA matrix. The homogeneous dispersion of CNTs-COOH in PVA is beneficial for high sensitivity and good switching characteristic at high humidities.

The DC current–voltage (I–V) curves of 10 wt % CNTs/PVA and 10 wt % CNTs-COOH/PVA films were measured to compare the electrical conductivity of CNTs and CNTs-COOH. The films were tested at room temperature with a humidity of about 30% RH. Although this is not a direct comparison between single CNTs and CNTs-COOH, the electrical conductivity of CNTs or CNTs-COOH in matrices is directly related to sensing properties of the films. As shown in Figure 8, I–V curves of the two films exhibit a very good linearity between 0 and 1.1 V. The resistance of 10 wt % CNTs-COOH/PVA film is about twice of 10 wt % CNTs/PVA, mainly attributed to the structural damage of the CNTs surface in the oxidation process, although the dispersion of CNTs-COOH in the matrix is more uniform than that of CNTs. The results demonstrate the electrical conductivity of 10 wt % CNTs-COOH/PVA has not changed much by treating CNTs with the mixed acids at a mild temperature. Meanwhile, the treated CNTs could disperse stably in water, which is beneficial for using as the filler of conductive composites and other applications. The improved balance between the dispersibility of CNTs-COOH and electrical conductivity of the composite films contributes to the much better humidity switching properties than the sensors based on pristine CNTs/PVA.

Long-term stability is very important for the practical value of a sensor. Stability of the 10 wt % CNTs-COOH/PVA sensor was tested by measuring the resistance at 85% RH for 7 days continuously. The humidity of 85% RH is a representative point, which could represent the swelling state of the composite film. As shown in Figure 9, there is an acceptable change in the resistances measured at different times, proving the good stability of the obtained sensor. We recorded the data at a same time after the sensor was put into the atmosphere of 85% RH, and the

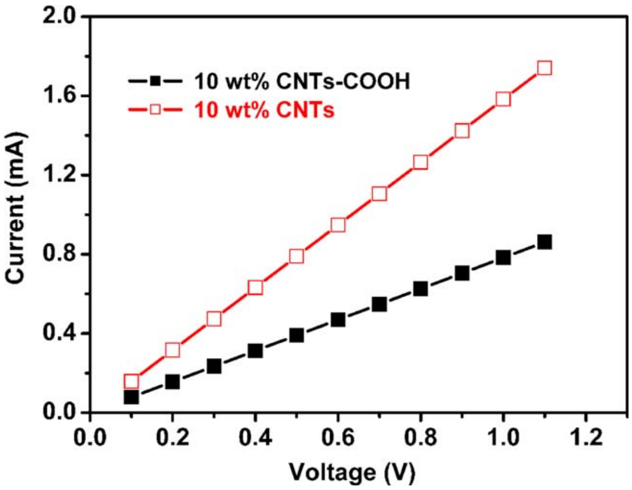

Figure 8. I–V curves of 10 wt % CNTs/PVA and 10 wt % CNTs-COOH/PVA sensors at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

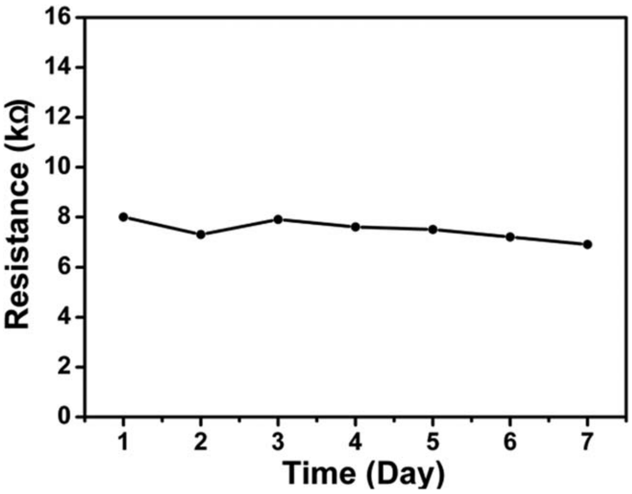

Figure 9. The resistances of the 10 wt % CNTs-COOH/PVA sensor measured at 85% RH for 7 days continuously.

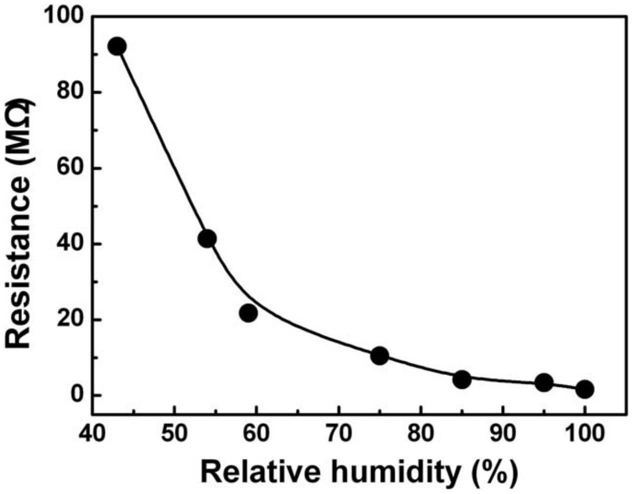

Figure 10. The resistances of PVA sensor at different RH.

fluctuation of resistance may originate from the change of sensitive film during the swelling and shrinkage processes. The switching characteristic of the sensor is still good with the little change, so such an extent of variation has little influence on the switching type sensor. These results demonstrate the obtained sensor is quite promising used in practical applications for long term monitoring of high humidities. The stability of the sensor is attributed to the strong interface interaction between CNTs-COOH and the matrix, and the fact that the PVA is very difficult to dissolve at room temperature. This may make the resulting sensor promising for practical applications such as long-term monitoring of high humidity levels.

Humidity Sensing Mechanism

The resistance change of composite films to RH is mainly attributed to two factors. First, the swelling of the matrix with increasing humidity increases the space between CNTs, which would decrease the conductivity of composite films. This is the main reason for the switching property at dew point, when the swelling of the composite films leads to sharp decrease of CNTs concentration. Second, as the physical absorption of H_2O molecules on the CNTs surface, the electronic donation into the CNTs compensates hole carriers of the p-type CNTs and results in the increase of resistance.[41,42] For CNTs-COOH, the charge transfer may result in a doubling of resistance from 11% to 95% RH, relating to the surface structure of CNTs, while the effect of pristine CNTs is much smaller.[37] In our systems, since the CNTs are dispersed in the PVA matrix, the charge transfer effect of CNTs is relatively less compared with the swelling of the composite films. In addition, the sensor based on pure PVA was also fabricated and the resistances at different humidities are shown in Figure 10. As can be seen, the resistance decreases with the increasing RH, and the resistance values are relatively high. The resistance is still as high as 3.4 MΩ at 95% RH, which is much larger than that of the composites, demonstrating the polymer matrix contributes little to the conductivity of the composite films.

CONCLUSIONS

The water-stable CNTs-COOH with no external additives were obtained by a simple oxidation process at a mild temperature. The humidity switching properties of CNTs-COOH/PVA were investigated with the composite films fabricated by a simple and efficient solution process. The CNTs-COOH/PVA sensor shows nonlinear response to RH, with good switching characteristic and high sensitivity, which are much better compared with pristine CNTs/PVA sensor. The improved properties are attributed to the uniform dispersion of CNTs-COOH in the composite films. More improvements may be realized by further balance between the dispersibility and the electrical conductivity of CNTs in different matrices. The good humidity switching properties demonstrate CNTs-based sensor a candidate for practical applications. These sensors are more beneficial to monitor and control certain range of humid atmospheres than common humidity sensors.

ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation Committee (NSFC, No. 51103053), Postdoctoral Science Foundation of China (PSFC, No. 2011M500608), Doctoral Fund of Ministry of Education of China (NO. 20110061120053) and Program from Changjiang Scholars and Innovativation Research Team in University (NO. IRT1017). The contribution of every listed author: Teng Fei: Analysis of data and drafting the paper. Kai Jiang: Fabrication and test of the sensors. Fan Jiang: The oxidation treatment and characterizations of CNTs. Ren Mu: The long-term stability measurement of the sensor. Tong Zhang: Designing research idea and revising the paper.

REFERENCES

1. Sakai, Y.; Sadaoka, Y.; Matsuguchi, M.; Kanakura, Y.; Tamura, M. *J. Electrochem. Soc.* **1991**, *138*, 2474.
2. Sakai, Y.; Sadaoka, Y.; Matsuguchi, M. *Sens. Actuators B* **1996**, *35*, 85.
3. Packirisamy, M.; Stiharu, I.; Li, X.; Rinaldi G. *Sens. Rev.* **2005**, *25*, 271.
4. Wang, J.; Xu, B. K.; Liu, G. F.; Zhang, J. C.; Zhang, T. *Sens. Actuators B* **2000**, *66*, 159.
5. Qi, Q.; Zhang, T.; Yu, Q. J.; Wang, R.; Zeng, Y.; Liu, L.; Yang, H. B. *Sens. Actuators B* **2008**, *133*, 638.
6. Qi, Q.; Zhang, T.; Wang, L. J. *Appl. Phys. Lett.* **2008**, *93*, 023105.
7. Su, P. G.; Sun, Y. L.; Lin, C. C. *Sens. Actuators B* **2006**, *113*, 883.
8. Wang, J.; Wu, F.-Q.; Shi, K.-H.; Wang, X.-H.; Sun, P.-P. *Sens. Actuators B* **2004**, *99*, 586.
9. Li, Y.; Hong, L. J.; Chen, Y. S.; Wang, H. C.; Lu, X.; Yang, M. J. *Sens. Actuators B* **2007**, *123*, 554.
10. Chen, H.; Peng, Z. K.; Fu, G. *Acta Phys. Sin.* **2009**, *58*, 7904.
11. Kim, D.-U.; Shim, J.-J.; Lee, C.-W.; Gong, M.-S. *Polymer (Korea)* **1999**, *24*, 617.
12. Sun, L. Y.; Qiu, F. B. *J. Transducer Tech.* **1995**, *5*, 22.
13. Barkauskas, J.; Vinslovaitė, A. *Mater. Res. Bull.* **2003**, *38*, 1437.
14. Dai, H. *Acc. Chem. Res.* **2002**, *35*, 1035.

15. Kong, J.; Franklin, N. R.; Zhou, C. W.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.
16. Li, J.; Lu, Y.; Ye, Q.; Cinke, M.; Han, J. *Nano Lett.* **2003**, *3*, 929.
17. Varghese, O. K.; Kichambre, P. D.; Gong, D.; Ong, K. G.; Dickey, E. C.; Grimes, C. A. *Sens. Actuators B* **2001**, *81*, 32.
18. Huang, X. J.; Sun, Y. F.; Wang, L. C.; Meng, F. L.; Liu, J. H. *Nanotechnology* **2004**, *15*, 1284.
19. Star, A.; Han, T.-R.; Joshi, V.; Stetter, J. R. *Electroanalysis* **2004**, *16*, 108.
20. Liu, L. T.; Ye, X. Y.; Wu, K.; Han, R.; Zhou, Z. Y.; Cui, T. H. *Sensors* **2009**, *9*, 1714.
21. Zilberman, Y.; Ionescu, R.; Feng, X.; Müllen, K.; Haick, H. *Acs Nano* **2011**, *5*, 6743.
22. Bradley, K.; Cumings, J.; Star, A.; Gabriel, J.-C. P.; Grüner, G. *Nano Lett.* **2003**, *3*, 639.
23. Jiang, W. F.; Xiao, S. H.; Feng, C. Y.; Li, H. Y.; Li, X. *J. Sens. Actuators B* **2007**, *125*, 651.
24. Su, P.-G.; Sun, Y.-L.; Lin, C.-C. *Sens. Actuators B* **2006**, *115*, 338.
25. Zhang, T.; Mubeen, S.; Bekyarova, E.; Yoo, B. Y.; Haddon, R. C.; Myung, N. V.; Deshusses, M. A. *Nanotechnology* **2007**, *18*, 165504.
26. Yoo, K. P.; Lim, L. T.; Min, N. K.; Lee, M. J.; Lee, C. J.; Park, C. W. *Sens. Actuators B* **2010**, *145*, 120.
27. Peng, H.; Jain, M.; Peterson, D. E.; Zhu, Y.; Jia, Q. *Small* **2008**, *4*, 1964.
28. Coleman, J. N.; Khan, U.; Gunko, Y. K. *Adv. Mater.* **2006**, *18*, 689.
29. Gibson, R. F.; Ayorinde, E. O.; Wen, Y. F. *Compos. Sci. Technol.* **2007**, *67*, 1.
30. Moniruzzaman, M.; Winey, K. I. *Macromolecules* **2006**, *39*, 5194.
31. Ma, P.-C.; Siddiqui, N. A.; Marom, G.; Kim, J.-K. *Compos. A* **2010**, *41*, 1345.
32. Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.-S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.
33. Zhang, B.; Fu, R. W.; Zhang, M. Q.; Dong, X. M.; Lana, P. L.; Qiu, J. S. *Sens. Actuators B* **2005**, *109*, 323.
34. Liu, W.-B.; Pei, S.; Du, J.; Liu, B.; Gao, L.; Su, Y.; Liu, C.; Cheng, H.-M. *Adv. Funct. Mater.* **2011**, *21*, 2330.
35. Schlea, M. R.; Brown, T. R.; Bush, J. R.; Criss, J. M.; Mintz, E. A.; Shofner, M. L. *Compos. Sci. Technol.* **2010**, *70*, 822.
36. Datsyuk, V.; Kalyva, M.; Papagelis, K.; Parthenios, J.; Tasis, D.; Siokou, A.; Kallitsis, I.; Galiotis, C. *Carbon* **2008**, *46*, 833.
37. Tang, M.; Dou, H.; Sun, K. *Polymer* **2006**, *47*, 728.
38. Cao, C. L.; Hu, C. G.; Fang, L.; Wang, S. X.; Tian, Y. S.; Pan, C. Y. *J. Nanomater.* **2011**, Art. ID 707303 (5 pages).
39. Hasimi, A.; Stavropoulou, A.; Papadokostaki, K. G.; Sanopoulou, M. *Eur. Polym. J.* **2008**, *44*, 4098.
40. Byrne, M. T.; Gun'ko, Y. K. *Adv. Mater.* **2010**, *22*, 1672.
41. Zahab, A.; Spina, L.; Poncharal, P.; Marlière, C. *Phys. Rev. B* **2000**, *62*, 10000.
42. Pati, R.; Zhang, Y.; Nayak, S. K.; Ajayan, P. M. *Appl. Phys. Lett.* **2002**, *81*, 2638.