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Functionalized Multi-Wall Carbon Nanotubes/Silicone Rubber Composite as Capacitive Humidity Sensor

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ABSTRACT: Functionalized multi-wall carbon nanotubes (MWCNTs) treated by mixed acids have been used to develop a capacitive humidity sensor based on MWCNTs/silicone rubber (SR) composite film. The MWCNTs/SR composites were prepared through conventional solution processed method. The micrographs of MWCNTs/SR composites were observed by transmission electron microscopy (TEM) and scanning electron microscope. The FT-IR spectra demonstrated the successfully grafting of —OH groups on the treated MWCNTs. The sensing properties of the composite at different relative humidity (RH) and frequency were characterized and linear sensing responses of the MWCNTs/SR composites to RH were observed. The treated MWCNTs/SR composite film (Tr-film) had higher sensitivity than that of the untreated MWCNTs/SR composite film (Un-film). Experimental data indicate that the Tr-film exhibits an excellent long-term stability, small hysteresis, and fine reproducibility. The response and recovery time of the Tr-film were 30 and 27 s, respectively. Thereby, such Tr-film had potential applications as humidity sensors. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40342.

KEYWORDS: capacitive humidity sensor; multi-wall carbon nanotubes; functionalization; composites; frequency characteristic

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INTRODUCTION

With the development of era, the needs for humidity sensors increase in many aspects, such as air conditioning systems, food quality monitoring, and medical equipment. Up to now, humidity sensors are mostly based on metal oxides,[1–3] porous silicon,[4–6] polymers,[7–9] and polyelectrolytes.[10–12] However, those humidity sensors have the same disadvantages: low sensitivity, long response, and recovery time. The material MWCNTs, discovered by Iijima in 1991,[13] have attracted much attention for their potentials in the fields of novel sensors, hydrogen storage materials, field-effect transistors, and field emission displays owing to its good chemical stability, unique electrical property, and high surface area to volume ratio. MWCNTs have large specific surface areas and interfaces, which make it has a strong interaction with the surrounding medium. Owing to the high surface area to volume ratio, MWCNTs is well suited for physical adsorption or chemical interaction with targeted measurand. Therefore, it is sensitive to a variety of environmental elements such as temperature and humidity.[14,15] Furthermore, randomly aligned MWCNTs can naturally form networks of porous structures, so MWCNTs are excellent materials for humidity sensing. Owing to these pores, capillary condensation happens in the MWCNTs films, which can amplify the capacitance response due to the higher dielectric constant of water.[16]

The capacitive-type humidity sensors use low power and show good linearity and exhibit better stability at higher temperature and higher humidity as compared to resistive humidity sensors. In recent years, many researchers are gradually concentrating on MWCNTs humidity sensors. Su et al. studied a low humidity sensor based on a quartz crystal microbalance (QCM) coated with MWCNTs/Nafion composite film, it showed excellent sensitivity and short response time.[17] Liu et al. discussed a resistive humidity sensor based on carbon nanotube and PDDA composite films, the resistances of MWCNTs/PDDA composite films increase exponentially with an increase in humidity, indicating the sensitivity to RH.[18] Bruzziet et al. studied a capacitive-type device at room temperature in the RH range 10–70%, and the sensor showed a linear dependence of the capacitance on RH.[19] However, few works have been focused on the frequency characteristics of the capacitive MWCNTs-based humidity sensor thus far, despite its essential effect on the performance of the sensor. Test frequency is an important factor affecting the humidity performance of MWCNTs based capacitive sensor. The dependent characteristics of the capacitance on RH of MWCNTs/SR composite film are distinguishing at different frequencies and the humidity sensitivities are different accordingly. Since sensors often work at various frequencies, it is necessary to study the frequency characteristics of the MWCNTs/SR composite film.

Moreover, it is also helpful to understand the humidity properties of the MWCNTs/SR composite film comprehensively.

In this work, MWCNTs/SR composite films are used to implement humidity experiments. Fabrication of this kind humidity sensor is simple and low cost, and hence wide application of this MWCNTs/SR composite film based humidity sensor can be obtained for humidity detection in the future.

EXPERIMENTAL

Materials

MWCNTs were purchased from Chengdu Organic Chemicals, Chinese Academy of Sciences. Before use, MWCNTs were dried in vacuum at 60°C for 24 h. The specifications of the MWCNTs are (i) diameter range—20–30 nm; (ii) length distribution—10–20 μm; and (iii) purity—>95% MWCNTs. The GD401 RTV SR was purchased from Chemical Institute of Sichuan. Saturated salt solutions were chose to provide humidity environment, and the RH are 11, 23, 33, 43, 59, 75, 85, and 98% separately. The RH varied from 11 to 98%, which is the typical operating range for the MWCNTs-based humidity sensors widely used in many measurement and control applications. An LCR meter purchased from Taiwan was used to measure the capacitances of MWCNTs/SR composite films, as a function of RH levels in the saturated salt solutions.

Composite Manufacturing

MWCNTs were functionalized at first: MWCNTs were added to the mixed solutions (3 : 1 H_2SO_4 : HNO_3), and then refluxed in the thermostatic oil bath for 60 min at 140°C. The obtained treated MWCNTs were then dried in a drying oven at 50°C. The acids treatment could greatly enhance the hydrophilia of MWCNTs by introducing —OH functional groups to the sidewalls and ends of MWCNTs. MWCNTs/SR composite films were fabricated through solution blending: 0.075 g MWCNTs were added to 3 mL Zippo premium lighter fluid(used as dispersant), followed by ultrasonic dispersion for 15min to achieve a uniform dispersion. Then 0.5 g SR was added into the mixed solution and dispersed for 15 min to get homogeneous mixtures. The obtained mixed solution was then spin-coated on the interdigital electrodes and cured at room temperature. Hereto, the MWCNTs/SR composite film was successfully fabricated, and the weight content of MWCNTs in the composite was 15%. Figure 1 depicts the whole fabrication process of the MWCNTs/SR composite film, and the size of the humidity sensor fabricated is 0.5 cm (length) × 0.5 cm (width) × 10 μm (thickness).

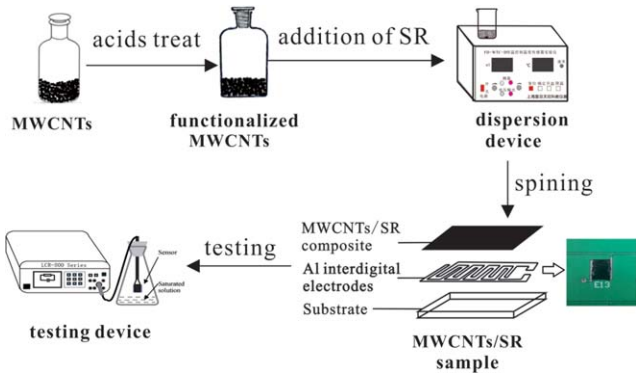

Figure 1. Fabrication process of the MWCNTs/SR composite film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The sensors were successively exposed to all the chambers with different RH levels. And the desiccation process of the sensor used to record hysteresis pattern was carried out simply: the sensor was moved from a high RH chamber to a low RH chamber, and the desiccation process depends on the natural desorption of the water molecules in MWCNTs. The uncertainty of the RH values is about ±1%. The samples were dried at 323 K for 30 min prior to electrical measurements.

RESULTS AND DISCUSSION

Characterization

Figure 2 is the SEM image of Un-film, and it shows that MWCNTs form networks of porous structures because of their random entanglement and alignment of nanotubes. It is observed that many small and irregular pores are created from MWCNTs. These networks of pores can be regarded as interconnected capillary voids that increase the exposed internal surface areas for the adsorption of water molecules. Due to the existence of these capillary pores, less vapor molecules from a lower RH level are required to saturate these pores and condense to liquid. Therefore, condensation can occur in these capillary pores earlier at a lower RH level rather than under the normal saturated vapor pressure at high RH.

The degree of dispersion and morphology of MWCNTs in the blend were studied by means of TEM. Figure 3 depicts the TEM micrograph of the Un-film and Tr-film. As can be seen from Figure 3(a), the untreated MWCNTs entangle with each other due to its special structure, which leads to the uneven dispersion in the SR matrix. Figure 3(b) shows that the treated MWCNTs become shorter and the degree of dispersion in the SR matrix gains great *improve*ment, as a result, the uniform dispersion in the SR matrix is obtained. The degree of functionalization of MWCNTs was discussed through Fourier transform infrared spectroscopy (FT-IR). Figure 4 shows the FT-IR spectra of the treated MWCNTs and untreated MWCNTs in the range

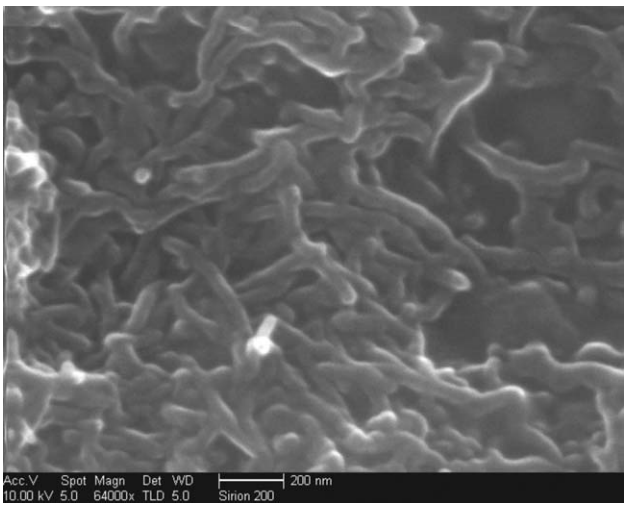

Figure 2. SEM image of the Un-film.

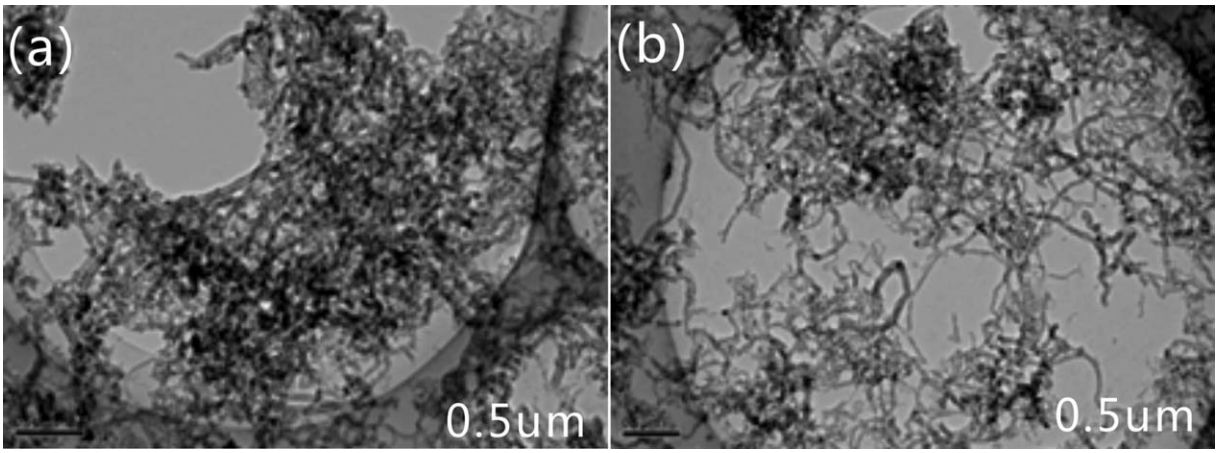

Figure 3. TEM images of the MWCNTs/SR composite films. (a) Un-film and (b) Tr-film.

of 4000 to 1000 cm^{-1}. The obvious peak at 3450 cm^{-1} in Figure 4(a) is due to the —OH functional groups. The acids treatment can greatly enhance the hydrophilicity of MWCNTs by introducing —OH functional groups to the sidewalls and ends of MWCNTs. Owing to the presence of these hydrophilic groups, more water molecules can be adsorbed in Tr-film compared with Un-film.

Humidity Properties and Analysis

The normalized capacitance changes versus different RH were monitored. In Figure 5, it shows the linear fit curves of the experiment data of the two composite films measured at room temperature. The round point section in Figure 5 is corresponding to the Un-film, while the quadrate point section indicates the capacitance changes of the Tr-film. The results show that the correlation coefficients (R) are 0.98628 (Un-film) and 0.98594 (Tr-film), respectively, indicating that the capacitances of both composite films increase almost linearly with RH. Furthermore, the linear fit equation of Un-film is $y = 0.00226x + 0.78788$, while the linear fit equation of Tr-film is $y = 0.00404x + 0.58741$. So it can be seen that both films are sensitive to RH, but the humidity sensing effect of Un-film is much weaker than that of Tr-film. The sensitivity of humidity sensor can be expressed as: Sensitivity $= \Delta C/C_0 \times 100\%$, where $\Delta C = C_{RH} - C_0$, C_0 refers to the capacitance when the RH is 11%, C_{RH} represents the capacitance at certain RH. Figure 6 demonstrates the relationship between sensitivity and RH. Obviously, the sensitivity of the Tr-film is twice as high as the Un-film at any RH level.

The humidity effect as shown in Figure 5 is due to the occurrence of capillary condensation effect in the MWCNTs. MWCNTs form porous structures in the films because of the random entanglement and alignment of the nanotubes, and many small and irregular pores are created from MWCNTs. Due to the existence of these pores, less vapor molecules from a lower RH level are required to saturate these pores and condense to liquid. Therefore, condensation can occur in these capillary pores earlier at a lower RH level rather than under the normal saturated vapor pressure at high RH. Because of the condensation of the water molecules, the dielectric constant of the sensor is changed, which leads to the different capacitance of the sensor.

The capillary condensation of vapors is the primary method of assessment of structural parameters of materials with pores in the range of 2–100nm.[20] Vapor condenses to water at a vapor pressure which is lower than the vapor pressure of saturation at a given temperature. Because of the porous structure of

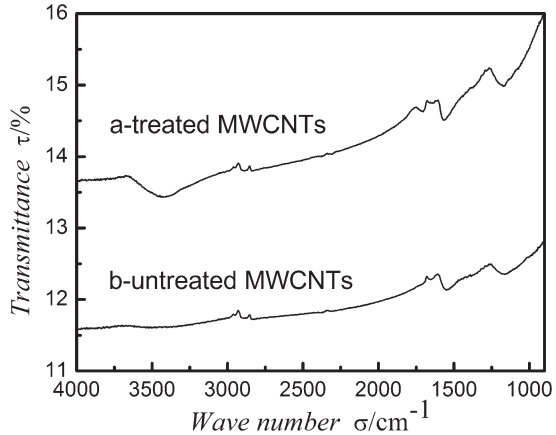

Figure 4. FT-IR spectra of MWCNTs (a) treated (b) untreated.

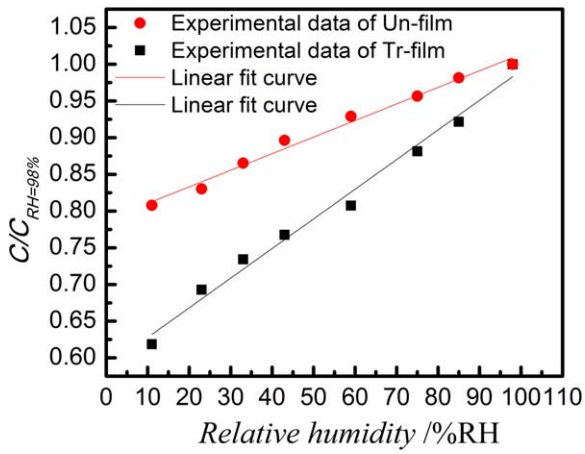

Figure 5. The normalized capacitance responses of Un-film and Tr-film against RH at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

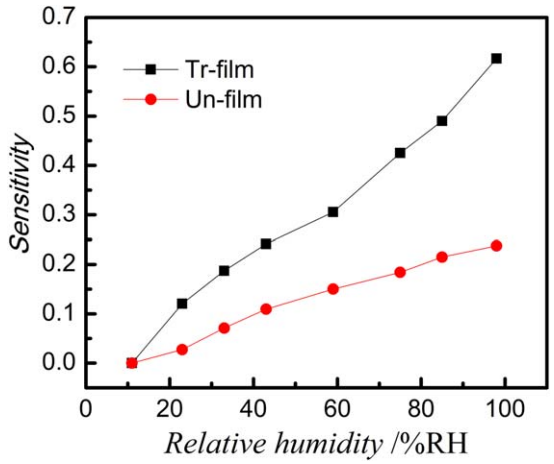

Figure 6. Sensitivity curves of Un-film and Tr-film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

MWCNTs film, a concave surface is produced in the micropores. At the same temperature the vapor pressure p corresponding to the concave surface is smaller than the saturated vapor pressure p_0.[21] Hence, vapor molecules could condense on the concave surface when $(P/P_0) < 1$. The condensation always happens from smaller pores to bigger ones which also can be depicted as the stronger the pressure becomes, the bigger the capillary pores where condensation happens are. Capillary condensation can take place in pores with a radius up to r_k at a particular RH and temperature. With a further increase in humidity, the water molecules tend to condense in capillary pores with a radius below the Kelvin radius r_k, the effect can be described by Kelvin's relation:

$$r_k = -2rV_l\cos\theta/RT\ln(p/p_0) \quad (1)$$

where θ represents the contact angle of liquid and wall of capillary pore; V_l refers to the molecular volume of liquid; r is the surface tension of liquid; R is the gas constant; T is the absolute temperature (K); r_k is the Kelvin radius of the capillary pores; p is the water vapor pressure, p_0 is the saturated water vapor pressure, and the p/p_0 is the RH.[21] Thus, p/p_0 is smaller than 1, and the higher the RH is, the bigger the Kelvin radius r_k becomes according to the formula (1).

The MWCNTs/SR composite films adsorb water vapors in the ambient humidity, and the water vapors absorbed condense to liquid at a vapor pressure due to capillary condensation effect. It is known that the relative dielectric constant of liquid water is about 80, which is much higher than that of water vapor (dielectric constant: 1). So owing to the condensation of the water molecules and the bigger relative dielectric constant of liquid water, the dielectric constant of the composite film increases, and the capacitance of the composite film increases accordingly. Furthermore, when the RH increases, more water vapors will be absorbed and condense to liquid in the film. Thus, the dielectric constant of the film increases with the increasing RH, and the capacitance of the MWCNTs/SR composite film will be bigger with the increasing RH just as shown in Figure 5. In addition, oxidative modification by acids can bring much hydrophilic groups to the sidewalls and ends of treated MWCNTs. As a result, more water molecules will be absorbed and condense to liquid in Tr-film than in Un-film due to these hydrophilic groups, which leads to the bigger capacitance changes of Tr-film in comparison with Un-film at the same RH level. As can be observed in Figure 6, the Tr-film has higher humidity sensitivity than the Un-film.

Frequency Dependence

In the following characterizations, we would mainly focus on the Tr-film due to its better humidity sensing performance than Un-film. The capacitance values of the Tr-film are 263.35, 203.27, 180.28, 160.65, and 140.76 pF when the frequencies are 1, 25, 50, 75, and 100 KHZ at ambient air humidity respectively. It indicates the capacitance decreases with the increasing test frequency.

Figure 7 depicts the normalized capacitance responses of the Tr-film to RH at different frequencies. It shows that the increasing test frequency will lower the capacitance sensitivity of the sensor. This is caused by capillary condensation happened in the MWCNTs. At high test frequency, owing to the dielectric relaxation phenomena, the formed liquid water could not have a complete polarization in the MWCNTs, and hence the effective dielectric constant of the liquid water decreases. As a result, the capacitance of the Tr-film decreases with the increasing test frequency. What is more, the degree of polarization becomes more and more incomplete when frequency ranges from low to high, and all these reasons lead to the lower sensitivity of Tr-film at high frequency in Figure 7.

Further Sensing Performances

The non-coincidence between the loading and unloading curves is known as hysteresis. Hysteresis is one of the most important elements to measure the quality of humidity sensor. For a perfect sensor device, its loading and unloading curves normally follow the same or almost same path. Figure 8 depicts the hysteresis of the Tr-film, it indicates that the hysteresis is tiny, and the humidification curve coincides with the desiccation curve on the whole RH. From Figure 8, it can be seen that the

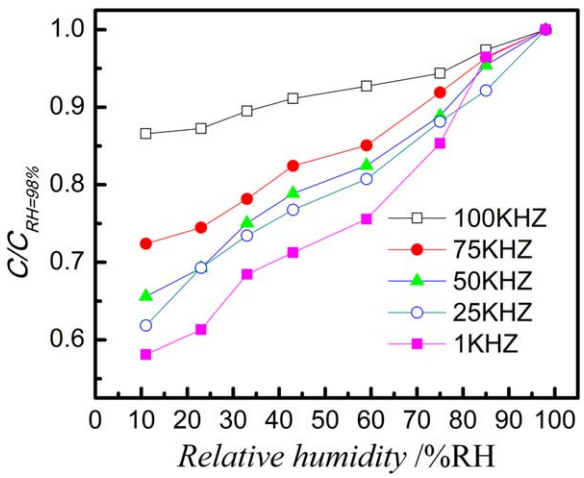

Figure 7. Normalized capacitance variations versus RH at different frequencies. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

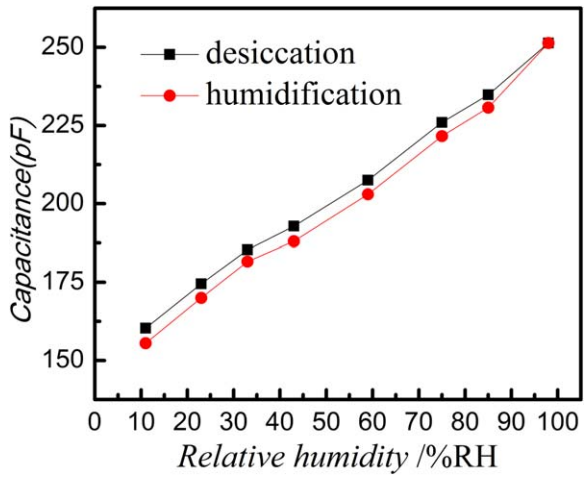

Figure 8. Hysteresis curve of the Tr-film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

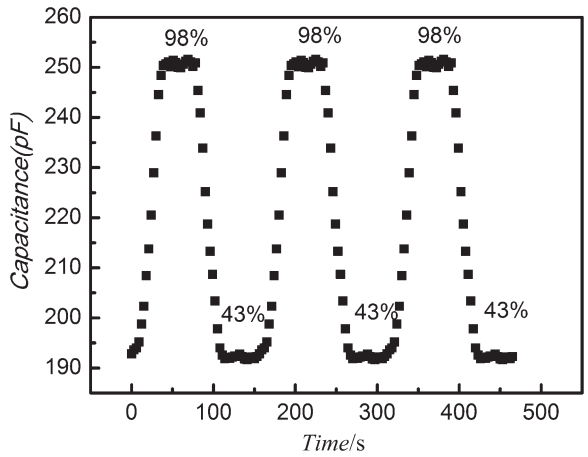

Figure 9. Repeatable responses of the Tr-film during three cycles between 43 and 98% RH.

maximum humidity hysteresis of Tr-film occurs at 43%RH, and the hysteresis (H) can be calculated by this formula: $H = \Delta C_{max}/S$, ΔC_{max} is the maximum capacitance difference at certain RH; S is the linear fit sensitivity in capacitance versus RH plot. And after calculation, the maximum humidity hysteresis H of Tr-film is 4.73%RH.

The response and recovery characteristics are essential characteristics for humidity sensors. The transient response behavior of the Tr-film to dynamic switches between 43%RH and 98%RH is given in Figure 9, indicating good reversibility of the response of the sensor. The sensor stayed 40 s at each RH. The response time of the sensor is about 30 s and the recovery time is about 27 s. The response time is longer than the recovery time, it can be inferred that capillary condensation will cost more time than the evaporation of water.

To compare these date with other sensing materials expressly, Table I lists the comparisons of different characteristics of the Tr-film and other sensing material. It can be observed that the Tr-film has high sensitivity and short response and recovery time, and it can be the candidate for humidity sensor. With regard to other sensing materials, they could not have high sensitivity and short response and recovery time at the same time. For example, nanostructured carbon-based sensor has short response and recovery time but low sensitivity, MWCNTs-enhanced based sensor has high sensitivity but long response and recovery time. So they are both not inappropriate for humidity sensor. For humidity sensors that can be applied to practical use, sensitivity, hysteresis, and response and recovery time should be considered comprehensively.

Moreover, tests for long-term stability were also carried out to evaluate the reliability of the sensor. The results are shown in Figures 10 and 11. The capacitance of the Tr-film was measured in 1 week and the RH were 33, 59, and 75%, respectively. As shown in Figure 10, only slight variation in capacitance at each RH is observed over time, proving good stability of the Tr-film. Figure 11 shows the capacitance versus RH curves for five round tests which are performed on five different weeks. The data show fine consistency. And according to Figure 11, the dependence of average value of capacitance on RH was plotted, as shown in Figure 12. The error bars indicate the maximum standard deviation of the capacitance is 6.02pF, showing the good repeatability of Tr-film.

CONCLUSIONS

In summary, the humidity performances of Tr-film and Un-film are measured, both films show linear dependence of capacitance on RH, but the Tr-film has higher sensitivity than the Un-film. Acids treatment can enhance the degree of dispersion of

Table I. Comparisons of Different Characteristics of the Tr-film Based Sensor with Other Sensing Materials

Sensing material					
Capacitive sensor	Sample thickness	ΔC/ΔRH	Response time	Recovery time	Hysteresis
Tr-film	10 μm	1.10pF/%RH	30 s	27 s	4.73%RH
Polyimide[22]	0.54 μm	0.31pF/%RH	70 s	70 s	8.97%RH
MWCNTs-enhanced[23]		2223.5nF/%RH	200 s	200 s	
Polyimide film with 1200 Å thick[24]	0.12 μm	0.86pF/%RH			1.75%RH
Nanostructured carbon[19]	10 μm	0.5pF/%RH	20 s	20 s	
Amorphous carbon[25]	500 μm		3 min	4 min	

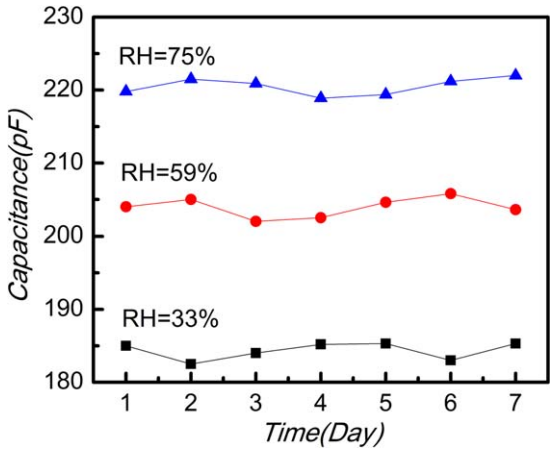

Figure 10. Long-term stability of the Tr-film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

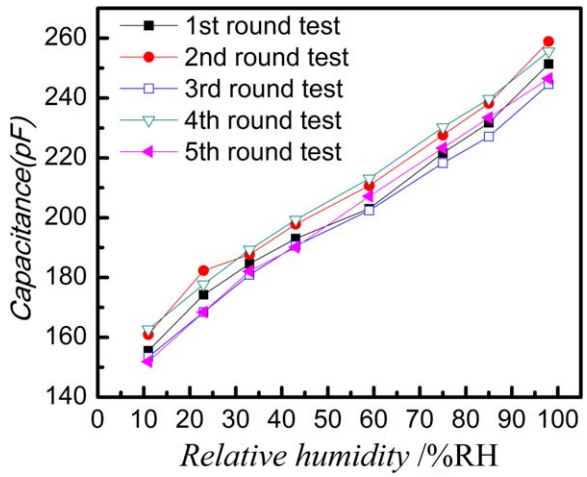

Figure 11. Capacitance responses versus RH curves for five round tests on five different weeks. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

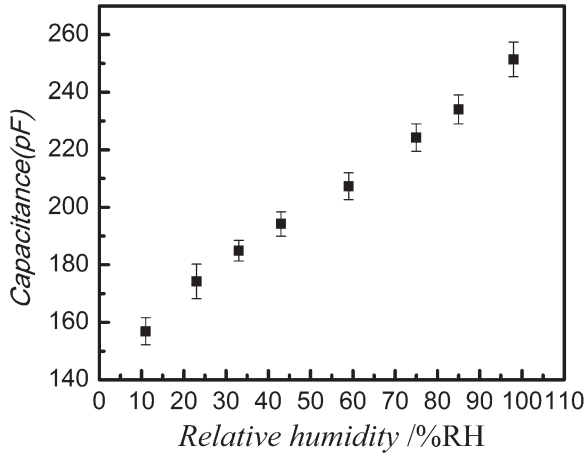

Figure 12. Dependence of the average value of capacitance of five round tests on RH.

MWCNTs in the SR matrix and bring much hydrophilic groups to the sidewalls and ends of treated MWCNTs, which results in the higher humidity sensitivity of the Tr-film in comparison with the Un-film. The frequency characteristic of the Tr-film is also measured, and the result shows that the capacitance of the Tr-film decreases with the increasing test frequency and the humidity sensitivity decreases conformably. The response time and recovery time of the Tr-film are 30 and 27 s respectively, and the maximum humidity hysteresis of the Tr-film is 4.73%. What's more, good stability and repeatability of the Tr-film are also observed. Owing to these good performances, Tr-film based humidity sensor can be the candidate for humidity sensor in the future.

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