Nanocomposites of carbon nanotubes and silicone-containing polyelectrolyte as a candidate for construction of humidity sensor

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There have been some reports on the use of nanocomposites for the construction of resistive-type humidity sensors in recent years. It was found that the composites sensing materials usually exhibit improved sensing properties, such as higher sensitivity, better stability, and quick response, in comparison with the single component [1–4]. Carbon nanotubes is a kind of promising inorganic nanomaterial with good mechanical and electrical properties. In addition, it is sensitive to humidity and gases at room temperature [5, 6]. In this report, nanocomposites of carbon nanotubes and a silicone-containing polyelectrolyte have been prepared and used to prepare resistive-type humidity sensors, and their humidity sensitive properties are investigated and compared with that of the polyelectrolyte.

Two types of carbon nanotubes were purchased from Shenzhen Nanotech Port Co. Ltd. The multi-wall carbon nanotubes (MWNT) has a diameter of 10–30 nm, and the purity is higher than 95%. The single multi-wall nanotubes (SWNT) has a diameter of less than 2 nm, and the purity is higher than 90%. Both nanotubes were treated with a mixture of sulfuric acid and nitric acid as reported in the literature [7]. The silicone-containing polyelectrolyte (Si-PE) was prepared as follows: The quaternary ammonium salt obtained from the reaction of dimethylaminoethyl methacrylate with n-brmomobutane was copolymerized with γ-methacryloxypropyl trimethoxy silane in methanol solution with azodiisobutyronitrile as the initiator under N_2 atmosphere at 60 °C for a certain time. The obtained solution was then diluted with methanol and precipitated in ether. The precipitate was washed with ether and dried in vacuum at 50 °C for 12 hrs. The chemical structure of the polyelectrolyte is shown in Fig. 1.

The chemically treated carbon nanotubes was dispersed in water or ethanol by magnetic stirring for 30 min, then ultrasonicated for 30 min. The procedure was repeated and the obtained suspending solution was mixed with the solution of the polyelectrolyte, magnetically stirred for 30 min, followed by ultrosonication for another 30 min. The solution so prepared was dip-coated on small interdigital gold electrodes (4 × 5 × 6 mm). After drying in air for a while, the electrodes coated with the sensing film were heated for a while to obtain the humidity sensor. Humidity responses of the sensors were measured using an in-house built electric circuit at $f = 1$ kHz, and constant humidities were provided by using different saturated salt solutions.

The Transmission electron microscopy (TEM) of the nanocomposites of the carbon nanotubes and the polyelectrolyte (Si-PE) was taken on a JEM-1200 EX instrument, and shown in Fig. 2. It can be seen clearly that the carbon nanotubes with hollow structures entangle with each other, and the diameters are in the range of 20–30 nanometer.

Fig. 3 shows the typical impedance response of the humidity sensors based on nanocomposites of carbon nanotubes with the polyelectrolyte and the polyelectrolyte alone. Over the whole tested humidity range (33–98%RH), the sensor based on the polyelectrolyte exhibits a linear response towards humidity change in semi-logarithmic scale, but the impedance is as high as $2.2 \times 10^7\ \Omega$ at a low humidity of 33%RH. In comparison, the sensor based on the nanocomposites exhibits much lower impedance over the whole humidity range, while the sensing linearity and sensitivity does not change. This indicates that the inclusion of the conductive carbon nanotubes in the sensing film can effectively decrease the impedance of the sensor without deteriorating other sensing properties, such as the sensitivity and linearity.

It is known that the solvent has some effect on the dispersion of the carbon nanotubes in the solution, hence the distribution of the nanoparticles in the prepared sensing film. In this paper, two solvents, water and ethanol, are used for the preparation of the nanocomposites of carbon nanotubes and the polyelectrolyte. Fig. 4 illustrates the effect of the solvent on the sensing behavior of the nanocomposites films and the polymer films alone. As shown in the figure, the humidity responses of the films based on the

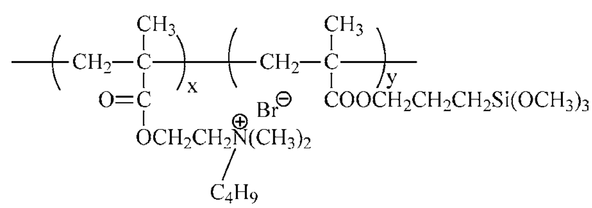

Figure 1 Chemical structure of the polyelectrolyte Si-PE.

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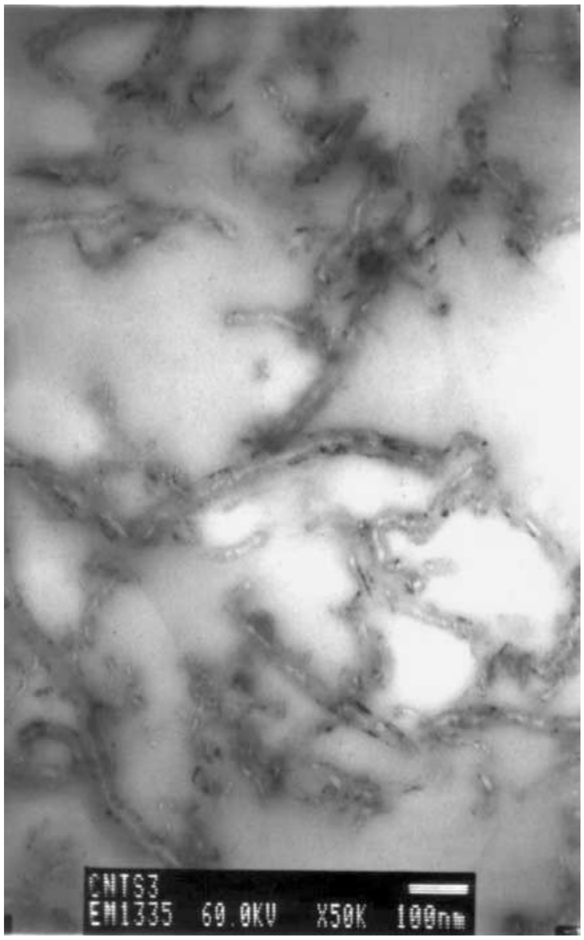

Figure 2 TEM photograph of nanocomposites of carbon nanotubes and Si-PE.

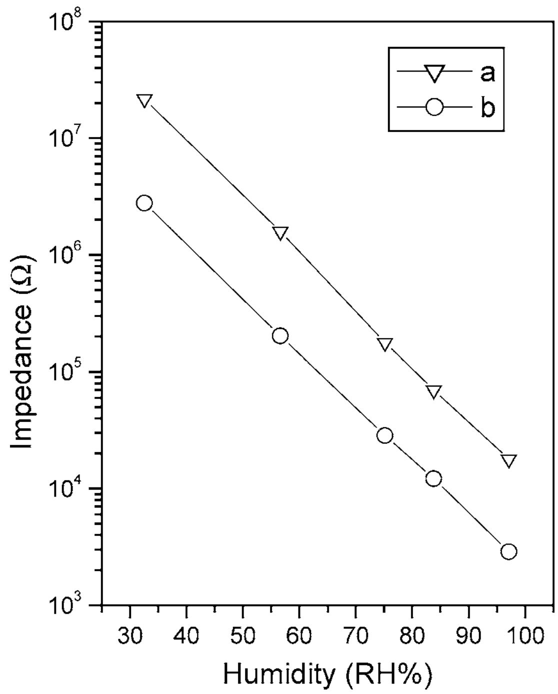

Figure 3 Impedance as a function of relative humidity for sensors based on (a) Si-PE and (b) nanocomposites of carbon nanotube and Si-PE.

polyelectrolyte are quite similar irrespective of the solvent. However, the sensing film of the nanocomposites prepared from ethanol has a lower impedance compared to that prepared from water, which is

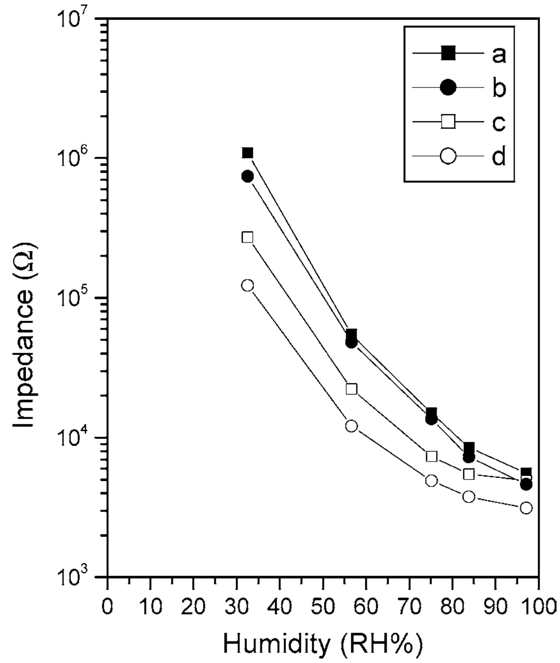

Figure 4 Impedance as a function of relative humidity for sensors based on (a) Si-PE in water, (b) Si-PE in ethanol, (c) nanocomposites of carbon nanotubes and Si-PE in water and (d) nanocomposites of carbon nanotubes and Si-PE in ethanol.

more apparent at low humidities. This implies that ethanol is a better solvent for the preparation of nanocomposites of carbon nanotubes with the polyelectrolyte.

In addition to the solvent, the type of carbon nanotubes also greatly affects the humidity response of the nanocomposites as shown in Fig. 5. Although the films of the nanocomposites containing both MWNT and SMNT show a greatly decreased impedance in the range of 33–98%RH in comparison with the film

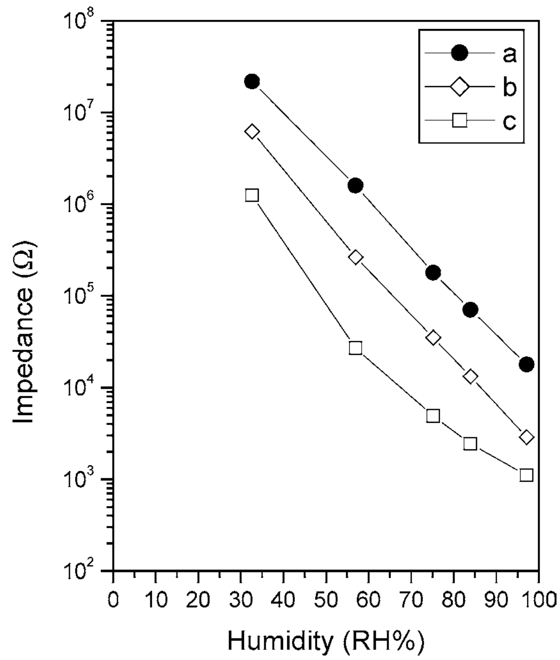

Figure 5 Impedance as a function of relative humidity for sensors based on (a) Si-PE, (b) nanocomposites of MWNT and Si-PE and (c) nanocomposites of SWNT and Si-PE.

of the polyelectrolyte, the lowest impedance is obtained with composites of SWNT and Si-PE and the decrease in the impedance is more than one order of magnitude over the tested humidity range. This suggests that SWNT is a more effective material for decreasing the impedance of humidity sensors. It is known that most of the resistive-type humidity sensors cannot detect low humidity due to the high impedance involved [8]. The formation of the nanocmposites of humidity sensitive polymers with the carbon nanotubes, which show reversible response to relative humidity [5], may provide a solution to prepare humidity sensors capable of detecting low humidities by taking advantage of the good conductivity of carbon nanotubes.

In conclusion, formation of nanocomposites of carbon nanotubes with polymer humidity sensitive materials can effectively decrease the impedance of the resistive-type humidity sensors without deteriorating other sensing properties. This may provide a promising method for preparing humidity sensors for detection of low humidity.

Acknowledgment
This project is financially supported by the National Natural Science Foundation of China.

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Received 15 January
and accepted 9 March 2004