Humidity sensitive properties of NaPSS/MWNTs nanocomposites

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In recent years, organic/inorganic nanocomposites have received great attentions and become attractive for many new electronic, optical or magnetic applications. Gas and humidity sensors based on the nanocomposites were also reported. Compared with the sensors based on single component, the sensors composed of composites may show improved sensing properties, such as higher sensitivity, faster response, better stability, etc. [1, 2] Carbon nanotubes are well-known inorganic nano-materials, and have been extensively investigated for building nano-electronic devices due to their unique electronic and mechanical properties. It is also reported that both single-wall nanotubes (SWNTs) and multi-wall nanotubes (MWNTs) are sensitive to humidity and various gases even at room temperature [3, 4]. In this paper, MWNTs were blended with sodium polystyrenesulfonate (NaPSS), a typical polyelectrolyte humidity-sensitive material, to prepare a nanocomposite for construction of the resistive-type humidity sensors. The humidity sensitive properties of the composite sensors have been investigated.

The multi-wall carbon nanotubes (MWNTs) were purchased form Shenzhen Nanotech Port Co. Ltd. (diameter: 10–30 nm, length: 0.5–500 μm, purity: >95%.) They were chemically treated by a modified literature method: untreated MWNTs were blended with a mixture of concentrated nitric and sulfuric acids (volume ratio = 1:3) by ultrasonication for 30 min, then heated at 140 °C for 40 min. followed by washing with water [5]. NaPSS was prepared by sulfonation of the commercial polystyrene and successive treatment with sodium hydroxide as reported in the literature [6]. The as-treated MWNTs were mixed with the aqueous solution of NaPSS and sodium carboxymethylcellulose (CMC), an additive used for improving the adhesion of the sensing film with the electrode, by repeated vigorous magnetic stirring and ultrasonication to give a well-dispersed suspension. A layer of humidity-sensitive film composed of the nanocomposite was prepared by dipping the small interdigitated gold electrode (6 × 5 × 0.5 mm) into the suspension so prepared. Both the width and gap of tracks of the electrode are 80 μm. The electrode covered with the film was first dried in air, then heat treated to construct a resistive humidity sensor.

The humidity responses of these sensors were measured with an in-house built electric circuit. The frequency of the applied voltage is 1 kHz. Different humidities were obtained by using a series of saturated salt solutions. The transmission electron microscopy (TEM) photographs of the nanocomposite of MWNTs and NaPSS were taken on a JEM-1230 instrument, and presented in Fig. 1. It is seen that the carbon nanotubes have the hollow structure and the diameters are in the range of 20–30 nm.

Fig. 2 shows the typical humidity responses of the humidity sensors based on nanocomposite of NaPSS and MWNTs (Fig. 2b) and NaPSS alone (Fig. 2a). The sensor based on NaPSS alone shows moderately linear response in the range of 33–87% RH in semi-logarithmic scale, but the linearity deteriorates when humidity further increases (87–97% RH). In addition, the impedance at a low humidity of 33% RH is as high as 2.7×10^6 Ω. In contrast, the sensor composed of the nanocomposite exhibits a highly linear response over the whole tested humidity range of 33–97% RH ($R^2 = 0.9996$), and the impedance is also greatly decreased over the whole tested humidity range. At the low humidity of 33% RH, the impedance is even decreased by almost one order of magnitude. Considering the fact that the polymer resistive-type humidity sensors usually have difficulty in detecting low humidity due to the high impedance involved [7], the low impedance of the nanocomposite with MWNTs may provide a solution for preparing humidity sensors capable of detecting the dry atmosphere. Fig. 3 shows the impedance response of the sensors with and without MWNT during the desiccation and adsorption process and both sensors exhibit a hysteresis of ∼3RH%. The hysteresis of NaPSS may result from the strong interaction of the SO_3^- group in the polymer with the adsorbed water molecules. The nanocomposite does not exhibit a larger hystersis since MWNTs show a reversible response to relative humidity [3].

The effect of the content of MWNTs in the nanocomoposite on the humidity response is illustrated in Fig. 4. As shown in the figure, when the content of MWNT in the precursor solution increases from 2 to 3 mg/mL, the impedance of the composite sensors decreases, especially at low humidity. In addition, the sensing linearity is greatly improved. A further increase in the content of MWNT leads to a larger impedance over the humidity range of 60∼98% RH, and the sensing linearity is also deteriorated. However, the impedance at the low humidity of 33% RH continues to decrease with the increase in the content of MWNTs, reaching only 1.1×10^5 Ω. The results show that the content of MWNTs has great effect on the sensing properties of the nanocomposite. Similar to the

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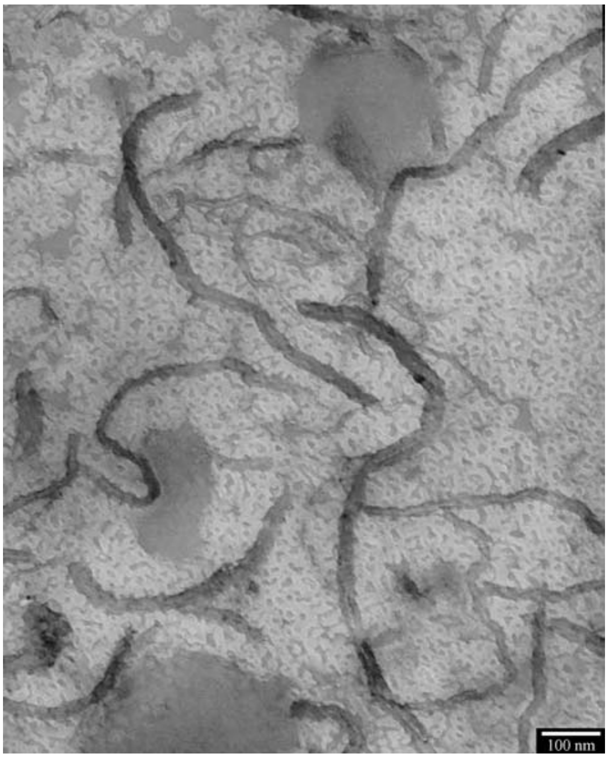

Figure 1 TEM photograph of nanocomposites of MWNTs and NaPSS.

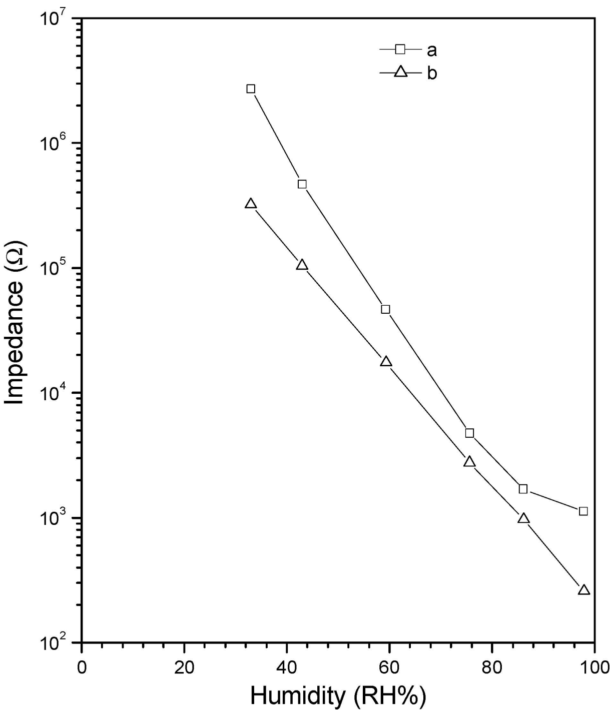

Figure 2 Impedance as a function of relative humidity for sensors based on (a) NaPSS and (b) NaPSS/MWNTs composites.

case of the humidity sensor based on the composite of SiO_2 with Nafion [8], the impedance of the nanocomposites at different humidities may be composed of the contributions of both NaPSS and the MWNTs. At a low humidity, the conduction of MWNTs may play an important role, and the impedance decreases with increase in the content of MWNTs in the composites, just as observed. At higher humidities, the contribution from NaPSS may become more important and the

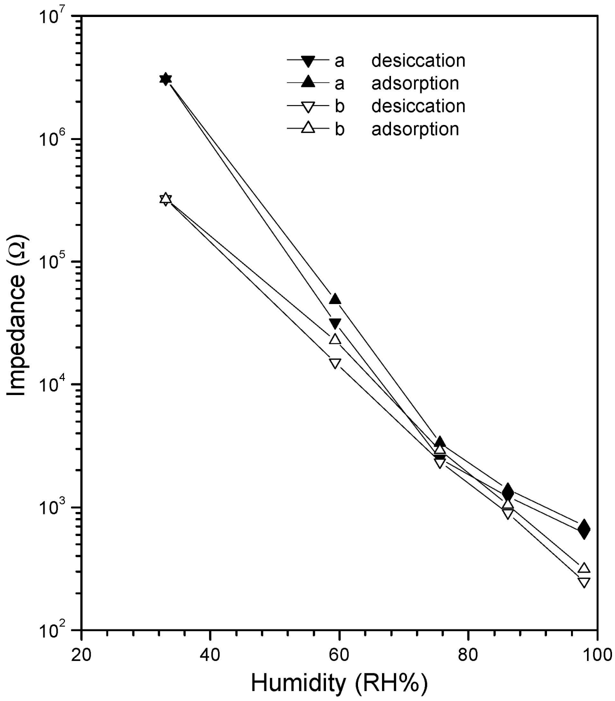

Figure 3 The hysteresis of sensors based on (a) NaPSS and (b) NaPSS/MWNTs composites.

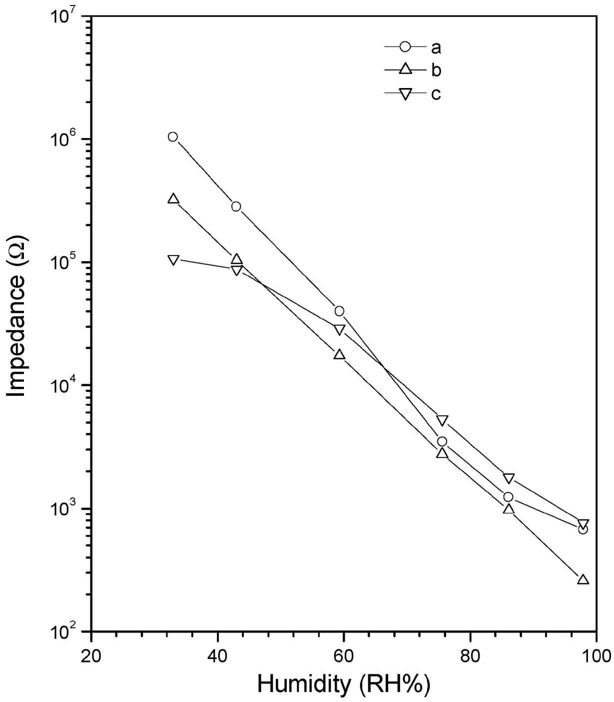

Figure 4 Impedance as a function of relative humidity for sensors based on NaPSS/MWNTs composites with different content of MWNTs (the content of MWNTs in the precursor suspension is (a) 2 mg/ml; (b) 3 mg/ml and (c) 4.5 mg/ml).

situation is more complex. As a result, it is necessary to control the content of MWNTs in the composite to obtain a good humidity response.

In conclusion, the resistive-type humidity sensors based on nanocomposite of NaPSS and MWNTs show a smaller impedance, especially at low humidity, and much better sensing linearity in the range of 33–97% RH in comparison with the sensor composed of NaPSS alone. The content of MWNTs has great effect on the sensing properties of the nanocomposites. The nanocomposites with MWNTs is promising for preparation of humidity sensors capable of detecting low humidity.

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