

A NOVEL RESISTIVE HUMIDITY SENSOR BASED ON SODIUM POLYSTYRENESULFONATE/TiO₂ NANOCOMPOSITES*

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Abstract A resistive humidity sensor was prepared based on sodium polystyrenesulfonate (NaPSS)/TiO₂ nanocomposites, and its electrical response to humidity was examined. The sensor exhibits better linearity, smaller hysteresis (< 4% RH) and quicker response (absorption: less than 2 s; desorption: less than 20 s) in comparison with sensor composed of NaPSS. The effect of concentration of NaPSS and TiO₂ on humidity response of sensors was discussed.

Keywords Humidity sensor, Nanocomposites, TiO₂, Sodium polystyrenesulfonate

INTRODUCTION

Humidity sensors have found wide applications in industrial production, process control, environmental monitoring, storage, electric applications, *etc.*, and research on humidity sensitive materials are gaining more and more attentions^[1–8]. Of the materials used for humidity sensors, polymers show the advantages of low price, quick response and easy integration, and have become the focus of research. However, they exhibit problems of low stability at high humidity, too high impedance at low humidity, drifting, *etc.* To overcome these shortcomings, polymers were usually chemically modified by grafting, crosslinking or formation of interpenetrating networks (IPN)^[9–11], Feng *et al.* also reported the formation of organic and inorganic composite thin film of Nafion/SiO₂^[3].

Organic/inorganic nanocomposites are a type of new materials receiving broad attention worldwide because many bulk properties were improved as compared with those of base polymers^[12, 13]. However, there have been no reports on their direct application in humidity sensors. In this paper, humidity sensors based on organic/inorganic nanocomposites of sodium polystyrenesulfonate (NaPSS) with TiO₂ were prepared and their humidity sensitive characteristics investigated.

EXPERIMENTAL

Preparation of Humidity Sensors

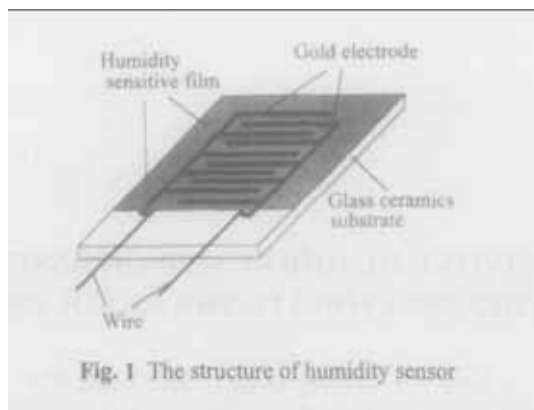
NaPSS was prepared by sulfonation of commercial polystyrene and successive treatment with sodium hydroxide. TiO₂ nanoparticles with average size of 20 nm were supplied by Shanghai Chemical Reagents Co..

NaPSS was dissolved in deionized water by heating and stirring together with sodium carboxymethylcellulose (CMC). To the solution, TiO₂ nanoparticles were added with strong magnetic stirring, then treated by ultrasonic agitation to give a milky opaque solution, which was deposited on an interdigital gold electrode (6 × 4 × 0.5 mm) by dip coating. The thus coated electrode was heated at 100°C for 30 min to give a resistive humidity sensor, whose structure is shown in Fig. 1.

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Measurements

Transmission electron microscopy (TEM) was carried out on a JEM-1200 EX instrument.

The humidity sensor was placed in a box where humidity was controlled by mixing dry and wet air, and the impedance of the sensor was measured with a digital multimeter (applied ac voltage = 2 volt, $f = 1$ kHz). The complex impedance spectra were measured at 1 volt with a Solartron 1255 frequency response analyzer coupled with 1286 Solartron electrochemical interface.

RESULTS AND DISCUSSION

Characterization of Nanocomposite film

The TEM picture of NaPSS/TiO₂ nanocomposite film is shown in Fig. 2. The dark spots are TiO₂ nanoparticles, while the lighter fiber-like region belongs to polymer. It can be seen that the particle sizes of TiO₂ are mainly in the range of 30–40 nm. This directly proved the formation of organic/inorganic composite on the nano scale.



Humidity Response of NaPSS and NaPSS/TiO₂ Nanocomposite Film

NaPSS is a typical polyelectrolyte used as humidity sensitive material^[14], and its response to humidity is shown in Fig. 3. This clearly shows that the logarithm of impedance of the NaPSS film decreases almost linearly with the increase of relative humidity over almost the whole humidity range (15% RH–90% RH), showing its high sensitivity (impedance changes about three orders of magnitude). However, a large hysteresis of ~10% RH is also observable, and its 90% response time between 11% RH and 97% RH was determined to be 2 s (absorption) and

3 min (desorption), respectively. This experimental fact can be explained from the chemical structures of NaPSS; the SO₃⁻ ions in the polymer chain interact strongly with water molecules absorbed, which resulted in slow desorption and large hysteresis.

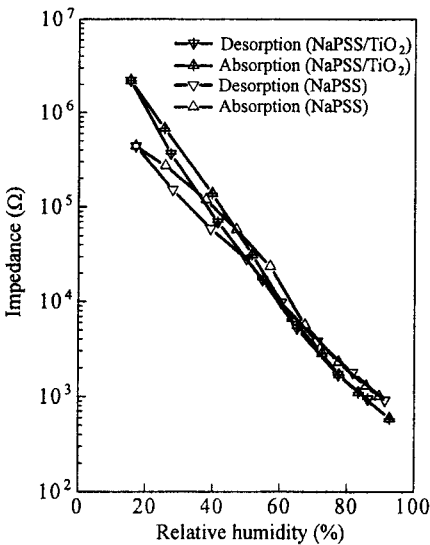


Fig. 3 Electrical response of NaPSS film and NaPSS/TiO₂ nanocomposite film to humidity

To improve its sensing behavior, NaPSS was blended with TiO₂, an inorganic humidity sensitive material^[15], to form nanocomposite thin film. In order to improve the stability of the mixture and to increase the adherence of the film to the gold electrode, CMC was added as an additive. The humidity response of the composite film is shown in Fig. 3. It can be seen that the composite film shows higher sensitivity (impedance changes almost four orders of magnitude in the tested humidity range) and better linearity in its semi-logarithmic response curve than the corresponding NaPSS film. Furthermore, its hysteresis also decreases greatly to less than 4% RH, and the 90% response time from 97% RH to 11% RH was even reduced to less than 20 s. All these results indicate that the formation of NaPSS/TiO₂ nanocomposite film can effectively improve the humidity-sensitive properties of these sensors by increasing its sensitivity, decreasing hysteresis and reducing response time.

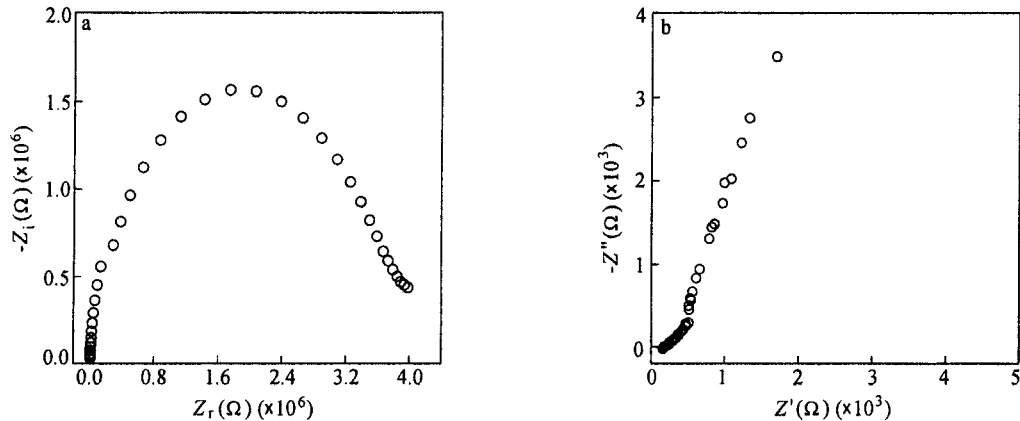


Fig. 4 Nyquist plot of NaPSS/TiO₂ nanocomposite film at different humidities
a) 11% RH; b) 85% RH

Complex Impedance Spectra of NaPSS/TiO₂ Nanocomposite Film

The Nyquist plots of the composite film at different humidities are given in Fig. 4. At low humidity, a semicircular curve was clearly observed, which is attributed to the film resistance. At high humidity, however, the film resistance becomes so small that a straight line due to the diffusion of the electroactive species at the electrode was observed instead (Warburg impedance). All these results indicate that the sensing of the composite film was based on ion transport mechanism, as we reported previously^[14].

Effect of Concentration of both NaPSS and TiO₂ on Humidity Response

The concentration of both NaPSS and TiO₂ in the nanocomposite film affects the humidity response of the film greatly, as given in Fig. 5 and 6. In Fig. 5, the concentration of NaPSS is 8.3 mg/cm³. When the content of TiO₂ was increased from 5 mg/cm³ to 10 mg/cm³ (curve a and b), the impedance of the sensor increased in the middle to high humidities. As a result, the linearity of the sensing curve was greatly improved. A further increase of TiO₂ content to 15 mg/cm³ (curve c) leads to an increase of impedance in low to middle humidities. In this case, however, linearity no longer existed.

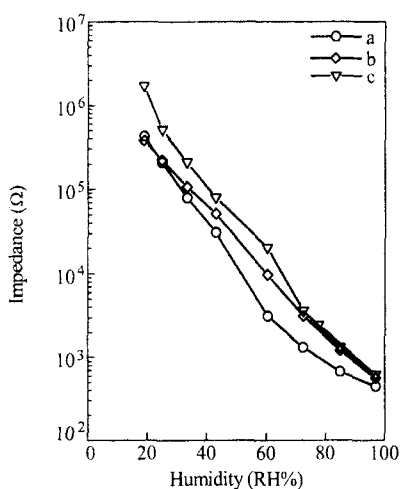


Fig. 5 Effect of concentration of TiO₂ on electrical response of NaPSS/TiO₂ composite film to humidity (NaPSS: 8.3 mg/cm³; TiO₂ content: a<b<c)

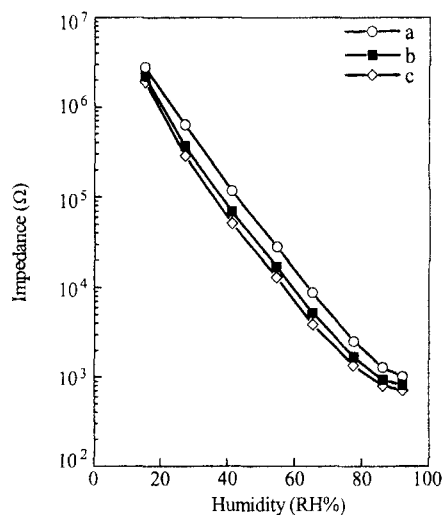


Fig. 6 Effect of concentration of TiO₂ on electrical response of NaPSS/TiO₂ composite film to humidity (NaPSS: 10 mg/cm³; TiO₂ content: a<b<c)

When the concentration of NaPSS was increased to 10 mg/cm³, the effects of the content of TiO₂ on the humidity response of composite film appear in a different way. With the increase of the content of TiO₂, the linearity of the semi-logarithmic response curve of the sensors remains good, but the impedance of composite film decreases almost uniformly in the tested humidity range, as shown in Fig. 6. Furthermore, the response time increases considerably. The 90% response time from 97% RH to 11% RH was determined to be 20 s and 185 s. for films containing TiO₂ of 5 mg/cm³ and 15 mg/cm³, respectively.

The above results show that only a suitable combination of concentrations of the two components can lead to the formation of composite films with good sensing behavior. And this was supposed to result from the effect of the concentration of NaPSS and TiO₂ on the dispersion of inorganic nanoparticles in the polymer matrix and the morphology of the composite film.

CONCLUSION

Sodium polystyrenesulfonate (NaPSS) was blended with TiO₂ to form nanocomposites. Resistive humidity sensors derived from the organic/inorganic nanocomposite thin film were prepared. The sensors show high sensitivity (impedance change by four orders of magnitude from 20%–90% RH), wide sensing range (20%–90%

RH), small hysteresis (< 4% RH) and quick response (2 s for absorption, and 20 s for desorption). Organic/inorganic nanocomposites can be a promising approach to the development of new humidity sensitive materials with good sensing characteristics.

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