A Novel Nanocomposite Sensor for Detection of Humidity

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Nanocomposite of iron oxide and polypyrrole were prepared by sol-gel process. The X-ray diffraction study of the nanocomposite has shown the presence of single cubic phase of iron oxide. The composite in the pellet form was used for humidity sensing investigations. The sensitivity of this sensor to humidity was found to increase even at high relative humidities. The device possesses highly stable and reproducible characteristics and has applications in pharmaceutical, medical and environmental industry along with the possibility of their application in detecting gases such as, CO₂, CH₄, and N₂.

Introduction

The increased concern about environmental and personal protection along with huge requirements for more accurate process control has created a need for measuring physical and chemical properties. This has resulted in continuous expansion in sensor development. The measurement and control of humidity is important in many areas including industry (paper and electronic), domestic environment (air conditioner), medicine (respiratory equipment), etc. Thus sensors highly sensitive to humidity are in great demand in medical and industrial fields. The sensitivity to humidity can be measured in terms of change in mechanical, optical, and electrical properties. The electrical detection based on the change in resistance or capacitance of the sensor on exposure to water vapour is most commonly used.

The inorganic oxides like aluminium oxide (Al₂O₃), titanium oxide (TiO₂), tin oxide (SnO₂) and iron oxide (Fe₂O₃) have been studied extensively and have emerged as economical humidity sensors in recent years. Use of special techniques of preparation and doping of SO₄, Ti, Sn, Zn, Si etc. in α-Fe₂O₃ has been found to improve the sensing capabilities.

There are several organic materials viz conducting polymers such as polypyrrole, polyaniline, polythiophene, and polyacetylene which find various applications as electronic and optoelectronic devices. The ability of conducting polymers to oxidize and reduce at specific electrochemical potential has made them useful as sensors. Many polymers such as polypyrrole, poly methyl methacrylate (PMMA), and poly vinyl carboxylate have shown good response to humidity and gases in terms of change in capacitance and resistance.

The conducting polymers show high sensitivity to gases and humidity as compared to inorganic sensors based on oxides due to their porous nature. However, the instability of conducting polymers in air and their poor processibility has limited their commercialization as sensors.

In the present paper the inorganic–organic hybrid nanocomposite containing polypyrrole as the organic part and iron oxide as the inorganic part has been used for studying their sensitivity to humidity. The nanocomposite has small grain size and high stability in air. This is most probably the first ever attempt made to study these composites as humidity sensors.

In order to determine the grain size and structural properties of the nanocomposites several structural investigations using X-ray, IR and SEM techniques have been carried out and the results are presented separately.
Experimental Details

The composite of iron oxide and polypyrrole was prepared by sol gel process. In this process the pyrrole monomer was added to a mixture of ferric nitrate and methoxy ethanol in a certain specific ratio. This mixture was heated at 150°C to evaporate the solvent, resulting in composite powder. The powder was then annealed at 300°C and then compressed into pellets of ~1.2 cm diam and ~0.1 cm thick for further studies.

The crystal structure of the powder was examined by using a Rigaku-Rotaflex diffractometer, using a Cu-kα (λ=1.5418 Å) at 40keV. The surface morphology was analyzed with the help of JEOL (JSM 840) Scanning Electron Microscope (SEM). The Fourier Transform Infra-Red (FTIR) spectra was recorded using the Nicolet 510 FTIR spectrophotometer.

The schematic experimental set up used for evaluation of nanocomposite sensor is shown in Figure 1. The pellets were placed in the sample holder having two pressure contacts. The contacts were made using silver paint. This was enclosed in a metallic chamber provided with two holes, one for attaching the hygrometer to measure the relative humidity and the other for the contacts from the sample holder to determine the resistance. The testo 601 capacitive hygrometer was used to measure the humidity and Keithley electrometer 610 was used to measure the resistance. The humidity inside the chamber was generated using two pressure method. By this method the relative humidity (RH) could be controlled up to ±1 per cent approx. The variations in resistance were studied as a function of RH values at room temperature.

Results and Discussions

The X-ray diffraction pattern for the nanocomposite is shown in Figure 2. The X-ray diffraction pattern for powder indicates the presence of single cubic phase of iron oxide with lattice constant a = 8.54 Å. Figure 3 shows the FTIR transmission spectra of the powder using KBr pellet was recorded in the range 400 cm⁻¹-4000 cm⁻¹ to confirm polymerization of pyrrole. The spectra shows peaks at 780 cm⁻¹, 1090 cm⁻¹, and 3400 cm⁻¹, indicating the presence of polypyrrole. The SEM study performed on the nanocomposite powder indicates the presence of highly branched chain structure (or a fibrillar morphology), as shown in Figure 4.

Humidity Sensors — RH vs Sensitivity

The sensitivity is defined as \( \frac{R_f}{R_d} \), where \( R_f \) is the resistance under dry conditions (in this case with relative humidity = 20 per cent) and \( R_d \) is the resistance at specified humidity. The sensitivity was determined for varying relative humidity.

Figure 5 shows the sensitivity as a function of humidity for nanocomposite. The sensor showed almost const
A continuous increase of sensitivity (S) with relative humidity (RH) with S approaching a value of 130 for highest relative humidity. Thus, in the present study we observe a continuous increase in sensitivity even at high RH values. This behavior is different from α-Fe₂O₃ humidity sensor which shows a distinct saturation at higher humidity values shown as dotted line in Figure 5 (obtained from ref. 6).

The response of sensor to humidity could be due to combination of the following two processes :

(a) The absorption of water on iron oxide surface has been shown to be a dissociative mechanism to form hydroxyl groups which are bound to lattice iron, as discussed earlier. The water vapour is adsorbed on the grain surface and in nanopores and reacts reversibly with lattice iron as:

\[ H₂O + O₀ + 2Fe₀ \rightleftharpoons 2(OH - Fe) + V₀^{00} + 2e⁻, \]

where \( O₀ \) is lattice oxygen at the oxygen site and \( V₀^{00} \) is vacancy created at oxygen site according to reaction:

\[ O₀ \rightleftharpoons O^₂⁻ + V₀^{00}. \]

The doubly ionized oxygen displaced from lattice reacts with \( H^⁺ \) coming from dissociation of water vapour to form hydroxyl groups, as given below:

\[ H^⁺ + O^₂⁻ \rightleftharpoons OH⁻. \]

Because of the free electrons given by this reaction the resistance decreases with increase in humidity. But the sensors based on iron oxide attain a saturation at high RH, suggesting the absence of any further active iron sites for reaction to occur and hence no change in resistance beyond a certain humidity was observed in earlier case.

A continuous increase in sensitivity with increase in RH values is observed in the present study. This could be probably due to the presence of polypyrrole which also reacts with water vapour (as shown in Figure 6), causing a counter balance or cancelling of the saturation characteristic of α-Fe₂O₃ humidity sensor.

Moreover, this polymer seems to have hydrophilic ions for charge compensation that are electrostatically bonded to matrix and adsorption of water increases mobility of ions and consequently resistance decreases. The combined mechanisms hence result in an increased response of the sensor at high relative humidities.
The sensor exposed to humid environment for prolonged duration of time exhibited no visible degradation in characteristics. The sensor recycled several times yielded very reproducible results. Preliminary investigation indicates that these devices have potential for detection of gases such as, CO₂, CH₄, and N₂ and have been reported elsewhere.²

**Conclusion**

The sensitivity to humidity of nanocomposite of iron oxide and polypyrrole prepared by the sol gel process has been studied. This nanocomposite sensor has shown a sharp increase in sensitivity even at high relative humidities, indicating a better response as compared to α-Fe₂O₃. The possible mechanism for such an increase has also been suggested.

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