Spectroscopic and Electrical Properties of Polyaniline/CeO$_2$ Composites and Their Application as Humidity Sensor

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ABSTRACT: Polyaniline/CeO$_2$ composites were synthesized by *in situ* chemical polymerization method using ammonium persulphate as an oxidizing agent. This is the single step polymerization process for the direct synthesis of emeraldine salt phase of polymer. The polymers were characterized by using FTIR spectral analysis, SEM, and XRD studies. Formation of conducting emeraldine salt phase is confirmed by spectroscopic techniques. High temperature conductivity measurements show ''thermal activated behavior.'' The change in resistance with respect to percentage relative humidity (% RH) is observed, when the pressed pellets of the polymer were exposed to the broad range of humidity (humidity ranging between 10 and 95% RH). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5533–5537, 2006

Key words: polymers; chemical synthesis; spectroscopy; conductivity; humidity sensing

INTRODUCTION

The study on conducting polymer (CP) has offered many advantages for sensor technology development. The CPs such as polypyrrole, polythiophene, poly(*p*-phenylene), and polyaniline (PANI) have been commonly used in scientific and industrial studies and in various applications as rechargeable batteries,[1,2] sensors,[3–6] and diodes in transistors and microelectronic devices.[7] Among all the CPs, PANI has received a great attention owing to its simple synthesis, good environmental stability, ability to dope with protonic acids, and moderately high electrical conductivity.[8]

In recent years, inorganic semiconducting oxides like zinc oxide (ZnO), aluminum oxide (Al$_2$O$_3$), titanium oxide (TiO$_2$), tin oxide (SnO$_2$), iron oxide (Fe$_2$O$_3$), etc., have been studied extensively and have emerged as economical sensors for monitoring toxic gases and humidity.[9–12] The sensitivity of these sensors to gas and humidity depends on its microstructure. This can be achieved by adopting special techniques of preparation or by doping impurities. It has been found that doping of SO$_4^{2-}$, Ti, Sn, Zn, Si, etc., in α-Fe$_2$O$_3$ has been found to improve the sensing capabilities.[13–16]

The inorganic sensors based on oxides have been found to be less sensitive to gases and humidity when compared with the CPs, which show high sensing behavior due to their porous nature. However, the instability of some of the CPs in air has limited their commercialization as sensors.[17]

Humidity is one of the most common constituents present in the environment. Therefore, sensing and controlling humidity is of great importance in the industrial processes, for human comfort, domestic purpose, in medical applications and agriculture. Recently, there has been a considerable increase in the demand of humidity control in various fields such as air conditioning systems, electronic devices, tire industries, sugar industries, and drying processes for ceramics and food.[18] The conventional materials used for sensing humidity are electrolytic metal oxides, alumina thin films, and ceramics.[19] However, polymers are identified as good candidates for practical applications, since they are compatible to oxides and ceramics and also they can be used at room temperature.[20–22] Of these, a disc type sensor would offer higher sensitivity toward humidity than a thin type film due to larger capacity toward water absorption.

In our earlier studies on humidity sensing and electrical properties of PANI/Co$_3$O$_4$ composites, we have reported good humidity sensitivity to the broad range of humidity (humidity ranging between 10 and 95% RH).[23] In the present article, we report the study on preparation, characterization, and successful utiliza-
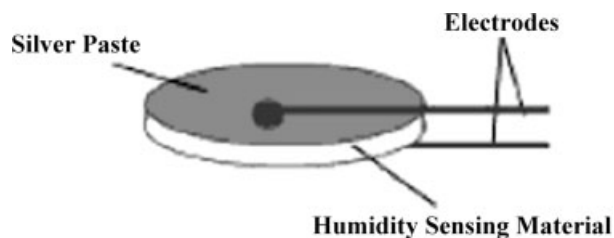
Figure 1 Sketch of capacitive type humidity sensors.

tion of PANI/cerium oxide (CeO_2) composites as a humidity sensor.

EXPERIMENTAL

Materials and methods

All chemicals used were analytical reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate ((NH_4)$_2S_2O_8$), hydrochloric acid (HCl), and cerium oxide (CeO_2) (sigma) were used as received.

Aniline (0.1 mol) was dissolved in $1M$ HCl to form aniline solution. Cerium oxide was added to the aniline solution with vigorous stirring to keep the cerium oxide suspended in the solution. To this reaction mixture, $0.1M$ of ammonium persulphate [(NH_4)$_2S_2O_8$], which acts as the oxidant was added slowly with continuous stirring at 0–5°C. After complete addition of the oxidizing agent, the reaction mixture was kept under stirring for 24 h. The greenish black precipitate of the polymer was recovered by vacuum filtration and washed with deionized water. The resultant precipitate was dried in an oven for 24 h to achieve a constant weight.

PANI/CeO_2 composites were prepared in weight percent ratio, in which the concentration of cerium oxide (10, 20, 30, 40, and 50 wt %) was varied. The test samples to be used as a sensor was prepared in pellet form (diameter: 10 mm; thickness: 3 mm) by applying pressure of $100M$ Pa using Pye-Unicam dye. The contacts were made using silver paste as electrodes on both sides. Figure 1 shows the sketch of the capacitive type of humidity sensor. The testo 601 capacitative hygrometer was used to monitor the humidity, and Keithley electrometer was used to measure the resistance.

The FTIR spectra of the samples were recorded on a PerkinElmer 1600 spectrophotometer in KBr medium. X-ray diffraction studies were performed by using Philips X-ray diffractometer with Cu Kα as the radiation source. The morphology of the composites in the form of pellets was investigated using Philips XL 30 ESEM scanning electron microscope (SEM). Temperature dependent electrical conductivity was measured by two-probe technique using a laboratory-made setup.

The planar resistance of the sensor was recorded by controlling the humidity in a closed chamber at room temperature. The humidity was first lowered by keeping $CaCl_2$ in a chamber. Controlled water vapors at room temperature were then introduced steadily for increasing the humidity inside the chamber from 10 to 95% relative humidity. Relative humidity inside the chamber was monitored by a standard precalibrated humidity meter.[24]

RESULTS AND DISCUSSIONS

Figure 2 shows the X-ray diffraction pattern for the composites having 50 wt % of cerium oxide in PANI. It is seen from Figure 2 that the cubic peak of CeO_2 indicates the crystalline nature of the composite. When comparing the XRD pattern of composite with that of CeO_2, the prominent peaks corresponding to 2θ = 33.51°, 56.04°, and 67.05°, are due to (200), (311), and (400) planes of CeO_2. The XRD diffraction studies performed on all the samples (10, 20, 30, 40, and 50 wt % cerium oxide) show that the peaks were found to be broadened, which were possible due to the formation of oxide particles. By comparing the XRD patterns of the composite and CeO_2, it is confirmed that CeO_2 has retained its structure even though it is dispersed in PANI during polymerization reaction.

Figure 3 shows the FTIR spectra of PANI-CeO_2 composites (50 wt % of CeO_2 in PANI). Polymerization of aniline can be confirmed by the presence of spectral peaks at 1566, 1487, 1298, 1244, and 1125 cm^{-1}, which may be due to PANI and 500 cm^{-1} peak corresponds to metal-oxygen stretching frequency as given in Table I.
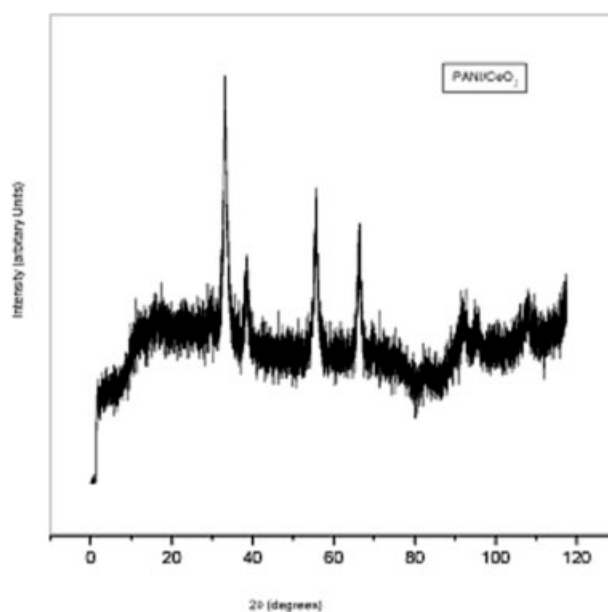

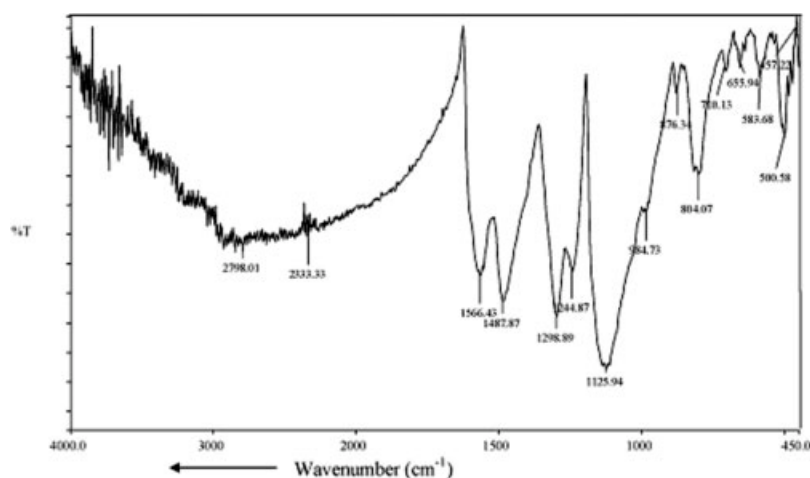**Figure 2** XRD spectra of PANI/CeO_2 composite (with 50 wt % of CeO_2 in PANI).

Figure 3 FTIR spectra of PANI/CeO₂ composite (with 50 wt % of CeO₂ in PANI).

The similar stretching frequency can also be found in other composites but intensity of metal oxygen peak increases as the wt % of CeO₂ is increased.[25,26] Metal oxygen stretching frequency of 494 cm^{-1} in pure CeO₂ shifted to 500 cm^{-1} in the composite indicates the weak interaction between CeO₂ and PANI.[27]

The SEM micrograph for 50 wt % of cerium oxide in PANI is shown in Figure 4. The composites possess grains and porous structure, and, further, the composites have capillary pores connected by pores. Such composites are likely to facilitate the adsorption of water vapors due to the large surface area and capillary pores. The SEM studies performed on all the samples indicated a transformation from a cluster pattern to a branched chain structure (or a fibrillar morphology) with increase in wt % of cerium oxide.[28]

Figure 5 shows the temperature dependent conductivity of PANI/CeO₂ (50 wt % of CeO₂ in PANI) composites. From the figure, it is observed that the conductivity is found to increase with the increase in temperature. Among the five composites, PANI/CeO₂ (50 wt % of CeO₂ in PANI) was seen to yield with highest conductivity. This sudden increase in the conductivity could possibly be explained on the basis of percolation theory. Conductivity is found to increase as the wt % of CeO₂ in PANI is increased. The increase in conductivity with increase in temperature is the characteristic of "thermal activated behavior." The decrease in resistance or increase in conductivity may be due to the increase of efficiency of charge transfer between CeO₂ and polymer chains with increase in temperature.[29,30] It is also found that the thermal curing affects the chain alignment of the polymer, which leads to the increase of conjugation length, and that brings about the increase of conductivity. Also, there had to be molecular rearrangement on heating, which made the molecular conformation favorable for electron delocalization.[31]

Figure 6 shows the characteristic response of PANI/CeO₂ composites (10, 30, and 50 wt % of CeO₂ of in PANI) as a function of relative humidity (% RH). From the figure, it can be noted that the resistance is varying almost linearly from 10 to 95% RH and is found to decrease from low humidity (dry state) to high humidity (wet state). At low humidity, when adsorption starts on the clean oxide surface, a layer of hydroxyl groups is formed. The water vapor molecules are chemisorbed through a dissociative mechanism by which two surface hydroxyls per water molecule are formed. At higher relative humidity, the water molecules adsorbed on the PANI/CeO₂ composite (50 wt % of CeO₂ in PANI) having grains and capillary pores enhance the electrolytic conduction as well as the protonic conduction by permitting capillary condensation of water molecules within the pores. The response time for sensing the humidity for an increase in relative humidity values by 10% was measured to be about 4–5 s, wherein it recovers back to the normal value in around 10 s. The samples were found to be stable more than 1 year.

The decrease in the resistance or increase in the conductivity with increasing humidity can be attributed to the mobility of the CeO₂ ion, which is loosely attached

TABLE I
IR Peak Position in PANI/CeO₂ Composite

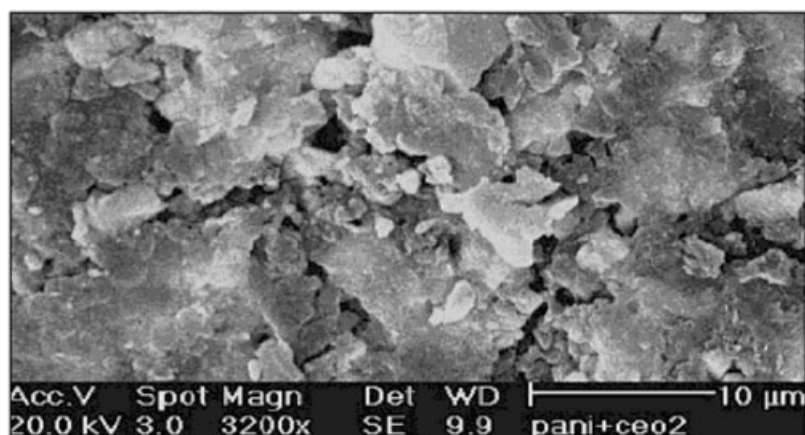| Wavenumber (cm^{-1})		Assignment
1566	PANI	Ring stretching
1487	PANI	Benzenoid ring stretching
1298	PANI	C—N stretching + CH bending
1244	PANI	C—N stretching + C—C stretching
1125	PANI	CH (ip) bending
500	PANI and CeO₂	ν_{m-o}

Figure 4 Scanning electron micrograph of PANI/CeO$_2$ composite (with 50 wt % of CeO$_2$ in PANI).

to the polymer chain by weak van der Walls' forces of attraction. At low humidity, the mobility of the CeO$_2$ ion is restricted because under dry conditions the polymer chains would tend to curl up into compact coil form. On the contrary, at high humidity, the polymer absorbs water molecules and gets hydrated, followed by the uncurling of the compact coil form into straight chains that are aligned with respect to each other. This geometry of the polymer is favorable for enhanced mobility of the CeO$_2$ ion or the charge transfer across the polymer chains and hence the conductivity.

Also, it has been reported that the conductivity of CP increases when the sample absorbs the moisture. Decrease of resistance with the increase in the humidity proves the adsorption of the water molecules, which makes the polymer more p-type in nature, i.e., the whole concentration is increased by the donation of

lone pair from the conducting complex toward the CeO$_2$ water molecules. Thus, the partial charge transfer process of conducting species with that of water molecules results in the decrease of sheet resistivity. At higher humidity level, the mechanism may be different. The almost linear variation with respect to percentage relative humidity (% RH) can be used in an amplifier circuit for converting the measured values into measurable % RH values. On careful observation of Figure 6, it is clearly seen that PANI/CeO$_2$ (50 wt % of CeO$_2$ in PANI) composite shows a linear response from 10 to 95% RH. On the other hand, in PANI/CeO$_2$ composite (10 and 30 wt % of CeO$_2$ in PANI), the resistance is found to drop down from 20 up to 50% RH in a linear fashion while, after 60% RH slightly saturation is observed with a very small decrease in the resistance up to 95% RH. In other words, we can say that, PANI/
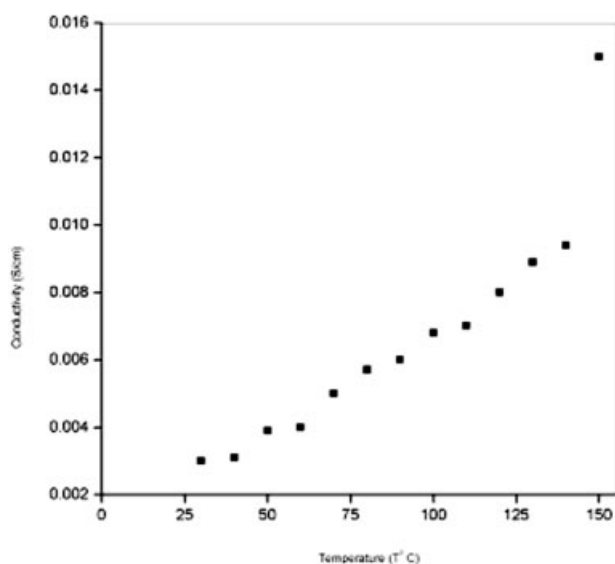

Figure 5 Temperature dependent conductivity of PANI/CeO$_2$ composite (with 50 wt % of CeO$_2$ in PANI).
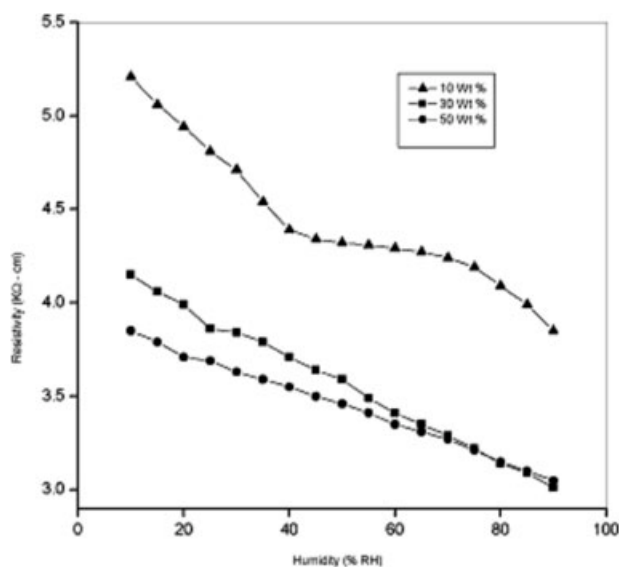

Figure 6 Variation of resistivity with change in relative humidity (%) for PANI/CeO$_2$ composites (10, 30, and 50 wt % of CeO$_2$ in PANI).

CeO_2 (10 and 30 wt % of CeO_2 in PANI) shows two step sensing response. Thus PANI/CeO_2 (50 wt % CeO_2 in PANI) shows better sensing properties and exhibits good linearity in sensing response curve.[32]

CONCLUSIONS

PANI/CeO_2 composites were synthesized by *in situ* chemical polymerization method using ammonium persulphate as an oxidizing agent. This is the novel polymerization process for the direct synthesis of emeraldine salt phase of the polymer. By comparing the XRD patterns of the composite and CeO_2, it is confirmed that CeO_2 has retained its structure, even though dispersed in PANI, during polymerization reaction. Formation of conducting emeraldine salt phases is confirmed by spectroscopic techniques. SEM micrograph clearly reveals the homogeneous distribution of CeO_2 in polymer. High temperature conductivity measurements show ''thermal activated behavior'' of the composite. The almost linear response of PANI/CeO_2 (50% of CeO_2 in PANI) composites to the broad range of humidity proves to be a competent material as humidity sensor.

References

1. MacDiarmid, A. G.; Yang, L. S.; Hunng, W. S.; Humphry, B. D. Synth Met 1987, 18, 393.
2. Mizumoto, M.; Namba, M.; Nishimura, S.; Miyadera, H.; Koseki, M.; Kobayashi, Y. Synth Met 1989, 28, 639.
3. Sukeerthi, S.; Contractor, A. Q. Ind J Chem Sect A 1994, 33, 565.
4. Ogura, K.; Saino, T.; Nakayama, M.; Shiigi, H. J Mater Chem 1997, 7, 2363.
5. Ogura, K.; Shiigi, H.; Nakayama, M.; Fujii, A. J Electrochem Soc 1998, 145, 3351.
6. Patil, R. C.; Ahmed, S. M.; Shiigi, H.; Nakayama, M.; Ogura, K. J Polym Sci Part A: Polym Chem 1999, 37, 4596.
7. Paul, W.; Ricco, A. J.; Wrighton, M. S. J Phys Chem 1985, 89, 1441.
8. Patil, R. C.; Patil, S. F.; Mulla, I. S.; Vijaymohanan, K. Polym Int 2000, 49, 189.
9. Cantalini, C.; Pelino, M. J Am Ceram Soc 1992, 75, 546.
10. Li, M.; Chen, Y. Sens Actuators B 1996, 32, 83.
11. Yagi, H.; Nakata, M. J Ceram Soc Jpn 1992, 100, 152.
12. Chung, W. Y.; Lee, D. D. Thin Solid Films 1991, 200, 329.
13. Cantalini, C.; Facio, M.; Rerri, G.; Pelino, M. Sens Actuators B 1993, 15/16, 298.
14. Nakatani, Y.; Sakai, M.; Matsuoka, M. Jpn J Appl Phys 1983, 22, 912.
15. He, F. J.; Yao, T.; Qu, B. D.; Han, J. S.; Yu, A. B. Sens Actuators B 1997, 40, 183.
16. Nakatani, Y.; Matsuoka, M. Jpn J Appl Phys 1982, 21, L758.
17. Skotheim, T. J., Ed. Handbook of Conducting Polymers; Marcel Dekker: New York, 1986.
18. Bracken, E. Sens Rev 1997, 17, 291.
19. Feng, C. D.; Sun, S. L.; Wang, H.; Segre, C. U.; Stetter, J. R. Sens Actuators B 1997, 40, 217.
20. Li, Y.; Yang, M. J.; Camaioni, N.; Casalbore-Miceli, G. Sens Actuators B 2001, 77, 625.
21. Lee, C. W.; Kim, Y.; Joo, S. W.; Gomg, M. S. Sens Actuators B 2003, 88, 21.
22. Somani, P. R.; Viswanath, A. K.; Aiyer, R. C.; Radhakrishnan, S. Sens Actuators B 2001, 80, 141.
23. Parvatikar, N.; Jain, S.; Kanamadi, C. M.; Chougule, B. K.; Bhoraskar, S. V.; Ambika Prasad, M. V. N. J Appl Polym Sci, to appear.
24. Jain, S.; Chakane, S.; Samui, A. B.; Krishnamurthy, V. N.; Bhoraskar, S. V. Sens Actuators B 2003, 96, 121.
25. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed.; Wiley: New York, 1986.
26. Ross, S. D. Inorganic, Infrared and Raman Spectra; McGraw-Hill: London, 1972; p 107.
27. Somani, P. R.; Marimuthu, R.; Mandale, A. B. Polymer 2001, 42, 2991.
28. Suri, K.; Annapoorni, S.; Sarkar, A. K.; Tandon, R. P. Sens Actuators B 2002, 81, 277.
29. Leclerc, M.; D'Aparno, G.; Zotti, G. Synth Met 1993, 55, 1527.
30. Zuo, F.; Angelopoulos, M.; MacDiarmid, A. G.; Epstein, A. J. Phys Rev B 1987, 36, 3475.
31. Kobayashi, A.; Ishikawa, H.; Amano, K.; Satoh, M.; Hasegawa, E. J Appl Phys 1993, 74, 296.
32. Kulkarni, M. V.; Viswanath, A. K. Sens Actuators B 2005, 107, 791.