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CO_2Sensing Behavior of PANi/CeO_2Composites

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***Abstract*—Carbon dioxide (CO_2) sensing using polyaniline (PANi)/ cerium oxide (CeO_2) composites has been studied in the present work. The composites prepared by insitu polymerization with 10,20,30,40 and 50 wt% of CeO_2 in polyaniline were characterized by FTIR, X-ray diffraction (XRD) and scanning electron microscopy (SEM) for confirmation of presence of CeO_2 in polyaniline matrix and the formation of the composites.On exposure of the composites to CO_2, change in resistance was observed with the increase in gas concentration. Maximum variation of resistance was observed in composite of 50wt% CeO_2 in polyaniline and maximum sensitivity for gas sensing was observed in the composite of 20wt% CeO_2 in polyaniline.**

***Index Terms*—Polyaniline, Cerium oxide, Composites, CO_2 sensing.**

I. INTRODUCTION

Conducting polymers such as Polyaniline, Polypyrrole, and Polythiophene etc. are finding potential applications in fabrication of solid state devices and chemical sensors. Among these polymers, polyaniline has gained wide spread importance because of its environmental stability, good electrical conductivity and ease of synthesis [1-12].The conductivity ofpolyaniline can be greatly altered by electrochemical redox, reversible acid/base doping and dedoping [13-14]. PANi exhibits gas sensing features at room temperature and hence is an attractive prospect for the development of a variety of gas sensors [15-17].Cerium oxide is a n-type semiconductor and its sensing behavior for various gases has been studied [18-20]. Its resistance decreases under the effect of reducing gases and increases under the effect of oxidizinggases .However, the metal oxide sensor operates at higher temperature which results in increased power consumption, reduced sensor life and limited portability. Nowadays attention is being given in synthesizing a new class of materials, known as conducting polymer composites. These composites are prepared by mixing suitably the organic and inorganic basematerials in proper form. These composite materials have fewdesirable properties from both the parent organic and inorganicclass of materials.[21–23].In the present paper, we are reporting the CO2 sensing behavior of polyaniline /CeO_2 composites.

II. EXPERIMENTAL

Synthesis of polyaniline – Cerium oxide composites was carried out by insitu polymerization technique. Analytical reagent-grade Ammonium persulfate , Hydrochloric acid and Cerium oxide (CeO2) were used for synthesis. Doubly distilled monomer aniline (0.1mol)was dissolved in 1M HCl to obtain aniline solution. Cerium oxide was added to this aniline solution with vigorous stirring to keep Cerium oxidesuspended in the solution.With continuous stirring at 0–5°C, 0.1M Ammonium persulfate,which acted as the oxidant, was added to this reactionmixture slowly. Stirring of reaction mixture was carried out for 24 hours. The polymercomposite in the form of greenish-black precipitate wasrecovered by vacuum filtration and washed with deionizedwater. The precipitate was dried in oven for 24 hours to achieve a constant weight,. In this way, polyaniline – Ceriumoxide composites with 5 different wt % of CeO_2 (10, 20,30, 40, 50) in polyaniline were synthesized. The test samples wereprepared in the pellet form (10 mm diameter and thicknessvarying up to 2 mm) by applying pressure of 10 Tons in aUniversal testing machine. The pellets were coated withsilver paste on either side. X-ray diffraction studies were performed by using Philips X-ray diffractometer with Cu $K_\alpha$as the radiation source.The FTIR spectra of the samples were recorded on a JASCO FT/IR 5300 spectrophotometer in KBr medium. The morphology of the composites in the form of pellets was investigated using Philips XL 30 ESEM scanning electron microscope (SEM).For CO_2 sensing.Thepellets were kept in the gas sensing chamber. Using a regulator and a flow meter, CO_2 is allowed to enter the gas sensing chamber at a constant rate of 20 ml/min. The variation in resistance of the composite pellets with increase in gas concentration is recorded at a regular interval of 20 seconds using a high accuracy dot-tech meter.

III. RESULTS AND DISCUSSIONS

A. *FTIR Spectra*

FTIR spectra of pure aniline and PANi/CeO_2 composite with 20 wt % of CeO_2 in PANi are shown in figure 1(a) and 1(b) respectively.The prominent peaks that are observed in polyaniline/CeO_2 composite are 2918 cm^{-1},1556 cm^{-1}, 1471 cm^{-1}, 1298 cm^{-1}, 1234cm^{-1},1107cm^{-1}, 790 cm^{-1}, 690 cm^{-1}, 617 cm^{-1},and 499 cm^{-1}.By careful observation of FTIR, the characteristic stretching frequencies in PANiare considerably shifted to lower wave numbers in PANi/CeO_2 composite. The data suggests that, there is a Vander walls kind of interaction between the polymer chain and CeO_2.

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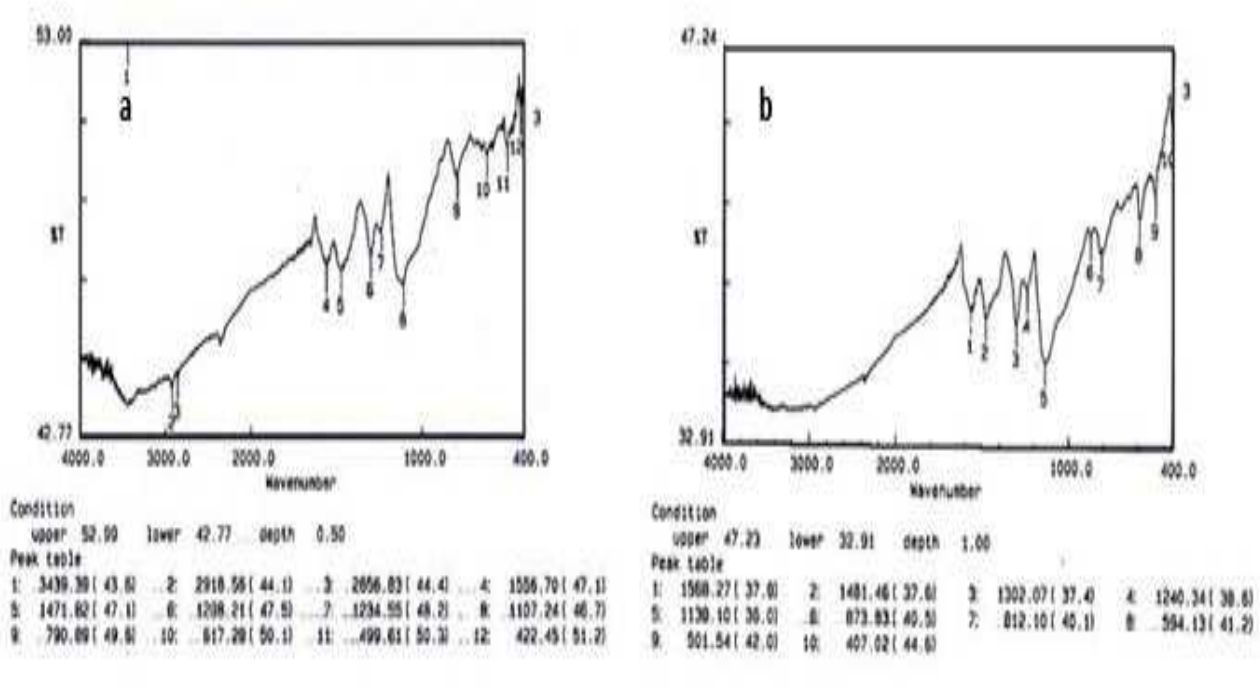

Figure 1 (a) FTIR Spectra of pure polyaniline (b) FTIR Spectra of PANI / CeO_2 Composite

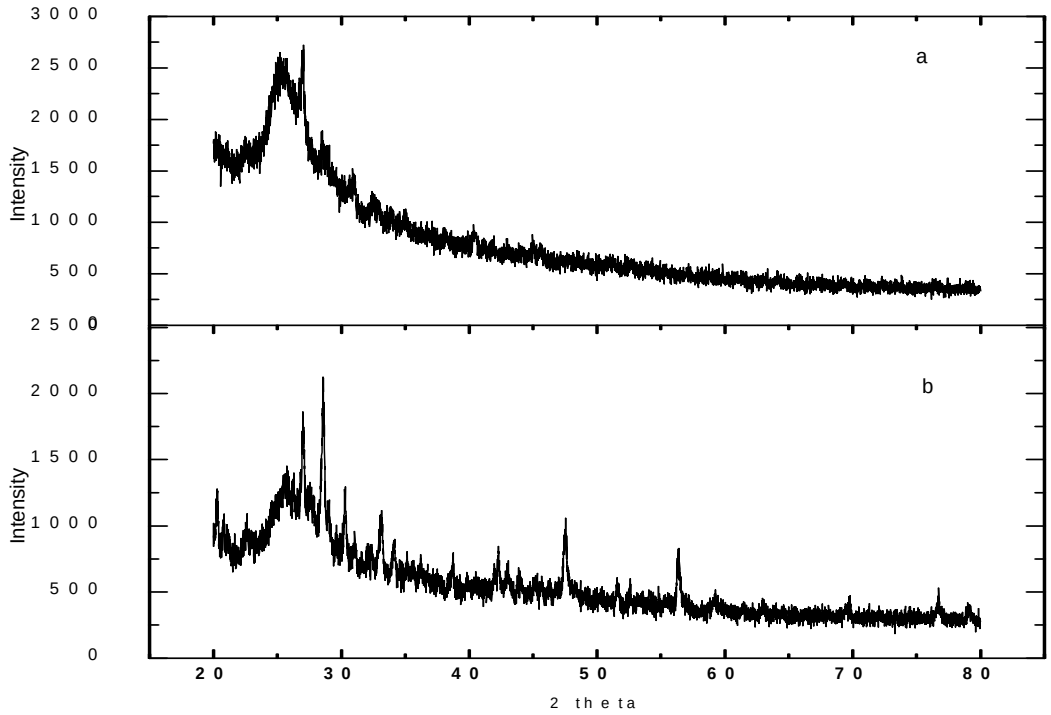

Fig.2 X-ray diffraction pattern of (a) pure PANi (b) 20 wt % of CeO_2 in polyaniline

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B. X – RAY DIFFRACTION

X-ray diffraction pattern of Polyaniline is shown in figure 2(a). The pattern shows a broad peak centered around $2\theta \approx 26^0$suggesting semi-crystalline nature of Polyaniline. X-ray diffraction pattern of Polyaniline – CeO_2 composite with 20 wt % of CeO_2 in polyaniline is shown in figure 2(b).The prominent peaks corresponding to $2\theta = 28.58^0$, 33.51^0, 47.55^0, 56.4^0 are due to (111), (200), (220), (311) planes of CeO_2 (JCPDS No. 34-0394). The cubicpeaks of CeO_2 indicates the crystalline nature of the composite. 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.

C. SCANNING ELECTRON MICROGRAPHS

Scanning electron micrograph of synthesizes conducting polyanilineis shown in figure 3(a). The micrograph of polyanilineis smooth and homogeneous. Since Hydrochloric acid is used as protonic acid in the preparation of polyaniline, the presence of microcrystalline structure can be seen which is not homogeneously distributed throughout. The presence of microcrystalline structures in polyaniline in these particular samples can be confirmed from XRD studies. The SEM micrograph of CeO_2 is as shown in figure 3(b).The SEM micrograph of polyaniline – CeO_2 composite with 20 wt % of CeO_2 in polyaniline is shown in figure 3(c). High magnification SEM image reveals the presence of CeO_2 particles uniformly distributed throughout the composite sample. A small variation in the particle dimensions of CeO_2 so dispersed in polyaniline has been observed. Also fibrillar morphology is observed in the composite.

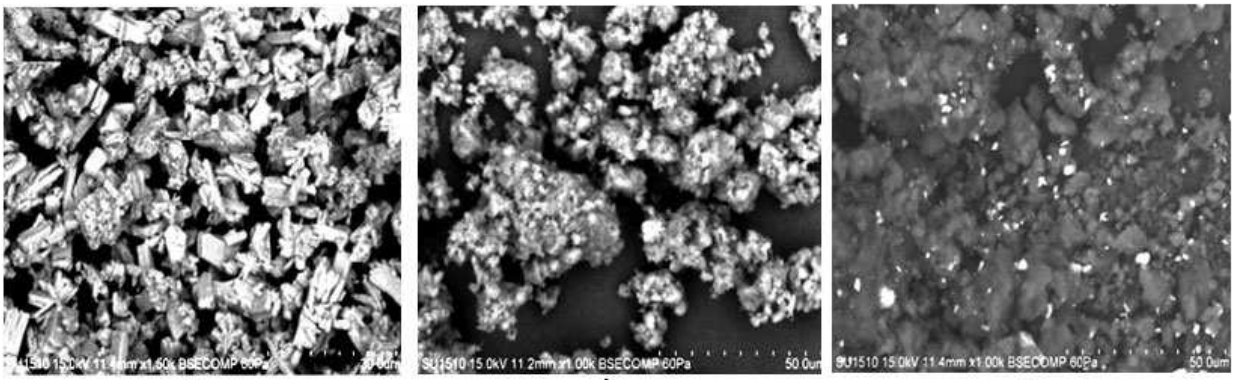

Fig. 3 SEM micrograph of (a) CeO_2 (b) purepolyaniline (c) PANi/CeO_2 composite with 20 wt% of CeO_2 in PANi

IV. SENSOR STUDIES

The change in resistance in pure PANi and PANi/CeO_2 composites when exposed to CO_2 is shown in figure 4(a). Among all the composites, 50wt % of CeO_2 in PANi exhibited maximum change in resistance. The sensitivity of PANi and PANi/CeO_2 composites for CO_2 sensing is shown in figure 4(b).Maximum sensitivity is observed in composite of 20 wt% of CeO_2 in polyaniline.

The variation in the resistance of the composites could be due the following reasons.

The CO_2 molecules induced and trapped into polymer matrix might cause it to swell leading to the disruption of conducting paths through the composites. This results in increased resistance of composites. After removal of gas, the polymer returns to original size, restoring the conducting paths.

CeO_2 is intrinsically n type semi conducting material.The possible mechanism of detection of corbon dioxide gas by CeO_2 is based on surface reactions. The adsorption of atmospheric oxygen atoms on the semi conductor surface and at grain boundaries of polycrystalline semiconductor traps the free electrons and creates an electrical double layer which acts as scattering centers for conducting electrons. When adsorbed oxygen atoms react with CO_2gas, the barrier height is increased resulting in increase of resistance . The overall conduction in a sensor element is determined by the surface reactions, the resulting charge transfer processes with the underlying semi conducting material and the transport mechanism through the sensing material and morphology of sensing layer [24].

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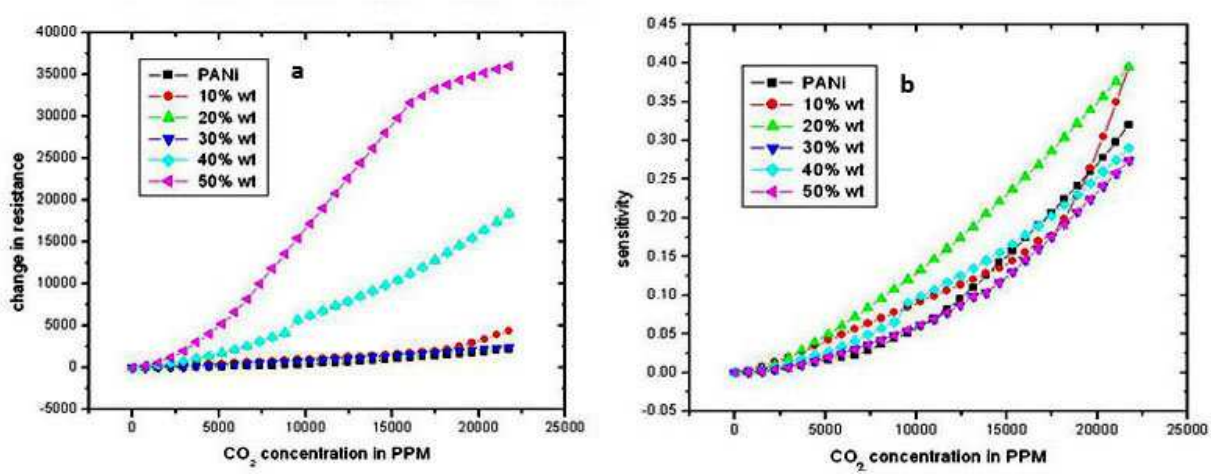

Figure 4 (a) Variation of resistance with gas concentration (b) sensitivity for CO_2 gas

Both the mechanisms mentioned above are responsible for variation of resistance in PANi/CeO_2 composites

V. CONCLUSIONS:

Polyaniline-Cerium oxide (PANi/CeO_2) composites of various weight percentages (10, 20, 30, 40, 50 wt%) were synthesized by insitu polymerization method. Retention of CeO_2 in polymer matrix was revealed in X-ray diffraction studies. Formation of PANi/CeO_2 composites was confirmed from FTIR studies. Uniform distribution of CeO_2 particles throughout the composite sample was revealed by SEM. On exposure to CO_2, change in resistance was observed in all the composites with increase in gas concentration. Maximum sensitivity for gas sensing was observed in the composite of 20 wt% CeO2 in polyaniline.

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