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Exploring potential electrical and LPG sensing properties of polyaniline-Co_3O_4 nanocomposite

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Polymer nanocomposites are an important class of materials in which recent researches are reported extensively due to their vast range of applications. Various synthetic methods are available in the literature and much importance is given to scalable processing techniques for sensing applications. The composite of polyaniline (Pn) doped with nanosized cobalt oxide (Pn/Co_3O_4) has been synthesized using a chemical oxidative polymerization of aniline in presence of various weight percentage of Co_3O_4. The structural and morphological characterizations of the prepared samples have been examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM) tool, respectively. AC conductivity of the prepared samples has been measured using the impedance technique within a frequency range of 10 KHz to 1 MHz at room temperature. Additionally, the DC electrical transport property of the composites have been experimented within a temperature range of 30-200°C. It is observed that the incorporation of nanosized Co_3O_4 into the PA matrix has an impact on the AC electrical properties of the samples. The variation in electrical resistance of both Pn and Pn/Co3O4 composites has been noted when exposed to 1000 ppm concentration of LPG gas. Both samples exhibit a quick resistance change on exposure to LPG gas with the Pn/Co_3O_4 composite demonstrating higher sensitivity and suitability for LPG sensing compared to Pn.

Keywords: Polyaniline, Co_3O_4, LPG, AC, DC, XRD, SEM

Conducting polymers dispersed with metal oxides constitute a new class of materials for various applications. Polyaniline (Pn) is one of the most interesting conducting polymer and also a promising material among the conducting polymers due to its interesting electrochemical properties, ease of synthesis, and optical properties. Additionally, due to its controlled electrical conductivity, redox characteristics, and stable environment, Pn is a particularly promising material for gas sensing applications. Pn has many active sites for gas adsorption and desorption on its backbone. Conducting polymer composite with nano sized metal oxides constitute special class of materials which enhances the properties and applications due to matrix mixing. As a result, the production of Pn composites comprising with nanosized metal oxides attracted researchers' attention in a variety of applications[1-5]. The widely used hazardous gas is liquefied petroleum gas (LPG) in domestic and commercial regions. The LPG comprises of many hydrocarbons in which propane and butane are in major compositions. Addition of ethyl mercaptan into the LPG shows significant odour when leaked. The low concentration, medium and high concentration of LPG tends to combine with air to create a flammable mixture and place very unique role in detection. Many gas sensor devices made up of metal oxide semiconductors on conducting polymers with metal oxides, plays a vital role as smart materials. The metal oxide semiconductors interact with the gas molecules to change its resistance and also depends on the temperature. Moreover the metal oxide semiconductors need much high operating temperature for lower concentration detection of gas. Therefore, the combination of metal oxide and the polymer such as conducting polyaniline play very important role in gas sensing device due to its controllable environmental stability, electrical conductivity and redox properties[6,7]. Cobalt oxide (Co_3O_4) is a p-type semiconductor that is particularly appealing for applications involving oxidation processes among the various metal oxides. The said oxide is matrixed in Pn forms semiconducting base for the use of gas sensors[8]. Therefore Co_3O_4 nanoparticles are used in many industries such as gas sensors[9], batteries[10], high performance super capacitors electrochemical cells[11] and fuel cells[10].

The present experimentation reports the synthesis of a Pn doped with cobalt oxide [Pn/Co_3O_4] using a chemical oxidative polymerization method. The Pn offers a high surface area for a gas sensing reaction. Nano sized Co_3O_4 materials nucleated over the polymer chains help to improve the conductivity and the stability. Prepared samples were characterized by characterisation tools for their phase formation. The AC characteristics of the samples were determined by the impedance technique at 10 KHz-1MHz range at RT, and the DC electrical transport properties of the composite were determined at 30 KHz-2000C range. The Pn/Co_3O_4 samples show an effect on the AC electrical properties. The electrical resistance change of the Pn and Pn/Co_3O_4 composite was measured at 1000 ppm LPG gas concentration. Both samples showed a rapid resistance change on LPG gas exposure. In addition, Pn/Co_3O_4 was found to be more sensitive to LPG sensing than Pn.

Experimental section

Materials and methods

The chemical used in the experiment were of analytic grade and solutions were prepared using double-distilled water. The Co_3O_4 was used to prepare Pn composites using chemical oxidative polymerization method. Pellets of Pn and Pn/Co_3O_4 composites with 12.4 mm diameter and 1.18 mm thickness were prepared by applying a pressure of 5 ton.

Preparation of Pn

Pn and Pn/Co_3O_4nanocomposites were prepared by *in situ* polymerisation of aniline by chemical oxidation method using ammonium per sulphate as an oxidizing agent. The aniline solution (0.2M) and hydrochloric acid (1NHCl) was prepared in separate beakers and are mixed with each other at RT. The mixer of aniline and hydrochloric acid was stirred under magnetic stirrer for 2 h to form aniline hydrochloride solution. Oxidation of PA was achieved by drop wise addition of 0.25M of ammonium persulfate as an oxidising agent in the reaction mixture over a period of 1h with continuous stirring and maintained temperature of about 5°C. Further the solution was stirred continuously using magnetic stirrer for 8 h in RT for complete oxidation reaction. Dark green coloured precipitate was obtained and is kept for overnight to sort out the particles at the base of the beaker. The as formed precipitate was filtered by using vacuum pump and washed with deionised water along with acetone and 1N HCl to remove other additives. The obtained sample was then dried in oven for 24 h at 50°C and was grinded in a pestle and mortar for fine powder[12].

Preparation of Pn/Co_3O_4nanocomposites

Different Pn/Co_3O_4nanocomposites were prepared by the addition of different weight percentage of Co_3O_4 in to the Pn matrix. 10wt%, 20wt%, 30wt%, 40wt% and 50wt% of Co_3O_4 powder was suspended in the mass fraction after substitution of oxidizing agent during *in situ* preparation of Pn as mentioned in the above procedure. Other reaction conditions remain same to form a dark green solution and contains required composite product. As earlier, the product is filtered and washed with deionised water along with acetone and dried. Further, the obtained product was grinded for its fine powder[13].

Analytical Techniques for characterisation

The sample's powder X-ray diffraction patterns are recorded using a JEOL JDX-8P diffractometer and CuKα radiation (1.54) at 30 kV. The JEOL JSM-6380 LA scanning electron microscope was employed to examine the particle morphology. Electrical studies at variable temperature were studied by Hioki LCR Q meter.

Results and Discussion

XRD study

Structural confirmations of the prepared samples were well studied by XRD tool. The XRD spectra for the pure Pn and Pn/Co_3O_4 nano composite samples were recorded in the range of 10° to 80° and are shown in Fig. 1. The XRD pattern of Pn (Fig 1(a)) shows a broad peak at 2θ angles at 28° can be assigned to the scattering from Pn at interplanar spacing, which is a characteristic of the van der Waals distances between stacks of Pn ring[14]. Existence of a broad peak in the said pattern indicates the amorphous nature of the sample. Fig. 1(b-f) shows indexed XRD pattern of Pn/Co_3O_4 nanocomposite at 10wt%, 20wt%, 30wt%, 40wt% and 50wt% of Co_3O_4 powder in the Pn matrix. Highly intensed Bragg's reflections are observed in all the patterns indicate the formation of crystalline nature of the samples. The XRD composite pattern exhibits well defined diffraction peaks obtained at 18.93°, 31.04°, 36.36°, 45.02°, 59.14° and 65.12° 2θ angles corresponding to the (hkl) planes (111), (220), (311), (400), (511) and (440), respectively for the phase of the cobalt oxide with reference to standard JCPDS card No. 42-1467[15-17]. In all the patterns, diffraction peak at 25°is observed, which is corresponding to PA. No characteristic peaks other than Co_3O_4 were observed which signify the purity of the samples. The average crystallite size of Pn was determined by using Scherrer's formula $D = K\lambda / \beta Cos\,\theta$, where $\lambda = 1.54060$ Å, θ is the Bragg angle, K is the Debye Scherrer constant and β is the peak full width at half maximum of the peak. The average crystallite size of Pn/Co_3O_4nanocomposite samples was found to be 23 nm.

SEM study

Morphology of the defined samples was well studied by SEM analysis. The SEM images of pure Pn and Pn/Co_3O_4 nano composite samples are shown in Fig. 2. The morphology of Pn (Fig. 2(a)) is irregular and non-fibrous with high density responses of the poor crystalline nature. SEM images of Pn/Co_3O_4 at10wt%, 20wt%, 30wt%, 40wt% and 50wt% of Co_3O_4 powder in the Pn matrix are shown in Fig. 2(b-f), respectively. These composite samples show irregularly arranged granular flakes with sharp edges with appearance of non-porous nature. Spherical particles with a few oval-like particles are randomly distributed. Also, spherical shape particles are uniformity distributed with several agglomerations. Fine particle networking with distribution of Co_3O_4 particles in the Pn matrix enhances the crystallinity of the composites as compared with pure Pn. Varied particles are irradiated with each other in the polymer matrix develops the diffracting phases in the amorphous polymer and upgrades the crystallinity of the composite samples[18-20].

AC electrical conductivity

The unique electrical conductivity character of polymers is due to the presence of π-conjugated system. The mechanism is often dominated by the conductivity of polymers, wherein the conjugated chain is traversed by mobile charge carriers, polaronsand bipolarons. In addition, charge carriers are included to the π-conjugated system once the polymer is doped[21]. In the present experiment, the AC conductivity measurements of the prepared samples were recorded by a two probe method. The frequency dependent AC electrical conductivity of Pn and

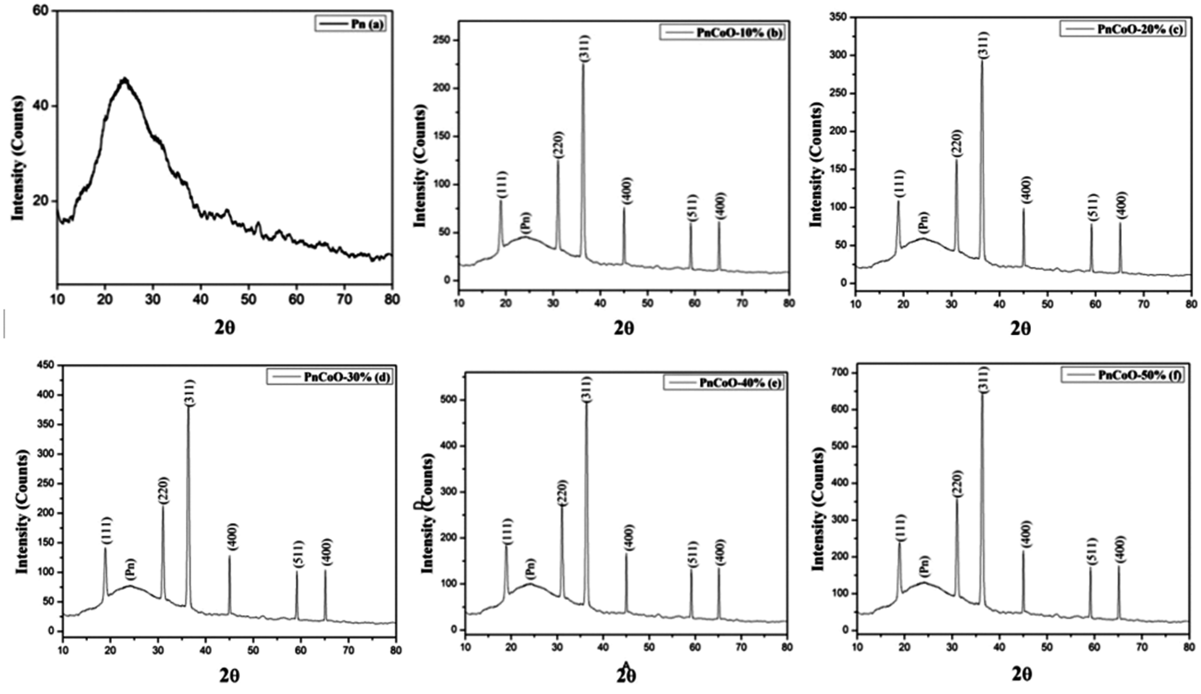

Fig. 1 — XRD pattern of (a) Pn (b-f) Pn/Co_3O_4nanocomposite with10wt%, 20wt%, 30wt%, 40wt% and 50wt% of Co_3O_4

Pn/Co_3O_4 nanocomposites was depicted in Fig. 3(a). The conductivity of the samples increases with increase in frequency of the samples. An increment of 1 order of conductivity of Pn/Co_3O_4 composite compared to the Pn was observed. Fig. 3(b) indicates the AC conductivity as function of different wt% of Co_3O_4. The conductivity of the composite material found increasing with increase in the content of Co_3O_4 in the Pn matrix[22-25]. This is due to the increase of isolated polarons and bipolarons and may be due to interfacial polarization[26].

DC electrical conductivity

The temperature dependent DC electrical conductivity of prepared samples was recorded to describe the charge transport mechanism in the Pn composites. The variation in the DC conductivity with change in temperature of Pn and Pn/Co_3O_4 composites was conducted and is represented in Fig. 4(a). The figure shows that, the DC conductivity of the pure PA and doped Pn samples increases with increase in temperature and exhibits the semiconductor behaviour and it is also found to increase with increase in the content of Co_3O_4 in the Pn matrix. This indicates that the Co_3O_4 particles give positive influence on composite towards increase in conductivity. The DC conductivity of composites showed higher conductivity compared to Pn due to increase of efficiency of charge transfer between the polymer chains and the dopant with increase in temperature. The conjugation length might have been increased which caused the increase in conductivity as

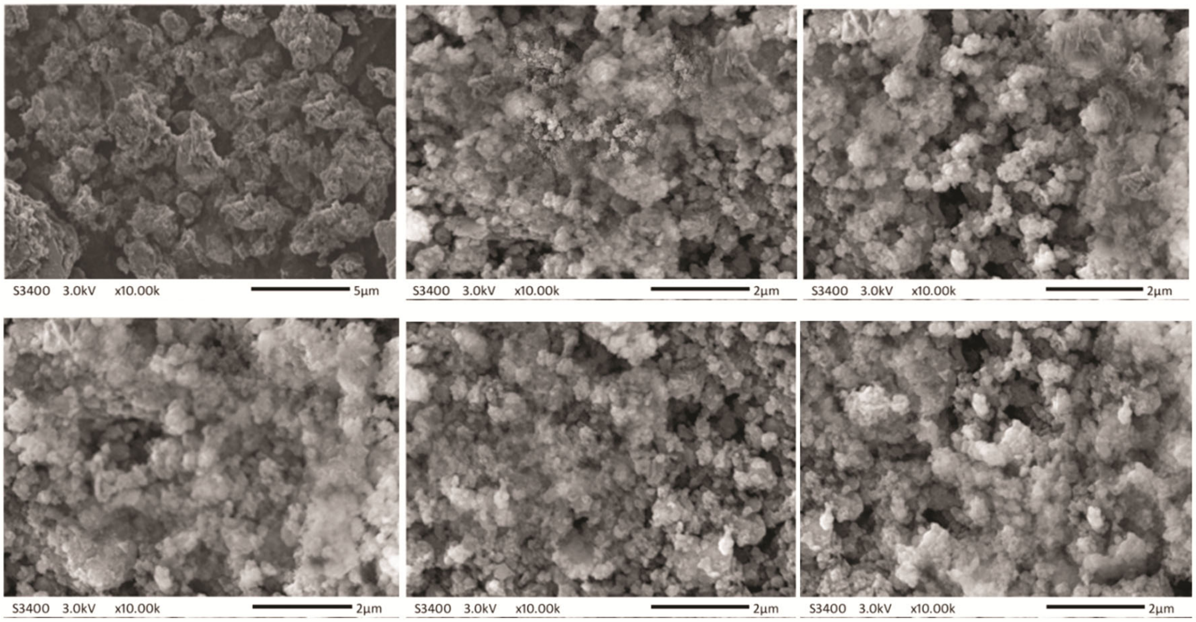

Fig. 2 — SEM image of (a) Pn(b-f) Pn/Co_3O_4nanocomposite with 10wt%, 20wt%, 30wt%, 40wt% and 50wt% of Co_3O_4

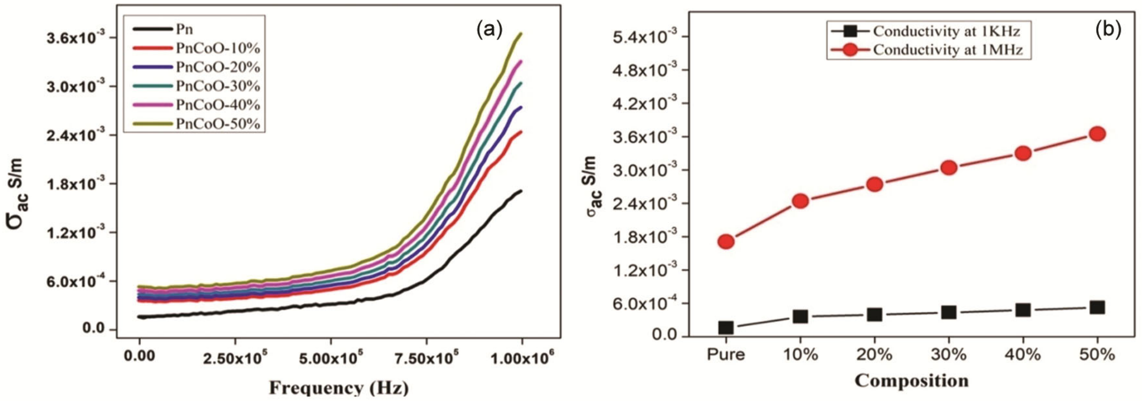

Fig. 3 — AC conductivity of Pn and Pn/Co_3O_4 composites a) as function of frequency b) as function of percentage of Co_3O_4

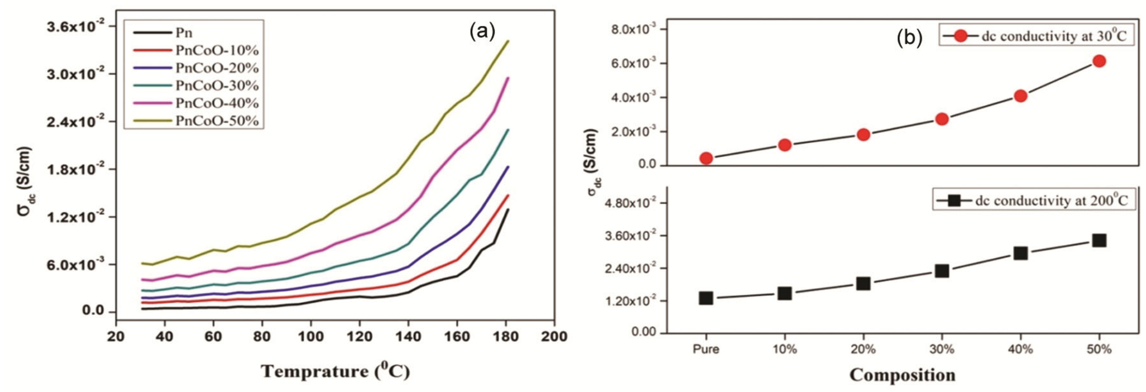

Fig. 4 — DC electrical conductivity of Pn and Pn/Co_3O_4 composite a) as function of frequency b) as function of percentage of Co_3O_4

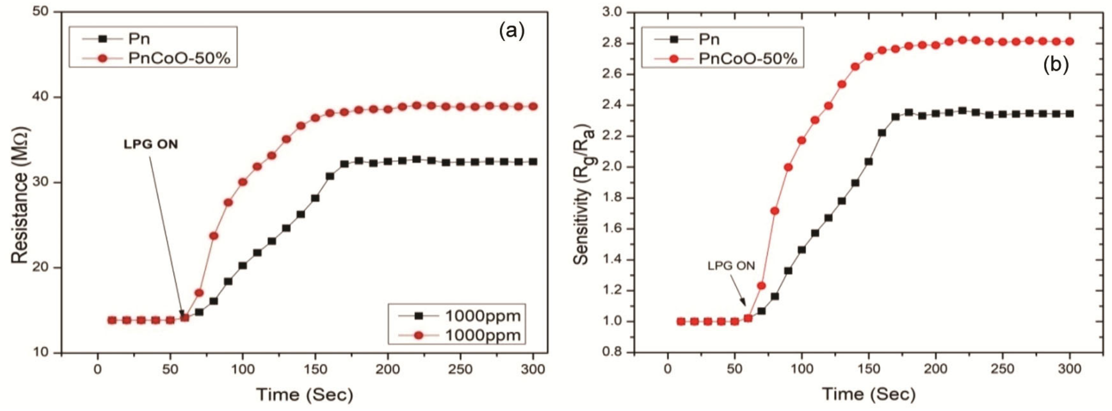

Fig. 5 — Variation of (a) resistance as a function of time for of Pn and Pn/Co_3O_4 composite (b) sensitivity as a function of time for of Pn and Pn/Co_3O_4 composite

thermal curing affects the chain alignment of polymer[27]. Fig. 4(b) indicates the DC conductivity as function of different wt% of Co_3O_4 in Pn matrix. The result shows that the Co_3O_4 has positive influence on the temperature dependent conducting property of the Pn. The DC conductivity of both samples increases in two phases, *i.e*. low temperature region and high temperature region. There is higher order increase in the conductivity at higher temperature phase and lowered conductivity at low temperature phase. The increase in conductivity of the samples at higher temperature is due to excitation of electrons to the conduction band[28-31].

LPG sensing studies

The gas sensing study of the Pn and 50wt% of Co_3O_4 dispersed PA is considered as a representative composite sample. Pn and Pn/Co_3O_4-50% composite samples upon interaction with LPG at 1000ppm concentration at RT was studied by calculating change in the resistance of sensing samples with time toward LPG exposure using two probe method. The variation in the electrical resistance and sensitivity of the samples as function of time at 1000ppm was depicted in Fig. 5(a) and 5(b), respectively. Initially, the resistance of the samples was found to be stabilized due to introducing air into the gas chamber using flow meter to establish the equilibrium between oxygen adsorbed at surface of the samples and atmospheric oxygen. The stabilized resistance at this state is known as resistance in the presence of air (Ra). When the resistance was found stabilized, then the LPG of 1000ppm concentration was injected in the gas chamber and the resultant change in the electrical resistance was noted. The resistance of the Pn and Pn/Co_3O_4 composite increases linearly with time when exposed to 1000ppm LPG concentration and reaches to steady state. It is observed from the plot that, the samples required 170 seconds to attain maximum resistance with composite at higher resistance compared to Pn. This increase in the resistance of the samples may due to the transfer of electrons from PA to gas molecules. A weak charge transfer between the polymer matrix and the analyte gas is the reason why electrons are removed by the gas in Pn[32]. This change in resistance is attributed to the fact that when LPG interacts with PA, the mobility decreases and resistance across the sample increases[33]. The change in the resistance is known as resistance in the presence of LPG (Rg). The higher change in the resistance of the composite was observed compared to PA. The change in sensitivity of the Pn and Pn/Co_3O_4 composite as a function of time is shown in Fig. 5(b). The sensitivity of the samples in terms of normalized resistance calculated by sensitivity = Ra/Rg and the Rg is the resistance of the sensor in presence of LPG gas and Ra is the initial stabilized resistance of the pallet. The composite material exhibits a higher change in sensitivity in comparison to Pn. These figures reveal that, the response of Pn and composite increases rapidly upon introduction of LPG gas and become stable within few seconds[34].

Conclusions

The successful synthesis of Pn and Pn/Co_3O_4 nanocomposite were achieved by chemical oxidative polymerisation technique in presence of oxidising agent. Prepared samples were well characterised for its phase confirmation. The increase in conductivity of the samples at higher temperature is due to excitation of electrons to the conduction band. The LPG sensing property describes almost linear variation in the composites electrical resistance are stable and assist in holding the molecules of the vapour and this to be a proficient material for sensing LPG. The composite shows greater sensitivity at 1000ppm compared to the Pn. Therefore, the composite can be a promising material for LPG sensing applications.

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