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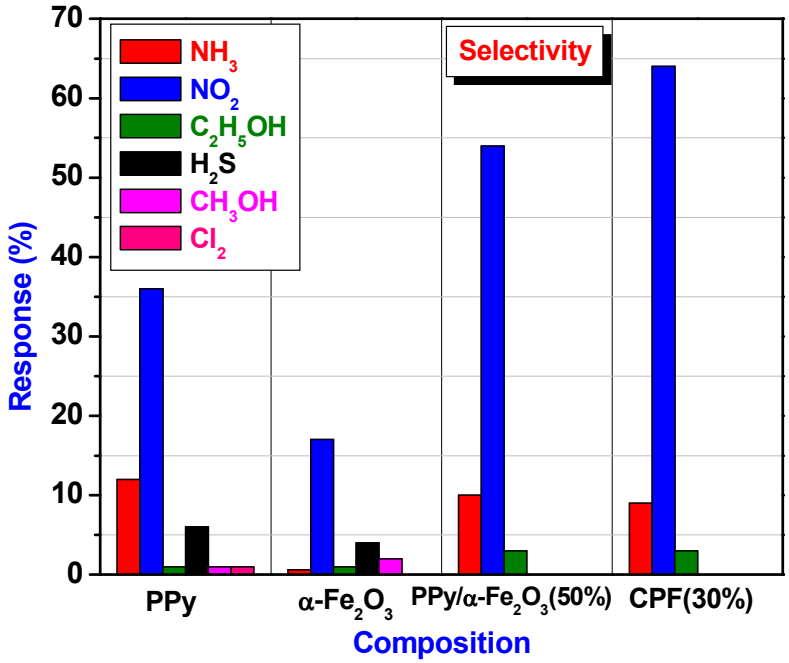

Camphor sulfonic acid doped PPy/α-Fe_2O_3 hybrid nanocomposites as NO_2 sensors

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Abstract

PPy/α-Fe_2O_3 hybrid nanocomposites with different weight percentages (10-50%) of CSA were successfully prepared by using solid state synthesis method. Thin films of prepared hybrid nanocomposites were deposited on glass substrates using spin coating technique and have been characterized using various techniques such as XRD, FESEM and TEM. The gas sensing performance of 10-50% CSA doped PPy/α-Fe_2O_3 nanocomposite thin films were studied towards NO_2, Cl_2, NH_3, H_2S, CH_3OH and C_2H_5OH gases. Among various compositions, 30% CSA doped thin films were found to be highly sensitive and selective towards NO_2 gas at room temperature i.e. chemiresistive response of 64% at 100 ppm with a reasonably fast response time of 148 sec. The sensor responses in relation to the CSA doping concentration and the gas concentration have been systematically studied. Additionally, other sensing properties such as reproducibility, cross-sensitivity, sensing linearity and stability were also studied and explored. The CSA doped PPy/α-Fe_2O_3 nanocomposites exhibited better response, stability and shorter recovery times as compared to PPy and PPy/α-Fe_2O_3 nanocomposites alone. Therefore, it is expected that such material with excellent gas sensing properties at room temperature can be used for high performance selective NO_2 sensors.

Keywords: CSA; PPy/α-Fe_2O_3 hybrid nanocomposites; NO_2 sensor; sensing properties;

1. Introduction

Gas sensor devices are used for the process control in chemical industries, prevention of hazardous gas leaks and for the detection of toxic pollutants. The current research in the field of gas sensors has been focused on the development of low cost efficient sensor devices for detection of toxic and hazardous gases, which have the characteristics of high response, selectivity towards target gas and rapid response time. Nitrogen dioxide, NO_2, is one of the toxic, flammable, colorless, hazardous and harmful gases, even at very low concentration; produced by many of the processes such as production of nitric acid, combustion of the exhaust of automotive engines, automobile exhaust fumes, industrial combustion of fossil fuel, home heaters and exhaust of motor vehicles, etc. [1]. Furthermore, NO_2 can be found in industries where the burning of diesel fuel takes place. Therefore, it is necessary to develop low cost sensors for the detection of NO_2 at a low concentration (5-100 ppm) has become increasingly important for industrial level in order to avoid risks that may occur due to nitrogen dioxide gas [2].

Inorganic nanostructured metal oxides such as ZnO, SnO_2, TiO_2, MoO_3, WO_3 and Fe_2O_3, etc. have been evaluated as gas sensing materials over the past several years [1-6].Furthermore, the disadvantages of the nanostructured metal oxide based sensors is their high temperature operation (200-450^oC) along with long term instability [4,5]. Conducting polymers have replaced nanostructured metal oxides for gas sensing activity owing to their operation under room temperature conditions [4]. Recently, conducting polymers such as polyaniline, polythiophene and polypyrrole have been extensively studied because of their good electrical and mechanical properties, which can be exploited in sensors and electrochromic devices [7, 8].Among the various conducting polymers, Polypyrrole (PPy) has attracted much interest because it is easily synthesized by chemical and electrochemical methods as well as it has excellent environmental

stability [9].Furthermore, PPy have been used as a good sensing material because of its gas sensing ability at room temperature conditions and easy sensor element processing [10,11]. However, there are also some disadvantages with PPy is its low chemical stability, insolubility and limited mechanical strength that are unfavorable for conducting polymer related applications. In order to overcome these problems, preparation of organic polypyrrole/inorganic nanoparticles hybrid nanocomposites has been considered to provide a suitable solution to the processability problem.

Over the past several years, organic/inorganic hybrid nanocomposite materials for gas sensing applications have been found an area of increasing research [12-15]. Combining the properties of the organic conducting polymers and inorganic metal oxides will help in the generation of the new class of gas sensing materials with synergistic or improved properties which can overcome the drawbacks coming from the single counterparts [16].

Doping is an effective and simple way to improve the gas sensing properties of the materials [17]. Furthermore, doping with various acids such as β-naphthalene sulfonic acid (NSA), camphor sulfonic acid (CSA), and dodecyl benzene sulfonic acid (DBSA) etc. influences the gas sensing properties by changing the chemical and structural nature of polymer and also creating more active centers which improves sensor response [18,19].

In the present work, we made an attempt to improve the gas sensing properties of PPy/α-Fe_2O_3 hybrid nanocomposites by adding different weight percentages (10-50%) of camphor sulfonic acid (CSA) dispersed into PPy/α-Fe_2O_3 hybrid nanocomposites using solid state synthesis method. Thin films of 10-50% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposites were fabricated using drop casting on glass substrates and characterized using various techniques such as XRD, FESEM and TEM , as well as their room temperature gas sensing performance towards various

oxidizing (NO_2,Cl_2) and reducing (CH_3OH, C_2H_5OH, H_2S, NH_3) gases were tested. For a comparison, thin films of PPy and PPy/α-Fe_2O_3 nanocomposites were also prepared separately and their gas sensing performance evaluated along with the 10-50% CSA doped PPy/α-Fe_2O_3 films for sensing NO_2 gas operating at room temperature.

To the best of our knowledge and literature survey, till today, there is no attempt has been made to prepare CSA doped PPy/α-Fe_2O_3 nanocomposites and study their room temperature gas sensing properties. So here, we made first ever attempt to study 10-50% CSA doped PPy/α-Fe_2O_3 thin films for the application of room temperature NO_2 gas sensor.

2. Experimental

2.1 Materials

Iron chloride hexahydrate (AR grade, Aldrich Chem. Ltd, India), methanol (AR grade, Sd Fine Chem. Ltd, India), Pyrrole (AR grade, Aldrich Chem. Ltd, India), ammonium per sulphate (AR grade, Sd Fine Chem. Ltd, India) and camphor sulfonic acid of 99.9% purity (AR grade, Aldrich Chem. Ltd, India).

2.2 Preparation of PPy/α-Fe_2O_3 nanocomposites

The PPy/α-Fe_2O_3 nanocomposites were prepared by solid state synthesis route by adding different weight percentage of α- Fe_2O_3 (10%-50%) nanoparticles in PPy matrix and has been described in our previous reports [20].

2.3 Preparation of CSA doped PPy/α-Fe_2O_3 nanocomposites

Hybrid nanocomposites of CSA doped PPy/α-Fe_2O_3 were prepared by adding different weight percentage of CSA (10%-50%) into PPy/α-Fe_2O_3 nanocomposite matrix by using solid state synthesis method. For formation of thin films, CSA doped PPy/α-Fe_2O_3 hybrid nanocomposites

were dissolved in m-cresol and stirred for 11 hours at room temperature to get casting solution. In order to prepare thin films, the casting solution was deposited on glass substrates (10x10mm) using drop casting and dried on hot plate at 50^{o}C for 10 min.

2.4 Characterization techniques

X-ray diffraction analysis of prepared samples was carried out using X-ray diffractometer (Model: PW-3710, Holland) with CuK_{α} radiation (λ = 1.5406 Å) in 2θ range of 10^{o}–80^{o}.

Surface morphology of the films was imaged using field emission scanning electron microscopy (FESEM) [Model: MIRA3 TESCAN] operating at 20 kV. The TEM image of prepared samples was carried out using Hitachi Model H-800 transmission electron microscopy. Thickness of the 30% CSA doped PPy/α-Fe_2O_3 film was recorded on Ambios XP-1 surface profilometer and it is found to be 597 nm.

In order to measure the room temperature gas sensing characteristics of the films, custom fabricated room temperature gas sensing measurement unit was used and which is reported elsewhere [16]. The change in the resistance of the films as a function of time was measured in fresh air ambient and in gas atmosphere. For the resistance measurement, two silver electrodes (1 cm apart from each other) are drawn on sensing materials for the contacts. Sensor was then mounted in an air tight stainless still chamber having volume of 250 cm^3. The change in resistance of the sensor films was measured using a Keithley 6514 System Electrometer, which was controlled by a computer. A desired concentration of the test gases (NO_2, NH_3, C_2H_5OH, Cl_2, H_2S, and CH_3OH) in the chamber is achieved by injecting a known quantity of gas using syringe. All the test gases were commercially procured from M/s Shreya Enterprises Pvt. Ltd. Mumbai, India. Once a steady state was achieved then the recovery of sensors was recorded by

exposing the sensors to fresh air, which is achieved by opening the lid of the stainless still chamber. The response (S) of the sensors was calculated using the relation,

$$S\ (\%) = |R_a - R_g| / R_a * 100\ \% \quad \text{..... (1)}$$

where R_a and R_g are the resistance values of the sensor films in fresh air and test gas respectively. Response time and recovery time of the sensor were defined as the times needed for 90% of total change in resistance upon exposure to test gas and fresh air, respectively.

3. Results and discussion

3.1 XRD analysis

Fig. 1(a) shows the X-ray diffraction pattern of 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite. The diffraction pattern of 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite showed sharp and well defined diffraction peaks, which are similar to that of reported PPy/α-Fe_2O_3 nanocomposite [20] indicating the diffraction pattern of PPy/α-Fe_2O_3 is not modified due to the presence of CSA and which attributed to the interaction between PPy/α-Fe_2O_3 nanocomposite and dopant CSA. Furthermore, the new diffraction peaks at $2\theta = 13.78^o$, 15.35^o, 16.27^o, 18.12^o, 19.46^o and 20.44^o in the diffraction pattern of CSA doped PPy/α- Fe_2O_3 hybrid nanocomposites belong to CSA and which are in good agreements with reported diffraction peaks available in literature [21,22].

3.2 FESEM and TEM analysis

FESEM micrograph of the 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite [Fig.1 (b)] shows spherical granular morphology in which spherical grains are agglomerated each other with high porosity and such a porous morphology is suitable for gas sensing application because porous surface morphology provides higher surface area to volume ratio as well as the gas

diffusion occurs more easily through porous structure hence increases the reaction between gas molecules and the surface of the films excepted to be higher response [23, 24].

The typical TEM image of 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite thin film [Fig. 1(c)] shows approximately spherical shaped nanoparticles, which are interconnected each other. Here the dark shaded α-Fe_2O_3 nanoparticles are found to be entrapped into light shaded PPy matrix with an average diameter is around 32 nm. The cross-section SEM micrograph of 30% CSA doped PPy/α-Fe_2O_3 film is shown in Fig.1 (d). It is seen that, the deposited film is strongly adherent to the substrate with 0.592 μm thickness and it is well matches with the thickness observed from Ambios XP-1 surface profilometer.

3.3 Gas sensing characteristics

3.3.1. NO_2 sensing properties of CSA doped PPy/α-Fe_2O_3 thin films

Our main aim is to develop and prepare a polymer based sensor material, which is stable, reproducible, more selective and operating at room temperature. Therefore, in the present study we made an attempt to improve the selectivity, sensitivity and stability of PPy/α-Fe_2O_3 hybrid nanocomposite sensor by addition of different weight percentage of camphor sulfonic acid (CSA) by solid state synthesis method. The gas sensing properties of pure PPy, α-Fe_2O_3 and PPy/α-Fe_2O_3 hybrid nanocomposites was described in our previous reports [16, 25, 26].

In the present experiment, room temperature gas sensing characteristics of 10-50% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite thin films was systematically investigated upon exposure to 100 ppm of various oxidizing and reducing gases such as NO_2 Cl_2, H_2S, NH_3, C_2H_5OH and CH_3OH using room temperature two-probe resistance measurement set-up.

Among 10-50% CSA doped compositions, 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite thin film showed highest response (64%) towards 100 ppm NO_2 gas. The response of different

doping concentrations of CSA into PPy/α-Fe_2O_3 nanocomposite towards fixed 100 ppm concentration of NO_2 gas is shown in Fig. 2(a). The higher sensor response of 30% CSA doped PPy/α-Fe_2O_3 nanocomposite thin film towards NO_2 gas is mainly due to the porous microstructure [shown in Fig. 1(b)] which could give a fine pathway for electron transfer in the gas sensing process as well as higher surface area to volume ratio of the film, which results in increases the reactions between NO_2 gas molecules and surface of the film and hence increases the sensor response [23, 24].

3.3.2 Selectivity study

Selectivity of the chemical sensor is an important consideration and it is defined as, the ability of a sensor respond to a certain gas in presence of other test gases. Fig.2 (b) shows the selectivity histogram of PPy, α-Fe_2O_3, PPy/α-Fe_2O_3 and 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite thin films.

The selectivity coefficient (K) of 'target gas' to 'another gas' is calculated using the following relation and the calculated results are displayed in table1,

$$K = (S_A/S_B) \quad \ldots\ldots (2)$$

Here S_A and S_B are the responses of sensor film to the target gas 'A' and another gas B, respectively.

Histogram shows, 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite thin film exhibit higher sensor response (64%) towards 100 ppm NO_2 gas with high selectivity. In the present study, the negligible cross response to NH_3 and C_2H_5OH gases is observed, which can leads to more reliable screening of nitrogen dioxide gas. Furthermore, no response is observed to H_2S, CH_3OH and Cl_2 gases, illuminating that the sensor based on the CSA doped PPy/α-Fe_2O_3 hybrid material

has good selectivity towards NO_2 gas and is found possible application for detecting highly toxic NO_2 gas in low ppm level at room temperature without interfering with other toxic gases.

Based on the observed results, it can be concluded that the formation of CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite is effective not only in enhancing the relative response factor of the sensor but also in making it selective for the detection of NO_2 gas at room temperature.

3.3.3 Response study of CSA doped PPy/α-Fe_2O_3 films towards NO_2 gas

We have systematically carried out the dependence of gas sensing response of 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite thin films towards NO_2 gas with different concentrations (5-100 ppm) at room temperature and the observed results are displayed in Fig.3 (a). It was observed that, the gas response increases linearly as the concentration of NO_2 gas is increased from 5 ppm to 100 ppm. The response of CSA doped PPy/α-Fe_2O_3 sensor was found to 7%, 12%, 14%, 26%, 40%, 55% and 64% with increasing NO_2 gas concentration from 5 to 100 ppm respectively. Above 100 ppm NO_2 gas concentration, the response of sensor was remaining constant, which indicates the sensor reaches saturation state above 100 ppm. The higher response towards NO_2 gas can be explained on the basis of different surface interactions between active layer of the film and adsorbed gas (herein NO_2). The lower NO_2 gas concentration leads to a lower surface coverage of gas molecules, resulting into lower surface interactions between the NO_2 gas molecules and the surface of the film. On the other hand, with increase in the NO_2 gas concentration increases the interactions between the NO_2 gas molecules and the surface of the film due to a larger surface coverage. If the concentration of gas increased above 100 ppm then the available surface area was found to be saturated with the NO_2 gas molecules, which eventually stabilized the interactions between the NO_2 gas molecules and the surface of the film [27]. Based on the above observation, the 100 ppm NO_2 gas concentration was found to be

sufficient. Thus, the maximum gas response (64%) was obtained at room temperature for the exposure of 100 ppm of NO_2 gas. The relationship between response and NO_2 gas concentration of 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite films is shown in Fig.3 (b).

3.3.4 Sensing mechanism

It is noted that, the gas sensing mechanism is based on the resistance changes occurring upon exposure to the various target gases as well as number of available active sites for the adsorption of various test gases on the surface of sensor [28, 29]. In order to enhancing the gas response of the sensors various parameters such as film thickness, crystallite size, porosity, nature and amount of dopant, catalysts and surfaces states plays an important role [30]. Here, we use dopant CSA to enhance the gas response of polymer based PPy/α-Fe_2O_3 hybrid nanocomposite sensor. The dopant CSA changes the chemical and structural nature of polymer nanocomposite and also creating more active centers for adsorption of gas [18, 19]. The response of CSA doped PPy/α-Fe_2O_3 films has been estimated from the measured value of resistance in presence of fresh air and NO_2 gas respectively. Fig.4 (a) shows the change in the resistance value of the sensing element (CSA doped PPy/α-Fe_2O_3 thin film) on exposure to 100 ppm of NO_2 gas as a function of time. The sudden decrease in the value of resistance is observed on exposure to oxidizing NO_2 gas. The recovery of the sensor is achieved by introducing fresh air into the test chamber. The interaction of oxidizing NO_2 gas (electron acceptor) with CSA doped PPy/α-Fe_2O_3 hybrid nanocomposites withdraw electrons from the CSA doped PPy/α-Fe_2O_3 hybrid nanocomposites, which results in increasing the conductivity of material (film resistance decreases). Figure 4 (b) shows proposed energy band diagram for CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite with the interaction of NO_2. Here, α-Fe_2O_3 (n-type) nanoparticles form a barrier layer with polymer matrix leading to the formation of depletion region (Wo). The interaction of the surface of CSA

doped PPy/α-Fe_2O_3 hybrid nanocomposite film with NO_2 gas sensing molecules affects the width of depletion region (Wo) and therefore, modulates the conductivity of the sensing element. The depletion region decreases (WNO_2) with the reduction of electrons (by adsorption of NO_2 gas molecules) in the CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite giving a high conductivity. In the present study, CSA enhances the rate of reaction by providing the additional active sites to the PPy/α-Fe_2O_3 nanocomposite. When the CSA doped PPy/α-Fe_2O_3 thin films were exposed to NO_2 gas then the corresponding changes are transferred immediately to the polymer matrix reflected as a fast drop in the resistance of the sensor film. Because of decrease in resistance the width of the depletion region decreased (WNO_2) and the conductivity of the material increased. Obviously, the gas sensing response has been significantly improved by introducing CSA into PPy/α-Fe_2O_3 hybrid materials. Therefore, it is suggested that this kind of hybrid nanocomposite can be reliably used for gas sensor material for detecting the low concentration of NO_2 gas at room temperature. For a typical sample response time of 148 sec. and recovery time of 3949 sec. was observed.

3.3.5 Reproducibility and Stability study

The reproducibility and stability of sensing device is also very important for practical applications of gas sensors. In order to check the reproducibility in sensing, the sample (30% CSA doped PPy/α-Fe_2O_3 thin film) was tested at 100 ppm for various cycles and the results are displayed in Fig.5 (a). The reproducibility in the sensing properties upon repeated exposure and removal of NO_2 gas can be clearly seen. It is well known that, polymer based sensors have common drawback of decrease in the sensor response due to aging inducted effects i.e. humidity effects. Therefore, the aging effect on the performance of 30% CSA doped PPy/α-Fe_2O_3 thin film sensor was studied.

Long term stability measurements performed on 30% CSA doped PPy/α-Fe_2O_3 thin film over a period of 40 days upon exposure of fixed 100 ppm NO_2 concentration and observed results are displayed in Fig.5 (b). From figure it is seen that, the performance of the sensor became stable after 15 days with 92% stability, which is higher than that of PPy (55%) and PPy/α-Fe_2O_3 nanocomposite (85%). The stability performance indicates that, the effect of humidity on NO_2 response properties of CSA doped PPy/α-Fe_2O_3 films remains negligible. The reliable detection of NO_2 gases in low ppm level (5 ppm) using CSA doped PPy/α-Fe_2O_3 films makes them attractive candidates for gas sensing application. More important, our CSA doped PPy/α-Fe_2O_3 films exhibit reversible gas sensing characteristics with good stability at room temperature and are adherent, therefore can have longer operating life.

4. Conclusions

The gas response study of camphor sulfonic acid doped organic–inorganic materials is in the beginning at present. In order to explore new gas sensing materials, and explain the gas sensing mechanism and supplement the deficiencies of the present sensing materials (CSA doped PPy/α-Fe_2O_3 nanocomposites) are all the emphases in the future. In present study, we have systematically investigated room temperature gas sensing characteristics of CSA doped PPy/α-Fe_2O_3 thin films a host of gases i.e. H_2S, NH_3, CH_3OH, C_2H_5OH, Cl_2 and NO_2.PPy/α-Fe_2O_3 hybrid nanocomposite thin films with various percentages (10-50 wt. %) of CSA were deposited on glass substrates using spin coating technique. It was found that, 30% CSA doped PPy/α-Fe_2O_3 sensor films are highly selective and sensitive towards NO_2 gas and exhibited a linear dependence of NO_2 sensor response between concentrations from 5 to 100 ppm. These sensors have fast response time of 148 seconds. The sensor responded towards NO_2 gas concentrations as low as 5 ppm and which is much lower than the lowest detection limit (25 ppm) of NO_2. All

the gas sensing results indicate that, the sensor based on CSA doped PPy/α-Fe_2O_3 thin film reproducibly detect low ppm level of NO_2 at room temperature with fast response time and good stability.

Acknowledgment

Authors (VBP) are grateful to DAE-BRNS, for financial support through the scheme no. 2010/37P/45/BRNS/1442.

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Figure captions:

Fig.1. (a) XRD pattern of CPF (30%) hybrid nanocomposite, (b) FESEM image of CPF (30%) nanocomposite thin film, (c) TEM image of CPF (30%) nanocomposite thin film and (d) Cross-section SEM image of CPF (30%) nanocomposite thin film.

Fig.2. (a) Response of 10-50% CSA doped PPy/α-Fe_2O_3 nanocomposite film for 100ppm of NO_2 and (b) Selectivity of PPy, α-Fe_2O_3, PPy/α-Fe_2O_3 and 30% CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite thin films.

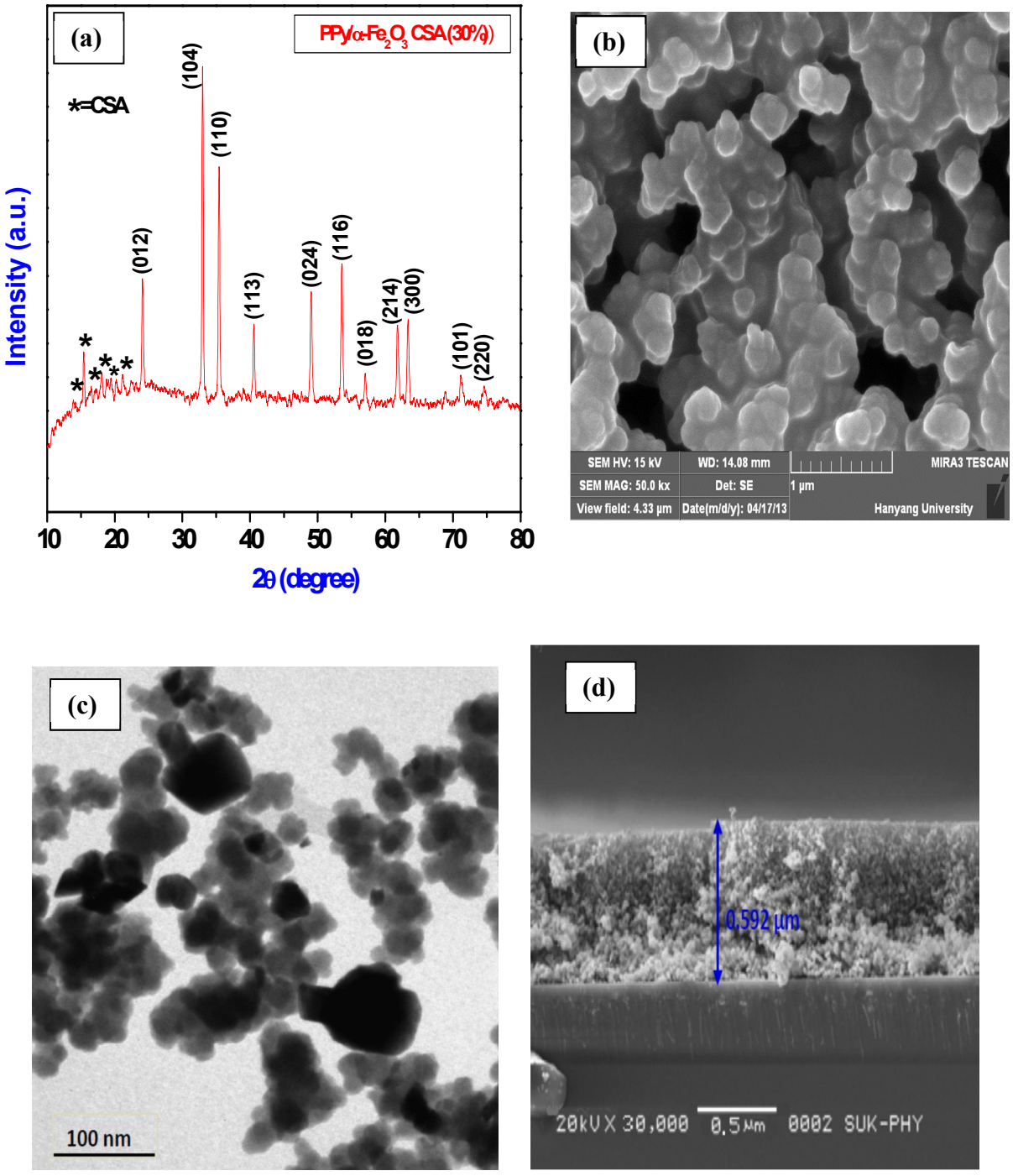
Fig.3. (a) Response to 30% CSA doped PPy/α-Fe_2O_3 thin film for various concentrations of NO_2 gas and (b) Relationship between response and NO_2 gas concentration to 30% CSA doped PPy/α-Fe_2O_3 thin film.

Fig.4. (a) Decrease in resistance of CSA doped PPy/α-Fe_2O_3 thin film with respect to time upon exposure to 100 ppm NO_2 and (b) Proposed energy band diagram for CSA doped PPy/α-Fe_2O_3 hybrid nanocomposite with the interaction of NO_2.

Fig.5. (a) Repeated response of 30% CSA doped PPy/α-Fe_2O_3 thin film to100 ppm NO_2 gas and (b) Stability study of PPy, PPy/α-Fe_2O_3 and 30% CSA doped PPy/α-Fe_2O_3 thin films.

Table caption:

Table1: K values of the sensor made by the film with CSA doped PPy/α-Fe_2O_3 for the NO_2 as a target gas.



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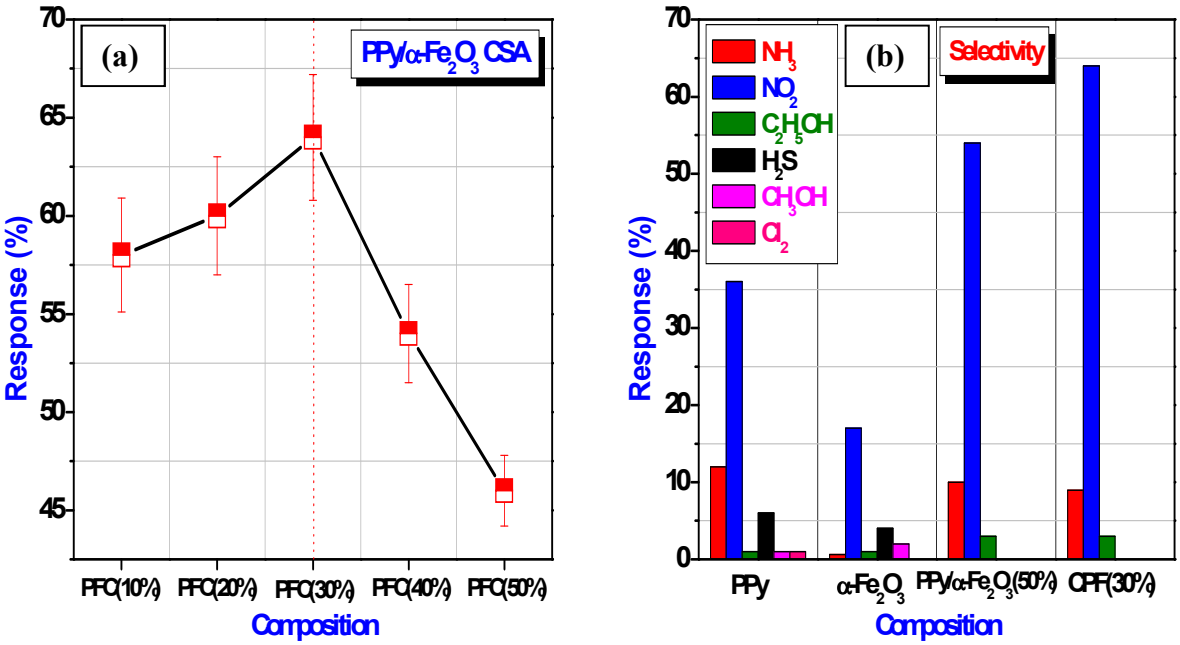

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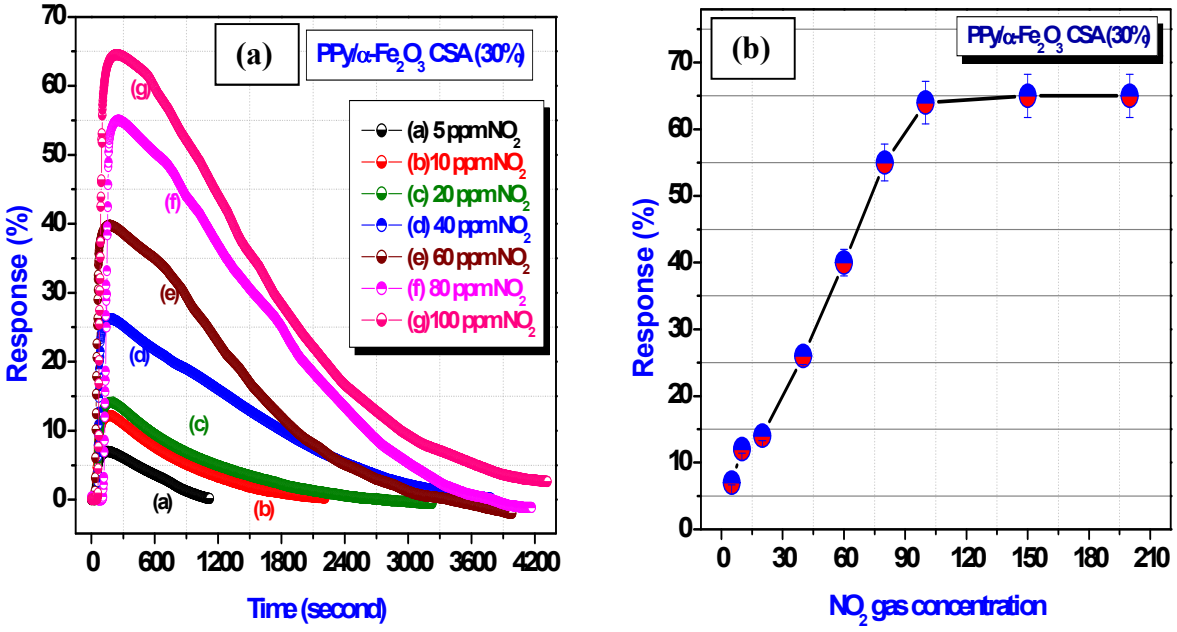

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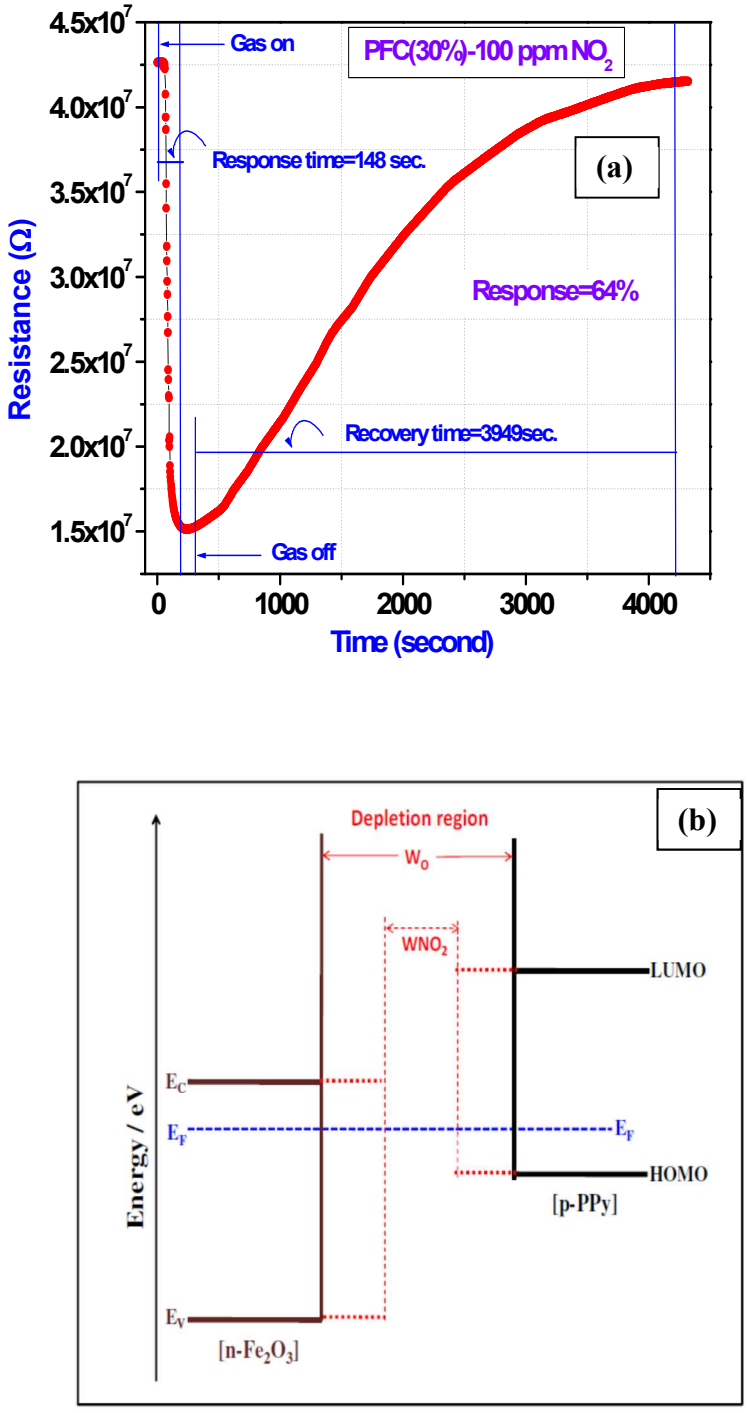

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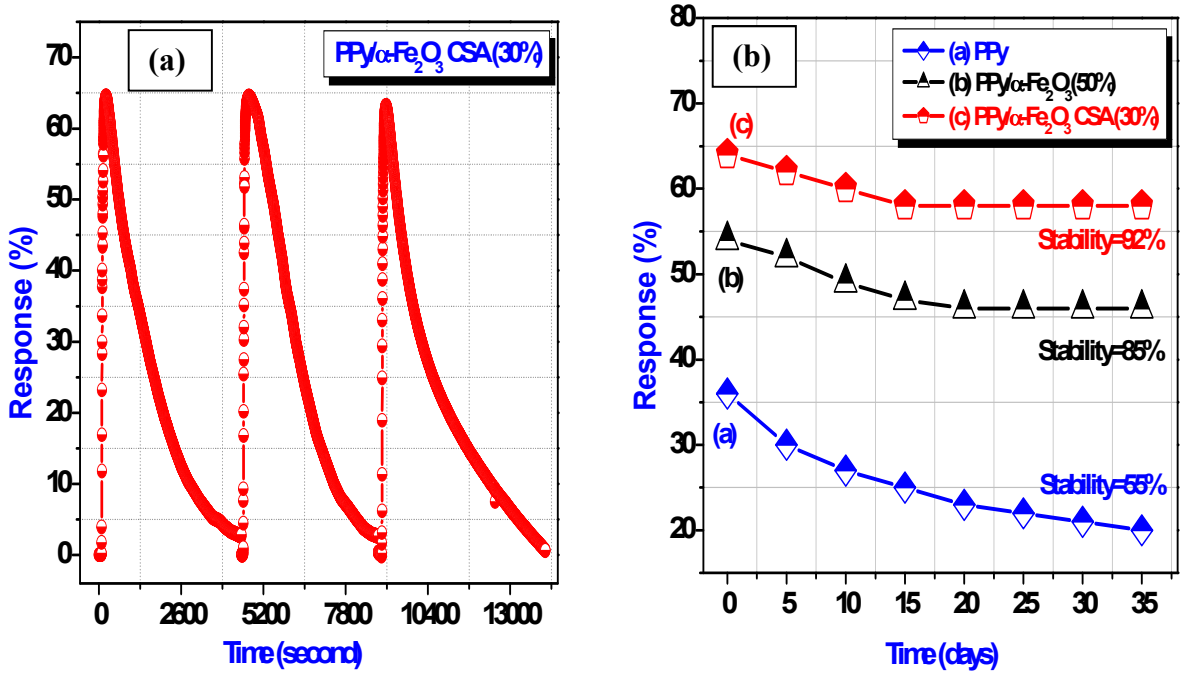

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