Methyl red/ polycarbazole composites: Humidity sensing characteristics and its adsorption isotherm study

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Abstract: Here, we have portrayed the development of novel polycarbazole - organic dye (methyl red) based composite material for humidity sensing application. Polycarbazole (PCz) was synthesized by well known chemical oxidative polymerisation method and PCz-dye composite material was developed via sonochemical technique. The porous nature of this organic moiety based composite material is apparent from FESEM micrograph. The optical property is simultaneously delineated by UV-Visible spectroscopy. The surface porosity of composite material is determined by BET analysis. This composite material is very sensitive towards humidity ranges from 8% to 97%. The best repeatability of the result is observed at very low (8% - 23% RH) and very high (75% - 97%) RH level. Moreover, the change in capacitance value in presence of different humidity level has been modelled using Redlich-Peterson isotherm model.

1. Introduction

Since its discovery in 2000, conducting polymer (CP) has attracted a great deal of interest as a fascinating model system for fundamental scientific research with the potential for several different promising applications. In conjugation with, Conducting polymers become a buzzing word rather than orthodox inorganic material for nano electronic device based application owing to its high flexibility, cheap price, facile synthesis procedure [1, 2] and so forth. Their effective redox activity [3] and charge transfer ability to the target analytes assessed its potentiality towards chemical sensing application in the global sensor industries. Polycarbazole (PCz) and its derivative are most important upcoming members in the ensemble of conducting polymers due to its promising photoconductive properties [4]. In recent, material researchers have explored this non-famous polymer towards different optical and electronics based applications such as electro-chromic devices [5], sensors [6] etc. Recently, Shakir.et.al and Baigh.et.al has shown ammonia sensing efficacy of polycarbazole based inorganic-organic composite at room temperature [7, 8]. Polycarbazole based composites have been also widely explored in the realm of bio sensing applications also [9]. Aromatic small molecule especially dye molecule is appended their potential towards chemical sensing application [10, 11] due to presence of different functional groups at its backbone. Humidity is one of the most significant parts in the nature. Over the few decades, organic semiconducting materials have come forward towards humidity detection [12] due to its easy synthesis procedure and easy operation at room temperature compared to inorganic metal oxides or sulphides. On basis of such literature in consideration, we have selected to prepare PCz / methyl red composites for humidity sensing application. Here, we have portrayed the synthesis and humidity sensing characteristics of PCz / methyl red composite material for the first
time. The significant sensitivity, low hysteresis offers it more importance towards humidity sensing application. Furthermore, Redlich Peterson model have been employed to understand the mode of water adsorption by this newly prepared composite material.

2. Experimental

A. Synthesis of MR dye /polycarbazole Composite

The pristine polycarbazole was synthesized by oxidative polymerization method [13]. For methyl red (MR) loading PCz, certain weight ratio of methyl red was mixed with fixed preweighted amount of PCz in DMSO and sonicated for 2 hr. The dispersed solution was stirred overnight for effective adsorption of dye at the surface of PCz. The different weight ratio of MR in PCz is labelled as CP1 (MR: PCz = 1: 1), CP10 (MR: PCz = 1: 10), CP 50 (1:50)

3. Material Characterization

The optical characterization of the composite along with its counterpart was performed by using UV–VIS-double-beam spectrophotometer (CECIL, Model no- CE7200). The morphological characterestics of the methyl red/PCz composites were studied by using TecnaiG2 30ST (FEI) Supra 35VP (Carl Zeiss) Field Emission Scanning Electron Microscope (FESEM). The N2 adsorption/desorption isotherm of said composite material is subsequently measured using [Quanta chrome Instruments version 3.0].

4. Humidity Sensor Fabrication and Set up

The humidity sensor for this experiment was fabricated on copper claded plastic board by copper etching technique. The distance between two copper electrodes is 2 mm. In this configuration, pristine PCz or composite material is employed between the gap of two electrodes and the composite material behaves as the sensing layer. Fig.1. shows the schematic picture of designed and fabricated humidity sensor. The humidity sensing attributes were studied by introducing the MR-PCz film sensor to various relative humid environments, prepared by saturated aqueous salt solutions. Firstly, the sensor was placed into fused CaCl2 (RH= 0 %), before exposing them to different RH concentrations of 8%, 23%, 53%, 75%, 85% and 97% in a closed conical yield prepared by saturated solutions of KOH, CH3COOK, Mg(NO3)2, NaCl, KCl and K2SO4 respectively. The capacitance value of the sensors was measured using Agilent U1253 B data logging/switch unit.

5. Result and Discussion

A. Morphological Analysis

The investigation of micro structural attributes is one of the most important tools compared to different characterisation technique because unique micro structural nature of conjugated polymer often significantly sweeps the sensing attributes towards different target analytes [14]. Figure 2 (a) has depicted the highly aggregated woolly like micro structural characteristics of pristine polycarbazole. The extended Fibrous like morphological features of methyl red is apparent from FESEM micrograph [Fig. 2(b)]. The morphological features of PCz / MR composite are totally different than pristine PCz and MR as observed from FESEM micrograph [Fig. 2(c)]. For MR loaded PCz, lumped agglomerated porous like structure is observed [Fig. 2(c)]. The porous nature of composite material is also further corroborated by BET analysis. The single phase homogeneous surface architecture of methyl red /PCz composite is apparent due to strong π–π staking and electrostatic interaction between methyl red and PCz.
B. UV-Visible Spectra Analysis
The significant interaction between polycarbazole and dye is analysed by UV-Visible spectra which have been shown in Fig. 3(a). Generally, the characteristic peaks for the pristine polycarbazole molecules are observed at about 297 nm in addition to a shoulder at 350 nm [15] on the UV spectrum relating to \(\pi - \pi^*\) transition of benzenoid ring and polaron level to \(\pi^*\) conduction band transition of quinoid ring [15]. The characteristics peak of methyl red was observed at 495 nm due to \(\pi - \pi^*\) transition [16]. The significant peak shift due to of \(\pi - \pi^*\) transition for pristine polycarbazole was revealed from UV-Visible spectra. After methyl red (MR) incorporation, it shifts toward blue end at the UV-Visible spectrum and appears at 293 nm which indicate that \(\pi - \pi^*\) electronic transition in PCz chain is somehow reduced in presence of MR via additional stacking interaction between MR and PCz.

C. Surface Area Analysis
The humidity sensing performance of any nanostructure material mainly governs by its surface area, pore size, pore volume distribution. The synthesized material with higher surface area can effectively expose higher number of functional group for interaction with target analytes [17]. Interestingly, we have observed that after incorporation of MR dye, effective surface area, pore size and pore volume of this composite material is highly improved. The improved surface area of methyl red / PCz composite arises due to facile adsorption of methyl red at the surface of PCz. The electrostatic interaction between (\(+N-H\)) group of PCz and (COO-) group of methyl red is one of the most important key factors of improving surface attributes of the composite material. Additionally, \(\pi-\pi\) stacking interaction between PCz and dye help them to curve a niche. The dye adsorption phenomenon and their consecutive impact on surface property of the pristine polymer are quite common for functional polymers [18]. The N\(_2\) adsorption – desorption hysteresis loop at higher relative vapour pressure (P/P\(_0\)) indicates capillary condensation took place due to presence of both well-defined micro and meso pores of PCz/MR dye composite. From Fig. 3(b), it is observed that H3 type hysteresis eventuates and desorption process are associated with connected inkbottle pores. H3 type hysteresis is generally observed in non rigid aggregated plate like particle. The nitrogen adsorption/desorption isotherm and pore size distribution of MR dye/polycarbazole composite are as shown in Fig. 3(b). Table 1 summarizes the average surface area; average pore volume and average pore diameter of pristine polycarbazole and MR dye /polycarbazole composite. An improvement of surface area is due to increase the distance of aggregated PCz chain by intercalation of dye molecule.

D. Humidity Sensing Characteristics
After rigorous morphological, optical characterization of this composite material, its humidity sensing attribute is investigated using different salt solution corresponds to different relative humidity. From Fig. 4(a), it is observed that MR /PCz composite are quite sensitive towards humidity. The capacitance of the humidity sensor [expressed as Eq. (1)] is determined by the area of the parallel electrodes (A), distance between electrodes (d) and relative dielectric permeability of the material. The dielectric constant of the sensing element (\(\varepsilon_d\)) is solely depends on polarizibility of the material [19, 20], which associated with dipolar, ionic or electronic polarizibility [21]. The electronic polarizibility in
conducting organic semiconductors arises due to the competitive displacement of the π-electrons with respect to the nucleus. The electronic polarizibility in methyl red comes due to presence of π-conjugated system.

The intermolecular charge transfer is responsible for good polarizibility in dye molecules [10]. For composite material, electronic polarizibility comes from both intra and intermolecular charge transfer. An adequate surface area, surface porosity as depicted in Table-1 is also responsible for effective humidity sensing attributes. The presence of the micro and meso pore also facilitates water molecule adsorption on the activated surface of the composite material which is clearly depicted by Eq.1 and 2 [22].

\[ C = \varepsilon_0 \varepsilon_d A/d \]  \hspace{1cm} (1)

\[ rk = 2\gamma M/ \rho RT \ln Ps / P \] \hspace{1cm} (2)

Where, \( rk \) is the radius, \( \gamma \) is surface tension, \( \rho \) is density and \( M \) is molecular mass of H\(_2\)O molecules. \( Ps \) is saturated vapour pressure and \( P \) is vapour pressure at fixed atmospheric condition.

From Fig. 4(a), it is observed that with increasing RH level, response value increases which corresponds that surface layer and interlayer diffusion phenomenon is responsible for water molecule adsorption. A closer look at capacitance vs. RH (%) profile at different dye loading deciphers that there is very little increase in response value upon different MR loading in PCz matrix. The saturation of response is also observed at the ranges of 23% RH to 53% RH. Fig. 4(b) has depicted time dependent dynamic response curve of CP10 at different RH and Fig. 4(c) has shown sensor repeatability curve which indicates sensor reproducible performance towards humidity detection. The best reproducible performance of the sensor was observed at low RH level (0% - 23%) and high RH level (75% - 97%).

Figure 2. FESEM micrograph of (a) pristine polycarbazole (b) pristine methyl red (c) methyl red polycarbazole composite (CP10)
Hysteresis is assigned as the difference in percentage for final setting point of RH when reached from above to when it is reached from below [10]. The hysteresis plot [Fig.4 (d)] has been employed to evaluate the performance of the sensors. Initially the sensors were subjected to the relative humidity increasing from 0% to 97% followed by a decrease in humidity level within the identical range. However, slight saturation of response during de-humidification process range at 23% RH to 43% RH took place indicating poor desorption from composite material at this stage. The calculated hysteresis value is obtained to be ~ 1.13%. An extremely low hysteresis value can makes this material as a good candidate for humidity sensing.

**Table-1:** BET analysis of methyl red /polycarbazole composite and pristine polycarbazole

| Name of sample | $S_{ads}$ (m$^2$/g.) | $S_{des}$ (m$^2$/g.) | Average Pore Volume (cc/g) | Average Pore diameter (nm) |
|----------------|-----------------------|-----------------------|---------------------------|---------------------------|
| CP 10          | 11.196                | 15.794                | 0.1395                    | 130.5                     |
| PCz            | 2.277                 | 1.063                 | 0.007                     | 6                         |

**E. Hysteresis Analysis**

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Figure 4. (a) Capacitance vs. RH (%) profile of dye / PCz composite (b) The response and recovery transient of CP10 in presence of different humid condition (c) The repeatability curve of MR/PCz composite (d) Hysteresis curve of CP10

F. Adsorption Isotherm Analysis

The plausible mode of water adsorption by methyl red/ PCz composite were investigated by well known Redlich Peterson adsorption model. The mathematical expression of the linear form of this model is given below [23],

\[
\ln \left( \frac{A \cdot C_e}{q_e - 1} \right) = g \ln (C_e) + \ln (a_R)
\]

which can be written as

\[
\ln (A \cdot RH/C - 1) = g \ln (RH) + \ln (a_R)
\]

where A is the Redlich–Peterson isotherm constant (L g⁻¹), aR is also having a constant unit g is an exponent that lies between 0 and 1. RH is the equilibrium phase concentration of the adsorbate (water vapour) C is the particle limiting adsorption capacity.
Figure 5. (a) Linear fitted curve of Redlich Peterson model (b) Plausible humidity sensing mechanism of methyl red / PCz composites

Table-2: Redlich Peterson adsorption analysis of CP10

| Composition | g    | aR  | A   | R²   |
|-------------|------|-----|-----|------|
| CP10        | 0.929| 6.30| 10  | 0.972|

The following regression coefficient value of the above fitting result (R² = 0.97) clearly indicates that the composite material strongly follows Redlich-Peterson isotherm. The basis of Redlich-Peterson isotherm adsorption model is of adsorbate at the heterogeneous and homogeneous amalgamated surface of adsorbent having different adsorption site [24]. So, for our composite material different adsorption/reactive site i.e. -COOH group of methyl red and =N-H group and dopant molecule (PTSA) of PCz are solely responsible [15] for humidity sensing phenomenon. Additionally, at low RH level, monolayer of water vapour is formed and after increasing RH level, the united adsorption phenomenon is enhanced when adsorption sites of sensing material are bridged with clusters of water molecules, which cover the pore of synthesized material and facile ion transfer takes place according to Grothus mechanism [25]. So, both monolayer and multilayer adsorption phenomenon occurs at the surface of material which is good agreement with Redlich-Peterson model.

6. Conclusion
So, in this article, we have demonstrated the sonochemical assisted preparation of polycarbazole/ MR composites and their subsequent utility in humidity sensing application for environmental and health monitoring. The synergetic electronic interaction of PCz moiety and dye (MR) molecules is observed from UV-Visible spectroscopy. The improved surface area of composite material compared to pristine PCz is apparent in BET surface area analysis. The morphological features of newly prepared material is analysed from FESEM micrograph. Interestingly, it was observed that the composite material is able to detect total humidity range (8% - 97% RH) with low hysteresis (~1%). The best repeatability arises at low RH (8% - 23%) and higher RH (75% - 97%). Furthermore, an effort was given to fit the
experimental capacitance value (with varying RH) into Redlich Peterson model for understanding the mode of water adsorption by this newly prepared composite material.

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