Chemical synthesis of polypyrrole/molybdenum trioxide composites for characterization and humidity sensing studies

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Abstract
In-situ polymerization of pyrrole (Py) is carried out with molybdenum trioxide (MoO₃) in the presence of oxidizing agent ammonium persulphate to synthesize the polypyrrole/molybdenum trioxide composites (PPy/MoO₃) by chemical oxidation method. The composites are synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt. % of MoO₃ in pyrrole. The powder X-ray diffraction (XRD) pattern suggests that, the composites exhibit semi-crystalline behavior. The Fourier Transform Infra-Red Spectroscopy (FTIR) reveals the stretching frequencies are shifted towards higher frequency side. The Scanning Electron Microscope (SEM) micrographs shown that, the MoO₃ particles are embedded in PPy chain to form multiple phases. The resistance of the polypyrrole/molybdenum trioxide composites on exposure to a humid environment increases from 40 Ω to 180 Ω for composites and 2.7 MΩ to 71.5 MΩ for the PPy/molybdenum trioxide (50%) with the increase in humidity response from 20 % to 90 %.

Keywords: Polypyrrole; Molybdenum Trioxide; Composite; Humidity; Sensor.

1. Introduction
Conducting polymer composites with some suitable compositions of one or more insulating materials lead to desirable properties. These materials are especially important owing to their bridging role between the world of conducting polymers [1] and that of nanoparticles. For application of conducting polymers, knowing how these conducting polymer composites will affect the behavior in an electric field is a long-standing problem and is of great importance. The discovery of doping in conducting polymer [2-4] has led to further dramatic increase in the conductivities of such conjugated polymers to values as high as 10⁶ Scm⁻¹.

Polypyrrole (PPy) is one of the most attractive polymers due to its special transport properties [5]. Molybdenum trioxide is most abundant of any molybdenum compound. It occurs as the rare mineral molybdate. The oxidation state [6] of molybdenum in this compound is +6.

The main applications of MoO₃ are as an adhesive between enamels and metals, as an additive to steel and corrosion-resistant alloys, as a co-catalyst, as a component in electrochemical devices and displays [7]. Molybdenum trioxide has also been suggested as a potential antimicrobial agent, e.g., in polymers. In contact with water, it forms H⁺ ions that can kill bacteria effectively [8].

Beside of demand of the humidity sensor, mainly electric output-based sensor, gradually increase, sensor development is also necessary to be carried out due to some drawbacks of the current sensors which were mainly affected by their sensing element material as reported by some researchers. Hence, investigations of new material sensor or combination of some materials have to be continuously proceeded to improve the sensor performance characteristics [9].

Humidity measurements displays an extensive influence and are widely applied in modern industry [10-11], agriculture [11-13], medicine [14-15], scientific research [16-17] and so on as well as people's daily lives. There is a substantial interest in the development of sensors for application in monitoring and detecting humidity in moisture-sensitive environment, such as glove boxes and...
clean rooms. Therefore, humidity sensors have attracted tremendous attention for the purpose of detecting the humidity. In order to optimize important properties like drift, accuracy, hysteresis or temperature influences of humidity sensors, recently new materials including metal oxide [18-19], ceramic [19-20] and polymers [21-22] have been designed as humidity sensors. Most commercially used humidity sensors with porous ceramics or metal oxides obviously are not suitable due to a large thickness or a complex integration process [18-20].

Especially, polypyrrole based composites, as one of the most interesting materials, have been identified as good candidates having a better humidity-sensitive characteristic, such as reliability, ease of processing and the low fabrication cost for the preparation of resistive-type humidity sensors.

Authors have synthesized the pure polypyrrole and its composites by chemical polymerization method in the presence of oxidizing agent. The synthesized composites are analyzed by the characterization techniques such as SEM, XRD and FTIR. The humidity sensing study is done for the synthesized samples and reported in this paper.

2. Experimental Details

2.1. Synthesis

The AR grade [Spectro Chem Pvt. Ltd.] pyrrole [23] purified is used and 0.3 M pyrrole solution is contained in a beaker which is placed in an ice tray mounted on a magnetic stirrer. 0.06 M ammonium persulphate [24] solution is continuously added drop-wise with the help of a burette to the above 0.3 M pyrrole solution. The reaction is allowed for 6 hours under continuous stirring by maintaining a temperature of 0°C to 5°C. The precipitated polypyrrole is filtered and dried in hot air oven and subsequently in a muffle furnace at 100°C. The yield of the polypyrrole is 3.2 g (100 weight percent).

For 0.3M pyrrole solution, 0.32 g (10 wt. %) of MoO_3 is added and mixed thoroughly, further 0.06 M ammonium persulphate is continuously added drop-wise with the help of a burette to the above solution to get a PPy/MoO_3 10 wt.% composite. Similarly, for 20, 30, 40 and 50 wt. %, 0.64 g, 0.96 g, 1.28 g and 1.6 g of MoO_3 [Sisco Research Lab Ltd] powder [25] is taken and the above procedure is followed to get the PPy/MoO_3 composites. The pure PPy and PPy/MoO_3 powder is pressed in the form of pellets of 10 mm diameter and 1-3 mm thickness using hydraulic press by applied 10-12 tons pressure. The conducting silver paste is applied to the pellets of synthesized composites for sensing measurements. The humidity response measurements are done by Humidity Sensor (V B Ceramic Consultant, Chenni, India) for the PPy/MoO_3 composites in the cooling temperature range between 70 ºC and 0 ºC.

2.2. Characterization

The X-ray diffraction patterns of the PPy/MoO_3 composites are recorded on X-ray Diffractometer (Bruker AXS D8 Advance) using CuKα radiation (λ = 1.5418 Å) in the 2θ range 20°-80°. The FTIR spectra of the PPy/MoO_3 composites are recorded on IR Affinity-1 (Shimadzu, Japan) spectrometer in KBr medium at room temperature. The SEM images of the PPy/ MoO_3 composites are recorded using Scanning Electron Microscope (Jeol 6390LV).

3. Results and Discussion

3.1. XRD Analysis

Figure 1a represents X-ray diffraction pattern of pure PPy, which has a broad peak at about 2θ = 25°, shown a characteristic peak of amorphous polypyrrole. In the XRD pattern of PPy/MoO_3 (40 wt.% composite), characteristic peaks are indexed by lattice parameter values. Main peaks are observed with 20 at 23.1°, 25.4°, 27.0°, 29.4°, 32.8°, 39.4°, 49.8°, 52.5° and 58.5° with respect to inter-planar spacing (d) 3.8 Å, 3.5 Å, 3.3 Å, 3.0 Å, 2.7 Å, 2.2 Å, 1.8 Å, 1.7 Å and 1.5 Å respectively. Careful analysis of X-ray diffraction of the PPy/MoO_3 (40 wt.%) composite suggests that it exhibits semi-crystalline behavior. Figure 1c represents XRD pattern of MoO_3 revealing the semi-crystalline nature [23-26].
3.2. FTIR Analysis

Figure 2: FTIR Spectra of a. pure PPy, b. PPy/MoO$_3$ (40% wt.) composite and c. MoO$_3$

The FTIR spectra of the pure PPy, PPy/MoO$_3$ (40%) composite & MoO$_3$ are shown in Figure 2. The characteristic stretching frequencies are observed at 1546.91, 1294.24, 1182.36, 1045.42, 964.41, 912.33, 804.32 and 619.15 cm$^{-1}$ may be attributed due to the presence of C = N stretching, N–H bending deformation, C–N stretching and C–H bending deformation frequencies. In comparison with pure PPy and MoO$_3$, the stretching frequencies are shifted towards higher frequency side. This indicates that, there is homogeneous distribution of MoO$_3$ particles in the polymeric chain due to the Vander Walls interaction between polymeric chain and MoO$_3$[28-35].

3.3. SEM Analysis

Figure 3.a: SEM Micrographs of the pure PPy

Figure 3.b: SEM Micrographs of the PPy/MoO$_3$ (40%) composite

Figure 3.c: SEM Micrographs of MoO$_3$

Figures 3.a, 3.b and 3.c show that, the SEM micrographs of the pure PPy, PPy/MoO$_3$ (40 wt. %) composite and MoO$_3$. It is seen clearly from the SEM micrograph of polypyrrole that, it has clusters of spherical shaped particles and chain pattern of the polypyrrole particles is observed. The chemically polymerized polypyrrole samples prepared with polypyrrole powder have a much larger specific surface than the electrochemically polymerized film. A granular morphology of the polypyrrole particle structures is measured from SEM micrograph and is found to be about 1 μm in diameter. The SEM micrograph of the composite shows that, the presence of spherical nature of polymer as clusters in the composite. MoO$_3$ particles are embedded in PPy chain to form multiple phases, presumably because of weak inter-particle interactions [36-40].

3.4. Humidity Sensing Study

The process by which the PPy/MoO$_3$ composites respond to humidity may be due to the interaction of the moisture with MoO$_3$ in the composite and the changes in resistance of the composites with respect to doping level of MoO$_3$ in PPy is influenced by the concentration of water molecules surrounding the polymer chain. At high humidity, water molecules are trapped by MoO$_3$, since MoO$_3$ has a higher affinity for water. In this situation, doping level of PPy becomes high and results in higher resistance. However, at low humidity, some water molecules are removed from MoO$_3$ and simultaneously PPy de-dopes, resulting in lower resistance [41].
It is observed that from Figure 4.1, the resistance increases with increasing humidity response, which reveals the susceptibility of the PPy/MoO$_3$ composites to humidity [42].

![Figure 4.2: Humidity responses as a function of cooling temperature for the PPy/MoO$_3$ composites](image)

The humidity response versus cooling temperature as well as time is shown in Figure 4.2 - 4.3 respectively. The humidity response is varied from 20 % to 90 % as a function of cooling temperature / time for the multi-phases [43-44].

The resistance as a function of weight percent of MoO$_3$ in PPy is shown in Figure 4.4 which is reveals that, the PPy/MoO$_3$ (30%) composite has higher resistance with respect to %Rh. The PPy/MoO$_3$ (50%) composite has higher resistance (MΩ) but, lower %Rh.

**Conclusion**

The polypyrrole/molybdenum trioxide composites are synthesized to tailor the transport properties. Detailed characterizations of the composites are carried out using SEM, XRD and FTIR techniques. The PPy/MoO$_3$ composites have shown that the resistance has dependence on humidity and exhibits a very good response to humidity sensing.

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**References**


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