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### Synthesis, Characterization and A.C. Conductivity Study of Polypyrrole/Zinc Tungstate (Ceramic) Composites

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#### Abstract

In-situ polymerization of pyrrole (Py) was carried out with Zinc Tungstate (ceramic) in the presence of oxidizing agent ammonium persulphate to synthesize polypyrrole (PPy)/Zinc Tungstate (ZnWO<sub>4</sub>) by chemical oxidation method. The PPy/ ZnWO<sub>4</sub> composites were synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt. % of NaVO<sub>3</sub> in Py. The surface morphologies of these composites were analyzed using Scanning Electron Microscopy (SEM), show that ZnWO<sub>4</sub> particles are embedded in PPy chain to form multiple phases. The Fourier Transform Infra-Red Spectroscopy (FTIR) reveals the stretching frequencies were shifted towards higher frequency side. The powder X-ray diffraction (XRD) spectrograph, suggests that they exhibit semi-crystalline behavior. Thermal analysis (TG/DTA) studies/testing were done and reported. The frequency dependent A.C. conductivity reveals that, the ZnWO<sub>4</sub> concentration in PPy is responsible for the variation of conductivity of the composites. Values of the conductivity were increases till wt. 50% ZnWO<sub>4</sub> in PPy. The dimensions of ZnWO<sub>4</sub> particles in the matrix have a greater influence on the conductivity values.

**Keywords:** Polypyrrole; Zinc Tungstate; Composites; Conductivity; Frequency.

#### Introduction

The discovery of electrical conductivity in molecular charge transfer promoted the development of conducting polymers which have been synthesized and show the excellent electrical properties. Conducting polymers, by virtue of their light weight and greater ease of fabrication, have replaced and are continuing to replace metals in several areas of applications. Conducting polymers have been prepared for a wide range of applications ranging from rechargeable batteries to smart windows.

Polypyrrole (PPy) has become one of the most studied electronically conducting polymers. It can be synthesized either chemically or electro-chemically. Polypyrrole is an intrinsic conducting polymer which can be made to have conductivities up to 1000 S cm<sup>-1</sup> rendering its versatile applications in batteries, electronic devices, functional electrodes, electro-chromic devices, optical switching devices, sensors and so on [1–5].

#### Experimental details

##### Synthesis

The AR grade [Spectro Chem Pvt. Ltd.] pyrrole [6] was purified by distillation under reduced pressure. 0.3 M pyrrole solution was contained in a beaker which was placed in an ice tray mounted on a magnetic stirrer. 0.06 M ammonium persulphate [7] solution was continuously added drop-wise with the help of a burette to the above 0.3 M pyrrole solution. The reaction was allowed for 5 hours under continuous stirring by maintaining a temperature of 0 °C to 3 °C. The precipitated polypyrrole was filtered and dried in hot air oven and subsequently in a muffle furnace at 100 °C. The yield of the polypyrrole was 3.6 g which has taken as 100 wt. %.

For 0.3 M pyrrole solution, 0.36 g (wt. 10%) of Zinc Tungstate (ZnWO<sub>4</sub>) was added and mixed thoroughly. Further 0.06 M ammonium persulphate was continuously added drop-wise with the help of a burette to the above solution to get PPy/ZnWO<sub>4</sub> (wt. 10%) composite. Similarly, for 20, 30, 40 and 50 wt. %, 0.72 g, 1.08 g, 1.44 g and 1.8 g of ZnWO<sub>4</sub>

[Sisco Research Lab Ltd.] powder [8] is taken and the above procedure is followed to get PPy/ZnWO<sub>4</sub> composites. The pure PPy and PPy/ZnWO<sub>4</sub> powder was pressed in the form of pellets of 1 cm diameter using hydraulic press. The conducting silver paste was applied to the pellets of synthesized composites to act as electrodes. The A.C. conductivity of the synthesized composites was measured in the frequency range from 10<sup>1</sup> Hz to 10<sup>7</sup> Hz [Hioki (Japan) Model 3532-50].

### Characterization

The SEM [6-12] images of the pure PPy, PPy/ZnWO<sub>4</sub> (wt. 50%) composite and ZnWO<sub>4</sub> were recorded using Scanning Electron Microscope (Jeol 6390LV). The FTIR [6-7, 10-12] spectra of were recorded on FTIR (Thermo Nicolet Avatar 370) spectrometer in KBr medium at room temperature. The XRD patterns were recorded on X-ray Diffractometer (Bruker AXS D8 Advance) [6-11] using Cu K<sub>α</sub> radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the 2 $\theta$  range 20°–80°. Thermal analysis studies/testing were done in the heat range from 40 °C to 740 °C at 10 °C/min for the pure PPy, PPy/ZnWO<sub>4</sub> (wt. 50%) composite and ZnWO<sub>4</sub> using Thermal Analysis System (TG/DTA) (Perkin Elmer Diamond TG/DTA).

## Result and discussion

### SEM Analysis

Figure 1.a represents the SEM micrograph of pure PPy. The figure represents the size and spherical nature of PPy particles. The elongated chain pattern of the polypyrrole particles was observed. Two particles sizes were measured as 162.21 nm and 176.37 nm. Figure 1.b represents the SEM micrograph of the PPy/ZnWO<sub>4</sub> (wt. 50%) composite. Here, particle size was increased with small change and measured as 162.75 nm. This has shown that, the ZnWO<sub>4</sub> particles were embedded uniformly in PPy chain to form multiple phases, presumably because of weak inter-particle interactions. In Figure 1.c, the SEM micrograph of ZnWO<sub>4</sub> shown semi crystalline nature [6-12].

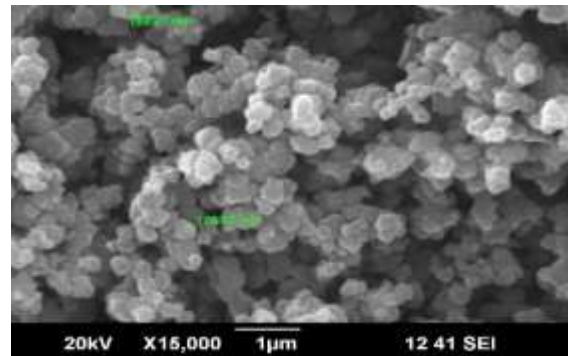


Figure 1.a SEM micrograph of the pure PPy

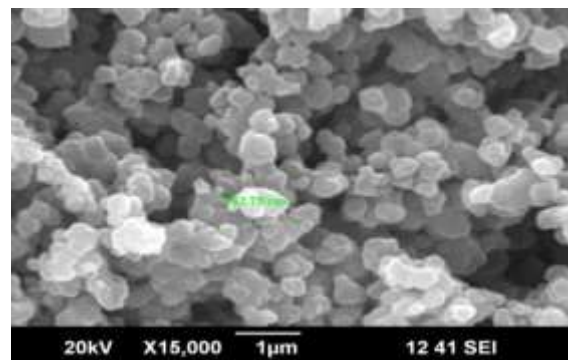


Figure 1.b SEM micrograph of the PPy/ZnWO<sub>4</sub> (wt. 50%) composite

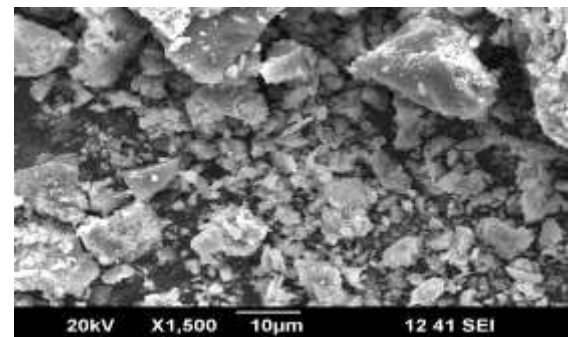


Figure 1.c SEM micrograph of the ZnWO<sub>4</sub>

### FTIR Analysis

The Figures 2.a, 2.b and 2.c have shown the FTIR spectra of pure PPy, PPy/ZnWO<sub>4</sub> (wt. 50%) composite and ZnWO<sub>4</sub>. Characteristic frequencies were observed at 1555 cm<sup>-1</sup>, 1476 cm<sup>-1</sup>, 1321 cm<sup>-1</sup>, 1202 cm<sup>-1</sup>, 1049 cm<sup>-1</sup>, 927 cm<sup>-1</sup>, 797 cm<sup>-1</sup> 619 cm<sup>-1</sup> for pure PPy. And characteristic frequencies were observed at 1567 cm<sup>-1</sup>, 1480 cm<sup>-1</sup>, 1328 cm<sup>-1</sup>, 1198 cm<sup>-1</sup>, 1109 cm<sup>-1</sup>, 1052 cm<sup>-1</sup>, 931 cm<sup>-1</sup>, 801 cm<sup>-1</sup> & 619 cm<sup>-1</sup> for PPy/ ZnWO<sub>4</sub> (wt. 50%) composite and 1518 cm<sup>-1</sup>, 1360 cm<sup>-1</sup>, 1049 cm<sup>-1</sup>, 963 cm<sup>-1</sup>, 911 cm<sup>-1</sup>, 842

$\text{cm}^{-1}$  &  $615 \text{ cm}^{-1}$  for  $\text{ZnWO}_4$  respectively may be attributed due to the presence of C = N stretching, N – H bending deformation, C – N stretching and C – H bending deformation frequencies. The stretching frequencies were shifted towards higher frequency side when pure PPy was compared with PPy/ $\text{ZnWO}_4$  (wt. 50%) composite. This indicates that, there is homogeneous distribution of  $\text{ZnWO}_4$  particles in the polymeric chain due to the Van der Waals interaction between polypyrrole chain and  $\text{ZnWO}_4$  [6-7, 10-14].

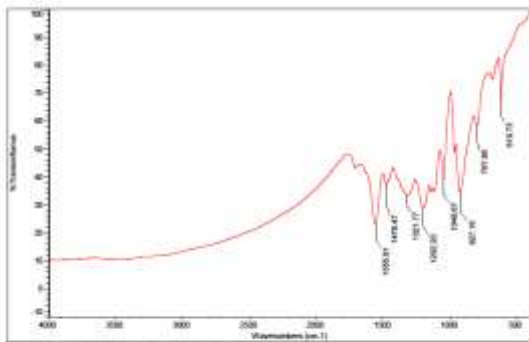


Figure 2.a FTIR spectrum of the pure PPy

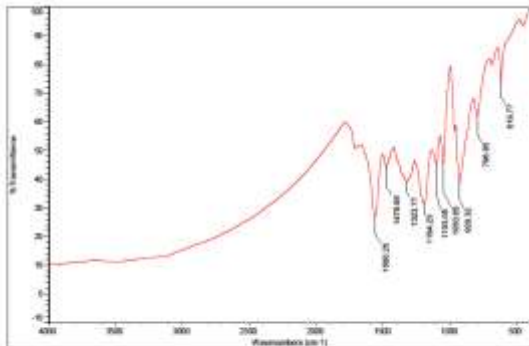


Figure 2.b FTIR spectrum of the PPy/ $\text{ZnWO}_4$  (wt. 50%) composite

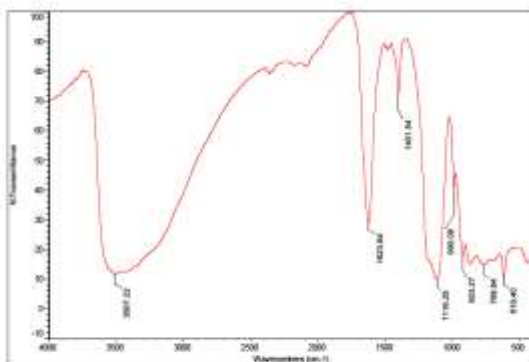


Figure 2.c FTIR spectrum of the  $\text{ZnWO}_4$

XRD Analysis

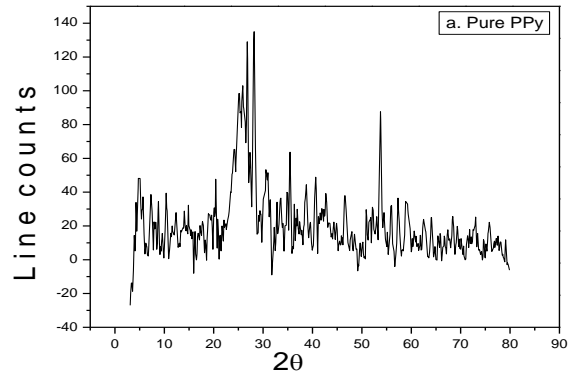


Figure 3.a XRD pattern of the pure PPy

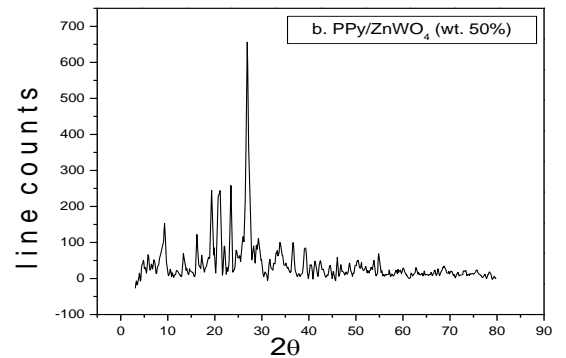


Figure 3.b XRD pattern of the PPy/ $\text{ZnWO}_4$  (wt. 50%) composite

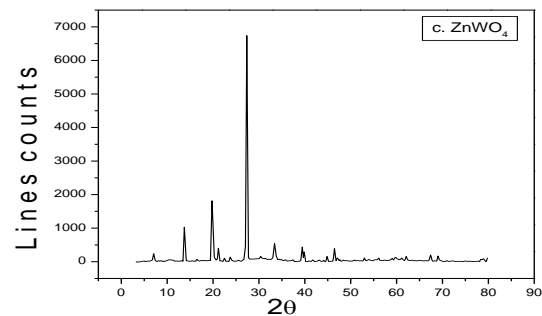


Figure 3.c XRD pattern of the  $\text{ZnWO}_4$

The Figure 3.a represents the XRD pattern of pure PPy. This has a broad peak at about  $2\theta=25^\circ$ , shown a characteristic peak of amorphous PPy. The XRD pattern of PPy/ $\text{ZnWO}_4$  (50 wt. %) composite shown in the Figure 3.b.

The characteristic peaks were indexed by lattice parameter values. The main peaks were observed with  $2\theta$  at  $9.31^\circ$ ,  $13.32^\circ$ ,  $16.19^\circ$ ,  $19.32^\circ$ ,  $21.12^\circ$ ,  $23.39^\circ$ ,  $26.89^\circ$ ,  $31.66^\circ$ ,  $36.63^\circ$ ,  $39.24^\circ$ ,  $41.32^\circ$ ,  $46.06^\circ$ , and  $54.85^\circ$  with respect to inter-

planar spacing (d) 9.48 Å, 6.64 Å, 5.46 Å, 4.59 Å, 4.20 Å, 3.79 Å, 3.31 Å, 2.82 Å, 2.45 Å, 2.29 Å, 2.18 Å, 1.96 Å, and 1.67 Å respectively. Careful analysis of the XRD of the PPy/ZnWO<sub>4</sub> (50 wt. %) composite suggests that, it exhibits semi-crystalline behavior. The Figure 3.c represents the XRD pattern of the ZnWO<sub>4</sub> revealing the semi-crystalline nature [6-11].

**TG/DTA Analysis**

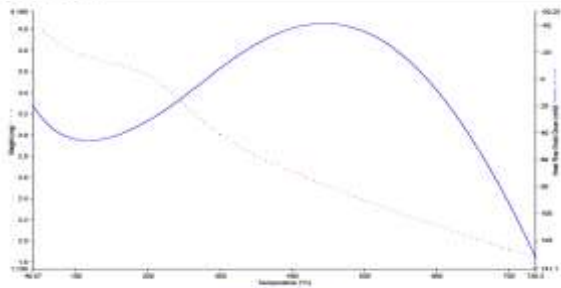


Figure 4.a TG/DTA thermograph of the pure PPy

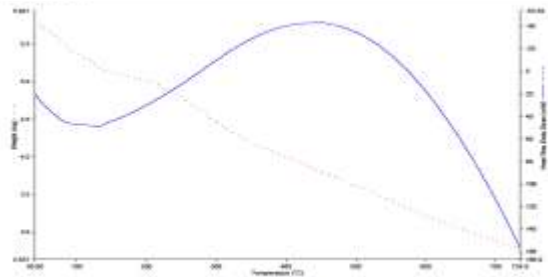


Figure 4.b TG/DTA thermograph of the PPy/ZnWO<sub>4</sub> (wt. 50%) composite

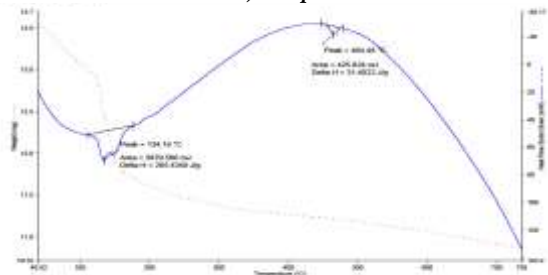


Figure 4.c TG/DTA thermograph of the ZnWO<sub>4</sub>

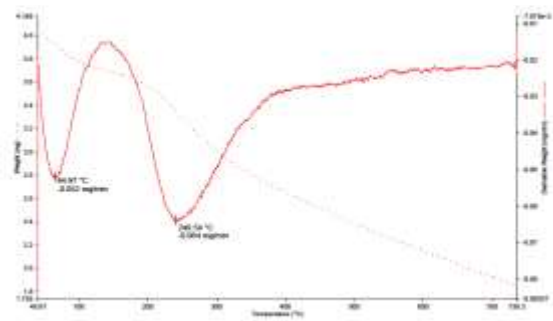


Figure 5.a TG/DTA thermograph of the pure PPy

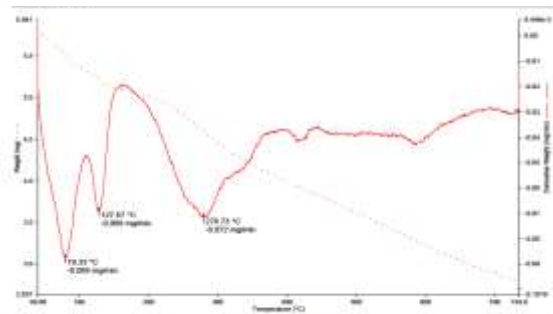


Figure 5.b TG/DTA thermograph of the PPy/ ZnWO<sub>4</sub> (wt. 50%) composite

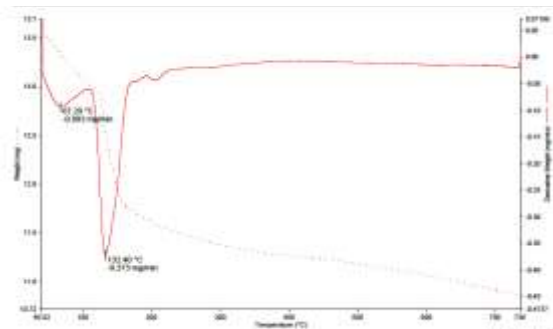


Figure 5.c TG/DTA thermograph of the ZnWO<sub>4</sub>

The most important and reliable factor in the study of heat stable polymers is the measurement or evaluation of thermal stability. Thermal properties and interaction between the polymers can also be noted from the oxidative degradation curves through thermo-gravimetric analysis (TG/DTA) studies. DTA is most commonly used to determine transition temperatures such as glass transitions, melting cross-linking reactions and decomposition. However, it measures only the total heat flow and the sum of all thermal transitions in the sample. The representative TG/DTA curves for pure PPy, PPy/ZnWO<sub>4</sub> (wt. 50%) composite ZnWO<sub>4</sub> are shown in Figures 4.a-4.c respectively. The residual weights ( $\gamma_c$ ) of the pure PPy, PPy/ ZnWO<sub>4</sub> (wt. 50%) composite and ZnWO<sub>4</sub>



were reported at 736.3 °C, 734.9°C and 736°C respectively. The materials have been heated from 40 °C to 740 °C under a constant heating rate of 10 °C/min and in the inert atmosphere of nitrogen gas. Variation of weight is almost linear and the maximum polymer decomposition temperature is there from 40 °C to 740 °C for all. In the Figure 4.a, two major weight loss stages for PPy were observed at 110 °C to 130°C and 736.3°C. In the Figure 4.b, two major weight loss stages for PPy/ZnWO<sub>4</sub> were observed at 135°C to 145°C and 734.8°C. And in the Figure 4.c, three major weight loss stages for PPy/ZnWO<sub>4</sub> were observed at 130°C to 134.16°C, 464.48 °C and 734.5 °C.

Derivative weight (mg/min) versus temperature is shown in Figures 5.a-5.c for the pure PPy, PPy/ZnWO<sub>4</sub> (wt. 50%) composite and ZnWO<sub>4</sub> respectively. For pure PPy, 0.052 mg/min is decomposed at 64.97 °C mg/min and 0.064 mg/min is decomposed at 240.54 °C with respect to total weight of the sample i.e. 4.057 mg. For PPy/ZnWO<sub>4</sub> (wt. 50%) composite, 0.088 mg/min is decomposed at 79.33 °C mg/min, 0.069 mg/min is decomposed at 127.67 °C mg/min and 0.072 mg/min is decomposed at 278.73 °C with respect to total weight of the sample i.e. 5.791 mg. For ZnWO<sub>4</sub>, 0.093 mg/min is decomposed at 67.29 °C mg/min and 0.373 mg/min is decomposed at 132.40 °C with respect to total weight of the sample i.e. 13.56 mg. It is found that, the weight loss caused by the volatilization of the small molecules in PPy/ZnWO<sub>4</sub> (wt. 50%) composite at different temperatures is slow compared to that of pure PPy and indicates its higher stability, which clearly proves that ZnWO<sub>4</sub> was inserted into the PPy to form composite and has increased the thermal stability of the composite material [15-23].

### A.C. Conductivity Study

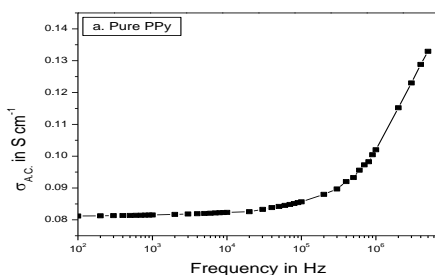


Figure 6.a Variation of A.C. conductivity as a function of frequency for PPy

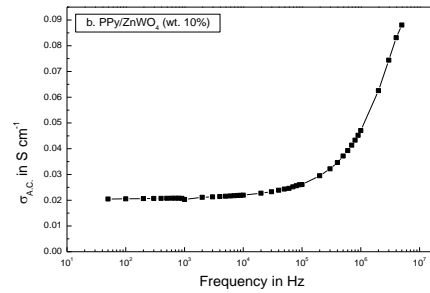


Figure 6.b Variation of A.C. conductivity as a function of frequency for PPy/ZnWO<sub>4</sub> composite (wt. 10%)

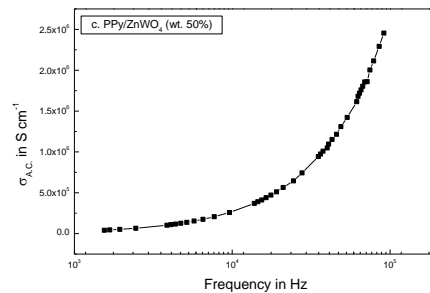


Figure 6.c Variation of A.C. conductivity as a function of frequency for PPy/ZnWO<sub>4</sub> composite (wt. 50%)

The variation of A.C. conductivity as a function of frequency for pure PPy, PPy/ZnWO<sub>4</sub> (wt. 10% and wt. 50%) composites is shown in Figure 6.a -6.c. It is observed that, the conductivity increases with frequency showing multiple phases of conductivity. It can also be seen that, the value of conductivity increases for 50 wt. % of ZnWO<sub>4</sub> in polypyrrole. This may be due to the extended chain length of polypyrrole which facilitate the hopping of charge carriers when the content of the ZnWO<sub>4</sub> is increased up to 50 wt. %. This percent weight is the percolation threshold for these composites. The composites obey percolation theory. The increase in conductivity for 50 wt. % may be due to the variation in the distribution of the ZnWO<sub>4</sub> particles which may support more number of charge carriers to hop between favorable localized sites causing increase in conductivity [9-10, 24-26].

### Conclusion

The PPy/ZnWO<sub>4</sub> composites were synthesized to tailor the transport properties. Detailed characterizations of the composites were carried out using SEM, FTIR, XRD and TG/DTA techniques. The results of A.C. conductivity of PPy and PPy/ZnWO<sub>4</sub> composites show a strong dependence on the weight percent of ZnWO<sub>4</sub> in polypyrrole. PPy/ZnWO<sub>4</sub> composites may find applications in sensors.

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