Synthesis, characterization and current study of polypyrrole/sodium metavanadate (ceramics) nano composites

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Abstract

In-situ polymerization of pyrrole was carried out with sodium metavanadate (ceramics) in the presence of oxidizing agent ammonium persulphate to synthesize the polypyrrole/sodium metavanadate composites by chemical oxidation method. The composites were synthesized with various compositions viz., 10, 20, 30, 40 and 50 weight percent of sodium metavanadate in polypyrrole. The surface morphologies of these composites were analyzed using Scanning Electron Microscope and shown that the sodium metavanadate particles are embedded in polypyrrole chain. The Fourier Transform Infra-Red graphs reveal the stretching frequencies are shifted towards higher frequency side. The powder X-ray diffraction patterns are suggests that, they exhibit semi-crystalline behavior. Thermal analysis studies were shown that, the composites have greater stability than the pure polypyrrole. The temperature dependent current reveals that, the sodium metavanadate concentration in polypyrrole is responsible for the variation of current of the composites. The value of the current is increases for 40 weight percent of sodium metavanadate in polypyrrole. The dimensions of sodium metavanadate particles in the matrix have a greater influence on the current values.

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1. Introduction

The discovery of electrical conductivity [1] in molecular charge transfer promoted the development of conducting polymers which have been synthesized and show the excellent electrical properties. Conducting polymers [2], 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 [3].

Polypyrrole has become one of the most studied electronically conducting polymer. It can be synthesized by either chemical or electro-chemical method [4]. PPy is a conducting polymer which can be made to have conductivities up to 1000 Scm⁻¹ rendering its versatile applications in batteries, electronic devices, functional electrodes, electro-chormic devices, optical switching devices, sensors and so on [5].

2. Experimental Details

2.1. Synthesis

The AR grade [SpectroChem 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 at temperature range of 0°C to 5°C. The precipitated PPy was filtered and dried in hot air oven and subsequently in a muffle furnace at 100 °C. The yield of the PPy was 3.6 g which has taken as 100 wt. %.

For 0.3M pyrrole solution, 0.36 g (10wt. %) of sodium metavanadate (NaVO₃) 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 a PPy/NaVO₃ (10%) composite. Similarly, for 20, 30, 40 and 50 wt. %, 0.72 g, 1.08 g, 1.44 g and 1.8 g of NaVO₃ [Sisco Research Lab Ltd.] powder[8] is taken and the above procedure is followed to get the PPy/NaVO₃ composites. The pure PPy and PPy/NaVO₃ composites powder was pressed in the form of pellets of 1 cm diameter and 1-2 mm thickness using hydraulic press by applied 10-
12 tons pressure. The current values were measured with respect to voltage at room temperature as well as the current values were measured at constant voltage for the synthesized composites in the temperature range 30 to 200 °C.

2.2 Characterization
The SEM images of the pure PPy, PPy/NaVO₃ (wt. 50%) composite and NaVO₃ were recorded using Scanning Electron Microscope (Jeol 6390LV). The FTIR spectra for the pure PPy, PPy/NaVO₃ (50%) composite and NaVO₃ were recorded on FTIR (Thermo Nicolet Avatar 370) spectrometer in KBr medium at room temperature. The XRD patterns for the pure PPy, PPy/NaVO₃ (50%) composite and NaVO₃ were recorded on X-ray Diffractometer (Bruker AXS D8 Advance) using Cu kα radiation (λ = 1.5418 Å) in the 2θ range 20°-80°. Thermal analysis studies/testing were done in the heat range from 40 to 740 °C at 10 °C/min for the pure PPy, PPy/NaVO₃ (50%) composite and NaVO₃ using Thermal Analysis System (TG/DTA) (Perkin Elmer Diamond TG/DTA).

3. Result and Discussion

3.1. SEM Analysis

Figure 1.a: SEM micrograph of the pure PPy

Figure 1.b: SEM micrograph of the PPy/NaVO₃ (wt. 50%) composite

Figure 1.c: SEM micrograph of NaVO₃

Figure 1. are presents the SEM micrograph of the 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. The SEM micrograph is shown that, the NaVO₃ particles were embedded uniformly in PPy chain to form multiple phases, presumably because of weak inter-particle interactions. The SEM micrograph of NaVO₃ in the Figure 1.c has shown high degree of crystalline nature [6-12].

3.2. FTIR Analysis

Figures 2.a, 2.b and 2.c have shown the FTIR spectra of the pure PPy, PPy/NaVO₃ (50%) composite and NaVO₃. The characteristic frequencies were observed at 1555 cm⁻¹, 1476 cm⁻¹, 1321 cm⁻¹, 1202 cm⁻¹, 1049 cm⁻¹, 927 cm⁻¹, 797 cm⁻¹, 619 cm⁻¹ for the pure PPy. And the characteristic frequencies were observed at 1567 cm⁻¹, 1480 cm⁻¹, 1328 cm⁻¹, 1198 cm⁻¹, 1109 cm⁻¹, 1052 cm⁻¹, 931 cm⁻¹, 801 cm⁻¹ & 619 cm⁻¹ for PPy/NaVO₃ (50%) composite and 1518 cm⁻¹, 1360 cm⁻¹, 1049 cm⁻¹, 963 cm⁻¹, 911 cm⁻¹, 842 cm⁻¹ & 615 cm⁻¹ for NaVO₃ 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 for the PPy/NaVO₃ (50%) composite. This indicates that, there is homogeneous distribution of NaVO₃ particles in the polymeric chain due to the Van der Walls interaction between the PPy chain and NaVO₃ [6-7, 10-14].
3.3. XRD Analysis

Figure 2.b: FTIR spectrum of the PPy/NaVO$_3$ (wt. 50%) composite

Figure 2.c: FTIR spectrum of NaVO$_3$

Figure 3.a: XRD pattern of the pure PPy

Figure 3.b: XRD pattern of the PPy/NaVO$_3$ (50%) composite
Figure 3.a represents the XRD pattern of PPy. This has a broad peak at about 2θ=25° shown a characteristic peak of amorphous PPy. The XRD pattern of the PPy/NaVO₃ (wt. 50%) composite has shown in the Figure 3.b. The characteristic peaks were indexed by lattice parameter values. The main peaks were observed with 2θ at 17.6°, 22.53°, 24.53°, 25.72°, 27.21°, 28.18°, 31.93°, 33.9°, 46.09°, 48.78° and 50.36° with respect to inter-planar spacing (d) 5.03 Å, 3.94 Å, 3.62 Å, 3.46 Å, 3.27 Å, 3.16 Å, 2.8 Å, 2.64 Å, 1.96 Å, 1.86 Å and 1.81 Å respectively. Careful analysis of the XRD of the PPy/NaVO₃ (wt. 50%) composite suggests that, it exhibits semi-crystalline behavior. The Figure 3.c represents the XRD pattern of the NaVO₃ revealing the semi-crystalline nature [6-11].

3.4. TG/DTA Analysis

The most important and reliable factor in the study of heat stable polymers is the measurement or evaluation of thermal stability. The graphs of derivative weight (mg/min) versus temperature were shown in the Figures 4.a-4.c for the pure PPy, PPy/NaVO₃ (50%) composite and NaVO₃ respectively. For the pure PPy, 0.052 mg/min is decomposed at 65 °C mg/min and 0.064 mg/min is decomposed at 240 °C with respect to total weight of the sample i.e. 4.057 mg. For the PPy/NaVO₃ (50%) composite, 0.047 mg/min is decomposed at 71 °C mg/min and 0.043 mg/min is decomposed at 289 °C with respect to total weight of the sample i.e. 4.580 mg. It is found that, NaVO₃ was inserted into the PPy to form composite and has increased the thermal stability of the composite material [15-23].

3.5. Current Study

Current versus voltage plot is as shown in the Figure 5.a. As voltage increase current also increase showing the metallic behavior of the pure PPy and its composites. At higher temperatures, the I-V characteristic for the PPy/NaVO₃ composites develops strong temperature dependence. Linearity of the I-V characteristic increases as temperature increases.
The variation of current is as function of weight percent of NaVO$_3$ in pure PPy. This may be due to the extended chain length of pure PPy which facilitate the hopping of charge carriers when the content of NaVO$_3$ is increased for wt. 40%. Further, the current is decreases for wt. 50% composite. The increase in current for wt. 40% may be due to the variation in the distribution of the NaVO$_3$ particles which may support more number of charge carriers to hop between favorable localized sites causing increase in current [24-25].

The variation of current is as function of weight percent of NaVO$_3$ in the pure PPy at different temperatures shown in the Figure 5.c. In all the composites, the current increases with respect to the temperature. The value of the current is increases for wt. 40% of NaVO$_3$ in PPy. This weight percent is the percolation threshold for these composites. Hence, the composites obey percolation theory [8-9, 26-29].

**Conclusion**

The PPy/NaVO$_3$ composites were synthesized to tailor the transport properties. Detailed characterizations of the composites were carried out using SEM, FTIR, XRD and TGA techniques. The results of current of the PPy/NaVO$_3$ composites were shown a strong dependence on the weight percent of NaVO$_3$ in the pure polypyrrole. The PPy/NaVO$_3$ composites may find applications in the field of sensors.

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**References**


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