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Synthesis and characterization of NLO active polypyrrole for optoelectronic applications

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Two Nonlinear optical (NLO) active Polypyrrole (PPy) powder samples have been synthesized by chemical oxidative polymerization method at room temperature. NLO test confirms the occurrence of second harmonic generation (SHG) in the PPy samples. The presence of monomer and dopants in the polymer were detected by FTIR analysis. The crystallinity and thermal stability of PPy also investigated via XRD and TGA techniques. UV Spectra confirms the π-electron mobility in the samples.

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Keywords: Chemical synthesis, X-ray diffraction, Nonlinear optics

1. Introduction

Over the last decades there has been an increasing interest and research activity on nonlinear optical properties of organic systems [1]. The NLO active organic materials are important materials, with prospects of application in optoelectronic devices. Polymeric materials are attractive candidates for incorporation into NLO devices [2]. PPy is a promising material for potential applications of electronic and optical devices [3].

Recently several results were reported on the synthesis of PPy [4 -7]. However, there have never been any reports on the NLO properties of PPy. Here, we report the synthesis and characterization of two NLO active PPy samples by varying the oxidizing agents. Conc. Nitric acid is used as a dopant of PPy. Ammonium per sulfate [$(NH_4)_2S_2O_8$] and potassium dichromate [$K_2Cr_2O_7$] were used as oxidizing agents to initiate the polymerization reaction. The SHG from the PPy was confirmed using Nd:YAG laser. Fourier transformation infrared spectroscopy (FTIR), X-ray diffraction (XRD), UV and thermo gravimetric analysis (TGA) were used for characterization and analysis.

2. Experimental

Pyrrole (Merck, India) was purified by vacuum distillation before use. Ammonium per sulphate (APS) and Potassium dichromate were purchased from Aldrich. Nitric acid (HNO_3 38 %) was obtained from (Loba chemical, India).The methanol and acetone were bought from Merck.

Polypyrrole was synthesized from pyrrole by chemical oxidative method at room temperature (0.1M) of pyrrole was dissolved in 1M HNO_3 aqueous solution drop wise to 100 ml of distilled water. Consecutively (0.1M) of oxidant was dispersed in 20ml of de-ionized water and added to the above solution which was being stirred for 2 hours. After the reaction product was recovered by filtration, washed with acetone and de-ionized water and then dried in vacuum oven at 60°C for 48 hours.

3. Characterization

The X-ray diffraction (XRD)analysis of PPy sample is performed using Bruker AXS D8 advance diffractometer with monochromatic Cu Kα radiation (λ=1.54Å).It is used to identify crystalline nature of the samples. Fourier transform infrared spectroscopy (FTIR) analysis is useful tool to determine the formation of dopant and functional groups. The FTIR spectroscopy analysis was scanned from 4000 to 400 cm^{-1} using thermonicolet V-200 FTIR Spectrometer by KBr pellet technique. The UV-Visible spectra of PPy samples were recorded employing Jasco V-530 dual beam spectrometer in m-cresol solvent. TGA measurements were utilized to investigate the thermal stability of PPy by employing perkin Elmer model thermo gravimetric analyzer in N_2 atmosphere between 40 to 1100 °C at a heating rate of 20°C/min. Second harmonic generation of synthesized polymer was measured using Kurtz and Perry powder technique.

4. Results and discussion

4.1 X-ray diffraction studies

XRD pattern show that the PPy powders are amorphous in nature. In each case broad peaks was observed at about $2\theta=27^{\circ}$ (Fig. 1) and $2\theta=21^{\circ}$ (Fig. 2). The broad peaks are characteristic of amorphous PPy [8].

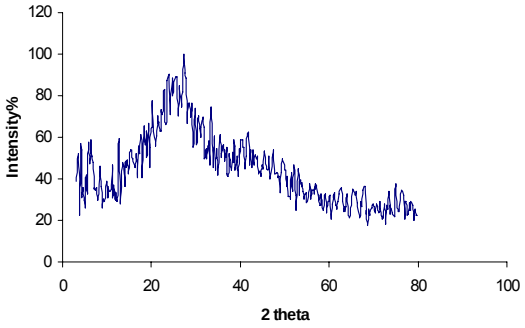

Fig. 1. XRD pattern of PPy-$(NH_4)_2S_2O_8$.

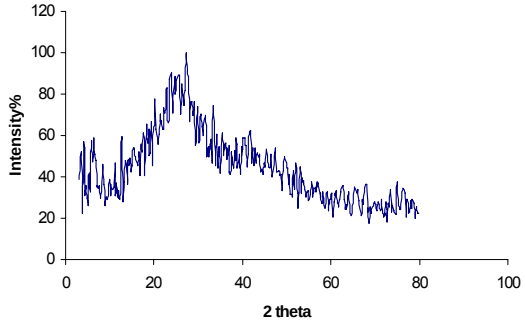

Fig. 2. XRD pattern of PPy-$K_2Cr_2O_7$.

4.2 FTIR spectrum analysis

The FTIR spectra of PPy-$(NH_4)_2S_2O_8$ and PPy - $K_2Cr_2O_7$ respectively (Fig. 3 and 4). The N-H symmetric stretching of pyrrole appears at 3431 and 3428cm^{-1} in both cases. The aromatic C-H asymmetric vibration was observed at 2923 and 2922 cm^{-1}. The storng band at 1384 cm^{-1} indicates the presence of NO_3^- ions of dopants in the polymer [9]. C-C stretching appears around 1458 and 1542 cm^{-1} [10]. The peak at 1123 and 1190 cm^{-1} is due to C-N stretching vibration and the peak at 1048 and 1041 cm^{-1} is due to C-H in plane deformation of pyrrole unit. The absorption band at 935 and 921 cm^{-1} is assigned to N-H wagging. The bands at 669 and 779 cm^{-1} were the characteristics of C-H out of plane ring deformation vibration [11]. Therefore FTIR analysis confirms the presence of pyrrole and the dopants.

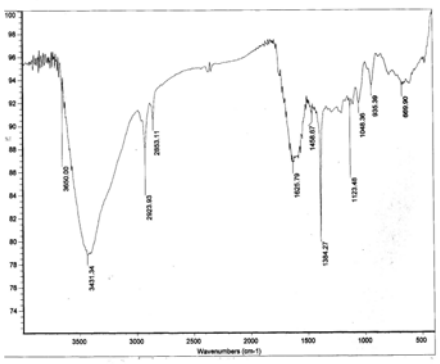

Fig. 3. FTIR spectrum of PPy-$(NH_4)_2S_2O_8$.

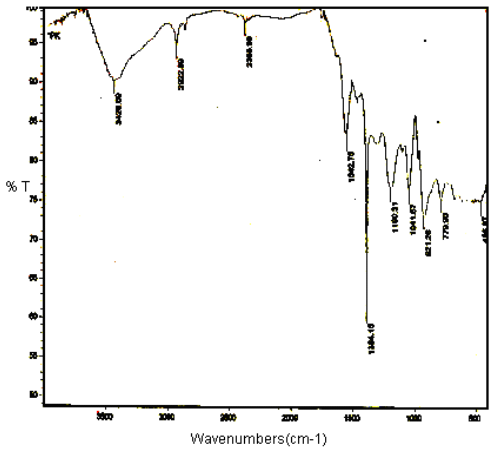

Fig. 4. FTIR spectrum of PPy-$K_2Cr_2O_7$.

4.3 UV absorption studies

The Figs. 5 and 6 reveal that the strong absorption at 600 nm for PPy-$(NH_4)_2S_2O_8$ and shorter wavelength at 380 nm for PPy-$K_2Cr_2O_7$ are attributed to the π-π* transitions in polypyrrole respectively. The band has undergone bathochromic shift owing to the extension of conjugation in the polypyrrole chain for longer wavelength 600 nm.

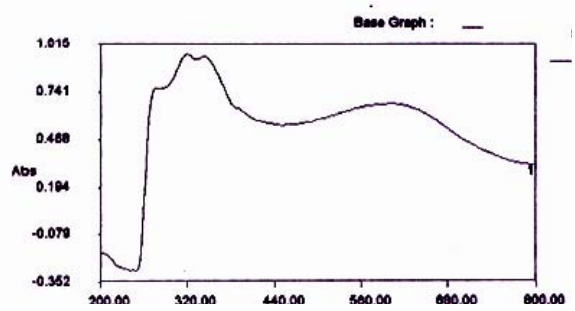

Fig. 5. UV- spectrum of PPy-$(NH_4)_2S_2O_8$.

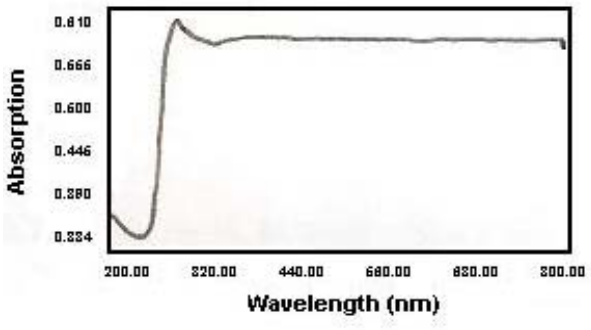

Fig. 6. FTIR spectrum of PPy-$K_2Cr_2O_7$.

4.4 Thermal analysis

The Figs. 7 and 8 depicts the thermo grams of PPy

samples synthesized using different oxidizing agents, two major stages of weight losses was observed in the PPy samples. The first weight loss was observed upto 180ºC, this loss could be attributed to the loss of water molecules from the polymer. The second stage observed within the range of 180ºC – 360ºC is related to removal of dopent ions from the polymer matrix. The weight loss observed after 400ºC is related to the degradation of the polymer itself. The thermo gram shows that the PPy powder samples are thermally stable upto certain lower temperature.

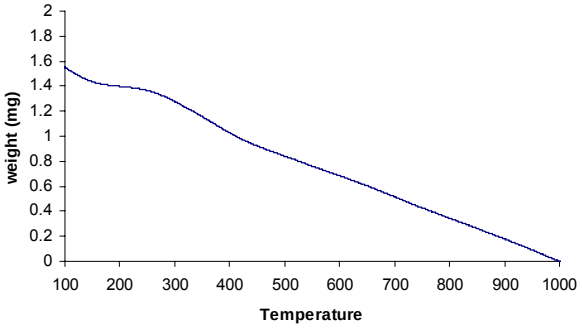

Fig. 7. TGA Curve of PPy-$(NH_4)_2S_2O_8$.

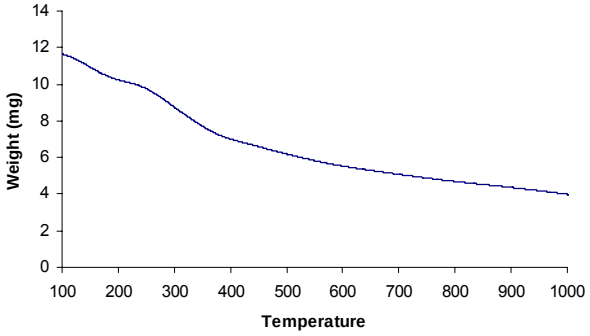

Fig. 8. TGA Curve of PPy-$K_2Cr_2O_7$.

4.5 Non linear optical analysis

The second harmonic generation of the synthesized polymers was measured using the Kurtz and Perry powder technique [12]. The powdered form of two PPy samples was densely packed capillary tubes and slides and subjected to NLO test using Nd: YAG laser. The input pulse energy of 2.41mJ/pulse was incident on the PPy powder. The second harmonic green signal was generated by the two samples. To measure the SHG intensity of the PPy, powdered form of microcrystalline KDP is used as a reference material. The present investigation results that SHG conversion efficiency of PPy-[$K_2Cr_2O_7$] was found to be 280mv and PPy-$(NH_4)_2S_2O_8$ was 380mv, which is higher than KDP (300mv) which was used as the reference material.

5. Conclusions

NLO active PPy was prepared successfully in the presence of two oxidizing agents. The properties of PPy were investigated using FTIR, UV, XRD, NLO and TGA techniques. It was found that, SHG conversion efficiency of PPy-$(NH_4)_2S_2O_8$ was 380mv, higher than KDP (300mv) which is used as a reference material. Therefore the above result indicates that, NLO active PPy-$(NH_4)_2S_2O_8$ is a considerable material for opto-electronic applications.

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