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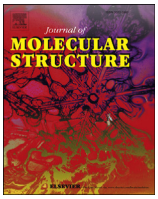

Effect of acid/base on the third-order optical nonlinearity of polypyrrole

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ABSTRACT

Polypyrrole (PPy) and its acid/base composites (PPy·H_2SO_4, PPy·HCl and PPy·$NH_3 \cdot H_2O$) were successfully synthesized and were characterized respectively by using fourier transform infrared, ultraviolet/visible absorption, X-ray diffraction, transmission electron microscopy and Raman spectroscopic techniques. The nonlinear optical properties of PPy and its acid/base composites were investigated using nanosecond Z-scan measurements at 532 nm. At the identical linear transmittance, the saturable absorption of pure PPy was changed to reverse saturable absorption by doping with acid (HCl and H_2SO_4) and base ($NH_3 \cdot H_2O$). The possible mechanisms for the different nonlinear properties were also discussed.

1. Introduction

The development of novel functional nanoscaled materials with superior properties has received great attentions due to the demand for new technologies that require high performance materials [1,2]. Conducting polymers with extended π-conjugation structures are a promising class of materials that possess unique properties that allow them to be used in a wide variety of applications in various scientific and technological areas such as chemical and biological sensors, polymeric rechargeable batteries, solid state devices, nonlinear optics, and corrosion resistance, and so on [3–5]. Particularly, these materials have emerged as a promising class of nonlinear optical (NLO) media for optoelectronic (including optical limiting) applications and there is considerable current interest in finding materials possessing large and ultrafast NLO responses along with other desirable chemical and physical properties [6–8]. The fundamental understanding of the relationship between molecular structure and NLO performances may be useful in preparing optimal materials for such applications.

Among these organic conducting polymers, polypyrrole (PPy) is becoming increasingly important for their potential applications and technological importance as electronic and optical devices, and it can be easily prepared by electrochemical and chemical oxidation methods and be doped with various dopants [9–11]. Therefore, PPy has the advantage of real applications in microelectronics and the information industry because of its controllable dielectric loss ability, ease of preparation, and good environmental stability. The physical and chemical properties of PPy mainly depend on the nature of the dopant, which can be improved by forming a polymer nanocomposite structure [12]. The electronical conductivities of PPy have been investigated extensively [13–16]. However, to the best of our knowledge, only a few informations exist concerning the NLO properties [17,18], especially the nonlinear absorption response, of this polymer in published literature.

Despite the technological importance, the effect of acid/base on the NLO properties of conducting polymers has not yet been well characterized. In this article, the polymer PPy was prepared by a conventional in situ chemical oxidative polymerization using ammonium persulfate (APS) as an oxidant. Hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and ammonium hydroxide ($NH_3 \cdot H_2O$) were chosen as the dopants. The preparation of such nanocomposites and their scrupulous characterization using FTIR, UV/vis, XRD, Raman, and TEM measurements have been presented in this aspect. Of special interest was to investigate whether this polymer has any appreciable NLO responses, and to study the effect of acid/base on the NLO properties by using Z-scan technique in the nanosecond regime at 532 nm. The results suggest that PPy-based

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nanocomposites with an appropriate dopant afford good candidates for optical limiting. Interesting but hitherto unknown results were indeed observed in the nonlinear optics of PPy and acid/base doped PPy (PPy·H_2SO_4, PPy·HCl and PPy·NH_3·H_2O). The synthetic technique provides a new approach to control the extrinsic morphology of PPy-based materials, and may be useful for developing new applications of these novel PPy nanocomposites in the promising nonlinear optical materials and other fields.

2. Experimental section

2.1. Materials and reagents

Pyrrole monomer (Shanghai Sinopharm Chemical Reagent Co. Ltd, China) was distilled under reduced pressure and stored under nitrogen in dark before use. Ammonium persulfate (APS, Shanghai Sinopharm Chemical Reagent Co. Ltd, China) as an oxidant was analytical grade and used as received. Other reagents were purchased from commercial suppliers and used without further purification. Deionized water was used throughout the whole composites preparation process.

2.2. Preparation of PPy and its nanocomposites

Polypyrrole (PPy) was prepared from pyrrole with APS as an oxidant by chemical oxidative method at room temperature. A typical polymerization is as follows (Scheme 1): 0.2 mL of pyrrole was dissolved in 20 mL deionized water, and then 0.1 g APS in 5 mL deionized water was added slowly by a constant pressure drop funnel. The resultant mixture was vigorously stirred at room temperature. The solution turned dark quickly, implying that the beginning of the polymerization. After 36 h, the mixture was poured into a large amount of methanol to terminate the reaction. The black precipitate was filtered and washed with deionized water, methanol, and ethanol several times to remove excess pyrrole, unreacted oxidant and other contaminants until the filtrate was colorless. The product (PPy) was dried under vacuum at room temperature for 2 days and grounded into fine powder. Doping was performed by immersing the PPy powder in aqueous solutions containing the dopants, i.e. H_2SO_4, HCl and NH_3·H_2O, respectively. Each solution was vigorously stirred for 36 h at room temperature. The resultant solid obtained by filtration was washed repeatedly with deionized water and dried, affording the desired PPy composites (PPy·H_2SO_4, PPy·HCl and PPy·NH_3·H_2O) with various dopants.

2.3. Instruments and measurements

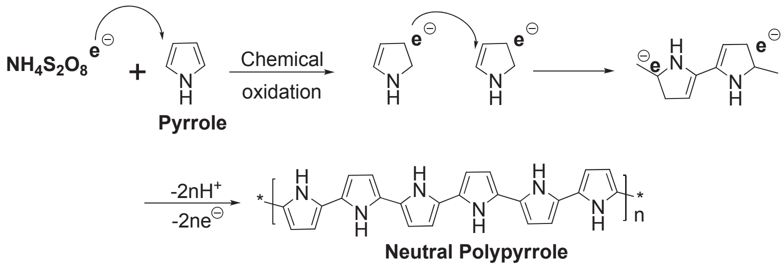
Fourier transform infrared (FTIR) spectra were measured with a MB154S-FTIR system (Canada) on powder samples using spectroscopic grade KBr pellet. Raman spectra were carried out at room temperature on a Renishaw Invia Raman Microscope. The 532 nm line of an Ar + radiation was used as the excitation resource, which was focused onto samples by using a microscope equipped with an a × 100 objective. The X-ray diffraction (XRD) analysis of all samples was recorded on a XD-3 diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) (Beijing Purkinje General Instrument Co., Ltd., China). It is used to identify crystalline nature of the samples. The ultraviolet/visible (UV/vis) spectra were obtained by a JASCO V-570 spectrophotometer using 1 cm quartz cuvette. TEM was conducted at 200 kV with a JEM-2100 (JEOL) instrument. Samples for TEM were prepared by placing a drop of a dilute dispersion of the as-prepared products on amorphous carbon-coated copper grids, which were then dried in air before being transferred into the TEM sample chamber.

The nonlinear absorption performances of all samples, including PPy, PPy·H_2SO_4, PPy·HCl and PPy·NH_3·H_2O, were assessed by the Z-scan measurement with linearly polarized 4 ns laser pulses at 532 nm with a repetition rate of 2 Hz. DMF suspension solutions of all samples in quartz cells of 2 mm thickness were placed at the focal point of a lens with a focal length of 50 cm, which was controlled by a computer, and then moved toward the *z*-axis of the incident beam. The incident and transmitted pulse light were measured by two energy detectors (Rjp-765 energy probe), which were linked to an energy meter (Rj-7620 ENERGY RATIOMETER, Laserprobe).

3. Results and discussion

3.1. FTIR studies

Fourier transform infrared spectroscopy (FTIR) has been shown to be an extremely powerful tool for surface characterization of materials, particularly when the nanocomposite is constituted by conducting polymer. FTIR analysis of PPy and its composites was carried out in the region of 4000–400 cm^{-1} to understand the chemical environment of the samples and shown in Fig. 1. The spectra display a rich band fingerprint region, implying all characteristic peaks of pyrrole functional groups [19]. The strong broadband at around 3425 cm^{-1} corresponds to the N–H stretching vibrations for nitrogen in the pyrrole rings and the O–H stretching of water from moisture [20]. The two very weak peaks 2973 and 2927 cm^{-1} can be assigned to the stretching vibration mode of aromatic C–H. The peaks observed at 1565 and 1479 cm^{-1} are due to the stretching vibrations of C=C and C–N of PPy ring, respectively, which may also represent the antisymmetric and symmetric pyrrole ring stretching modes; the peak around at 1195 cm^{-1} corresponds to the breathing vibration of the pyrrole ring, whereas the medium peak at 784 cm^{-1} originates from the C–H wagging vibration, and the peaks near 1047, 941, and 684 cm^{-1} can be ascribed to the C–H in-plane, C–H out-of-plane deformation vibrations, C–C out-of-plane ring deformation or C–H rocking, respectively [21]. A shoulder peak observed at 1297 cm^{-1} is predominantly because of the C–C in-ring stretching



Scheme 1. Chemical oxidative polymerization of pyrrole.