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Ecofriendly method to synthesize poly (*o*-aminophenol) based on solid state polymerization and fabrication of nanostructured semiconductor thin film

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ABSTRACT

Poly (ortho-aminophenol) (POAP) has been successfully synthesized by mechanochemical solid state polymerization (MCSSP) as a green method which is simple, rapid, free hazard solvent, economically route and environmental friendly method. POAP has been synthesized by using developed Mortar Grinder RM200 without using solvents in the preparation process and has been compared with the POAP synthesized by interfacial polymerization method (IP) as traditional method. The comparison between the two techniques was carried out by justifying various analyses such as, Fourier transform infrared spectra, ultra violet visible spectra (UV–Vis), X-ray diffraction, thermogravimetric analysis, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX). The analysis revealed that there is a good agreement between the MCSSP and IP method to synthesize POAP. POAP synthesized by MCSSP method has nearly the same high crystallinity of POAP synthesized by IP method. The energy band gap (Eg) was detected for POAP solution (DMF) synthesized by the two methods. Eg was found to be 1.74 eV and 1.95 eV for POAP synthesized by MCSSP and the IP method respectively. A thin film of POAP either synthesized by MCSSP or IP method was fabricated. Morphological and optical properties of the thin film have been investigated using SEM/EDX, AFM, and UV–Vis test. POAP thin film was located in the semiconductor materials range.

1. Introduction

Among the available essentially conducting polymers, polyaniline (PANI) or polyaniline derivatives have been attracted supreme interest on account of its low-cost monomer precursor, easy to synthesize, has a good thermal stability, tunable properties and abundant application opportunities [1–8]. A novel room-temperature solid-state oxidative method for the fabrication of PANI/single-walled carbon nanotube (PANI/MWNTs) composites was demonstrated, and found that the solid-state polymerization is an effective method for fabricating the composites of carbon nanotubes with a polyaniline type conducting polymer [9,10]. As an extension of the traditional synthesis method, the solid-state synthesis method has many advantages: reduced pollution, low cost, simple, rapid, free hazard solvent, economically route and considered environmental friendly method. Now, it is widely used for synthesizing polyaniline type conducting polymers for various applications [11-14]. By solid state polymerization method volatile organic solvents during polymerization are overcome [15].

The oxidation proceeding in the absence of solvents is of special interests to understand the chemistry of polymers oxidation and is an easy single-step method to prepare new materials.

The aim of the present study is to report for the first time synthesis of POAP based on MCSSP method compared with conventional standard interfacial polymerization method. Physicochemical properties of the resulting POAP are discussed in detail by comparative studies of FTIR, UV–vis, XRD, SEM, AFM and the energy band gap (Eg) value. Also the present study aims to prepare a nanostructured polymer thin film from the POAP synthesized by the traditional interfacial polymerization and mechanochemical solid state polymerization. The thin film has various

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potential industrial applications, such as antifouling biosurfaces, medical implants, advanced membranes, solar cells, adhesion, lubrication and friction modification. The spin coating method was used to fabricate the POAP thin film and the film thickness was determined by ellipsometer. The morphological properties of the fabricated thin films were investigated by AFM and SEM analysis and the optical properties were investigated by UV–vis spectra.

2. Experimental

2.1. Materials and methods

All reagents were used as received without further purification. Ortho-amino phenol (Aldrich) ammonium persulphate (Merck), ethanol (Merck), chloroform (Merck) Isopropanol (Shanghai chemicals), acetone (Merck) and dimethyl formamide (Merck) were used as purchased.

2.2. Synthesis of POAP

2.2.1. Synthesis of POAP based on mechanochemical solid state polymerization method

Typically, 1.6 g *o*-aminophenol monomer and 4.1 g ammonium persulphate initiator in solid state were mixed by a mechanical stirrer (950 rpm) for 10 min at room temperature and then was kept for 4 h. The resulting solid mixture was grinded by using a Grinder RM 200 for 10 min. During the milling process a dark gray color was gradually observed and increased with time which indicates the progress of the polymerization reaction of POAP. The same resulting color (dark Gary) was obtained during the conventional interfacial polymerization method. The resulting solid mixture from grinding process was washed with 100 ml of ethanol: distilled water (1:1) in order to dissolve unreacted monomer, oligomer and excess initiator. The resulting dispersion was filtrated; the solid retained on the filter paper (POAP) was washed with distilled water, followed by ethanol for several times. The resulting polymer sample (1.2 g) was dried at 60 °C for 24 h and marked by POAPs.

2.2.2. Synthesis of POAP based on interfacial polymerization method

The two phase polymerization was performed in 200 ml bottles at room temperature. The same weights from monomer and initiator which used in the previous MCSSP method were used in the interfacial polymerization method to carry the comparison between the two methods. 1.6 g OAP monomer was dissolved in chloroform, 4.1 g ammonium persulphate initiator was dissolved in distilled water. Separately, ammonium persulphate solution was added gently to alongside of monomer container. POAP was gradually appeared between the organic and aqueous layers in the reactor. The entire aqueous phase was filled homogeneously by POAP. Non-aqueous phase was removed from the bottom using separating funnel. POAP was collected by filtration. The resulting precipitate was washed with distilled water, followed by ethanol several times to remove unreacted monomer, oligomers and excess of the oxidizing agent. The resulting POAP (1.4 g) was dried at 60 °C for 24 h and marked by POAPi.

2.2.3. Preparation of POAP thin film

The POAP thin film was fabricated by deposition of POAP solution onto clean optically flat quartz substrates. A quartz substrate was cleaned by detergent, followed by ultrasonic cleaning for 10 min with isopropanol and acetone. The quartz substrate was rinsed with bi-distilled water for several times and then dried with inert gas. A 0.018 g of the POAP was dissolved in 0.5 ml DMSO. The resulting DMSO solution of POAP was stirred under magnetic at 60 °C for 25 min. The resulting PAOP solution was spin coated on the quartz substrate by spin coater SPIN150 at speed of 2000 rpm for 40 s. The resulting film was kept dry in a clean environment conditions and then kept in an evacuated dictator for testing. The film thickness was measured by M-2000 Ellipsometer and was found to be 150 nm.

2.3. Characterization

2.3.1. FT-IR analysis of POAP powder

The FT-IR spectra of the POAP powder were recorded using 130 FT-IR Spectrometer, Spectrum RX 1. The samples were prepared in the pellet form by mixing the powder with KBr by the ratio 1:10 and pressing it in the Perkin Elmer hydraulic device using 5 tons pressure.

2.3.2. XRD of POAP powder

The X-ray diffraction spectra of the POAP samples was carried out by Burker D8 advanced XRD (x-raydiffractometer using the Cu-Kα radiation wavelength ($\lambda = 1.54$ Å). The scanning range was set from 5° to 80°. The operating conditions were 40, divengency slit: 1 mm, Ni filter, LynxEye one dimensional detector and Detector slit 3 mm. The crystallinity analysis is calculated based on the peak area from EVA software.

2.3.3. SEM/EDX of POAP powder

The morphological study for POAP powders was carried out using scanning electron microscope (SEM), FE-SEM Zeiss Leo Supra 55. Samples were sputtered by a thin film of gold to improve the conductivity.

2.3.4. UV–visible absorption spectra measurements and optical band gap of POAP solution

The UV–visible absorption spectra of prepared POAP samples were measured using Shimadzu UV spectrophotometer (M160 PC) at room temperature in the range 200–800 nm. The POAP samples were dissolved in dimethyl formamide (DMF) solvent and DMF has been taken as a reference during the measurement performance. The optical band gap (Eg) was measured from the absorption spectra data. Eg was calculated from Tauc's relation for direct transitions [16,17].

2.3.5. Molecular weight determination

Molecular weights of POAPi and POAPs have been determined by Gel Permeation Chromatography using waters 515/2410 Gel Permeation Chromatograph (GPC, Waters, America) and a Styragel column calibrated with polystyrene standards and series 2410 refractive index detector. Mobile phase is tetrahydrofuran (THF), the flow rate is 1 ml/min, and the temperature is 40 °C.

2.3.6. Thermogravimetric analysis (TGA) of POAP powder

The Thermogravimetric analysis of the resulting POAP sample was applied by TGA, Q50, TA instruments. The experiment was carried out under N_2 atmosphere with heating rate of 10 °C/min from 30 °C to 1000 °C.

2.3.7. UV–vis NIR spectra measurement of POAP thin film

UV–Vis absorption spectra of POAP thin film (150 nm) was recorded by a Shimadzu UV-3600 UV–vis NIR spectrophotometer at room temperature.

2.3.8. AFM of POAP thin film

The surface roughness and morphology of POAP nanostructure thin films were studied using an AFM (Bruker dimension icon