

Optical and structural properties of BTCA doped polyaniline nanoparticles at room temperature

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Abstract

BTCA doped Polyaniline was synthesized by in-situ chemical polymerization method at room temperature. BTCA acts as a dopant and soft template for the synthesis of PANI nanoparticles. The prepared samples were characterized by FT-IR, XRD, SEM and PL. FT-IR spectrum confirms the presence of dopant in the polyaniline structure. The optical band gap was found to be 1.90 eV. X-ray diffraction patterns showed crystalline structure due to planar nature of benzenoid and quinoid functional groups. The intensity of the peak reflections are (100) and (110) planes. Spherical agglomerate like morphology. PL study shows emission peak at 420nm.

Introduction

Polyaniline (PANI) is considered to be one of its most interesting photocatalytic materials due to its low monomer cost, environmental stability, larger conductivity, and porous structure [1], [2]. The main disadvantage of PANI is its low solubility due to its rigid backbone [3,4]. Various approaches have been tried to improve its processability, with two notable attempts at overcoming these drawbacks being chemical modification, such as doped PANI with organic acids and substituted derivative of PANI, respectively. Organic acids such as salicylic acid, benzoic acid, oxalic acid [5], dodecylbenzenesulfonic acid [6], and poly(4-styrenesulfonic acid) [7] have been used to dope PANI through an oxidative chemical process.

Among organic acids, 1,2,4,5-benzenetetracarboxylic acid (BTCA), also known as pyromellitic acid, is a tetrafunctional chemical that acts as a crosslinking modifier to control crystallisation rate and increase melting point enthalpy due to benzeneization at the centre of BTCA [8,9]. Furthermore, Karkietal suggested that BTCA might be used as an attractive multivalent model functioning as a switch in an H-bonding supramolecular network, which could be realised for developing new photoactive array applications [10].

The Current chemical methods for fabricating polyaniline nanostructures (tubes, wires, rods, fibres) generally require specific materials that control the structure, i.e. an insoluble solid model such as zeolite channels [7], porous membranes [8, 9], opal, and so on, as well as organic templates such as surfactants, polymers, and large organic dopants[11].

At room temperature, BTCA doped PANI nanoparticles were produced using a chemical oxidation technique in this study. The optical, structural, and morphological properties are thoroughly explored.

2. Materials and Methods

In a typical synthesis, 1 M aniline monomer and 1 M Benzenetetracarboxylic acid (BTCA) were dissolved in 100 ml of de-ionized water, and then 1M ammonium persulfate (APS) was added to the mixture while stirring continuously for 30 minutes. For 24 hours, the polymerization reaction was carried out under static circumstances at room temperature. The resulting precipitate was washed with water, acetone, and methanol in that order. For 24 hours, the sample was maintained in a vacuum oven at 60° C.

3. Results and discussion

3.1 PL properties of BTCA doped PANI

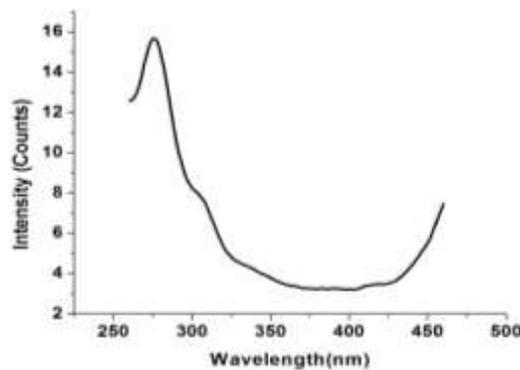


Fig.1 Photoilluminescence properties of BTCA doped Polyaniline

Fig. 1 depicts the photoilluminescence characteristics of BTCA doped polyaniline. The peak was discovered at 420nm. This peak is caused by transitions from the polaronic band to the PANI band structures.

3.2 X-ray diffraction pattern of BTCA doped PANI

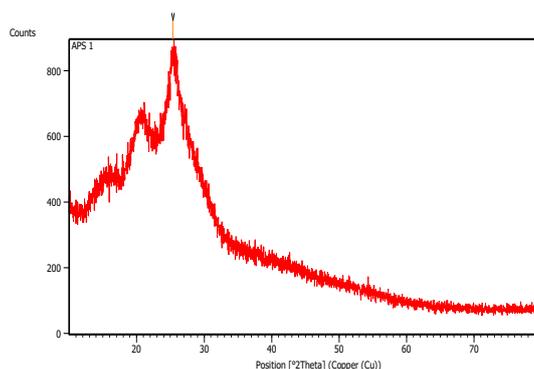


Fig.2 X-ray diffraction of BTCA doped PANI

The X-ray diffraction pattern of BTCA doped PANI is shown in Fig.2. Two distinct peaks are found at $2\theta = 20^\circ$ and 25° . These peaks corresponded to the planes (100) and (110). This result demonstrates that PANI in salt form is formed when PANI is doped with benzoic acid [12]. Polymers are often thought to be amorphous, yet the synthesised polymer has a crystalline structure due to the fibre character and planar nature of the benzenoid and quinoid functional groups. The face-to-face inter-chain stacking distance between aromatic rings of PANI chains is attributed to the peak at $2\theta = 25^\circ$ [13].

3.3 FT-IR spectra of BTCA doped PANI

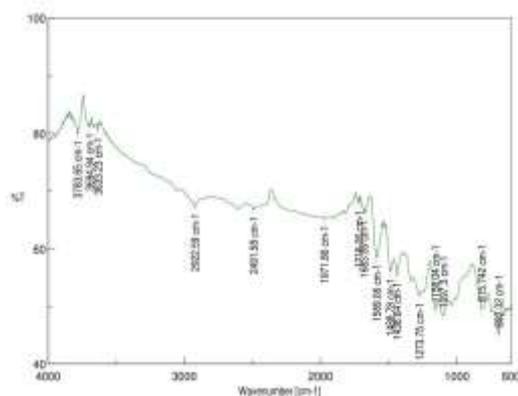


Fig.3 FTIR spectra of BTCA doped PANI

Fig.3 shows the infrared spectrum of PANI-benzenetetracarboxylic acid salt. PANI-benzoic acid salt exhibited bands at 1589 and 1488 (for N-H bending) [14]. C-N stretching mode vibrations cause the characteristic peak at 1273.75 cm. This mode was identified as a single band at 815 cm-1, which falls within the range 800-860 cm-1 described for 1-4 disubstituted

benzene. The PANI salt exhibited a significant absorption band at 1158 cm⁻¹, which has been linked to high electrical conductivity and a high degree of electron delocalization.

3.5 Optical band gap of BTCA doped PANI

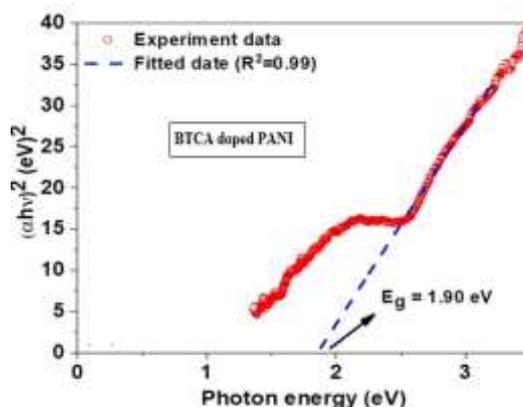


Fig.4 The absorption band gap of BTCA doped PANI

The absorption band gap of BTCA doped PANI is measured from the absorption coefficient data as a function of wavelength using Tauc relation (2).

$$(\alpha hv)^n = B(hv - E_g) \quad (2)$$

where, α is the absorption coefficient, hv is the photon energy and n are a constant which depends on the probability of transition. Fig. 4 shows the variation of $(\alpha hv)^2$ vs. hv . The calculated wavelength of the absorption band gap energy value was found to be 1.90 eV.

3.6 Morphological studies of BTCA doped PANI

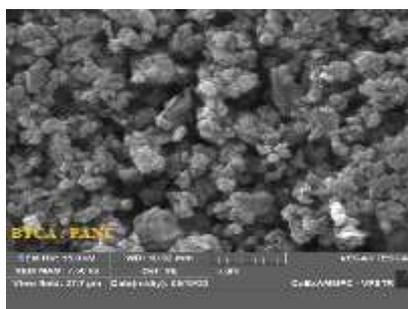


Fig.5 Morphological studies of BTCA doped PANI

Figure 5 shows SEM images of BTCA doped PANI. PANI has a spherical agglomeration shape.

Conclusion

BTCA doped PANI was synthesized by chemical route at room temperature. The sample was characterized by XRD, PL, FT-IR spectroscopy, UV spectroscopy and SEM. The

FT-IR analysis reveals PANI's characteristic peaks. A PL investigation shows an emission band at 420nm. The morphology of the spherical agglomeration is revealed by the SEM image. An XRD analysis indicates the crystalline and salt forms of polyaniline. The energy value of the absorption band gap was found to be 1.90 eV.

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