FABRICATION AND STRUCTURAL ANALYSIS OF POLYPYRROLE–FUNCTIONALIZED CARBON NANOTUBE COMPOSITES THROUGH OXIDATIVE POLYMERIZATION

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Abstract:

In this work, a novel nanocomposite was developed using polypyrrole (PPy), a well-known conducting polymer. The polymerization of pyrrole and the functionalization of multi-walled carbon nanotubes (MWCNTs) were carried out through an in-situ chemical method. Initially, the MWCNTs were functionalized using formaldehyde and potassium hydroxide solutions. The resulting PPy/MWCNT nanocomposite was characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy. The electrical properties of the synthesized composite were evaluated using the standard four-probe technique. Structural analyses from XRD, FTIR, and Raman studies confirmed both the successful polymerization of pyrrole and the formation of the PPy/MWCNT nanocomposite. Furthermore, DC electrical conductivity measurements revealed a sharp increase in conductivity, with conductivity values rising proportionally to the concentration of functionalized carbon nanotubes in the composite.

Keywords: Polypyrrole (PPy), Multi-Walled Carbon Nanotubes (MWCNTs), Conductivity

1. Introduction

Conducting polymers (CPs) were first synthesized in the 1960s and are considered the latest generation of polymeric materials. Unlike conventional polymers, which are typically insulators, CPs possess electrical and optical properties comparable to those of metals and inorganic semiconductors, while retaining the desirable characteristics of organic polymers, such as ease of synthesis and flexibility in processing. This unusual behavior arises from their unique molecular structures. Polymers with conjugated π-electron backbones (i.e., systems with alternating C=C bonds) display distinctive electronic properties, including low-energy optical transitions, low ionization potentials, and high electron affinities. As a result, these polymers can undergo oxidation and reduction more readily and reversibly than conventional polymers [1].

Electronically conducting polymers (ECPs), such as polypyrrole (PPy), polythiophene (PT), and polyaniline (PANI), exhibit unusually high electrical conductivity in the doped state. Owing to this property, they have attracted significant attention from both chemists and physicists [2]. ECP films behave like redox polymers and show great potential in diverse applications, including electrocatalysis, solar energy conversion, corrosion protection, and electronics [3].

Conducting polymers can be synthesized either chemically or electrochemically, with electrochemical synthesis being the most widely used method due to its simplicity, speed, and precise controllability. Among these, polypyrrole is one of the most extensively studied conducting polymers because it can be easily deposited from aqueous and non-aqueous media, adheres well to various substrates, and demonstrates excellent electrical conductivity and stability. Electrochemical polymerization produces thin films of a few micrometers on electrode surfaces, whereas chemical oxidation results in fine-grained materials. However, the yield and quality of the polymer films depend on several factors, including the nature and concentration of the monomer and counter ion, solvent, cell parameters (such as electrode type and applied potential), as well as temperature and pH conditions [4-5].

2. Synthesis of Polypyrrole/MWCNTs composites

(a) Preparation of polypyrrole

The preparation of polypyrrole involves the polymerization of freshly distilled pyrrole, a monomer of the conducting polymer polypyrrole. The pyrrole monomer is distilled by heating it to its boiling point, during which cooling pumps are used to collect the purified pyrrole while the volatile impurities are removed [6].

For the chemical polymerization of pyrrole, ferric chloride ($FeCl_3$) is employed as the oxidizing agent. In this experiment, 6.4932 g of $FeCl_3$ was dissolved in 100 mL of 0.1 M hydrochloric acid (HCl) and the solution was kept under constant stirring. After one hour, 0.7 mL of freshly distilled pyrrole was added, and the mixture was stirred continuously for 24 hours. The resulting product was filtered and thoroughly washed to remove unreacted pyrrole and other impurities. The material was then dried in a hot air oven, ground into fine powder, and stored for further characterization and investigations [7].

(b) Preparation of Polypyrrole / 10 wt% CNT composites

Polypyrrole/CNT composites were synthesized via an in-situ polymerization method to ensure effective bond formation within the sample. For this, 6.4932 g of ferric chloride ($FeCl_3$) was dissolved in 100 mL of 0.1 M hydrochloric acid (HCl) under constant stirring. Subsequently, 0.06776 g of CNTs (corresponding to 10 wt%) was added to the solution, followed by the addition of 0.7 mL of freshly distilled pyrrole. The reaction mixture was stirred continuously for 24 hours [8].

The resulting product was filtered, thoroughly washed to remove impurities and unreacted pyrrole, and then dried in a hot air oven. The dried material was ground into fine powder and stored for further investigations. The same procedure was repeated to prepare composites with 5 wt% and 3 wt% CNT loadings [9].

3. Result analysis & Discussions

Figure (1) presents the XRD patterns of pure polypyrrole (PPy) and its composites with MWCNTs at varying concentrations. The XRD spectrum of PPy exhibits a broad peak at 25° and a sharper one at 11.79°, which can be attributed to the regular repetition of monomer units and the ordered arrangement of the polymer backbone. In the case of the composites, additional peaks appear at 35°, 43°, and 50°, corresponding to the crystalline planes of MWCNTs. The broad peak around 25° is observed in both PPy and MWCNTs, confirming their coexistence in the composite structure.

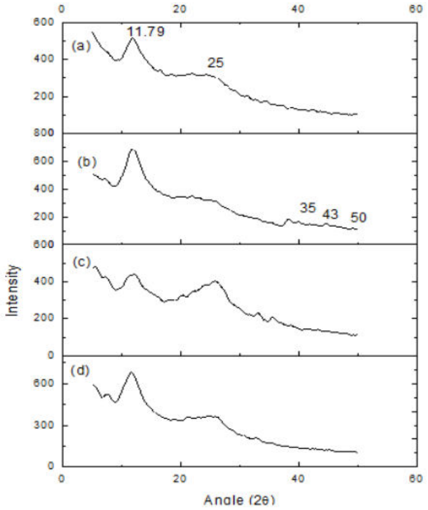

Figure1. XRD Spectrum of (a) PPy (b)PPy/MWCNT (10wt%) (c) PPy/MWCNT (5wt%) (d) PPy/MWCNT (3wt%) composites

Figure (2) shows the FTIR spectra of PPy and PPy/MWCNT composites. Characteristic absorption bands of PPy are observed at 785 cm⁻¹, 1125 cm⁻¹, 1259 cm⁻¹, 1459 cm⁻¹, 2369 cm⁻¹, and 3580 cm⁻¹. The band at 3580 cm⁻¹ corresponds to hydrogen-bonded N–H stretching vibrations, while the peaks at 1459 cm⁻¹ and 1259 cm⁻¹ are attributed to C–N stretching modes in the pyrrole ring. The band at 785 cm⁻¹ corresponds to out-of-plane C–H vibrations. These assignments confirm the formation of polypyrrole.

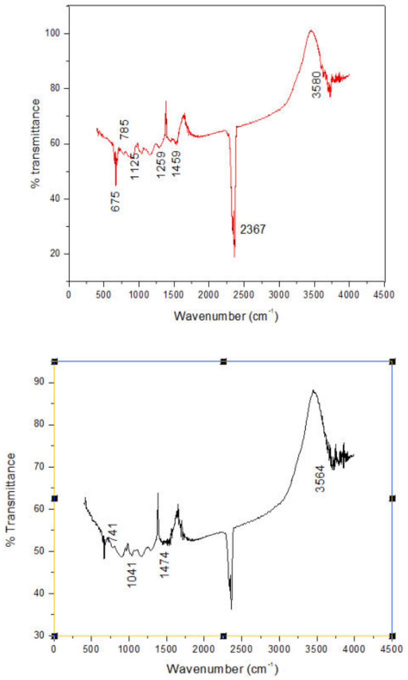

Figure 2. FTIR Spectraof (a) PPy (b)PPy /CNT composites

Incorporation of MWCNTs results in peak shifts, indicating interactions between MWCNTs and the nitrogen sites of PPy. Specifically, bands at 3580 cm⁻¹, 1125 cm⁻¹, and 785 cm⁻¹ shift to lower wavenumbers, while the band near 1425 cm⁻¹ shifts to a higher wavenumber. No uniform red or blue shift is observed, suggesting changes in bond strengths—weakening of N–H, C–H, and C–C bonds and strengthening of the C–N bond in the composites as shown in figure.3.

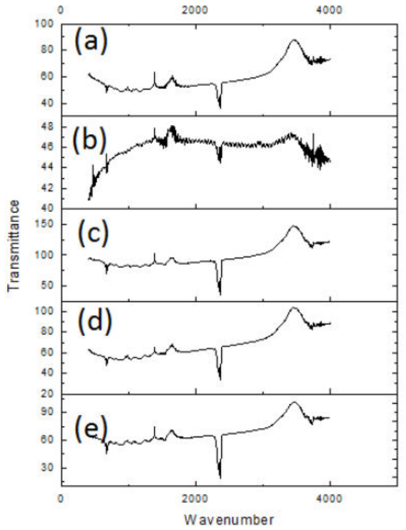

Figure 3. FTIR Spectra of (a)PPy (b)functionalized CNT (c) 10wt%PPy/CNT (d)5wt%PPy/CNT (e) 3wt%PPy/CNT

The Raman spectra of PPy, MWCNTs, and PPy/MWCNT composites are shown in Figure (d). Pure MWCNTs display a characteristic G-band at 1591 cm⁻¹, associated with the graphite wall, and a D-band at 1334 cm⁻¹, attributed to disordered graphite. In the composites, these peaks shift to 1559 cm⁻¹ (G-band) and 1317 cm⁻¹ (D-band), along with the emergence of a new peak at 2659 cm⁻¹, indicating modifications caused by MWCNT functionalization and interaction with PPy in figure.4.

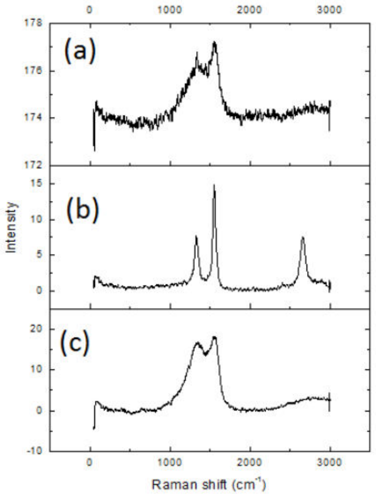

Figure 4. Raman spectra of (a) PPy (b)functionalized MWCNT (c)10 wt% PPy/ MWCNT composites

The investigation aimed to synthesize high-quality PPy/MWCNT composites suitable for electrode applications in supercapacitors. Although powder samples with electrical conductivity in the range of 5–20 S/cm were successfully obtained, producing high-quality thin films of these composites remains a challenge. Functionalization of MWCNTs was primarily intended to improve their processability for film formation. The current results confirm that PPy/MWCNT nanocomposites hold promise as electrode materials for supercapacitors due to their favorable conductivity range. However, further optimization of synthesis parameters and functionalization techniques is essential to achieve high-quality thin film devices.

Conclusion

The prime objectives of this work were successfully achieved. The synthesis of the PPy/MWCNT nanocomposite was accomplished to a significant extent. The structural characteristics of the newly prepared composite were examined using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy, while its electrical properties were evaluated through the standard four-probe technique. The results from XRD, FTIR, and Raman analyses confirm the successful polymerization of pyrrole monomers and the formation of PPy/MWCNT nanocomposites.

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