Synthesis, Characterization of Polyaniline and Polyaniline Encapsulated Cellulose isolated from Sugarcane Bagasse and its study on Electronic Properties

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ABSTRACT

In recent years, synthesis of conducting polymeric composites has attracted a great deal of attention due to their wide applications in various fields. In the present investigation, we report on the synthesis of polyaniline cellulose nanocomposite via oxidation polymerization method. Here the addition of ammonium peroxydisulfide as oxidizing agent into a reaction mixture of aniline and cellulose as solid support at room temperature leads to the formation of polyaniline encapsulated cellulose nanocomposite. The nanocomposite was isolated and then characterized by using various analytical techniques to understand the composition and the surface morphology of the PANI-Cellulose nanocomposite. The structure of the nanocomposites was analysed using X-ray Diffraction method (XRD) and UV-visible spectroscopy instruments. The electrochemical behaviour of the polymer nanocomposite was studied by cyclic voltammetry in supporting electrolyte medium. Electrical measurement of composite together with increase in its conductance, thereby makes it a possible future material for high temperature application purposes, resulting in PANI-Cellulose nanocomposite having high thermal and electrical conducting property compared to polyaniline.

Keywords: PANI, PANI-Cellulose, Nanocomposite, Oxidation polymerization, Electro catalytic activity.

1. INTRODUCTION

Nowadays, cellulose with a conducting polymer has a great deal of application in new functional papers and packaging applications, such as anti-static and electro-magnetic shielding papers and antibacterial papers [1, 2]. Among the conducting polymer used for coating fiber, micro/nano structured Polyaniline (PANI) conductive polymeric composites have received considerable attention because of unique properties, including chemical and electrical properties, simple preparation, low cost and excellent environmental stability [3]. These characteristics have led to the application of PANI in various micro/nano materials and devices [4]. The optical, microwave absorption and magnetic functions of PANI micro/nano structures have also drawn significant research interest because of their potential to meet the needs of various technological applications. Polymer modification by surfactants is an attractive and interesting method of preparing polymer composites. Polymers have been widely studied in solution and in solid states because of their interesting physical properties, including easy solubility morphology and reversible fusibility [5-7].

Cellulose is an abundant and renewable raw material, suitable for industrial manufacturing [8]. Cellulose and its derivatives have been applied to many aspects of our life for over 150 years and have been used for recent applications in fields such as electronics, biomaterials, and pharmaceuticals, where cellulose structure and properties have
been found to be valuable [9, 10]. These chains are stabilized by the hydrogen bonds and van der Waals forces between the hydroxyl groups on the D-glucose units, resulting in regions with both amorphous and crystalline character. Cellulose is well-known as the main component of the plant cell wall, which permits the passage of nutrients like water, ions, and small molecules, and maintains the cell shape with strong tensile strength. The native cellulose fibers applied here function like a cell wall that uptakes electrolyte from the bulk electrolyte bath. Previously, porous cellulose fibers have been applied as a template for the synthesis of noble metal nanoparticles less than 10 nm, and different wood tissues have been utilized to grow zeolites, demonstrating the mesoporous structure of the cellulose fibers. Meanwhile, the electron-rich oxygen atoms of the polar hydroxyl and ether groups in cellulose can also interact with electropositive transition metal cations. Recently it has been reported that palladium nanoparticles supported cellulose filter papers can be prepared by a simple dip coating method which was used as an efficient catalyst for the Suzuki-Miyaura cross coupling reaction [11].

2. EXPERIMENTAL

2.1. Materials
Cellulose was extracted from raw sugarcane bagasse materials, Aniline, Pyrrole monomer (Aldrich chemicals) was distilled under reduced pressure, and Ammonium persulfate (APS, Aldrich chemicals). All aqueous solutions were prepared with double-distilled water.

2.2. Cellulose isolation
Extraction of cellulose from sugarcane bagasse was carried according to the following methodology (Rodrigues Filho et al., 2000): a mixture of 76mL NaOH (0.25M) and 4g of dry, ground bagasse was kept at room temperature for 18h. Then, this mixture was filtered, washed with distilled water and refluxed with a HNO₃/ethanol solution (20% v/v) for 3h, changing the alcoholic solution every hour. After the reflux, the bagasse was washed with distilled water to remove the acid and oven dried at 105°C for 3h [12].

2.3. Instrumentation

UV-Visible spectral studies were carried out by using Shimadzu UV-Visible Spectrophotometer, Japan (Model UV-1800). FT-IR spectra were recorded using a Perkin Elmer (360 model, USA) IR double beam spectrophotometer. Morphological and structural investigations were carried out using field emission scanning electron microscopy (FE-SEM, SU6600, Hitachi, Japan). Electrochemical experiments were carried out using a CHI 660A electrochemical instrument, USA and Gamry model 330, USA. The working and counter electrodes were glassy carbon electrode (GCE) (3mm dia) and platinum wire as auxiliary electrode. An Ag/AgCl electrode was used and has a reference electrode (Ag/AgCl/KCl). Bioanalytical system (BAS, USA) polishing kit was used to polish the GCE surface.

3. RESULTS AND DISCUSSION

3.1. UV-Vis spectrum of PANI-Cellulose

Figure 1 shows the UV-Vis spectra of PANI shows at 400nm attributed to the polaron π* transition in the Emerladine Salts (ES). The dark green product dispersed water shows three absorption peaks. The absorption spectrum of PANI shows bands around 355nm - 450nm corresponding to π – π* within the benzenoid moieties which is due to the formation of a doping level owing to the ‘exciton’ transition, caused by inter-band charge transfer from benzenoid to quinoid moieties, respectively. The localized polaron peak around 750nm indicates a compact coiled (tightly coiled chains) conformation of PANI in its conducting form [13]. The absorption spectrum for PANI-Cellulose clearly shows that PANI was successfully coated Cellulose. PANI-Cellulose shows bands around 375nm corresponding to PANI coated cellulose.

3.2. FT-IR spectrum

FT-IR spectrum of CF and PANI-Cellulose are shown in figure 2. A peak at 3452cm⁻¹ is due to O-H stretching vibrations, the other two peaks at 2367 and 2078 cm⁻¹ are assigned due to the aliphatic C-H stretching vibrations. Major peaks at 1639 and 1409cm⁻¹ are due to the asymmetric and symmetric stretching of the carboxylate group (-COO), and a sharp peak at 1409cm⁻¹ is due to C-O-C stretching vibrations, respectively. In the case of PANI/CF peaks at 2835, 2367 and 1639cm⁻¹
(weak bands) for aliphatic C-H stretching vibrations and carbonyl stretching vibrations of CF respectively. From the above studies it is confirmed that the PANI was successfully modified over the surface of cellulose [14].

![Figure 1. UV-Vis spectra of PANI and PANI-Cellulose composite](image1)

![Figure 2. FT IR spectrum of cellulose, PANI and PANI-Cellulose composite](image2)

### 3.3. X-Ray diffraction studies

The XRD patterns of Cellulose, pure PANI and PANI-Cellulose nanocomposite are compared in figure 3. It can be seen that diffraction of Cellulose shows a typical peak at 14.8, 16.7 and 23.5 [15]. The pure PANI has a primary characteristic peak at 25.2° attributed to the scattering from the periodicity perpendicular to PANI chains and the one at 20.3° to the alternating distance between layers of polymer chains [15]. The diffraction peaks of PANI-Cellulose composite is similar to PANI, and no obvious diffraction peak at about 200 of cellulose appears, since the content of cellulose in the composite is very small and the cellulose is uniformly dispersed in the composite materials [16].

![Figure 3. X-ray Diffraction of Cellulose, PANI and PANI-Cellulose composite](image3)

### 3.4. Electrochemical behaviour of PANI, PANI-Cellulose /GCE

Cyclic voltammogram of PANI-Cellulose modified GCE in presence 0.1M KCl is shown in figure 4. As an electrolyte a scan rate 50mV/s in the potential range from -1.0V to 1.0V is noted. There is no peaks obtained for the bare GCE (a) Two set of redox peaks were observed in case PANI-Cellulose in 0.1M KCl medium. A well-defined first redox peaks at +0.19V and – 0.16 V (vs. Ag/AgCl_sat) and the second redox peaks at +0.5V and + 0.24 V (vs. Ag/AgCl_sat) were shown in figure 4. In the positive sweep the first redox peak is due to the formation of radical cations (polaronic emeraldine) and the second redox couple is the formation of diradical dications (represented by the resonance structures: bipolaronic pernigraniline and protonated quinonedimine) through the oxidation of PANI salt form. These two set of redox peaks is due to the interconversion of benzenoid form of polyaniline to quinoid form. It is confirmed that emeraldin salt form of polyaniline deposited on the surface of the cellulose nanofiber [17, 18].

### 3.5. FE-SEM image of PANI-Cellulose

The surface morphology of the PANI and PANI-Cellulose was observed using field emission scanning electron microscopy (FE-SEM). The FE-SEM images of PANI and PANI-Cellulose composites obtained from the in situ polymerization of PANI on cellulose are shown in figure 5. The change in surface morphology was seen in the case polyaniline modified cellulose nanofibers [18].
Figure 4. The electrochemical responses of the bare GCE (a), PANI/GCE (b), PANI-Cellulose/GCE (c) in 0.1 M KCl at a scan rate 50 mV (A)

Figure 5. FE-SEM images of PANI and PANI-Cellulose composite (A and B)

3.6. I-V studies of PANI and PANI-Cellulose

Figure 6 shows the I-V studies of PANI and PANI-Cellulose composite at room temperature. I-V of PANI is completely symmetrical with respect to the polarity of the applied voltage. This curve shows the non-ohmic relation and this linear increase with current and applied voltage. The charge conduction is not only carried by free carriers (hole & electron) such as semiconductors but also it is carried by the formation of polarons and bipolarons, as applied voltage increases and increase with the formation of polarons and bipolarons rapidly to high values of current through the sample [19, 20, 21].

The current–voltage characteristic of PANI-Cellulose composite was taken at room temperature as shown in figure 7 and indicates that cellulose coated polyaniline behave as Schottky effect. The forward bias corresponds to the positive potential to the polyaniline with respect to cellulose. The I-V studies of the PANI–Cellulose indicates the formation of the depletion layer at PANI-Cellulose interface. This is due to the increase in the voltage current and also increase at higher voltage linear peak appear for PANI but at higher voltage, non-linear peak will appear for PANI-Cellulose composite due to non-polaron and free electron carrier of composite [19,20].

Figure 6. I-V of PANI

Figure 7. I-V of PANI-Cellulose

4. CONCLUSION

This study confirms and extends the broad spectrum of electronic properties I-V Spectra and CV for PANI and PANI-Cellulose so far that they are capable of high current and rectifying the effect and polaron, non–polaron shows the linear & non–linear cases for PANI and PANI-Cellulose composite. The UV-Visible, IR&XRD shows the formation of composite.

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