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Surface Modification of Cellulose Nanofiber with Polyaniline using Aniline Monolayer as Seed for Chemical Oxidation Polymerization of Aniline

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A simple method is adopted to prepare conducting polyaniline thin film on cellulose filter paper by chemical oxidative polymerization. In order to improve the adhesion of polyaniline on cellulose nanofiber aniline terminal, silane monolayer was used as catalyst to initiate polymerization reaction. It was also showed that aniline dimer modified cellulose nanofiber shows an enhanced polyaniline growth and acting as seed for the polyaniline growth. The polyaniline modified cellulose fibre filter paper was then characterized with UV-visible spectroscopy, FT-IR, FE-SEM and electrochemical studies. Polyaniline modified filter paper strips can be used for naked eye sensing of ammonia and hydrazine in environmental samples.

Keywords: Cellulose nanofibre, Polymerization, Polyaniline, Modified filter paper.

INTRODUCTION

Conductive polymers have unique electrical and opto-electronic properties are interesting features to use in a variety of commercial applications [1]. Polyaniline (PANI) is one of the well-studied conducting polymers because of its easy synthesis and inherent electrical properties and thus it can be used in numerous applications including super capacitors, batteries, chemical and biological sensors, electrical conductors and in antistatic coatings [2-6]. However, PANI has some disadvantages for example; it has low dispensability and poor solubility in most of the solvent, which limit its applications. To improve the electronic properties various strategies have taken to overcome all inherent limitations. To avoid length operating procedure for the fabrication of sensor device, *in situ* chemical as well as electrochemical polymerization approach have been made. Recently, biopolymer template chemical oxidative polymerization of pyrrole and aniline emerges as the energy storage devices and gas sensor applications [3]. Moreover, polyaniline composite of biopolymers can be synthesized by chemical oxidative polymerization method in which biopolymers is functioning as template and the nanocomposite have shown a lot of applications in environmental cleanup of toxic heavy metal pollutants and removal of textile dye [7-10].

The fabrication of a flexible and electrically conductive nanocellulose based polyaniline composite film is one of interesting research in recent days. By this way, it is possible to fabricate high conductive flexible sensor devices. Some of the natural polymers including nanocellulose have been used as solid support to grow polyaniline with controlled film thickness by controlling of reaction conditions. Earlier studies have shown that the controlled growth of polyaniline film on solid support based monolayer modified surface in which the monolayer functionalized with its respective monomer or dimer as seed to grow a high density polyaniline [11-13]. Recently, it has been shown that polyaniline modified cellulose fibre was synthesised and then used for removal of toxic pollutants like Cr(VI) and Hg(II) from environmental sources [9]. In that study, the polymerization of aniline in the presence of nanocellulose to improve the physical and electrochemical properties of PANI and noted that polyaniline containing nitrogen is capable coordination with these metal salts. Hydroxyl groups that cover the surface of cellulose allows to react well with a variety of materials including conducting polymers.

Recent studies proved that cellulose nanofibers derived from natural sources have shown a lot of applications including surface modifications with gold, silver and palladium nanoparticles for catalytic applications, electrochemical sensors and

Surface Enhanced Raman Scattering (SERS) studies [14-18] and also have been utilized for surface modification by various reactions in biotechnology such as targeted drug delivery and biochemical sensing of microbes [19]. In present study, a use of cellulose nanofiber as template to grow polyaniline after pre-treatment with aniline terminal monolayer as seed is demonstrated. The advantage of the present method, a stable covalent bonded polyaniline film was obtained over cellulose nanofiber and can be enable to use for various sensor applications. Surface modification of silicon and glass substrate to generate the polymer pattern as well as microelectronic applications using suitable functionalized molecules [20]. Similar strategy have been taken to modify cellulose paper surface to growth polyaniline uniformly in a controlled manner under optimized experimental conditions and then a detailed studies have been carried out to study the surface characteristics and sensor applications.

EXPERIMENTAL

Aniline, *N*-phenyl-1,4-phenylenediamine (aniline dimer), *N*-[3-(trimethoxysilyl)propyl}aniline, potassium hydroxide and ammonium persulfate (APS) were used as received from commercial sources. Whatman filter papers were also purchased from the commercial sources. All solvents used as received without any further distillation.

The UV-visible spectral studies were carried out using Shimadzu UV-1800 UV-visible spectrophotometer, Japan. FTIR analysis was performed on the samples using the Bruker FT-IR spectrometer in the absorption mode over a range of 4000-400 cm^{-1}. FESEM analysis was carried out using a JEOL JSM-7600 Field emission scanning electron microscope, a secondary detector, 3.0 probe size and 20 kV acceleration voltages. The samples were mounted on the aluminium stub followed by coating a thin layer of gold to avoid charging.

Surface modification of cellulose with aniline monolayer: Fresh glass slides were cleaned with alcoholic KOH solution to clean graze and waxes from the glass surfaces and then placed in hot piranha solution for 2 h. Care must be taken while handling piranha solution (a mixture of 30 mL of 30 % hydrogen peroxide with 70 mL of conc. H_2SO_4). Finally, the glass slide were cut into small pieces (1 cm × 2 cm) and then placed in a 1% methanolic solution of silane and allowed stay at room temperature for 1 day. Then, the aniline functionalized glass slides was removed and then washed with methanol and dried under nitrogen atmosphere. Similarly, filter paper pieces were placed in a freshly prepared silane solution for period of 3 h and then washed with dry methanol and dried under N_2 atmosphere. To functionalized aniline dimer, the glass plates and filter paper pieces were placed in a solution of 1% aniline dimer in dry methanol containing Nalgene 100 mL polypropylene wide mouth boxes with air tight lit.

Polymerization and deposition of polyaniline: The aniline was purified by distillation in vacuum. The substrate modified with SAMs (self assembled monolayers) was placed in an aqueous solution containing aniline (4 mL) and 1 M HCl (200 mL) solution using plastic clamps and equally spaced. Another solution containing $(NH_4)_2S_2O_8$ (2.3 g) and 1 M HCl (100 mL) was added to initiate polymerization. The substrates were taken out after 5 min and placed in an aqueous solution of aniline (8 mL) in 1 N HCl (200 mL) for 30 min to reduce the oxidation state of polyaniline from the pernigraniline to the emeraldine [20]. The substrates were then immersed in 1 M HCl for 1 min and dried under a stream of nitrogen. To prepare polyaniline Emeraldine base, a polyaniline modified substrate was placed in aqueous NH_3 (1%) for few minutes.

RESULTS AND DISCUSSION

Surface morphology: Polyaniline protected cellulose nanofiber and cellulose based filter papers were prepared and then characterized with various experimental techniques to study the surface functional groups before and after surface pre-treatment. The appearance of green colour indicates the formation of Emeraldine salt form of conducting polyaniline. The morphology of polyaniline protected cellulose fibres are shown in Fig. 1. A thin film coating of polyaniline on cellulose fibre paper where bare unmodified cellulose filter paper is seen the individual fibres of cellulose. Due to surface initiated polymerization studies a high density coating polyaniline can be prepared.

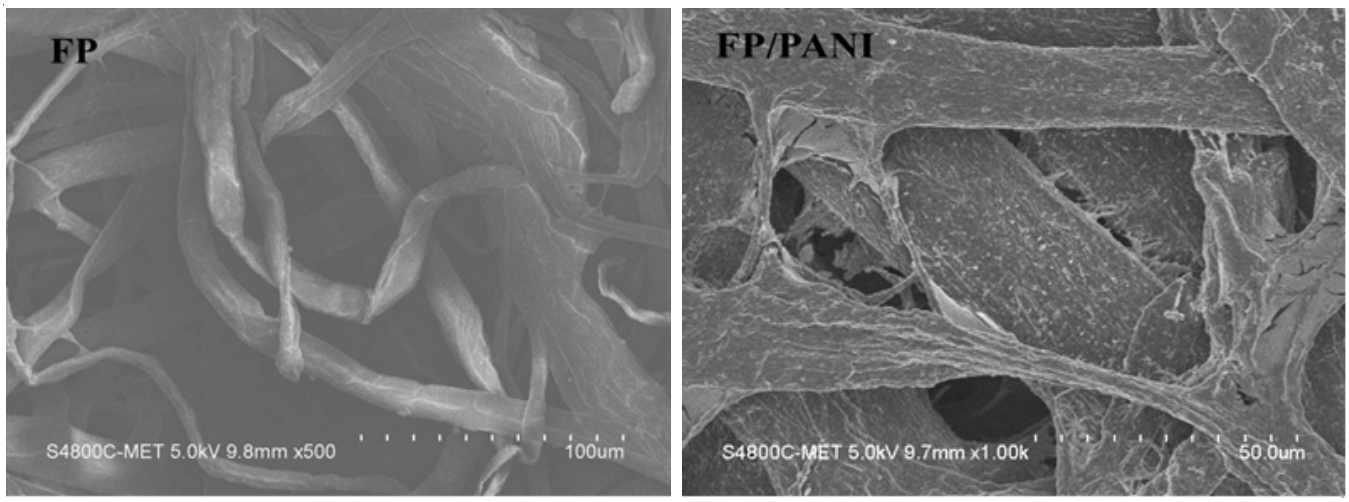

Fig. 1. Morphology of polyaniline protected cellulose fibres

FT-IR analysis: The surface functional groups and the Emeraldine salt and base forms can be measured by FT-IR studies. The FTIR spectra of polyaniline and polyaniline modified cellulose fiber are shown in Fig. 2. The bands appearing at around 1593 and 1487 cm^{-1} are associated with the aromatic ring stretching of the C-C–C bonds and these peaks that are referred as the stretching vibrations of N–B–N and N=Q=N (B = benzenoid, Q = quinonoid), respectively. The peaks appearing at around 1306 cm^{-1} correspond to C=O stretching mode. The peak observed at around 1238 cm^{-1} in the case of PANI (EB)-FP had red-shifted to 1155 cm^{-1} in the spectrum of PANI (ES)-FP. These peaks correspond to a vibration mode of the $–NH^+$ structure. The peak around 1021 cm^{-1} corresponded to C-O stretching mode. The peaks around 820 cm^{-1} corresponded to C-H out of plane bending. Almost all peaks of PANI (EB)-FP have slightly red-shifted in PANI (ES)-FP, which is steady with the previous reports [21,22].

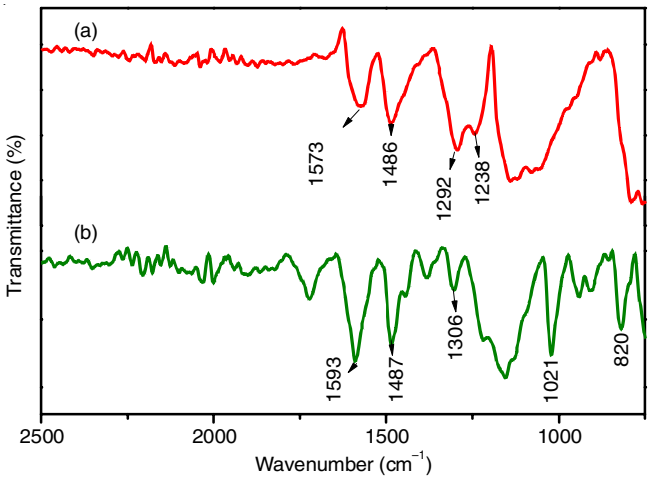

Fig. 2. FTIR of (a) PANI and (b) PANI protected cellulose fibres

UV-visible analysis: The UV-visible spectral behaviour of polyaniline grown on filter paper exhibit two major peaks for polyaniline emeraldine salt form where as a shift in peak position by exposing with ammonia as shown in Fig. 3. Herein, a glass plate was used for the deposition of both aniline silane monolayer and aniline dimer. These studies provide an information of pH induced structural changes of polyaniline and their corresponding UV-visible spectral envisage the interconversion of benzenoid form of polyaniline backbone into quinonoid form of aniline linkages (Fig. 4).

Electrochemical studies: The electrochemical behaviour of polyaniline deposition cellulose fiber and polyaniline was carried out in 0.5 M HCl medium at the appearance of two sets of peak indicates the interconversion of benzenoid and quinonoid form of polyaniline in 0.5 M HCl medium. The influence of potential scan on peak current values also recorded. The linear raise in peak current values indicate the adsorption controlled electron transfer processes of the surface bound polyaniline. The influence of peak potential against the pH of the medium also recorded at different pH ranges from pH 1 to pH 10 (Fig. 5). The polyaniline modified cellulose nanofiber based paper strips can be used for naked eye sensing ammonia and hydrazine in environmental samples.

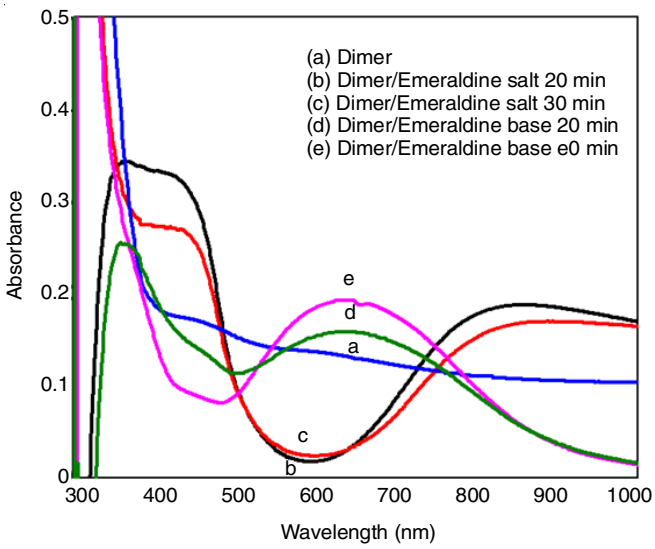

Fig. 3. UV-visible spectral behaviour of polyaniline grown on filter paper

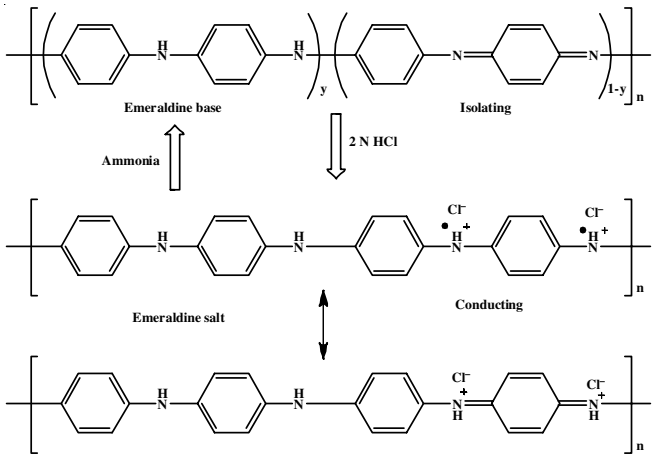

Fig. 4. Interconversion of benzenoid and quinonoid form of polyaniline

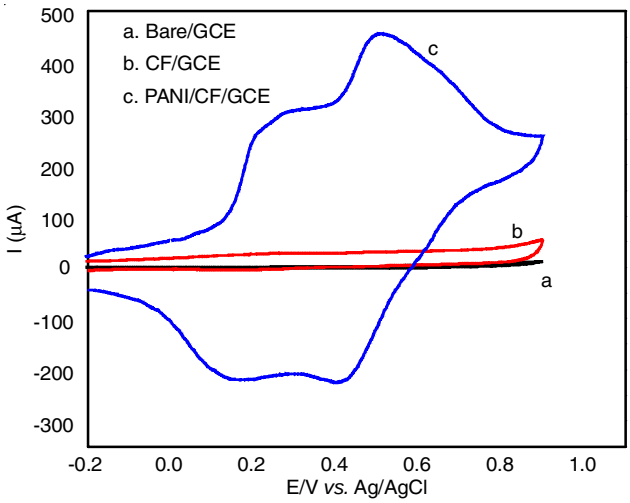

Fig. 5. Cyclic voltammetry behaviour of polyaniline on cellulose fiber in 0.5 M HCl medium; bare GCE (a); CF (b); and PANI/CF at 50 mV/s scan rate

Conclusion

A simple method to prepare polyaniline film on cellulose filter paper is reported. It is observed that aniline terminal silane

and aniline dimer as seed for effective growth polyaniline on cellulose nanofibers with strong adhesion properties. Extensive characterization studies provide the evidence of deposition of polyaniline in controlled oxidative polymerization approach. Cellulose nanofiber functionalized with conducting polyaniline film can be used for various electrochemical sensors applications.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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