

Electrochemical Grafting of Chitosan on Polyaniline and Its Characterization

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Abstract

Chitosan was grafted with polyaniline by electrochemical polymerization. Electrochemical polymerization was carried out by coating chitosan on the surface of graphite working electrode by cyclic voltammetry then PANi grew onto chitosan in acidic solution and a graft copolymer was produced. Prepared sample obtained from electrochemical polymerization was characterized by FTIR spectroscopy which confirmed that chitosan grafted polyaniline was formed. Cyclic voltammograms gave redox peaks of PANi which developed at 0.2 V and 0.68 V and of chit-g-PANi at 0.4 V and 0.75 V and current was found to be proportional to the scan rates. Specific capacitance were found to be 189.82, 191.95 F/g and 353.33 Fg⁻¹ for chitosan, PANi and chit-g-PANi respectively which indicate that chit-g-PANi has highest specific capacitance. This chit-g-PANi on the surface of graphite was applied to measure the pH of different solution having different concentration using a pH meter, a linear trend was obtained from pH 1 to 13 and slopes of 66.786 and 58.5 mV/pH were found for acidic (1-7 pH) and basic (9-13 pH) solutions respectively. The slope of 66.346 mV/pH was found in glass electrode for 1 to 13 pH.

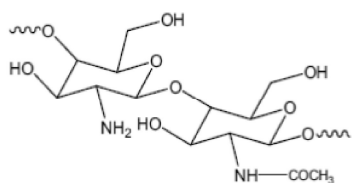
Keyword: *chitosan, chitin, polyaniline, graft copolymer, electrochemical polymerization, conducting polymer*

Introduction

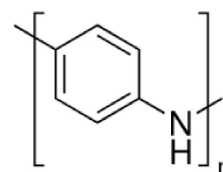
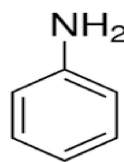
Chitosan is a biodegradable, non-toxic, non-allergenic, naturally occurring high molecular weight biopolysaccharide¹. Due to the biodegradability and structural properties of chitosan, it is also widely used in wastewater treatments, separation membranes, drug delivery systems, and biosensors². Chitosan can remove anionic metals species (chromate, phosphate, and nitrate) through electrostatic attraction or hydrogen bonding due to the presence of amine (-NH₂) and hydroxyl (-OH) functional groups and also the presence of these groups makes chitosan as a potential adsorbent for anchoring a variety of transition metals³.

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Polyaniline is the oldest polymers among other known intrinsically conducting polymer (ICP). Polyaniline was found for the first time during anodic oxidation of aniline in sulfuric acid at 1862 by H. Letheby of the College of London Hospital and at that time a partly conductive material was obtained which was probably polyaniline⁵. Due to its ease of synthesis this conducting polyaniline was well known and it has other interesting property like environmental stability, unique acid/ base doping/ dedoping and oxidation chemistry⁶.

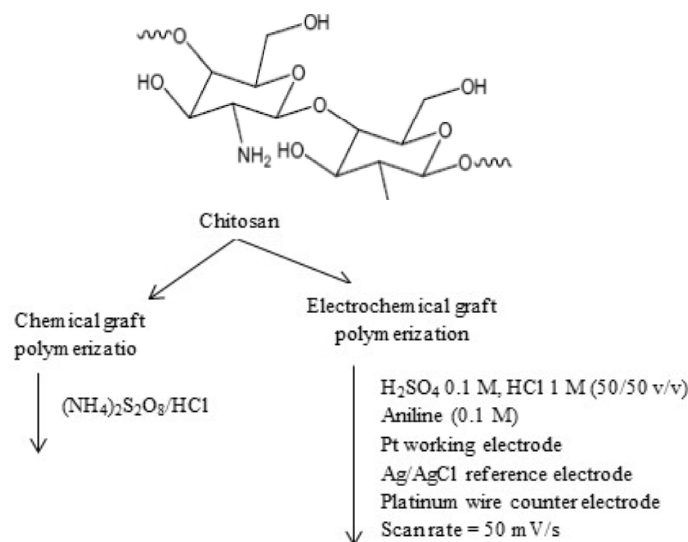


Scheme 1: Structure of chitosan with chitin



Scheme 2: (a) Aniline monomer (b) Polyaniline

Polyaniline grafted chitosan can be used as an adsorbing material for copper ions⁷. Bio/conducting composite materials have been used as effective adsorbent for the removal of dyes, heavy metals and fluoride ions from aqueous solution⁸. Chitosan grafted polyaniline was synthesized by chemical and electrochemical polymerization. Chitosan grafted polyaniline is written as chit-g-PANi.



Scheme 3: Schematic illustration of chemical and electrochemical formation of chitalin (chi-g-PANi)⁴

Experimental Methods

Materials

The sample of pure chitosan, aniline monomer (Molecular Wt. 93.13 g, specific density 1.021 g L⁻¹ was double distilled), ammonium persulfate (APS), acetic acid, nitrogen gas, graphite rod from batteries,

sulphuric acid (0.1 M), hydrochloric acid (1 and 3 M), sodium hydroxide (1 M), Na_2HPO_4 , NaH_2PO_4 , sodium ammonium hydroxide (Thermo Fisher scientific India) were available from laboratory of Central Department of Chemistry, TU and all these chemicals were of analytical grade and required concentration of solutions were diluted in distilled water.

Preparation of Chit-g-PANi by Electrochemical Polymerization

Exact 0.75 mL of conc. acetic acid was added in 250 mL volumetric flask for making 0.25% acetic acid. 1 g chitosan and 100 mL of 0.25% acetic acid was mixed in beaker and then stirred for 4 hours in magnetic stirrer and then prepared chitosan solution was filtered by cotton pad or cotton cloth to remove the un-dissolved particles. Electrochemical polymerization was carried out by coating chitosan on surface of graphite rod working electrode and then PANi was grown onto chitosan in acidic solution. Graphite electrode was made by joining circuit on graphite rod of batteries. Chitosan graft polyaniline was prepared by applying intended potential to the electrode using potentiostat. PANi was deposited onto chitosan coated graphite rod where electrolytic solution consisted of 0.1 M aniline in 20 mL of equal ratio mixtures (50:50) of 0.1 M sulphuric acid and 1 M hydrochloric acid in water (i.e. 10 mL of 0.1 M sulphuric acid and 10 mL of hydrochloric acid). The potential range for electrochemical polymerization and the scan rates were -0.25 to 1 V and 50 mVs^{-1} respectively for 25 cycles. A dark green layer was observed on the surface of the graphite rod.

The measurement of cyclic voltammetry was done in different scan rates (20 mVs^{-1} , 40 mVs^{-1} , 60 mVs^{-1} , 80 mVs^{-1} , 130 mVs^{-1}) for 15 cycles. The potential range was 0.3 to 1.4 V and open circuit potential (OCP) was +0.272 V.

Measurement of pH by Chit-g-PANi Coated Graphite Electrode

Potentials of these buffer solutions were measured from pH 1.2 to 12.8 with the chit-g-PANi coated graphite electrode as indicator electrode and the standard calomel electrode (SCE) as a reference electrode. A Fisher Accumet pH meter was used to measure all the pH and potential of the prepared solutions. Glass electrode was also used to measure the potential of the prepared solutions which were already measured by chit-g-PANi coated graphite electrode to experiment the response of chit-g-PANi coated graphite electrode in comparison with glass electrode.

Results and Discussion

FTIR spectra of all samples were recorded by using IRTracer-100 of SHIMADZU spectrophotometer at room temperature in the range of $4000\text{--}400 \text{ cm}^{-1}$. But only the mid spectrum IR range contains the characteristic peaks of chit-g-PANi. Sample of chit-g-PANi obtained from electrochemical polymerization gave spectra. In chit-g-PANi, the peak at $3000\text{--}3500 \text{ cm}^{-1}$ was of quite reduced intensity and broad due to the overlapping of O-H stretching of chitosan and N-H stretching of aniline groups at PANi Grafts.

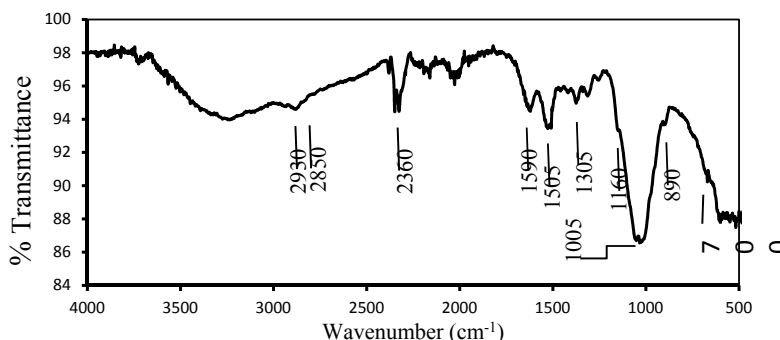


Figure 1: FTIR spectrum of chit-g-PANi obtained from electrochemical polymerization

Chitosan gave strong peak around 3490 cm^{-1} in IR spectrum due to the stretching variation of O-H, the extension of N-H, and inter hydrogen bonds of the polysaccharide. The peak at $3200\text{-}3500\text{ cm}^{-1}$ was of quite reduced intensity and broad in graft copolymer due to overlapping of O-H stretching of chitosan and N-H stretching of aniline groups at PANi Grafts. Intensity of this peak with respect to chitosan reduces due to the appreciable amounts of O-H bonds and N-H bonds at chitosan have been grafted with PANi chain.

Cyclic Voltammetry (CV) of Chit-g-PANi

The CV of various samples was plotted by using Potentiostat/Galvanostat controlled by Polarization software interfaced with IBM computer. Figure 1.5 (a) shows cyclic voltammograms of chitosan grafting on graphite electrode.

First curve shows the oxidation of chitosan moieties in the precursor starts to be oxidized for polymerization and for redox behavior and which are showed in the first curve and it is completely electroactive. These peaks appeared again after several cycles.

PANi formation has started at the chitosan in the precursor film and the ohmic conduction occurs between the electrode which is implied by the higher increase of maximum current and shifting of its peaks to higher potential and the polymerization rate increases for the succeeding potential cycles. The graphite electrode is covered with a thick layer and the solution near the graphite electrode surface has become an intensive green color.

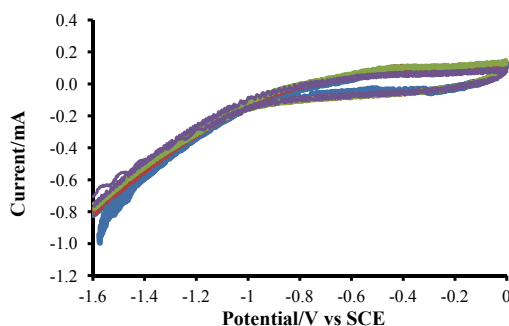


Figure 2: Cyclic voltammograms of chitosan deposition

Here in figure 2, two pairs of redox peaks are seen and the voltammograms show similar shapes as in the case for PANi². It can be said that during cycling of these two polymers, the identical redox process occurs. Two pairs of redox peaks A/a and B/b develop at 0.4 and 0.75 which can be seen in the figure 3 that resemble the behavior of PANi. The curve shapes of chit-g-PANi almost give the electrochemical behavior of PANi with the same conditions of electrochemistry. Current is highest in value when scan rate is 130 mVs⁻¹ but lowest current was observed in lower scan rate i.e., 40 mVs⁻¹.

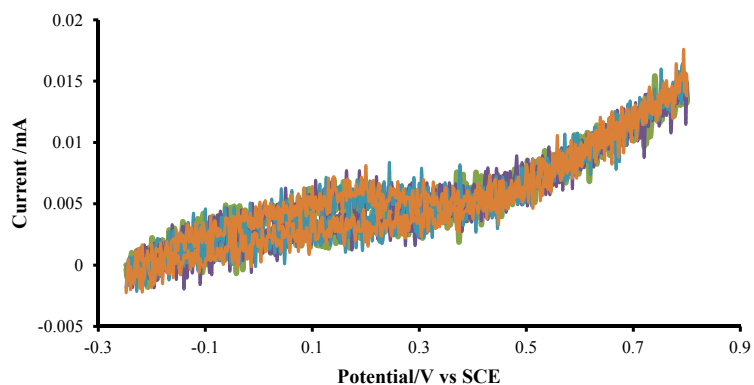


Figure 3: Cyclic voltammograms of 0.1 M aniline

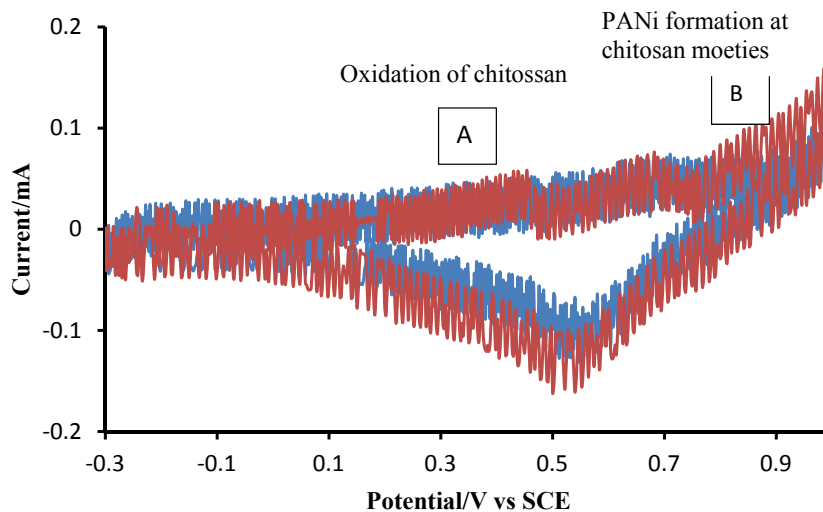


Figure 4: Cyclic voltammograms of graft copolymer formation of chit-g-PANi

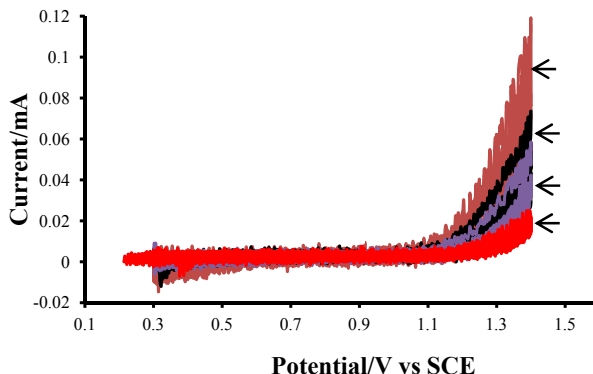


Figure 5: Cyclic voltammograms of blank of chit-g-PANi in different scan rates

Capacitive study

$$\text{Capacitance (C)} = \frac{\text{Average Current}}{\text{Scan Rate}} \dots\dots\dots \text{(v)}$$

$$\text{Specific Capacitance (SC)} = \frac{\text{Capacitance}}{\text{Weight of Active Materials}} \dots\dots\dots \text{(vi)}$$

Table 1: Specific capacitance of samples from CV

Samples	Specific Capacitance (Fg ⁻¹)
Chitosan	189.825
PANi	191.949
Chit-g-PANi	353.329

From the study of Figure of CV, chit-g-PANi has larger voltammetry output current, so capacitor with good capacitance can be anticipated with the use of this material. Specific capacitance for the composite material was calculated by taking average current obtained from the CV. The specific capacitance value thus calculated from the CV curve is shown in table 3.3. The specific capacitance for sample chit-g-PANi was found to be highest (353.329 F g⁻¹) while lowest for chitosan (189.825 Fg⁻¹).

pH Sensing by Chit-g-PANi Electrode

Chit-g-PANi coated graphite electrode gave the significant response when potentials were recorded from acidic solutions to basic solutions. A linear trend from pH 1 to 13 was obtained. A slope of 66.786 mV/pH in acidic solution (1-7 pH) and 58.5 mV/pH in basic solution (9-13 pH) were observed for chit-g-PANi coated graphite electrode. It was observed that the surface of the polyaniline film was deposited very smoothly on graphite rod.

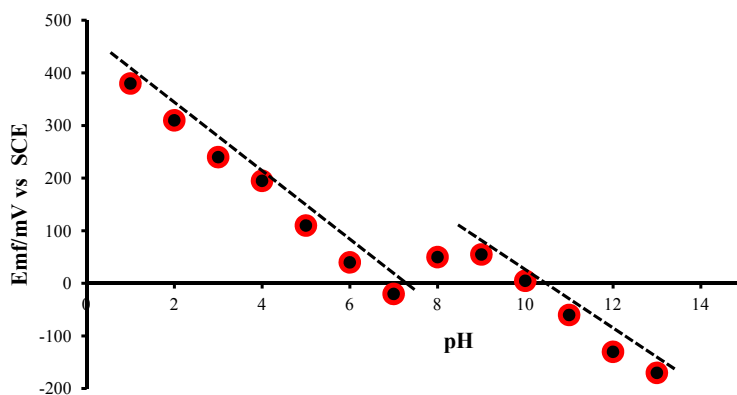


Figure 6: Response of the chit-g-PANi electrode

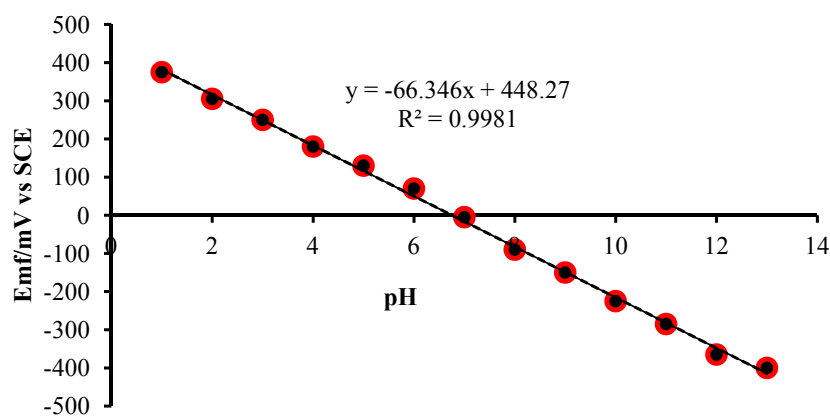


Figure 7: Response of the glass electrode

Conclusions

Chitosan graft PANi was made by electrochemical polymerization. Chit-g-PANi synthesized by electrochemical method has higher conductivity and physical properties. Chitosan graft PANi was characterized by FTIR which gave different spectrum that confirmed the formation of chit-g-PANi copolymer was obtained. No residual monomer was found in the graft copolymer, even after storage for long periods.

Cyclic voltammograms gave redox peaks of PANi which developed at 0.2 V and 0.68 V and of chit-g-PANi at 0.4 V and 0.75 V and blank of chit-g-PANi was done in different scan rates. The value of specific capacitance of chit-g-PANi was found to be 353.329 F/g which is higher than that of PANi and chitosan whose values were 189.825 F/g and 191.949 F/g respectively.

Chit-g-PANi coated graphite electrode was made for the measurement of pH which is a non-glass pH electrode, pH of the acidic and basic solutions were measured by using obtained copolymer graphite electrode and also by glass electrode. In this measurement, a linear trend was obtained and slopes of 66.786 mV/pH for acidic solutions and 58.5 mV/pH for basic solutions were observed. Slope of 66.346 mv/pH was observed from glass electrode for different buffer solutions. Prepared chit-g-PANi electrode can be used for the measurement of pH with several precautions.

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