This chapter primarily deals with the methods and materials used for synthesizing different types of Polyaniline (PAni) based nanostructured materials. This is followed by the discussion of the principles and specifications of different analytical techniques employed for the physico-chemical characterization of the synthesized materials. Various parameters related to Swift Heavy Ion (SHI) irradiation are mentioned in this chapter. The biochemical assays used for investigating the antioxidant activity and biocompatibility of these materials are also briefly described. Thereafter, the methodology adopted for the fabrication of quartz crystal microbalance (QCM) sensors modified by Polyaniline (PAni) based nanostructured materials has been discussed.

### 3.1. Materials

Monomer aniline (Merck) was used for the synthesis of polyaniline (PAni) based nanostructured materials. Aniline was distilled under reduced pressure and stored in dark prior to use. Hydrochloric acid (HCl) and camphor sulfonic acid (CSA) purchased from Merck were used as dopants. Ammonium peroxydisulfate (APS) also obtained from Merck was used as the oxidant. For the synthesis of Polyaniline (PAni) nanofiber reinforced PVA nanocomposites, Polyvinyl alcohol (PVA) ($M_w = 145000$) purchased from Merck was used. Glycerol (Merck) was used as the plasticizer for the synthesis of PAni nanofiber reinforced PVA nanocomposites. All other chemicals, solvents and reagents used in the synthesis and purification process were of analytical grade and used as received without any further purification. The physical properties of the materials used for the synthesis of different PAni based nanostructured materials in the present work are tabulated in Table 3.1.
Table 3.1: Some physical properties of the materials used in synthesis

<table>
<thead>
<tr>
<th>Physical properties of the monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Aniline</td>
</tr>
</tbody>
</table>

Physical properties of dopants, oxidant and plasticizer used in synthesis

<table>
<thead>
<tr>
<th>Physical properties of solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvents</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Acetone</td>
</tr>
<tr>
<td>Methanol</td>
</tr>
<tr>
<td>Ammonium persulfate</td>
</tr>
<tr>
<td>Ethanol</td>
</tr>
<tr>
<td>Glycerol</td>
</tr>
</tbody>
</table>

3.2. Synthesis of polyaniline nanofibers

Polyaniline (PAni) nanostructures have been synthesized using several techniques such as well-controlled solution synthesis [326, 327], soft-template methods such as micellar [403, 404], microemulsion and reverse microemulsion polymerization [150, 151, 405], hard-template methods [153], template free methods [146], seeding polymerization [325] interfacial polymerization [155, 324] and electro-spinning technology [153]. In the present work, we have used
interfacial polymerization and rapid mixing polymerization techniques for the synthesis of PANi nanofibers and PANi nanofibers reinforced PVA nanocomposites, respectively [155, 324, 329, 330]. Interfacial polymerization has been preferred over other techniques for the synthesis of PANi nanofibers because this technique is very simple and gives a good yield of high quality PANi nanofibers without the use of any template.

Polaraniline (PANi) nanofibers doped with dopant acids viz., hydrochloric acid (HCl) and camphor sulfonic acid (CSA) have been synthesized using the interfacial polymerization technique [155, 324]. The block diagram for the synthesis of PANi nanofibers by interfacial polymerization in shown in Fig. 3.1.

Figure 3.1: Block diagram for the synthesis of polyaniline nanofibers using interfacial polymerization

It is known from the early years of conducting polymer research that polyaniline fibrils of ~ 100 nm in diameter can be synthesized “naturally” during electropolymerization on the surface of the electrodes [144, 166]. Recent works indicates that uniform polyaniline nanofibers can be obtained without the need for any template simply by controlling the electrochemical polymerization kinetics [166]. It has been discovered that the basic morphological unit for chemically synthesized polyaniline also appears to be nanofibers with diameters of tens of nm [330]. The secondary overgrowth of polyaniline on the initially
formed nanofiber scaffolds is responsible for the formation of micron sized particulates of PAni in the final product [329]. Interfacial polymerization is a method by which this secondary overgrowth can be restricted and high quality nanofibers can be obtained.

In interfacial polymerization, a heterogeneous biphasic (organic-aqueous) system is formed by gently pouring an aqueous solution of the dopant and oxidant over an organic solution of the monomer or vice-versa depending on the difference in density between the two phases. However, it is preferred to have the aqueous phase above the organic phase mainly because of the fact that it is easier to collect the PAni nanofibers formed during the reaction. Since the as formed polyaniline product is synthesized in its hydrophilic emeraldine salt form, it diffuses away from the reactive interface into the aqueous layer. This makes more reaction sites available at the interface and suppresses lateral overgrowth. In this way, the nanofibers formed at the interface are collected from the aqueous phase without severe secondary overgrowth.

3.3. Synthesis of polyaniline nanofiber reinforced PVA nanocomposites

Polyaniline nanofiber reinforced PVA nanocomposites have been synthesized using an in-situ rapid mixing polymerization. The block diagram depicting the synthesis procedure of PAni nanofiber reinforced PVA nanocomposites films is shown in Fig. 3.2. The process for preparing the PAni nanofiber reinforced polymer nanocomposite films consists of making an aqueous solution of the non-conducting polymer (PVA) and a plasticizer. A definite amount of HCl is added to the solution in order to make its pH less than or equal to 3 (three). The monomer aniline and oxidant are added simultaneously in the molar ratio of 2:1 and the obtained solution is rapidly stirred using a magnetic stirrer. The colour of the clear solution gradually changes to green indicating the formation of PAni nanofibers. The solution is then heated at around 50\textsuperscript{o}-60\textsuperscript{o} C (323-333 K) to make the solution viscous, subsequently it is cast into petri-dish and the solvent is allowed to evaporate slowly giving transparent green films of the PAni nanofiber reinforced PVA nanocomposites of thickness around (30 mm.
3.4. Swift Heavy Ion (SHI) irradiation

Swift heavy ion (SHI) irradiation experiments have been carried out in the Material Science (MS) beam line at Inter University Accelerator Centre (IUAC), New Delhi under ultrahigh vacuum \(\sim 10^{-6}\) Torr. The swift heavy ions having high energies (> 1 MeV/\(\mu\)) are provided by the 15 UD Pelletron accelerator at IUAC [406].

The schematic view of the 15 UD Pelletron at IUAC and its different parts are shown in Fig. 3.3. It is basically a tandem electrostatic Van de Graff type accelerator, in vertical configuration, which can go upto a maximum terminal voltage of 16 MV and capable of accelerating any ion from proton to uranium upto an energy of around 200 MeV depending upon the suitable negative ion source and the charge state. The pelletron accelerator consists mainly of two parts: (a) ion source and (b) the accelerating column with many auxiliary parts in between. In the top portion of the tank there are three different ion sources, viz., R.F. source (ALPHATROSS), Source of Negative Ions by Cesium Sputtering (SNICS) and direct extraction negative ion source (Duoplasmatron), which can produce different negative ions to be injected in pelletron tank. These three ion sources working on three different principles can produce almost every type of
negative ions. Duoplasmatron works on the principle of gas discharge, SNICS uses surface ionization and R.F. source utilizes high frequency gas discharge.

The negative ions emerging from the ion source are first accelerated to 250 keV by the high voltage deck potential and different optical elements focus and inject the same into the vertical accelerating tube. The injector magnet does mass selection by bending the ions by 90° and then injects them into the accelerating tube. The singly ionized negative ions then follow a vertical downward path and get accelerated through the accelerating tube path. It consists of a vertical insulating cylindrical tank of height 26.5 m and diameter 5.5 m, filled with SF$_6$ (Sulphur hexafluoride) at high pressure (> 200 psi) as an insulating gas. In the top portion of the tank there is an ion source system consisting of a high negative potential deck, SNICS, vacuum system, power supplies and controls of the ion source required to produce and inject the negative ions into accelerating tank. The ion source system is followed by the high voltage accelerating terminal of height 3.18 m and diameter 1.52 m inside the tank. The terminal is connected to the tank vertically through ceramic titanium tubes called accelerating tubes. A potential gradient is maintained through these tubes from high voltage to ground, from top.
of the tank to the terminal as well as from the terminal to the bottom of the tank. The insulating column which supports the high potential terminal consists of thirty 1 MV modules, 15 on either side of the terminal. The upper portion of the column is referred to as low energy section and the portion below the terminal as the high energy section. The shorted section with no potential gradient, commonly known as the Dead Section, is provided each in the low and high energy sections for equipment housing. Both are provided with an electron trap and a sputter ion pump. The low energy dead section (LEDS) is also provided with an electrostatic quadrupole lens while the high energy dead section (HEDS) is equipped with a second foil striper assembly. A shorting rod system is also provided for temporarily shorting selected column modules without entering the pressure vessel. Two insulating shafts run one from each ground end to the terminal and are used to drive four 400 cycle per second (cps) generators, which provide power for the equipments like heater lenses, pumps, foil changer etc., housed in the column, dead sections and terminal. The charging of high voltage terminal to 15 MV is done by using the pelletron charging chains. There are two independent sub systems with one charging chain in each, so that each chain is required to supply \(100 \mu A\) current. Negative ions from the ion source are focussed by different optical instruments and then injected by the injector magnet into accelerator with some small energy (>>300 KeV) provided by the negative potential deck at the ion source. In the terminal, negative ions are stripped off few electrons by the positive ions which are again accelerated as they proceed towards the bottom of the tank at the ground potential.

The beam energy gained by the ion in the accelerating tube at the end of the tube is determined by,

\[ E_{\text{beam}} = (q + 1)V_T \]  

(3.1)

where \(V_T\) is the terminal voltage, \(q\) is the number of positive charges on the ion after stripping. These high energy ions were analyzed to the required energy with the help of 90° bending magnet known as analyzer magnet and directed to the desired experimental area with the help of switching magnet which can deflect the beam into any one of the seven beam lines in the beam hall for the experiments.
Fig. 3.4 (a, b) shows the Materials Science (MS) beam line and the samples loaded in a ladder. For ion irradiation, the samples of area 1cm × 1cm are mounted on a sample holder (ladder) made up of copper. The ladder in the Material Science (MS) chamber is rectangular and 24 samples can be loaded with six samples on each side at a time. After sample loading the ladder is inserted in the MS vacuum chamber. Vacuum inside the irradiation chamber is maintained with the help of a rotary and turbo-molecular pump at ~10^{-6} torr during irradiation. All the samples in the present work have been irradiated at normal beam incidence.

3.4.1. Parameters related to Ion beam

3.4.1.1. Fluence

One of the most important parameter related to ion beams during swift heavy ion (SHI) irradiation is the fluence. Fluence ($\phi$) is defined as the total number of irradiating ions incident per square centimeter (ions/cm$^2$) of the sample. Fluence of an ion beam depends upon the time of irradiation (t), beam current and charge state according to following relation:

$$\text{Fluence} (\phi) = \frac{\text{Time} \times \text{Beam current} \times \text{pnA}}{\text{Charge state}}$$  \hspace{1cm} (3.2)
Beam currents for ion irradiation experiments are usually taken in the range of 1-5 nA.

\[
1 \text{ pnA (particle nano-ampere)} = \frac{10^{-9} \text{Coul} \cdot \text{sec}^{-1}}{1.6 \times 10^{-19} \text{Coul}} = 6.25 \times 10^9 \text{ particles/sec} \quad (3.3)
\]

3.4.1.2. Count

The fluences during the irradiation have been recorded by using a counter. Following relation relates the counts and the fluence

\[
\text{Counts} = \frac{\phi q e}{S} \quad (3.4)
\]

where \(\phi\) is the fluence, \(q\) is the charge state of the ion beam, \(e\) is the electronic charge \((1.6 \times 10^{-19} \text{ Coulomb})\) and \(S\) is the scale of the counter.

3.4.1.3. Beam energy

The energy of the accelerated ion beam depends on charge state \((q)\) of the ion and the terminal voltage \(V_T\) according to the relation

\[
E (\text{MeV}) = (q + 1)V_T + V_{\text{inj}} \quad (3.5)
\]

For the 15 UD pelletron at Inter University Accelerator Centre, New Delhi, India, the terminal potential \(V_T\) is in the range of 10 MV to 15 MV and injector potential \((V_{\text{inj}})\) is in the range of 250 to 350 keV. The projected range of \(O^{7+}\) ion beam used in the present work has been calculated using the SRIM-2007 code (SRIM-Stopping Ranges of Ions in Matter) [407].

<table>
<thead>
<tr>
<th>PA\text{ni based nanostructured materials}</th>
<th>Ion</th>
<th>Energy (MeV)</th>
<th>(S_e) (eV/Å)</th>
<th>(S_n) (eV/Å)</th>
<th>Projected Range ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA\text{ni nanostructures}</td>
<td></td>
<td>4.739E+01</td>
<td>2.673E-02</td>
<td>124.55</td>
<td></td>
</tr>
<tr>
<td>PA\text{ni nanofiber reinforced PVA nanocomposites}</td>
<td>(O^{7+})</td>
<td>90</td>
<td>4.490E+01</td>
<td>2.546E-02</td>
<td>131.78</td>
</tr>
</tbody>
</table>

Table 3.2 gives the incident energy, corresponding electronic energy loss \((S_e)\), nuclear energy loss \((S_n)\) and projected range obtained from SRIM-2007 code for \(O^{7+}\) ion beam in the polyaniline (PA\text{ni}) based nanostructured materials that are investigated in the present work.

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3.5. **Characterization techniques**

3.5.1. **Electron microscopy**

The tremendous advancement in the field of nanoscience and nanotechnology can mainly be associated with the development of sophisticated instruments capable of characterizing the nanomaterials. Electron microscopy is the most efficient technique for investigating the structural and morphological details of nanomaterials.

3.5.1.1. **Transmission electron microscopy**

Transmission electron microscopy (TEM) is the premier tool for understanding the internal microstructure of materials at the nanometer level. Electrons have an important advantage over X-rays in that they can be focused using electromagnetic lenses. One can obtain real-space images of materials with resolutions on the order of a few tenths to a few nanometers, depending on the imaging conditions, and simultaneously obtain diffraction information from specific regions in the images (e.g. small precipitates) as small as 1 nm [408].

Transmission electron microscope (TEM) uses a high voltage electron beam to create an image. The electrons are emitted by an electron gun, commonly fitted with a tungsten filament cathode as the electron source. The electron beam is accelerated by an anode typically at +100 keV (40 to 400 keV) with respect to the cathode, focused by electrostatic and electromagnetic lenses, and transmitted through the specimen that is in part transparent to electrons and in part scatters them out of the beam. When it emerges from the specimen, the electron beam carries information about the structure of the specimen that is magnified by the objective lens system of the microscope. The spatial variation in this information (the “image”) is viewed by projecting the magnified electron image onto a fluorescent viewing screen coated with a phosphor or scintillator material such as zinc sulfide. The image can be photographically recorded by exposing a photographic plate directly to the electron beam, or a high-resolution phosphor may be coupled by means of a lens optical system or a fibre optic light-guide to the sensor of a CCD (charge-coupled device) camera. The image detected by the CCD may be displayed on a monitor or computer. Resolution of the TEM is
limited primarily by spherical aberration, but hardware correction of spherical aberration has allowed the production of images with resolution below 0.5 Å (50 pm) at magnifications above 50 millions [409].

The TEM studies have been carried out using JEOL JEM 100 CX II transmission electron microscope installed at the Sophisticated Analytical Instrumentation Facility (SAIF), North-Eastern Hill University (NEHU), Shillong, Meghalaya, India shown in Fig. 3.5 (a). The micrographs have been taken at 100 kV accelerating voltage at different magnifications according to need. The samples have been prepared on carbon coated copper grids for viewing under TEM.

Figure 3.5: (a) Transmission electron microscope (JEOL JEM 100 CXII) at SAIF, NEHU, Shillong and (b) Scanning electron microscope (JEOL JSM 6390 LV) installed at Tezpur University used for acquiring electron micrographs in the present work.

3.5.1.2. Scanning electron microscopy

The scanning electron microscope (SEM) is one of the most widely used instruments in materials research laboratories and is common in various forms in fabrication plants. The SEM study has been carried out using a JEOL JSM 6390 LV model scanning electron microscopy [shown in Fig. 3.5 (b)] installed at Central Instrumentation Facility (CIF), Tezpur University, Assam, India to examine the
surface morphology and porosity. The micrographs have been taken at an accelerating voltage varying between 5-15 kV and magnification is fixed according to need from 2000X to 10000X. The samples have been coated with platinum and placed on carbon tape before viewing.

Scanning electron microscopy is central to microstructural analysis and therefore important to any investigation relating to the processing, properties, and behaviour of materials that involve their microstructure. The SEM provides information relating to topographical features, morphology, phase distribution, compositional differences, crystal structure, crystal orientation, and the presence and location of electrical defects [410]. The SEM electron beam is a focused probe of electrons accelerated to moderately high energy and positioned onto the sample by electromagnetic fields. The SEM optical column is utilized to ensure that the incoming electrons are of similar energy and trajectory. These beam electrons interact with atoms in the specimen by a variety of mechanisms when they impinge on a point on the surface of the specimen. For inelastic interactions, energy is transferred to the sample from the beam, while elastic interactions are defined by a change in trajectory of the beam electrons without loss of energy. Since electrons normally undergo multiple interactions, the inelastic and elastic interactions result in the beam electrons spreading out into the material (changing trajectory from the original focused probe) and losing energy. This simultaneous energy loss and change in trajectory produces an interaction volume within the bulk. The signals resulting from these interactions (e.g. electrons and photons) will each have different depths within the sample from which they can escape due to their unique physical properties and energies.

Lenses in the SEM are not a part of the image formation system but are used to demagnify and focus the electron beam onto the sample surface. This gives rise to two of the major benefits of the SEM: range of magnification and depth of field in the image which allows surfaces at different distances from the lens to appear in focus, and provide three dimensional information [410].

The interaction of high energy electrons with the sample results in the generation of Backscattered electrons (BSEs) and Secondary Electrons (SEs). BSEs are electrons from the incident probe that undergo elastic interactions with the
sample, change trajectory, and escape the sample. These make up the majority of electrons emitted from the specimen at high beam voltage and their average energy is much higher than that of the SEs. The intensity of the BSE signal is a function of the average atomic number ($Z$) of the specimen, with heavier elements (higher $Z$ samples) producing more BSEs. The BSE intensity and trajectory are also dependent upon the angle of incidence between the beam and the specimen surface. The topography or physical features of the surface are then imaged by using these properties of the BSE signal to generate BSE topographic images. Secondary electrons (SEs) of low energy (typically 2 to 5 eV), on the other hand, are due to inelastic interactions and are influenced more by surface properties than by atomic number. The SE is emitted from an outer shell of a specimen atom upon impact of the incident electron beam. The depth from which SEs escape the specimen is generally between 5 and 50 nm due to their low energy. Secondary electrons are generated by both the beam entering the specimen and BSEs as they escape the specimen; however, SE generation is concentrated around the initial probe diameter. Secondary electron intensity is a function of the surface orientation with respect to the beam and the SE detector and hence produces an image of the specimen morphology [410].

3.5.2. Powder X-ray diffraction (XRD)

X-ray scattering and spectroscopy methods can provide a wealth of information concerning the physical and electronic structure of crystalline and non-crystalline materials in a variety of external conditions and environments. X-ray powder diffraction is one of the most widely used probes for crystal structure determination. This technique is based on the scattering of X-rays by crystals governed by the Bragg’s law. Powder X-ray diffraction is used to determine the atomic structure of crystalline, semi-crystalline and amorphous materials without the need for large (~100 $\mu$m) single crystals. X-ray diffraction patterns give information about crystal structure parameters like crystallite size (domain length in case of semi-crystalline polymers), d-spacing, diffraction planes, structure, phase and lattice constants. In addition to the crystal structure, XRD is applied for various other purposes such as chemical analysis, stress, strain, particle size measurements, phase equilibrium, determination of orientation for single crystals
or the ensemble of orientations in a polycrystalline or polymeric aggregate, order-disorder transformation etc. The intensities and angles of the diffracted X-ray beams are related to the atomic arrangement of the crystal. In case of polymeric materials, XRD is used to determine the proportions of the crystalline and amorphous phases in terms of the degree of crystallinity. X-ray diffraction is also used to determine the domain length in case of polymers. Polymers are semi-crystalline materials. Their crystallinity is attributed to chain folding or to the formation of single or double helices, for at least part of their chain length [411]. This local range of order in polymer chains is referred to as the domain length (L) and can be in the range of angstroms (Å). The X-ray diffraction patterns for the polyaniline (PAni) based nanostructured materials reported in the present work have been recorded using a Rigaku Miniflex diffractometer with Cu Kα radiation (λ = 1.5406 Å) shown in Fig. 3.6. The angular range spread over the region between 10° and 70° in 2θ, in steps of 0.05°. The X-ray diffraction patterns have been used to determine the d-spacings, domain length (L), strain (ε), and the degree of crystallinity. The methodology adopted for the quantitative estimation of these structural details of the PAni based nanostructured materials specifically the d-spacings, domain length (L), strain (ε) and the degree of crystallinity are discussed in the next two subsections (Sections 3.5.2.1 and 3.5.2.2).

Figure 3.6: Rigaku Miniflex X-ray diffractometer installed at the Department of Physics, Tezpur University
3.5.2.1. Calculation of d-spacing, domain length (L) and strain (ε)

The d-spacings have been deduced from the angular position 2θ of the observed peaks in the X-ray diffraction patterns of the PANi based nanostructured materials, according to the Bragg’s formula

\[ \lambda = 2d \sin \theta \] (3.6)

Line broadening in the X-ray diffraction patterns may be attributed to two major factors: the size and strain components. The former depends on the size of coherent domains (or incoherently diffracting domains), which is not limited to the grains but may include effects of stacking and twin faults and sub-grain structures (small-angle boundaries, for instance); and the latter is caused by any lattice imperfection (dislocations and different point defects) [412]. The theory is quite general and has been successfully applied to all forms of materials, including oxides and polymers [413].

In the present work, the domain length (L) and strain (ε) of the PANi based nanostructured materials have been calculated using a single line approximation technique employing Voigt function [414]. The measures of dispersion used in earlier studies of crystal imperfections by means of diffraction broadening have been the width of the line profile at half the maximum intensity (FWHM, 2w) and the integral breadth (β). However, uncertainties arising from the correction of the instrumental broadened in the profile have led to the introduction of the Fourier and variance methods [415]. These methods allow a detailed and accurate analysis of imperfections to be undertaken, but are solely dependent on the quality of the data, necessary expertise and computing facilities that are available to analyse the data.

A limitation in the use of the FWHM or integral breadth is the need to ascribe an analytical function to the line profiles. Earlier workers have assumed that they are Cauchy (Lorentzian) or Gaussian in form, but it has been demonstrated later on [416] that a closer approximation is given by the convolution of these curves, namely the Voigt function. The Voigt function has been adopted by many groups for an analysis of diffraction broadening based on the integral breadth of a single line and the approach has also been used to obtain the domain size and strain in deformed tungsten [414 and refs. therein]. An
explicit equation for the Voigt function has been introduced by Langford in 1978 [417], which shows that the breadths of the Cauchy and Gaussian components can easily be found from the ratio of the FWHM of the broadened profile to its integral breadth (2w/β). Later on Keijser et al. [414] reported that graphical methods or interpolation from tables can be avoided by using empirical formulae and thus the required calculations can be simplified greatly. While it is always desirable to use data from several reflections whenever practicable, the method can be used in single-line analysis.

The measured line profile \( h \) is the convolution of the standard profile \( g \) with the structurally broadened profile \( f \). Assuming, \( h \), \( f \) and \( g \) to be Voigt functions [417], we get,

\[
h_c = g_c \otimes f_c \quad \text{and} \quad h_g = g_g \otimes f_c \tag{3.7}
\]

where subscripts C and G denote the Cauchy and Gaussian components of the respective Voigt profiles. From Eq. (3.7) it follows that the integral breadths of \( f_c \) and \( f_g \), are given by

\[
\beta_c^I = \beta_c^b - \beta_c^s \quad \text{and} \quad (\beta_c^I)^2 = (\beta_c^b)^2 - (\beta_c^s)^2 \tag{3.8}
\]

The constituent Cauchy and Gaussian components can be obtained from the ratio 2w/β for the \( h \) and \( g \) profiles. However, to avoid graphical methods or interpolation from tables, an empirical formula has been given as [414]:

\[
\beta_c = (a_0 + a_1 \varphi + a_2 \varphi^2) \beta \tag{3.9}
\]

and

\[
\beta_g = \left[ b_0 + b_{12} \left( \varphi - \frac{2}{\pi} \right)^{\frac{1}{2}} + b_1 \varphi + b_2 \varphi^2 \right] \beta \tag{3.10}
\]

where \( \varphi = \frac{2w}{\beta} \), \( a_0 = 2.0207 \), \( a_1 = -0.4803 \), \( a_2 = -1.7756 \), \( b_0 = 0.6420 \), \( b_{12} = 1.4187 \), \( b_1 = -2.2043 \) and \( b_2 = 1.8706 \).

The maximum error introduced by Eqs. (3.9) and (3.10) is about 1%, and in the majority of cases the error is much less than this. In order to separate size and strain effects, it has been assumed that the size and strain profiles have a Voigtian profile. If two or more reflections are available, size and strain effects can be determined from the variation of \( \beta_c^I \) and \( \beta_g^I \) with hkl [417]. However, in a single-
line analysis it is assumed that the Cauchy component of the profile is solely due to crystallite size (domain length in case of polymers) and that the Gaussian contribution arises from strain [418]. In a single-line analysis the apparent crystallite or domain length (L) is given by [414]:

$$L = \frac{\lambda}{\beta \cos \theta}$$ \hspace{1cm} (3.11)

and the strain (ε) is given as

$$\varepsilon = \frac{\beta \lambda}{4 \tan \theta}$$ \hspace{1cm} (3.12)

where \( \beta \) is measured on a \( 2\theta \) scale and, if \( K_\alpha \) radiation is used, \( \lambda \) and \( \theta \) are the wavelength and angular position of the \( \alpha_1 \) component.

### 3.5.2.2. Degree of crystallinity

Domain length (L) is a measure of the local range of order (ordering in a single polymer chain) of a polymer whereas the overall ordering in the polymer samples are generally described in terms of the degree of crystallinity. The degree of crystallinity gives quite a good estimation of the amount of crystalline phase present in a polymer sample. A typical X-ray diffractogram for a polymeric material consists of a broad amorphous hump superimposed with some sharp peaks as shown in the Fig. 3.7 (a). The total area under the diffractogram is the sum of the crystalline peaks and broad amorphous hump.

If a typical X-ray diffractogram has two crystalline peaks with areas \( K_1 \) and \( K_2 \) superimposed on a broad amorphous hump with an area \( K_3 \) as shown in Fig. 3.9 (b), then the degree of crystallinity (\( \kappa \)) of the polymer will be

$$\kappa = \frac{\alpha_c (K_1 + K_2)}{\alpha_c (K_1 + K_2) + \alpha \lambda K_3}$$ \hspace{1cm} (3.13)

where \( \alpha_c \) and \( \alpha \lambda \) are proportionality constants for the crystalline and amorphous phases, respectively. Assuming \( \alpha_c = \alpha \lambda \) for reasonable accuracy in polymers, the Eq. (3.13) for the degree of crystallinity may be written as

$$\kappa = \frac{K_1 + K_2}{K_1 + K_2 + K_3} = \frac{K}{K_0}$$ \hspace{1cm} (3.14)

In order to express the degree of crystallinity in the form of percentage, the above Eq. (3.14) can be modified as
\[ \kappa = \frac{K_1 + K_2}{K_1 + K_2 + K_3} \times 100\% = \frac{K}{K_0} \times 100\% \] (3.15)

where \( K \) is the sum of the areas of all the crystalline peaks in the diffractogram and \( K_0 \) is the total area under the diffractogram. In the present work the area has been calculated by dividing the X-ray diffractogram into minute square grids \( (0.5 \times 0.5 \text{ mm}^2) \) and counting the number of grids. The degree of crystallinity of a polymer is affected by the secondary valence bonds that can be formed, the structure of the polymer chain (range of order), the physical treatment and the molecular weight of the polymer.

Figure 3.7: (a) Typical X-ray diffractogram of a semi-crystalline polymer and (b) XRD patterns showing the superposition of crystalline peaks and an amorphous hump.

3.5.3. FTIR spectroscopy

Infrared spectroscopy has been a workhorse technique for analysis of materials in the laboratory for over seventy years. Fourier Transform Infrared Spectroscopy (FTIR) is a powerful analytical tool for characterizing and identifying organic molecules, chemical bonds (functional groups) and the molecular structure of organic compounds. Fig. 3.8 describes the layout of a simple FTIR spectrometer. The key modules of a FTIR spectrometer are the
source, the Michelson interferometer and the detector. To use the FTIR instrument, the IR radiation from a continuous source is directed onto the sample of interest and the intensity is measured using an infrared detector. The Michelson interferometer provides the means for the spectrometer to measure all optical frequencies simultaneously. The interferometer modulates the intensity of the individual frequencies of radiation before the detector picks up the signal.

![Figure 3.8: Layout of a simple FTIR spectrometer](image)

Part of the infrared radiation is absorbed by the sample and the rest is transmitted. The wavelength of infrared radiation absorbed is characteristic of stretching/ bending vibrational modes of a chemical bond. The most useful range for identification of the compounds is the near and mid-infrared region as most of the molecular vibrations lie in these frequency regions. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each material is a unique combination of atoms, no two compounds
produce exactly similar infrared spectra. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of different kind of materials. A single vibrational energy change is accompanied by a number of rotational energy changes, consequently vibrational spectra appear as bands rather than as discrete lines. Band positions are presented as wave numbers (in cm\(^{-1}\)). Band intensities are expressed either as transmittance ‘T’, the ratio of the radiant power transmitted by the sample or the absorbance ‘A’, logarithm to the base 10 of the reciprocal of the transmittance, \(A = \log_{10}(1/T)\). Determination of frequencies, at which the sample absorbs IR radiation, allows the identification of the sample’s chemical make-up, since functional groups are known to absorb radiation at specific frequencies. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

The FTIR spectroscopy study of the polyaniline (PAni) based nanostructured materials have been conducted for understanding the bond structure, compositional and doping studies of the conducting polymers. The FTIR spectra have been recorded using a Perkin Elmer spectrum 100 spectrophotometer installed at Tezpur University, Assam, India.

3.5.4. Ultraviolet-Visible (UV-Vis) spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy is one of the more ubiquitous analytical and characterization techniques in materials science. UV-Vis absorption spectroscopy provides key information about the electronic transitions and hence the electronic structure of the material. There is a linear relationship between absorbance and absorber concentration, which makes UV-Vis spectroscopy especially attractive for making quantitative measurements. Ultraviolet-visible absorption spectroscopy involves the absorption of ultraviolet/visible light (wavelengths (\(\lambda\)) between 190 and 900 nm) by a molecule raising electrons from a ground/ lower electronic state to an excited/ higher electronic state.

In organic molecules and polymers, the UV-Vis spectrum can help in identifying chromophores and the extent of electronic delocalization [419]. Similarly, absorption measurements can be correlated with bulk physical properties [420]. For inorganic complexes, the UV-Vis spectrum can provide
information about oxidation states, electronic structure, and metal-ligand interactions. For solid materials, the UV-Vis spectrum can measure the band gap and identify any localized excitations or impurities [410].

There are several types of electronic transitions possible in a molecule including: $\sigma$ to $\sigma^*$ (alkanes), $\sigma$ to $\pi^*$ (carbonyl compounds), $\pi$ to $\pi^*$ (alkenes, carbonyl compounds, alkynes, azo compounds), $\eta$ to $\sigma^*$ (oxygen, nitrogen, sulphur and halogen compounds) and $\eta$ to $\pi^*$ (carbonyl compounds). Transitions from the highest occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO) require the least amount of energy and are, therefore, usually the most important. Some electronic transitions are “forbidden” by certain selection rules.

UV-Vis spectroscopy studies of the polyaniline (PAni) based nanostructured materials have been carried out for the study of optical absorption characteristics and hence the energy band structure using a Shimadzu model UV-2450 spectrophotometer as shown in the Fig. 3.9 (a). Pristine and irradiated PAni nanofibers have been dispersed in milli-Q water in a quartz cuvette before taking UV-Vis measurements. The UV-Vis spectra of the PAni nanofibers reinforced nanocomposites films over glass substrates have been acquired after subtraction of glass background.

Figure 3.9: Photographs of (a) UV-Visible spectrophotometer (Shimadzu UV-2450) installed at Department of Physics, Tezpur University and (b) The Renishaw in-Via Raman microscope installed at IUAC, New Delhi.
3.5.4.1. Calculation of optical band-gap

The optical absorption coefficient ($\alpha$) has been calculated from the absorbance ($A$) using Eqs. (3.16 and 3.17) after correction for reflection:

$$I = I_0 \exp(-\alpha x)$$  

Eq. (3.16) may be written as

$$\alpha = \frac{2.303}{x} \log\left(\frac{I}{I_0}\right) = \frac{2.303}{x} A$$  

where $x$ is the thickness of the sample; and $A$ is the absorbance.

If we consider $d$ to be the thickness of the quartz cuvette used for the UV-Vis experiments then the equation for the absorption co-efficient [Eq. (3.17)] may be modified as:

$$\alpha = \frac{2.303 A}{d}$$  

The optical band gap may be evaluated for the values of the absorption coefficient using the following relation:

$$\alpha = \sum \alpha_i = \sum \frac{A_i (h\nu - E_{g_i})^{m_i}}{h\nu}$$  

where the value of $E_{g_i}$ and $m_i$ correspond to the energy and the nature of the particular optical transition with absorption coefficient $\alpha_i$.

For allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, the value of $m_i$ corresponds to 1/2, 2, 3/2 and 3, respectively [421]. In an allowed direct transition the electron is simply transferred vertically from the top of the valence band to the bottom of the conduction band, without a change in momentum (wave vector). On the other hand, in materials having an indirect band gap, a transition from the valence to the conduction band must always be associated with a phonon of the right magnitude of crystal momentum.

3.5.5. Micro-Raman ($\mu$R) spectroscopy

In the present work, the micro-Raman ($\mu$R) spectra of the polyaniline (PAni) based nanostructured materials have been acquired using a Renishaw in-Via Raman microscope with Ar ion laser and excitation wavelength of 514.5 nm. The power has been varied from 0.5-1.0 mW and exposure time from 10-20 s.
according to the requirement of the sample analysed. Fig. 3.9 (b) shows the Raman microscope installed at Inter University Accelerator Centre (IUAC), New Delhi.

Raman spectroscopy is based on the inelastic scattering of light by matter and is capable of probing the structure of gases, liquids, and solids, both amorphous and crystalline. In addition to its applicability to all states of matter, Raman spectroscopy has a number of other advantages. It can be used to analyze tiny quantities of material (e.g., particles that are ~1 mm on edge), as well as samples exposed to a variety of conditions such as high temperature and high pressure and samples embedded in other phases, so long as the surrounding media are optically transparent [410].

Raman scattering results from incident radiation induced transitions in the atoms/molecules of the scattering medium. The transition can be rotational, vibrational, electronic, or a combination (but first-order Raman scattering involves only a single incident photon). In a Raman experiment, the sample is irradiated with monochromatic radiation. If the sample is transparent, most of the light is transmitted, a small fraction is elastically (Rayleigh) scattered, and a very small fraction is inelastically (Raman) scattered. The inelastically scattered light is collected and dispersed, and the results are presented as a Raman spectrum, which plots the intensity of the inelastically scattered light as a function of the shift in wavenumber of the radiation. Each peak in the spectrum corresponds to one or more vibrational modes of the solid. Total number of peaks in the Raman spectrum is related to the number of symmetry-allowed, Raman active modes. Some of the modes may be degenerate and some may have Raman intensities that are too low to be measured, in spite of their symmetry allowed nature. Consequently, the number of peaks in the Raman spectrum will be less than or equal to the number of Raman active modes. The practical usefulness of Raman spectroscopy resides largely in the fact that the Raman spectrum serves as a fingerprint of the scattering material.

The challenge for the so-called nanotechnologies is to achieve perfect control of nanoscale related properties. This obviously requires correlating the parameters of the synthesis process (self assembly, microlithography, sol-gel,
polymer curing, electrochemical deposition, laser ablation) with the resulting nanostructure. Not all conventional techniques are suitable for that purpose but Raman Spectroscopy (RS) has proven to be quite useful for that purpose. For quite a long time this technique has mainly been devoted to fundamental research, but instrumental progress (laser miniaturization, CCD detection, notch filters and data processing softwares) have rendered it a general characterization method. Not only can it provide basic phase identification but subtle spectra alterations can be used to assess nano-scale structural changes and characterize micromechanical behaviour [410].

3.5.6. Current-Voltage (I-V) characteristics

The accurate determination of a material’s conductivity is critical for understanding material composition or device performance. The method used to determine conductivity depends on whether the material is a bulk sample or a thin film. Two-point measurement using an inexpensive ohmmeter is perhaps the simplest approach for the measurement of conductivity in case of bulk samples, although its accuracy is limited and fairly large samples are required. A current-voltage (I-V) characteristic is a relationship, typically represented as a chart or graph, between an electric current and a corresponding voltage, or potential difference. The conductivity or resistivity of a bulk sample is based on accurate measurement of both resistance and the sample dimensions. The resistance is the ratio of the voltage measured across the sample to the current driven through the sample or of the voltage applied across the sample to the measured current.

For a homogeneous bar of length, \(L\), and uniform cross-section, \(A\), the resistance, \(R\), is related to the resistivity, \(\rho\), by

\[
R = \frac{\rho L}{A}
\]  

(3.20)

I-V characteristic curves are used to model the behavior of electronic devices such as bipolar junction transistors (BJTs), heterojunction bipolar transistors (HBTs), junction field effect transistors (JFETs) and various kinds of diodes such as Zener, rectifying, Schottky, laser, light emitting diodes etc. I-V characteristics of the samples investigated in the present thesis have been studied using a Keithley 2400-C source meter interfaced with a PC using a GPIB port as
shown in the Fig. 3.10 (a). The I-V characteristic curves acquired using 2-point probe has been used to determine the resistivity and the conductivity of the samples of a particular thickness and length.

Figure 3.10: Photographs of (a) Keithley 2400-C source meter and (b) HIOKI 3532-50 LCR HiTESTER installed at Materials Research Laboratory, Department of Physics, Tezpur University

3.5.7. **Dielectric relaxation spectroscopy**

Dielectric relaxation spectroscopy has been widely employed to investigate the charge transport mechanism and relaxation phenomenon in conducting polymers [422, 423]. The overall electric behaviour can be studied by employing different formulations such as the complex impedance \( Z^* \), complex permittivity \( \varepsilon^* \) and complex modulus \( M^* \) as discussed in the next subsections. In the present work, a Hioki 3532-50 LCR meter connected with stainless steel circular electrodes (radius=0.5 cm) [Fig. 3.10 (b)] has been used to acquire the data for complex impedance (\( Z \)), phase angle (\( \theta \)), capacitance (\( C \)), and other parameters have been calculated from the acquired data using different transformation equations.

In general, the ac electric response is a superposition of the dielectric response of the bound charges (dipoles) along with the hopping of the localized charge carriers and to the response produced by the molecular structure deformations due to the diffusion of charge carriers [422]. Different types of polarization mechanisms can co-exist in the same material. Besides the conductivity and dipolar polarization, there are electrode effects, interfacial effects and space charge relaxations. The correct interpretation of the experiments is obtained by verifying the reliability and physical grounding of the model by
which the fitting procedure is carried out. The dielectric function $\varepsilon^*$ is used to study the polarization mechanisms, whereas the complex impedance $Z^*$ and the electric modulus $M^*$ usually are used to describe the conductivity relaxation mechanisms of the materials [424].

3.5.7.1. Permittivity formalism

The real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of the complex permittivity ($\varepsilon^*$) is calculated from the measured values of the capacitance ($C$) and the loss tangent ($\tan\delta$) using the Eqs. 3.21 and 3.22, respectively.

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$

(3.21)

$$\varepsilon'' = \varepsilon' \tan\delta$$

(3.22)

where $C$ is the measured capacitance, $d$ is the thickness of the sample, $A$ is the area of the pellet and, $\varepsilon_0$ is the permittivity of free space.

3.5.7.2. Impedance formalism

The real ($Z'$) and imaginary part ($Z''$) of the complex impedance ($Z^*$) can be written as:

$$Z' = |Z| \cos(\phi)$$

(3.23)

and

$$Z'' = |Z| \sin(\phi)$$

(3.24)

where, phase angle $\phi = \tan^{-1} \frac{Z''}{Z'}$ and $|Z| = \sqrt{Z'^2 + Z''^2}$.

The real ($Z'$) and imaginary part ($Z''$) of the complex impedance ($Z^*$) has been calculated according to the Eqs. (3.23) and (3.24) using the measured values of $|Z|$ and phase angle ($\phi$) over the frequency range of 50 Hz - 5 MHz acquired by the HIOKI LCR meter.

3.5.7.3. Modulus formalism

Complex electric modulus or inverse complex permittivity ($M^*$) is defined by the equation,

$$\frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''} = \frac{\varepsilon'^2}{\varepsilon'^2 + \varepsilon''^2} + \frac{j\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + jM''$$

(3.25)

where $j = \sqrt{-1}$ and $M'$ and $M''$ are the real and the imaginary part of complex modulus ($M^*$), respectively, which have been calculated by transforming the data obtained for the real and imaginary parts of permittivity using the Eq. (3.25).
3.5.8. **AC conductivity measurements**

The variation in AC conductivity of the PANi based nanostructured materials as a function of frequency and temperature have been derived using the measured values of the conductance $G(\omega)$ according to the Eq. (3.26). The values of conductance have been acquired using the HIOKI LCR meter [Fig. 3.10 (b)].

$$\sigma(\omega) = G(\omega) \frac{d}{A}$$  \hspace{1cm} (3.26)

where $d$ is the thickness and $A$ is the cross-sectional area of the sample.

3.6. **Positron Annihilation lifetime spectroscopy**

The sensitivity of positrons to lattice defects, particularly vacancy-type defects, in condensed medium has made it possible to use it extensively as an atomic level probe to study defects in a wide variety of solids including polymers [425, 426]. Positron annihilation lifetime (PAL) measurements at room temperature were carried out at Variable Electron Cyclotron Centre (VECC), Kolkata, India. A 4 $\mu$ Ci $^{22}$Na positron source was used as the positron source and was sandwiched between two identical thick films of PANi nanofiber reinforced PVA nanocomposites. The sandwich was then placed in between two ultra fast BaF$_2$ scintillators (2.5 cm diameter and 2.5 cm thick) coupled to two XP2020Q photomultiplier tubes. These scintillation counters grafted into a slow–fast coincidence assembly constituted the PAL coincidence spectrometer. A time resolution of 190 ps was achieved in this setup. Not less than 0.5 million total coincidence counts were recorded in each of the spectra. The lifetime data were analyzed by using the computer program PATFIT-88.

3.7. **Antioxidant activity assay**

The antioxidant assays of the material were performed both with respect to time and concentration of the samples following the method of Serpen et al. [427]. 0.2–0.8 mg of the material was applied to 3.0 ml of 100 $\mu$M DPPH solution in HPLC grade MeOH. The reaction mixture was vortexed for 30 secs and incubated in the dark for 15 min, after which the wavelength scanning was performed using the Shimadzu 2450 UV–Vis spectrophotometer [Fig. 3.9 (a)]. In order to study the time dependence of the antioxidant activity the maximum concentration of each
sample was applied to the 3 ml DPPH solution and the spectra were recorded with 5 min interval from \( t = 0 \) to 30 min. The DPPH degradation was calculated using the formula:

\[
\% \text{ of DPPH scavenging} = \left( \frac{A_B - A_S}{A_B} \right) \times 100
\]

where \( A_B \) is the absorption of the blank and \( A_S \) is the absorption of the sample.

### 3.8. Haemolysis prevention assay

The haemolysis prevention activity was studied following the procedure of Miki et al. [428]. Blood was collected from a slaughter house ethically maintained by Tezpur local district administration (Assam, India) using 1/10th volume of 3.8% sodium citrate out of the total blood volume. Blood was then centrifuged in a 50 ml centrifuge tube using an MPW centrifuge at 3000 rpm for 5 min. The supernatant containing platelet-poor plasma was discarded and the pellet containing RBC was suspended in 10 volumes of phosphate buffer saline (PBS) of pH 7.4. The process was repeated two more times to completely remove the buffy coat of RBC. Finally the cells were suspended in PBS to get a uniform suspension of cells. The polyaniline nanofiber samples were suspended in PBS at a concentration of 5 mg/ml and sonicated for 10 min. From the suspension 20 \( \mu l \) of material was pipetted out into the test tubes. \( \text{H}_2\text{O}_2 \) was added to get 100 \( \mu M \) concentrations in 3 ml. After allowing the reaction to occur for 5 min, the tubes were subjected to 3 ml blood and incubated for 1 h at 37\(^\circ\) C. After incubation, the samples were centrifuged at 3000 rpm for 5 min to pellet out RBC cells. The supernatants were carefully separated using a 1 ml micropipette and used for absorption studies at 540 nm. The percentage of haemolysis prevention was calculated using the relation as follows:

\[
\% \text{ of haemolysis prevention} = \left( \frac{A_B - A_S}{A_B} \right) \times 100
\]

where \( A_B \) is the absorption of the blank and \( A_S \) is the absorption of the sample.

### 3.9. Characterization of QCM based chemical sensors

The characterization of the PANi nanofiber reinforced PVA nanocomposite modified Quartz crystal microbalance (QCM) sensors have been carried out using
a QCM set-up. Fig. 3.12 shows the photograph of the experimental set up of a QCM 200 Quartz crystal microbalance oscillator interfaced with a PC using RS-232 port for on-line data acquisition. The inset of the figure shows a 5 MHz AT-cut quartz crystal coated with gold electrodes.

![Experimental set-up of the Quartz crystal microbalance (QCM) interfaced with a PC. The inset shows a gold coated quartz crystal oscillator.](image)

Figure 3.11: Experimental set-up of the Quartz crystal microbalance (QCM) interfaced with a PC. The inset shows a gold coated quartz crystal oscillator.

### 3.9.1. Response time of the sensor

Sensors do not change output state immediately when an input parameter change occurs. Rather, it will change to the new state over a period of time, called the response time. The response time can be defined as the time required for a sensor output to change from its previous state to a final settled value within a tolerance band of the correct new value. This concept is somewhat different from the notion of the time constant of the system. This term can be defined in a manner similar to that for a capacitor charging through a resistance and is usually less than the response time. The response time of the sensor has been determined using the response characteristic curves for the sensor for different concentration of the analytes.
3.9.2. Linearity of the sensor

The linearity of a sensor is an expression of the extent to which the actual measured curve of a sensor departs from the ideal curve. Linearity is often specified in terms of percentage of nonlinearity, which is defined as:

\[ \text{Nonlinearity (\%)} = \frac{D_{\text{in(max)}}}{IN_{\text{f.s.}}} \times 100 \]  

(3.28)

where

- Nonlinearity (\%) is the percentage of nonlinearity
- \( D_{\text{in(max)}} \) is the maximum input deviation
- \( IN_{\text{f.s.}} \) is the maximum, full-scale input

The static nonlinearity defined by Eq. (3.28) is often subject to environmental factors, including temperature, vibration, acoustic noise level, and humidity. It is important to know under what conditions the specification is valid and departures from those conditions may not yield linear changes of linearity.

3.9.3. Sensitivity of the sensor

Definitions of sensitivity fall into two contrasting categories. In some fields, sensitivity is the ratio of response to cause. Hence increasing sensitivity is denoted by a progressively larger number. In other fields, sensitivity is the ratio of cause to response. Hence increasing sensitivity is denoted by a progressively smaller number.

Sensitivity is often defined as the ratio of the magnitude of response to the magnitude of the quantity measured. Another definition is taken as the minimum input signal required to produce a specified output signal having a specified signal-to-noise ratio. In general, the sensitivity of the sensor is commonly defined as the slope of the output characteristic curve (\( dy/dx \)) or, more generally, the minimum input of physical parameter that will create a detectable output change.