CHAPTER II

Synthesis and characterisation of PANI-TiO$_2$ hybrid by one-pot method

2.1. Literature review

*Polyaniline*

With the discovery of organic conducting polymers (OCPs) in 1960, an attractive subject of research was initiated because of the interesting properties and numerous application possibilities of OCPs. It was expected that OCPs would find their potential applications in multidisciplinary areas such as electrical, electronics, thermoelectric, electrochemical, electromagnetic, electromechanical, electro-luminescence, electro-rheological, chemical, membrane and sensors [1-4]. However, many of the potential uses for OCPs have yet to be explored because of a number of obstacles that need to be overcome. The conductivities of OCPs are in the range of inorganic semiconductors. This is because of their low mobility $10^{-4}$ to $10^{-5}$ cm$^2$ per volt second even though the number of charge carriers are as high as $10^{21}$ to $10^{25}$ per cm$^3$ (inorganic semiconductors have only $10^{16}$ to $10^{18}$ per cm$^3$, but mobility is $10^2$ to $10^5$ cm$^2$ per volt second). The conductivity can be enhanced by developing better oriented, defect-free conducting polymers. Among the available OCPs, PANI is found to be the most promising because of its ease of synthesis, low cost monomer, tunable properties and better stability compared to other OCPs. PANI has properties that are not often found with other conducting polymers. It exists in a variety of forms that differ in degree of oxidation or extent of protonation or both. It is a typical phenylene-based polymer having a chemically flexible – NH group in a polymer chain flanked either side by a phenylene ring. It is a unique polymer because it can exist in a variety of structures depending on the value of (1–y) in the general formula which is given below:
The forms (viz. pernigraniline, emeraldine and leucoemeraldine), their mutual transformations and their roles in the chemical polymerisation of aniline are important. The forms and transformation are given below;

Absorption spectra of its various protonated forms and corresponding bases are reported. PANI can be prepared by various methods of which chemical and electrochemical routes are commonly used. Aniline can be chemically oxidized with oxidizing agents like ammonium persulphate (APS) to yield PANI. The APS has advantages like high redox potential, no interfering ions and non-metallic oxidizing agent. PANI can be prepared electrochemically by galvanostatic, potentiostatic or potential sweeping methods. The applications of PANI cover a wide range including microelectronics, membrane technology, lithium batteries, conductive textiles, electrochromic devices and sensors.

The electronic properties of PANI can be reversibly controlled by protonation as well as by redox doping. Therefore, PANI could be visualized as a mixed oxidation state polymer composed of reduced \(\text{–NH–B–NH–}\) and oxidized \(\text{–N=Q=N–}\) repeat units where \(\text{–B–}\) and \(\text{=Q=}\) denote a benzenoid and a quinoid unit respectively forming the polymer chain, the
average oxidation state is given by \((1-y)\). Depending upon the oxidation state of nitrogen atoms that exist as amine or imine configuration, PANI can adopt various structures in several oxidation states, ranging from the completely reduced leucoemeraldine base state (LEB) \(y-1 = 0\), to the fully oxidized pernigraniline base state (PNB), where \(1-y = 1\). The “half” oxidized \((1-y = 0.5)\) emeraldine base state (EB) is a semiconductor and is composed of an alternating sequence of two benzenoid units and a quinoid unit. The protonated form is the conducting emeraldine salt (ES). The electronic structure and excitations of these three insulating forms (LEB, PNB, EB) are contrasted. However, the LEB form can be p-doped (oxidatively doped), the EB form can be protonic acid doped and the PNB form can be n-doped (reductively doped) to form conducting ES systems. The EB, intermediate forms of PANI can be non-redox when doped with acids to yield the conductive emeraldine salt state of PANI. It can be rendered conductive by protonating (proton doping) the imine nitrogen, formally creating radical cations on these sites. This doping introduced a counter ion (e.g. Cl\(^-\) if HCl was used as the dopant), and the counter ion was affixed to the parent polymer by partially sulphonating the benzene rings in the polymer, resulting in a so-called “self-doped” polymer. Both organic acids such as camphor sulphonic acid, and inorganic acids such as HCl are effective, with the organic sulphonic acids leading to solubility in a wide variety of organic solvents, such as chloroform and m-cresol.

Polyaniline is known for its electrochromic activity; it shows multiple colour changes (transparent yellow-green-blue) depending on the electrochemical reactions in the potential range from -0.2 to 0.8 V against standard calomel electrode. The cyclic voltammogram of polyaniline film in 0.1M H\(_2\)SO\(_4\) aqueous solution showed two anodic peaks at 0.2 and 0.7 V, together with large capacitive background currents. The colour of polyaniline films change from transparent yellow to green at the anodic peak around 0.2 V and gradually changed from green to dark blue at potentials higher than 0.3 V. The colour change from transparent yellow to green is due to the formation of Wurster-type radical cations at 0.2V, and that of from green to blue is due to the formation of a diimine structure and doped states with \((SO_4)^{2-}\) in the polymer at potentials above 0.3 V. The deterioration of electrochromic property is caused by hydrolysis of the diimine structure formed by oxidation at 0.7 V [5].
**Conduction mechanism in PANI**

The electrical conductivity ($\sigma$) in any system is proportional to the product of the density of charge carriers ($n$), the charge carried by each carrier ($e$) and the mobility of each carrier ($\mu$). $\sigma = en\mu$, where ‘$e$’ is the unit electronic charge ($1.6\times10^{-19}$C), ‘$n$’ in m$^{-3}$ and $\mu$ in m$^2$/Vs [6]. The carrier concentration, its mobility and the type of carrier can be estimated from a Hall effect measurement. For the negatively charged carriers ($n$-type semiconductors), the Hall voltage is positive and for the positively charged carriers ($p$-type semiconductors), the Hall voltage is negative. The experimental results show that the majority charge carriers in PANI are holes, which indicates that the PANI is a $p$-type semiconductor [7,8]. The delocalized $\pi$ bonds available in the system are responsible for the semi-conducting properties. The $\pi$ orbital produces the valance band and the $\pi^*$ forms the conduction band. The difference in energy between ground ($\pi$) and excited ($\pi^*$) orbitals is called the band gap or band energy. The value of this band gap determines both the electrical and optical properties of semi-conducting polymers. As the band gap energy decreases, the $\pi-\pi^*$ transition becomes easier, resulting in a high conductivity. The band gap energy of PANI can be estimated from UV analysis [9,10].

Various models have been proposed for the electrical conduction mechanism in PANI. From the temperature dependent conductivity, the models proposed are quasi one-dimensional (1D) variable range hopping (VRH), 3D VRH, a combination of 1D and 3D VRH, charging energy limited tunneling (CELT) for granular metals and a heterogeneous model where temperature dependence of conductivity shows from nonmetallic to metallic [11]. Quasi-1D VRH indicates that the conductivity of PANI is highly anisotropic, since it is much higher along the polymer chains. This quasi-1D metal resistivity shows a small magnitude at low temperatures and a sharp increase at higher temperatures. In disordered semiconductors with localized states in the band gap, conduction occurs by hopping (i.e. phonon-assisted tunneling between electronic localized states centered at different positions).

Owing to the local anisotropy of the samples caused by the polymer chains (one-dimensionality), the percolation behavior (formation of connected paths of highly doped
regions) is very difficult to predict and the observed conductivity will very often be a combination of VRH in lightly doped regions and tunneling between more heavily doped domains in the PANI and its composites. PANI behaves as a semi-crystalline, heterogeneous system with a crystalline (ordered) region dispersed in an amorphous (disordered) region. It is similar to a Quasi-Metallic Island surrounded by a non-metallic amorphous zone. The crystalline domains are metallic in nature, where conduction occurs through electron delocalization or hopping of the charge carrier due to the ordered structure. The conduction in the metallic region occurs by the hopping of charge carriers through the polaron structure. A polaron structure is formed after protonation of the emeraldine base. This crystalline section is responsible for the conductivity of PANI. However, metallic grains are surrounded by an amorphous non-conducting region consisting of disordered or folded chains. The overall conductivity of PANI depends on bridging among conductive regions. Tunneling of charge carriers occurs between conducting and non-conducting phases [12].

Three terms soliton, polaron and bipolaron are used to explain the conduction mechanism of PANI and other OCPs. Soliton, sometime called as conjugational defect, is lone electron created in the polymer backbone during the synthesis of conductive polymer, in very low concentration. Conjugational defect is a misfit in the bond alternation so that two single bonds will touch. Soliton can be generated in pairs, as soliton and antisoliton. Three methods were used to generate additional solitons; chemical doping, photogeneration and charge injection. An electron will be accepted by the dopant anion to form a carbocation (positive charge) and a free radical during the chemical doping (oxidation) of the polymer chain, known to organic chemists as radical cation or polaron to physicists. Both the soliton and polaron can be neutral or charged (positive or negative). In the doping process, the heteroatoms (nitrogen) will be protonated and become a bipolar form. The motionless charged states are known as carbonium (+ve) and carbanion (-ve) radicals by organic chemist. The conventional distortion of molecular lattice can create a localized electronic state; thereby lattice distortion is self-consistently stabilized. Thus, the charge coupled to the surrounding (induced) lattice distortion to lower the total electronic energy is known as polaron (i. e. an ordinary radical ion) with a unit charge and spin = ½. A bipolaron consist of two coupled polarons with charge = 2e and
spin = 0. The polaron and bipolaron have a unique property called “spin-charge inversion”. Whenever they bear charge, they have no spin and vice versa. Bipolarons are not created directly but must form by the coupling of pre-existing polarons or possibly by addition of charge to pre-existing polarons [13].

When EB is doped with different acids, a polaron is formed. Such polaron is not delocalized completely, but is delocalized only a few monomeric units deforming the polymeric structure. The energy associated with this polaron represents a destabilized bonding orbital. It has a higher energy than the valence band, (to the nearest band theory approximation) and lies in the band gap. If another electron is subsequently removed from the already oxidized polymer, another polaron or a bipolaron will be created. Low doping level gives rise to polarons (EB) and with increase in the doping level more and more polarons interact to form bipolarons (PNB). The polaron structure is responsible for electrical conduction through the hopping mechanism in the crystalline region and hopping may be intra-chain or inter-chain. In the polaron structure, a cation radical of one nitrogen acts as the hole and these holes are charge carriers. The electron from the adjacent nitrogen (neutral) jumps to that hole and that hole then becomes neutral. Consequently, the holes start to move. As a result, on the second nitrogen another hole is created. Thus in the polaron structure, an electron starts moving along the polymer chain towards one particular direction and the corresponding hole is set into motion along the chain length in the opposite direction leading to an electrical conduction along the chain. However, in the case of a bipolaron structure, this type of movement of the electron and hole is not possible since the two holes are adjacently located. The reason for the conductive nature of the emeraldine salt and the insulating nature of the PNB might be explained by this conduction theory. In the LEB or the PNB structure, the electronic environments of all the nitrogens along the polymer chain are similar. Protons from the dopant can be attracted by any nitrogen atom and there may be a few (more than two) protonated nitrogens or free nitrogens situated side by side across the chain. Hence, there is less chance for chain regularity, creating less chance for the formation of polaron which is responsible for the conduction. As a result, protonated LEB is insulating in nature. More
details of different conduction mechanism are given by Bhadra et al and it is beyond the scope of this study [14].

**Drawbacks of PANI**

The potential applications of PANI have been limited due to its infusibility, very low solubility in most of the available solvents, hygroscopic and much lower conductivity compared to that of metals [15]. However, the conductivity of PANI is improved after doping. Another method used to improve the conductivity of PANI is to control its structure, i.e. the preparation of perfect EB through over oxidation followed by reduction. Processability can be improved by introducing alkyl substituent or by coating on flexible textile materials.

**TiO₂**

Titanium dioxide (TiO₂) also called as titania, is the naturally occurring oxide of titanium. It has got a wide range of applications in day-today life. It is used as pigment (CI 77891), sunscreen and food colour (E171). The research interest for TiO₂ mainly focus on its photocatalytic and UV absorbing properties. There are three main types of TiO₂ structures: rutile, anatase and brookite. The size dependence of the stability of various TiO₂ phases has been reported [16]. Rutile is the most stable phase for particles above 35 nm in size. Anatase is the most stable phase for nanoparticles below 11 nm. Brookite has been found to be the most stable for nanoparticles in the 11-35 nm range. These have different activities for photocatalytic reactions, but the precise reasons for differing activities have not been elucidated in detail. Rutile has three main crystal faces, two that are quite low in energy and are thus considered to be important for practical polycrystalline or powder materials [17]. These are: (110) and (100). The most thermally stable is (110). It has rows of bridging oxygens (connected to just two Ti atoms). The corresponding Ti atoms are 6-coordinate. In contrast, there are rows of 5-coordinate Ti atoms running parallel to the rows of bridging oxygens and alternating with these. The exposed Ti atoms are low in electron density (Lewis acid sites). The (100) surface also has alternating rows of bridging oxygens and 5-coordinate Ti atoms, but these exist in a different geometric relationship with each other. The (001) face is thermally less stable, restructuring above 475°C. There are double rows of bridging oxygens
alternating with single rows of exposed Ti atoms, which are of the equatorial type rather than the axial type.

Anatase has two low energy surfaces, (101) and (001), which are common for natural crystals. The (101) surface, which is the most prevalent face for anatase nanocrystals, is corrugated, also with alternating rows of 5-coordinate Ti atoms and bridging oxygen, which are at the edges of the corrugations. The (001) surface is rather flat, but can undergo a (1 x 4) reconstruction. The (100) surface is less common on typical nanocrystals, but is observed on rod-like anatase grown hydrothermally under basic conditions. This surface has double rows of 5-coordinate Ti atoms alternating with double rows of bridging oxygens. It can undergo a (1 x 2) reconstruction. It was reported in 1942 by Earle that rutile and anatase TiO$_2$ in the form of powders are n-type semiconductors and the conductivity decreases with increasing O$_2$ partial pressure at temperatures above 600°C [18]. The effect of O$_2$ was explained on the basis of an equilibrium involving thermal release of O$_2$ from the lattice.

Titania exhibits some unique dielectric and chemical properties that can be utilized in various technological applications such as photocatalysts [19-22], ceramic membranes [23], humidity sensors [24-25] and gas sensors [26]. It is frequently used in the form of powder or a loose compact consisting of small particles with sizes on the nanometer scale. Several methods have been developed to synthesize titania nanometer-sized particles, such as gas condensation method [27] and sol-gel method [28-29]. The microemulsion approach is a promising method to prepare nanometer-sized particles. An inverse microemulsion system [30] has been employed to synthesize nanometer-sized particles.

**PANI-TiO$_2$ Composites/hybrids**

Polymer–semiconductor nanocomposites generate a new field for the development of advanced materials in science and technology [31]. The composites of TiO$_2$ with different polymers such as conducting PANI [32–35], PPY [36] and poly(phenylenevinylene) (PPV)
have been studied for their unique properties. PANI–TiO$_2$ hybrids/composites are explored for enhanced catalytic activity, optical properties and electrical properties.

**Methods of preparation of PANI–TiO$_2$ hybrids/composites**

There are several innovative methods reported for the synthesis of composites or hybrids as the inherent intractability of PANI prevents it from composite formation in conventional blending methods.

**In-situ polymerisation:** In-situ polymerisation is the most employed method where aniline is chemically polymerized in the presence of TiO$_2$ and thus PANI is physically incorporated with TiO$_2$ [38-41]. In this typical procedure, weighed amount of TiO$_2$ in HCl is sonicated for better dispersion and aniline in HCl is added. This is kept under vigorous stirring for some time and then oxidizing agent such as APS is added. The temperature is usually kept low as 0°C and polymerisation time is above 2 h. The powder obtained is the required composite. The conductivity can be modified by further doping with sulphonic acids. Su et al reports composites of higher conductivity by doping with DBSA and XSA [42]; they were successful in producing free standing films from homogeneous suspensions in m-cresol. The conductivity ranged from 2-5 S/cm.

**Enzymatic synthesis:** Enzymatic synthesis has attracted significant attention because it is carried out under mild conditions, in comparison to those used for chemical polymerisation. Horseradish peroxidase (HRP) and soybean peroxidase (SBP) are oxido-reductase enzymes capable of oxidizing aromatic amines in the presence of hydrogen peroxide [43-45]. These enzymes can be derived from non-contaminant renewable sources and have high reaction selectivity to aromatic compounds and they cut down the oxidation by-products to water [46]. For these reasons, peroxidase catalyzed polymerisation of aniline is considered to be an environmental friendly route. Most of the research related to enzymatic polymerisation of aniline was carried out using polyelectrolyte templates such as sulphonated polystyrene [47-48], poly(vinylphosphonic acid) [49] and deoxyribonucleic acid (DNA) [50]. In an enzymatic
route for the synthesis of PANI-TiO$_2$ reported by Nabid et al, horseradish peroxidase (HRP) was used to catalyze the polymerisation and H$_2$O$_2$ as oxidant [51]. The presence of sulphonated polystyrene (SPS) affected the polymerisation reaction. Polyaniline was deposited on the surface of TiO$_2$, forming a core-shell structure. These nanoparticles displayed a great effect on the electron exchange assistance, because the reversibility is better for PANI/TiO$_2$/Pt electrode with the $\Delta E$ value of 39 mV in comparison to that of PANI/Pt electrode with the $\Delta E$ value of 281 mV.

**Electrochemical method:** The first attempt at electrochemical synthesis of TiO$_2$/PANI composite was performed by electropolymerisation of aniline in the presence of TiO$_2$ nanoparticles [52]. In a later work, a more complicated multistep procedure involving polymerisation of aniline and subsequent electrodeposition of TiO$_2$ is suggested [53]. Ilieva et al [54] studied photoelectrochemical responses of layers of PANI-TiO$_2$; they produced two types of layer: (i) TiO$_2$-PANI single-layers were produced by starting the electropolymerisation in the TiO$_2$ particle containing solution; (ii) PANI/TiO$_2$-PANI bi-layers were produced by starting the polymerisation in TiO$_2$ free solution and synthesizing a first pristine PANI layer and then transferring it to the TiO$_2$ containing solution for further growth of a second TiO$_2$-PANI layer. The thickness of the bi-layer structures was modified by varying the thickness of the first PANI layer and keeping the number of scans used for producing the outer TiO$_2$-PANI composite layer constant.

**Self assembly method:** In a preparation process of the PANI-TiO$_2$ hybrid/composites, $\gamma$-amino-propyltriethoxysilane was used as a coupling agent to form a dense aminopropylsilane monolayer with active sites for the graft polymerisation of aniline. After TiO$_2$ nanoparticles were surface modified by this coupling agent forming a self-assembled monolayer (SAM), conductive polyaniline layer was chemically grafted, resulting in PANI/SAM-TiO$_2$ composites. These composites showed better photocatalytic activity and thermal stability [55]. Aminobenzoate monolayer which was chemically adsorbed on the TiO$_2$ nanocrystal surface also acted as the grafting sites for aniline. This is reported to yield uniform core-shell nanocomposite. The thickness of polyaniline layer coating on the TiO$_2$ nanocrystal
surface was controlled to 2-5 nm; they reports to have fabricated dye-sensitized solar cell with a short circuit current density of 0.19 mA/cm² and an open circuit voltage of 0.35 V using the TiO₂/polyaniline nanocomposite film as a sensitized electrode. It is also reported that polyaniline in the nanocomposite acted as a visible-light sensitizer in a photoelectrochemical reaction. The sensitization effect increased with increasing binding strength between polyaniline and TiO₂ [56]. In a similar method, negatively charged TiO₂ nanoparticles are made to act as template for aniline polymerisation. Authors call it template polymerisation, and they obtained core-shell nanoparticles. First, the TiO₂ surface was modified to be negatively charged using Chem-Solv (aqueous alkaline alcohol) for 8 h under ultrasonication. The negative-charged TiO₂ nanoparticles were then used as templates for polymerisation. Second, the added aniline monomers were adsorbed in the form of anilinium cations on the negative TiO₂ surface by an electrostatic attraction. After the addition of ammonium persulphate as an initiator, the adsorbed anilinium cations polymerized immediately on the TiO₂ templates. In-situ oxidative template polymerisation of aniline was successfully performed on the surface of negatively charged TiO₂ nanoparticles with mean diameter of ca. 40nm using ammonium persulfide as an oxidant at pH 1 and 25°C [57]. PANI/TiO₂ composite nanofibres were successfully synthesized by interfacial polymerisation. For the interfacial self-assemble polymerisation, its conditions are mild without employing/removing template approach and the product is easy to be handled and the yield is high [58]. Polyaniline/TiO₂ microspheres with 2.5-3.6 μm in average diameter were synthesized by a template-free method in the presence of salicylic acid (SA) as the dopant by Zhang et al [59]. It was found that the morphology, conductivity and hydrophilicity of the PANI-SA/TiO₂ microspheres were affected by the content of TiO₂ nanoparticles. The micelles composed of SA anions and anilinium cations containing TiO₂ were proposed to interpret the formation mechanism of the self-assembled composite microspheres.

**Template polymerisation:** Different types of templates including “soft” and “hard” templates like anodized alumina, micelles, and surfactants are used for preparing PANI-TiO₂ composites [60]. In one of such methods, core–shell sulphonated-PS sphere was used as templates for preparing composite capsules and hollow Spheres of PANI-TiO₂. With this easy
and effective approach, hollow Fe$_3$O$_4$–PANI spheres with uniform cavity size and shell thickness can be produced. The template particles are prepared by simple sulphonation of PS microspheres, and aniline is polymerized on the surface of sulphonated-PS spheres. This was coated with TiO$_2$ by sol-gel process. The polystyrene cores were dissolved in N,N-dimethylformamide (DMF) solvent, forming hollow TiO$_2$–PANI spheres. The conductivity of TiO$_2$–PANI/PS composite capsules reduces to 2.76×10$^{-2}$ S/cm, much lower than that of the PANI/PS capsules (0.10 S/cm). This was mainly caused by TiO$_2$ nanoparticles, which partly block the conductive path [61]. Li et al prepared PANI/TiO$_2$ composite by in-situ polymerisation of polyaniline on the surface of TiO$_2$ template obtained by the sol–gel process via cotton template [62]. PANI/TiO$_2$ nano-composites with different amount of nanometer TiO$_2$ were synthesized by using reverse micelle formed from cationic surfactant cetyltrimethyl ammonium bromide (CTAB) as the template [63].

**Photo polymerisation:** Aniline can be photo-polymerized into polyaniline [64]. As TiO$_2$ being good photocatalyst, aniline adsorbed on TiO$_2$ can be photocatalysed to form PANI-TiO$_2$ hybrids. But this method is not well explored.

**Inverse emulsion method:** PANI–TiO$_2$ hybrids/composites by inverse emulsion method have been reported [65]. They carried out polymerisation in an organic solvent (chloroform, CHCl$_3$) in the presence of a protonic acid (HCl) as a dopant and an emulsifier (cetyl trimethylammonium bromide). The resultant PANI-TiO$_2$ nanocomposites were with the diameter range of 50–200 nm. Electrical conductivities were found to be 0.38 S/cm for bulk PANI and 0.11 S/cm for PANI-TiO$_2$ nanocomposites.

**One-pot polymerisation:** One-pot synthesis for TiO$_2$ and PANI-TiO$_2$ was done from various precursors such as tetra butyl titanite and titanium tetra chloride. The synthesis method reported by Wei et al has resulted in mesoporous titania in anatase phase. It required several hours for the completion of reaction [66]. The method used by Han et al was mentioned as one-pot method by the authors [67], in which they use TiO$_2$ as such with aniline and
polymerized. This is as similar to the in-situ polymerisation method with only difference by the addition of surfactant. The anionic surfactant (SDS) has a positive impact on the conductivity of the composites. By increasing its concentration, the shell thickness of produced core-shell composites increased and the TiO$_2$ was well dispersed into the PANI by incorporating the surfactant. PANI-TiO$_2$ hybrid materials were synthesized in supercritical CO$_2$ using two different methods. In the first method, separately synthesized TiO$_2$ particles were mixed with aniline to perform polymerisation in supercritical CO$_2$. The second method included the preparation of aniline-TiO$_2$ hybrids through a sol-gel reaction of titanium isopropoxide in the presence of aniline. Further polymerisation of aniline-TiO$_2$ hybrids in supercritical CO$_2$ produced PANI-TiO$_2$ hybrid particles. The final products showed the intrusion of PANI into the internal structure of TiO$_2$. PANI-TiO$_2$ nanocomposites synthesized with the first method showed a relatively low electrical conductivity of $3.78 \times 10^{-2}$ S/cm at 20°C. The electrical conductivity of the hybrid particles produced using the second method increased to $7.75 \times 10^{-2}$ S/cm. Through SEM and TEM analyses it was confirmed that the PANI has been interpenetrated into the three-dimensional network of the TiO$_2$ when the second method was used [68]. A sol–gel preparation method is used by Roy et al [69] to synthesize PANI- TiO$_2$ and is described as follows: Aniline/ HCl and titanium nitrate hydrated /citric acid are taken in 1 : 3 ratio and are stirred thoroughly for 1 h. To this mixture, APS and a-dextrose are added with constant stirring using magnetic stirrer at 70°C for 5–6 h. Finally, a green gel is obtained. The gel is further refluxed with 0.1N HCl to enhance the protonation processes. They formed core-shell composite with properties amiable for gas sensors. The hybrids were synthesized via a sol-gel process by Xiong et al [70], followed by oxidative polymerisation, using a bifunctional compound to bridge the two phases. If a bridging compound is added, it gives strong covalent bonding and interesting electrochemical properties.

Unique properties of PANI-TiO$_2$ hybrids

UV–Vis diffuse reflectance spectral study of TiO$_2$ nanoparticles, PANI, and PANI/TiO$_2$ nanocomposites by many researchers showed that polyaniline/TiO$_2$
nanocomposites can strongly absorb the UV light and also absorb the visible and near-IR light, whereas the TiO$_2$ can absorb light with wavelengths below 400 nm only. This shows that PANI can act as sensitizer of TiO$_2$ [71].

In a detailed study by Hao et al, the sensing property is explained in terms of pinning of Fermi levels [72]. They studied the cyclic voltammetric behavior of TiO$_2$ electrode and PANI-TiO$_2$ electrode in [Fe(CN)$_6$]$_3$ electrolyte. In the dark, the TiO$_2$ nanoporous film electrode exhibits reversible cyclic voltammetry peaks corresponding to the oxidation of [Fe(CN)$_6$]$_4$ and reduction of [Fe(CN)$_6$]$_3$, which indicates a free flow of electrons in both directions. But in the case of PANI- TiO$_2$ electrodes, the reduction peak of [Fe(CN)$_6$]$_3$ was not detected indicating that the electrons in the conduction band of TiO$_2$ nanoporous film do not flow to the electrolyte. And also in photocurrent studies, it was seen that photogenerated electrons in the conduction band of TiO$_2$ nanoporous film have free flows to both directions. Hence, the energy bands of TiO$_2$ nanoporous film are unbent. The photocurrents of PANI-TiO$_2$ electrode were larger than that of the TiO$_2$ nanoporous film electrode. The PANI film formed above TiO$_2$ could suppress the flow of electrons to the electrolyte.

When the PANI-TiO$_2$ electrode is excited by light, the photogenerated electrons from the PANI conduction band can be quickly injected into the conduction band of TiO$_2$, while the holes migrate to the interface between TiO$_2$ nanoparticles and electrolytes to oxidize. The band energies of these two semiconductors do not favor the flow of electrons to the electrolyte. When the TiO$_2$ is sensitized by acid-doped PANI, the photocurrent generation extends into the visible and infrared regions. A maximum value can be seen in the region of 600-700 nm (2 eV). The electron structure and charge transport of acid-doped PANI are complexed. It was reported [73] that acid-doped PANI had a strong electronic absorbance in the infrared region. When it was excited by infrared light, the acid-doped PANI generates photocurrents. Roe et al. reported [74] that the transition of electrons created by photoexcitation to the conduction band might take place. Kim [75] assigned the 2 eV transition as an n$\rightarrow$$\pi^*$ transition from the nonbonding lone pair state to the conduction band, this transition opened a channel for optical pumping of charges into the conduction band of acid-doped PANI with 2 eV photons. Kim et
al [76] also observed the photocurrents obtained with 2 eV light excitation. The energy level of conduction band is about 2.7 eV for acid-doped PANI [77] and the energy level of conduction band is about 4.0 eV for TiO$_2$ [78]. Thus, when the TiO$_2$ is sensitized by acid-doped PANI, the photoexcited electrons in the conduction band of acid-doped PANI can be injected into the conduction band of TiO$_2$. Thus the acid-doped polyaniline as a sensitizer for TiO$_2$ improves the conversion efficiency of light to electricity.

The size and morphology of PANI-TiO$_2$ matters a lot. When PANI layer is thick, the electrons and holes created by photoexcitation might be recombined before the electrons reach the TiO$_2$ nanoparticles due to the low mobility of the electrons and holes created by photoexcitation in doped PANI. In other words, it is due to the large intrinsic capacitive currents of the polymer material combined with loss of transfer efficiency for the photo-generated electrons in the bulk of thick composite layers. The electrochemical response is reduced in thick PANI layers. Despite the loss of electroactivity, it seems that the PANI structure provides sufficient conductivity and thus the photoelectrochemical response observed at TiO$_2$-PANI remains unaffected.

Mickova et al [79] reported that irreversibility of redox couple in PANI/TiO$_2$ composite films is higher than in PANI films. In comparison with PANI and the composite, the oxidation peak potentials for all the PANI-TiO$_2$ hybrids produced by Xiong et al [70] are reduced significantly, and that the magnitude of the peak potential shift increases with the amount TiO$_2$ in the hybrids. They propose that the reason for the decrease in the oxidation potentials for the hybrids is that the electron donor (PANI) - acceptor (TiO$_2$) interaction causes a decrease in the energy of the highest occupied molecular orbital (HOMO) and ionization potential of PANI, thus enabling PANI to be oxidized at a lower potential. This feature is also shown by the lower band gap of the hybrids, compared to PANI and the PANI/TiO$_2$ composite. This gives rise to improved electrochromic response and good optical contrast. The conductivity of PANI-TiO$_2$ was higher than pristine PANI. The dielectric properties were improved.
Applications of PANI-TiO$_2$ composites / hybrids

- **Photocatalysis:** PANI-TiO$_2$ composites / hybrids are widely used as photocatalyst for the degradation of organic pollutants. The efficiency can be enhanced many folds with respect to neat TiO$_2$ catalyst. The interaction between PANI and TiO$_2$ may be of significance to promote the migration efficiency of carriers and induce a synergetic effect to enhance the photocatalytic and photo electro catalytic activities [80]. The photocatalytic degradation in the solid polymer matrix proceeded much faster than the direct photolytic degradation under air [81]. The catalytic mechanism and further details will be further discussed in chapter IV.

- **Smart corrosion resistant coatings:** Coatings prepared from polyaniline-nano-TiO$_2$ particles synthesized by in-situ polymerisation were found to exhibit excellent corrosion resistance much superior to PANI in aggressive environments. The corrosion studies were carried out on steel plates coated with formulations containing 10 wt% polyaniline prepared with different concentrations of nano-TiO$_2$. The open circuit potential (OCP) was found to shift with time from -0.38 V to more anodic side (-0.2 V) much above that of bare steel (-0.5 V) indicating better protection. The presence of nano-TiO$_2$ was found to be vital in this corrosion prevention and the shift of OCP to anodic side. From these data, one could envisage more than 100 times improvement in the corrosion resistance especially for polyaniline prepared with 4.18 wt% nano-TiO$_2$. The exceptional improvement of performance of these coatings has been associated with the increase in barrier to diffusion, prevention of charge transport by the nano-size TiO$_2$, redox properties of polyaniline as well as very large surface area available for the liberation of dopant due to nano-size additive [82]. Sathyanarayanan et al evaluated the corrosion protection performance of the coatings containing PANI and PANI-TiO$_2$ composite on steel by immersion test in 3% NaCl for 60 days and salt fog test for 35 days. The performance of the coatings in both the tests was investigated by open circuit potential measurements and EIS technique. It has been found that the open circuit potential values of PANI-TiO$_2$ composite containing coating are nobler by 50–200mV in comparison to that of coatings with PANI. Besides, the
resistance values of the coating containing PANI-TiO₂ composite were more than 107 \( \Omega \text{cm}^2 \) in the 3\% NaCl immersion test after 60 days and 109 \( \Omega \text{cm}^2 \) in the salt fog test of 35 days, which were two orders high in comparison to that of PANI containing coatings. The better performance of PANI-TiO₂ composite containing coatings may be due to uniform distribution of polyaniline which can form uniform passive film on the iron surface [83].

- **Sensors**: PANI is known to be a good pH sensor and gas sensor [84]. On compositing with TiO₂, the sensing activity is reported to be enhanced. Thin films of PANI and TiO₂/PANI composites were deposited on copper inter-digited electrodes (IDE) by spin coating method to prepare the chemiresistor hydrogen gas sensor [85]. The response of chemiresistor sensors for H₂ gas was evaluated by monitoring the change in electrical resistance at room temperature. It was observed that the PANI-TiO₂ composite thin film based chemiresistor sensors show a higher response as compared to pure PANI sensor. The gas sensors of the composite nanofibres with different PANI to TiO₂ ratios were fabricated on home-made gold electrodes, and the sensing property for ammonia gas detection was investigated at room temperature by Li et al [86]. Results showed that the composite nanofibre sensor could detect as low as 25 ppb ammonia gas, which is superior to the PANI nanofibre without TiO₂ nanoparticles. The sensing sensitivity of the composite nanofibres strongly depended on the ratio of PANI to TiO₂. The sensitive property of PANI-TiO₂ sensors to NH₃ at room temperature was also studied by Jiang et al [87]. With planar interdigitated electrodes, PANI/TiO₂ composite thin film gas sensor doped by hydrochloric acid and para toluene sulphonic acid (PTSA) respectively were prepared by combining in-situ chemical oxidation polymerisation and electrostatic self-assembly technique at the room temperature. The results show that the sensitivity, response and recovery characteristic, and the stability of PANI/TiO₂ composite thin film doped by hydrochloric acid are superior to that of PANI/TiO₂ composite thin film doped by PTSA. This study was helpful for the development of NH₃ sensitive device with low cost and high sensitivity. The gas sensing test by Izzuddin et al [88] revealed that PANI-TiO₂ were responsive towards ethanol vapour exposure with 2 weight percent TiO₂ / PANI film
exhibited the best sensitivity. However, over longer exposure cycles, it was observed that 3 wt% TiO$_2$/PANI have a better stability.

**Fuel Cells:** Composites of PANI and TiO$_2$ nanoparticles were investigated for applications in direct methanol fuel cell and alcohol sensors. Anilinium sulphate and TiO$_2$ with nanometric size were electropolymerised in 0.5M H$_2$SO$_4$ solution on carbon paper. Oxidation and response to methanol was measured by chrono amperometry and electrochemical impedance spectroscopy [89]. A unique nanostructured PANI-TiO$_2$ composite was synthesized by Qiao et al and explored as an anode in Escherichia coli microbial fuel cells (MFCs). The results of X-ray diffraction, morphology, and nitrogen adsorption-desorption studies demonstrate a networked nanostructure with uniform nanopore distribution and high specific surface area of the composite. Optimization of the anode showed that the composite with 30 wt% PANI gives the best bio- and electrocatalytic performance. A possible mechanism to explain the excellent performance was proposed. In comparison to previously reported work with E.coli MFCs, the composite anode delivers 2-fold higher power density (1495 mW/m$^2$). Thus, it has great potential to be used as the anode for a high-power MFC and may also provide a new universal approach for improving different types of MFCs [90]. PANI-TiO$_2$ composites are stable during the electrooxidation of ascorbic acid; hence they can be used as an alternative catalyst for direct ascorbic acid fuel cells. In a study by Ganesan et al, polyaniline was grafted onto a mixture of rutile and anatase TiO$_2$ nanoparticles by in-situ chemical oxidative polymerisation. Compared to the neat polyaniline, PANI-TiO$_2$ composites showed higher capacitance and also higher activity per mass of polyaniline [91].

**Dye sensitized solar cells (DSSC):** The dye absorbed TiO$_2$/PANI electrode based DSSCs significantly improved the conversion efficiency, and may attribute to the high charge carrier transportation between the TiO$_2$ and the PANI layer. It was demonstrated by Ameen et al that TiO$_2$/PANI and dye absorbed TiO$_2$/polyaniline electrodes were prepared by plasma-enhanced polymerisation using aniline monomer for the fabrication of DSSCs. The structural and the crystalline studies demonstrated the formation of TiO$_2$/PANI thin film, where the
PANI molecules are well penetrated into the porous nanocrystalline TiO$_2$ thin film. The electrical conductivity of pristine PANI was greatly improved by the incorporation of TiO$_2$ into TiO$_2$/PANI electrode. The fabricated DSSC with dye absorbed TiO$_2$/PANI electrode exhibited a reasonably well overall conversion efficiency of 0.68%. An impedance study was performed to describe the high JSC, FF, and conversion efficiency of dye absorbed TiO$_2$/PANI electrode based cells [33]. The photoconductivity of PANI-TiO$_2$ composite has been enhanced markedly. Feng et al discussed this effect by taking the photoinduced charge transfer between PANI and TiO$_2$ into consideration. A composite of PANI encapsulating TiO$_2$ with nanometer size has been synthesized by in-situ emulsion polymerisation. Panicle dimensions have been measured and the nature of the association between the components has been observed using SEM and TEM techniques. The interaction between PANI and TiO$_2$ and the nature of chain growth have been investigated and explained according to the results of FTIR. The mechanism of charge transport in these composites has also been studied by measuring the DC conductivity of all samples and the temperature-conductivity relation [92].

**Effect of surfactants**

The potential incorporation of a surfactant into a conducting polymer is likely to improve the electrical, thermo-oxidative and hydrolytic stability due to the introduction of bulky hydrophobic component. Yavuz et al [93] observed TiO$_2$/PANI–cationic surfactant has the highest conductivity value whereas TiO$_2$/PANI–anionic surfactant has the lowest one. The magnetic properties of the TiO$_2$/PANI composites have been considered by measuring the magnetic susceptibility. The mass magnetic susceptibility of TiO$_2$/PANI composites exhibited negative values. From that result, they concluded that the composites in all situations are diamagnetic, i.e. having bipolaron conduction mechanism. The yield is higher in the presence of surfactants case than no surfactant case. The incorporation of bulky surfactant anion into TiO$_2$/PANI may be the cause for the increase in the polymer yield. This incorporation can be ionic interaction between the polycations and the surfactants moiety during polymerisation.
PANI coated TiO$_2$ have been prepared with ammonium persulphate as an oxidant in aqueous sodium dodecyl sulphate micellar solution [67, 94]. The addition of a small amount of TiO$_2$ nanoparticles greatly increased electrical conductivity from 5.89 to 14.2 S/cm. These nanosized powders could transfer into the organic phase. With increase in the amount of SDS, the dispersibility into the organic solvent was increased. Consequently, the electrical conductivity of the product was also decreased. The obtained composites showed 14.16 S/cm of conductivity at maximum while the value was almost independent on the polyaniline coating ratio in range of 100-20wt%. The conductivity value of composite with 20wt% polyaniline was 70000 times higher than that of raw titania. Modified titania had properties of polyaniline and titania together. In addition, these composite showed the photoconductive response against the UV irradiation, which might show the existence of P-N junction between titania and polyaniline.

**Aim of the present study**

On the basis of literature cited above, it was found that one-pot method of synthesis for PANI-TiO$_2$ can yield hybrids with desired properties. Hence, work has been designed and executed to explore the possibilities of One-pot method for the synthesis of PANI-TiO$_2$ hybrids. As anatase phase was more advantageous and active, it was aimed to obtain anatase TiO$_2$ hybrided with PANI. Acetic acid medium was tried as a means to obtain anatase form of TiO$_2$ and to reduce the ill-effects of strongly acidic pH. The variation in properties with respect to TiO$_2$ content was also studied. The hybrids were subjected to ageing and the loss in electrical conductivity was studied.

**2.2. Experimental section**

**Chemicals used**

The chemicals used in for the are given below:

<table>
<thead>
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<th>Chemical</th>
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Aniline | ADLAB | 98% (distilled before use)
--- | --- | ---
Titanium tetrachloride | Loba | 99%
Hydrazine hydrate | Loba | AR grade
Ammonium persulphate (APS) | Merck | AR grade
Camphor sulphonic acid (CSA) | Sigma-Aldrich | AR grade

**Synthesis of PANI-TiO$_2$ by conventional and one-pot method**

Anatase grade TiO$_2$ was synthesized by hydrolysis of TiCl$_4$ followed by calcination as reported by Reddy et al [95]. For this, 5 mL of TiCl$_4$ digested in Con.HCl was diluted with water to get a concentration of 2 M. An aqueous solution of hydrazine hydrate (5 M) was added drop-wise until the pH was about 7.5. The mixture was kept under constant stirring on a magnetic stirrer for 1 h at room temperature. Then the precipitated TiO$_2$.nH$_2$O was filtered and washed repeatedly with hot distilled water to make it free from chlorine. This was then dried overnight at 90°C and ground to fine powder form. This polycrystalline TiO$_2$ powder was then calcinated at different temperatures (400, 500, 600°C). The calcination time also was varied from 2 to 12 h and the resulted samples were characterized using XRD. The TiO$_2$ anatase powder at optimized calcinating time was selected for further studies and designated hereafter as TiO$_2$.Cal. A 0.16 g (2.0 x 10$^{-3}$mol) of this TiO$_2$.Cal was added with 0.6 mL aniline (6.3 x 10$^{-3}$mol) in 20 mL of 1 M HCl, stirred for 1 h and then polymerized with aqueous solution of 1.5 g of APS (6.5 x 10$^{-3}$mol) and 0.7 g CSA (3.0 x 10$^{-3}$mol) for 2 h. The precipitate thus obtained was washed well with distilled water, dried at 60°C and designated as PT$_{cal}$. This hybrid was of PANI-TiO$_2$ ratio 1:0.3. Pristine PANI was prepared by conventional chemical polymerisation with APS as oxidant and CSA as dopant for reference purpose.

**One-pot method of synthesis** of PANI-TiO$_2$ was done in HCl and designated as PT$_{HCl}$. One-pot synthesis of PANI-TiO$_2$ was again done in acetic acid and designated as PT$_{CH_3COOH}$. A 2 mL (18.1 x 10$^{-3}$mol) of TiCl$_4$ was slowly dissolved in 10 mL ethanol under vigorous stirring to obtain the ethanolic solution of TiCl$_4$. Then, 2 mL of the above solution and 0.6 mL of aniline were injected synchronously into a flask containing 40 mL of acid (1 M
HCl was used for PT\text{HCl}, while 1 M acetic acid was used for PT\text{CH3COOH}). Thereafter, each system was heated to 80°C for 4 h under constant stirring to obtain TiO\textsubscript{2} nanoparticles adsorbed with aniline. Then, these systems were cooled to room temperature. APS and CSA as in the case of PT\text{cal} were added drop-wise into each. The polymerisation was allowed to proceed for 2 h under room temperature to ensure the completion of the reaction. Finally, each products were filtered and washed repeatedly with distilled water and then dried at 60°C for 6 h. Pristine TiO\textsubscript{2} were prepared in HCl and acetic acid media (as per above procedure, without the addition of aniline and polymerization) and designated as TiO\textsubscript{2,HCl} and TiO\textsubscript{2,CH3COOH} respectively.

**Effect of TiO\textsubscript{2} concentration**

The amount of TiO\textsubscript{2} plays an important role in the properties of hybrids in all literature reported. Hence, five different PT\textsubscript{CH3COOH} were synthesized by varying the amount of TiCl\textsubscript{4} precursor and their electrochemical impedance spectra were compared. These samples were also analyzed with XRD and SEM. The samples were designated as PT\textsubscript{x}, where x denotes the ratio of TiO\textsubscript{2} with respect to aniline.

**Effect of CSA concentration**

The concentration of CSA with respect to aniline was varied and the effect in electrical conductivity was studied.

**Effect of Oxidant concentration**

Oxidant concentration is said to influence the properties of hybrid. In many cases, higher oxidant concentration increased the electrical conductivity. Hence, input ratio of oxidant (APS) to aniline monomer in the system of PT\textsubscript{CH3COOH} was varied and EIS spectra were compared. Hybrids containing one higher concentration and one lower concentration were prepared and compared with having oxidant-monomer ratio as 1:1.

**Characterisation**
The X-ray diffraction (XRD) measurements of the materials were performed using X'Pert–PRO X-ray diffractometer. All samples were analyzed in the range between 10 and 80° as 2θ and Cu as anode (K-Alpha -1.54060 Å). Fourier transform infrared (FT-IR) spectra were taken using a Shimadzu 8400S spectrometer, using KBr pellet method. Thermogravimetric analysis (TGA) was performed using EXSTAR Model 6000 instrument with a heating rate 20°C/min over a temperature range between 40 and 750°C in air. Scanning electron microscopy (SEM) images were obtained using a HITACHI S3000H instrument. Transmission electron microscopy (PHILIPS CM200 operating at 20 kV) was employed to determine the particle size. The elemental analysis was done with Elementar analysensysteme GmbH varioMicroV1.6.1. The mode of operation was CHNS. The electrochemical impedance experiments were performed for pelleted materials of 1 cm in diameter (prepared using hydraulic press) sandwiched between two symmetrical stainless steel electrodes in AUTOLAB electrochemical impedance bridge with FRA software. Impedance measurements were made in the frequency range of 10 mHz to 100 KHz at an amplitude of 10 mV. Five measurements of thickness were taken with a screw guage and averaged. Several researchers have described the conductivity of PANI through impedance spectroscopy [96-97]. Conductivity in semen can be obtained using the formula $\sigma = \frac{t}{R \times a}$, where R is the resistance, t is the thickness and a is the area. The resistance of pellets was also measured by conventional two probe method using digital multimeter.

2.3. Results and discussion

Conventional and one-pot method of synthesis

Three different TiO$_2$ and PANI-TiO$_2$ hybrids were synthesized; first by conventional method and other two by one-pot method. The yield of colourless TiO$_2$ powder obtained from calcination through conventional method (TiO$_{2\text{cal}}$) was 2.5 g, which corresponds to 1:1 molar ratio. This supports the mechanism of hydrolysis reported in the literature [95]. TiCl$_4$ in HCl undergoes hydrolysis yielding TiO$_2$.nH$_2$O, which on calcination gives anatase TiO$_2$ depending upon the calcinating temperature and time. The degree of crystallinity increased on increasing temperature (fig.2.1). The peaks become more clear and intense on increasing the temperature. The average particle size was calculated by scherrer formula and compared (fig.2.2). At
400°C, an increase in calcinating time resulted in increased size whereas in other two temperatures, the size decreased when the calcinating time was increased. The reason may be that the amorphous nature dominates in the former temperature and crystalline nature dominates in latter two temperatures. On comparing the particle size as a function of temperature for time duration of 2 h, a linear size increment is observed. From the results, it is observed that TiO₂ calcinated at 500°C for 2 h gave anatase TiO₂ with desired properties and hence selected for further studies.

In the synthesis of other two (TiO₂.HCl and TiO₂.CH₃COOH), ethanol was used to digest TiCl₄. The yellow gel of TiCl₄ in ethanol turned colourless on the addition of acid (HCl or CH₃COOH). This mixture upon heating and stirring for 4 h gave white precipitate of TiO₂. The amount of ethanol used for digesting TiCl₄ played an important role in the formation of TiO₂. TiO₂ was not formed when the ratio of TiCl₄ to ethanol was below 1:4 (fig.2.3).

From the fig.2.3, it is clear to note that TiO₂ was not formed (absence of characteristic XRD peaks) during synthesis at 1:2 and 1:3 ratios of TiCl₄ to ethanol. TiCl₄ in ethanol may undergo reaction as TiCl₄ + 4C₂H₅OH \rightarrow Ti(OC₂H₅)₄ + 4HCl [98], which need least 1:4 ratio to satisfy molar reaction. Thus, a ratio of 1:5 was found to be optimum, since a ratio less than 1:4 did not favor the reaction and a ratio greater than 1:5 led to the formation of ester. Hence, the ratio of 1:5 was taken as optimum and used for further studies.

0.4 g of colourless rutile powder (TiO₂.HCl) was obtained from 1 mL of TiCl₄. The molar ratio corresponds to this yield is 0.8:1. The loss may be due to some parallel hydrolysis yielding Ti(OH)₄. TiCl₄ may react with water in ethanol to form TiClₓ(OH)₄₋ₓ and HCl. TiClₓ(OH)₄₋ₓ form Ti(OH)₄ that is soluble in acidic medium and is removed on filtration. This loss was not observed in the case of TiO₂.CH₃COOH and yield corresponding to 1:1 molar ratio was obtained.

The formation of anatase grade TiO₂<sub>an</sub> (JCPDS file no 89-4921, body centered) and anatase grade TiO₂<sub>CH₃COOH</sub> (JCPDS file no 89-4203, tetragonal primitive) and rutile grade TiO₂<sub>HCl</sub> (JCPDS file no 89-4920, tetragonal primitive) hybrids with PANI are clearly noticed
from the XRD result (fig.2.4). The average particle size obtained from scherrer formula was 24, 26 and 11nm respectively for TiO$_2$cal, TiO$_2$HCl and TiO$_2$CH$_3$COOH.

The 101 plane at 2$\theta$ of 25.2 confirms anatase phase and 110 plane at 27.4 confirms rutile phase. The crystallinity index was calculated using the formula CI = [Ic/ (Ic+Ia)] x100, where Ic is the intensity of major crystalline plane (i.e. 101 for anatase and 110 for rutile) and Ia is the intensity of amorphous region in XRD pattern. The crystallinity index decreases in the order TiO$_2$Cal > TiO$_2$CH$_3$COOH > TiO$_2$HCl > PT$_{cal}$ > PT$_{HCl}$ > PT$_{CH_3COOH}$ (Table 2.1).

The reason for TiO$_2$HCl to be rutile and TiO$_2$CH$_3$COOH to be anatase can be explained by the crystal structure of each phase. Although rutile and anatase have tetragonal structures consisting TiO$_6^{2-}$ octahedra, the linkages of octahedra are different. Rutile involves corner and edge sharing linkages, whereas anatase has only edge sharing [99], thus rutile is thermodynamically more stable than anatase, which is kinetically more feasible [16]. The presence of HCl as solvent medium may reduce the rate of reaction forming Ti (OC$_2$H$_5$)$_4$ and favors backward reaction. This makes some of TiCl$_4$ to remain as such. Thus, the reaction may follow another pathway as explained by Zhu et al [100]. Ti (OC$_2$H$_5$)$_4$ and TiCl$_4$ species react and form Ti-OH bonds. These Ti-OH bonds break on continuous supply of heat and convert into TiO$_2$ rutile. The presence of weak vibrational band around 2360 cm$^{-1}$ corresponding to some unreacted alkoxides (Ti-OCH$_3$ bond) in the FT-IR spectra of TiO$_2$-HCl also supports this [101]. On the other hand, in the presence of acetic acid, the reaction may prefer a two step reaction as outlined below [98,102];

$$\text{TiCl}_4 + 4\text{C}_2\text{H}_5\text{OH} \rightarrow \text{Ti} (\text{OC}_2\text{H}_5)_4 + 4\text{HCl} \quad \text{(step 1)}$$

$$\text{Ti} (\text{OC}_2\text{H}_5)_4 + 4\text{CH}_3\text{COOH} \rightarrow \text{TiO}_2 + 4\text{CH}_3\text{COOCH}_3 + 2\text{H}_2\text{O} \quad \text{(step 2)}$$

Due to kinetic feasibility, anatase TiO$_2$ is formed here. This can also be evidenced as the system turned to milky white within one hour in acetic acid medium, while it took about two hours in HCl medium. An ageing time of 72 h was essential for ethanolic TiCl$_4$ solution for the effective formation of hybrids. The formation of HCl in the acetic acid medium was well supported as the pH of reaction mixture was lower than that of 1 M neat acetic acid. This has
favored polyaniline formation, since aniline was not fully polymerized in neat acetic acid (1M). The formation of anilinium ion is difficult in high pH [103].

The amount of TiO$_2$ present in the hybrids was estimated by residue analysis (residue weight after incineration at 650°C). When the % component of TiO$_2$ in the feed was at 25%, the % component of TiO$_2$ in the hybrids was estimated at 11.8, 24.1 and 24.5 for PT$_{cal}$, PT$_{HCl}$ and PT$_{CH3COOH}$ respectively. The XRD pattern also shows that TiO$_2$HCl and TiO$_2$CH$_3$COOH are more amorphous, but when it comes to hybrids, all three have the similar degree of amorphous nature (Table 2.1).

FT-IR spectra of pristine PANI, different TiO$_2$ and hybrids are given (fig.2.5). The FT-IR spectra for hybrids show all the prominent peaks of PANI, but mostly shifted to higher frequency. The peak around 600 cm$^{-1}$ and 1600 cm$^{-1}$ are the characteristic peaks of TiO$_2$. The new band around 2360 cm$^{-1}$ of hybrids shows the charge transfer interaction between TiO$_2$ and PANI with PANI molecules coordinated to Lewis acid site, Ti$^{4+}$ [104]. The blue-shift of bands is more prominent in PT$_{HCl}$ and PT$_{CH3COOH}$ than PT$_{cal}$, indicating more intense interactions (Table 2.2). Such shifting also confirms the covalent bond formation [57]. In the hybrids, the typical peak around 1250 cm$^{-1}$ is ascribed to S=O with reduced intensity due to low interaction of CSA. Thus, it is inferred that the interaction due to CSA is diminished in hybrids when compared to pristine PANI. This may be the cause for the decreased electrical conductivity of hybrids when compared to pristine PANI. The intensity of FT-IR peak at 1629 cm$^{-1}$ indicates an increase in dipole moment attributed to surface charges present in TiO$_2$-CH$_3$COOH. This surface charge facilitates the adsorption of aniline. The ratio of $I_{1600}/I_{1500}$ is an indicator representing emeraldine form of PANI if the value is 1. The values are noticed as 1.3, 0.8 and 1.0 for PT$_{I}$, PT$_{HCl}$ and PT$_{CH3COOH}$ respectively. This shows that conducting emeraldine form is mostly present in PT$_{CH3COOH}$. PT$_{cal}$ is over-oxidised (value is > 1) and PT$_{HCl}$ is under-oxidised (value is < 1). In the case of PT$_{cal}$, aniline adsorbed on TiO$_2$-Cal may be low and available APS may be high, which could be the reason for over oxidation. In PT$_{CH3COOH}$, the presence of acetic acid favors the formation of perignaline form [106], which oxidizes itself and hence results emeraldine form. It can be suggested that TiO$_2$CH$_3$COOH may act as template for PANI formation as in the case reported by Kim et al [57].
Thermogravimetric Analysis (TGA) curve reveals that the PT$_{\text{cal}}$ has more number of weight losing steps than PT$_{\text{CH3COOH}}$ (fig.2.6). The weight loss around 100°C corresponds to moisture content. The degradation of polymer starts around 300°C [105]. The multiple steps of PT$_{\text{cal}}$ show the presence of oligomers. The lower percentage of TiO$_2$ in PT$_{\text{cal}}$ is once again evidenced with lower residue weight. The Differential Thermal Analysis (DTA) curves also support the formation of oligomers with endothermic peaks (fig.2.7). More number of endothermic peaks could be seen in PT$_{\text{cal}}$ than in other two. The exothermic peak around 500°C is not discrete. All these thermal data supports that PT$_{\text{HCl}}$ and PT$_{\text{CH3COOH}}$ having similar thermal behavior and PT$_{\text{Cal}}$ having different behavior.

The SEM images of different TiO$_2$ and PANI-TiO$_2$ hybrids are given in fig.2.8 to fig 2.13. The shape and size of TiO$_2$ also varies with respect to the synthesis method and medium. TiO$_2$$_{\text{cal}}$ and TiO$_2$$_{\text{CH3COOH}}$ are spherical in morphology whereas TiO$_2$$_{\text{HCl}}$ is branch like. The size of the particles well decreased in one-pot synthesis. This also makes one-pot synthesis more advantageous. When the morphology of hybrids is compared, PT$_{\text{CH3COOH}}$ is more regularly packed than other two. PT$_{\text{cal}}$ is like bundles of rags and PT$_{\text{HCl}}$ is aggregated as layers placed one above the other like sedimentary rocks. This structure of PT$_{\text{HCl}}$ and the comparatively large gap between the particles may be the result of fast polymerisation in HCl medium. The three dimensional well arranged rectangular blocks of PT$_{\text{CH3COOH}}$ may be due to regulated polymerisation over TiO$_2$ surface in acetic acid medium. Apart from chemical modification, morphological characteristics also pave way to improved properties of PT$_{\text{CH3COOH}}$.

The results of electrochemical impedance spectroscopic (EIS) study showed that the electrical conductivity of PANI got reduced on hybriding with TiO$_2$ (fig.2.14). This is in accordance to previous reports [42, 106]. From bode plots and conductivity values (fig.2.15 and Table 2.3), it can be inferred that conductivity has increased in the order PT$_{\text{cal}}$ < PT$_{\text{HCl}}$ < PT$_{\text{CH3COOH}}$ < PANI. The impedance plot of pristine PANI was similar to that reported by Hue et al [107]. Dyre [108] proved that nyquist plot as obtained for pristine PANI is a simpler representation of an amorphous semiconductor in which charge transport occurs through hopping. The fitted circuit was Rs (Rp Cp) for PANI and PT$_{\text{CH3COOH}}$. The bode plots in EIS responses of PANI and PT$_{\text{CH3COOH}}$ were almost similar with a blue shift in the case of
\( \text{PT}_\text{CH}_3\text{COOH} \) suggesting the need of higher energy. \( \text{PT}_\text{cal} \) and \( \text{PT}_\text{HCl} \) have similar pattern of bode plot, which is in accordance with the reports suggesting ideal dual rail behavior \cite{109}. \( R(P_t \text{Cp}[W]) \) was the fitted circuit for these two hybrids. The large decrease in the electrical conductivity for \( \text{PT}_\text{cal} \) may be due to the high crystallinity of incorporated TiO\(_2\text{cal} \). \( \text{PT}_\text{HCl} \) had a Warburg denoting the porosity of the material. The porosity and under oxidized state of PANI might be the major causes for the higher resistance. The rutile form of the hybrid is less electrical conductive than anatase form of hybrid, which may contribute a minor account for high resistance of \( \text{PT}_\text{HCl} \). There exists a P-N junction in all three hybrids, which offers the capacitance. The observed distortion of Nyquist diagrams indicates the contribution of a phase constant element. It is speculated that this additional term may reflect the granular structure of conducting hybrids. The experimental data show that within the experimental errors the equivalent electric circuit contains no inductive element. In the whole frequency range investigated, the resistive character was found to be dominant. The frequency dependence of the conductivity proved that the charge transport mechanism is an one dimensional hopping. The two probe method indicated the DC conductivity and is higher than AC conductivity at lower frequency (table 2.3). The AC conductivity obtained from EIS increased with applied frequency. This may be due to the disappearance of capacitive hindrance at P-N junction at higher frequencies.

On comparing the conductivity of hybrids with pristine PANI, it was seen that hybrids are much lower in conductivity. This may be due to lower CSA doping in the hybrids. CSA may be prevented from effective doping in the presence of TiO\(_2\). CHNS/O analysis was done in order to estimate the approximate CSA content (table 2.4). It was observed that the sulphur content was lower in hybrids synthesized using one-pot synthesis. Hence, it can be assumed that CSA content is lower in the hybrids. The reaction in one-pot synthesis is shown in the scheme (fig 2.16) and CSA have surfactant action more than doping action. As shown by Baito et al, prior to polymerisation, there may be a bonded interaction between aniline and TiO\(_2\). TiO\(_2\) may be negatively charged and attaches aniline, which in-turn become cationic. This polymerises in the presence of APS. Here, TiO\(_2\) itself acts as an electron acceptor, giving no room for CSA. But, presence of CSA was also essential for the ordered arrangement of hybrid, which is discussed later in this chapter.
PT$_{CH3COOH}$ was found to be better than other two hybrids in terms of electrical conductivity, morphology and other properties. TiO$_2$ formed in this case was confirmed to be of anatase form and medium was not highly acidic. Both were advantageous and so PT$_{CH3COOH}$ was taken as efficient and hence used for further studies.

**Effect of TiO$_2$ content in the hybrid PT$_{CH3COOH}$**

TiO$_2$ content in PT$_{CH3COOH}$ was varied by varying the initial ratio of aniline to TiCl$_4$ (1:0.1, 1:0.2, 1:0.3, 1:0.4, 1:1). The obtained hybrids were designated as PT$_{0.1}$, PT$_{0.2}$, PT$_{0.3}$, PT$_{0.4}$ and PT$_1$ respectively. Pristine PANI was represented by PT$_0$. The electrical conductivity was one of the primary aims, so hybrids with higher TiO$_2$ content were not studied. The synthesized hybrids were characterized using XRD, SEM and EIS. The hybrids were named as PT$_{0.1}$, PT$_{0.2}$, PT$_{0.3}$, PT$_{0.4}$, and PT$_1$ in accordance with their TiO$_2$ content.

XRD patterns of PT$_{CH3COOH}$ hybrid show that 101 plane of anatase phase is present in all hybrids at 2$\theta$ around 25.4 (Fig.2.17). The XRD peak corresponding to PANI (ascribed to the periodicity parallel to the polymer chain) 2$\theta$=21° was observed clearly in PT$_{0.3}$. This peak was not seen in lower ratios of TiO$_2$, which indicates that PANI formed was not ordered in that ratio. This owed that the HCl released form TiCl$_4$ was essential for the initiation of polymerisation. When TiCl$_4$ was low with respect to aniline, HCl released was insufficient for making aniline to aniline hydrochloride. Hence, effectiveness of polymerisation reaction was lower. It can be concluded that effective hybrids are formed when the ratio of aniline to TiO$_2$ is $\geq$1:0.3.

The SEM images of the hybrids are given in figures (Fig.2.18 to Fig.2.22). The image of PT$_{0.3}$ is already shown in fig.2.13. PANI acquires definite shape and morphology on addition of TiO$_2$. The SEM images show that PT$_{0.2}$ and PT$_{0.3}$ have ordered arrangement. This may be attributed to the regulated polymerisation of aniline on the surface of TiO$_2$. On increasing the content of TiO$_2$, it collapses, may be due to agglomeration or excess of TiO$_2$ particles. The morphology of PT$_{0.1}$ was similar to PT$_0$ while that of PT$_1$ was similar to TiO$_2$CH$_3$COOH.

The electrical conductivity of all hybrids was lower than that of pristine PANI. This decrease may be attributed to lower CSA doping. The electrical conductivity of PANI is said
to be strongly dependent on dopants. CSA is one of the important dopant conferring high conductivity to PANI [14]. As already discussed, CSA content is lower in hybrids than PANI and hence hybrids have lower conductivity. Conductivity increases initially with the increasing amount of TiO$_2$ in the hybrid up to the ratio of 1:0.3 (PANI: TiO$_2$) and then decreases. The nyquist and bode plots obtained from EIS analysis of hybrids are given (fig.2.23 and fig 2.24). The electrical conductivity obtained from EIS and two-probe method is tabulated in table 2.5. The electrical conductivity depends on TiO$_2$ content. The initial increase in conductivity may be because of the extended conformation configuration of PANI. The electrical conductivity can be enhanced by developing better orientated defect-free conducting polymers. In this case, TiO$_2$ could act as suitable template for the formation of well oriented polyaniline. This might influence the increase in conductivity observed up to C$_{0.3}$. When the TiO$_2$ content was further increased, it might hinder the carrier transport between different molecular chains of polyaniline. Alternatively, the interaction at the interface of polyaniline and TiO$_2$ may lead to the reduction of the conjugation length in polyaniline chains. There exist a capacitive element and the AC conductance at lower frequencies was lowered. This capacitance may be due to the P-N junctions produced by space charge polarisation and interfacial polarisation, i.e., positive charges are displaced along the field and negative charges shift in the opposite direction creates an internal electric field which partly compensates the external field inside the composites. It is this spontaneous alignment that give rise to the nonlinear polarisation behavior of these composites. When frequency increases, the polarisation fades away as their relaxation time is much larger. Hence, AC conductivity becomes higher at higher frequencies. The capacitive behavior was not seen prominent in PT$_1$. Higher amounts of TiO$_2$ gave large resistive component to PT$_1$.

From the above studies, it was seen that PT$_{0.3}$ had better electrical properties than other hybrids and hence taken for further studies. The TEM image and SEAD pattern of PT$_{0.3}$ is given in fig.2.25. The image clearly shows the encapsulation of TiO$_2$ particles by PANI forming core shell hybrids. The image is similar to that reported by Roy et al [69]. The particle size of TiO$_2$ was about 20nm. The SAED pattern shows a continuous ring pattern corresponding to finer grain size. The TEM images of the TiO$_2$ and PANI-TiO$_2$ composite show the granular structures. PANI provides strength and stiffness to the TiO$_2$ composite, and
acts as a binder that distributes external load. In addition to increasing the rigidity of the polymer matrix, the particles are added to modify rheological property. The PANI matrix macromolecules with TiO\(_2\) in SEM image displays a very rigid and extended structure. This may be attributed to the formation of intra residue hydrogen bonds between the molecules and the surfactant effect offered by CSA, resulting in a regularly arranged structure.

**Effect of CSA concentration**

The role of CSA in hybrids was analysed for the hybrid PT\(_{0.3}\) by varying the concentration of CSA. Hybrid was also synthesized without CSA and electrical conductivity was noted. Lower ratio of CSA (1:0.25 with respect to aniline) and higher ratio of CSA (1:1 with respect to aniline) were taken and compared to that with 1:0.5 ratio. The bode plot is given in fig.2.26. The electrical conductivity was much lower for the hybrid synthesised in the absence of CSA. The conductivity increases with CSA, though the increment is not significant at higher ratio. The SEM image of hybrid without CSA shows that there is no ordered arrangement (fig.2.27). Thus CSA works as a surfactant and essential for the morphological and other important properties.

**Effect of APS concentration**

From the fig.2.28, the optimum ratio of APS to aniline was found to be 1:1. Further increase in the amount of APS led to over oxidation and resulted in decrease in conductivity. This amount is lower than the reported ratio of 1:1.5 by many other researchers. Hence it is assumed that presence of TiO\(_2\) as well as acetic acid medium contributes for the lower consumption of APS.

**Effect of ageing**

Pristine PANI and hybrid PT\(_{0.3}\) were aged in atmospheric condition for one week and electrical conductivity was noted (fig.2.29). There was a large decrease in conductivity of pristine PANI, while it was negligible in the case of hybrid. With PANI, the electrical conductivity deteriorates mainly because of three reasons (dedoping, oxidation and chemical
crosslinking) as pointed out by Travers et al [110]. Pristine PANI is prone to all these effects. Atmospheric oxygen penetrates and contributes to major deterioration. This oxidative ageing may be prevented in hybrids due to the closely packed ordered morphology and increase in corrosion resistance [83]. Thus the conductivity is maintained and shelf life is increased.
Fig. 2.1. XRD patterns of TiO$_2$ calcinated for 2 h at

a) 400°C, b) 500°C, c) 600°C.
Fig. 2.2. Effect of treatment time on the size of TiO$_2$
Fig. 2.3. XRD pattern of products formed at different ratios of TiCl$_4$ to ethanol

a) 1:2, b) 1:3, c) 1:4, d) 1:5
Fig. 2.4. XRD patterns of

a) PANI, b) TiO$_2$Cal, c) PT$_{cal}$, d) TiO$_2$HCl, e) PT$_{HCl}$, f) TiO$_2$CH$_3$COOH, g) PT$_{CH_3COOH}$
Table 2.1. Crystallinity Index of the TiO$_2$ and hybrids

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$cal</td>
<td>98.30</td>
</tr>
<tr>
<td>TiO$_2$HCl</td>
<td>85.32</td>
</tr>
<tr>
<td>TiO$_2$CH$_3$COOH</td>
<td>85.70</td>
</tr>
<tr>
<td>PT$_{cal}$</td>
<td>82.92</td>
</tr>
<tr>
<td>PT$_{HCl}$</td>
<td>82.63</td>
</tr>
<tr>
<td>PT$_{CH_3COOH}$</td>
<td>81.63</td>
</tr>
</tbody>
</table>
Fig. 2.5. FT-IR Spectra of

A = pristine PANI,
B = a) TiO$_2$-Cal, c) TiO$_2$-HCl, e) TiO$_2$-CH$_3$COOH,
C = b) PT$_{cal}$, d) PT$_{HCl}$, f) PT$_{CH_3COOH}$
### Table 2.2. FT-IR peak assignments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Functional groups and their peak positions (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti-O</td>
</tr>
<tr>
<td>PANI</td>
<td>-</td>
</tr>
<tr>
<td>PT_{cal}</td>
<td>591</td>
</tr>
<tr>
<td>PT_{HCl}</td>
<td>619</td>
</tr>
<tr>
<td>PT_{CH₃COOH}</td>
<td>605</td>
</tr>
</tbody>
</table>
Fig. 2.6. TGA curves of a) PT_{cab}, b) PT_{HCl}, c) PT_{CH3COOH}
Fig. 2.7. DTA curves of a) $PT_{\text{cal}}$, b) $PT_{\text{HCl}}$, c) $PT_{\text{CH}_3\text{COOH}}$. 
Fig. 2.8. SEM image of TiO$_2$cal.
Fig. 2.9. SEM image of TiO$_2$HCl
Fig. 2.10. SEM image of TiO$_2$CH$_3$COOH
Fig. 2.11. SEM image of PT_{Cal}
Fig. 2.12. SEM image of $\text{PT}_\text{HCl}$
Fig. 2.13. SEM image of $PT_{CH3COOH}$
Fig. 2.14. Nyquist plots for a) PANI, b) PT$_{cab}$, c) PT$_{HCl}$, d) PT$_{CH3COOH}$. 
Fig. 2.15. Bode plots of the hybrids

a) PANI, b) PT$_{\text{cals}}$, c) PT$_{\text{HCl}}$, d) PT$_{\text{CH}_3\text{COOH}}$
Table 2.3. Electrical conductivity of hybrids

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity measured by</th>
<th>EIS method (S/cm)</th>
<th>Two-probe method (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANI</td>
<td></td>
<td>1.12 x 10^{-1}</td>
<td>1.33 x 10^{-1}</td>
</tr>
<tr>
<td>PT&lt;sub&gt;cal&lt;/sub&gt;</td>
<td></td>
<td>2.03 x 10^{-4}</td>
<td>2.57 x 10^{-4}</td>
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<tr>
<td>PT&lt;sub&gt;HCl&lt;/sub&gt;</td>
<td></td>
<td>6.79 x 10^{-4}</td>
<td>7.24 x 10^{-4}</td>
</tr>
<tr>
<td>PT&lt;sub&gt;CH3COOH&lt;/sub&gt;</td>
<td></td>
<td>9.84 x 10^{-3}</td>
<td>1.39 x 10^{-2}</td>
</tr>
</tbody>
</table>
Fig. 2.16. Scheme showing the formation of hybrids

A- Mechanism proposed by us

B- Mechanism proposed by Yuvaz and Gok [93]
### Table 2.4. Elemental composition of pristine PANI and hybrids

<table>
<thead>
<tr>
<th>Sample</th>
<th>CHNS analysis</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>PANI</td>
<td>41.8</td>
<td>4.0</td>
</tr>
<tr>
<td>PT&lt;sub&gt;cal&lt;/sub&gt;</td>
<td>27.6</td>
<td>2.6</td>
</tr>
<tr>
<td>PT&lt;sub&gt;HCl&lt;/sub&gt;</td>
<td>27.4</td>
<td>2.6</td>
</tr>
<tr>
<td>PT&lt;sub&gt;CH3COOH&lt;/sub&gt;</td>
<td>27.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>
Fig. 2.17. XRD patterns of hybrids

a) PT₁, b) PT₀.₄, c) PT₀.₃, d) PT₀.₂, e) PT₀.₁
Fig. 2.18. SEM image of $PT_0$
Fig. 2.19. SEM image of PT$_{0.1}$
Fig. 2.20. SEM image of PT$_{0.2}$
Fig. 2.21. SEM image of PT$_{0.4}$
Fig. 2.2. SEM image of PT$_1$
Fig. 2.23. Nyquist plots for $\text{PT}_{\text{CH}_3\text{COOH}}$ with varying amounts of $\text{TiO}_2$;

a) PANI, b) PT$_{0.1}$, c) PT$_{0.2}$, d) PT$_{0.3}$, e) PT$_{0.4}$ f) PT$_1$
Fig. 2.24. Bode plots for $\text{PT}_{\text{CH}_3\text{COOH}}$ with varying amounts of TiO$_2$;

a) PANI, b) PT$_{0.1}$, c) PT$_{0.2}$, d) PT$_{0.3}$, e) PT$_{0.4}$ f) PT$_1$
Table 2.5 Electrical conductivity of hybrids

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity measured by</th>
<th>EIS method (S/cm)</th>
<th>Two-probe method (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT₀</td>
<td></td>
<td>1.12 x 10⁻¹</td>
<td>1.33 x 10⁻¹</td>
</tr>
<tr>
<td>PT₀₁</td>
<td></td>
<td>8.79 x 10⁻⁴</td>
<td>1.24 x 10⁻³</td>
</tr>
<tr>
<td>PT₀₂</td>
<td></td>
<td>4.84 x 10⁻³</td>
<td>9.39 x 10⁻³</td>
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<tr>
<td>PT₀₃</td>
<td></td>
<td>9.84 x 10⁻³</td>
<td>1.39 x 10⁻²</td>
</tr>
<tr>
<td>PT₀₄</td>
<td></td>
<td>7.59 x 10⁻⁴</td>
<td>8.32 x 10⁻⁴</td>
</tr>
<tr>
<td>PT₁</td>
<td></td>
<td>1.59 x 10⁻⁴</td>
<td>1.74 x 10⁻³</td>
</tr>
</tbody>
</table>
Fig 2.25. TEM Image of PT_{0.3}.

SAED pattern of PT_{0.3}
Fig. 2.26. Effect of CSA concentration

a) $PT_{CH_3COOH}$ without CSA

$PT_{CH_3COOH}$ with CSA  

b) 1: 0.25,  c) 1:0.5,  d) 1:1
Fig. 2.27. SEM image of PT$_{0.3}$ without CSA
Fig. 2.28. Effect of APS concentration on electrical conductivity

![Graph showing the effect of APS concentration on electrical conductivity with different ratio annotations.](image-url)
Fig. 2.29. Conductivity decay

a) Pristine PANI
b) PT$_{\text{CH}_3\text{COOH}}$
c) Pristine PANI after 1 week
d) PT$_{\text{CH}_3\text{COOH}}$ after 1 week
2.4. Summary

- PANI-TiO₂ hybrids were successfully prepared by conventional as well as by one-pot method.
- The problem of lower integration of TiO₂ into the polymer matrix in the case of in-situ polymerisation of conventional method could be solved by one-pot synthesis.
- The reaction medium in one-pot synthesis has played a major role in determining the crystallographic form of TiO₂.
- TiO₂ formed in the presence of acetic acid medium was of anatase type only, while rutile was formed in HCl medium.
- Literature study reveals strong mineral acid like HCl is suitable for PANI synthesis. We have attempted to use week organic acid like acetic acid for the same. It also favored the formation of emeraldine form with lower amount of APS.
- The electrical conductivity increases initially and then decreases with respect to TiO₂ content. Based on the morphology, electrical conductivity and ageing factor, the best hybrid was found to be PT₀.3.
- The electrical conductivity of the hybrids was lower than that of pristine PANI.
- Regular and ordered arrangement of hybrid was not seen in the absence of CSA as dopant. The optimum amount of CSA for better electrical conductivity was half the molar ratio of aniline present in the system. Above this level, there was no significant increase in electrical conductivity.
- Optimum ratio of APS to input amount of aniline was 1:1, and above this value has led to decrease in electrical conductivity that could be due to over oxidation.
- The conductivity decay due to ageing was lower in the case of hybrid when compared to pristine PANI.
References