Antimicrobial and Photocatalytic activity of Polyaniline-SiO$_2$ nanocomposites

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Abstract - **Nanocomposites having organic and inorganic particles provide a completely new class of materials with novel properties. The nano porous silica (SiO$_2$) is one of the interesting inorganic particles because of its applications in numerous areas like coatings, catalysis, medicine and drug delivery, high-tech industries, etc. Polyaniline (PANI) has unique electrical, optical and photoelectric properties, and most importantly, it is cheaper than other conducting polymers. In this article, PANI and PANI-SiO$_2$ nanocomposite were synthesized by *in-situ* chemical oxidative polymerization in the presence or absence of SiO$_2$ nanoparticles in 1M sulphuric acid medium using potassium perdisulphate (PDS) as oxidant. The polymerisation yield were noted and is enhanced the yield as well as the rate of reaction or the growth of polymerization due to influence of SiO$_2$. The synthesised PANI and PANI-SiO$_2$ were characterized by the measurement of DC conductivity, UV-visible and FTIR spectra. Conductivity studies shows that the presence of SiO$_2$ nanoparticle affected the increase in the degree of oxidation and the percentage of protonation. UV-visible spectral studies show that the incorporation of nano porous SiO$_2$ on PANI due to both peak position and intensity varied. FTIR spectra confirmed the characteristics vibrational band of quinoid, benzenoid, C=N and C-N moieties and of SiO$_2$ in the samples. The antimicrobial activity of the synthesized material PANI and PANI-SiO$_2$ were tested against four bacteria, E-Coli, Pesudononas, Klebaiella, S.aureus strain using disc diffusion method. The nanocomposite doped polymer possesses excellent antibacterial property which is allow its use in packing material to protect the food stuff from early deterioration paints and drug delivery etc. Photocatalytic results exhibits degrading efficiency increased with influence of SiO$_2$ nanoparticles in the polymer nanocomposites. From the above observations the PANI-SiO$_2$ nanocomposites gives diverse effect and for different fields.**

Keywords — *PANI-SiO$_2$, DC conductivity, UV-visible, FTIR, antimicrobial, Photocatalytic*

I. INTRODUCTION

Polyaniline (PANI) is one of the most studied conducting polymers for electronic, optical, chemical sensors and biosensors due to its tunable conducting property, thermal stability, and unique doping/dedoping and redox properties [1, 2]. However, the poor mechanical properties, insolubility in common solvent and low processability have some drawbacks. In order to overcome these problems, the strategies have been developed such as conventional electro-active conducting polymer composites with unique properties [2]. Synthesis of conductive composites of polyaniline and inorganic metal oxide doping compounds could provide materials with modified properties [3-5]. Among these inorganic materials, nano porous silica (SiO$_2$) has received great attention due to its unique properties and

wide application [6, 7]. The incorporation of metal oxide nanoparticles could effectively improve the electrical, optical and dielectric properties of the polyaniline composite and these properties are very much sensitive by tuning the quantum properties. Nanocomposites containing organic polymers and inorganic particles provide a completely new class of materials with novel properties [8]. In fact in these nanocomposites, the advantages of the inorganic material and the organic polymer are combined together. In recent years, conducting polymer/inorganic hybrid materials have been extensively studied because of their potential applications in chemistry, physics, electronics, optics and biotechnology [9.10]. The physical and chemical properties of final conducting polymer/inorganic composite can be tailored through proper selection of conducting polymer type and inorganic

material for particular purposes. Although there are plenty of conducting polymers, little work has been done on using conducting polymer to modify SiO2 to decompose organic pollutions. As a typical conducting polymer, PANI has unique electrical, optical and photoelectric properties, and most importantly, it is cheaper than other conducting polymers. Some researchers have investigated the effect of incorporation of PANI to the photocatalytic performance of TiO2 [11, 12, 13]. One of the research reported that PANI acts as a sensitizer to the neat TiO2 by triggering TiO2 to absorb photon under visible irradiation [13, 14]. Compared to the neat TiO2, the PANI-TiO2 nanocomposites showed better photocatalytic activity in the photodegradation of methyl orange under sunlight [13]. Another research revealed that the modification of TiO2 by PANI improved the photocatalytic degradation of phenol due to the synergetic effect of PANI and TiO2 [11]. PANI modified TiO2 nanocomposite not only absorbs the UV light but also significantly absorbs the visible and near IR [12]. PANI has a forbidden band gap of 2.8 eV, showing strong absorption in the region of visible light. Hence, it may function as a sensitizer to TiO2 so PANI modified TiO2 has better photocatalytic activity than neat TiO2 [13]. Beside TiO2-PANI, many studies have been done to explore the properties of TiO2-SiO2. It is revealed that addition of SiO2 to TiO2 improved some characteristic of pristine TiO2 like the surface area, the homogeneity, and its absorptivity. The changes of these properties improved the photocatalytic activity of TiO2 [15]. Silica-modified TiO2 was also reported to exhibit a better photocatalytic performance than TiO2 itself [16]. The improved performance came especially from two important things, the interaction between TiO2 and SiO2 and improved adsorption of the pollutant on the silica over pure TiO2. Principally, there are two types of interaction of TiO2 and SiO2 that is physical with such weak forces as van der Waals, and chemical with the formation of Ti-O-Si bonds [17]. The degree of interaction depends on the preparation methods and synthesis conditions [18]. These materials have been considered to be used not only as catalytic supports but also as catalysts through the generation of new catalytic active sites [16, 19]. Therefore, this study proposed to modify the properties of PANI with SiO2 and also compare with PANI. Firstly, SiO2 was synthesized through the green synthetic method from rise husk and then the dispersed SiO2 was added to PANI. PANI was introduced to the powder of the SiO2 by in situ polymerization of aniline. Therefore in this study, at first PANI-SiO2 nanocomposite was synthesized by in-situ chemical oxidative polymerization in the presence of SiO2 nanoparticles. The photodegradation of methylene blue (MB) under visible light was used to evaluate the photocatalytic performance of the resulted powders.

II. Experimental Methods

2.1 Preparation of Nano porous silica

Silica powder is extracted from the locally available bio source like Rise husk. The major steps in this procedure are ash preparation, reflux conditioning, Gel formation and synthesis of nano porous silica. Rise husk was washed thoroughly with water to remove the soluble particles, dust and other contaminants present where by the heavy impurities. The rice husk was then dried in air oven at about $110^{o}C$ for 24hours and ash was obtained. 20gm of white ash was added to 100ml of 1M NaOH solution. The solution is then boiled for 1hour in reflux condition. Extract sodium silicate solution from ash. The solution was left to cool for a few hours. The cooled solution was then filtered using Whatmann 1 filter paper to separate the residue. The sodium silicate solution is cooled in condition. The pH of the solution was adjusted to 6 with 1N HCl within a few minutes the solution turns to gel. The gel was washed thoroughly with distilled water to remove the sodium chloride by centrifugation method. Configuration is done for about 5 times at an rpm of 5000 for 10 minutes. The obtained silica gel is dried at $105^{o}C$ for 6 hour and silica powder is prepared. The powder silica is further heated at about 400 ^{o}C for 4 hours in a Muffle Furnace to obtain Nano Porous Silica

2.2 Preparation of Polyaniline

2ml aniline solution in 100ml aqueous 1 M sulphuric acid medium was added with 4.0 g potassium perdisulphate as oxidizing agent dissolved in 100 ml of aqueous 1M sulphuric acid in drop wise addition. The stirring of the reaction mixture was continued for half an hour. After addition of potassium perdisulphate, chemical oxidative polymerisation was allowed to proceed further for overnight in a refrigerator. The precipitate formed was filtered. Washed with 1M sulphuric acid, DD water, acetone and then with ethanol until the filtered become colorless. The precipitate was dried in an air oven at $80^{o}C$ for about 4 hour. The dried polymer sample was grind into a fine powder and the yield was noted. The sample was stored in air-proof sealed plastic covers.

2.3 Preparation of Polyaniline-SiO2 nanocomposites

2ml aniline solution in 100 ml aqueous 1M sulphuric acid medium was added with 50 mg of nano porous silica and stirred well. The chemical oxidative dispersion polymerization of aniline in aqueous 1M sulphuric acid in the presence of SiO2 was polymerized in 100 ml of aqueous 1 M sulphuric acid medium by using 4.0 g potassium perdisulphate as oxidizing agent in drop wise addition. The stirring of the reaction mixture was continued for half an hour. After addition of potassium perdisulphate, chemical oxidative polymerization was allowed to proceed further for overnight in a refrigerator. The precipitate formed was filtered. Washed with 1M sulphuric acid, DD water,

acetone and then with ethanol until the filtered become colorless. The precipitate was dried in an air oven at 80°C for about 4 hour. The dried polymer sample was grind into a fine powder and the yield was noted. The sample was stored in air-proof sealed plastic covers.

2.4 Spectroscopic methods

The electronic spectra (UV-Visible) were recorded on a Shimadzu UV-2401 PC spectrophotometer. In each measurement m-cresol was used as a solvent. The measurement was carried out *PG &* Research Department of Chemistry, Adithanar College of Arts and Science, Tiruchendur. The FTIR spectra were recorded on a spectrophotometer Nicolet Magna-750 using KBr pellets at Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli.

2.5 Measurement of DC Conductivity

DC conductivity of the powdered polymer samples were measured at room temperature on pressed pellets with the help of a hydraulic press by applying 3 metric ton pressure. These pellets were then subjected to DC electrical conductivity measurements in four probe (Scientific Equipment and Service, Roorkee, Model DFPO2). Current (I)-Voltage (V) measurements of the pellet were made at different positions, which yielded more or less the same value within the experimental error. Conductivity was measure by using Ohm's law

$V = IR$

Where I is the current (in amperes) through a resistor of resistance R (in Ohms) and V is the drop in potential (in volts) across it. The reciprocal of resistance (R^{-1}) is called conductance. I and V values were plotted according to Ohm's law and the resistances were obtained from the slope of the plot. Conductivity values were then computed from the values of resistance and dimensions of the pellet using the following equation,

Conductivity $(\sigma) = (1/R) \times (l/\pi r^2)$.

Conductivity $(\sigma) = 0.8/R$ S.Cm^{-1}.

Where R is the resistance, l is the thickness of the pellet and r is the radius of the pellets.

2.6 Studies of Antimicrobial activity

Test strains were cultured in disc diffusion method. The medium pH value 7 was checked after addition of each agent and the resulting pH was not altered. Bacteria were maintained on Muller-Hinton agar. The tubes were incubated for 24 hours at 37°C and visible culture growth was recorded. Bacterial cultures were placed on non inhibitory solid media (Muller-Hinton agar) for 24 hours to detect survivors; the plates were allowed to stand for 10-15 minutes, to allow for culture absorption. The 8 mm size wells were punched into the agar with the head of sterile micropipette tips. Wells were sealed with 1 ml of molten agar to prevent leakage from the bottom of the plate. The bacteria were plated onto solid nutrient agar plates. Using a

micropipette, 100 µL of the test solution samples (PANI and PANI-SiO$_2$) were poured into each of the wells on all plates. After incubation at 22-25 ± 2°C for 24 hrs, the size of zone of inhibition was measured with a ruler up to 1 mm resolution. A solvent blank m-cresol was run as a negative control whereas, the antibiotic Chloramphenicol was used as a positive control.

2.7 Studies of Photocatalytic Activity

The photocatalytic activity under visible light in the literatures is followed [11, 5]. The prepared samples were evaluated for photocatalytic activities by monitoring the degradation of MB dye in the aqueous phase. In a typical experiment, 30 mg of the prepared samples powder were dispersed in 100 mL of an aqueous solution of MB with an initial concentration of 40 mg/L in a quartz vessel. The adsorption–desorption equilibrium was achieved by stirring the mixture in a dark environment for 30 min. The photocatalytic degradation was then conducted by irradiating the above mixture using a 150-W tungston Lamp emitting solar light at a distance of 15 cm from solution. To maintain the uniform dispersion of photocatalyst particles, the mixture was stirred continuously. Then, 2 ml of the dye suspension were withdrawn at a regular time interval and centrifuged. The UV–Visible absorption spectra of the supernatant solution were analyzed using a UV–Visible spectrometer in quartz cuvettes to monitor the characteristic absorption peak of MB at 665 nm.

Then the absorption of MB aqueous solution was measured by UV-Vis spectrophotometer. Degradation efficiency can be calculated using the following equation:

$\eta = (1- At/A0)$ (1)

where At and A0 are the concentrations of the solution after illumination for t minutes and before illumination (t = 0) respectively.

III. RESULTS AND DISCUSSIONS

3.1 POLYMERIZATION YIELD

The chemical oxidative dispersive polymerization of aniline in the presence or absence of colloidal solution of nano porous silica was carried out in 1 M aqueous sulphuric acid medium using PDS as oxidizing agent. The preparation yield of PANI and its nanocomposites with nano porous silica are reported in the table 1.

Table 1 The yield, conductivity and UV-Visible spectral data of polymer samples.

Sample	Aniline	PDS	SiO$_2$	Yield (g)	Σ	UV-Visible spectral Data in m-cresol
PANI	0.10M	0.10M	-	1.82	0.8805	403, 547, 562, 762
PANI-SiO$_2$	0.10M	0.10M	50mg	2.02	1.9897	556, 752

This clearly indicates that the incorporation of nano porous silica is enhanced the polymerization yield as well as the rate of reaction or the growth of polymerization. This effect happens when Nano porous silica act as incorporating agents due to the formation of Pani-SiO$_2$ nanocomposite. It is simple to control the nanocomposite structure using nano porous silica. Since nanocomposites made from nano porous silica display essential stability and the polymer growth is efficiently stable and enhanced.

3.2 DC CONDUCTIVITY

All the polymer sample was measured by four probe DC conductivity measurement as shown in Table 1. This was found that the conductivity values were changed with different composition of synthesised PANI-SiO$_2$. The nanocomposites PANI-SiO$_2$ had greater conductivity than PANI. The conductivity was enhanced along with incorporation of SiO2 nanoparticle. The incorporation of SiO2 nanoparticle caused the content of positive charge in the formation PANI also increased. The presences of these cations lead to the distance between the conduction band and valence band wider. The presence of SiO2 nanoparticle also affected the increase in the degree of oxidation and the percentage of protonation and. The increase in the degree of oxidation lead to the change of the formation of polaron, so that the incorporation of SiO2 nanoparticles in polymerization of aniline resulted in increasing the value of the conductivity of PANI.

3.3 UV-VIS SPECTRAL STUDIES

PANI and PANI-SiO$_2$ materials are dissolved in m-cresol. It can be dissolved slowly. All the samples are observed (π-π^*) extended conjugation at around 350-385nm; (n-π^*) polaronic peak around 530-570 nm and above 800 nm has a emeraldine base form in tail structure. All the samples shape of graph, intensity of peak height and intensity of positions is different. It indicates that all polymer materials have different compositions. The solubility of composites materials are high due to high intensity of peak. The observed figure 1 and table 1 demonstrates UV-visible spectra for PANI and PANI-SiO$_2$ in m-cresol solvent. In the spectra two major absorption peaks were observed at 556 nm and 752 nm respectively.
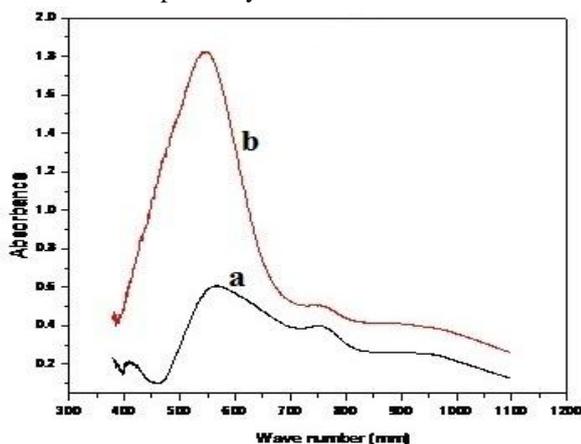
Figure 1 UV-Visible spectra of a) PANI and b)PANI-SiO$_2$

The peak at 403nm is due to π-π* transition which is related to the extent of conjugation between the adjacent phenylene rings in the polymeric chain and the peak at 556nm is owing to the shifting of electron from benzenoid ring to quinoid ring at and the peak at 752nm is caused by π-polaron transition.

3.4 FTIR SPECTRAL STUDIES

The FTIR spectra of all the polymer samples were presented in the given the Table 2. The characteristics vibrational band of quinoid, benzenoid, C=N and C-N moieties and of dopant ions appear at the usually observed positions in the FTIR spectra of the samples. The C=C stretching vibration of quinoid and benzoid became stronger and the relative absorption band d at 1526 and 1426 cm^{-1} shift to change in values. The FTIR spectra of the PANI-SiO2 are shown in figure 2b. The peak at 1112 cm-1 can be attributed to the aromatic C-H in plane bending modes respectively. The 1290 cm-1 is corresponding to aromatic C-N stretching modes. The peak 1591 cm-1 corresponds to N-H bending vibrations of primary amine. The peak 620-700 cm-1 corresponding to out of the plane C-H bending modes. In this figure characteristic bands corresponding to SiO2 are seen at 400-600 cm-1. PANI-Sio2 , the peak at 1110 cm-1 shows that Aromatic C-H in plane bending modes. The peak at 1290 cm-1 aromatic C-N stretching modes. And 1540 cm-1 corresponds to N-H bending vibration of primary amine. The peak at 638 cm-1 out of C-H plane bending modes.

Table 2 Comparative FTIR Spectral data for PANI and PANI-SiO$_2$

PEAK ASSIGNMENT	PANI	PANI-SiO2
Out of C-H plane bending	627	638
Meta substituted ring	792	799
N-H bending vibration of primary amine	1591	1540
Aromatic C-N stretching	1290	1290
Aromatic C-H in plane bends	1112	1110
Silicon dioxide		400-600

3.5 STUDIES OF ANTIMICROBIAL ACTIVITY

The antimicrobial activity of the polyaniline materials against different microorganisms was monitored with positive and negative control of chloramphenical and solvent. The disc diffusion method was used to determine the zone of inhibition. The material exhibited a very good inhibitory effect against E-Coli, Pseudononas, S. Aureus and Klebstella relative to standards chloramphenicol as shown in table 3. The antimicrobial property of the material seems to arise due to changes in the micro environment in the vicinity of organism particle contact area causing damage to the cell membrane on intimate contact between the cell and particle. The solvent m-Cresol has weak antimicrobial activity as such using the disk

diffusion method according to the procedure described by Hwang and Ma.

Table 3 Antimicrobial activity of PANI AND PANI- SiO₂

Micro organism	Zone of inhibition (mm)- media: Muller Hinton Agar			
	Chloram phenicol (PC)	PANI m-cresol	PANI+ SiO2 m-cresol	m-Cresol
E. Coli	23.0	23	22	17
Pseudomonas	23.0	22	24	16
Klebsiella	24.0	20	25	17
S. aureus	22.0	23	25	16

The antimicrobial activity of the synthesized material Pani and Pani-SiO₂ were tested against four bacteria, E-Coli, Pesudononas, Klebaiella, S.aureus strain using disc diffusion method. The result clearly shows that the materials are reactive against all tested bacterial strains and can be used as potential antibacterial agent. The result concerning antibacterial activity were ordered as strong activity (> 23nm) , moderate activity (> 12-15mm). The nano composite doped polymer possesses excellent antibacterial property which is allow its use in packing material to protect the food stuff from early deterioration paints and drug delivery etc. This work demonstrates a practical way of producing polymer nanocomposite with some unique properties for diverse application.

3.6 STUDIES OF PHOTOCATALYTIC ACTIVITY

The photocatalytic performance of PANI-SiO2 nanocomposites for liquid-phase degradation of MB has been measured for a maximum absorption at about 665 nm. The photocatalytic performance is shown in Fig 2. The activity of Without Catalyst, PANI and PANI-SiO2 nanocomposites can be evaluated by comparing the photocatalytic efficiency of PANI and its nanocomposites of SiO2 are given in Table 4.

Table 4 Photocatalytic acitivities of PANI and PANI-SiO₂

Time (sec)	Blank	PANI	PANI +SiO₂
0	0	0	0
15	1.5	1.5	2.1
30	1.8	1.9	4.3
45	2.2	2.3	6.2
60	2.2	2.5	9.3
75	2.4	3.8	12.2
90	2.4	5.2	14.1
105	2.8	7.6	16.5
120	2.8	9.8	18.5
135	2.8	12.4	20.2
150	2.8	15.2	22.8
165	3.0	17.4	25.1
180	3.1	19.7	28.7

As can be seen from the Fig 2 and Table 4, the photocatalytic degrading efficiency was increased with influence of nanoparticles in the polymer nanocomposites.
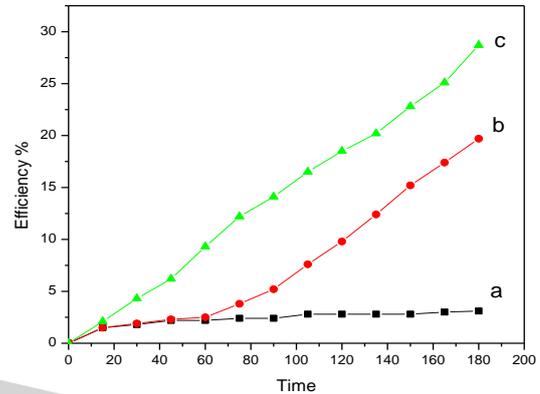
Figure 2 Photocatalytic efficiency of a)Without Catalyst b)PANI and c) PANI-SiO₂

IV. CONCLUSION

The present study indicates the growth and yield of polymerization is enhanced due to inclusion of nano porous silica. The inclusion of nano porous silica in PANI is confirmed by measurement of DC conductivity, UV-visible and FTIR spectral studies. The transition of charge carriers is analyzed in benzenoid and quinonoid ring structrues of the prepared conducting PANI-SiO2 nanocomposite by using UV-visible and FTIR spectra. The antimicrobial activity of the synthesized material PANI and PANI-SiO₂ were tested against four bacteria, E-Coli, Pesudononas, Klebaiella, S.aureus strain using disc diffusion method. The result clearly shows that the materials are reactive against all tested bacterial strains and can be used as potential antibacterial agent. The result concerning antibacterial activity were ordered as strong activity (> 23nm) , moderate activity (> 12-15mm). The nano composite doped polymer possesses excellent antibacterial property which is allow its use in packing material to protect the food stuff from early deterioration paints and drug delivery etc. This work demonstrates a practical way of producing polymer nanocomposite with some unique properties for diverse application.

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