RESEARCH ARTICLE

Optimization and Thermal Effects of Polyaniline Nanomaterial Synthesized by Chemical Oxidative Polymerization Method

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Abstract

Scientific zone has a great attention to the polyaniline (PANI) nanomaterials which is an organic, conductive and a conjugated polymer. It has variety of applications such as in batteries, microelectronics displays, antistatic coatings, electromagnetic shielding materials and actuators.[1] PANI was synthesized by using chemical oxidative polymerization method. The preparation process carried out by the main reagent aniline (C_6H_7N) with the ammonium peroxydisulpate (APS) (($NH_4)_2S_2O_8$) which act as an oxidant and hydrochloric acid (HCL) as a dopant in an ambient temperature. The synthesized polymer materials are annealed at different temperatures such as 200°C, 300°C and 400°C. After annealed treatment, the weight percentage of polymer material are changed were decreases with increase the temperature of pure PANI (0.441g), 200°C(0.172g), 300°C (0.147g), 400°C (0.105 g). Then the obtained polymer materials are characterized by FTIR, UV-Visible, Particle size analysis (PSA) and Antibacterial analysis. FTIR is used to determine the functional group of polymer nanomaterials. UV-Visible exhibits the quantitative information about the polymer nanomaterials by using its band gap. The size of the individual partic les and the size distribution range of the respective samples are determined by the Particle Size Analyzer (PSA). Antibacterial activity is used to find the polymer nanomaterials which kills bacteria, or bacteriostatic, which slow down the growth of bacteria. These profiling techniques are used to find the properties like functional group, quantitative information, particle size, antibacterial activity of respective polyaniline nanomaterial samples.

Keywords: Polymer material, FTIR, UV-Vis, Antibacterial activity

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1. Introduction

Nature provides many materials within the size of nanoscopic ranges with some ideal functions. The intermediate dimension range between 1-100nm defines the mesoscopic range or nanoscopic range. Nano materials are the size dependent materials which has some ideal properties like chemical property which depends on reactivity and catalysis then the thermal property depends upon the melting temperature of nano materials, mechanical property depends on adhesion, capillary forces then the optical property leads to the absorption and scattering of light then the electrical properties defined by the tunneling of current through the required nano materials and the super paramagnetic effect defines the magnetic properties of the nano materials.[2] Manipulation of matter in atomic, molecular and supramolecular scales defines the nanotechnology. Nano particles has unexpected properties that they are small enough to confine their electrons and produce quantum effect.[3] The nano materials have large surface area. Then there is huge debate going on among the scientist about the future implications of nano technology.

F. FERDINARD RUNGE was the first one who discovered the polyaniline by the initial oxidation of aniline in the year 1834, then HENRY LETHEBY concluded this discovery with his experiment which is the first electrochemical oxidation of aniline in the year 1862. PANI is a cheaper monomer when it is compared to polyacetylene and other conducting polymers. The first ever preparation of "a blue substance" undergoes the electrolysis of aniline sulfate (AS), it decolorizes partially when it is treated with reducing agent. In the early times,

PANI was named as "ANILINE BLACK", because of its dark pigment color of PANI, so this PANI is used for dying of textile fabrics. PANI has a reversible redox behavior with this behavior, it has some applications such as super capacitor, gas sensor, PH sensor, fuel cell applications etc.., PANI with its frequency dependent conductivity, and it involves in the electromagnetic interference (EMI) shielding applications.[6-15] To produce a polymer, we use chemical oxidative polymerization method. In this method, the abstractions of two hydrogen atoms from a monomer produce a polymer. This method of experiment is used to demonstrate the heterogeneous precipitation polymerization technique. Then the optimization of PANI was done by this chemical oxidative polymerization method

2. EXPERIMENTAL PROCEDURE

The chemical oxidative polymerization method is used to optimize the polyaniline (PANI). Firstly, we should wash the laboratory glass wares that are all needed for this experiment with the required detergent then distilled water and acetone, and then dry the glass wares. The main reagent aniline is taken in the amount of 0.1M as 0.19313ml, then it is diluted with the 100ml of distilled water in the conical flask and the mixture is placed in the magnetic stirrer for 10 minutes at 500 rpm. After 10 minutes, HCL of 1M as 3.0898ml is added to the aniline mixture then stirrer it for 30 minutes. Here, the oxidizing agent is ammonium peroxydisulpate (APS). We have to take the 0.5M as 2.852g of ammonium peroxydisulpate (APS) is mixed with 25ml of distilled water and the required APS solution is added in drop wise in the aniline and HCL concentration and this concentration is admitted to rapid mixing by using an additional flask. While adding this APS solution on the aniline and HCL mixture, the colour of solution turned from white to sky blue and then dark blue. At last, the color of the mixture is turned to dark green which shows the property of polymerization. The required solution is admitted to stirrer for 24 hours at 500 rpm. The whatmann filter paper is used to filter the required solution after 24 hours of stirring process. At last, we get a dark green color precipitate if polyaniline. And the required precipitate of precipitate of polyaniline is washed with the 20ml of acetone and 25ml of ammonium solution which is used to take away the excess acidity and impurity from the obtained polyaniline precipitate. The obtained substance is dried under vacuum at 60° C for 4 days. Then the agate mortar is used to grind the required substance of polyaniline. Therefore, we get the fine powder of polyaniline with the weight percent is 1.766g. The fine powder of polyaniline is divided into 4 parts with the weight percent of 0.4 gram of each. First part of 0.4g of polyaniline is kept as a pure substance and the other three samples are admitted to the heat treatment at the temperature 200° C, 300° C, and 400°C. After the heating process, the substances are again grinded with the agate mortar and kept in the sample tubes.

3. RESULTS AND DISCUSSIONS

3.1 Fourier Transform Infrared Spectroscopy

The determination of functional groups of Pure PANI, PANI (200°C), PANI (400°C) possessed by using KBr pellets. The range from 400-4000cm^{-1} shows the FTIR spectrum of Pure PANI, PANI (200°C), PANI (400°C) in Fig. 1. The spectrum of Pure PANI, PANI (200°C) and PANI (400°C) acquires O-H Stretching group with the alcohol compound class with the characteristic peaks at 3197.98 cm^{-1}, 3030.17 cm^{-1} and 3170.97 cm^{-1} then it appears to be a weak and broad peak. Then it acquires the N-H bending group with amine compound class at 1625.99cm^{-1}, 1589.34 cm^{-1} and 1598.99 cm^{-1} then it appears to be a medium peak. C-F stretching for the peaks at 1303.88 cm^{-1}, 1290.38 cm^{-1} and 1224.80 cm^{-1} with the fluoro compounds and it appears to be a strong peak. Then the spectrum possessed with the C-O stretching with the aliphatic ether compounds and their peak values at 1136.07 cm^{-1}, 1114.86 cm^{-1} and 1114.86 cm^{-1}, then the peak appears to be strong at this ranges. C-Br stretching with halo compounds with the peak values at 615.29 cm^{-1}, 607.58 cm^{-1} and 623.01cm^{-1} and it appears to be a strong peak. Therefore, we can clearly notice the observable changes in the spectrums of PANI (200°C) and PANI (400°C) with the spectrum of pure PANI. So the tempering treatment can alter the spectrum of pure PANI. Hence, the Fourier Transform Infrared spectrograph results that the presence of functional group, changes in the spectrum under annealed treatment and the characteristic functional group and their peak values are tabulated in Table.1.[7, 8]

3.2 UV-Visible Spectroscopy

UV-Visible exhibits the quantitative information like absorption spectra, optical properties about the polymer nanomaterial by using its band gap. Fig.1 shows the absorption spectra of (a) Pure PANI, (b) PANI (200°C) and
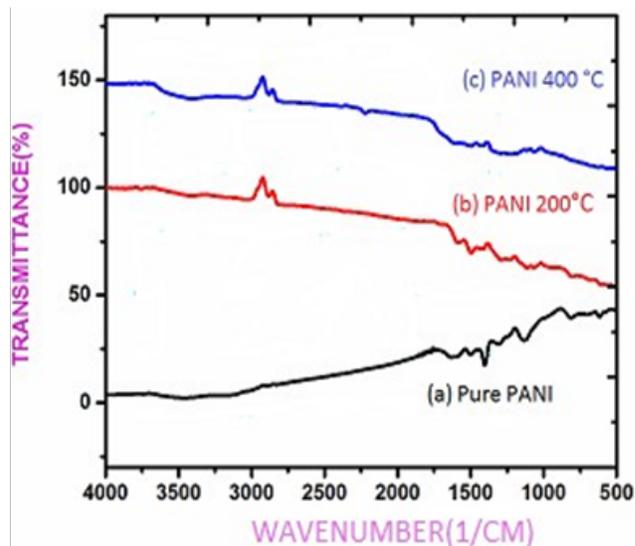

Fig. 1: FTIR Spectra of (a) Pure PANI, (b) PANI (200°C) and PANI (400°C)

Table 1: FTIR wave number Region of pure PANI, PANI (200°C) and PANI (400°C) Nanomaterial

S.No	Functional Group	Wave Number (Cm^{-1})			Appearance	Compound Class
		Pure PANI	**PANI (200°C)**	**PANI (400°C)**		
1.	O-H Stretching	3197.98	3030.17	3170.97	Weak, broad	Alcohol
2.	N-H Bending	1625.99	1589.34	1598.99	Medium	Amine
3.	C-F Stretching	1303.88	1290.38	1224.80	Strong	Fluoro compounds
4.	C-O Stretching	1136.07	1114.86	1114.86	Strong	Aliphatic Ether
5.	C-Br Stretching	615.29	607.58	623.01	Strong	Halo compounds

PANI (400°C) nanomaterial. The fundamental law to find the optical band gap energy Eg = hc/λmax, where λmax be the maximum absorption wavelength in nm, h be the Planck's constant and c be the velocity of light. In pure PANI, the absorption band can be divided into two characteristics at around 205 nm and 1027 nm, that are assigned to n-π* excitation of benzenoid ring to the quinoid ring and π-π* transition of the benzenoid ring and their band gap energies are 6.048 eV and 1.2074 eV. Then the spectrum of PANI (200°C) has wavelength at around 217 nm and 1065 nm which has the n-π* excitation of benzenoid ring to the quinoid ring and π-π* transition of the benzenoid ring and their values of band gap energies are 5.7142 eV and 1.1643 eV, and then for PANI-400°C

has 206 nm 290 nm, this both have same transition like n-π* excitation of benzenoid ring to the quinoid ring and their band gap energy values would be 6.0194 eV and 4.278 eV.[5,8]

Therefore, the absorption peaks in pure PANI, PANI (200°C) and PANI (400°C) are shows that there is a difference in the required spectrum of PANI-200°C and PANI-400°C with the spectrum of pure PANI. This result shows the thermal effects of pure PANI by using UV-Visible spectrums. Hence the band gap energy of corresponding nanomaterial and their electron transition are tabulated in table: 3.2.1.[6, 7]

3.3 Particle size analysis

The size of the individual particles and the size distribution range of the respective samples are determined by the particle size analyzer. Fig: 3.3.1 represents the peaks of particle size distribution for the samples like (a) pure PANI, (b) PANI (200°C) and (c) PANI (400°C). Then the peaks drawn with the particle diameter (nm) and the normalized particle amount (Cum) in %.

Pure PANI has 27.074 μm of particle diameter for normalized particle amount (cum) of 25%, then it has 171.504 μm of particle diameter for normalized particle amount (cum) of 50% and it acquires 240.738 μm of particle diameter for normalized particle amount (cum) of 75%. For PANI (200°C) sample, the particle diameter was 41.99 μm for the 25% of normalized particle amount (cum), then it has 347.600 μm of particle diameter for 50% of normalized particle amount and for 75% of normalized particle amount, it attains the 409.141 μm of particle diameter, and for PANI (400°C) sample, 25% of normalized particle amount has 59.093 μm of particle diameter then 50% of normalized particle amount
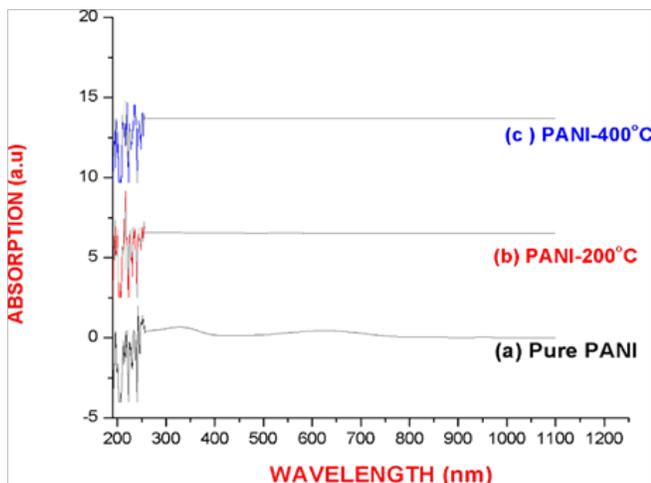
Fig 2: UV-Vis Spectra of (a) Pure PANI, (b) PANI (200°C) and PANI (400°C) Nanomaterial

Table.2. UV- Vis data and their characteristic assignments of Pure PANI, PANI (200°C) and PANI (400°C) Nanomaterial

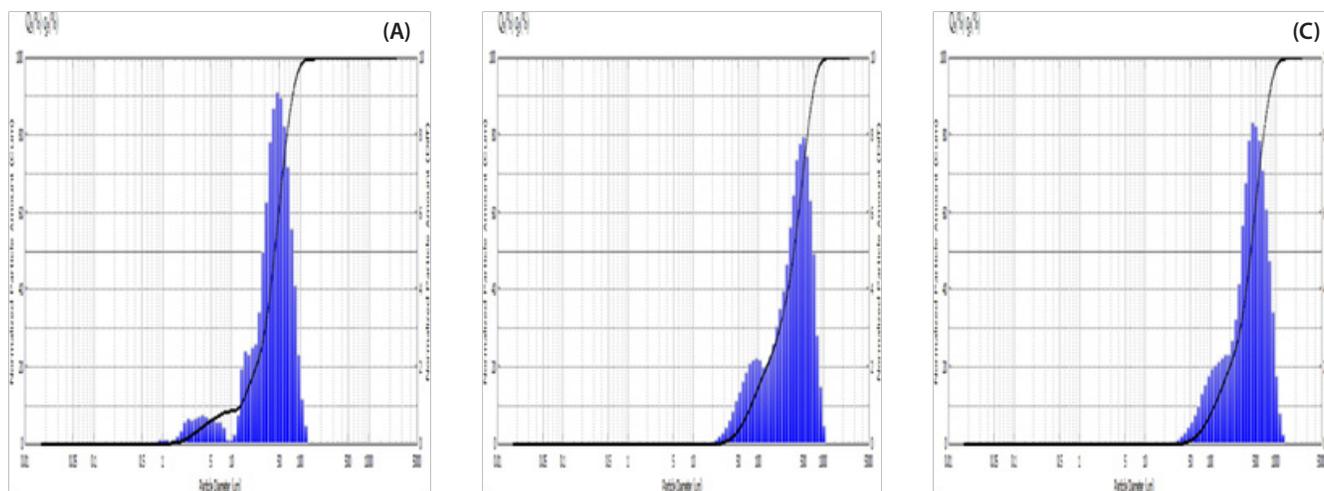| S.No.	Sample Name	Wavelength(nm)	Absorption	Band gap Energy(ev)	Electron Transition
1.	Pure PANI	205 1027	-4.000 0.007	6.048 1.2074	n- π* π-π*
2.	PANI (200°C)	217 1065	2.633 0.016	5.7142 1.1643	n- π* π-π*
3.	PANI (400°C)	206 290	-4.000 0.003	6.0194 4.2758	n- π* n- π*

Fig. 3A to C: Particle size spectra of **(A)** pure PANI, **(B)** PANI (200°C) and **(C)** PANI (400°C) nanomaterial

has 521.535 μm of particle diameter and 75% of normalized particle amount has 592.011 μm of particle diameter. Therefore, we conclude that the particle size diameter can increase with the increase in temperature of pure PANI for the 25%, 50%, and 75% of normalized particle amount and their values are tabulated in Table: 3.3.1.[4, 5]

3.3 Antibacterial analysis

Table 3: Particle size diameter and cum% of pure PANI, PANI (200°C) and PANI (400°C) nanomaterial

Sample Name	Particle diameter (μm)		
	Cum%		
	For 25%	For 50%	For 75%
Pure PANI	27.074	41.99	59.093
PANI (200°C)	171.504	347.600	521.535
PANI (400°C)	240.738	409.141	592.011

Determination of antimicrobial activity by agar well diffusion method

The determination of antimicrobial activity of pure PANI, PANI (200°C) and PANI (400°C) nanomaterial by using well diffusion method
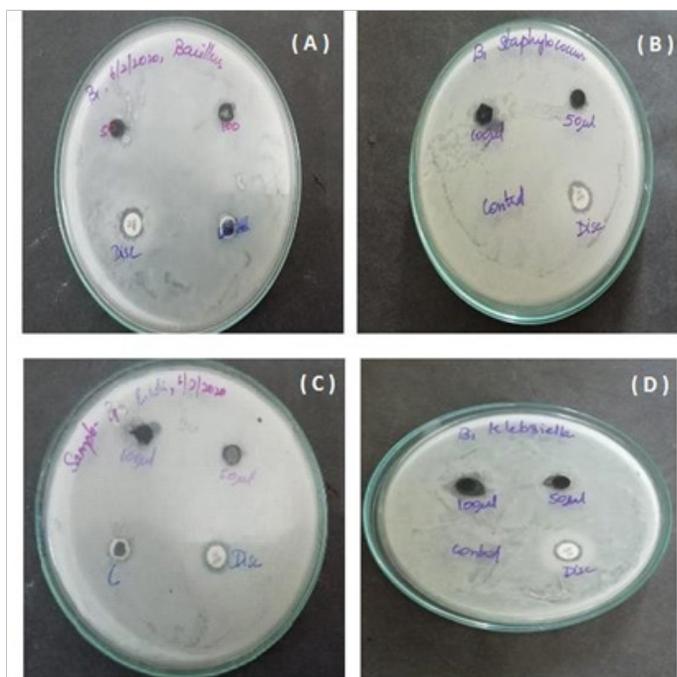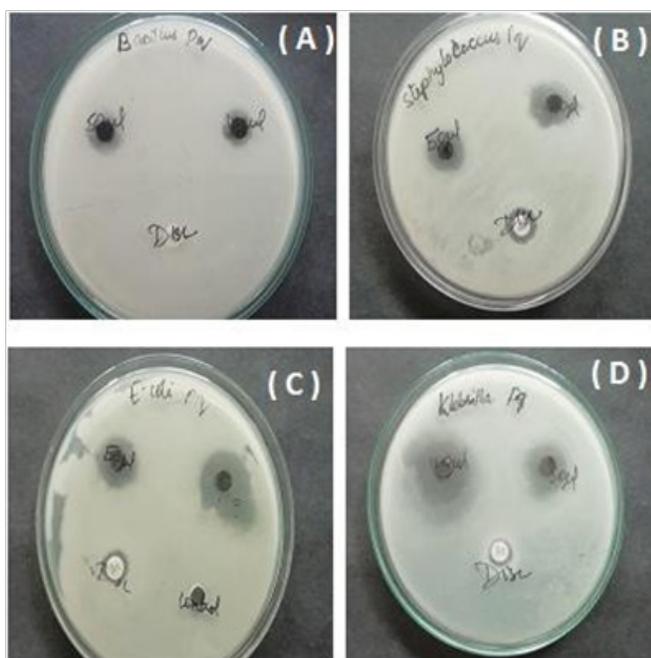

Fig. 4.1: Photographs of antimicrobial results of pure PANI nanomaterial for gram positive (A) bacteria Bacillus cereus, (B) Staphylococcus aureus and gram negative (C) bacteria Escherichia coli, (D) Klebsiella pneumonia.
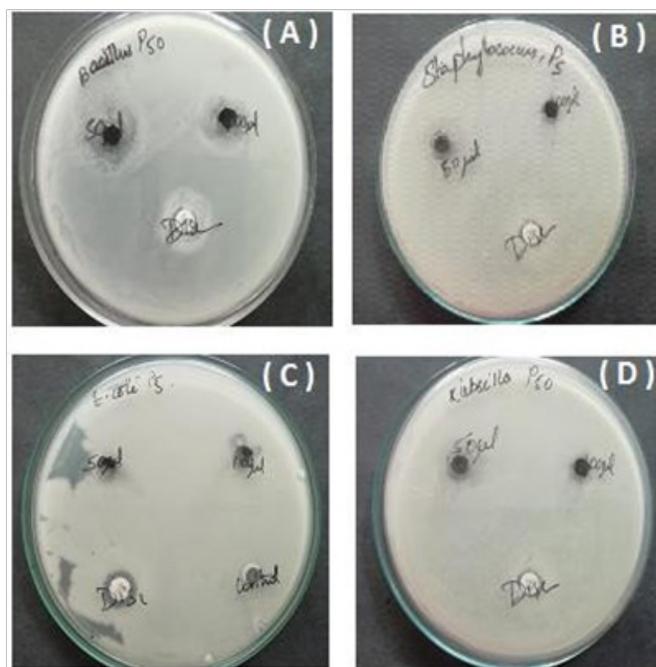
Table 4: Results of antimicrobial activity of pure PANI, PANI (200°C) and PANI (400°C) nanomaterial

S.No.	Sample Name	Zone of Inhibition in diameter (mm)							
		Microorganism							
		Gram positive				Gram negative			
		Bacillus cereus		Staphylococcus aureus		Escherichia coli		Klebsiella pneumonia	
		50 (μl)	100 (μl)	50 (μl)	100 (μl)	50 (μl)	100 (μl)	50 (μl)	100 (μl)
1.	Pure PANI	0	0	10	15	0	0	10	18
2.	PANI (200°C)	0	0	15	19	15	20	15	20
3.	PANI (400°C)	0	0	0	0	0	0	0	0

Fig. 4.2: Photographs of antimicrobial results of PANI (200°C) nanomaterial for gram positive (A) bacteria Bacillus cereus, (B) Staphylococcus aureus and gram negative (C) bacteria Escherichia coli, (D) Klebsiella pneumonia

Fig. 4.3: Photographs of antimicrobial results of PANI (400°C) nanomaterial for gram positive (A) bacteria Bacillus cereus, (B) Staphylococcus aureus and gram negative (C) bacteria Escherichia coli, (D) Klebsiella pneumonia.

Liquid Mueller Hinton agar media and the Petri plates were sterilized by autoclaving at 121°C for about 30 minutes at 15 lbs pressure. Under aseptic conditions in the laminar airflow chamber, about 20ml of the agar medium was dispensed into each Petri plate to yield a uniform depth of 4mm. After solidification of the media, 18 hrs culture of Gram positive microorganisms such as Bacillus cereus(MTCC 430), Staphylococcus aureus (MTCC 3160), Gram negative microorganisms such as E.coli (MTCC 1698) and Klebsiella pneumoniae (MTCC10309) obtained from IMTECH, Chandigarh were swabbed on the surface of the agar plates. Well was prepared by using cork borer followed with loading of 50 µl and 100 µl. Each sample is distinct well with sterile distilled water as negative control and ampicillin (30mcg/disc) as positive control. The sample loaded plates were then incubated at 37°C for 24 hours to observe the zone of inhibition. Table.4. Represents the antibacterial activity of PANI (200°C) sample is much higher than the pure PANI and PANI (400°C). Then the samples like pure PANI, PANI (200°C) and PANI (400°C) doesn't have the ability to kill the gram positive bacteria bacillus cereus and the sample PANI(400°C) has zero zone of inhibition. So the pure PANI and PANI (200°C) has the ability to kill the bacteria like Staphylococcus aureus and Klebsiella pneumonia with the certain amount of zone of inhibition noted in the table.4. Therefore, the PANI (200°C) can kill the bacteria like Staphylococcus aureus, Escherichia coli and Klebsiella pneumonia with certain amount of zone of inhibition except the gram positive bacteria Bacillus cereus.

Hence sample PANI (200°C) has a good antibacterial activity than the pure PANI and PANI (400°C).[1-3]

4. Conclusions

The pure polyaniline (PANI) nanomaterial has been optimized by the chemical oxidative polymerization method under ambient temperature. Then the pure PANI is admitted to thermal effects at 200°C and 400°C. The functional group and the compound class of pure PANI, PANI (200°C) and PANI (400°C) has obtained by FTIR analysis. Then UV-Vis analysis gives the quantitative information about the respective samples. The particle size distribution of the pure PANI increase with the increase in te temperature. Then the PANI (200°C) has higher antibacterial performance than the pure PANI and PANI (400°C). Annealed treatment results that the weight percentage of polymer material decreases with increase the temperature of pure PANI (0.441g), PANI- 200°C (0.172g), PANI- 300°C (0.147g), PANI- 400°C (0.105g). Hence the optimized pure PANI behavior can alter by increasing the temperature of it.

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