THE EFFECTS OF VARIOUS ACIDS DOPED POLYANILINE MORPHOLOGIES AND ANTIBACTERIAL ACTIVITY OF POLYANILINE

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ABSTRACT

The work reported here is converging on the synthesis of the conducting polyaniline (PANI) and its doping with several acids in the occurrence of oxalic acid. In the first step polyaniline was synthesized via chemical oxidation polymerization method. The doped PANI samples was subjected to several characterization techniques. Fourier transform infrared spectroscopy (FTIR) was used to control significant functional groups and reaction progress, while UV-Vi's spectroscopy was used to not only authorize the reaction optimization, but also to trace several characteristic peaks of PANI and its doped version. Both spectroscopic results sustenance the formation and successful doping of PANI. Similarly, X-ray diffraction (XRD) was practical to inspect the nature and phase changes of the synthesized polymer materials. This specified that the material properties of the samples were affected by changing the composites of reactant molecules. Overall, the obtained polymer was semi crystalline. Scanning electron microscopy (SEM) was also active to investigate the morphology, surface properties and regular size of the particles. It was seen that the normal size of the polymer chain is in the micrometer range with rock-like structural geometry.

Keywords: Polyaniline; antibacterial activity; PANI morphology

1. INTRODUCTION

Polyaniline (PANI) is a conductive polymer which can simply be synthesized by both the chemical and electrochemical approaches [2]. The chemical technique is a very possible route for the mass production of PANI and does not need a conducting substrate and is not expensive. Polyaniline composites including transition metals are still a burgeoning attention as a super capacitive material due to the formation of metal-PANI hetero junctions [1]-[5]-[6]-[8]. Here we demonstrate a facile chemical synthesis of ternary doped super capacitive polyaniline using transition metal as a coolant with an inorganic acid dopant using the oxidant ferric chloride, which itself acts as a dopant. More remarkably the rational combination of external binary dopants can successfully modify PANI morphology. The low cytotoxicity

and biocompatibility of polymeric materials have led to the probable use of polymers in biomedicine. Among the various types of polymers are of great interest in biomedical applications due to good cellular response. The antibacterial effects were assessed from the diameter of zone of inhibition and minimum inhibitory concentration values.

2. Materials and methods

2.1 Materials

The monomer aniline (BDH) was freshly distilled and collected at its boiling point (184 °C) and stored in a vacuum desiccator. Oxalic acid[$C_2H_2O_4$] and phthalic acid[$C_8H_6O_4$] were recrystallized from water. Ammonium Persulfate (APS) [$(NH_4)_2S_2O_8$] was purchased from Merck. Solvents of analytical grade such as DBSA (Dodecyl Benzene Sulfonic Acid) [$C_{18}H_{30}O_3S$], acetone were used in the present work.

2.2 Synthesis procedures

2.2.1 Synthesis of oxalic acid doped PANI

The oxalic acid doped PANI was synthesised by chemical polymerisation method. 0.1M aniline, 0.1M dodecyl benzene sulphonic acid is added and 0.2M oxalic acid dopant were assorted and stirred with the above solution. Then 0.3M APS was added dropwise to this solution with continuous stirring. Finally, the resultant composite was filtered out under vacuum and washed using distilled water. Thus, prepared samples were dried for 24 hours at 120^0C in vacuum oven and grained.

2.2.2 Synthesis of phthalic acid doped PANI

The phthalic acid doped PANI was synthesised using chemical polymerisation process. 0.1M aniline, 0.1M dodecyl benzene sulphonic acid is added and stirred and 0.2M phthalic acid dopant was added to the solution. The polymer composite (Aniline-DBSA-Phthalic acid-APS) were equipped with continuous stirring for 3 hours. Thus, prepared samples were dried for 24 hours at 120^0C in vacuum oven and grained.

2.2.3 Synthesis of Calotropis procera doped PANI

The Calotropis procera doped PANI was produced using chemical polymerization method. 0.1M aniline, 0.1M dodecyl benzene sulphonic acid was added and 3.2 ml Calotropis procera milk dopant were mixed and stirred with the solution. The oxidant 0.3M APS was added dropwise to above solution with continuous stirring. The polymer composite (Aniline-DBSA-Phthalic acid-APS) were arranged with continued stirring for 3 hours. Thus, prepared samples were dried for 24 hours at 120^0C in vacuum oven and grained.

3. Results and discussion

The prepared powdery samples are characterized and investigated for Optical, functional and surface morphological studies.

3.1. Optical Absorption Spectra (UV - Vis Spectra)

A Jasco UV V-770 spectrophotometer was used to record the electronic absorption spectra of the polymers in the range of 200 - 800 nm. Fig 3.1(a-c) demonstrates UV-Visible spectra of PANI doped with Oxalic, Phthalic acid and Calotropis respectively. A wide peak in visible region (~ 720 nm) can be allocated to dictation absorption band, which is attributed to bipolaron formation on quinoid segment in the polyemeraldine chain.

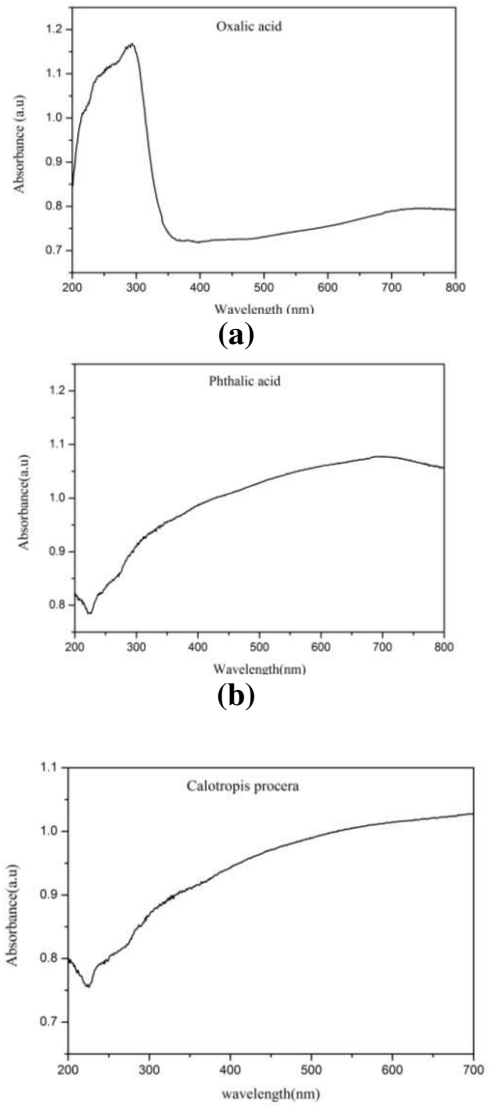


Fig. 3.1 UV - Vis spectra of (a) Oxalic (b) Phthalic and (c) Calotropis acids doped Polyaniline

A peak at 304 nm in PANI doped with phthalic acid (Fig. 3.1b) and a peak at 325nm in PANI doped with Calotropis acid (Fig 3.1c) can be assigned to π - π * transition absorption band due to the excitation of benzene ring. The peaks at 325nm in Fig 3.1c can be attributed to the leucoemeraldine salt phase of the polymer.

3.2 Functional group Analysis (FT-IR)

A PerkinElmer Spectrum-2000 Fourier transform IR (FT-IR) spectrophotometer was used to gain the IR spectra between 500 and 4000 cm^{-1}. Fig 3.2 a-c displays FTIR Spectra of PANI doped with oxalic, phthalic and Calotropis acids respectively.

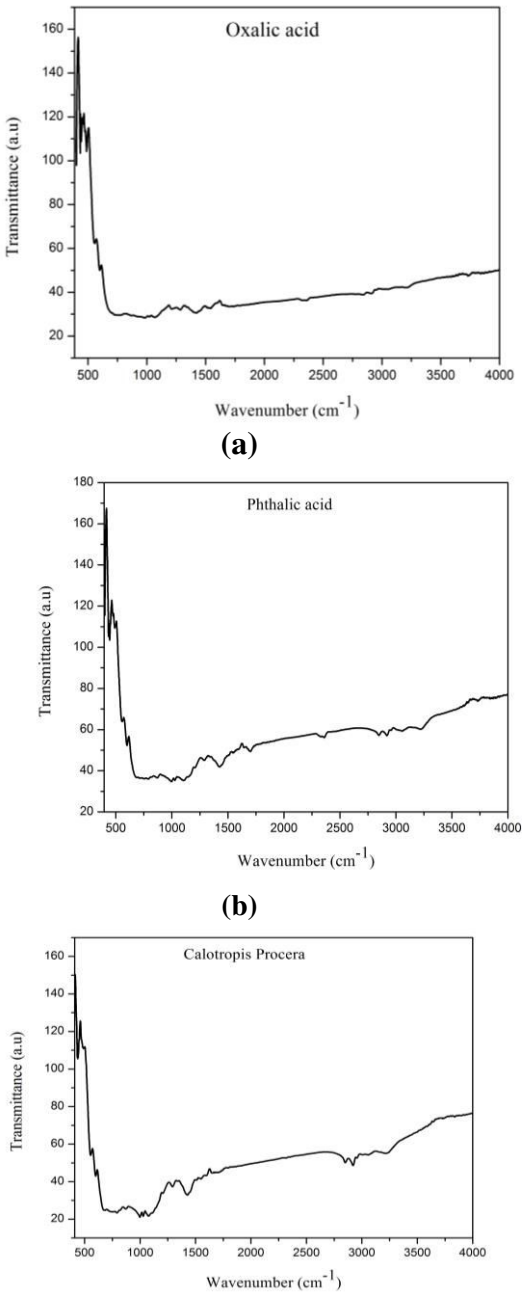


Fig.3.2 FT-IR Spectra of (a) Oxalic (b) Phthalic and (c) Calotropis acids doped Polyaniline

An intense band at 818 cm^{-1} is detected in all the polymers, which is the characteristic of the para disubstituted aromatic rings through which the polymerization proceeds. The polymers show two intense bands at 1158 and 622

cm^{-1} are shown in Fig. 3.2(a), on behalf of in plane and out of plane C-O-H bending motions of benzenoid rings. In the C-O-H stretching region, the aromatic C-O-H is easily recognized at 3128 cm^{-1} is shown in Fig .3.2(a). A peak at 1468 cm^{-1} shows the stretching of benzenic rings. The stretching bands that are characteristics of an aromatic amine are noticed in the region between 1259 cm^{-1} and 1320 cm^{-1}. Bands at 1600 cm^{-1} and 1500 cm^{-1} are allocated to the non-symmetric C6 ring stretching modes. The higher frequency vibration at 1600 cm^{-1} has a major influence from the quinoid rings. The lower frequency mode at 1500 cm^{-1} depicts the presence of benzenoid rings. The presence of both these bands simply displays that the polymer is composed of amine and imine units. A peak at 1053 cm^{-1} shows rocking (presence of HSO_3^- group).

Wavenumber (cm^{-1})			Ascription
Oxalic acid	Phthalic acid	Calotropis acid	
502	502	502	S=O
607	607	607	S-C
814	814	814	C-H
1050	1050	1050	S=O
1106	1106	1106	C-H
1241	1241	1241	$C-N^+$
1290	1290	1290	C=N
1490	1447	1447	C=C & C-N
1569	1569	1569	C=C
2926	2926	2926	C-H

The peak at 1261 cm^{-1} portrays the stretching in polaron form of the PANI emeraldine salt SO_3^{2-} group is present at the wavelength 512 cm^{-1}. The wavelength at 1188 cm^{-1} looks like the aromatic in-plane bending of the prepared polyaniline.

The occurrence of many bands in the IR spectra may be attributed due to the following factors:

3.3. Surface morphology (SEM)

The SEM micrographs of the polyaniline doped with phthalic acid are shown in Fig.3.3. It approves new aspect of morphological growth demonstrating that when phthalic acid is used as doping agent, it guides to the formation of PANI nanostructures.

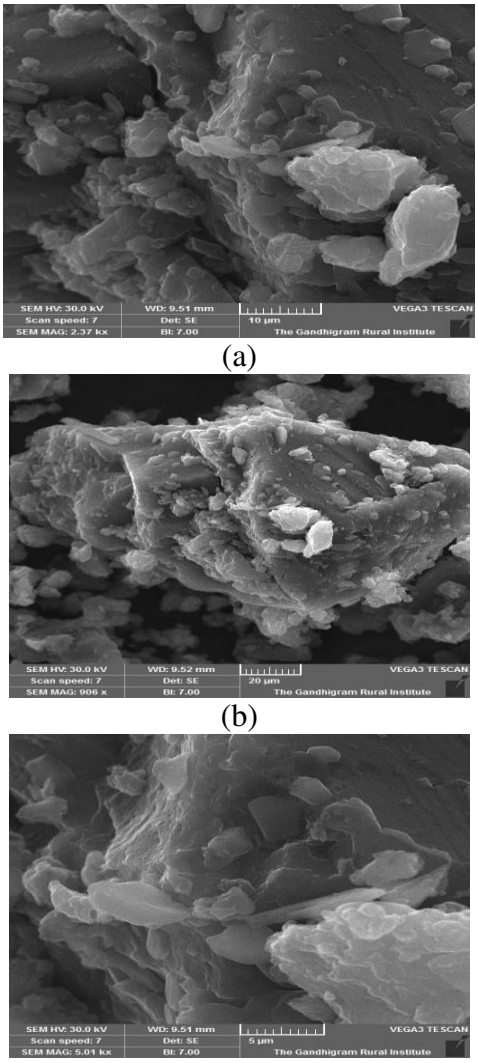


Fig. 3.3 SEM images of various magnification of phthalic acid doped PANI (5 µm, 2 µm and 1µm)

The resulted polymer exhibits rock-like structure derived from the aggregation of small granules. The rock structure was compact and dense in phthalic acid doped PANI. These features continue unaffected even at higher

magnifications, suggesting the compactness of the surface.

3.4. Antibacterial activity analysis

Bacterial Strains

Antibacterial activity of Polyaniline nanocomposites was individually tested on pathogenic gram-negative bacteria via., gram positive, sporulating, and facultative Bacillus subtilis strains and Escherichia coli (Clinical strain).

Standardization of Bacterial Strains

The synthesized samples were analyzed for its antibacterial activity against the gram positive, sporulating, and facultative Bacillus subtilis strains by means of Agar - well diffusion method. One milliliter of bacterial suspension was injected in a LB Broth overnight and was spread on Luria Bertani broth agar plates using sterile cotton swabs for 12 h as shown in figure.
Bacillus subtilis, known also as the hay bacillus or grass bacillus, is a Gram-positive, catalase-positive bacterium, found in soil and the gastrointestinal tract of ruminants and humans.

Fig.3.4 Antibacterial activity against the gram positive, sporulating, and facultative Bacillus subtilis strains using Agar - well diffusion method

Antibacterial Testing by the Agar Diffusion Method

Determination of bactericidal activity of various acid doped PANI was done by agar well diffusion method. Inoculums of bacterial strain were plated by means of sterile swabs onto petri dishes holding almost 25 ml of Luria Bertani broth agar, where 7 mm wells were made and filled with 50 µl (microlie) of all the samples (50 µg concentration) and DMSO is used as control.

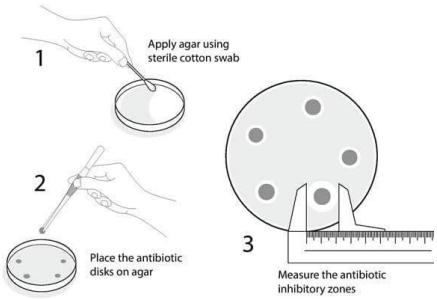
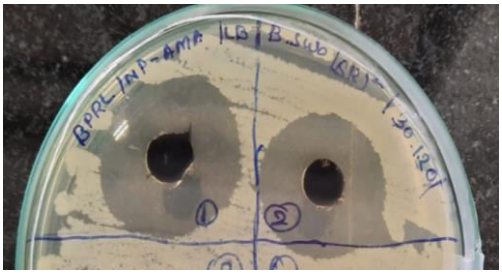
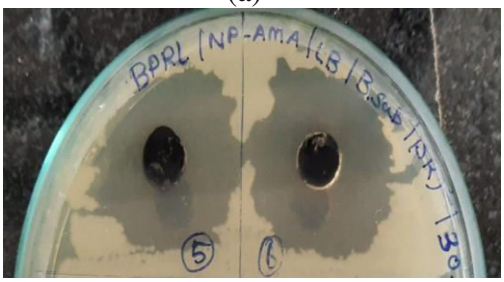


Fig 3.5 Zone of inhibition measurement

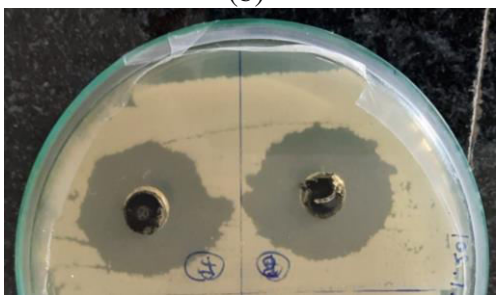
Antibacterial activity



(a)



(b)



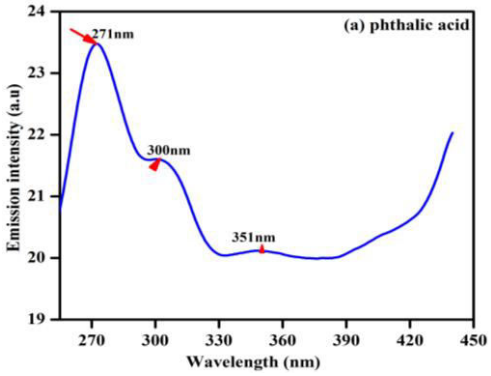
(c)

Fig. 3.6 Antibacterial activity of (a) oxalic acid, (b) phthalic acid (c) Calotropis acids doped Polyaniline

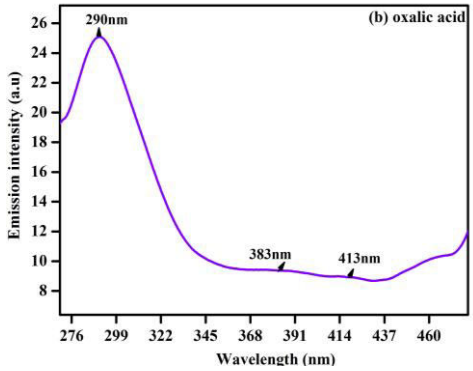
Antibacterial efficiency of PANI doped with oxalic acid, phthalic acid and Calotropis acid against one gram-positive human the gastrointestinal tract of ruminants and humans viz sporulating and facultative Bacillus subtilis strains.

3.5. Optical Emission Spectra (PL Spectra)

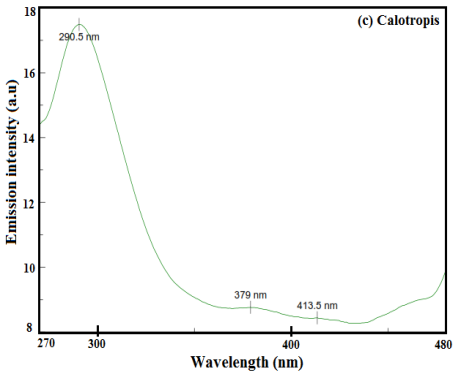
The photoluminescence spectra of aniline doped with several acids are shown in Fig 3.7(a-c). For the three samples, the photoluminescence emission is observed the sharp peek at around 292 nm as shown as Fig. 3.7(a-c). Fig. 3.7a shows the spectrum of PANI with two peeks at 290,300 and 351nm. The wavelength of excitation selected for all the samples is 365 nm. This is because the π to π * transition of the benzenoid unit, the unit accountable for photoluminescence in PANI, corresponds to around 350nm.



(a)



(b)



(c)

Fig. 3.7 PL Spectrum of (a) phthalic acid, (b) oxalic acid, and (c) calotropis doped polyaniline

The direct band gap energy value was calculated by using the formula,

$$E_g = hc/\lambda \qquad (4)$$

Where h is a constant (6.634 x 10^{-34} J/S). C is the velocity of light (3 x 10^{8} m/s) and λ is emission wavelength in emission spectrum. The calculated wavelength of the emission band gap energy values is recorded in the below Table.3.1

PHTHALIC ACID		OXALIC ACID		CALATROPIS MILK	
Wavelength	**Band gap**	**Wavelength**	**Bandgap**	**Wavelength**	**Band gap**
271	4.55ev	290	4.27ev	290.5	4.27ev
300	4.12ev	383	3.32ev	379	3.27ev
351	3.59ev	413	3.00ev	413.5	3.00ev

Table 3.1 Emission bandgap of various acid doped PANI

3.6 Structural analysis (XRD)

X-Ray diffraction pattern of several acids and natural product doped Polyaniline are recorded in the range of

20˚- 80˚ and are shown in Fig.3.8 (a-c) respectively. In each case X - Ray diffraction pattern of PANI has a broad peak about 2θ=21° to 25° which shows the characteristic peak of polyaniline. Fig 3.8(a-c) indicated that polyaniline had a semi crystalline structure because no sharp peak can be perceived in the XRD pattern.

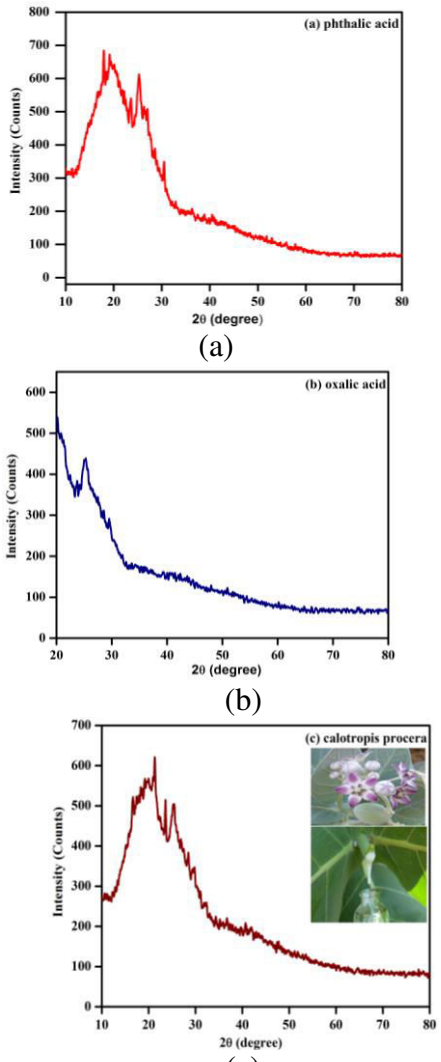


Fig. 3.8 XRD pattern of (a) phthalic acid, (b) oxalic acid, and (c) Calotropis doped polyaniline

The weak peaks at 2θ of 25^0 observed due to polymer chains placed parallel and closed to each other and produced crystalline zones that are surrounded by amorphous areas. The peak at 25.1^0 is attributed to prediocity perpendicular to the polymer chain, whilst those other peaks are due to the fact that the branches of oxalic acid are doped well in the PANI chains. The XRD pattern also recommends that PANI-oxalic acid, which proposes that the semi-crystalline nature of the polymer could be enhanced by doping oxalic acid into the polyaniline molecular chains.

Samples	Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Crystal size D(nm)	Dislocation density δ x10^{15}m	micro strain ε	Interplanar spacing d_{nkl}
Phthalic acid	25.25	128.10	0.65	3.52	5.31	0.035	0.147	0.751
Oxalic acid	25.26	85.78	0.80	3.52	4.32	0.053	0.181	0.752
Calotropis milk	21.27	107.95	0.53	4.17	7.45	0.018	0.124	0.757

***Table 3.2** XRD parameters of various acid doped Polyaniline.*

XRD of the synthesized samples is carried out by means of CuKα radiation (λ=1.54A˚). The size was calculated using Debye-Scherrer's formula.

$$D=k\lambda/\beta\cos\theta \qquad (1)$$

where, λ is the X-ray wavelength (1.5406 Å), k is the shape factor (~ 0.89), D is the average diameter, θ is the Bragg angle in degrees and β is the line broadening measured by half-height in radian.

The dislocation density (δ) can be evaluated from Williamson and Small man's formula,

$$\delta=1/D^2 \qquad (2)$$

Micro strain of the nanoparticles can be calculated by using the formula [3]

$$\varepsilon = \beta\cos\theta/4 \qquad (3)$$

The X-ray diffraction pattern of PANI has a broad peak at about $2\theta=25.16^0$ and the three overlapping sharp peaks at 21.27^0 and 25.25^0. The semi crystalline

peaks and amorphous corona of the angular intensity profile are used to estimate the percent of crystallinity of the polymer systems. Since the XRD results displayed that the phthalic acid doped PANI has better semi crystallinity then Calotropis doped PANI.

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