"Multi-Component Template Effects"- Preparation of Highly Porous Polyaniline Nano Rods using Crude Lemon Juice and its Application for Selective Detection of Catechol

Vineeta Gautam[1, 2$,] *Karan P. Singh*[2**], *Vijay L. Yadav*[1*]

1. Department of Chemical Engineering & Technology, IIT-BHU, Varanasi-521005, U.P., India
2. Mahamana Innovative Technologies Welfare Society, Nawabganj, Bareilly-242606, U.P., India

E-mail : contactmitws@gmail.com, vlyadaviitbhu2014@gmail.com, gautamvinita09@gmail.com

Number of pages: 31

Figures: 22

Tables:11

Supplementary information for publication

1. **Important assumption and presumption of concept "Multi-component Template Effects"**
2. **HR-SEM images**
3. **TEM images**
4. **XRD**
5. **AFM images**
6. **BET surface area and BJH pore size distribution**
7. **Comparative table of FT-IR frequency**
8. **NMR analysis**
9. **UV-Visible spectra**
10. **Effect of pH on cyclic voltammograms**
11. **Cyclic voltammograms of PANI (L) and PANI (H)**
12. **Differential Pulse Voltammetry and Chronoampereometry**
13. **Cyclic Voltammetric response of different analytes**

S1: Important assumption and presumption of concept "Multi-component Template Effects"

1. The main objective is to identify the template like effects on the morphologies of synthetic polymer/nano particle under the influence of suitable natural extract. Small amount of natural extract in the reaction mixture could redefine the inter-facial properties, strength of π–π interaction, hydrophobic/hydrophilic affinities and electrostatic forces. This effect could be considered as a subclass of soft template synthesis.
2. The word "synergistic" used to indicate creative, innovative and combined effect of molecules present in the reaction mixture on the morphology of nano materials/synthetic polymers. In this research work lemon juice was used to prepare PANI, we observed that PANI-lemon have well defined rod shape architecture, due to the linear alignment of individual chains (confirmed from HR-SEM, TEM and AFM), whereas no such modifications was observed in PANI-citric acid. Filtered lemon juice has the nominal amount of suspended solid. It is presumed that the filtered natural extract have no solid substrate or analogue. Thus, we define "Multi-component Template Effects" as a combined template like effect of matrix molecules on the morphology of synthetic polymer / nano particles.
3. It is presumed that this approach does not bring any serious issues on the purity of synthetic polymeric products because the filtered aqueous extract has very nominal amount of suspended solids and most of the soluble molecules could be easily removed during washing with appropriate solvents by adopting suitable doping-dedoping-redoping procedures. However, a permanent impression of matrix (i.e. pseudo template) has been persisted on the morphologies of synthetic polymer. The three PANI samples have same structure and functional groups (confirmed from FTIR spectra), but differ in their spatial arrangement (confirmed from microscopic analysis).
4. The natural extracts obtained from a specific source have approximately a similar composition (however, concentration of component could change seasonally), thus a reproducible effect on the morphology could be obtain by using same natural extract in similar conditions.
5. Addition of a small amount of suitable plant extract in the reaction mixture could be eco-friendly, cost effective approach to modify morphology of nano particles.
6. This concept can implement to the synthesis of a variety of synthetic polymers / metal nano particles by using a suitable plant extracts.
7. Any living system has many molecules in the matrix, and a variety of nanomaterials are produced by nature. Synergism is the key concept of any biosynthesis. The discussions are open to illustrate the synergistic effect of a multi-component biological system and implementation of this concept for the synthesis of many new man-made nanomaterials.

Figure S2: HR-SEM image at different resolution

Figure S 2A - PANI-HCl

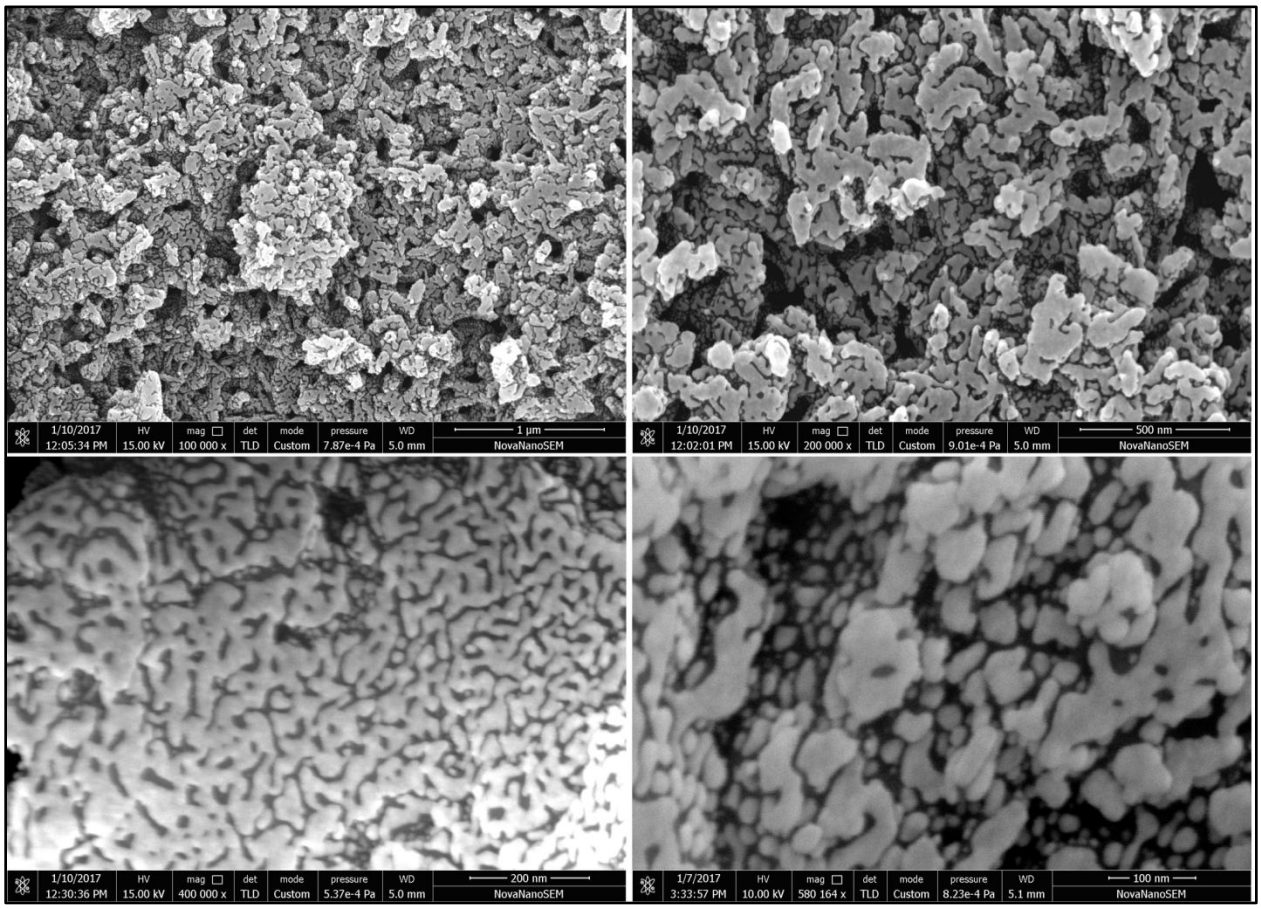


Figure S 2B: PANI-citric acid

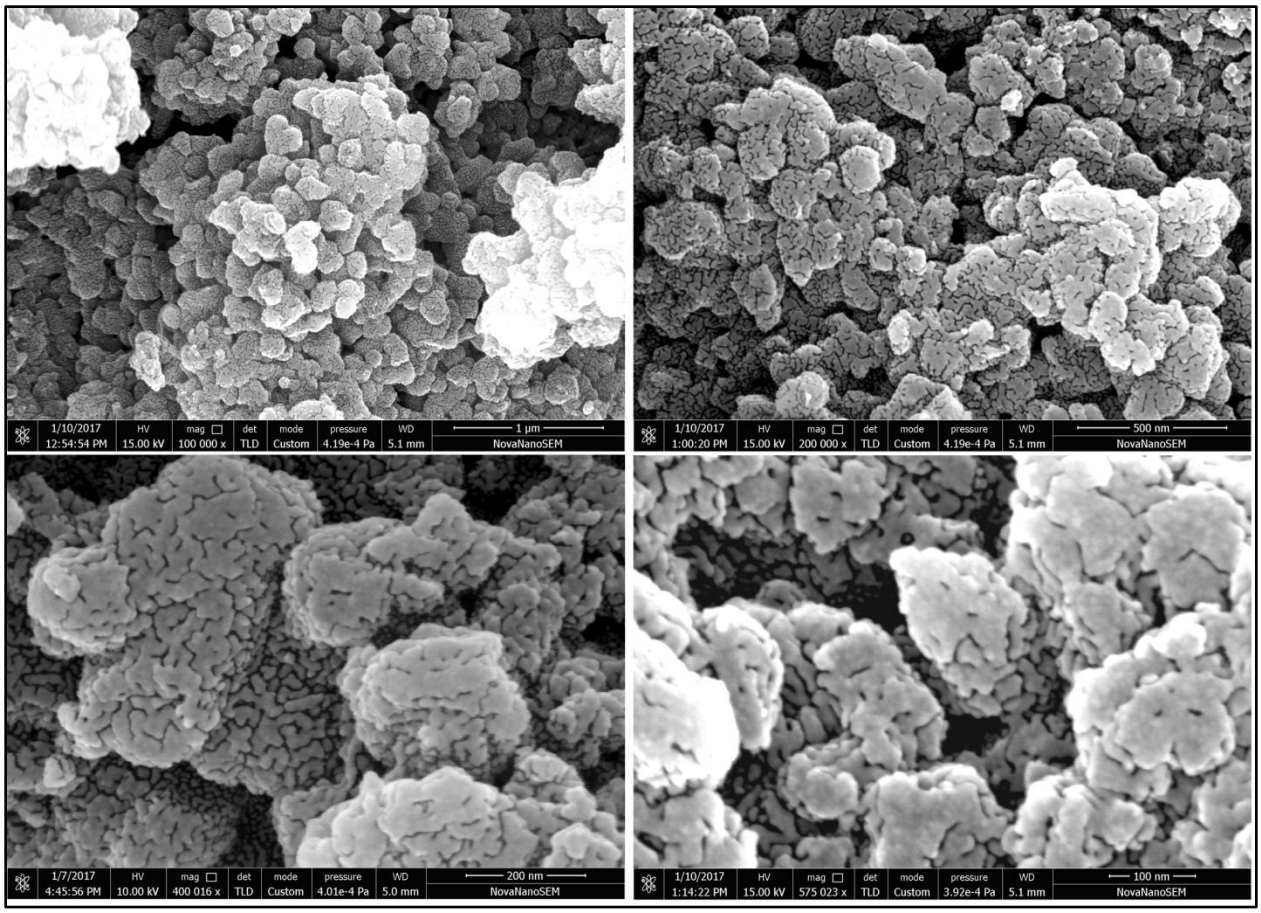


Figure S 2C: PANI-lemon (L) (Prepared in low concentration of lemon juice extract)

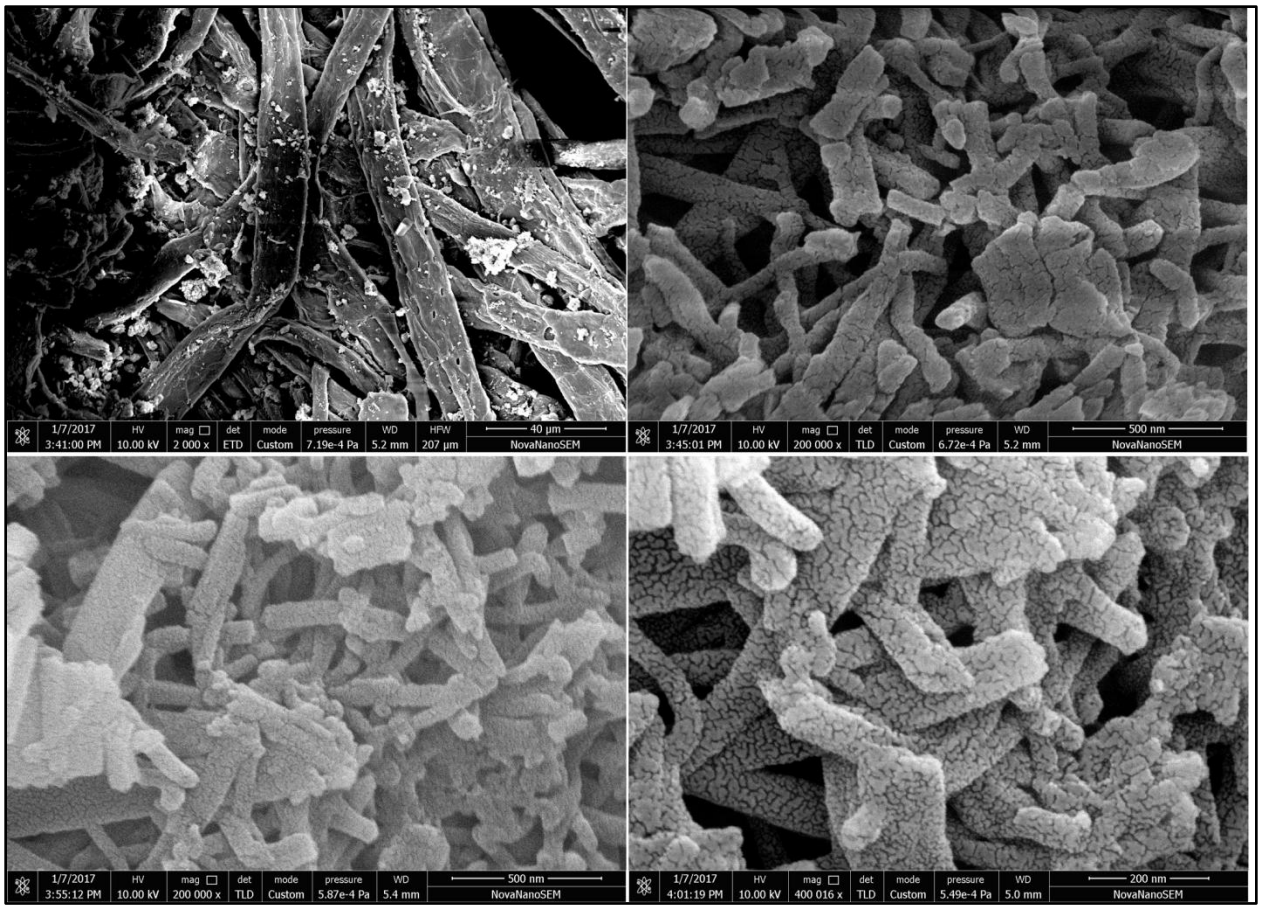


Figure S2D - PANI-lemon (H) (Prepared in high concentration of lemon juice extract)

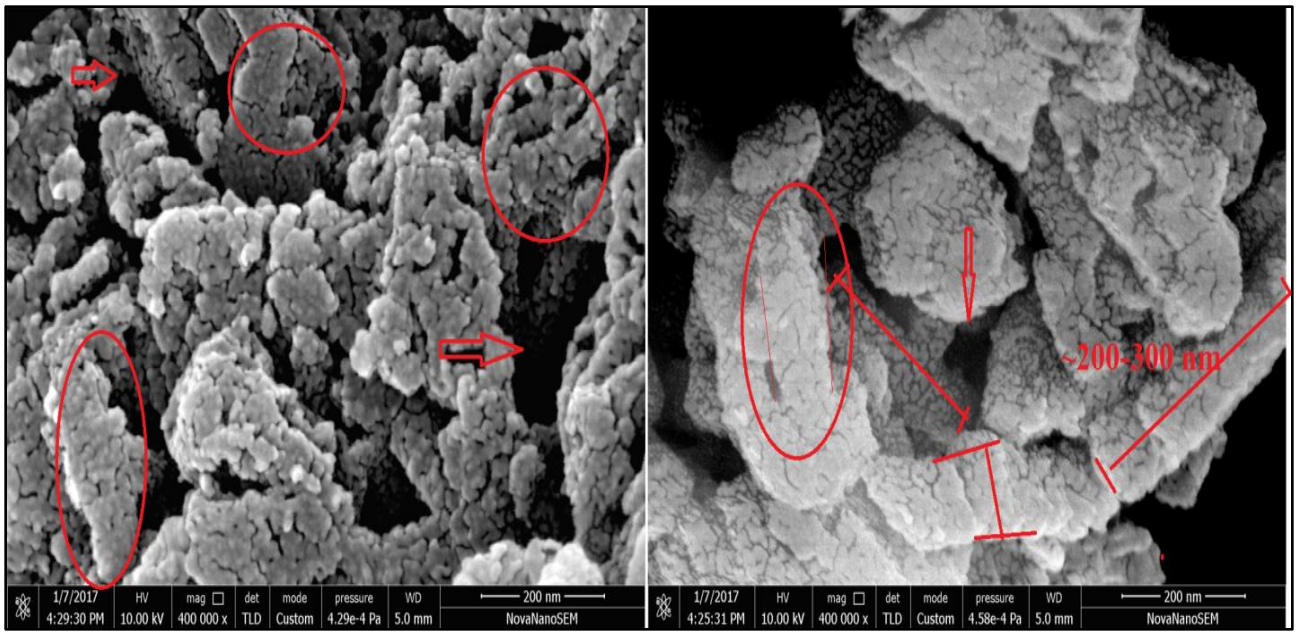


Figure S3: Additional TEM images and electron diffraction pattern

Figure S 3A: PANI-HCl

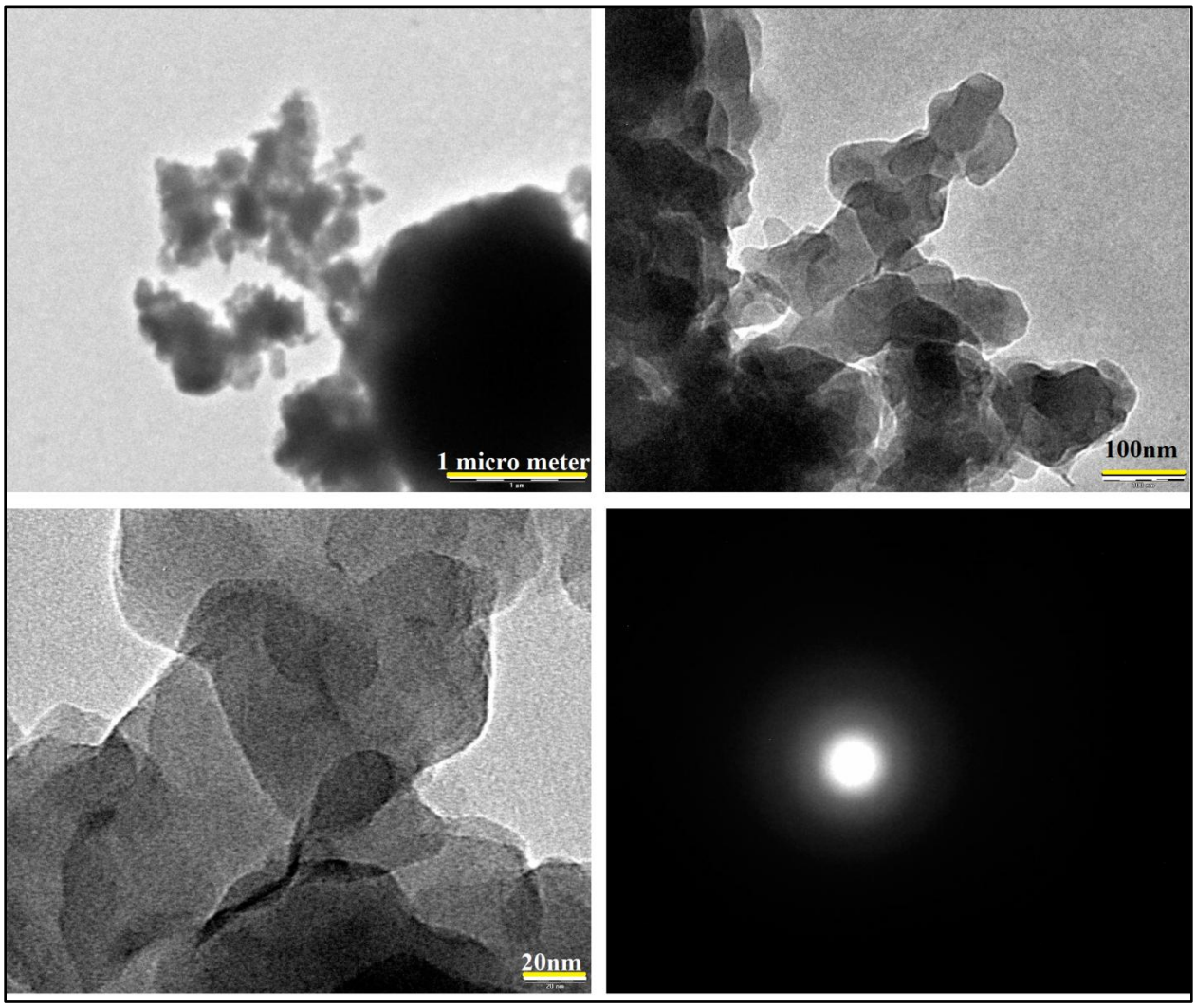


Figure S 3B: PANI-Citric acid

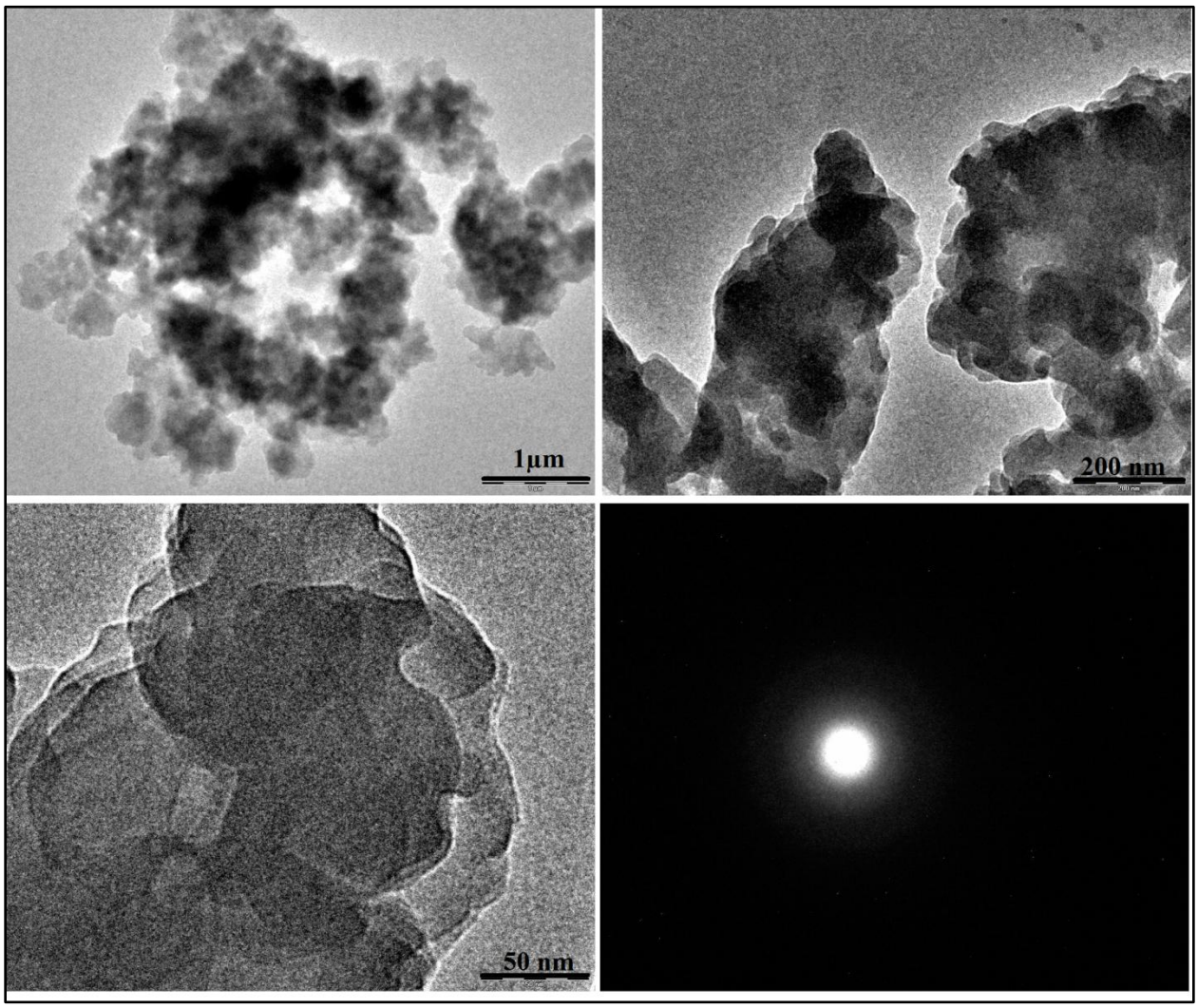


Figure S 3C: PANI-Lemon (L)

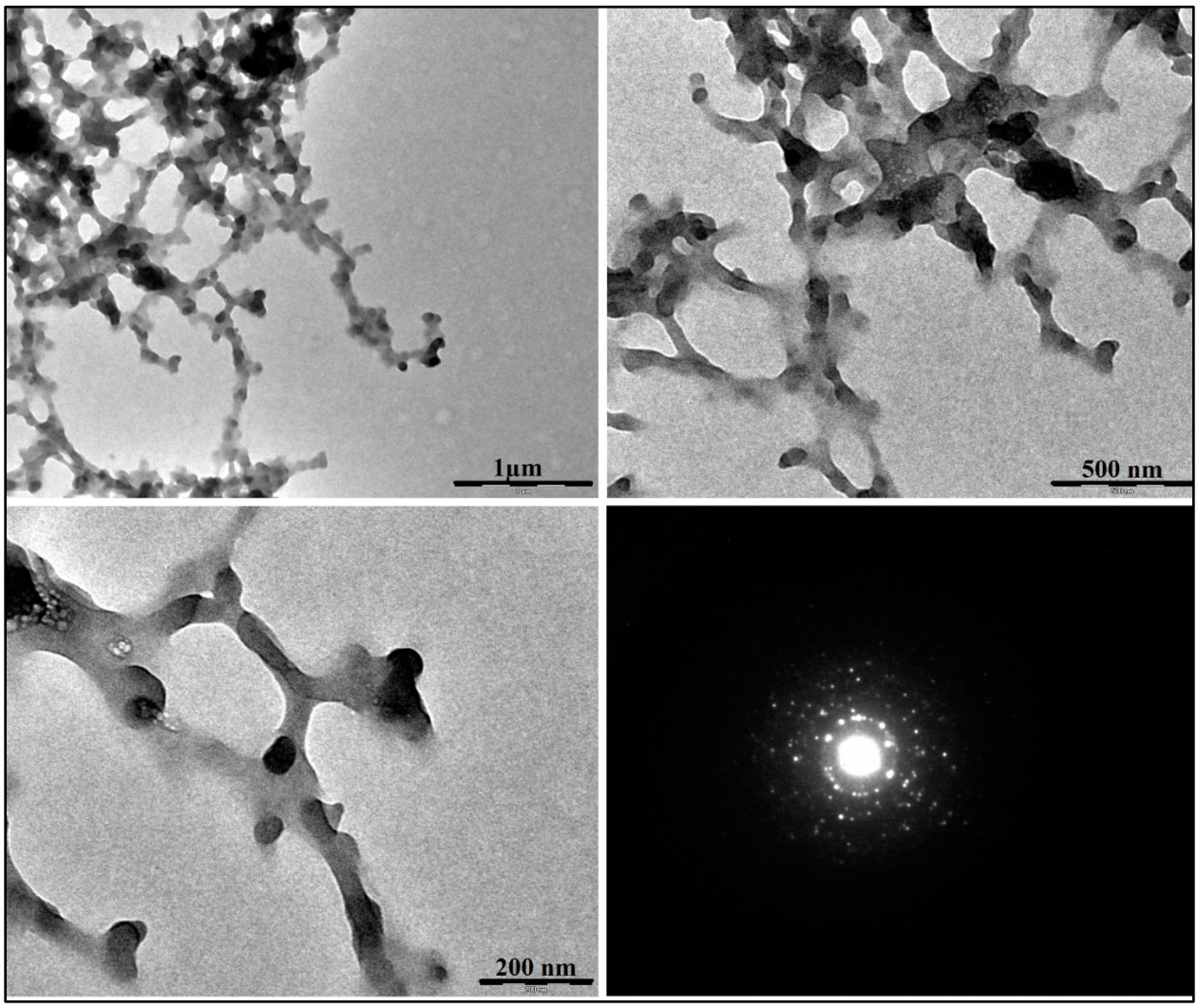
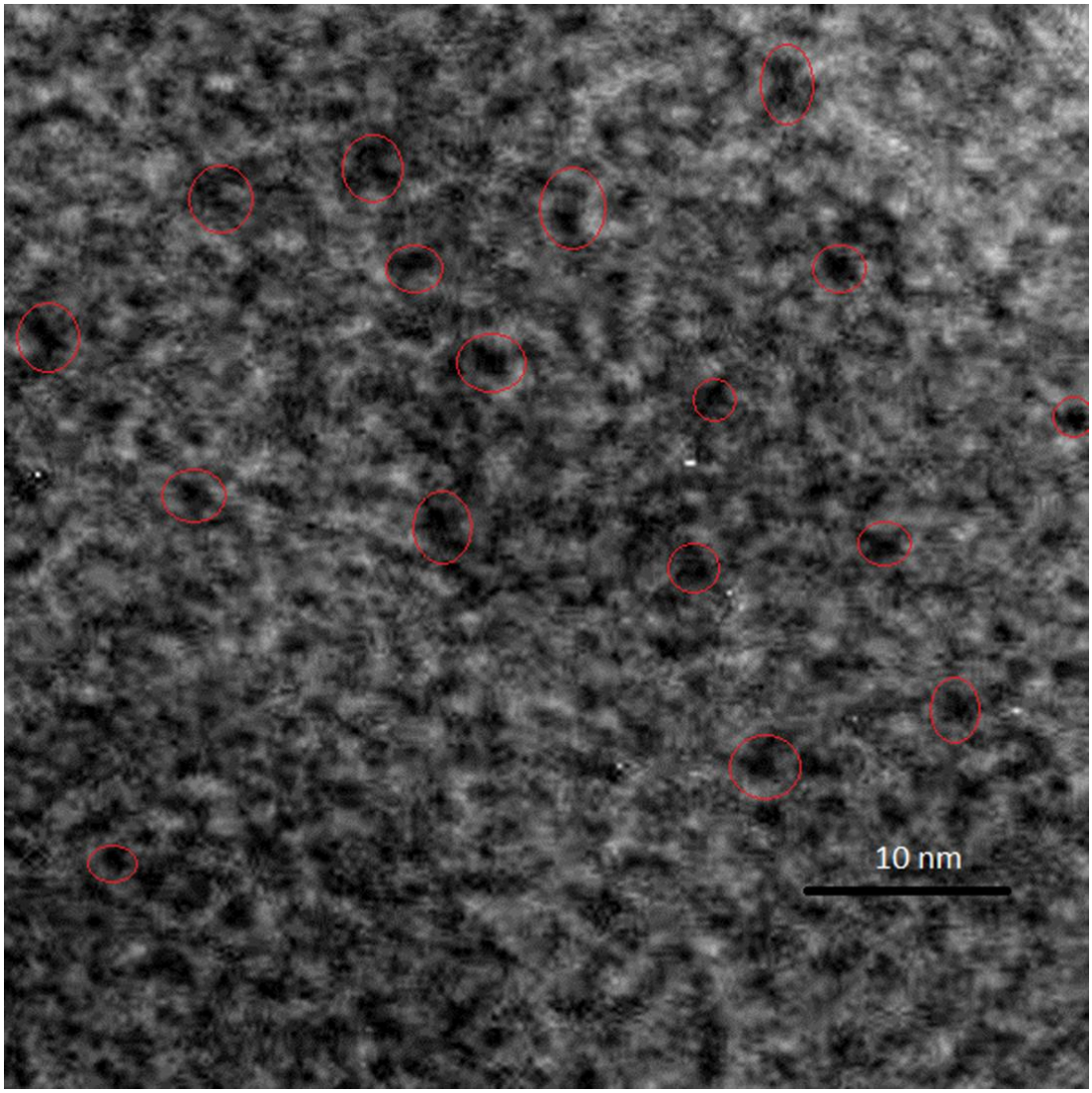


Figure S 3D: Zoom image of surface of nano rod

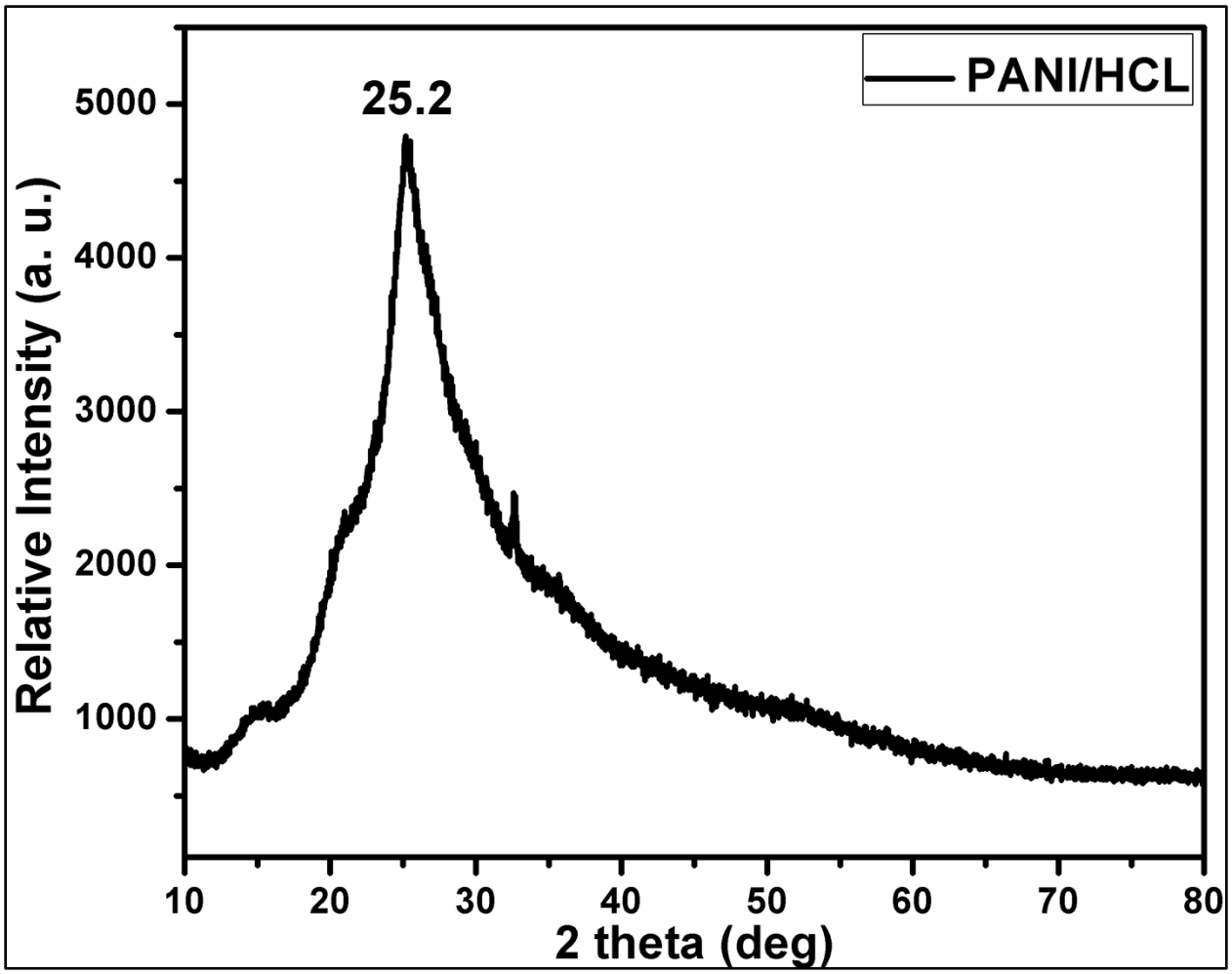


The zoom TEM image of PANI-Lemon-L exhibited that the surface of nano rods has small pore size structure ~ 4-5 nm.

Figure S 4: XRD analysis

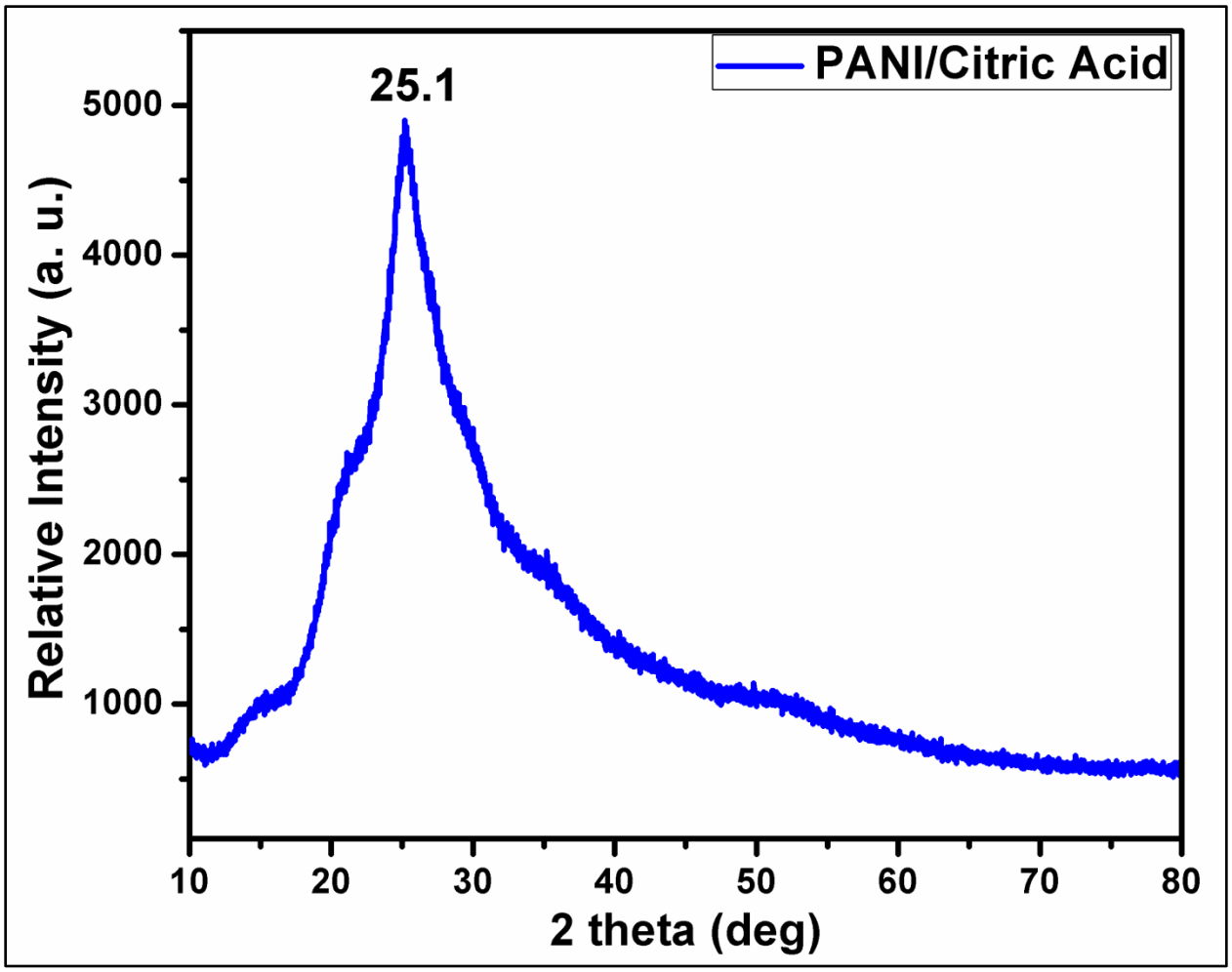
In the X-ray absorption analysis, PANI sample was exposed to a beam of X-rays of suitable energy. The angles of deviation and relative intensities of the deviated beams were measured to examine the phase homogeneity. The position of the Bragg's peaks obtained from X-ray powder diffractograms shows the alignment of benzenoid and quinoid ring plain of PANI chains responsible for crystalline structure. We observed similar XRD as reported by earlier workers, except that some additional sharp peaks appeared in PANI-lemon.[23,46] A large number of sharp peaks are a strong evidence for the semi-crystalline nature of PANI-lemon. Thus, XRD analysis strongly demonstrates that the lemon juice influence on the crystalline nature of Polyaniline. The PANI-lemon exhibits its strongest peak at $2\Theta = 22.83^{o}$, its second strongest peak at 26.36^{o}, a medium intensity peak at 16.0^{o}, 34.4^{o} and a weak peak at 30.0^{o}. PANI-HCl and PANI-citric acid show strong peaks at $2\Theta = 24.94^{o}$ and 24.49^{o}, respectively. The crystallite size calculated at the strongest peak of PANI-HCl, PANI-Citric acid, PANI-Lemon are 12.7 Å, 13.8 Å and 46.7 Å, respectively. The crystallite sizes are very less which indicate small size crystallites were arranged together as a bigger cluster. Thus, the X-ray powder diffractograms are consistent with the results of the other morphological studies. Crystalline PANI products display a better metallic behavior (in term of conductivity) than amorphous products. Tiwari et.al. showed that polycrystalline PANI based material showed better electrochemistry.[51]

Figure S 4A – PANI-HCl



No.	2-theta(deg)	d(ang.)	Height (counts)	FWHM(deg)	Size (ang.)	Rel. int. I (a.u.)
1	15.23(3)	5.812(11)	149(12)	2.45(14)	34(2)	2.21
2	24.94(4)	3.568(5)	1447(38)	6.72(11)	**12.7(2)**	58.07
3	26.05(4)	3.418(5)	1419(38)	9.4(2)	9.1(2)	100.00
4	32.687(8)	2.7374(6)	239(15)	0.16(2)	535(72)	0.22

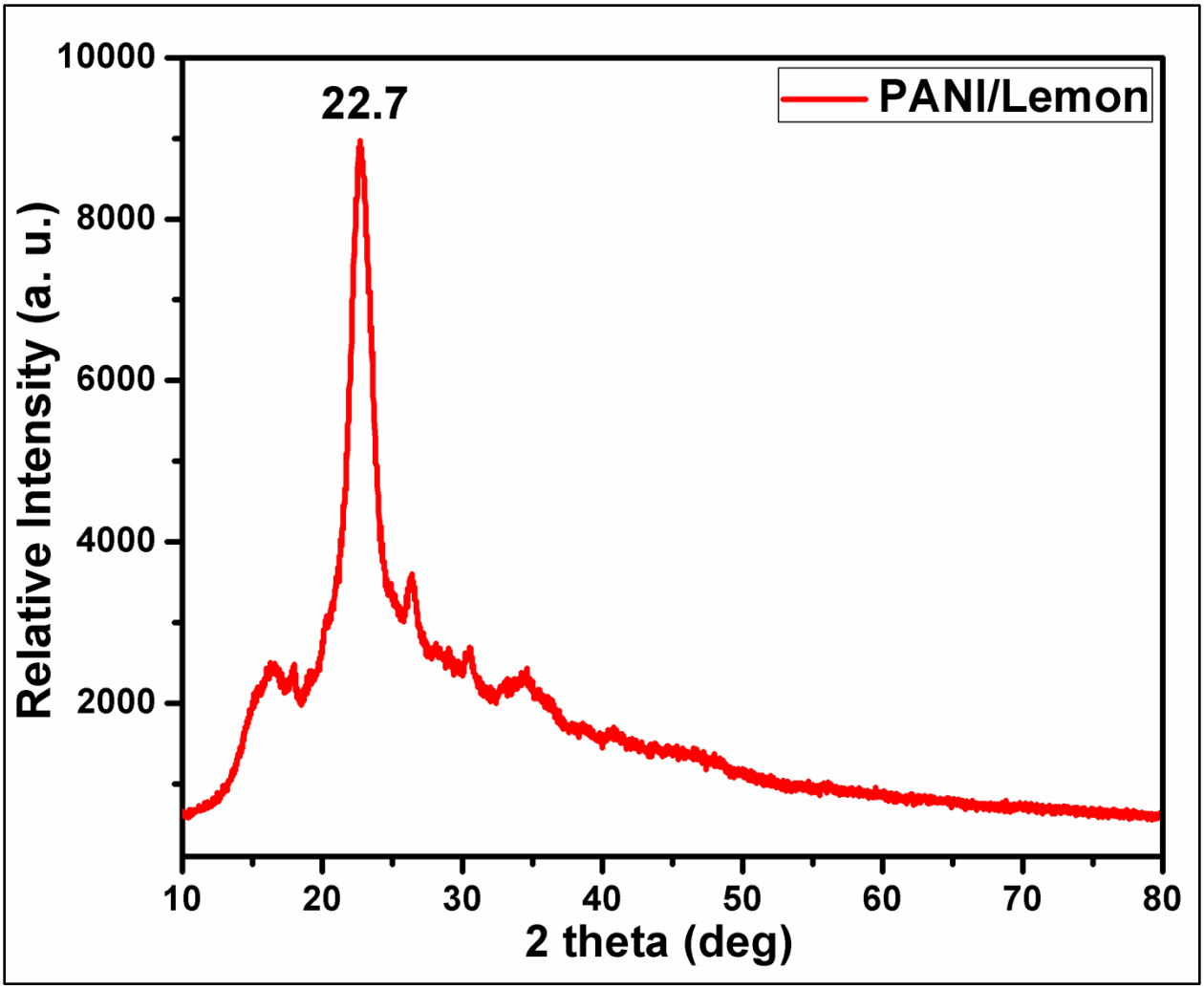
Figure S 4B – PANI-citric acid



PANI/Citric Acid

No.	2-theta(deg)	d(ang.)	Height(counts)	FWHM(deg)	Size (ang.)	Rel. int. I(a.u.)
1	14.97(9)	5.91(3)	47(7)	1.3(3)	62(12)	0.60
2	22.49(6)	3.950(10)	1060(33)	6.12(18)	**13.8(4)**	62.97
3	25.13(2)	3.540(3)	1369(37)	7.19(8)	11.82(13)	100.00

Figure S 4C – PANI-lemon

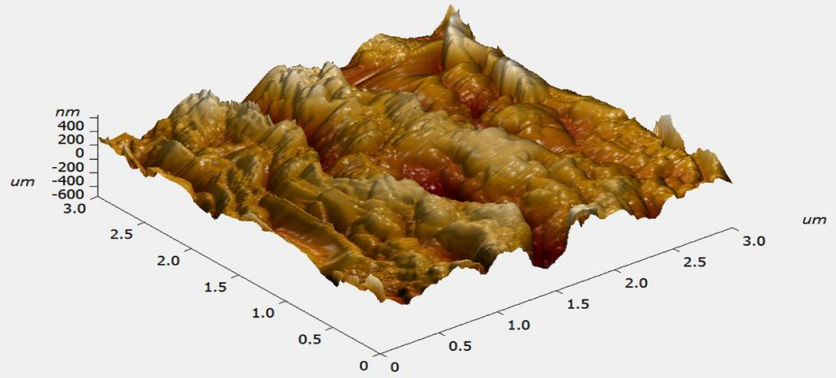


No.	2-theta(deg)	d(ang.)	Height(counts)	FWHM(deg)	Size (ang.)	Rel. int. I(a.u.)
1	16.0(2)	5.54(8)	296(17)	1.8(2)	48(5)	6.21
2	22.833(17)	3.892(3)	4030(63)	1.812(16)	**46.7(4)**	100.00
3	26.366(12)	3.3776(15)	427(21)	0.61(4)	139(8)	3.34
4	34.4(3)	2.60(2)	90(9)	1.0(3)	88(23)	1.02

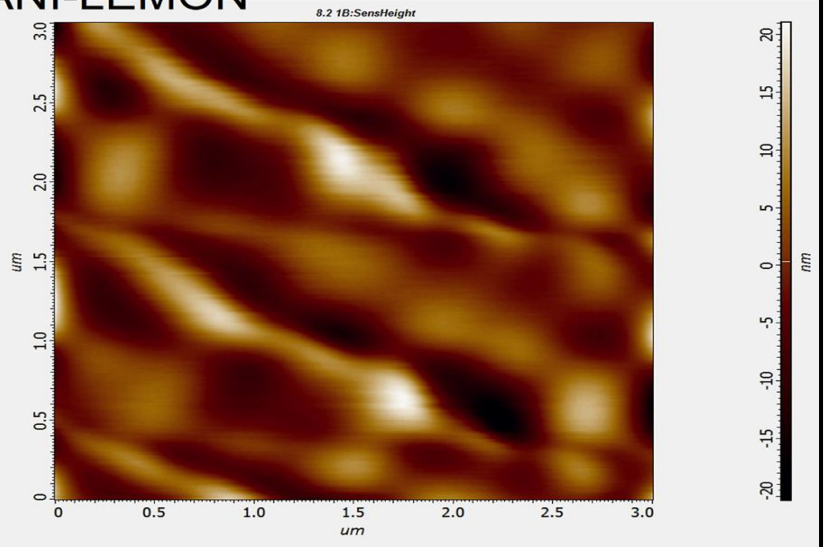
Figure S 5: AFM images of PANI-HCl and PANI-lemon

The AFM is a form of scanning probe microscopy technique which is very useful to investigate the morphology and topographical information of conductive polymers at very high resolution. This allows a 3D profile of the surface to be produced at magnifications over one million times, giving than optical or scanning electron microscopes. The AFM imaging was performed on as spin coated samples on a glass slide in the tapping mode. AFM images reveal that PANI-lemon has uniformly porous surface structure, whereas PANI-HCl irregular topology and arrangement.

PANI-HCl



PANI-LEMON



PANI-LEMON

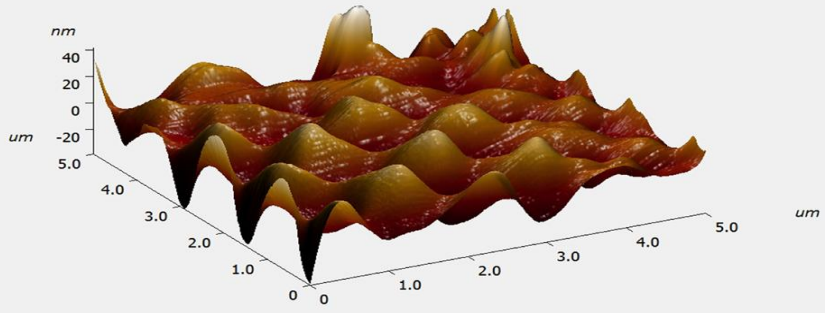


Figure S6: BET anf BJH analysis

Figure S6A: Comparison of Nitrogen adsorption and desorption isotherms, surface area vs relative pressure and pore volume vs pore diameter plots for PANI-HCl, PANI-citric acid, PANI-lemon (L) and PANI-lemon (H)

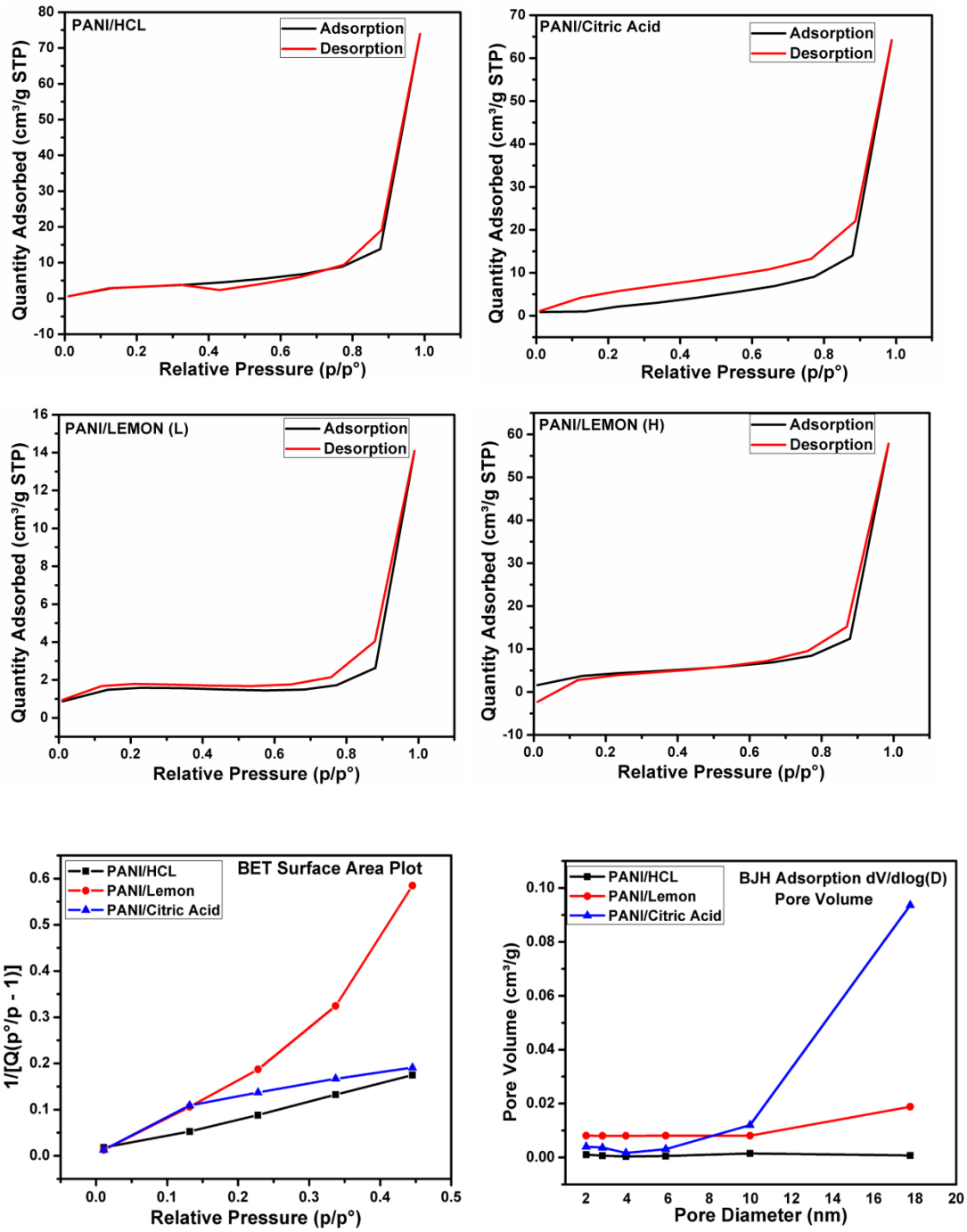


Table S 6 B:

Surface area and porosity report for PANI-HCl, PANI citric acid, PANI-lemon (L) and PANI-lemon (H)

	PANI-HCl	**PANI –citric acid**	**PANI-lemon (L)**	**PANI-lemon (H))**
Surface Area				
Single point surface area at p/p°	0.337322115 : 11.1067 m^2/g	0.337927487 : 8.8169 m^2/g	0.337334884 : 4.5264 m^2/g	0.337604362: 14.0121 m^2/g
BET Surface Area	**11.6179 m^2/g**	**10.8535 m^2/g**	**3.6671 m^2/g**	**13.4519 m^2/g**
BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	26.6512 m^2/g	24.7164 m^2/g	4.8483 m^2/g	19.9279 m^2/g
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	31.1460 m^2/g	26.7748 m^2/g	5.3847 m^2/g	22.7516 m^2/g
Pore Volume				
BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter	0.113779 cm^3/g	0.098609 cm^3/g	0.020872 cm^3/g	0.087712 cm^3/g
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter	0.114403 cm^3/g	0.095775 cm^3/g	0.021839 cm^3/g	0.088851 cm^3/g
Pore Size				
BJH Adsorption average pore diameter (4V/A):	17.0768 nm	15.9585 nm	17.2200 nm	17.6058 nm
BJH Desorption average pore diameter (4V/A	14.6925 nm	14.3082 nm	16.2230 nm	15.6210 nm

Table S 6 C

Data point

Isotherm Linear Plot Adsorption

Relative Pressure (p/p°)	Quantity Adsorbed (cm^3/g STP)		
	PANI/HCl	PANI/Lemon(L)	PANI/Citric Acid
0.01083	0.61354	0.86723	0.8629
0.13171	2.87912	1.48393	0.99731
0.22789	3.34584	1.58255	2.13965
0.33732	3.8501	1.56911	3.05916
0.44532	4.5898	1.4876	4.20412
0.55484	5.54337	1.44212	5.49102
0.66343	6.81974	1.48788	6.92608
0.77144	8.89189	1.7221	9.07335
0.87685	13.82433	2.63661	14.00146
0.98722	73.95835	14.08585	64.18851

Isotherm Linear Plot Desorption

Relative Pressure (p/p°)	Quantity Adsorbed (cm^3/g STP)		
	PANI/HCl	PANI/Lemon(L)	PANI/Citric Acid
0.98722	73.95835	14.08585	64.18851
0.88078	19.1583	4.03995	22.06235
0.77616	9.42314	2.13874	13.25655
0.65276	5.92501	1.76468	10.81453
0.54014	3.99094	1.67785	9.3304
0.43045	2.34337	1.69303	8.2408
0.32137	0.75905	1.75055	7.00314

BET-Surface area plot

Relative Pressure (p/p°)	1/[Q(p°/p - 1)]		
	PANI/HCl	PANI/Lemon(L)	PANI/Citric Acid
0.01083	0.01784	0.01245	0.01304
0.13171	0.05269	0.10618	0.1089
0.22789	0.08821	0.18687	0.13708
0.33732	0.13221	0.32442	0.16685
0.44532	0.17492	0.58493	0.19068

Isotherm Log Plot Adsorption

Relative Pressure (p/p°)	Quantity Adsorbed (cm^3/g STP)		
	PANI/HCl	PANI/Lemon(L)	PANI/Citric Acid
0.01083	0.61354	0.86723	0.8629
0.13171	2.87912	1.48393	0.99731
0.22789	3.34584	1.58255	2.13965
0.33732	3.8501	1.56911	3.05916
0.44532	4.5898	1.4876	4.20412
0.55484	5.54337	1.44212	5.49102
0.66343	6.81974	1.48788	6.92608
0.77144	8.89189	1.7221	9.07335
0.87685	13.82433	2.63661	14.00146
0.98722	73.95835	14.08585	64.18851

BJH Adsorption dV/dlog(D) Pore Volume

Pore Diameter (nm)	Pore Volume (cm^3/g)		
	PANI/HCl	PANI/Lemon(L)	PANI/Citric Acid
17.75973	7.27904E-4	0.01879	0.09365
9.97201	0.00147	0.00808	0.01202
5.87812	5.3119E-4	0.00806	0.00308
3.94291	3.51678E-4	0.00802	0.00168
2.80063	6.63078E-4	0.00801	0.00366
2.00771	0.00104	0.00808	0.00398

Isotherm Log Plot Desorption

Relative Pressure (p/p°)	Quantity Adsorbed (cm^3/g STP)		
	PANI/HCl	PANI/Lemon(L)	PANI/Citric Acid
0.98722	73.95835	14.08585	64.18851
0.88078	19.1583	4.03995	22.06235
0.77616	9.42314	2.13874	13.25655
0.65276	5.92501	1.76468	10.81453
0.54014	3.99094	1.67785	9.3304
0.43045	2.34337	1.69303	8.2408
0.32137	0.75905	1.75055	7.00314

Table S 7: FT-IR spectra ascription of PANI before and after treatment with catechol

PANI-HCl (cm^{-1})		PANI-Citric acid (cm^{-1})		PANI-Lemon (cm^{-1})		Ascription
	Catechol treated		Catechol treated		Catechol treated	
806	805	805	805	791	816	C-H
						CH ring out-of-plane bend; CCC ring out-of-plane deformation
1130	1130	1130	1130	1132	1141 Decrease in intensity	N=Q=N
1231	1231	1231	1231	1238	1242	CCC ring in-plane deformation; CN stretch
1297	1286	1297	1287	1298	1297	NH out-of-plane bend; CN strength; CC stretch CH ring in-plane bend
1499	1488	1487	1488	1495	1466	C=C (Benzenoid)
1577	1577	1566	1566	1570	1588 Decrease in intensity	C=C (Quinoid)
				1630		CC stretch; CH ring in-plane bend; CN stretch

Figure S 8: NMR analysis.

NMR spectroscopy is a significant technique to acquire thorough molecular, structural and doping information about PANI. Important information on PANI spectra has been well reported in the literature.[55-56] ^{1}H NMR spectrum of PANI-HCl, PANI-citric acid and PANI-lemon (L, H) in DMSO-D6 solutions exhibited characteristic sharp peaks of aromatic and primary/secondary amine and some weak peaks due to dopants. PANI-HCl shows a triplet (7.096, 7.196, and 7.298) which is correlated with the protonation level of PANI chains. In case of PANI-lemon, the spectra have a wide single peak at 7.082 δ, attributed to fast proton exchange between primary and secondary amines, symmetric arrangement of PANI chains, and equivalent chemical environment for aromatic protons. Proton exchange leads to a broadening of the OH and coupled hydrogen signals. Symmetry among polyaniline chains facilitates the proton exchange reactions. Thus, we inferred PANI-lemon has linear alignment of chains. Chloride ion also acts an anionic dopant so we get a peak ~ 2.5 δ. Citric acid (3'-hydroxybiphenyl-3-carboxylic acid) is a weak organic tribasic carboxylic acid, so we have obtained complex NMR spectra.

Figure S 8A: Proton NMR of PANI-HCl

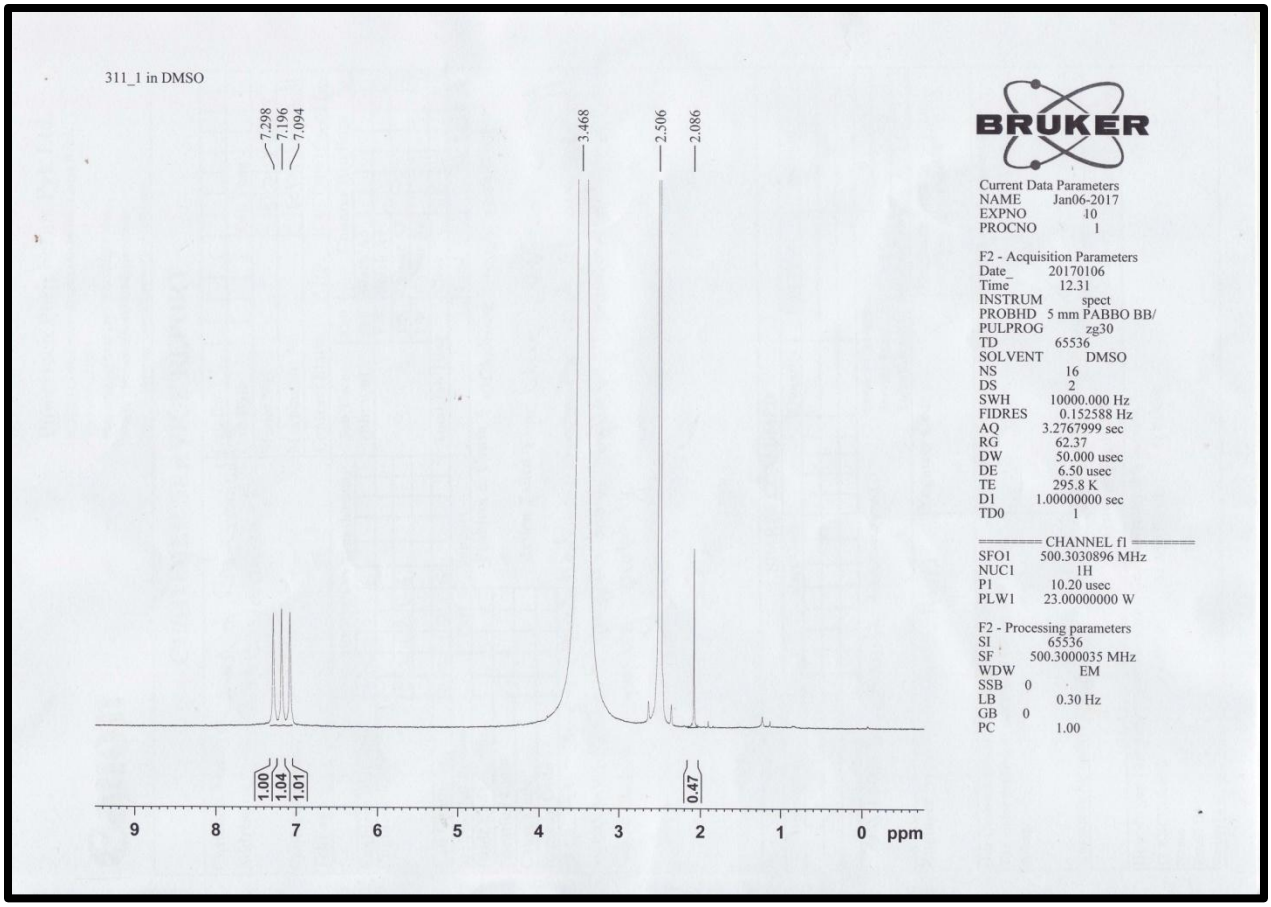


Figure S 8B : Proton NMR of PANI-citric acid

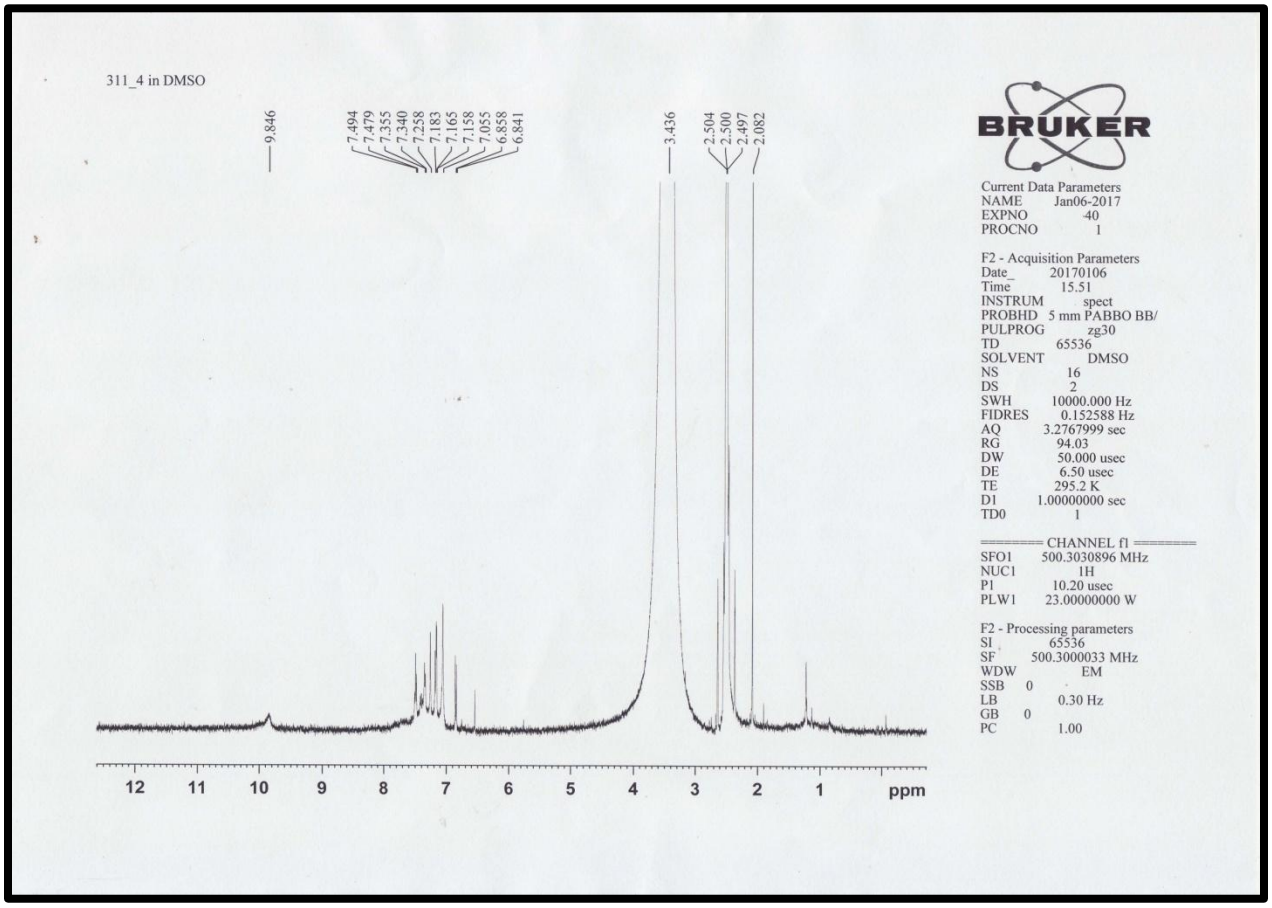


Figure S 8C: Proton NMR of PANI-lemon (L)

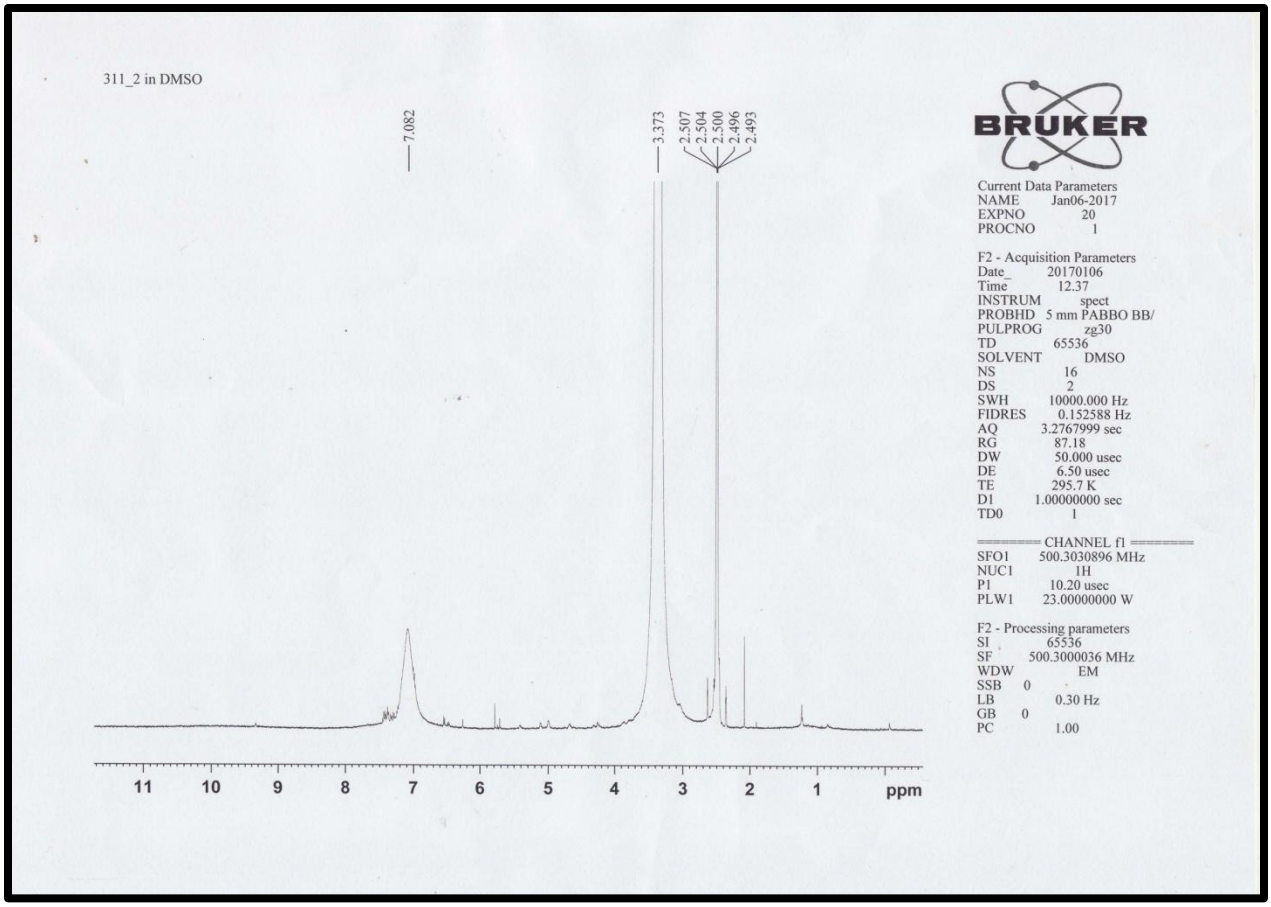


Figure S 8D: Proton NMR of PANI-lemon (H)

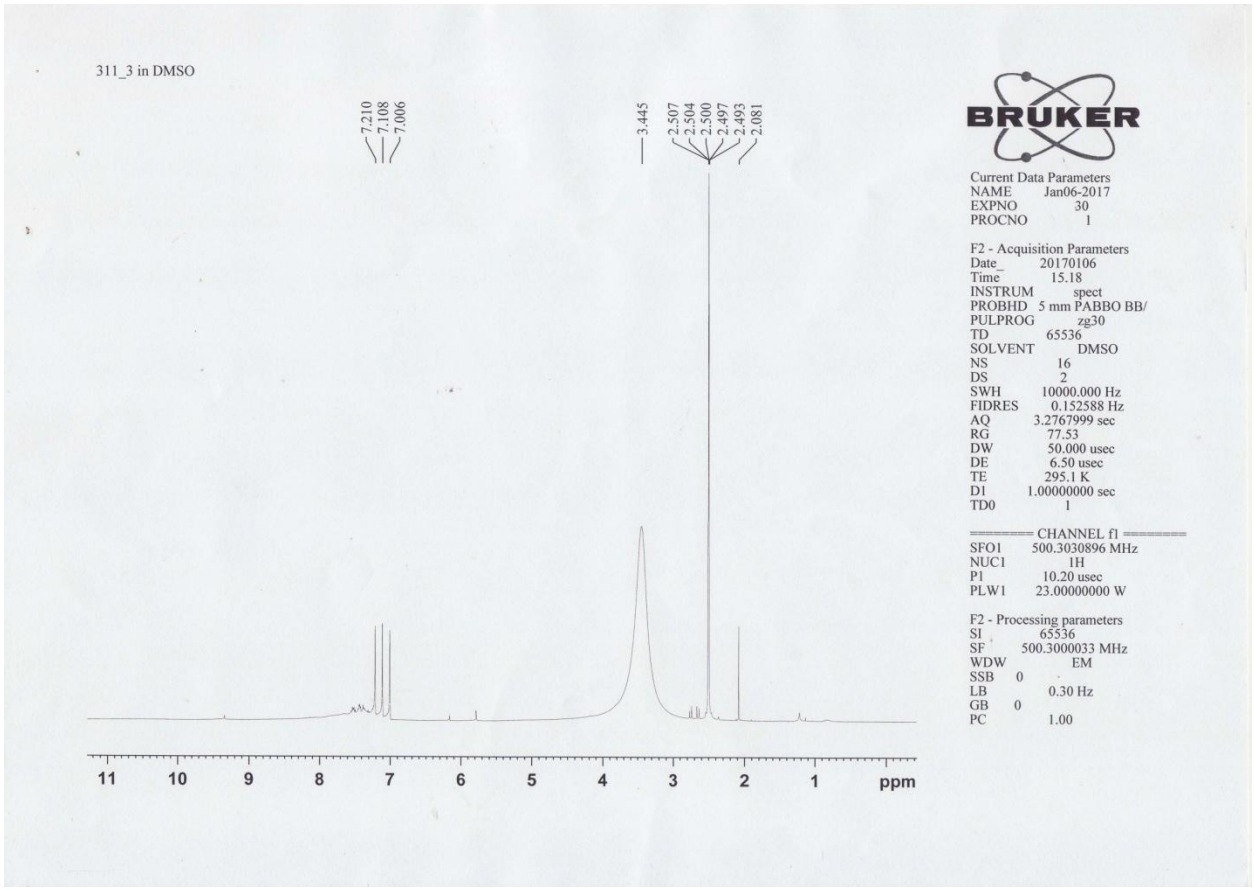


Figure S 9: Comparative electronic spectra for PANI-HCl, PANI-citric acid and PANI-lemon

(before and after treatment with dilute solution of catechol).

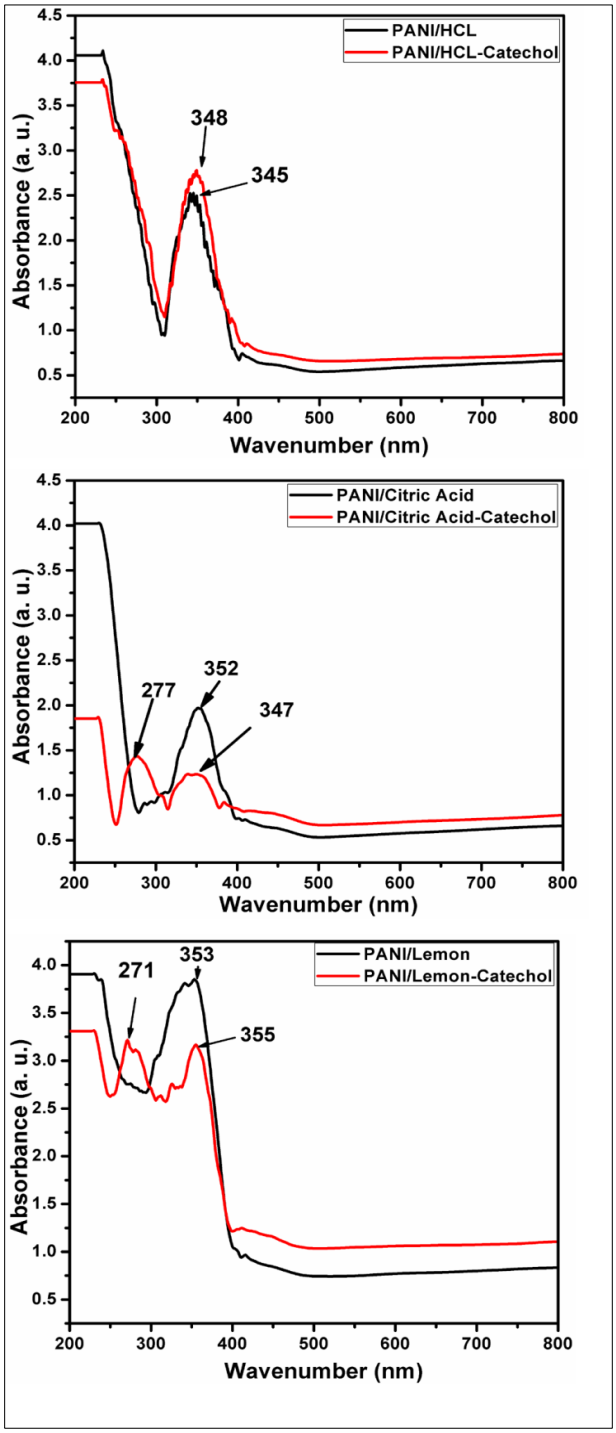


Figure S10: Effect of pH

Supplementary information 10A: Cyclic Voltammograms of carbon paste electrodes modified with PANI-lemon in the phosphate buffer solution of different pH- 1, 3, 5 and 7.

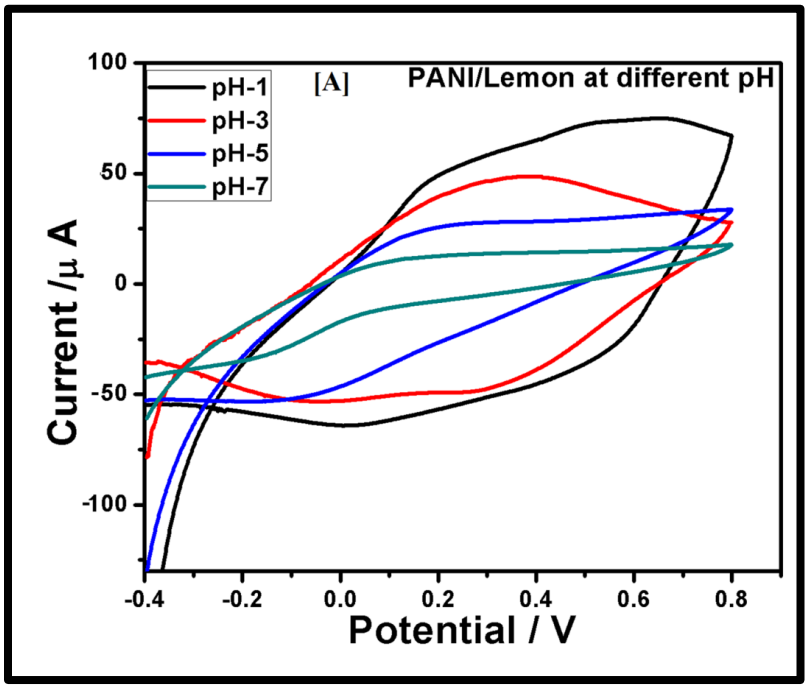
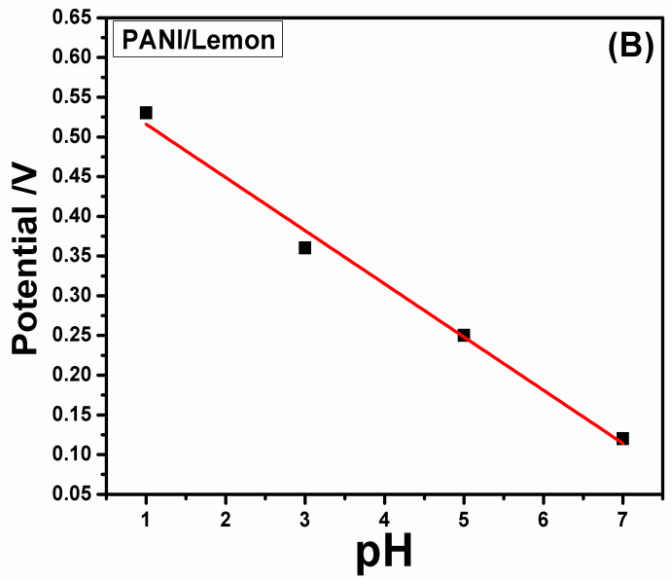


Figure S 10 B, C: Variation in peak potential and peak current with respect to variation in pH of the solution



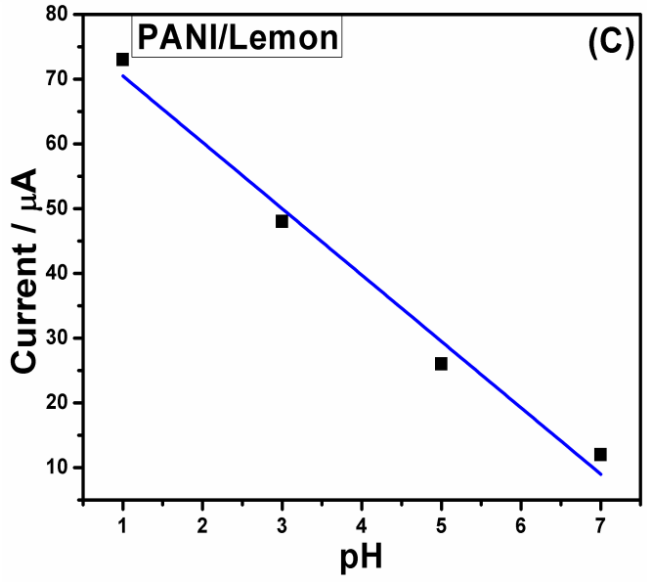


Figure S 11:

Cyclic voltammograms of PANI (L) and PANI (H)

Effect of lemon juice concentration on electrochemical behavior and catechol response, A- Cyclic Voltammograms of PANI-Lemon (L) [prepared in lower concentration (0.5%) of lemon juice, B- Cyclic Voltammograms of PANI-Lemon (H) [prepared in higher concentration (2%) of lemon juice]

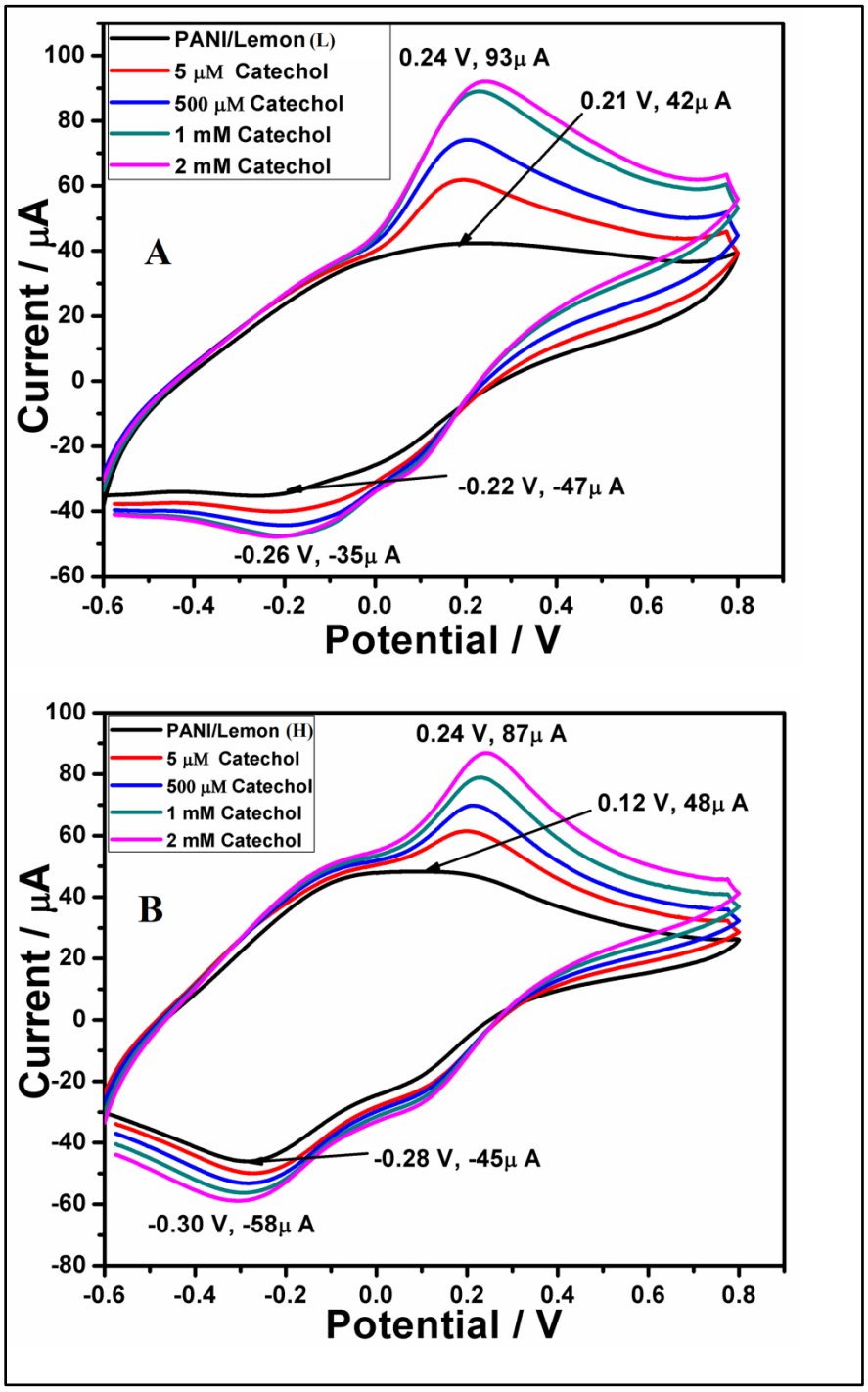


Figure S12: Response of PANI-lemon modified carbon paste electrode in the presence of different concentrations of catechol in PBS-7, (A) DPV (B) Chronoampereometry.

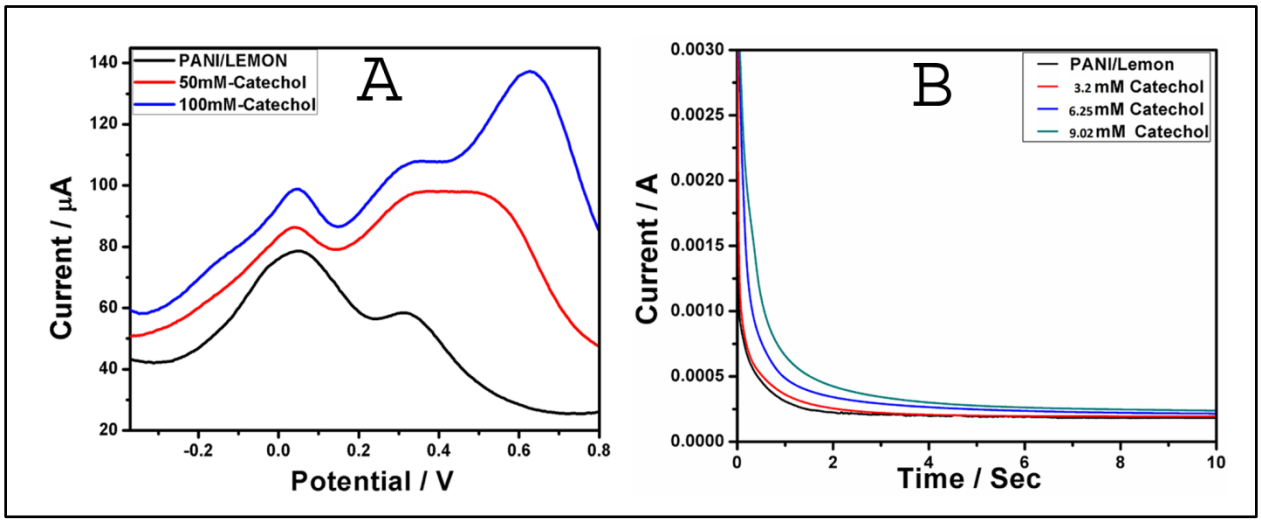


Figure S13 - Cyclic Voltammograms of PANI-lemon modified Graphite paste electrode in Phosphate buffer solution of pH-7 with 1 mM analyte (a) Phenol, (b) Para Nitro Phenol, (c) H_2O_2, (d) Glucose, (e) Gallic acid, (f) Citric acid, (g) Catechol, (h) Adipic acid (i) Ascorbic acid.