

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLETYPE

Self assembled polyaniline nanofibers with enhanced electromagnetic shielding properties

Nina Joseph ^a, Jobin Varghese ^{a, b} and Mailadil Thomas Sebastian ^{*a, b}

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

5 DOI: 10.1039/b000000x

Polyaniline nanofibers have been synthesized by simple chemical polymerization method without using any structure directing agents and organic solvents. Investigated the effect of various reaction conditions on the morphology and electromagnetic interference (EMI) shielding properties of polyaniline nanofibers. Detailed study of various reaction conditions indicates that stable surfactant free, room temperature
10 oxidation of aniline hydrochloride by ammonium persulfate at low oxidant to monomer ratio in acidic media yields self-assembled uniform polyaniline nanofibers. The nanofibers have excellent EMI shielding efficiency of about 71-77 dB in the frequency range of 8.2-18 GHz.

1. Introduction

The emerging growth of the electric and electronic industry leads
15 to increased use of electronic products and telecommunication equipments which in turn cause the problem of electromagnetic interference (EMI). EMI has received attention, as it affects human health, reduces the lifetime and performance of the instruments. It also affects the safety operation of many electronic
20 devices from day to day life to space exploration.¹ This problem can be solved by shielding all electronic equipments against electromagnetic interference.² Shielding of electromagnetic radiation in the microwave frequency region unusually high
25 frequencies of 8.2-18 GHz (X and Ku band) has great importance because of its utilization in the commercial, military and biological fields.¹ Extensive research has done for the development of new lightweight microwave shielding materials with high efficiency and strength. In aerospace applications, metallic shields are commonly used but have the disadvantages of
30 high density and weight.³

Over the past few decades, conducting polymers have been an area of immense interest owing to the growing technological applications. The applications are in rechargeable batteries,^{4,5} EMI shielding,^{6,7} microelectronics,^{8,9} sensors,^{10,11} electrochromic
35 displays,¹² photovoltaic devices¹³ etc. That is due to their light weight, versatility, processability and tunable electrical properties.¹⁴⁻¹⁷ Among the various conducting polymers, polyaniline (PANI) has gained particular attention for use in commercial applications. That is because of its superior
40 conductivity control through doping with relatively natural polymerization of high yield, low cost, low density, environmental stability, interesting redox reversibility and excellent corrosion resistance.¹⁸⁻²⁴ Hence polyaniline finds potential applications as corrosion protection of metals, light-emitting devices, biocompatible materials, catalysts, electrodes,
45 sensors, control of electromagnetic radiation and antistatic

coatings.²⁵⁻²⁹ The intrinsic conductivity of polyaniline makes it a viable material in the field of EMI shielding over wide frequency range of 100 MHz-20 GHz. In addition, polyaniline exhibits
50 notable EMI shielding through absorption that provides shielding against potential internal EMI, which differs from the dominant metal based shielding mechanism of reflection which is very interesting for military applications.³⁰ Mn_{0.5}Zn_{0.5}Fe₂O₄ polyaniline composite prepared by in situ emulsion
55 polymerization exhibits shielding effectiveness (SE) of 35 dB in the X-band (8.2 - 12.4 GHz).³¹ While the polyaniline-MWCNT nanocomposites has EMI SE of about 28-39 dB in the Ku-band (12.4-39.2 GHz) frequency range.³¹ EMI shielding of 55 dB obtained in the Ku-band for DBSA (Dodecyl Benzene Sulfonic
60 Acid) doped polyaniline nanostructures.³² Polyaniline tubes consisting of reduced graphene oxide decorated with iron oxide nanoparticles exhibit a shielding effectiveness of 51 dB in the X-band.³³ In Recent times, Polyaniline based composites report shielding effectiveness of 100 % at X and Ku-band frequency
65 range.³⁴ As a result, polyaniline based EMI shielding materials are of high demand.

Nanofiber is the most attractive nanostructure of polyaniline because of large aspect ratio, high specific surface area, and excellent processability.³⁵ Traditional polymerization with
70 common mineral acids produces polyaniline with granular morphology.³⁶ Many synthetic methods have been developed to synthesize one-dimensional polyaniline structures through aniline chemical oxidation assisted by templates like zeolite, track-etched polymeric membranes, anodized alumina, polymer fibers etc.³⁷⁻⁴⁰
75 Another method of synthesis of nanofibers is by the addition of surfactants that act as structure directing agents.⁴¹⁻⁴⁵ There are several other approaches for the synthesis of polyaniline nanofibers such as interfacial polymerization, seeding polymerization, dilute polymerization, ultraviolet light, gamma
80 ray radiation, ultrasonic irradiation, microwave assisted polymerization., etc.^{36,46-52} Most of these methods yield nanofibers on a limited scale, often require tedious synthesis

process as well as post-synthesis process to remove templates and surfactants. In the present case, we report a simple, template or emulsifier free (self-assembled)⁵³ synthesis of an excellent EMI shielding polyaniline nanofibers at room temperature by chemical polymerization route. The present paper investigated the effect of

Table 1 Reaction conditions and conductivity of prepared polyaniline nanofibers

reaction medium, surfactant, temperature, stirring and reaction time on the morphology and shielding properties of polyaniline nanofibers in the frequency range of 8.2-18 GHz.

No	APS/ Aniline hydrochloride	Solvent	Temperature (°C)	Surfactant	Stirring	Reaction time (hrs)	Sample code	Conductivity (S/cm)
1	1.35	water	0	0.12 SDBS	No	36	P1	0.06
2	1.35	1 M HCl	0	0.12 SDBS	No	36	P2	1.50
3	1.35	1 M HCl	RT(28)	0.12 SDBS	No	36	P3	6.00
4	1.15	1 M HCl	RT (28)	0.12 SDBS	No	36	P4	11.00
5	1.35	1 M HCl	RT (28)	No	No	36	P5	10.00
6	1.15	1 M HCl	RT (28)	No	No	36	P6	18.50
7	1.35	1 M HCl	RT (28)	No	Yes	36	P7	7.50
8	1.15	1 M HCl	RT (28)	No	Yes	36	P8	14.50
9	1.15	1 M HCl	RT (28)	No	No	1	P9	9.00
10	1.15	1 M HCl	RT (28)	No	No	12	P10	10.70
11	1.15	1 M HCl	RT (28)	No	No	60	P11	15.00

2. Methodology and characterization

The reactants used in the synthesis of polyaniline were aniline hydrochloride monomer (Alfa Aesar, Ward Hill, MA, USA), ammonium persulfate (APS) (Aldrich, Chemical Company, Inc., Milwaukee, WI, USA) and sodium dodecylbenzenesulfonate (SDBS) (Aldrich, Chemical Company, Inc., Milwaukee, WI, USA). The aniline hydrochloride monomer is less toxic than liquid aniline and persulfate ammonium salt was preferred to the potassium counter part because of its better solubility in water and is a commonly used oxidant. The synthesis was achieved by the drop wise addition of APS dissolved in water into the aniline hydrochloride solution in water with an oxidant monomer molar ratio of 1.35 at 0 °C. Sodium dodecylbenzenesulfonate (SDBS) was used as the surfactant (0.12M) and the reaction mixture was kept undisturbed at 0 °C for 36 hrs.⁴⁵ The polyaniline (emeraldine HCl salt) powder precipitate obtained was filtered and washed with water and methanol to remove excess acids and by products from polymerization. Resulting powder was dried in vacuum oven at 60 °C for 24 hrs. The reaction conditions were varied as given in Table 1 to observe their effects on the formation of polyaniline and its EMI shielding property. In the reaction process, the acidity of the reaction mixture was increased by replacing water with 1 M HCl and temperature at which reaction was kept stable was changed from 0 °C to room temperature (25-30 °C). The surfactant was also removed and the stable condition was changed to stirring for 36 hrs to analyze its effects. As well as the APS to aniline hydrochloride molar ratio was varied from 1.35 to 1.15 and the reaction was kept at different time duration of 1-60 hrs.

The polymerization yield is found to depend on the reaction conditions. The polymerization yield increased from 78 % (P1) to

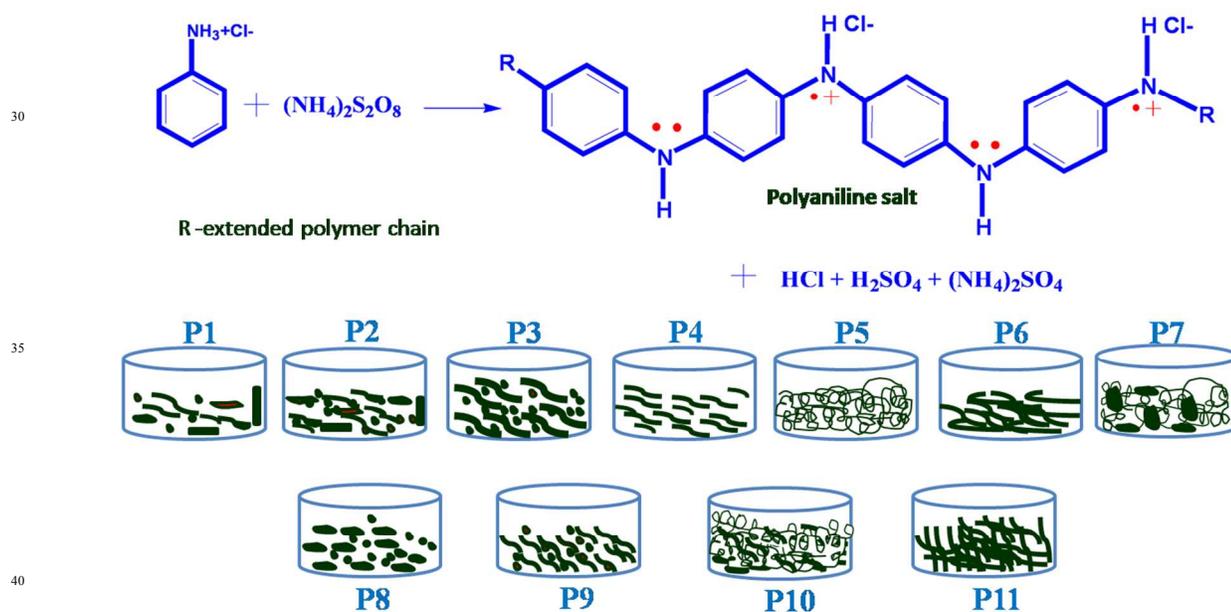
81 % (P2) when the acidity of the reaction mixture was increased, while the reaction temperature was kept fixed at 0 °C. The polymerization yield further increased to 85 % with change in reaction temperature to room temperature (P3). However, with changing APS/aniline hydrochloride molar ratio from 1.35 to 1.15 (P4), the polymerization with the same reaction temperature of room temperature exhibits yield of 89 %. The removal of surfactant further improves the polymerization yield to 91 % for P5 and maximum yield of 95 % is achieved for P6. It is found that higher yield can be achieved by unstirred polymerization, as P7 and P8 exhibit yield of 86 % and 90 % respectively. The polymerization yield obtained when duration of the reaction was varied to 1 (P9), 12 (P10), 60 (P11) hrs was 84 %, 87 % and 93 % respectively. It is clear from these results that higher yields were obtained, as compared with 7-10% for interfacial polymerization,⁵⁴ 13.4-42.3% for rapid mixing polymerization and dilute polymerization.^{55,56}

The morphology of the synthesized polyaniline structures was analyzed using Scanning Electron Microscope (SEM) (JEOL, JSM-5600LV, Tokyo, Japan) and Transmission Electron Microscope (TEM) (FEI Tecnai-G2 30S-TWIN, FEI Company, Hillsboro, OR). The phase purity of the polyaniline was measured using X-ray diffraction (XRD) pattern using CuK α radiation (X'Pert PRO MPD X-ray diffractometer, PANalytical, Almelo, Netherlands) and ¹H NMR spectroscopic measurement was done using Bruker 500 MHz NMR spectrometer. The FTIR analysis was obtained by PerkinElmer spectrum two IR spectrometer and UV-Vis absorption spectrum by Shimadzu 3600 UV-vis-NIR spectrophotometer. The EMI shielding measurements were performed by waveguide method using vector network analyzer (Agilent Technologies E5071C, ENA series, 300 kHz-20 GHz, CA) from the magnitude of complex scattering parameters S₁₁ and S₁₂. The obtained polyaniline powders were pressed into 1 mm thick samples of dimension 22.86 × 10.8 mm for X band (8.2-

12.4 GHz) and 15.80×7.90 mm for Ku band (12.4-18 GHz) frequency range measurements. The DC conductivity of the samples was measured using four probe method from the current and voltage relationships using current source Aplab 9710 P and nanovoltmeter Keithley 2182 A using the same samples used for X band shielding measurements.

3. Results and discussion

The reaction conditions play a vital role in the morphology and properties of polyaniline. Scheme 1 represents the polymerization of polyaniline by the oxidation of aniline hydrochloride by ammonium persulfate (APS) and the products obtained during various reaction conditions. The different reaction conditions and the product designation of the obtained polyaniline structures are depicted in Table 1.



Scheme 1 Polymerization of aniline monomer by ammonium persulfate yielding polyaniline emeraldine salt of varying morphology

The lower the acid concentration, the lower the amount of nanofibers obtained in the final product. A decrease in the acid concentration leads to an increase in the granular particles over the nanofibers which are clear from Figure 1 (a) and (b). Aniline monomer themselves is considered as molecular templates for the growth of polyaniline nanofibers which is further enhanced by the increase in acid concentration.⁵⁷ The HCl which is a strong polar solvent may play an important role in connecting the polyaniline particles leading to the self-assembled fiber structure by suppressing secondary growth.⁴⁶ The obtained fibers are non-uniform with average diameter less than $1 \mu\text{m}$.

3.1.2 Effect of reaction temperature

The nucleation behaviour of polyaniline depends on the polymerization rate and hence is temperature sensitive.⁴⁶ At lower temperature of 0°C , the new nuclei will more likely to create heterogeneous nuclei which induce aggregation. Hence granular particles could be obtained and is evident in the SEM images given in Figure 1 (a) and (b). Excessive active centres and quick reaction rate in the reaction process is achieved with

3.1. Morphology

3.1.1. Effect of reaction medium

The polyaniline morphology appears to be affected by the solvent used in the polymerization process. Non-uniform agglomerated fibers (P1) of varying sizes along with granular and rod structures are observed for polymerization carried out in water medium (Figure 1 (a)). A change in the morphology is observed for 1 M HCl (P2) with some polyaniline tubes also obtained along with fibers, rods and particles as depicted in Figure 1 (b). The fibrillar polymer growth is found to be enhanced with 1 M HCl, since the quality and uniformity of polyaniline is affected by the acid concentration in the aqueous phase.³⁶

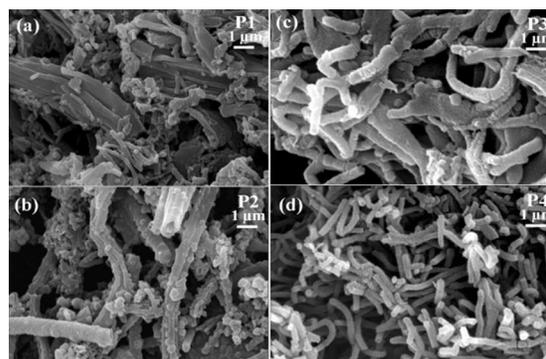


Fig. 1 SEM images of synthesized (a) P1 (b) P2 (c) P3 and (d) P4 powders

increase in temperature (P3) which in turn leads to higher transient concentration. Hence nanofibrous structure of polyaniline with average diameter of 750 nm is obtained as shown in Figure 1 (c). The nanofibers are found to be more uniform in size and appearance with fewer particle aggregates, when polymerization is carried out at room temperature (28°C).

3.1.3 Effect of oxidant monomer molar ratio

The monomer to oxidant ratio has significant effect on the morphology of synthesized polyaniline. Nanofibers with more uniform diameter of about 500 nm and shorter length (nanorods) are obtained with change of oxidant monomer molar ratio from 1.35 to 1.15 (P4) as depicted in Figure 1(d). The obtained nanofibers look similar both in size and uniformity. Granular particles will be formed when ammonium persulfate (oxidant) content is low due to insufficient activation centres which results in secondary nucleation. High oxidant content leads to excess active centres which hinder one dimensional growth and coral like aggregates are formed. The oxidant monomer molar ratio of 1.15 and 1.35 can yield polyaniline nanofibers as evident from the SEM images Figure 1 (d) and (c) respectively.

3.1.4 Effect of surfactant

Fine fibrous structure of polyaniline with smaller diameter and clean surfaces are obtained with the removal of surfactant for both molar ratios as shown in Figure 2 (a) and (b) (P5 and P6). The obtained nanofibers are more uniform in diameter than those with surfactant.

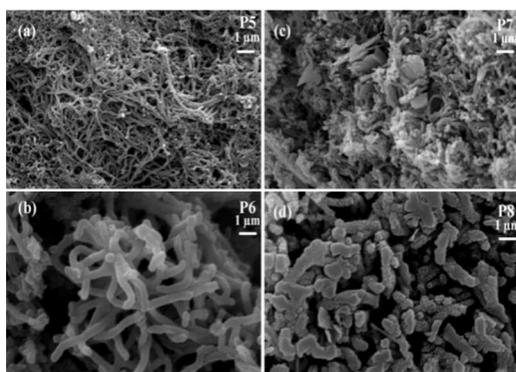


Fig. 2 SEM images of synthesized (a) P5 (b) P6 (c) P7 and (d) P8 powders

This may be due to the presence of some amount of surfactant on the surface of nanofibers which deteriorates its quality. The average diameter of nanofibers obtained are 100 and 200 nm respectively for oxidant monomer molar ratio of 1.35 (P5) and 1.15 (P6). The nanofibers synthesized with oxidant to monomer molar ratio of 1.15 have good uniformity in diameter and are found to be interconnected to form branched structures. The formation of nanofibers synthesized with oxidant monomer ratio 1.35 is found to be incomplete. There are regions of coagulation along with some particles as evident from the SEM image (Figure 2 (a)), which indicate that the formation of polyaniline nanofibers is not uniform.

3.1.5 Effect of stirring

The stable preparation condition is varied by providing a constant stirring of 600 rpm for 36 hrs and is found to have affected the morphology of polyaniline nanofibers for both molar ratios (P7 and P8). Fibrous morphology appears to be destroyed with stirring and hence broken fibers are obtained for both molar ratios (1.35 and 1.15) as evident from Figure 2 (c) and (d) respectively. Mechanical shear force leads to the collision of initial nanofibers inducing heterogeneous nucleation resulting to the loss of fibrillar morphology.⁵⁸

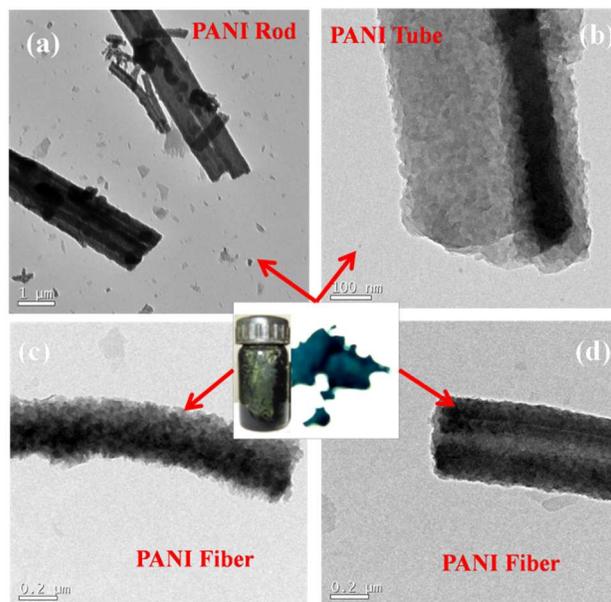


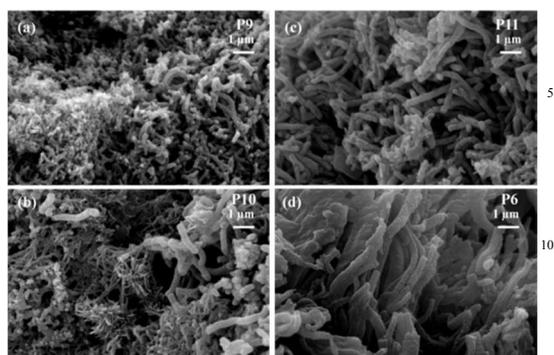
Fig. 3 TEM images of synthesized polyaniline structures

The TEM images of the polyaniline obtained by varying the reaction conditions are given in Figure 3, which gives the morphology of obtained polyaniline (PANI) rods, tubes and fibers. PANI rods shown in figure 3 (a) are of shorter length and are obtained with oxidant monomer molar ratio of 1.15 at room temperature for reaction time of 36 hrs in the presence of surfactant (P4). The PANI tube (figure 3 (b)) with tubular morphology is observed with increase in the acidity of the reaction medium for oxidant monomer molar ratio of 1.35 at 0 °C (P2). The PANI fiber depicted by the TEM image given in figure 3 (c) is synthesized with oxidant monomer molar ratio of 1.15 (P6) at room temperature for reaction time of 36 hrs without any surfactant. On the other hand, the PANI fiber (P3) synthesized with oxidant monomer molar ratio of 1.35 at room temperature for reaction time of 36 hrs in the presence of surfactant is depicted in the figure 3 (d). The diameter of these two PANI fibers is different and was synthesized at different reaction conditions.

3.1.6 Effect of reaction time

The reaction time is found to play an important role to obtain high quality uniform sized nanofibers. The reaction time of the reaction process with molar ratio 1.15 is varied for 1, 12 and 60 hrs (P9, P10, P11) and is found to influence the morphology significantly as shown in Figure 4 (a), (b) and (c) respectively. It can be found that the diameter of nanofibers obtained is not uniform for 1 hr and 12 hrs of reaction time, while that for 60 hrs no significant improvement is observed. Thus reaction time of 36 hrs is observed to be ideal to obtain uniform nanofibers (P6). The fractured surface of uniaxially pressed rectangular sheet of polyaniline nanofibers (P6) is shown in Figure 4 (d) which clearly reveals that the fibrous morphology is maintained after pelletization. Uniform sized nanofibers are obtained without using any structural directing molecules at room temperature due to the combined effect of various reaction conditions. The acid complexes with the monomer to form micelles that guide the self-assembled growth of nanofibers formed at the initial stage of polymerization. The room temperature facilitates the reaction process while the stable condition promotes the growth of fibers

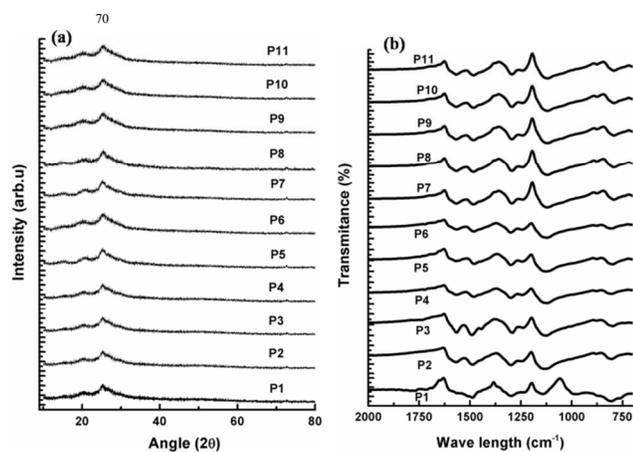
which all leads to the suppression of secondary growth of polyaniline yielding uniform polyaniline nanofibers.⁵⁹



15 **Fig. 4** SEM images of (a) P9 (b) P10 (c) P11 powders and (d) fractogram of the sheet of P6

3.2 Structural characterization

The crystallinity and orientation of conducting polymers are of great interest, as highly ordered systems have a metallic
20 conductive state. X ray diffraction pattern of metallic polyaniline consist of three peaks at 2θ values of 15° , 20° and 25° .⁶⁰ The XRD of the synthesized polyaniline nanofibers (Figure 5 (a)) also has three peaks at 2θ values of 15° , 20° and 25° indicating the crystallinity of the obtained nanofibers. The peaks centred at 20°
25 and 25° respectively correspond to the periodicities parallel and perpendicular to the polymer chain. The peak at 2θ of 25° indicates the formation of doped polyaniline nanofibers since this
30 peak is the characteristic of highly doped emeraldine salt of polyaniline.⁶¹ The formation of doped polyaniline nanofibers is also evident from the spectroscopic studies. The ^1H NMR spectrum of P6 in DMSO- d_6 is shown in the Figure S1 (Supporting Information). The solvents resonate at 2.5 ppm from the residual d_6 and the polyaniline nanofibers (emeraldine salt)



70 **Fig. 5** (a) XRD and (b) FT-IR spectra of synthesized polyaniline nanofibers at various reaction conditions

resonate at 7.01, 7.11, 7.22 ppm due to the presence of proton on
35 phenylene and distributed phenylene units.⁶²

The FTIR spectra of the obtained polyaniline nanofibers are depicted in the Figure 5 (b). The band at 804 cm^{-1} confirms the para-coupling structure of the polymer as it correspond to the out of plane deformation of C-H in the 1,4-di substituted benzene ring, which is identical to emeraldine salt of polyaniline.^{63,64} The
40 band around 1300 cm^{-1} correspond to C-N stretching of secondary aromatic amine. The band characteristic of conducting protonated polyaniline is found at 1240 cm^{-1} , which corresponds to π electron delocalization induced in the polymer by
45 protonation. The characteristic absorption peaks around 1490 cm^{-1} and 1560 cm^{-1} are attributed to the C=C stretching mode of benzenoid (B-NH-B) and quinonoid (-N= Q= N) rings respectively.⁶⁵⁻⁶⁷ The band observed at 1140 cm^{-1} of P1 corresponds to C-H flexural vibration of aromatic ring and is
50 associated with the high degree of electron delocalization which is the characteristic of conducting polyaniline. This peak shifts to lower frequency of around 1120 cm^{-1} for all other polyaniline nanofibers indicating their high doping degree due to the
55 increased concentration of HCl during their synthesis.^{64,46} These results agree with the conductivity and EMI shielding properties of these nanofibers and are higher than that of P1. The solid state absorption spectra depicted in Figure 6 (a) reveals the emeraldine state of obtained nanofibers with two prominent bands attributed to the π - π^* transition and charge transfer exciton transition
60 formed in a benzenoid ring with its adjacent quinoid ring.³¹ The protonated emeraldine form of obtained polyaniline nanofibers is confirmed by the presence of three distinct bands in the absorption spectra of P6 in DMSO given in Figure 6 (b). The additional absorbance at 410 nm corresponds to polaron- π^*
65 transition is the characteristic of emeraldine salt of polyaniline suggesting the presence of polaronic concentration.^{33,68} These polarons interact effectively with the incident EM radiation leading to the good EMI shielding properties of obtained polyaniline nanofibers as shown in Figure 6 (c).

3.3 Conductivity and EMI shielding effectiveness

The conductivity of the synthesized polyaniline structures are given in Table 1. It is observed that the synthesis conditions had a
75 considerable effect on the conductivity of the synthesized polyaniline structures. The electrical conductivity increases from 0.06 S/cm (P1) to 1.5 S/cm (P2) with change in reaction medium from water to 1 M HCl. Conductivity of 6 S/cm is obtained when polymerization temperature is increased from 0°C to room
80 temperature (P3). Change of molarity further improves the conductivity and increases to 11 S/cm (P4) with change in oxidant monomer molar ratio from 1.35 to 1.15 at room temperature. Conductivity of 10 S/cm (P5) and 18.5 S/cm (P6) is achieved by the removal of surfactant for oxidant monomer molar
85 ratio of 1.35 and 1.15 respectively. The conductivity is found to be decreased with stirring as well as with change of reaction time. These results conclude that all these polyaniline structures exhibit high conductivity which can provide good EMI shielding properties⁶⁹ and is evident from figure 6 (c).

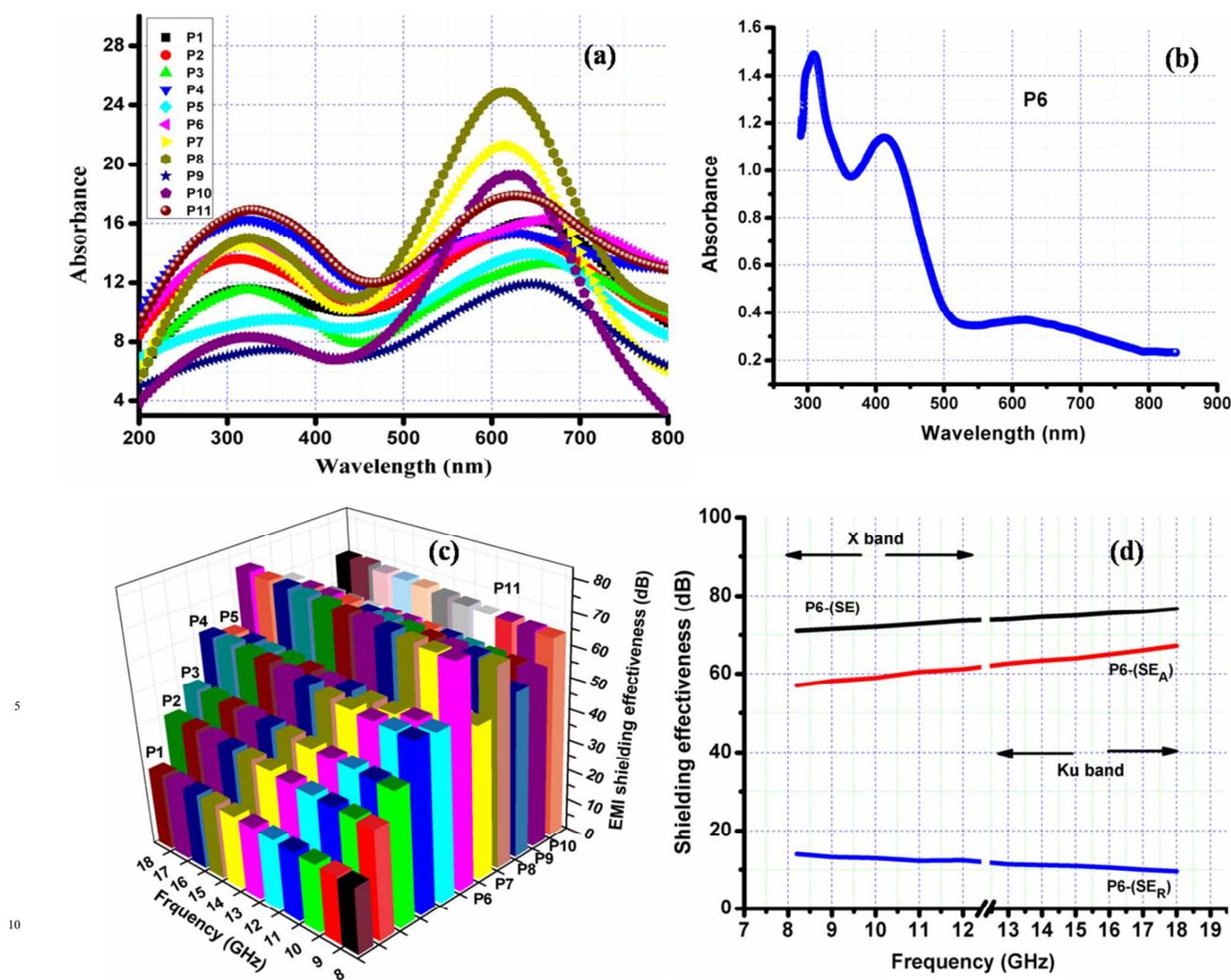


Fig. 6 (a) Solid state UV-Vis spectra of polyaniline nanofibers (b) Absorbance spectrum of P6 in DMSO, frequency dependence of (c) SE of synthesized polyaniline nanofibers and (d) SE, SEA and SER of P6 in the frequency range of 8.2-18 GHz

The electromagnetic interference (EMI) shielding effectiveness (SE) is the measure of shielding against the penetration of electromagnetic radiation into a material. It includes the measure of power lost due to absorption (absorption shielding effectiveness (SE_A)) and reflection by the material (reflection shielding effectiveness (SE_R)) during transmission. It is given as

EMI shielding effectiveness

$$SE \text{ (dB)} = SE_R + SE_A,$$

$$SE_A \text{ (dB)} = -10 \log [(S_{21}^2)/(1 - S_{11}^2)]$$

$$SE_R \text{ (dB)} = -10 \log (1 - S_{11}^2),$$

where S_{11} and S_{12} are the magnitude of scattering parameters.^{70,71}

The frequency variation of the SE of polyaniline nanofibers in the X and Ku band frequency range (8.2-12.4 & 12.4-18 GHz) is given in the Figure 6 (c). It is found that the shielding effectiveness is greatly influenced by the synthesis conditions. The polyaniline synthesized with monomer oxidant molar ratio of 1.35, stable for 36 hrs at 0 °C with water as reaction medium (P1)

has average SE of 23 dB and increases to 38 dB with 1 M HCl medium (P2) over the measured frequency range. This increase in the shielding effectiveness is due to the dual advantage provided by the increase in acid concentration. It enhances nanofibrillar morphology of the polymer resulting in the larger amount of nanofibers. Polymerization proceeds faster in the presence of excess 1 M HCl i.e at higher acidity than in its absence and serves as the anion dopants to yield a product of enhanced conductivity.⁷² An increase in the shielding effectiveness is observed with change in the reaction temperature from 0 °C to room temperature (P3) and average SE of 45 dB is obtained. An increase in the rate of reaction with increase in temperature leads to the formation of more nanofibers. The formed nanofibers provide connectivity for the charge carries which improves the conductivity and thus enhance the shielding property.

The change of oxidant to monomer molar ratio to 1.15 (P4) leads to further increase in the average SE to 58 dB in the X and Ku band frequency range. This may be due to the formation of increased amount of uniform sized nanofibers with good conductivity at this molar ratio. The removal of surfactant further improves the shielding efficiency and average SE for molar ratio

1.35 increases from 45 dB of P3 to 56 dB for P5, while that for 1.15 molar ratio the increase is from 58 dB of P4 to 74 dB (P6) in this frequency range. This can be attributed to the formation of more uniform polyaniline nanofibers without surfactants and presence of trace amount of surfactant on the surface of nano fibers may also degrade their conducting property.

The shielding effectiveness of P7 and P8 at the measured frequency range indicates that stirring for 36 hrs degrades the shielding property. This is due to the damage of fibrillar morphology by stirring as clear from Figure 2 (c) and (d) which leads to the decrease in conductivity as. All the observed results indicate that among all the synthesized polyaniline fiber structures, P6 which is the surfactant free polyaniline with good morphology of uniform sized nanofibers (Figure 2 (b) and 4 (d)) has good shielding effectiveness. This polyaniline is obtained by keeping the reaction stable for 36 hrs at room temperature in excess of 1 M HCl with 1.15 oxidant to monomer molar ratio as given in the Table 1. The effect of reaction time on the SE is analyzed by varying the reaction time of P6 and found that the reaction time also influences the shielding property of polyaniline structures. The P9 is found to have low shielding effectiveness than P10 at this frequency range. This is due to non-uniform polyaniline nanofibers obtained for 1 hr and 12 hrs of reaction time (Figure 4 (a) and (b)). The 60 hrs reaction time slightly decrease the shielding effectiveness and average SE of 67 dB is obtained in the 8.2-18 GHz frequency range. The SE of all the obtained polyaniline nanofibers shows a slightly increasing trend with frequency due to the increase in the conductivity with frequency.⁷³

The total shielding effectiveness is the combined effect of SE_A and SE_R . The frequency dependence of SE, SE_A and SE_R of P6 over the X and Ku band frequency range is shown in Figure 6 (d). The SE of P6 is almost independent of frequency with slightly increasing trend and varies from 71-77 dB. Hence it can provide a broad band width for shielding. The SE_A is showing an increasing trend with frequency and increases from 57-67 dB in the measured frequency range. A decreasing trend with frequency is observed for SE_R and varies from 14-10 dB in the 8.2-18 GHz frequency range indicating that the dominant shielding mechanism is absorption. All other synthesized polyaniline structures also follows similar trend with absorption as the dominant shielding mechanism. Thus uniform sized polyaniline nanofibers with excellent shielding property are obtained which can prove to be potential candidates for EMI shielding applications.

Conclusion

Polyaniline nanofibers were synthesized by chemical oxidation of aniline hydrochloride by ammonium persulfate. The effect of solvent, temperature, surfactant, stirring, reaction time, and oxidant to monomer molar ratio on the morphology and EMI shielding properties of polyaniline nanofibers were investigated to generate nanofibers of good morphology with excellent shielding properties. Based on the results it was observed that these reaction conditions greatly influence the morphology and EMI shielding property of synthesized polyaniline nanofibers. Uniform polyaniline nanofibers of average diameter 200 nm and EMI shielding effectiveness of 71-77 dB was obtained in the frequency range of 8.2-18 GHz. This polyaniline nanofiber was synthesized by a simple surfactant free room temperature oxidation of aniline hydrochloride by ammonium persulfate at

stable condition for 36 hrs with oxidant to monomer molar ratio of 1.15 in an excess of 1 M HCl. Hence a simple, economic, scalable and environmentally friendly synthesis method is achieved to attain uniform nanofibers with attracting EMI shielding properties which elucidates the difficulties in other tedious nanofiber synthesis methods.

Notes and references

^a Department of Electrical Engineering, Microelectronics and Materials Physics Laboratory, University of Oulu, 90570 Finland

⁷⁰ E-mail: mailadils@yahoo.com,

^b Materials Science and Technology Division, CSIR-NIIST, Thiruvananthapuram, Kerala, India.

⁷⁵ † Electronic Supplementary Information

¹H NMR spectroscopy of P6 in DMSO-d₆

- [1] N. Joseph, S. K. Singh, R. K. Sirugu du, V. R. K. Murthy, S. Ananthakumar, M. T. Sebastian, *Mater. Res. Bull.* 2013, 48, 1681, H. A. Reshi, A. P. Singh, S. Pillai, R. S. Yadav, S. K. Dhawan and V. Shelke, *J. Mater. Chem. C*, 2015, Advanced Article, DOI:10.1039/C4TC02040E.
- [2] D. A. Weston, *Electromagnetic Compatibility: Principles and Applications*, Marcel Dekker, New York 2001, X. C. Tong, *Advanced Materials and Design for Electromagnetic Interference Shielding*, CRC Press, United States 2009.
- [3] Y. Wang, X. Jing, *Adv. Technol.* 2005, 16, 344.
- [4] Kh. Ghanbari, M. F. Mousavi, M. Shamsipur, *Electrochim. Acta*, 2006, 52, 1514.
- [5] C. Y. Wang, V. Mottaghitalab, C.O. Too, G. M. Spinks, G. G. Wallace, *J. Power Sources*, 2007, 163, 1105.
- [6] A. Bhattacharya, A. De, *Prog. Solid State Chem.* 1996, 24, 141.
- [7] Taka T. *Synth. Met.* 1991,41, 1177.
- [8] J. Unsworth, B. A. Lunn, P. C. Innis, Z. Jin, A. Kaynak, N. G. Booth, *J. Intel Mat. Syst. Str.* 1992, 3, 380.
- [9] Angelopoulos M. *IBM J.Res. Dev.* 2001, 45, 57.
- [10] R. Gangopadhyay, A. De, *Sens. Actuator B*, 2001, 77, 326.
- [11] H. Liu, J. Kameoka, D. A. Czapski, H. G. Craighead, *Nano Lett.* 2004, 4, 671.
- [12] T. Kobayashi, H. Yaneyama, H. Tamura, *J. Electroanal. Chem.* 1984, 161, 419.
- [13] E. W. Paul, A. J. Ri cco, M. S. Wrighton, *J. Phys. Chem.* 1985, 89,1441.
- [14] P. Chandrasekhar, *Conducting Polymers, Fundamentals and Applications: A Practical Approach*, Kluwer Academic, Netherlands 1999.
- [15] T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds, *Handbook of Conducting Polymers*, Marcel Dekker, New York 1998.
- [16] G. Cao, *Nanostructures and Nanomaterials: Synthesis, Properties, and Applications*, Imperial College Press, London 2004.
- [17] A. Kaynak, *Mater. Res. Bul.* 1996, 31, 845.
- [18] J. Joo, *Appl. Phys. Lett.* 1994, 65, 2278.
- [19] P. Alexander, N. Ogurtsov, A. Korzhenko, G. Shapoval, *Prog. Polym. Sci.* 2003, 28, 1701.
- [20] N. Gospodinova, L. Terlemezyan, *Prog. Polym. Sci.*,1998, 23, 1443.
- [21] L. Zhang, M. Wan, Y. Wei, *Macromol. Rapid Commun.*, 2006, 27, 366.
- [22] D. Chen, Y. E. Miao, T. Liu, *ACS Appl. Mater. Interfaces*, 2013, 5, 1206.
- [23] D. K. Moon, M. Ezuka, T. Maruyama, K. Osakada and T. Yamamoto, *Macromolecules*, 1993, 26, 364.
- [24] P. M. McManus, R. J. Cushman, S. C. Yang, *J. Phys. Chem.*,1987, 91, 744.
- [25] S. Bhadra, D. Khatgir, N. K. Singha and J. H. Lee, *Prog. Polym. Sci.*, 2009, 34, 783.

- [26] S. Sivaram, *Polymer Science Contemporary Themes*, Tata McGraw-Hill, India 1991.
- [27] M. Aldissi, *Intrinsically Conducting Polymers: An Emerging Technology*, Kluwer Academic, Netherlands 1993.
- [28] Y. Chen, E. T. Kang, K. G. Neoh, C. H. Wang and K. L. Tan, *Synth. Met.*, 2000, 110, 47.
- [29] C. H. Wang, Y. Q. Dong, K. Sengothi, K. L. Tan and E. T. Kang, *Synth. Met.* 1999, 102, 1313, T. A. Skotheim and J. R. Reynolds, *Handbook of Conducting Polymers third edition: Conjugated Polymers—Processing and Applications*, CRC Press, United States 2007.
- [30] M. A. Dar, R. K. Kotnala, V. Verma, J. Shah, W. A. Siddiqui and M. Alam, *J. Phys. Chem. C*, 2012, 116, 5277.
- [31] P. Saini, V. Choudhary, B. P. Singh, R. B. Mathur and S. K. Dhawan, *Mater. Chem. Phys.* 2009, 113, 919.
- [32] P. Saini and M. Arora, *J. Mater. Chem. A*, 2013, 1, 8926.
- [33] A. P. Singh, M. Mishra, P. Sambyal, B. K. Gupta, B. P. Singh, A. Chandra and S. K. Dhawan, *J. Mater. Chem. A*, 2014, 2, 3581.
- [34] R. R. Mohan, S. J. Varma, M. Faisal and S. Jayalekshmi, *RSC Adv.*, 2015, 5, 5917, P. Sambyal, A. P. Singh, M. Verma, M. Farukh, B. P. Sinng and S. K. Dhawan, *ACS Adv.*, 2014, 4, 12614.
- [35] D. H. Zhang and Y. Y. Wang, *Mater. Sci. Eng. B*, 2006, 134, 9.
- [36] J. Huang and R. B. Kaner, *J. Am. Chem. Soc.*, 2004, 126, 851.
- [37] C. G. Wu and T. Bein, *Science*, 1994, 17, 1757.
- [38] C. R. Martin, *Science*, 1994, 23, 1961.
- [39] R. V. Parthasarathy and C. R. Martin, *Chem. Mater.*, 1994, 6, 1627.
- [40] H. Dong, S. Prasad, V. Nyame and W. E. Jones Jr, *Chem. Mater.*, 2004, 16, 371.
- [41] Z. Zhang, Z. Wei and M. Wan, *Macromolecules*, 2002, 35, 5937.
- [42] W. Li and H. L. Wang, *J. Am. Chem. Soc.*, 2004, 126, 2278.
- [43] G. Li and Z. Zhang, *Macromolecules*, 2004, 37, 2683.
- [44] G. Li, H. Peng, Y. Wang, Y. Qin, Z. Cui and Z. Zhang, *Macromol. Rapid Commun.*, 2004, 25, 1611.
- [45] G. Li, S. Pang, J. Liu, Z. Wang and Z. Zhang, *J. Nanopart. Res.*, 2006, 8, 1039.
- [46] R. Li, Z. Chen, J. Li, C. Zhang and Q. Guo, *Synth. Met.* 2013, 171, 39.
- [47] X. Zhang, W. J. Goux and S. K. Manohar, *J. Am. Chem. Soc.*, 2004, 126, 4502.
- [48] N. R. Chiou and A. J. Epstein, *Adv. Mater.*, 2005a, 17, 1679.
- [49] J. Li, H. Tang, A. Zhang, X. Shen and L. Zhu, *Macromol. Rapid Commun.*, 2007, 28, 740.
- [50] S. K. Pillalamarri, F. D. Blum, A. T. Tokuhiko, J. G. Story, M. F. Bertino, *Chem. Mater.*, 2005, 17, 227.
- [51] X. L. Jing, Y. Y. Wang, D. Wu and J. P. Qiang, *Ultrason. Sonochem.*, 2007, 14, 75.
- [52] M. R. G. Nikolaidis, D. R. Stanisavljev, A. J. Eastal and Z. D. Zujovic, *Macromol. Rapid Commun.*, 2010, 31, 657.
- [53] Y. Yao, E. Metwalli, J. F. Moulin, B. Su, M. Opel and P. Müller-Buschbaum, *ACS Appl. Mater. Interfaces*, 2014, 6, 18152.
- [54] J. X. Huang, S. Virji S, B. H. Weiller, R. B. Kaner, *J. Am. Chem. Soc.* 2003, 125, 314.
- [55] N. R. Chiou, A. J. Epstein, *Synth. Met.* 2005, 153, 69.
- [56] N. R. Chiou, A. J. Epstein, *Adv. Mater.* 2005, 17, 1679.
- [57] N. R. Chiou, L. J. Lee, and A. J. Epstein, *Chem. Mater.*, 2007, 19, 3589.
- [58] D. Li and R. B. Kaner, *J. Am. Chem. Soc.*, 2006, 128, 968.
- [59] H. D. Tran, J. M. D'Arcy, Y. Wang, P. J. Beltramo, V. A. Strong and R. B. Kaner, *J. Mater. Chem.*, 2011, 21, 3534.
- [60] K. Lee, S. Cho, S. H. Park, C. Heeger, W. Lee and S. H. Lee, *Nature*, 2006, 441, 65.
- [61] J. P. Pouget, M. E. Jozefowicz, A. J. Epstein, X. Tang and A. G. MacDiarmid, *Macromolecules*, 1991, 24, 779.
- [62] Shaolinmu and Y. Yang, *J. Phys. Chem. B*, 2008, 112, 11558.
- [63] Y. Zhu, J. Li, H. He, M. Wan and L. Jiang, *Macromol. Rapid Commun.*, 2007, 28, 2230.
- [64] H. Ding, J. Shen, M. Wan and Z. Chen, *Macromol. Chem. Phys.*, 2008, 209, 864.
- [65] S. R. C. Vivekchand, K. C. Kam, G. Gundiah, A. Govindaraj, A. K. Cheetham and C. N. R. Rao, *J. Mater. Chem.*, 2005, 15, 4922.
- [66] H. R. Tantawy, D. E. Aston, J. R. Smith and J. L. Young, *ACS Appl. Mater. Interfaces*, 2013, 5, 4648.
- [67] N. K. Guimard, N. Gomez and C. E. Schmidt, *Prog. Polym. Sci.*, 2007, 32, 876.
- [68] C. C. Yang, Y. J. Gung, W. C. Hung, T. H. Ting and K. H. Wu, *Compos. Sci. Technol.*, 2010, 70, 466.
- [69] R. Ramasubramaniam, J. Chen, H. Liu, *Appl Phys Lett.* 2003, 83, 2928.
- [70] D. Annapurna and K. D. Sisir, *Microwave Engineering*, Tata McGraw Hill, India 2009.
- [71] N. Joseph and M. T. Sebastian, *Mater. Lett.*, 2013, 90, 64.
- [72] J. Stejskal, I. Sapurina, J. Prokeš and J. Zemek, *Synth. Met.*, 1999, 85, 105, 195.
- [73] D. D. L. Chung, *Carbon*, 2001, 39, 279.