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Prologue: Nanofibers

Gustavo M. Do Nascimento

1. Introduction

The preparation of polymers with morphology well determined in the nanometric range is one of the great challenges in the polymer science and technology. The possibility to prepare nanofibers (or nanofibers) brings the opportunity to produce polymers with new or reinforced properties. Many ways have been developed to synthesize polymeric nanofibers, for instance, the polymerization into media having large organic acids. The interfacial polymerization can also form nanofibers at an aqueous-organic interface. Hence, a great variety of “bottom-up” approaches, such as electrospinning, interfacial, seeding, and micellar, can be employed to obtain pure polymeric nanofibers. The preparation of nanostructured polymers by self-assembly with reduced post-synthesis processing warrants further applications, especially in the field of biotechnology and removable resources. The notable applications include tissue engineering, biosensors, filtration, wound dressings, drug delivery, and enzyme immobilization. In this chapter, the state-of-the-art results of synthesis, spectroscopic characterization, and applications of polyaniline nanofibers will be reviewed. The main goal of this work is to contribute to the rationalization of some important results obtained in this wonder area of polymeric nanofibers.

2. Nanofibers

Despite that nanofibers are produced for a long time, only in recent years, the scientific interest in this field has rapidly increased. The reason for that is, probably, owing to the improvement of the synthetic pathways in the production of better nanofibers. In addition, the combination of spectroscopic and microscopic techniques leads to a better correlation between structure and properties of nanofibers. **Figure 1** shows that in 2018, more than 6000 papers having “nanofiber” or “nanofibre” as keyword were published. In addition, **Figure 2** shows that at least 20 different research fields have more than 1000 papers published related to “nanofiber” or “nanofibre.” These two graphs clearly show that nanofibers are one of the focuses in the science of advanced materials.

Our group has dedicated to the preparation and characterization of polyaniline nanofibers [1–10]. Among the different techniques used for structural investigation, resonance Raman spectroscopy is the most important technique for these systems. Thus, in this chapter, mainly the Raman results obtained for polyaniline (PANI) will be discussed.

3. Nanofibers of conductive polymers

Nowadays, the preparation of conductive polymers with organized morphology and structure is a desired deal. Since the discovery of poly(acetylene) doping process

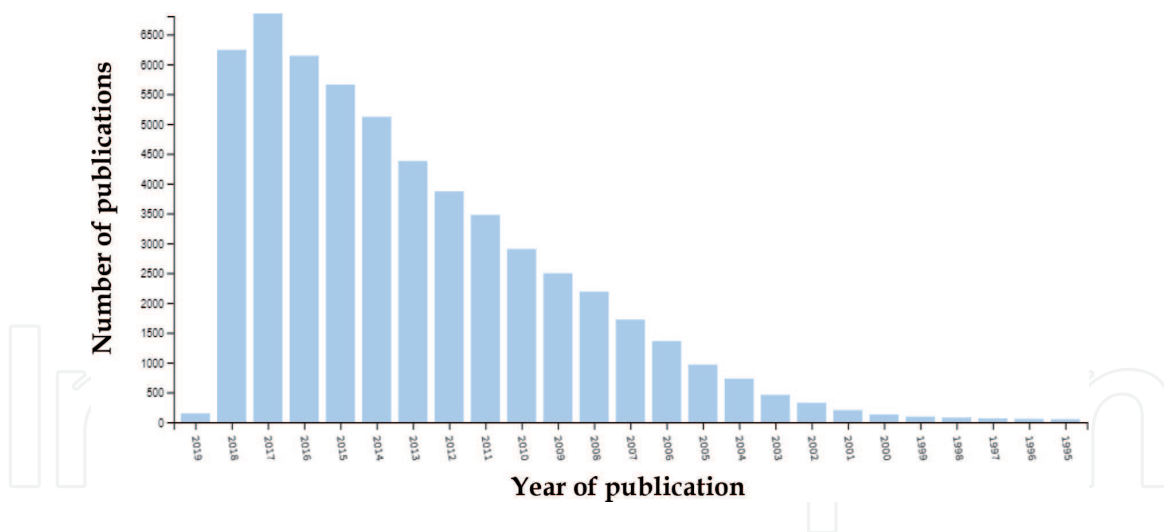


Figure 1.

Number of publications by year having the keyword “nanofiber” or “nanofibre” in the text. The research was done in November 25, 2018, using Web of Science database. The total score found are 54,611 papers.

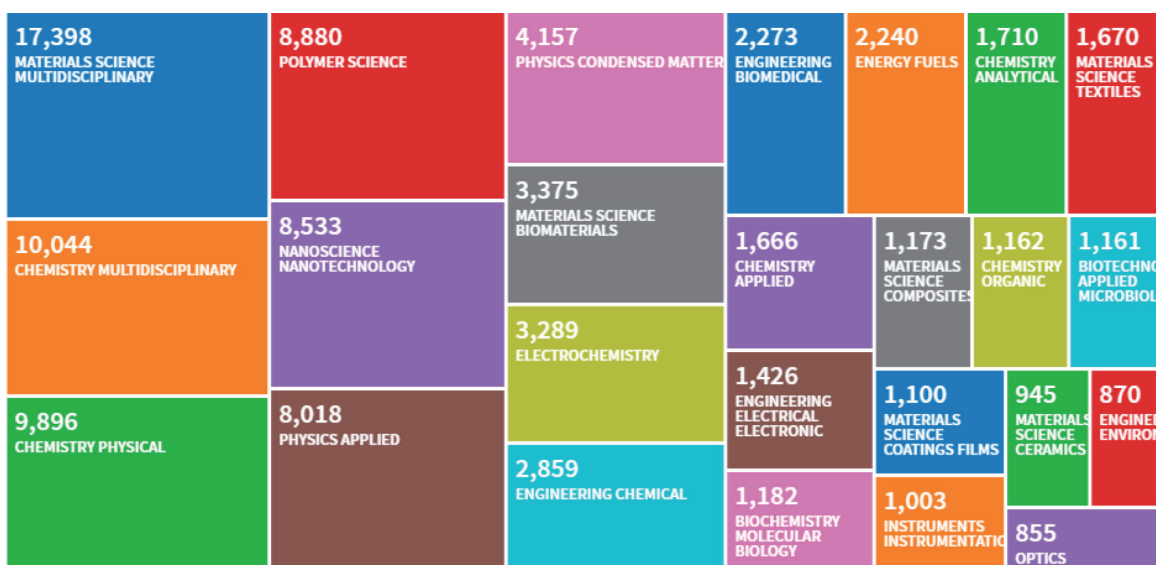


Figure 2.

Number of publications by year having the keyword “nanofiber” or “nanofibre” in the text divided by the main research areas or categories. The research was done in November 25, 2018, by using Web of Science database.

in the early 1970s [11–16] and posterior investigation of its properties mainly done by Hideki Shirakawa, Alan J. Heeger, and Alan G. MacDiarmid (see **Figure 3**), the field of conductive polymers brings many contributions to different applications: from batteries to organic light-emitting diode (OLED) displays. The preparation of nano-structured conductive polymers can turn the polymer more efficiently to applications. The doping process [17–25] in conjugated polymers is characterized by the passage from an insulating or semiconducting state with low conductivity, typically ranging from 10^{-10} to 10^{-5} Scm^{-1} , to a “metallic” regime (ca. $1-10^4 \text{ Scm}^{-1}$; see **Figure 3**).

Reversibility is one main characteristic of chemical doping; in fact, the polymer can return to its original state without major changes in its structure. Counterions stabilize the doped state in the polymeric chain. The conductivity can be modulated only by adjusting the doping level, varying from non-doped insulating state to highly doped or metallic. All conductive polymers (and their derivatives), for example, among others, may be doped by p (oxidation) or n (reduction) through chemical and/or electrochemical process [16–18]. The doping process can also be characterized by no loss or gain of electrons from external

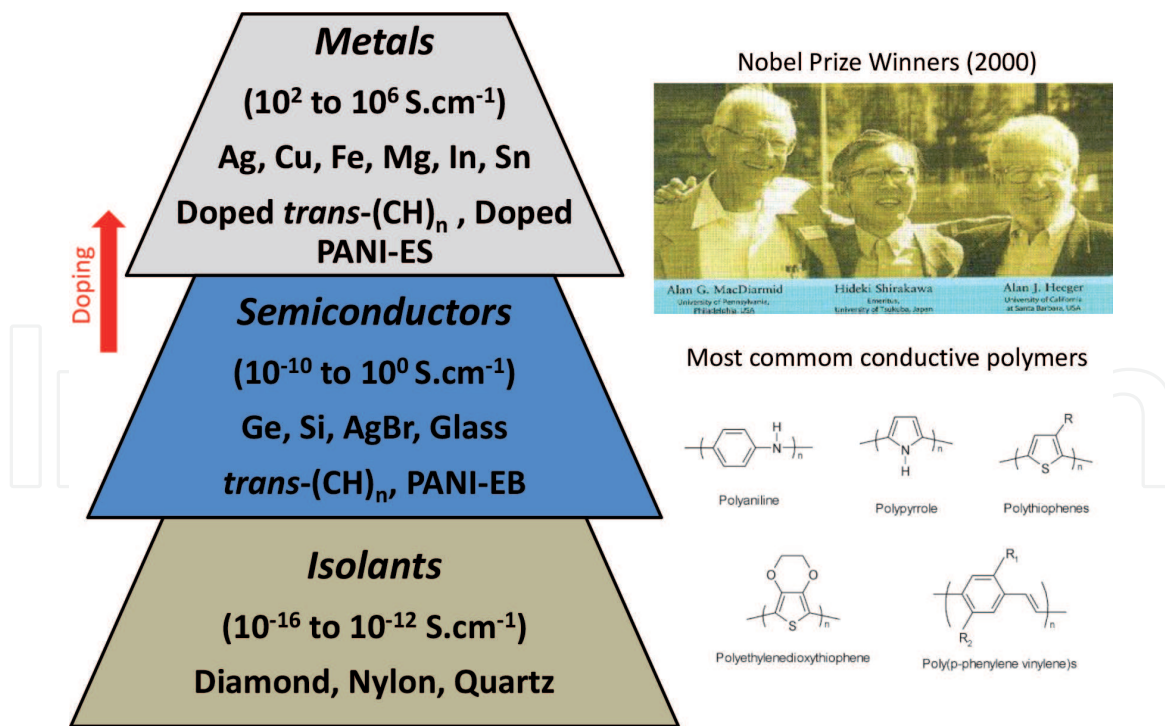


Figure 3. The Nobel winners (Hideki Shirakawa, Alan J. Heeger, and Alan G. MacDiarmid) and the chemical structures of the most common conductive polymers. The conductivity values for different materials are displayed in comparison with conducting polymers before and after the doping process. The doping causes (addition of nonstoichiometric chemical species in quantities commonly low $\leq 10\%$) dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer.

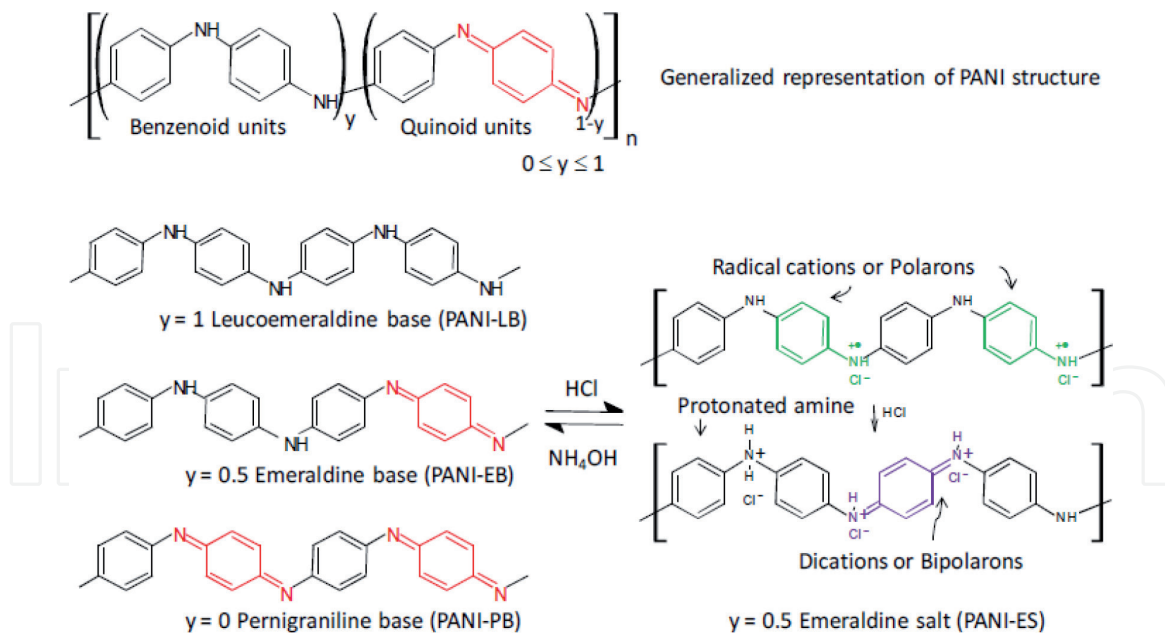


Figure 4. Generalized representation of chemical structure of PANI and its most common forms.

agents. This is the point for polyanilines (see **Figure 4**), and this process is named internal redox process.

PANI-ES is formed after protonation with the appearance of the free radical tail of band in the NIR spectral region (starting from ca. 1.6 eV or 780 nm), which is attributed to a charge transfer from the highest occupied energy level of the benzene ring (HOMO) to the lowest unoccupied energy level of a semiquinone (polarons) ring (LUMO) [25].

PANI nanofibers can be prepared by using different routes, and the resulting polymer shows improvement in its electrical, thermal, and mechanical stabilities. The conventional synthesis of polyaniline, based on the oxidative polymerization of aniline in the presence of a strong acid dopant, typically results in an irregular granular morphology with a very small percentage of nanoscale fibers. Highly uniform PANI nanofibers with diameter ranging from 30 to 120 nm, depending on the dopant, are prepared by interfacial polymerization [26, 27]. The diffusion of the formed product from the interfacial solvent-solvent region to the bulk of the solvent can suppress uncontrolled polymer growth by isolating the fibers from the excess of reagents. In fact, the addition of certain surfactants to such an interfacial system grants further control over the diameter of the nanofibers. Isolation of the nanostructured PANI from the solution can be achieved by filtration in a nanoporous filters or dialyzed, and then the cleaned solution containing the nanofibers is centrifuged in order to separate the nanofibers from the solution.

Another approach is the synthesis of PANI nanofibers or nanotubes by making use of large organic acids. These acids form micelles upon which aniline is polymerized and doped. Fiber with diameters from 30 to 60 nm can be modulated by reagent ratios [28–31]. PANI nanofibers can also be obtained in ionic liquids (ILs) as synthetic media [2, 6]. There is a large variety of ionic liquids, and the most used ones are derived from imidazolium ring, pyridinium ring, quaternary ammonium, and tertiary phosphonium cations. The most unusual characteristic of these systems is that, although they are liquids, they present structural organization and can act as a template-like system, and PANI nanofibers are obtained when the aniline is polymerized in these media.

4. Raman spectroscopy of polyaniline nanofibers

Raman spectroscopy is a technique par excellence for probing the vibrational frequencies by inelastic scattering the incident light (see **Figure 5**) [32–35]. In the conventional Raman spectroscopy, the intensities of the Raman bands are linearly proportional to the intensity of the incident light and proportional to the square of the polarizability tensor. However, when the laser line falls within the region of a permitted electronic transition, the Raman bands that are tightly coupled or associated with the excited electronic state have a tremendous increase of about 10^{5-6} times; this is what characterizes the resonance Raman effect. In the case of multi-chromophoric system, like polyaniline, just by tuning an appropriate laser radiation on an electronic transition of the polymer, the spectrum changes dramatically (see **Figure 6**).

PANI shows a characteristic Raman bands for each oxidized or protonated form [36–40]. The presence of a free carrier tail absorption in the UV–VIS–NIR spectra for both PANI nanofibers/nanotubes prepared with NSA (β -naphthalenesulfonic acid) or with DBSA (dodecylbenzenesulfonic acid) confirmed that polymeric chains have an extended conformation. In addition, the band at 609 cm^{-1} is sensible to conformation changes of the PANI chains [1, 3]. The studies of doping and heating behavior of PANI-NSA nanofibers show the loss of the fibrous morphology of PANI after treatment with HCl solution [4]. However, the PANI nanofibers are more susceptible to cross-linking (bands at 578 and 1340 cm^{-1} ; see **Figure 6**) than conventional PANI, and after heating at 200°C , it is possible to dope the polymer with HCl and maintain the nanostructured morphology.

PANI nanofibers prepared from interfacial polymerization were also characterized by Raman spectroscopy. Bands at 200 and 296 cm^{-1} related to $\text{C}_{\text{ring}}\text{-N-C}_{\text{ring}}$ deformation and lattice modes of polaron segments of PANI practically disappear in the Raman spectra of PANI nanofibers. The changes indicate the increase of the

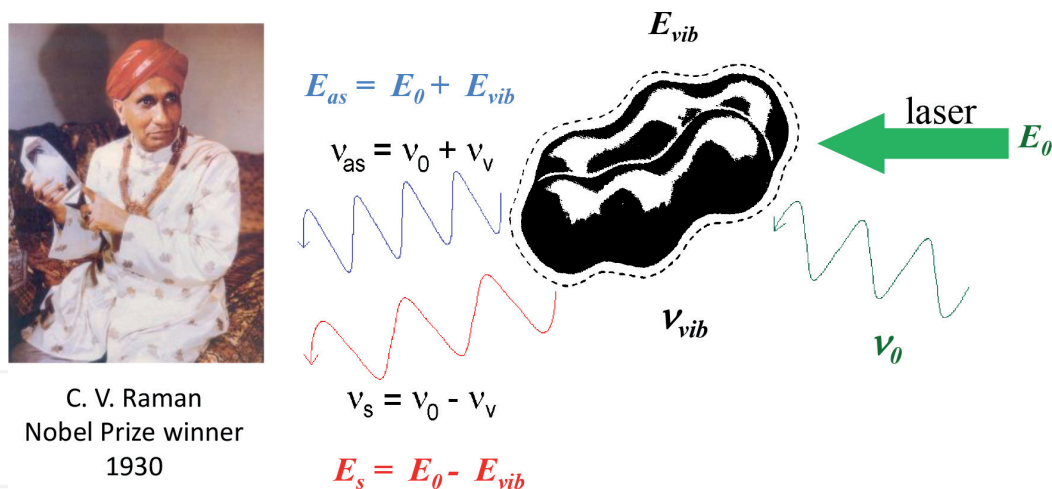


Figure 5. Schematic representation of Raman effect. The Raman scattering was discovered by C. V. Raman and is characterized by inelastic scattering of the incident radiation (ν_0) with laser energy (E_0). The scattered light has two components: Stokes radiation (ν_s) with lower energy than E_0 ($E_s < E_0$) and the anti-stoke radiation (ν_{as}) with higher energy than E_0 ($E_{as} > E_0$).

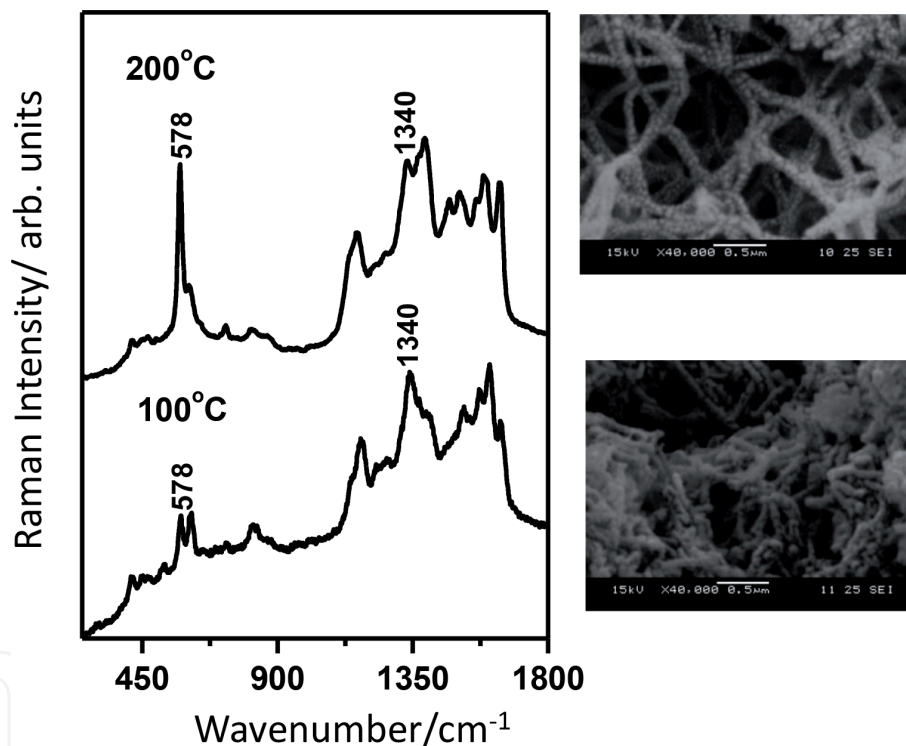


Figure 6. Resonance Raman spectra of PANI-NSA after heating at indicated temperatures and doping with HCl. For comparison the SEM images are also given.

torsion angles of the $C_{\text{ring}}\text{-N-C}_{\text{ring}}$ segments. In addition, the FTIR spectra for PANI nanofibers display higher changes in the region from 2000 to 4000 cm^{-1} . Both data are associated to the formation of bipolarons (protonated, spinless units) in the PANI nanofiber backbone higher than the conventional PANI. The PANI nanofiber morphology permits major diffusion of the ions inside the polymeric matrix leading to a more effective protonation of the polymeric chain [5]. In addition, only for PANI nanofibers with a diameter of 30.0 nm, low dispersion of the $\nu\text{C}=\text{N}$ band is seen (see **Figure 7**). The Raman dispersion is associated to the electron-phonon coupling into a conjugated structure. In other words, very low D values indicated more electronic homogeneity into the PANI nanofibers, due to the stacking of quinoid-quinoid rings, leading to high torsion $C_{\text{ring}}\text{-N-C}_{\text{ring}}$ angles.

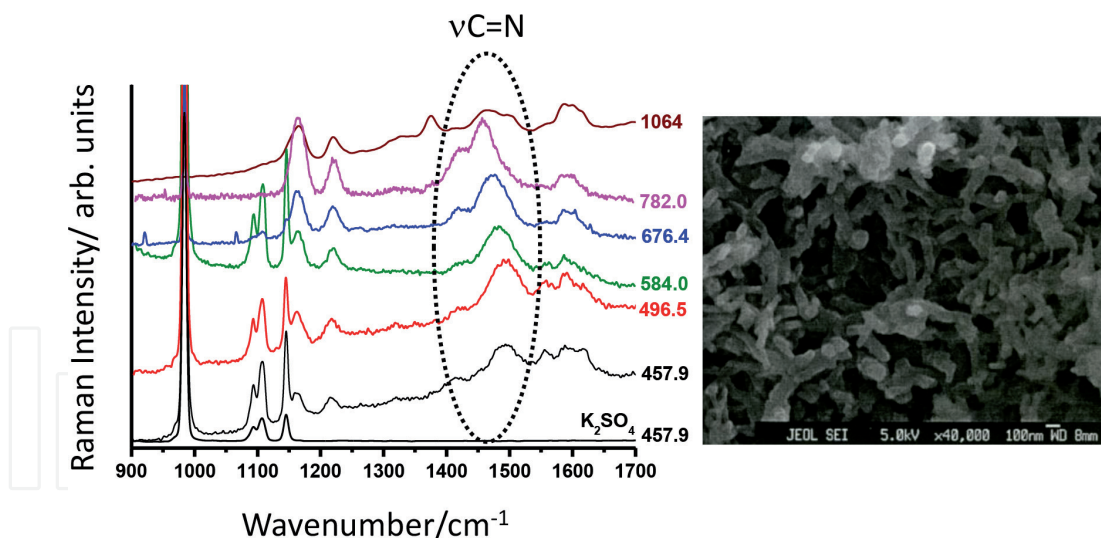


Figure 7.
Raman dispersion of PANI nanofibers.

5. Conclusion

The structural studies of the polyaniline nanofibers by using resonance Raman spectroscopy, as the main technique, have been decisive to elucidate intra- and interchain interactions and chemical and thermal stabilities of PANI nanofibers. The presence of phenoxazine rings is observed in PANI nanofibers formed in micellar media. The presence of these rings is crucial for stacking and stabilization of the fibers. In addition, the changes in bands at low energies are associated with an increase in the torsion angles of $C_{\text{ring}}-N-C_{\text{ring}}$ segments due to the formation of bipolarons (protonated, spinless units) in the PANI nanofibers. The major diffusion of the ions inside the nanofiber gives a more effective protonation. However, only with the previous thermal treatment, it is possible to retain the nanofiber morphology.


Hence, the π -stacking between quinoid rings and the presence of π - π stacking formed by phenoxazine rings can be the driving forces for the formation of the fiber morphology of PANI. The quality of the PANI nanofibers can be monitored by the influence over the Raman dispersion curves. Finally, the example of characterization of PANI nanofibers by using Raman spectroscopy can be applied to other nanofiber materials with the improvement of future nanofiber structural studies.

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