Nanoflakes to nanorods and nanospheres transition of selenious acid doped polyaniline

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Abstract

Morphology transition of selenious acid doped polyaniline from nanoflakes to nanorods and nanospheres was explored by changing the selenious acid—aniline (dopant—monomer) mole ratio in the aniline polymerization. The transition of polyaniline nanospheres to nanorods occurred when the dopant—monomer mole ratio was between 1 and 0.5. The formation of polyaniline nanorods was dominant when the dopant—monomer mole ratio is 0.5. At mole ratio 0.5, nanorods were obtained with the diameter at around 150 nm. At mole ratio 1, both the nanorods and nanospheres were formed and formation of the nanosphere is favored when the mole ratio is more than 1. When the mole ratio was low (0.125—0.03), polyaniline showed flakes like morphology. The morphology transition was studied by scanning electron microscopy and the molecular structure was confirmed by X-ray diffraction, FTIR and UV—vis spectroscopy. A simple and practical route to synthesize polyaniline nanostructures was demonstrated using selenious acid as effective dopant. The mechanism governing the formation of the polyaniline nanostructures is discussed.
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1. Introduction

Conjugated polymers are promising materials for applications as electronics and sensors due to their electrical properties, mechanical flexibility, and relative ease of processing [1—3]. Controlled electrical conductivities can be obtained if molecularly ordered polymers are prepared with fewer conjugation interrupting defects [4—7]. Among the conjugated polymers, polyaniline (PANI) is a conducting polymer that has been widely studied for electronic and optical applications. Unlike other conjugated polymers, PANI has a simple and reversible acid/base doping/dedoping chemistry, enabling control over properties such as free volume [8], solubility [9], electrical conductivity [10], and optical activity [11,12]. In recent years, one-dimensional (1D) PANI nanostructures have attracted growing attention due to the potential advantages as an organic conductor that exhibits low dimensionality. Such materials are potentially useful for applications such as chemical sensors that depend on ultra-small, high surface area features [13]. A variety of chemical methods have been employed to synthesize 1D PANI nanostructures such as rods, wires, tubes, and fibers. Examples include template directed synthesis [14]; the addition of surfactants [15], micelles [16] or seeds [17]; interfacial polymerization [18,19]; rapidly mixed polymerization [20] and sonochemical synthesis [21].

Wan et al. [22] have synthesized microtubules of PANI using $(NH_4)_2S_2O_8$ as an oxidant in the presence of a dopant, naphthalenesulfonic acid (NSA), without a template. The "template-free" formation of these PANI microtubules is attributed to self-assembling of NSA molecules and/or aniline salts into a microstructured intermediate [22,23] that acts as a supramolecular

template [24] and self-doping reagent. Zhang et al. [25] have synthesized PANI nanostructures (nanorods and nanotubes) by self-assembly using inorganic acids.

The essentials of doping PANI and its derivatives were explained by Heeger [26] and MacDiarmid and Epstein [27]. In addition, various dopants such as TiO_2, $FeCl_4^-$, $LiClO_4$, $LiBF_4$, $Zn(ClO_4)_2$ and $LiPF_6$ have been studied [28−31]. The study of doping PANI with non-organic dopants, such as palladium and platinum compounds, is still in progress [32,33]. Recently, polymers containing a chalcogenide, selenium, have exhibited promising properties as organic superconductors. Tetraselenesulfalene and other Se containing organic compounds have displayed metal to semiconductor (insulator) transitions at low temperatures. PANI salt doped with selenium [34] are of great interest in understanding fundamental processes and have possible application in preparing semiconducting quantum dots dispersed within PANI matrix. Joshi and Lokhande [35] have reported the fabrication of heterojunctions using electrochemically deposited isotype *p*-selenium-*p*-polyaniline from a single bath solution. Generally, various synthetic methods reported PANI nanostructures with the aid of sulfonic acid dopants.

In this study, a simple, scalable procedure for producing highly crystalline selenious acid (SELA) doped PANI nanostructures was demonstrated by rapid addition of an initiator solution to an aqueous monomer−dopant solution, followed by static reaction condition at 0−5 °C. The morphology transition of PANI was observed when the dopant−monomer mole ratio was varied. In addition, the effect of dopant−monomer mole ratio on the morphology of the resulting selenious acid doped PANI was observed and the formation mechanism was discussed. The morphology transition was studied by scanning electron microscopy (SEM) and the molecular structure of the nanostructures was confirmed by X-ray diffraction (XRD) FTIR and UV−vis spectroscopy.

2. Experimental

2.1. Synthesis

In a typical experiment, 0.9313 g of aniline was dissolved in 25 ml aqueous solution containing 0.02−1.29 g selenious acid at 0−5 °C. To this solution, 25 ml aqueous solution containing 1.14 g ammonium persulfate was added in bulk and the reaction mixture was kept under static condition for 6 h at 0−5 °C. After the reaction time the product was filtered, washed with water followed by acetone and dried in oven at 50 °C for 6 h. In the reactions, the selenious acid was varied from 0.003 M to 0.2 M, i.e., mole ratio of dopant−monomer mole ratio is varied from 0.03:1 to 2:1 (0.03−2) by keeping monomer−initiator ratio constant as 1:1. The known amount of product was dedoped by aqueous 1 M sodium hydroxide solution. Selenious acid doped polyaniline salt was stirred in 1 M sodium hydroxide solution for 12 h at 25 °C. The solution was filtered, washed with excess distilled water and finally with acetone to obtain the dedoped form of polyaniline salt (polyaniline base). The powder was dried at 60 °C till constant weight.

2.2. Characterization

The surface morphology of the PANI nanostructures was observed by scanning electron microscope (SEM) (JEOL, JSM-840A) operated at 15 kV. XRD experiments for PANI nanostructures were performed at the beamline 10C1 of the Pohang Accelerator Laboratory. The beam conditions were wavelength of 0.1540 nm, beam size of 0.5 mm (H) × 0.3 mm (V), and energy resolution of $\Delta E/E = 2 \times 10^{-4}$. In the case of a symmetric $\theta-2\theta$ scan for the analysis of texture, ordering, and microstructures, the experimental conditions were 0.5− 50°, a 0.05° step size, and a 2 s data collection time for each data point. The PANI nanostructures were separately characterized by FTIR spectroscopy. The sampling part of FTIR spectrometer (ABB Bomem Inc., Quebec City, Quebec, Canada) was modified by collimating IR radiation from interferometer and then the corresponding intensity was recorded by a DTGS detector. Spectra were collected for each sample (64 scans with a resolution of 4 cm^{-1}). Pellet samples were also prepared by mixing 2 mg of sample with KBr powder homogeneously and pressed to 10 t/cm^2. FTIR spectra of the resulting pellet were collected using normal configuration. The conductivity of polyaniline nanostructures was found using Loresta GP MCP-T600, Mitsubishi Chemical, four probe conductivity meter at room temperature. UV−vis spectrum of the polyaniline base sample was recorded at ambient temperature using Mecasys OPTIZEN 2120 UV spectrophotometer. Solution for the absorption spectrum of polyaniline base was prepared by dissolving the samples in 1-methyl-2-pyrrolidone and filtered through whatman 41 filter paper. Absorption spectra of the dilute solution were recorded in the range 1100−300 nm using a pair of matched 3 ml stoppered silica cells of 10 mm path length.

3. Results and discussion

3.1. Morphology

The PANI nanostructures were synthesized using selenious acid dopant and ammonium persulfate initiator. The aniline polymerization was carried out in selenious acid (0.2−0.003 M) solution containing 0.1 M aniline, 0.1 M ammonium persulfate. The reaction was allowed to proceed for 6 h at 0−5 °C. After the reaction time, the product was filtered and washed with water followed by acetone. Then the product was dried in oven at 50 °C for 6 h. In all the reactions, the mole ratio of monomer aniline and initiator ammonium persulfate was 1. Satisfactory arrays of ordered PANI nanorods were obtained when a minimum amount of selenious acid dopant was used (dopant− monomer mole ratio of 0.5). In addition, it was determined that the formation of nanorods was strongly dependent on the dopant−monomer mole ratio. For example, PANI salt displayed only an agglomerated nanosphere morphology when the dopant−monomer mole ratio was 2 (Fig. 1a). However, some mole ratios (e.g., from 0.5 to 1.0) more favorably formed rod-like PANI nanostructures (Fig. 1b and c). Below the mole ratio of 0.125, the nanorod morphology changed to nanoflakes.
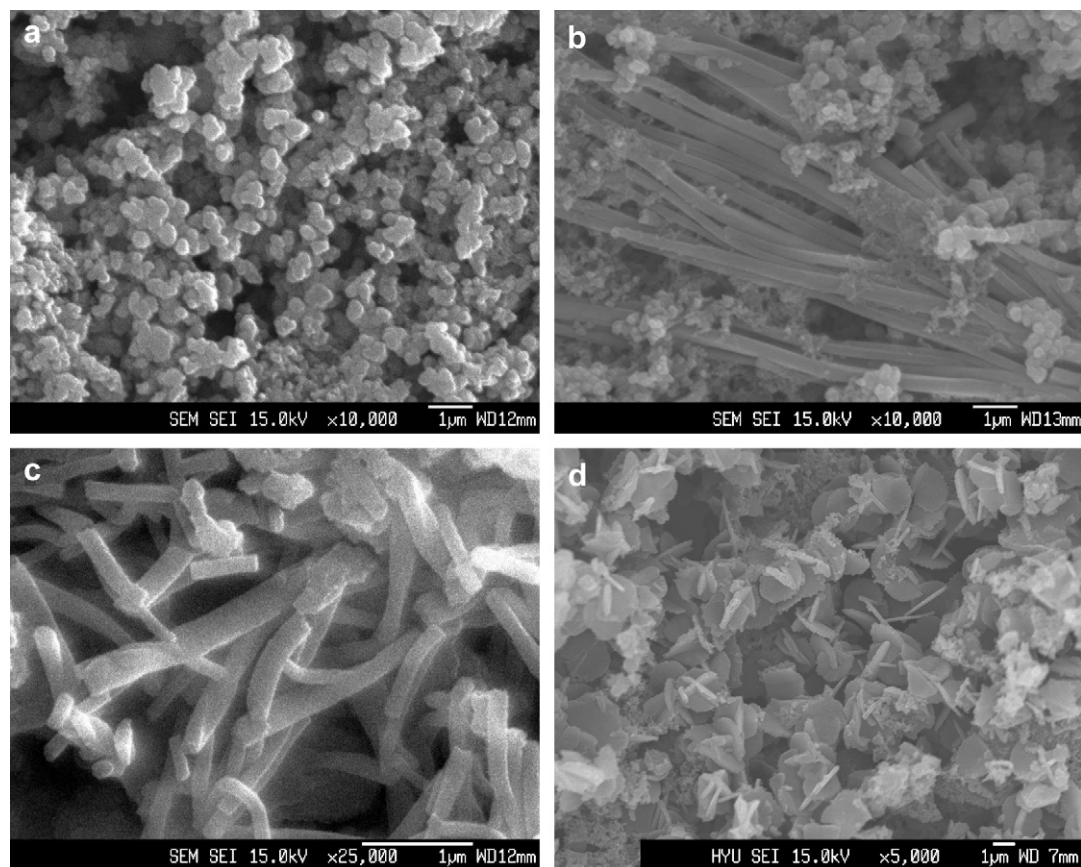
Fig. 1. SEM images of PANI nanostructures (a) nanospheres, (b) mixture of nanospheres and nanorods, (c) nanorods and (d) nanoflakes.

Flake-like morphology was favored when the mole ratio was 0.03 (Fig. 1d), as summarized in Table 1.

3.2. Proposed mechanism for the formation of PANI nanostructures via rod/sphere shaped micelle

The reason for the different morphology in polyaniline system is potentially related to micelle formation. Hassan and co-workers [36] reported that PANI nanoparticles were prepared in rod-like micelles by a sphere to rod transition in anionic sodium dodecyl sulfate micelles with the addition of

Table 1
Effect of the dopant–monomer mole ratio on the morphology and size of selenious acid doped PANI nanostructure[a]

Dopant–monomer mole ratio	Morphology	Average diameter	Conductivity[b] (S/cm)
0.03	Flakes	~1 μm	3×10^{-4}
0.125	Flakes and nanorods[c]	~1 μm and 150 nm	9×10^{-4}
0.50	Nanorods	~150 nm	8×10^{-3}
1.0	Nanorods and nanospheres	~150 nm	8×10^{-3}
2.0	Nanospheres	~150 nm	2×10^{-2}

[a] The reaction was carried out for 6 h at 0 °C in static condition.
[b] Polyaniline nanostructures were made into pellet to measure room temperature conductivity.
[c] Nanorods were about 150 nm in diameter and 1–1.5 μm in length.

aniline hydrochloride and ammonium persulfate. Recently Chan and co-workers [37] reported that the hydrophobic moiety of the structure-directing agent directed the formation of cylindrical micelles. The same group [38] reported the synthesis of ordered PANI nanorods using hydrophilic Allura Red AC as the structure-directing agent and that the formation of ordered arrays was due to the formation of well-aligned rod-like micelle aggregates. Both investigations utilized structure-directing agents (surfactant and dyes) and dopants. In this study, structure-directing agents like hydrophobic/hydrophilic dyes and surfactants were not utilized and only a dopant for synthesizing the well ordered PANI nanorods was employed.

As a representative system we have proposed the rod and sphere like micelle formation for the polyaniline nanorod and nanosphere. The formation mechanism of PANI nanorods from SELA dopant was similar to Chan et al.'s report. When aniline was mixed with the selenious acid solution, the selenious acid–aniline salt (SELA–ANI) was formed through an acid/base reaction. The SELA–ANI salt can form micelle-like arrangements, acting as templates to form nanostructures under certain conditions as shown in Fig. 2. In SELA–ANI salt, the phenyl ring acts as a hydrophobic end and $HSeO_3$ is hydrophilic, thus forming a micelle-like arrangement. When the selenious acid–aniline (dopant–monomer) ratio was greater than 1, more aniline molecules were complexed with selenious acid to form the sphere shaped micelles, such that very few aniline molecules were free to diffuse into the SELA–ANI
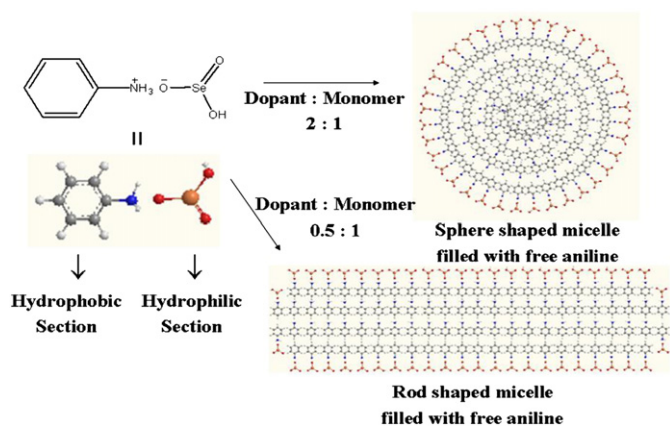
Fig. 2. Mechanism for the formation of PANI nanostructures via rod/sphere shaped micelle.

Fig. 3. XRD plots of PANI nanostructures of (A) nanospheres, (B) nanorods and (C) nanoflakes.

micelle to form PANI nanospheres when combined with initiator solution. When the dopant–monomer ratio was 0.5, few aniline molecules were protonated and more free aniline molecules were uncomplexed. These free aniline moieties diffused into the SELA–ANI micelles, elongating the micelles to form rod-like micelles. These rod-like micelles combine with the initiator solution to produce PANI nanorods. The same can be applicable for flake-like nanostructure also. The proposed formation mechanism of selenious acid doped PANI nanosphere and nanorod is shown in Fig. 2.

3.3. Nanostructures and crystallinity

To further investigate the solid-state properties, the PANI nanostructures were analyzed by XRD. Synchrotron X-ray scattering measurements were performed at Pohang Light Source (10C1) in Korea with X-ray wavelength of 1.24 Å.

In general, a polymer chain in a matrix has both amorphous and crystalline domains, and the percentage of respective domains varies depending upon the backbone. PANI backbone is highly rigid due to the linear structure and less flexible to chain folding that would induce a crystalline domain. Therefore, undoped PANI chains are normally observed as highly amorphous polymers. In the presence of sulfonic acids, the dopant–polymer undergoes various interactions, which tend to organize the polymer chains in highly ordered arrays.

The XRD patterns of the PANI nanostructures are shown in Fig. 3. It is very clear from the spectra that all the samples had two broad peaks at approximately $2\theta = 20°$ and $25°$. The peak centered at $2\theta = 20°$ was ascribed to periodicity parallel to the polymer chain and the $2\theta = 25°$ peak was due to the periodicity perpendicular to the polymer chain [39]. The change in XRD pattern by different morphologies of PANI is a special and interesting feature which reflects the importance of XRD analysis for structural and morphological analysis. The change in XRD peak intensity with surface morphology is well known for PANI systems [40]. The XRD patterns of PANI nanorods and nanoflakes (Fig. 3B and C) showed new sharp, intense and distinct peak at around $2\theta = 6°$ which is obtained due to the presence of ordering in the polyaniline
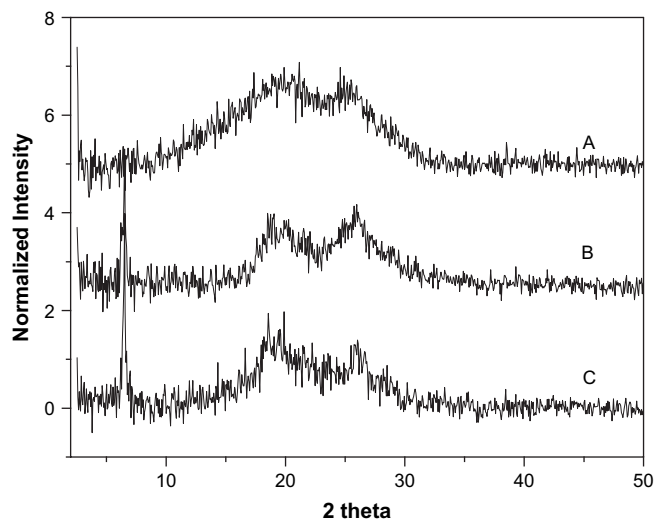
nanostructures. This new peak was not observed in the case of polyaniline nanospheres (Fig. 3A). In the PANI nanosphere, the new peak was absent, indicating a less ordered PANI structures.

3.4. FTIR spectroscopy

The PANI nanostructures (nanospheres, nanorods, and nanoflakes) were separately characterized by FTIR spectroscopy. The FTIR spectra of all the PANI nanostructures were essentially similar to PANI salt prepared using sulfuric acid dopant [41] (Fig. 4). The characteristic peaks at 1585 cm^{-1} and 1495 cm^{-1} were related to the quinonoid and benzenoid structures, respectively. The bands at 1290 cm^{-1} were assigned to the CN stretching of the secondary aromatic amine. The C–H out-of-plane bending mode has been used as a key to identify the type of substituted benzene. For polyaniline salt, this mode was observed as a single band at 830 cm^{-1}, which falls in the range of $800-860 \text{ cm}^{-1}$ reported for 1,4-di-substituted
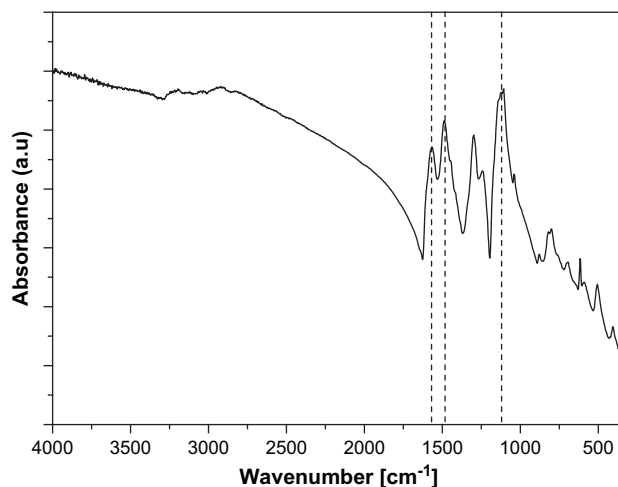

Fig. 4. FTIR spectrum of PANI nanorods.

benzene [42]. Additionally, the characteristic peaks were similar to the PANI doped with β-NSA [42] and inorganic acid [25].

3.5. UV–vis spectroscopy

The UV–vis spectra of polyaniline base and polyaniline salt have been reported in the literature. Absorption spectrum of polyaniline base [43–45] shows two distinct absorption bands located at around 320 nm and 620 nm depending on the method of preparation and/or processing of polyaniline. The band at around 320 nm and 620 nm may be assigned to the excitation of the amine and imine segments of the polymer chain, respectively. For polyaniline in the salt form, the peak at 620 nm disappeared except for an absorption at 320 nm, whereas a new peak above 725 nm occurred. This new peak is due to the polaron which has been demonstrated [45–48].

In the present study, the selenious acid doped polyaniline salt is not soluble in most of the organic solvents. However, polyaniline base is soluble in 1-methyl-2-pyrrolidone. The UV–vis spectra of polyaniline bases which are prepared by dedoping of polyaniline nanostructures using sodium hydroxide are very nearly the same. As a representative, the UV–vis spectrum of polyaniline base prepared by dedoping PANI nanosphere in sodium hydroxide is shown in Fig. 5. The UV–vis spectrum of polyaniline base showed a broad band at around 320 nm and another band at around 610 nm. These two peaks are assigned to the excitation of the amine and imine segments of the polymer chain, respectively, and this is consistent with literature reports of polyaniline base.

3.6. Conductivity

To measure conductivity PANI nanostructures were pressed into a pellet of 10 mm diameter and ca. 2 mm thickness under pressure. The conductivity measurement of PANI pellets was measured at room temperature using Loresta GP MCP-T600, Mitsubishi Chemical, four probe conductivity meter at room temperature. Samples were dried in vacuum before making

Fig. 5. UV–vis spectrum of dedoped PANI nanosphere.

into pellets. The resistance was measured at 10 different points and average resistance was calculated. PANI nanoflakes had a low conductivity in the range of 3×10^{-4} S/cm, whereas nanorods and nanospheres showed an increase in conductivity, with values of 8×10^{-3} S/cm and 2×10^{-2} S/cm, respectively.

The conductivity of the nanorods and nanospheres was similar, with both slightly lower than conventional PANI systems. The differences in conductivity may be due to the lower dopant concentration. Interestingly, in the present investigation, the morphology of the nanorods significantly affected the conductivity. Although more (approximately four times in excess) dopant (0.2 M) was used for the nanospheres, no significant increase in the conductivity was observed. However, less dopant was used to synthesize (0.05 M) highly ordered and crystalline PANI nanorods with a reasonable conductivity. It is also evident from the nanorod SEM image that a good conductive network was formed, therefore indicating that compared to the amount of dopant used, morphology has more effect on solid-state properties such as conductivity and crystallinity. The direct correlation of PANI morphology with solid-state ordering was observed for the PANI system. Compared to the PANI nanospheres and nanoflakes, the high solid-state ordering and self-assembly of PANI nanorods was contributing to reasonable conductivity despite the amount of dopant present. The behavior suggests that the morphology, as well as solid-state ordering of PANI, played a major role in the conductivity of PANI nanostructures.

4. Conclusions

In summary, large quantities of uniform selenious acid doped polyaniline nanostructures were synthesized by a template-free simpler route using selenious acid dopant and ammonium persulfate oxidant. This approach is an easy, inexpensive, and scalable one-step method to produce uniform nanostructures with controllable average diameters in bulk quantities. It was found that the morphology of the nanostructures could be easily controlled by the concentration of selenious acid and aniline. Polyaniline with nanoflakes, nanorods and nanospheres was obtained when the selenious acid–aniline mole ratio is 0.03, 0.5 and 2, respectively. The morphology transition was studied by SEM studies and molecular structure of the polyaniline nanostructures was confirmed by XRD, FTIR and UV–vis spectroscopic techniques. In this work, PANI has been synthesized with various morphologies such as nanospheres, nanorods and nanoflakes using only one dopant and without the use of any surfactant or template. The morphology transition from nanospheres to nanorods was observed by simply changing the amount of dopant. The direct correlation of PANI morphology with solid-state ordering and conductivity was observed for the PANI system. Due to the reasonable conductivity, crystallinity, nanosize and high surface area, these PANI nanostructures may have potential application as chemical sensors or actuators, gas-separation membranes and neuron devices. Because of the versatility of this method in producing nanostructures of polyaniline, we anticipate that nanostructures
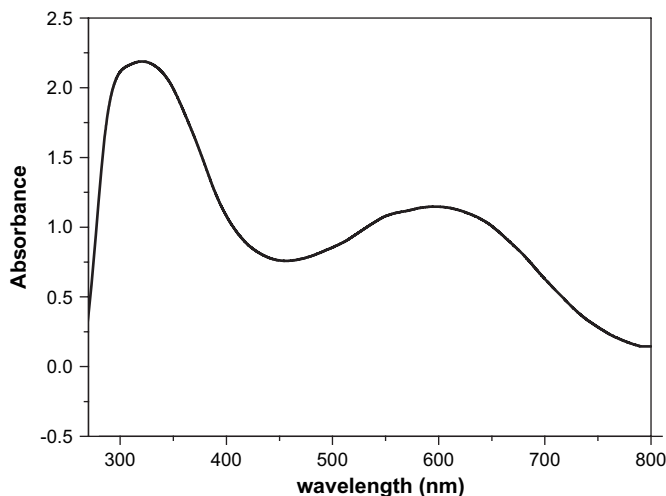
of other polyaniline derivatives and other conducting polymers could be synthesized in a similar fashion.

Acknowledgements

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