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Synthesis, characterization and morphology of polyanthranilic acid micro- and nanostructures

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Abstract Polyanthranilic acid (PANA) nanofibres, nanorods, nanospheres and microspheres were synthesized by polymerization of anthranilic acid using ammonium peroxydisulfate (APS) as oxidant without hard or soft templates. Polymerization of anthranilic acid was carried out in aqueous solutions of strong (hydrochloric) and weak (acetic) acids. The influence of synthetic parameters such as oxidant, initiator, dopant acid and its concentration, redox initiator, and reaction medium on the morphology and particle size of PANA have been investigated. PANA nanofibres and nanorods were obtained via redox polymerization of anthranilic acid initiated by $FeSO_4$ as redox initiator. PANA nanospheres and nanofibres were also obtained when used aromatic amines as initiators. When polymerization carried out in the solution of weak (acetic) acid the microsphere morphology obtained and the particle size increase with increasing the concentration of weak acid. PANA nanorods were obtained also by polymerization of anthranilic in ethanol-water mixture unlike interfacial polymerization of anthranilic acid (in chloroform-water) that give PANA microspheres. The morphology and particle size of PANA was studied by scanning electron microscope (SEM) and transmission electron microscope (TEM). The average diameter of nanostructures obtained ≤100 nm. The optical bandgap of microspheres and nanofibers polymeric products were determined using UV-vis spectroscopic technique and found to be 2.0 eV and 1.6 eV, respectively. The bandgap decreased with decreasing the particle size. IR spectrum confirmed the structure of PANA nanofibres (synthesized with $FeSO_4$ as redox initiator) in emeraldine form. The thermal stability of polymer obtained was determined by thermal gravimetric analysis (TGA). The molecular weight was determined also by gel permeation chromatography (GPC).

Keywords Polyanthranilic acid · Ammonium peroxydisulfate · Morphology · Nanofibres · Nanospheres · Nanorods · Microspheres

Introduction

During the past decades, polymernanoparticles (PNP) have raised a great interest in the world of research due to their various physical, chemical properties and their numerous possible applications in electronics, photonics, conducting materials, sensors, medicine, biotechnology, pollution control and environmental technology [1–9]. Polyaniline (PANI) and its derivatives are considered to be one of the most promising classes of organic conducting polymers due to their well-behaved electrochemistry, easy protonation reversibility, excellent redox recyclability [10], good environmental stability [11], electrochromism [12], ease of doping [13] and ease of preparation. In addition, PANI can be used as an electrode material [14, 15], in microelectronics [16], as an electrochromic device [17], in radiation shielding and in recordable optical discs. On the contrary, the commercial usefulness of PANI has been limited by its intractable nature especially in the doped form which is normally produced chemically as an insoluble powder [18].

However, its insolubility in most of the common solvents and poor mechanical property are restricted its applications in devices. A number of attempts have been made to improve the processibility of PANI by polymerization of aniline derivatives with alkyl, sulfonic, and carboxyl groups substitution [19]. The carboxyl functionalized PANI "polyanthranilic acid" (PANA) has overcome this problem due to its solubility in common organic solvents. Recently, PANA was synthesized via different

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oxidizing agents and also used for processible composites formation [20]. Acid functionalized PANA-multi wall carbon nanotubes (MWCNTs) nanocomposite has overcome the problem of both PANI and CNTs due to its solubility [21]. Nanostructures PANI (nanofibres and nanotubes) produced during polymerization of aniline have received ever increasing attention during last years [22–28]. PANI is unique among the family of conjugated polymers since its doping level can be readily controlled through an acid doping/base dedoping process [29].

Although many papers have been published in the field of PANI conducting polymer nanostructures [22–28], no any paper has discussed the synthesis and characterization of PANA nanostructures.

In the present study, for the first time PANA nanostructures such as nanofibres, nanorods and nanospheres have been synthesized with average diameter ≤100 nm using different polymerization conditions and demonstrate that it is a very general route to create PANA nanostructures.

These nanostructures have received intensive interest because they possess optical properties in the visible region implying the possibility of using these materials in solar energy applications.

Experimental

Materials

Ammonium peroxydisulfate (APS) was obtained from Merck, India. Anthranilic acid was obtained from Rolex India Ltd, India. Diphenyl amine (RDH) and P-phenylene diamine (FLUKA) were used without further purification. $FeSO_4.7H_2O$ was obtained from Aldrich, USA. Hydrochloric acid and acetic acid from (Merck, India). Deionized water was used to the preparation of the aqueous solutions. All solvents were of analytical grade and used as received.
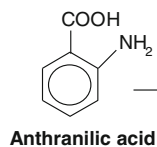
Synthesis of PANA nanofibres and nanorods by polymerization initiated by redox initiator

In a typical synthesis, anthranilic acid (0.19 g, 1.4 mmol) and $FeSO_4.7H_2O$ (0.09 g, 0.3 mmol) were dissolved in 20 ml of 0.1 M HCl solution with a magnetic stirring to form a transparent aqueous solution. Afresh solution of APS (0.12 g, 0.5 mmol) in 20 ml of 0.1 M HCl solution was rapidly added to the above solution containing anthranilic acid and $FeSO_4$. Upon the addition of APS, a series color change is observed with naked eye: yellow and reddish brown. The polymerization reaction was carried out for 6 h at room temperature without any disturbance. The dark brown precipitate was filtered off, washed with 0.1 M of HCL followed by deionized water several times, and dried at room temperature for 24 h to give PANA nanofibers. The same polymerization method was carried out in the dark to give PANA nanorods.

Synthesis of PANA nanospheres and nanofibres by polymerization initiated by aromatic amines

0.002 g (0.012 mmol) of an initiator (diphenyl amine) is dissolved in a minimal methanol. This solution is mixed with a solution of the anthranilic acid (0.2 g, 1.4 mmol) in 5 ml of 1 M HCl to form a mixture. This mixture is rapidly mixed with a solution of APS (0.05 g, 0.22 mmol) in 5 ml of 1 M HCl. Upon addition of oxidant, the characteristic color changes associated with the formation of the PANA is observed within several seconds. The reaction mixture is then left unagitated for 1 day, after which time the crude product was filtered off, washed with 0.1 M of HCL followed by deionized water several times, and dried at room temperature for 24 h to give PANA nanospheres. The same polymerization method was carried out by using p-phenylene diamine instead of diphenyl amine to give PANA nanofibres.

Scheme 1 Polymerization of anthranilic acid at different polymerization conditions

Synthesis of PANA nanorods by polymerization in ethanol/water mixture

Typically, the reaction was performed in a 20 ml glass vial. 0.44 g (3.2 mmol) of anthranilic acid was dissolved in 10 ml ethanol. APS (0.18 g, 0.8 mmol) was dissolved in 10 ml deionized water and rapidly mixed with a solution of anthranilic acid. The polymerization reaction was carried out for 24 h at room temperature without any disturbance. The precipitate was filtered off, washed with 0.1 M of HCL

followed by deionized water several times and dried at room temperature for 24 h to give PANA nanorods.

Synthesis of PANA microspheres by interfacial polymerization

The interfacial reaction was performed in a 20 ml glass vial. 0.44 g (3.2 mmol) of anthranilic acid was dissolved in 10 ml of chloroform as organic phase. APS (0.18 g, 0.8 mmol) was dissolved in 10 ml of 1 M HCL and rapidly mixed with a

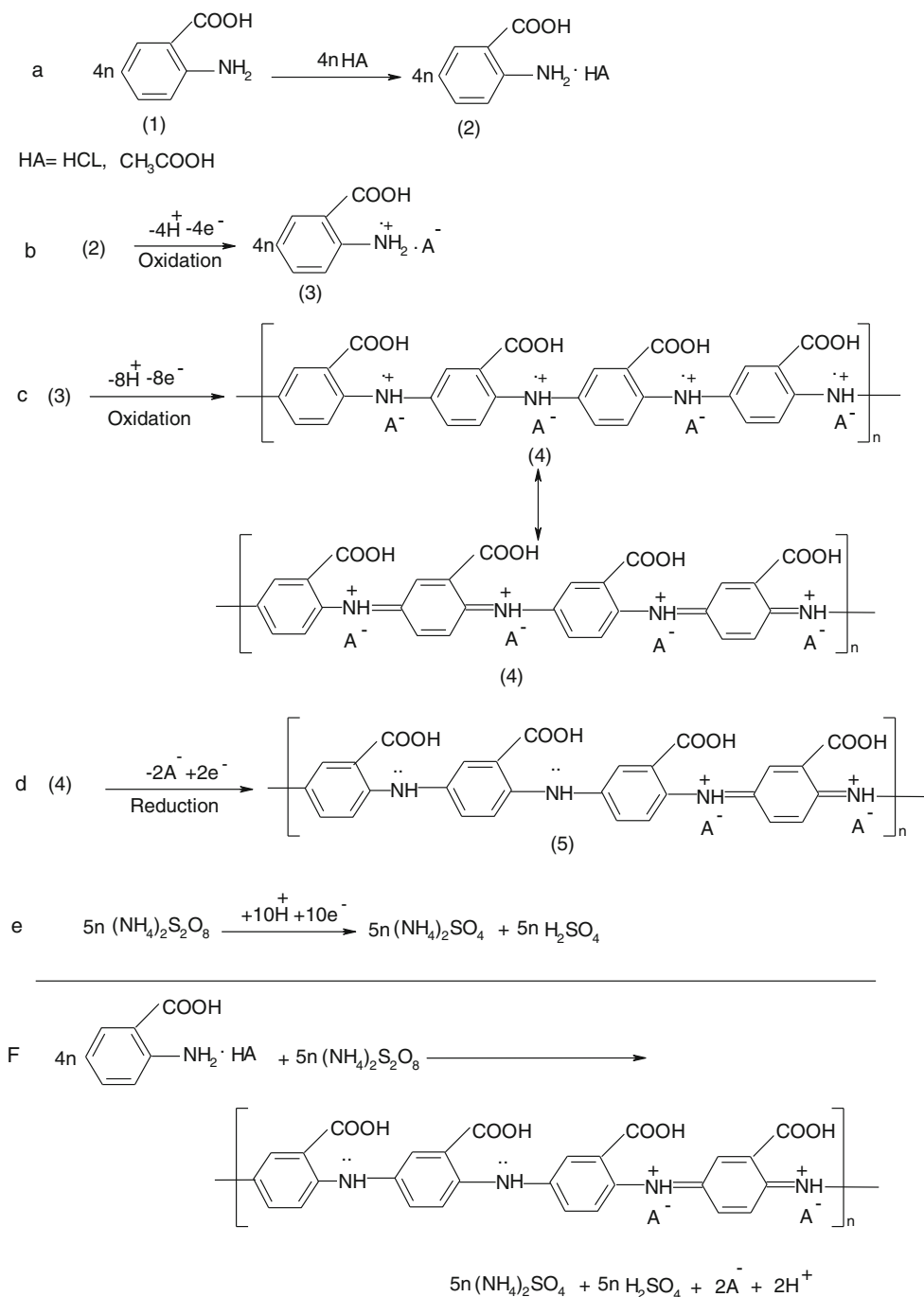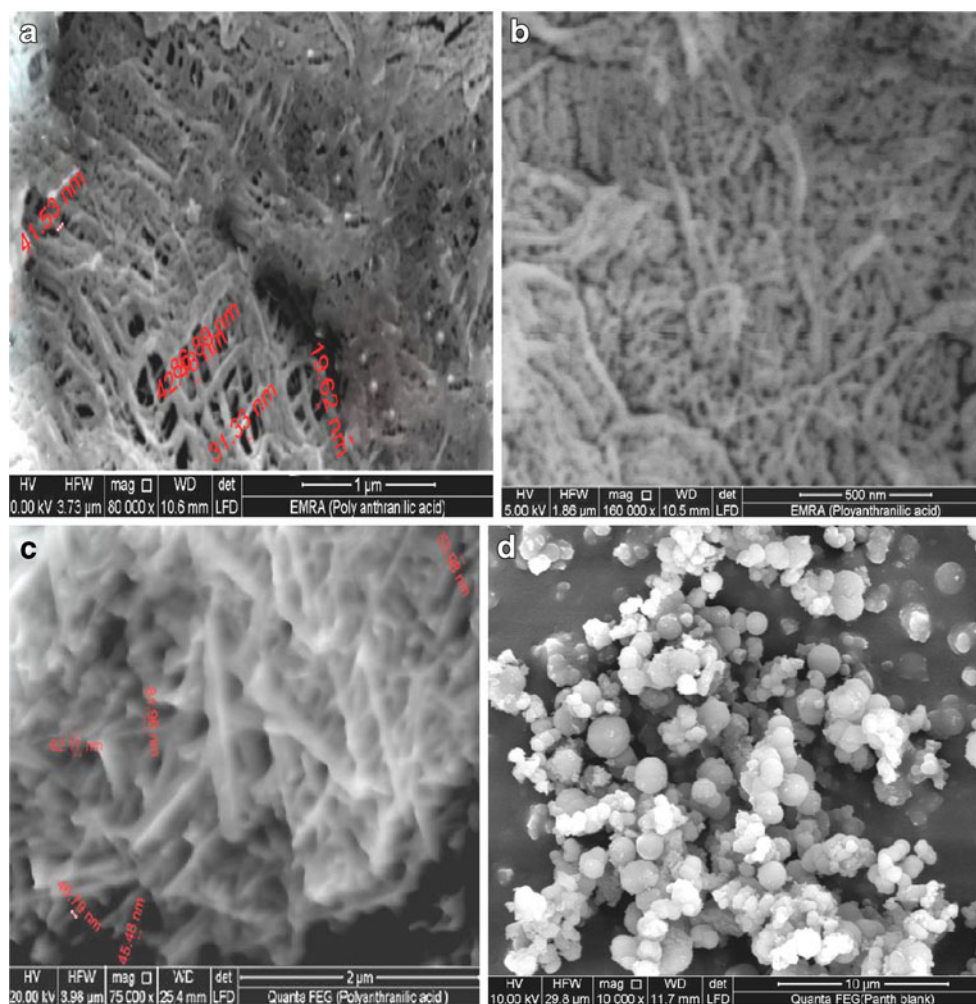Scheme 2 Mechanism of anthranilic acid polymerization

Fig. 1 SEM images of PANA. **a** nanofibres at 0.1 M HCL/FeSO$_4$, **b** nanofibres at 0.5 M HCL/FeSO$_4$, **c** nanorods at 0.1 M HCL/FeSO$_4$(in dark) and **d** microspheres at 0.1 M HCL in absence of FeSO$_4$

solution of anthranilic acid. The polymerization reaction was carried out for 24 h at room temperature without any disturbance. The precipitate was filtered off, washed with 0.1 M of HCL followed by deionized water several times and dried at room temperature for 24 h to give PANA microspheres.

Fig. 2 SEM images of **a** PANA nanospheres/diphenyl amine and **b** PANA nanofibres/p-phenylene diamine in 1 M HCL
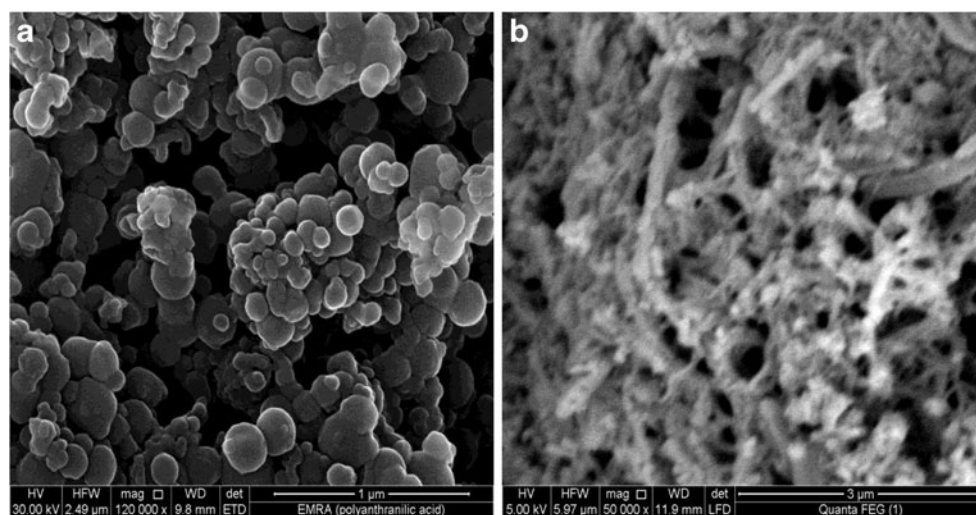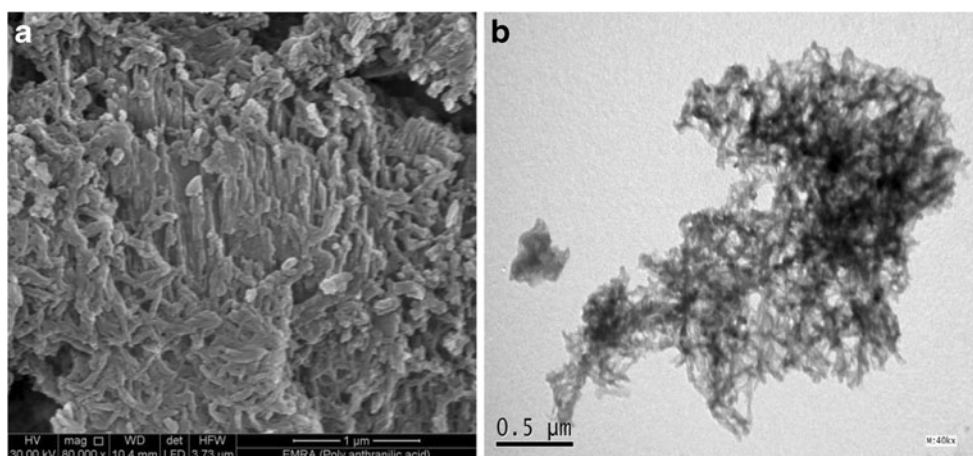
Fig. 3 SEM (**a**) and TEM (**b**) images of PANA nanorods prepared in ethanol-water mixture

Synthesis of PANA microspheres by polymerization in aqueous medium of acetic acid

1.37 g (9.9 mmol) of anthranilic acid was oxidized with 2.85 g (12.5 mmol) of APS in an aqueous medium of acetic acid at room temperature. Anthranilic acid was dissolved in 50 ml of acetic acid at different concentrations (0.5 M, 1 M). Solution of oxidizing agent dissolved in 50 ml distilled water was added drop-wise to the monomer solution with constant stirring. After complete addition, the solution was kept for stirring for 30 min and then incubated for 24 h at room temperature. The precipitate was washed with the same concentration of acetic acid followed by deionized water and kept for drying at room temperature for 24 h.
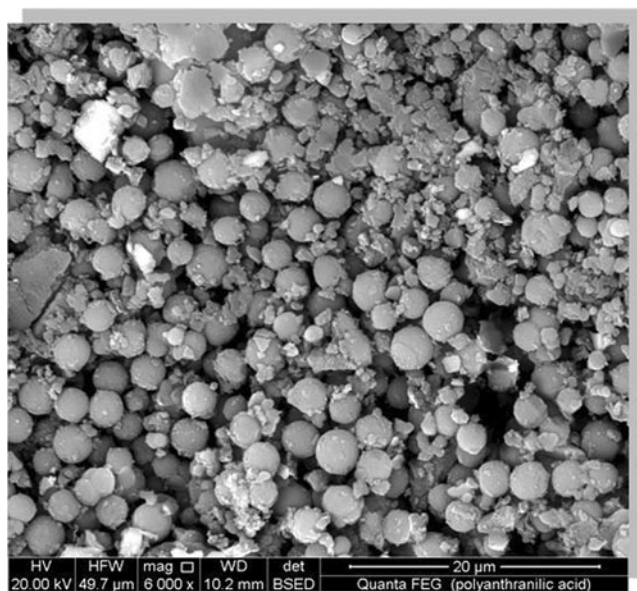

Fig. 4 SEM images of PANA microspheres prepared via interfacial polymerization

Morphological properties of polymer

The morphology and particle size of PANA samples prepared by different methods were determined by scanning electron microscope (SEM) (QUANTA 250 SEG, HOLANDA) and transmission electron microscope (TEM) (JEOL [JEM- 1230 electron microscope]).

FT-IR measurements

The IR spectrum of the PANA was measured as KBr pellets using FT/IR-BRUKER, Vector 22 (Germany) Spectrophotometer.

UV-vis absorption measurements

The UV-vis absorption spectra for the PANA of nanofibres and microspheres were measured using $T_{80}+$ UV/vis Spectrometer. PG instruments Ltd, Britain.

Determination of molecular weight by gel permeation chromatography (GPC)

Molecular weights of the prepared polymers were measured using Gel permeation Chromatography type; 1,100, Germany. The measurements were conducted at ambient temperature using dimethyl formamide (DMF) as the mobile phase at flow rate of 1.0 ml/min. PANA samples were dissolved in the same solvent as the mobile phase at concentration of 5 mg/ml. The column was calibrated using polystyrene standards.

Thermal gravimetric analysis

Thermal analysis experiments including thermal gravimetric analysis (TGA) and Differential scanning calorimetry (DSC) for the PANA nanofibres and

Fig. 5 SEM images of PANA microspheres **a** 0.5 M CH₃COOH, **b** 1 M CH₃COOH
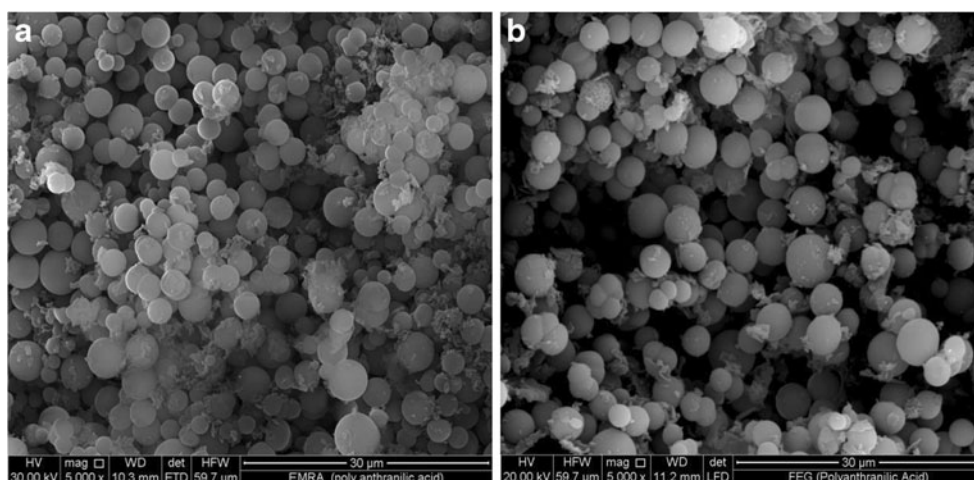
microspheres were carried out using SDT Q600 V20.5 Build 15 Thermogravimetric Analyzer. The experiment was performed in a dynamic atmosphere of nitrogen from room temperature to 700 °C at heating rate of 10 °C/min.

Results and discussion

Synthesis of PANA nanostructures

PANA nanofibres, nanorods, nanospheres and microspheres were synthesized by polymerization of anthranilic acid using ammonium peroxydisulfate (APS) as oxidant without hard or soft templates. Scheme 1 illustrates the polymerization of anthranilic acid at different polymerization conditions. Mechanism of anthranilic acid polymerization was illustrated in Scheme 2.
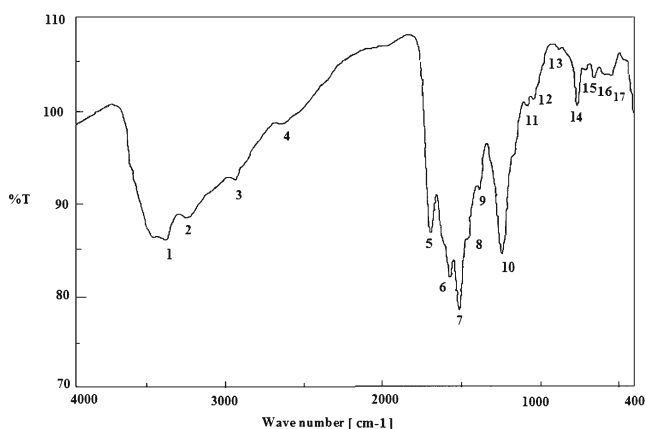

Fig. 6 FT-IR spectrum of PANA nanofibres at 0.1 M HCL/FeSO₄

Morphological properties of polymer

The morphology and particle size of PANA samples were investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM). Figure 1(a,b) shows typical SEM images of the synthesized PANA prepared by redox polymerization initiated by FeSO₄ as redox initiator at different conditions. Figure 1 shows PANA nanofibres with average diameter of 43 and 21 nm in case of 0.1 M and 0.5 M of HCL, respectively. We observed that the particle size of nanofibres decreased with increasing the concentration of HCL. However, PANA nanorods (with average diameter of 57 nm) were obtained by the same method except that the polymerization was carried out in the dark. Figure 1(c) shows SEM image of PANA nanorods. This observation may be due to optical properties effect of PANA. Figure 1(d) shows PANA microspheres synthesized in the absences of redox initiator (FeSO₄) at 0.1 M HCL. It reveals that the addition of Fe^{+2} in conventional polymerization system leads to a change in bulk morphologies of PANA from microspheres to nanofibres and nanorods [24]. When APS is added into solution containing anthranilic acid and FeSO₄ APS can react with Fe^{2+} ions instantaneously to produce sulfate radical anions because Fe^{+2} ions have a lower oxidation potential than anthranilic acid. The classical chemical formula expressed as follows: $S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + SO_4^{-\cdot} + Fe^{3+}$ [30]. The rate of polymerization of anthranilic acid with the aid of Fe^{2+} ions has a substantial increase compared with that without the aid of Fe^{2+} ions [24]. Accelerating the rate of polymerization will rapidly produce high oligomer concentration to favor homogeneous nucleation, which reduces the secondary nucleation sites on the preexisting nanofibres and nanorods [31, 32]. PANA nanostructures (nanospheres and nanofibres) were obtained by polymerization of anthranilic acid in the presence of aromatic amine as initiator. The morphology of polymer could be

Fig. 7 Emeraldine form for PANA
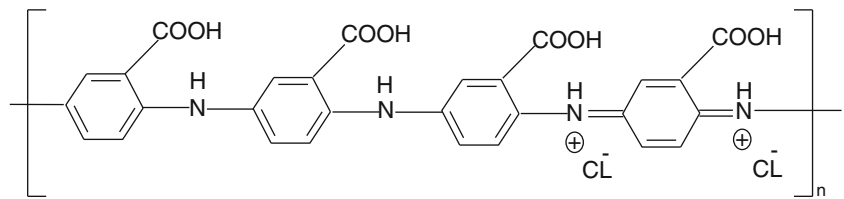
influenced by selection the initiator. Therefore, in the presence of diphenyl amine PANA nanospheres were obtained with average diameter of 89 nm at 1 M HCL. Whereas, in the presence of p-phenylene diamine PANA nanofibres were obtained with average diameter of 100 nm at 1 M HCL. Figure 2 shows the SEM images of PANA nanospheres and nanofibres obtained via polymerization of anthranilic acid initiated by aromatic amines. It is believed that the change in the observed morphology in the absence and presence of initiator Figs. 1(d) and 2(a, b), respectively can be attributed to the rate enhancement caused by the introduction of the initiator [33]. It is believed that in the presence of an initiators, the formation of reactive nuclei is much faster, and as a result they will undergo homogenous nucleation leading to nanostructures (nanofibres and nanospheres) rather than heterogeneous nucleation leading to agglomerated structures. It has also been shown that homogenous nucleation promotes the formation of nanofibres and nanospheres [34]. PANA nanorods were obtained also by polymerization of anthranilic in ethanol-water mixture in absence of functional dopant acid (HCL). Figure 3 shows SEM and TEM images of PANA nanorods with average diameter of 25 nm. The results obtained in this work indicated that the interfacial polymerization of anthranilic acid lead to microstructures PANA. Figure 4 shows SEM image of PANA microspheres obtained by interfacial polymerization based on a two phase oxidative polymerization technique using mild acid (1 M HCL) and chloroform as immiscible solvents. The mechanism for the formation of microspheres may be explained based on the micelles droplets of anthranilic acid formed in the reaction solution at the interface of the two phases due to stirring [35]. Micelles droplets formed and stabilized at the interface due to the hydrophilic (NH_2 and COOH groups) and hydrophobic (benzene rings) nature of the anthranilic acid monomer. Moreover, anthranilic monomer also have tendency to self stablize during polymerization. When the addition of an oxidant, which is hydrophilic, the polymerization took place at the interface produce small spherical nanostructures [36]. It is well known that the oxidative polymerization of aniline and its derivative is an exothermic process. Hence the heat released during the oxidation of anthranilic acid will increase the local temperature of droplets, which results in the fusion of droplets to form the larger microspheres. PANA microspheres were obtained by polymerization of anthranilic acid in weak acid. Figure 5 shows SEM images of PANA microspheres obtained by polymerization in acetic acid with average diameter of 1.7 and 2.8 μm at 0.5 M and 1 M of CH_3COOH, respectively. We observed that the particle size increased with increasing the concentration of acetic acid. Although polyaniline nanotubes was obtained via polymerization of anthranilic acid in solution of acetic acid [26], PANA microspheres was obtained at the same condition of polymerization, which
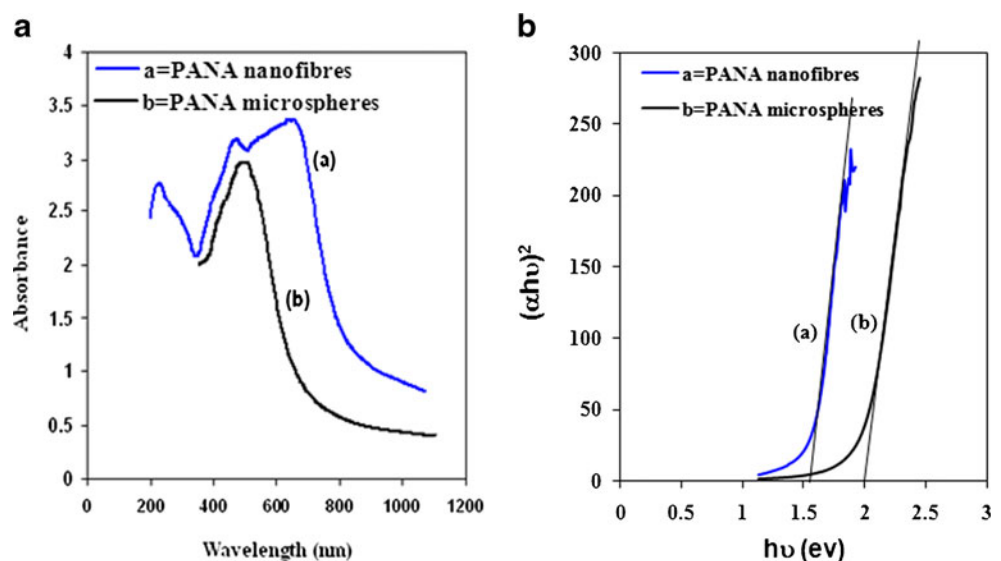
Fig. 8 **a** UV-vis spectra of PANA nanofibres at 0.1 M HCL/$FeSO_4$ and microspheres at 0.1 M HCL in absence of $FeSO_4$, **b** $(\alpha h\upsilon)^2$ vs. $h\upsilon$ plot for bandgap estimation
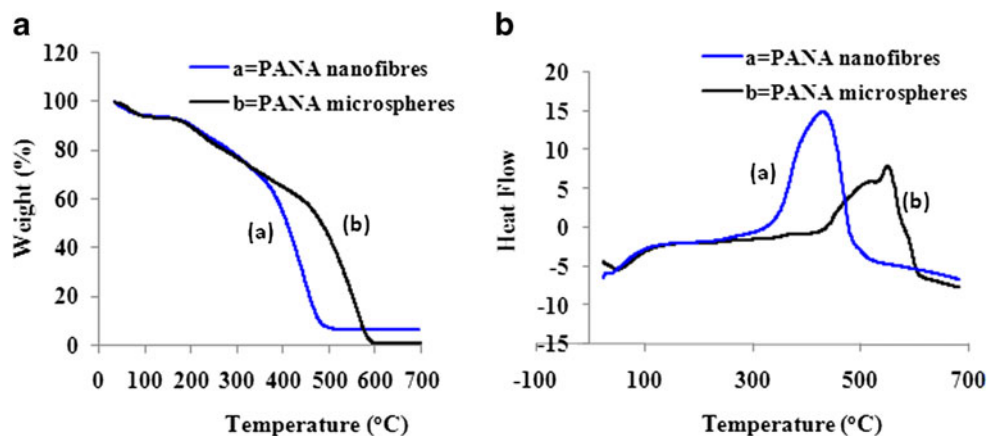
Table 1 GPC results of moleculer weight for PANA microspheres and nanofibres synthesized by polymerization of anthranilic acid in the absence and presence of $FeSO_4$, respectively as redox initiator

Samples	Average molecular weight(Mw)	Number average(Mn)	Polydispersities
PANA microspheres	16,851	11,970	1.4
PANA nanofibres	19,014	15,189	1.2

Table 2 TGA of PANA microspheres and nanofibres

Samples	1st step (°C)	2nd step (°C)	3rd step (°C)
PANA microspheres	50–108	108–189	471
PANA nanofibres	50–85	85–184	386

may be due to the presence of COOH group. This means that microspheres PANA are formed by polymerization of anthranilic acid in absence of $FeSO_4$, interfacial polymerization and polymerization of anthranilic acid in acetic acid.

FT– IR spectrum of PANA

Infrared absorption spectra are long know and well established in characterizing the chain structure of polymers. The IR spectrum for PANA (Fig. 6) shows strong band for the C=O stretching at $1,684$ cm^{-1} and band at $3,373$ cm^{-1} assigned to OH group. The $3,230$ cm^{-1} band can be assigned to NH group. The spectrum shown in Fig. 6 exhibit main bands at $1,565$ cm^{-1} and $1,509$ cm^{-1} corresponding to the C=C stretching frequency of benzenoid and quinoid rings, respectively. Another absorption peak at $1,241$ cm^{-1} is mainly due to C–N stretching of secondary aromatic amine [37]. The $1,083$ cm^{-1} band can be assigned to a vibration mode of the $-NH^+=$ structure, which is formed by protonation [38]. The broad nature of this peak is owing to the high degree of electron delocalization [39] which was expected because of the greater degree of oxidation. The band appearing at 755 cm^{-1} corresponds to the C–H out-of-plane bending vibration of the benzene rings. These data reveals to emeraldine form for PANA as shown in Fig. 7.

UV-vis absorption measurements

Figure 8(a) illustrates UV-vis spectra of PANA nanofibres and microspheres. UV-vis spectrum of PANA nanofibres showed three peaks as shown in Fig. 8(a). The first peak at 280 nm corresponds to $\pi-\pi^*$ transition in benzenoid ring, second peak at 480 nm attributed to the $n-\pi^*$ transition or the excitonic transition due to partial oxidation of polymer and can be assigned to represent the intermediate state between lecuoemeraldine form containing benzenoid ring and emeraldine form containing the conjugated quinoid ring. Third peak of PANA spectrum at about 680 nm corresponds to exciton-like transition quinoid ring or diimino unit [40]. This band is blue shifted (shorter wavelength) in PANA microspheres,

The bandgaps of PANA nanofibres and microsperes products (synthesized by polymerization of anthranilic acid in the presence and absence of $FeSO_4$, respectively as redox initiator) were evaluated from the absorbance spectra of PANA. The optical band gaps of PANA nanofibres and microsperes were estimated by fundamental relation given by Tauc [41].

$$\alpha h\upsilon = B(h\upsilon - Eg)^n \qquad (1)$$

where α is the absorption coefficient, h υ the energy of absorbed light, $n=1/2$ for direct allowed transition and B is proportionality constant. Energy gap (Eg) was obtained by plotting $(\alpha h\upsilon)^2$ vs $h\upsilon$ and extrapolating the linear portion of $(\alpha h\upsilon)^2$ vs $h\upsilon$ to zero, as shown in Fig. 8(b). The band gaps

Fig. 9 **a** TGA, **b** DSC curves of PANA nanofibres at 0.1 M HCL/$FeSO_4$ and microspheres at 0.1 M HCL in absence of $FeSO_4$

Table 3 DSC of PANA microspheres and nanofibres

Samples	Exothermic peak (°C)
PANA microspheres	583
PANA nanofibres	447

of PANA nanofibres and microspheres were estimated to be 1.6 eV and 2 eV, respectively, It may be pointed out here that the band gap of PANA microspheres is significantly larger than nanofibres. This is due to the change occurring in each of morphology and particle size, where the optical band gap depends on the change in particle size. From UV-vis spectra the optical absorption of PANA lies in visible region.

Molecular weight determination of polymer

Molecular weights of the prepared PANA were determined by GPC and listed in Table 1. Table 1 showed that PANA nanofibres have higher molecular weight (Mw), number average (Mn) than that found for microspheres polymer, unlike, microspheres PANA have higher polydispersities than that found for nanofibers. It is believed that in the presence of $FeSO_4$ as redox initiator may bais formation of nanofibres by accelerating growth of the nanofibres a long the axis of polymer chain leading to higher molecular weight.

Thermal gravimetric analysis

TGA is widely used to study the thermal stability and all physical process involving the weight changes with temperature. In addition, it is also employed to investigate the thermal degradation, phase transition and crystallization of polymers.

Thermal analysis in Fig. 9(a) showed that there are three major stages of weight loss for both PANA nanofibres and microspheres. In case of PANA nanofibres the first stage with weight loss of 5 % at temperature up to 85 °C results from the loss of water molecules from the polymer and perhaps out of gassing of unknown small molecules. The second stage that commences after 85 °C until 184 °C of weight loss 8 % which associated with the loss of acid dopant bound to the PANA chain and the evolution of CO_2. The third stage of weight loss 31 % at 386 °C represents degradation of skeletal PANA chain structure after dopant has been removed. Above 447 °C, the results obtained are associated with the residues only. From DSC results Fig. 9(b) showed that there is exothermic peak at 447 °C (Tables 2 and 3).

In case of PANA microspheres, the first stage with weight loss of 6 % at temperature up to 108 °C results from the loss of water molecules from the polymer and perhaps out of gassing of unknown small molecules. The second stage that commences after 108 °C until 189 °C of weight loss 10 % which associated with the loss of acid dopant bound to the PANA chain and the evolution of CO_2. The third stage with weight loss of 49 % at 471 °C represents degradation of skeletal PANA chain structure after dopant has been removed. Above 583 °C, the results obtained are associated with the residues only. From DSC in Fig. 9(b) showed that there is exothermic peak at 583 °C.

TGA and DSC results showed that the change in morphology and particle size from microspheres to nanofibres decreased the stability of the prepared PANA While, the stages of degradations were shifted to lower temperatures values.

Conclusion

Polyanthranilic acid nanofibres, nanorods and nanospheres have been synthesized by polymerization of anthranilic acid using ammonium peroxydisulfate (APS) as oxidant without hard or soft templates at different conditions for the first time. Moreover, PANA microspheres have been synthesized by polymerization of anthranilic acid via interfacial polymerization, solution polymerization in aqueous solution of acetic acid, and polymerization in absence of redox initiator ($FeSO_4$). The morphology and particle size of nanostructures ($\leq$ 100 nm) were studied using scanning electron microscope (SEM) and transmission electron microscope (TEM). The optical properties and thermal stability of nanofibres prepared by rapid polymerization imitated by redox initiator ($FeSO_4$) were compared with microspheres obtained at the same conditions of polymerization in absence of $FeSO_4$ as redox initator. The results obtained from optical measurements showed that λ max of PANA nanofibres (680 nm) is longer than λ max of PANA microsperes (580 nm). This indicates that the maximum wavelength of PANA microspheres is shifted to shorter wavelength (blue shift). The optical bandgap of PANA nanofibres is narrower than the optical bandgap of PANA microsheres. The optical bandgap decreased with decreasing the particle size. The optical absorption of PANA lies in visible region implies the possibility of using these materials in solar energy applications. Thermal analysis results showed that PANA microspheres are more stable than nanofibres.

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