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Morphological study of novel architecture titanium dioxide nanowires decorated polyaniline nanocomposites and its electrical properties

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ABSTRACT

Polyaniline-Titanium nanowires (PANi/TiO_2 nanowires) composites were prepared in presence of organic/inorganic acid medium. Firstly, TiO_2 nanoparticals (P_{25}) were converted to TiO_2 nanowires through hydrothermal process using 10% NaOH, subsequently the aniline was polymerized by the addition of ammonium persulfate in the presence of acetic acid and sulfuric acid medium using 10 % TiO_2 nanowires to form PANi/TiO_2 nanowires composites. The prepared composites have been characterized by UV-Visible and FT-IR. The UV-Visible spectra and composites exhibited an additional band at around 445nm, which represents the formation of polyaniline in the presence of TiO_2 nanowires. The FT-IR spectra of the PANi/TiO_2 nanowires composites demonstrates the change of the intensity of the bands at 1595 and 1468 cm-1 correspond to C = C of quinoid and benzoid rings as compared to that of pure PANi, which reveals that the PANi in the composites is richer in quinoid units than the pure PANi. The SEM and TEM distinguished that the morphology of the PANi/TiO_2 nanowires composites varied from 1D nanofibers to 2D leaves and 3D granules and rose-like micro/nanostructures depends on the reaction conditions. Moreover, the electrical conductivity of the prepared composites showed no significant decrease in conductivity compare with pure polyaniline prepared in absence of TiO_2 nanowires this due to the network structure of TiO_2 nanowires and to be in the order of 10^{-2} S/ cm in case of using acetic acid and 10 S/cm in case of using sulfuric acid.

KEYWORDS

Polyaniline;
Titanium nanowires;
Composites;
Nanofibers;
Morphology;
Conductivity.

INTRODUCTION

Polyaniline (PANi) is one of the best promising materials in conducting polymers, due to its potential applications in optical and microelectronic devices, sensors[1, 2], catalysts, drug delivery, energy storage systems, electrodes[3, 4] environmental stability in a conducting form, corrosion protection[5, 6], release devices[7, 8], and oxidation or protonation adjustable electrooptical properties[9-11]. A key property of a conductive polymer is the occurrence of conjugated double bonds along the backbone of the polymer chains. In conjugation, the bonds between the carbon atoms are alternately single and double, the oxidation of aniline monomer in the inorganic acid media by chemical polymerization using ammonium peroxydisulfate as oxidant has become the most extensively used synthetic route to conducting PANi. As well as, the obtained PANi has some disadvantages that PANi is inherently brittle and poor in processability due to its insolubility in common organic solvents to overcome these difficulties by using functionalized protonic acids[12], and surfactants such as SDBS and SDS[13]. Moreover, the problems of low stability and workability of pure PANi can be avoided throughout the synthesis of composite materials coupling the properties of PANi and the new composites or simple mixing of the components in melts or in solution does not always cause high dispersion of PANi as a result of incomplete or poor compatibility of the components[14]. In this case it is more efficient to carry out polymerization of aniline in the dispersed matrix polymer which allows the formation of a thin layer of PANi on the surface of particles. The preparation of PANi counts on the reaction conditions and several factors should be substantial in the control of the properties and morphology of PANi[15, 16] such as, the chemical nature of the oxidants, the nature of the acid protonating the aniline monomer, reaction temperature, the reaction intermediates during the oxidation, the concentrations of the reactants (aniline/oxidant) and their molar proportions, solvent using in the polymerization process, the additives (e.g. colloidal stabilizers, emulsifiers, and metal oxide nanoparticals). Moreover, the preparation of PANi/nanocomposites by conventional blending, mixing in solution or melt form become very difficult. A number of methods have been used to prepare PANi/nanocomposites, the commonly method used to prepare the nanocomposites is the intercalation of aniline (aniline hydrochloride) into the gallery of clay layers followed by in-situ polymerization[17-19]. Emulsion polymerization is also used for preparation of PANi/ clay nanocomposites[20-22], where the emulsifier in the emulsion system contributes to maximization of the affinity between hydrophilic host (clay) and hydrophobic guest (aniline), this composites showing electrical conductivity as well as good physical properties[23].

Synthesis of one- dimensional nanostructures TiO_2 possess various sizes and morphologies in nanoscale (e.g. nanorods, nanowires and nanotubes) and it is important for a wide range of fields and applications[24-27]. Also, TiO_2 utilizes in a wide range of significant technological applications where a more detailed understanding of the essential aspects of TiO_2 surfaces or interfaces would potentially have a positive impact. Also, TiO_2 nanoparticls have received great attention in photovoltaic cells, batteries, electrochemical sensing, optics, photonic crystals, catalysis and photocatalysis[28], photovoltaics[29, 30], UV blocking, smart coatings, and functional fillers in textiles, paints, paper, and cosmetics[31, 32] this because of their unique electrical, optic properties, and it has a very wide band gap. While many of these applications require high surface and interfacial areas, it is advantageous to have TiO_2 in the form of nanoparticls or nanowires. While, TiO_2 can be synthesized in a number of nanostructures and phases, including nanoparticls[33], polycrystalline nanowires[34], and nanotubes[35-38]. Many papers on PANi/ TiO_2 composites have been published[39-43]. In previous work by Zhang et al. they succeed to fabricate polyaniline in presence of TiO_2 composite nanotubes and the PANi/ TiO_2 composite microspheres[44]. They found that the morphology, size, molecular structure, electrical properties, and wettabilities of these micro/ nanostructures are affected by the content of TiO_2 nanoparticls in the composites.

The most of polyaniline preparations are carried out in dilute hydrochloric acid or they use aniline hydrochloride as a monomer[45]. Other inorganic acid, eg sulfuric acid[46] has infrequently been used in the expectation of enhanced conductivity of the PANi. Moreover, polyaniline prepared in the presence of weak organic acids, such as (Acetic acid) has a conductivity of the order of 10^{-2} to 10^{-1} S cm^{-1}, these values being comparable with those for PANi prepared by the oxidation of aniline in the absence of any acid and this is a surprisingly good level of electrical conduction. In the case the polyaniline prepared embracing frequently of sulfate counter-ions, fashioned by the reduction of peroxydisulfate. This fact should also be taken on your consideration in the current study, in viewing the use of various acids either weak organic acid (acetic acid) or strong inorganic acid (sulfuric acid) which are likely to be the main counter-ions in the prepared polyaniline nanocomposites in existence of TiO_2 nanowires as nanofillers and in the presence of those two acids in addition to study the different morphology of the prepared polyaniline nanocomposites ant its electrical conductivity.

MATERIALS AND METHOD

Materials

Titanium dioxide powder (P25, Degussa, ~25 nm in diameter), was used as received. Aniline hydrochloride monomer (99% purity, Aldrich) was distilled under reduced pressure and stored at low temperature prior to use. Ammonium persulphate (APS), Sodium hydroxide (NaOH) and Sodium chloride (NaCl) were used as received from Alfa Aesar and all other organic solvents used in this study were of analytical grade and used without further purification.

Preparation of the sodium titanate nanowires

In a classic nanosynthesis[47], 0.2 g of TiO_2 nanoparticles (P25) in aqueous solution of NaOH (10M, 40ml) was placed into a Teflon-lined autoclave. The mixture was stirred to form a milky suspension, then sealed and hydrothermally treated at 200-240 °C for ~3 days. Subsequently, the resultant white precipitate (the sodium-titanate nanowires) was separated by filtration, and washed with an aqueous solution of sodium chloride (1.0 M) so as to get the $Na_2Ti_3O_7$ nanowires. The resultant powdery sample was then oven-dried at 80 °C for 6 hr.

Preparation of polyaniline and polyaniline / TiO_2 nanowires composites

The preparation of pure polyaniline through the oxidation polymerization by oxidizing aniline hydrochloride with ammonium persulphate in an aqueous medium without any extra acid at room temperature as very simple method and has been used as a reference[45]. Using 0.2 mol/L of aniline hydrochloride monomer was dissolve in 100 ml of 0.1 M HCl and 0.25 mol/L ammonium persulphate as initiator was added drop by drop for ½ h., then the polymerization take place by adding the initiator. The reaction left under stirring over night to complete the polymerization process the prepared polyaniline was collected on a filter, washed with three times by 0.1 M HCl, and also with acetone. Polyaniline powder was dried in air and then in vacuum at 60°C. The preparation of polyaniline/TiO_2 nanowires composites through the oxidation polymerization, the desire amount of TiO_2 nanowires based on the monomer concentration was dispersed in an aqueous solution containing sulfuric acid (0.1 or 0.2 mol/L) in round flask using an ultrasonicator for 30 min. Then 0.2 M of aniline monomer was added to the round flask, stirring for 10 min afterward 0.25 M of ammonium peroxydisulfate was dissolved in water and added dropwise to the acidic aqueous solution for ½ h, briefly stirred at room temperature, and left at rest to polymerize for 24 h., subsequently polyaniline was collected on a filter, washed with three 100-mL of portions of 0.1 M HCl, and also with acetone. Polyaniline powder was dried in air and then in vacuum at 60 °C. Otherwise acetic acid was used as organic acid in different concentrations to prepare polyaniline in presence of different concentration of TiO_2 nanowires (5 and 10%), the same experiments were repeated at 0 °C for the acetic acid and sulfuric acid.

Characterization

The XRD was carried out in a Bruker D8 Advance X-ray diffractometer with CuK-α radiation (λ= 0.1542 nm, 40 kV, 30 mA). The lattice spacing was calculated via Bragg's equation. PANi/TiO_2 nanowires composites samples used for XRD were pasted to a glass slide by separating the samples homogenously on it. The samples were placed in a vertical configuration (transmission) for the collection of XRD data. The microstructure of the samples was examined for very dilute suspensions of the corresponding nanocomposites in water using JEOL JEM-1230 transmission electron microscope (TEM) with acceleration voltage of 80 kV. The microscopy probes of the nanocomposites samples were prepared by adding a small drop of the water dispersions onto a Lacey carbon film-coated copper grid then allowing them to dry in air. Also, scanning electron microscope (SEM), Tescan VEGA-II, USA, operated at 20 kV. FT-IR spectra were recorded using Perkin Elmer Fourier transform infrared spectroscopy. The AC conductivity measurements were carried out on pressed discs in the temperature range 30–120 °C at frequencies from 100 Hz up to 100 kHz using Hioki Z-Hitester 3531 LCR Bridge and Hioki 9261 Test Fixture, Japan.

RESULT AND DISCUSSION

The design of novel molecular structure and the expansion of a new doping method is a challenge for the fabrication of polyaniline composites of high quality, and high solubility. Additionally, the toxicity of the aniline monomer is of concern with considers to an environmentally friendly synthesis (i.e., green chemistry), and requests to be tackle for commercial applications, furthermore, the efficient polymerization of aniline monomer is accomplished simply in an acidic medium, where aniline survives as an anilinium cation. The organic and inorganic acids of different concentrations have been used in the syntheses of polyaniline in presence of TiO_2 nanowires.

FT-IR spectroscopy

Figure 1 shows the FT-IR spectra of the TiO_2 nanowires, PANi and PANi/TiO_2 nanowires composites. It was observed that, TiO_2 nanowires having characteristic peaks at 908 and 512 cm^{-1} which are assigned to the Ti–O–Ti stretching vibrations. The bond Ti–OH observed below 3498 cm^{-1} indicates the existence of hydrogen bonding, while the characteristic bands in IR spectra of PANi occur at 3488, 1595, 1468, 1328, 227, 1125, and 780 cm^{-1}. The spectra of PANi exhibit the bands at about 1595 and 1468 cm^{-1} correspond to C = C stretching of quinoid and benzoid rings vibrations, respectively[48], indicating the oxidation state of PANi (emeraldine salt). As commonly observed for emeraldine salts, the benzenoid band at 1468 cm^{-1} is stronger than that of the quinoid band at 1595cm^{-1}. The strong characteristic band appearing at 1125 cm^{-1} was explained by MacDiarmid and co-workers[48] as the ‘‘electron-like band’’ and is considered to be a measure of the delocalization of the electrons and, thus, is indicative of the conductivity of PANi. Also, the incorporation of TiO_2 nanowires leads to the shift of some FT-IR bands of prepared polyaniline composites. The characteristic bands in the spectra of PANi/ TiO_2 nanowires prepared in 0.4 mol/l of acetic acid observed plus to the characteristic bands of PANi, are at 1479, 1425,1202, 1070, 750 and 696 cm^{-1} (Figure 1d). The bands at 1479 and 1425 cm^{-1} are related to mix C–C stretching, and C–H and C–N bending vibrations observed in the spectra of the aromatic oligomers[49, 50]. The peak at 1070 cm^{-1} is possibly due to the S=O stretching vibration and suggests the presence of sulfonic groups on the aromatic rings[51]. When polymerization of aniline was performed in solutions 0.2 mol/l of sulfuric acid there are bands at at 3485, 1586, 1446, 1328, 1187, and 748 cm^{-1} (Figure 1c). Also, there are blue shift in the wave numbers for the bands obtained form PANi/TiO_2 nanowires composites (Figure 1c, d) compared with that obtained from pure PANi (Figure 1b) as shown in TABLE 1. Furthermore, it can be noted that the hydrogen-bond absorption at 3230 cm^{-1} is strengthened in the presence of TiO_2 nanowires in the polyaniline composites which suggested that there is strong interaction between the polyaniline and TiO_2 nanowires through hydrogen bonds between PANi and hydroxyl group of TiO_2 nanowires.

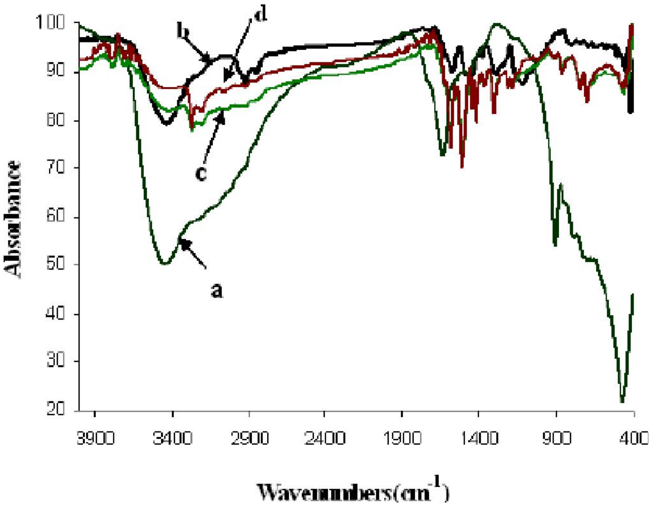

Figure 1 : FTIR spectra of the samples obtained through oxidative polymerization: (a) TiO2 nanowires; (b) Polyaniline in absence of TiO2 nanowires; (c) polyaniline/ TiO2 nanowires composites prepared using acetic acid 0.2 mol/l; (d) polyaniline/ TiO2 nanowires prepared composites using sulfuric acid 0.2 mol/l.

UV-Visible spectra

Figure 2 shows the UV–vis absorption spectra of polyaniline/TiO_2 nanowires (10 %) prepared in different in acidic medium. Noticeably, the prepared polyaniline/TiO_2 nanowires (10%) composites not only can strongly absorb the UV light but also be able to absorb the visible and near-IR light. The characteristic peaks of polyaniline appear at two bands close to 325 and 620 nm. The absorption peaks at 325 and the absorption in the visible region at ~ 620 nm are due to the π–π* (benzenoid) and n- π* (quinoid) transitions of the emeraldine salt of the polyaniline backboned[52], respectively. These results are reliable with that reported by other authors[53, 54]. Amusingly, the absorption spectra of the PANi/TiO_2 nanowires (10 %) composites illustrated three characteristic peaks at 325, 445, and 630 nm. The additional absorption peak at ~ 445 nm it perhaps due to the electronic state provoked by the doping of the carboxylic groups of the acetic acid into the imine sites of PANi[55]. Moreover, this peak illustrated that the interaction between the TiO_2 nanowires and polyaniline layer that facilitates electron delocalization between the composites, and also improved the electrical conductivity of the polyaniline composite[52]. The two peaks assigned to the excitation of the benzenoid and quinoid segments were shifted slightly in the PANi/TiO_2 nanowires composites and demonstrate the existence of a site selective interaction between the quinoid ring of the PANi and TiO_2 nanowires[56]. It is well known that the electronic absorption spectra of the conjugate polymer are strongly associated to degree of doping, conjugation length, and the type of solvent used to prepare the polymer solution.

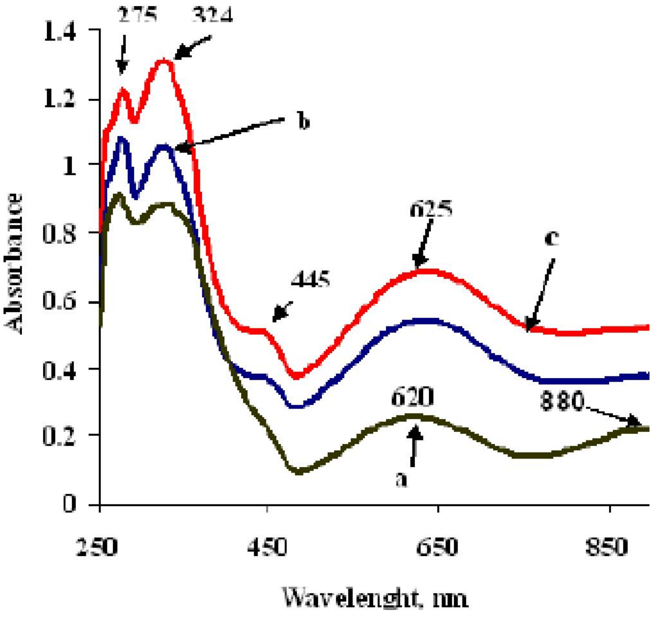

Figure 2 : UV-visible spectra of a) polyaniline prepared by classical method as well as PANi/TiO2 nanowires composites prepared by oxidation process in different acidic medium b) 0.2 M of sulfuric acid, and c) 0.2 M of acetic acid.

TABLE 1 : The blue shift of FT-IR band of Polyaniline and Polyaniline/ TiO_2 nanowires composites

Samples	C=C benzenoid ring cm^{-1}	C=C quinoid ring cm^{-1}
PANi in absence of TiO_2 nanowires	1468	1146
PANi/ TiO_2 nanowires (10%) using 0.2 mol/l of sulfuric acid	1446	1187
PANi/ TiO_2 nanowires (10%) using 0.2 mol/l of acetic acid	1425	1202

XRD diffraction patterns

Figure 3 confirms the X-ray diffraction patterns of TiO_2 nanowires, polyaniline, and polyaniline / TiO_2 nanowires composites prepared using different acidic medium using 10% TiO_2 nanowires throughout the oxidative polymerization using ammonium persulphate and aniline monomer. The XRD of TiO_2 nanowires (Figure 3 a) produced through the hydrothermal synthesis step could be indexed to the sodium titanate, $Na_2Ti_2O_4(OH)_2$, which has the body-centered orthorhombic crystal structure shown above the corresponding XRD. The body-centered orthorhombic $Na_2Ti_2O_4(OH)_2$ is made up of TiO_6 octahedra that share edges to form two dimensional sheets. These sheets are held together and electrostatically stabilized with Na^+ and OH^- in between the layers. Conversely, the peak of diffraction of TiO_2 nanowires appears at 2θ = 11° (d = 8.1 Å), 2 θ = 31° (d = 3 Å) and 2 θ = 45.5° (d = 2.16 Å). While, the Bragg diffraction peaks of 2θ = 25.5° (d = 3.574 Å), 2 θ = 20.8° (d = 4.34 Å), 2 θ = 8.7° (d = 10.2 Å)[57], and 2 θ = 15.2° (d = 5.9 Å) can be found in the pure polyaniline, as shown in (Figure 3b). Also it can be distinguished that when using 10% of TiO_2 nanowires in the polyaniline/TiO_2 nanowires composites using 0.2 mol/l of sulfuric acid and 0.2 mol/l of acetic acid at room temperature (Figure 3c, d) respectively, the peaks of diffraction of polyaniline at 2θ = 25.5° (d = 3.574 Å), and 2 θ = 20.8° (d = 4.34 Å) become very weak and broaden and the peak of TiO_2 nanowires in the XRD spectra in the nanocomposites were absent this because the low concentration of TiO_2 nanowires in the matrix and the addition of TiO_2 nanowires was hinders the crystallization of the polyaniline molecular chain. This is due to when the polyaniline is engrossed on chain of absorbed polyaniline is tethered, and the degree of crystallinity decreases.

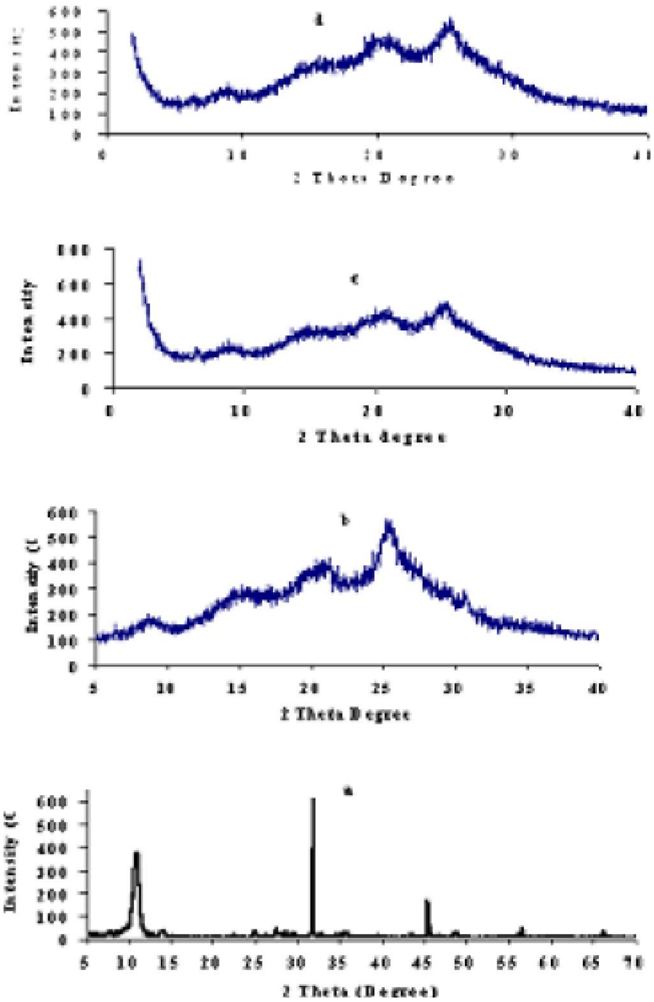

Figure 3 : XRD diffraction pattern of a) TiO2 nanowires, b) pure polyaniline, c) PANi/ (10%) TiO2 nanowires composites prepared using 0.2 mol/l of sulfuric acid, d) PANi/ (10%) TiO2 nanowires composites prepared using 0.2 mol/l of acetic acid.

Figure 4 illustrates the X-ray diffraction patterns of polyaniline obtained through oxidative polymerization of aniline in presence of 10% TiO_2 nanowires using 0.2 mol/l of sulfuric acid and 0.2 mol/l of acetic acid at 0 °C. when using sulfuric acid as inorganic acid medium, there are two peaks at 2 θ = 5.86° (d = 15 Å), and 2 θ = 10.82° (d = 8.2 Å) that indicate that the formation of short oligomers composed of several aniline units, rich in phenazine structures which appear at 2 θ = 5.86° whereas the other peaks appear at 2 θ = 10.82° for TiO_2 nanowires which proven by SEM micrograph which is stronger than that of polyaniline/ TiO_2 nanowires prepared using 0.2mol/l acetic acid, The results suggest that the formation of polyaniline nanofibers on the surface of TiO_2 nanowires.

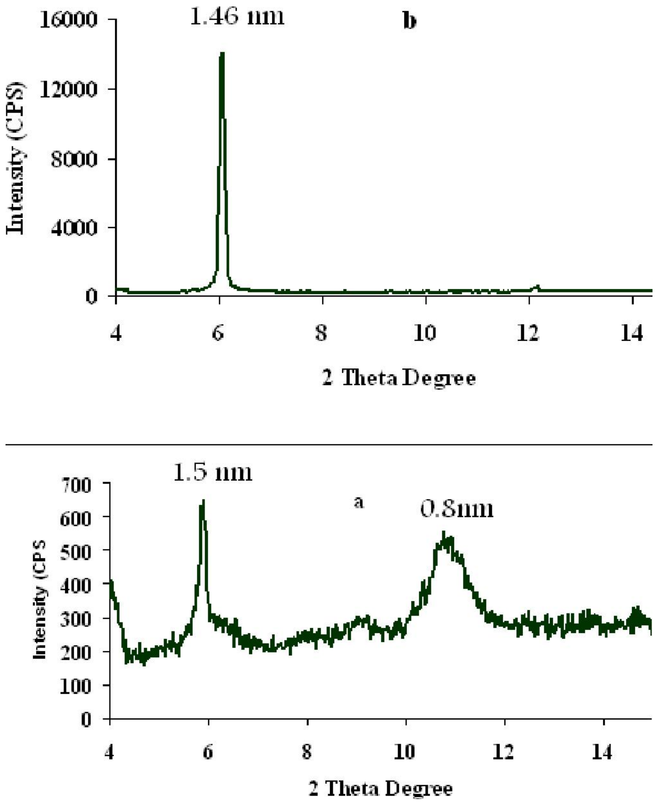

Figure 4 : XRD diffraction pattern of, a) PANi/ TiO2 nanowires (10%) composites prepared using 0.2 mol/l of acetic acid prepared at 0 oC, b) PANi/ TiO2 nanowires (10%) composites prepared using 0.2 mol/l of sulfuric acid prepared at 0 oC.

Morphology

Scanning electron microscope (SEM)

The study demonstrated that SEM results when appropriately interpreted and combined with TEM results give a much clearer picture of the formation of different morphology of PANi. Corresponding, these two techniques offer information to help us to achieve significant relationships between the polymer-inorganic nanocomposites nanostructure. Also, the morphology of the prepared PANi particles by oxidative polymerization using organic/inorganic acid medium in presence of 10 % of TiO_2 nanowires is frequently difficult to control, and is most often nanofibers rather than globular micro/nanostructure. Moreover, the construction of granular, leaves, rose and fibers micro/nanostructures morphologies of conductive polymers in presence of TiO_2 nanowires were highly attractive, due to a high length/diameter ratio (i.e. high aspect ratio) of TiO_2 nanowires.

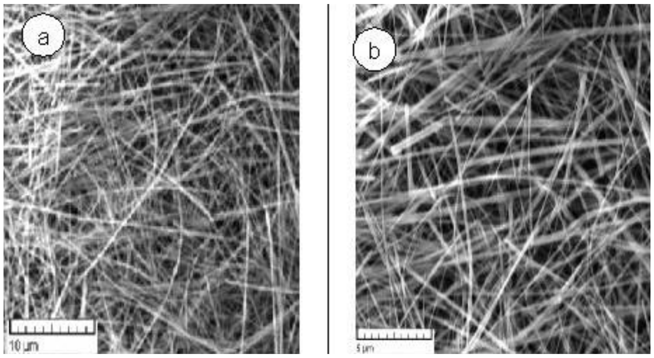

Figure 5 : SEM micrographs of TiO2 nanowires prepared by hydrothermal method using 10 M NaOH for 72 hr. at 220-240 oC, for clarity using different magnifications (a, b).

The SEM microgaphs of polyaniline TiO_2 nanowires was done and for the sake of clarity, each photograph is shown in different magnifications. The TiO_2 nanowires are clearly obvious in the SEM image (Figure 5a, b) as tangled, ropes with a smooth surface. For the PANi/ TiO_2 nanowires composites, the changes in the morphology are remarkable. Also, for the prepared composites, when the polymerization take place using 0.4 mol/L of sulfuric acid as strong acidic medium in presence of TiO_2 nanowires facilitated the formation of PANi particles on the surface of the TiO_2 nanowires by formation of core-shell polyaniline/ TiO_2 nanowires composite, as shown in (Figure 6).

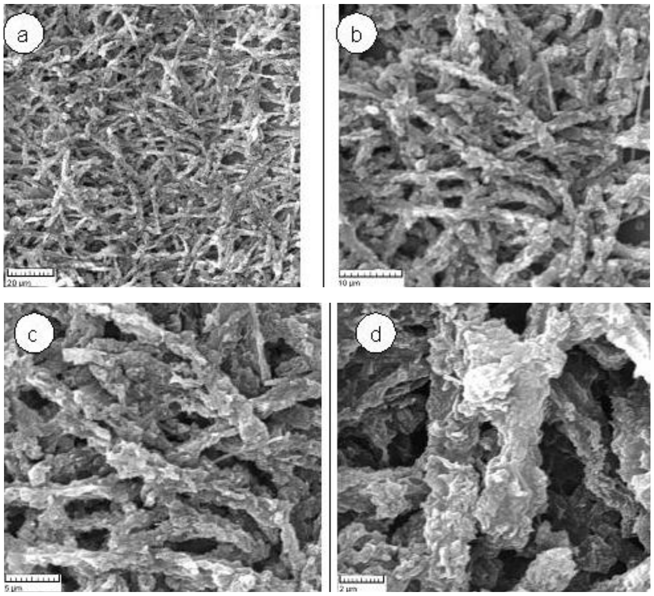

Figure 6 : SEM micrographs of polyaniline/ TiO2 nanowires composites prepared by oxidation polymerization using 0.2 M Sulfuric acid (H2SO4) using 10 % of TiO2 nanowires, at room temperature at different magnifications (a, b, c, and d).

By carrying out the polymerization process of aniline in 0°C the incredible morphology of PANi nanofibers on the surface of TiO_2 nanowires as network like-structure this because of the high aspect ratio of TiO_2 nanowires which lead the formation of polyaniline nanofibers on its surface as observed in (Figure 7).

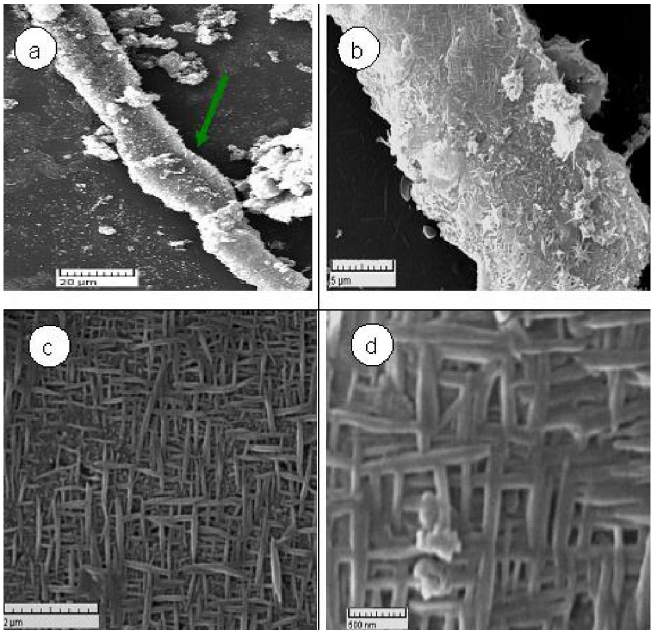

Figure 7 : SEM micrographs of polyaniline/ TiO2 nanowires composites nanofibers prepared by oxidation polymerization using 0.2 M Sulfuric acid (H2SO4) using 10 % of TiO2 nanowires, 0 oC, for clarity using different magnifications (a, b, c, and d).

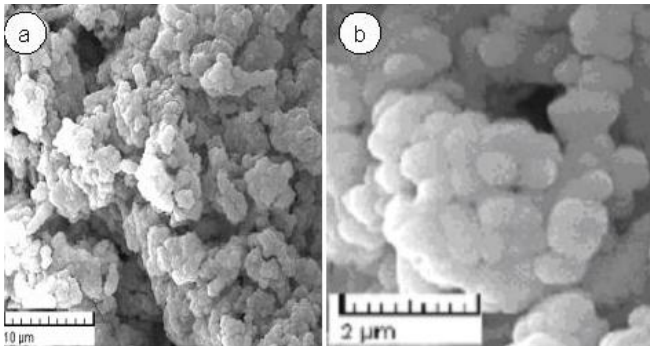

Figure 8 : SEM micrographs of polyaniline (Granular structure) prepared by oxidation polymerization using 0.2 M acidic acid in absence of TiO2 nanowires, for clarity using different magnifications (a, b).

Additionally, The SEM distinguished that the morphology of the PANi/ TiO_2 nanowires composites changed from 1D nanofibers to 2D leaves and 3D rose-like microstructures by changing either the concentration of TiO_2 nanowires during the polymerization process or by change the reaction temperature, Figure 8 showed that the formation of granular structure of polyaniline when using 0.4M of acetic acid in the absence of TiO_2 nanowires at room temperature and the APS/ANI molar ratio was 1:1.25. The formed polyaniline exhibits granular particles or a sponge like structure of pure PANi obtained in a standard polymerization. Granular morphology is the most typical form for PANi prepared in the typical way[58].

It can be thought that the granule structure of PANi has a core–shell structure. The core is contained phenazine nucleates and the shell is composed of radically oriented stretched PANi chains. The ordering of chains is lower at the globule edge, and the PANi chains become randomly oriented close to the granule surface[59]. When the polymerization of aniline occurs by loading 5 % of TiO_2 nanowires, the morphology of the prepared composites is totally differ and leave-like micro/nanosturacture PANi/ TiO_2 nanowires composites will be formed as shown in (Figure 9) and for more directness, each photograph is shown in two magnifications for the PANi/ TiO_2 nanowires composites and the change in the morphology of the prepared composites are extraordinary, However, Figure 10 revealed that the formation of 3-dimensional polyaniline rose like micro/nanostructure in case of loading the concentration of TiO_2 nanowires to 10 % depend on the monomer concentration and the composition of the two kinds of particles depends on the content of TiO_2 nanowires charged. With increasing TiO_2 nanowires content, the contact area between polyaniline and TiO_2 nanowires increased, the absorbed polyaniline increased, and the content of free polyaniline decreased, which leads to the formation of rose–like micro/nanostructure with a more uniform composite structure.

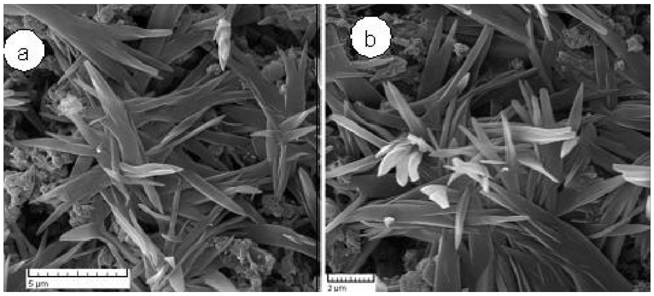

Figure 9 : SEM micrograph of polyaniline/ composites(leaves –like micro/nanostructure) prepared by oxidation polymerization using 0.2 M acidic acid by the addition of 5 % TiO2 nanowires for clarity using different magnifications (a, b).

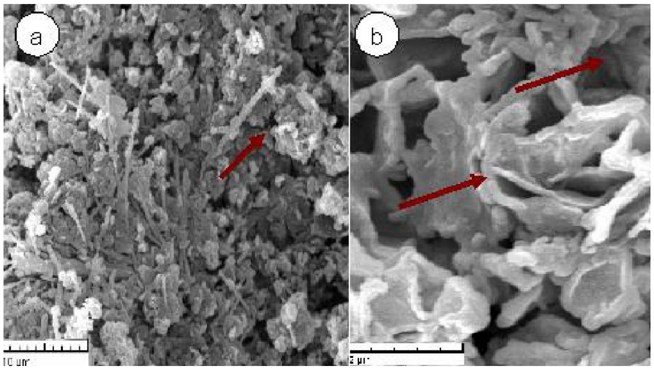

Figure 10 : SEM micrographs of polyaniline composites (rose –like microstructure) prepared by oxidation polymerization using 0.2 M acidic acid (HAC) by the addition of 10 %TiO2 nanowires, for clarity using different magnifications (a, b). Arrows indicated the formation of rose –like microstructure.

The rich diversity of PANi structures prepared in 0.4 mol/L^{1} acetic acid is better visualized on SEM micrographs (Figure 11) and may be the result of the existence of TiO_2 nanowires that lead to the formation of PANi nanofibers when using solution of acetic acid due to the high surface areas of the TiO_2 nanowires works as core coated by the shell of polyaniline which causing the arrangement of PANi nanofibers on the surface of TiO_2 nanowires this phenomena was observed also in case of using sulfuric acid as inorganic acid. It can be concluded that the PANi nanofibers takes place by using TiO_2 nanowires in organic acid medium and PANi is produced as nanofibers having a diameter of tens of nanometers and a length of a few micrometers. Also, the construction of nanofibers is based on the mechanism of the stacking of phenazine nucleates, from which polymer chains grow. The nanofibers radius is determined by the length of the polymer chains, i.e. by their molecular weight. At higher aniline concentrations the radius increases during the polymerization. The use of ammonium peroxydisulfate as oxidants with a high oxidation potential, favors secondary nucleation. Simultaneously with the growth of nanofibers, the formation of new nucleates takes place close to their surface. Also, the mechanism of a template process has been accessible in explanation[60]. As well, the formation of polyaniline composites with a core-shell structure still remains a puzzle and needs new technologies and new methods

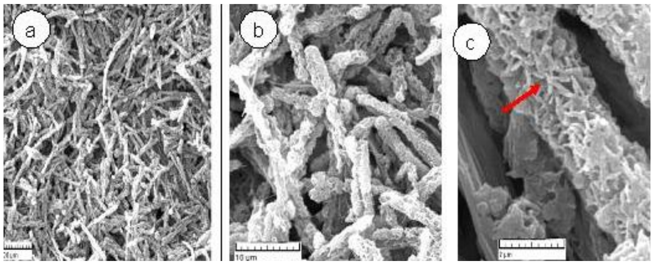

Figure 11 : SEM micrograph of polyaniline composites (fibers-like micro/nanostructure) prepared by oxidation polymerization using 0.2 M acidic acid by the addition of 10 %TiO2 nanowires at 0 oC at different magnifications (a, b, and c).

Transmission electron microscope (TEM)

Figure 12 revealed that the TEM micrographs of TiO_2 nanowires, pure polyaniline and polyaniline composites constructed by oxidative polymerization using sulfuric acid in presence of TiO_2 nanowires at room temperature. Figure 12a suggests that (i) the bundled TiO_2 nanowires mostly stay in a stacked (i.e. one sitting on the other) and warped form due to an interfacial bonding that holds all the nanowires together in a bundle, and (ii) the recognizable space in between the nanowires in the bundles is due to the interfacial bonding as weak as, likely a H-bonding. (Figure 12b) shows the pure polyaniline without any TiO_2 nanowires which represent nanofiber form of polyaniline. The average diameter of the produce nanofibers was about 20 nm. These thinner polyaniline nanofibers aggregated to bundles by van der Waals' forces. By loading 10% of TiO_2 nanowires during the polymerization process of polyaniline at 0 °C the TEM image confirms to type of nanofibers one for the surface of TiO_2 nanowires (Figure 12c) and the other for polyaniline nanofibers as network on the surface of TiO_2 nanowires as revealed by SEM (Figure 12 d). Interestingly, the oxidative polymerization of aniline monomers provides a route to the direct configuration of nanofibers of PANi- TiO_2 nanowires composites when the polymerization takes place at room temperature, the formation of polyaniline nanofibers in case of using two type of acids (Figure 12e, f) and there is no change in the TEM image by increasing the reaction temperature from zero to room temperature in presence of 10% TiO_2 nanowires.

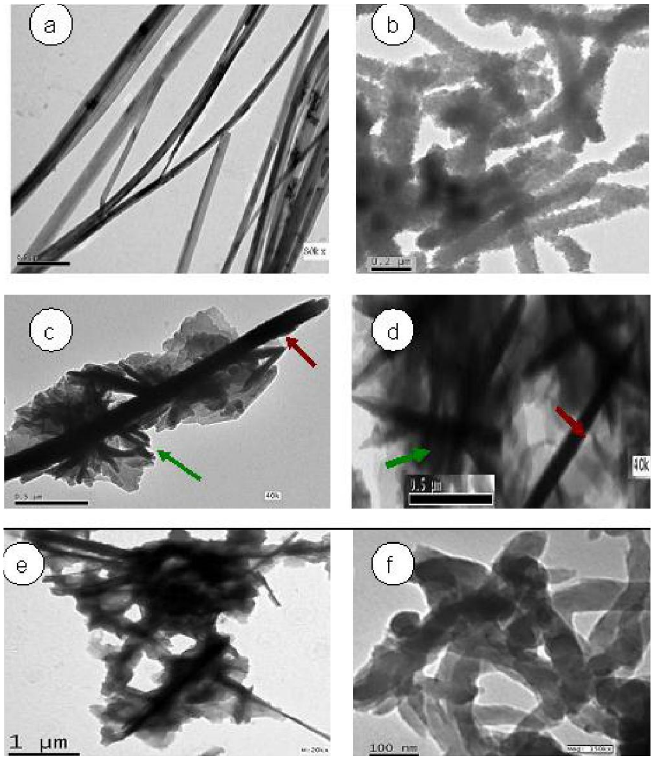

Figure 12 : TEM micrographs of a) TiO2 nanowires; b) pure PANi without TiO2 nanowires; c) PANi-10 % TiO2 nanowires prepared using acetic acid at 0 oC; d) PANi-10 % TiO2 nanowires prepared using Sulfuric acid at 0 oC; e) PANi-10 %TiO2 nanowires prepared using acetic acid at room temperature; f) PANi-10 % TiO2 nanowires prepared using Sulfuric acid at room temperature.

Electrical conductivity

The electrical conductivity of polyaniline is a significant parameter for most applications of conducting polymers, in the presence of the single crystallinity and multilayered TiO_2 nanowires could provide direct electrical pathways for photogenerated electrons and enhance the electron transport rate in the polyaniline nanocomposites, when 0.2M aniline monomer was oxidized with 0.25M ammonium peroxydisulfate in presence of 10% TiO_2 nanowires and using an aqueous medium containing 0.2 mol/L of sulfuric acid and 0.2 mol/L of acetic acid. The electrical conductivities of polyaniline composites obtained through oxidative polymerization using 10% of TiO_2 nanowires in presence of acidic acid increasing from $6.6x10^{-3}$ to $8.2 x10^{-2} Scm^{-1}$ by decreasing the temperature from 25°C to 0°C. While the conductivity of polyaniline prepared in absence of TiO_2 nanowires using 0.4 mol/L of acetic acid is 9.6 x10^{-1} Scm^{-1}. As well, the conductivities of composites prepared using 0.2 mol/L of sulfuric acid also increasing from 1.48 to 2.12 Scm^{-1} by decreasing the temperature from 25°C to 0°C compared with the pure polyaniline prepared in absence of sulfuric acid which around 3.2 Scm^{-1} as shown in TABLE 2. This increasing in the conductivity by decreasing the temperature is not easy to clarify but an assumption is accessible. Ring sulfonation in the polyaniline chains may take place during polymerization by the attack of peroxydisulfate radicals. Such a process might be more concerned in the polymerization at low temperature, which proceeds for long time. The sulfoxy groups would then participate in internal protonation[61] a self-doping, thus moderately increasing the conductivity. This hypothesis is supported by the elemental analysis of the PANi bases which revealed the presence of 0.3 wt% sulfur[45]. In addition, this results suggest that the conductivity decreased by the addition of TiO_2 nanowires during polymerization process.

TABLE 2 : The electrical conductivity of polyaniline and polyaniline/ TiO_2 nanowires composites.

Samples	Acid Concentrations	Conductivity Scm^{-1}		Percent of TiO_2 nanowires
		25 °C	0 °C	
Pure Polyaniline	0.2 mol/l of sulfuric acid	3.2	--	----
	0.2mol/l of acetic acid	9.6 x10^{-1}	---	-----
PANi/ TiO_2 composites	0.2 mol/l of sulfuric acid	1.48	2.12	10 %TiO_2 nanowires
PANi/ TiO_2 composites	0.2mol/l of acetic acid	6.6x10^{-3}	8.2 x10^{-2}	10 %TiO_2 nanowires

CONCLUSION

TiO_2 nanoparticals (P_{25}) were successfully converted to TiO_2 nanowires via hydrothermal process using 10% NaOH, PANi/TiO_2 nanowires composites by polymerized the aniline monomer using potassium persulfate as oxidant in the presence of acetic acid and sulfuric acid medium using 10 % TiO2 nanowires. The prepared PANi/TiO_2 nanowires composite exhibits an additional band at around 445nm in the UV-Visible spectra, which confirmed the formation of polyaniline in the composite. The FT-IR spectra of the PANi/TiO_2 nanowires composites demonstrates the shift in the C = C of quinoid and benzoid rings vibrations as compared to that of pure PANi. The morphology of the prepared PANi/TiO_2 nanowires composites were distinguish by SEM and TEM and varied from 1D nanofibers to 2D leaves and 3D granules and rose-like micro/ nanostructures counts on the reaction conditions. Furthermore, The electrical conductivity of the prepared PANi/TiO_2 nanowires composites was evaluated and no significant decrease in conductivity compare by pure polyaniline prepared in absence of TiO_2 nanowires because of the TiO_2 nanowires works as network structure on the polyaniline composites and to be in the order of 10^{-2} S/ cm in case of using acetic acid and 10 S/ cm in case of using sulfuric acid.

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REFERENCES

[1] S.Huang, B.H.Virji, R.B.Weiller, Kaner; J.Am.Chem.Soc., **125**, 14 **(2003)**.
[2] S.H.Hosseini, A.A.Entezami; Polym.Adv.Technol., **12**, 482 **(2001)**.
[3] T.Cao, L.Wei, S.Yang; Langmuir., **18**, 750 **(2002)**.
[4] H.Gharibi, M.Zhiani, A.A.Entezami, R.A.Mirzaie, M.Kheirmand, K.Kakaei; J.Power Sourc., **155**, 138 **(2006)**.
[5] C.Jeyaprabha, S.Sathiyanarayanan, G.T.J. Venkatachari; J.Appl.Polym.Sci., **101**, 2144 **(2006)**.
[6] N.Ahamad, A.G.MacDiarmid; Synth.Met., **78**, 103 **(1996)**.
[7] L.M.Lira, S.I.Codoba De Torresi; Electro.Chem.Commun., **7**, 717 **(2005)**.
[8] B.Massoumi, A.A.Entezami; Polym.Int., **51**, 555 **(2002)**.
[9] A.J.Heeger; J.Phys.Chem., **B105**, 8475 **(2001)**.
[10] J.M.Pernaut, J.R.Reynolds ; J.Phys.Chem., **B104**, 4080 **(2000)**.
[11] G.MacDiarmid, J.C.Chiang; A.F.Richter; **18**, 285 **(1987)**.
[12] M.Abdel Rehim, A.M.Youssef, E.Hassan, N.Khatab, G.Turky; Synthetic Metals, **160**, 1774 **(2010)**.

[13] O.T.Kala, J.Laakso, K.Vakiparta, E.Virtanen, H.Ruohonen, H.Jarvinen, T.Taka, P.Passiniemi, J.Sterholm, E.Y.Cao, A.Andreatta, P.Smith, A J.Heeger; Synth.Met., **69**, 97 **(1995)**.

[14] A.A.Pud, N.A.Ogurtsov, A.Korzhenko, G.S.Shpoval; Progr.Polym.Sci., **28**, 1701 **(2003)**.

[15] W.Zhong, Y.Wang, Y.Yan, Y.Sun, J.Deng, W.J.Yang; Phys.Chem., **B111**, 3918 **(2007)**.

[16] F.Leroux, G.Goward, W.P.Power, L.F.Nazar; Electrochem.Soc., **144**, 3886 **(1997)**.

[17] T.A.Kerr, H.Wu, L.F.Nazar; Chem.Mater., **8**, 2005 **(1996)**.

[18] Q.Wu, Z.Xue, Z.Qi, F.Wang; Polymer, **41**, 2029 **(2000)**.

[19] G.M.Nascimento, V.R.I.Constantino, M.L.A.Temperini; Macromolecules, 35 **(2002)**.

[20] J.W.Kim, S.G.Kim, H.J.Choi, M.S.Jhon; Macromol.Rapid Commun., **20**, 450 **(1999)**.

[21] B.H.Kim, J.H.Jung, S.H.Hong, J.S.Joo, A.J.Epstein, K.Mizoguchi, J.W.Kim, H.J.Choi; Macromolecules, **35**, 1419 **(2002)**.

[22] Z.H.Bi, Y.C.Hung, C.Liang, J.L.Yu, J.H.Ying, H.T.Po, H.H.Tar, S.H.Ko; Polyme., **49**, 4218 **(2008)**.

[23] E.Ruiz-Hitzky, P.Aranda, B.Casal, J.C.Galvan; Adv.Mater., **7**, 180 **(1995)**.

[24] Z.R.Tian, J.A.Voigt, J.Liu, B.McKenzie, M.J.McDermott, M.A.Rodriguez, H.Konishi, H.F.Xu; Nat.Mater., **2**, 21 **(2003)**.

[25] E.Hosono, S.Fujihara, K.Kakiuchi, H.Imai; J.Am.Chem.Soc., **126**, 7790 **(2004)**.

[26] M.Law, L.E.Greene, J.C.Johnson, R.Saykally, P.D.Yang; Nat.Mater., **4**, 5 **(2005)**.

[27] K.S.Leschkies, R.Divakar, J.Basu, E.Enache-Pommer, J.E.Boercker, C.B.Carter, U.R.Kortshagen, D.J.Norris, E.S.Aydil; Nano.Lett., **7**, 1793 **(2007)**.

[28] X.Peng, A.Chen; Adv.Funct.Mater., **16**, 1355 **(2006)**.

[29] M.Gratzel; Nature, **414**, 338 **(2001)**.

[30] R.Asahi, T.Morikawa, T.Ohwaki, K.Aoki, Y.Taga; Science, **293**, 269 **(2001)**.

[31] S.Liu, A.Chen; Langmuir., **21**, 8409 **(2005)**.

[32] B.O'Regan, M.Gratzel; Nature, **353**, 737 **(1991)**.

[33] J.E.Boercker, E.Enache-Pommer, E.S.Aydil; Nanotechnology, **19**, 095604 **(2008)**.

[34] D.Gong, C.A.Grimes, O.K.Varghese, W.C.Hu, R.S.Singh, Z.Chen, E.C.Dickey; J.Mater.Res., **16**, 3331 **(2001)**.

[35] G.K.Mor, K.Shankar, M.Paulose, O.K.Varghese, C.A.Grimes; Nano Lett., **5**, 191 **(2005)**.

[36] G.K.Mor, O.K.Varghese, M.Paulose, K.Shankar, C.A.Grimes; Sol.Energy Mater.Sol.Cells, **90**, 2011 **(2006)**.

[37] K.Zhu, N.R.Neale, A.Miedaner, A.J.Frank; Nano Lett., **7**, 69 **(2007)**.

[38] M.Paulose, K.Shankar, O.K.Varghese, G.K.Mor, B.Hardin, C.A.Grimes; Nanotechnology, **17**, 1446 **(2006)**.

[39] K.Gurunathan, D.C.Trivedi; Mater.Lett., **45**, 262 **(2000)**.

[40] S.Su, N.Kuramoto; Synth.Met., **114**, 147 **(2000)**.

[41] W.Feng, E.Sun, A.Fujii, H.Wu, K.Niihara, K.Yoshino; Bull.Chem.Soc.Jpn., **73**, 2627 **(2000)**.

[42] H.Xia, Q.Wang; Chem.Mater., **14**, 2158 **(2002)**.

[43] A.M.Youssef, M.Abdel Rehim, N.Khatab; 43rd IUPAC World Polymer Congress (Macro2010), 11-16 July Glasgow, UK., **(2010)**.

[44] L.J.Zhang, M.X.Wan; J.Phys.Chem. **B107**, 6748 **(2003)**.

[45] A.A.Haroun, A.M.Youssef; Synth.Met., **161**, 2063 **(2011)**.

[46] K.G.Neoh, K.L.Tan, T.C.Tan, E.T.Kang; J.Macromol Sci.Chem., **A27**, 347 **(1990)**.

[47] J.Stejskal, R.G.Gilbert; Pure.Appl.Chem., **74**, 857 **(2002)**.

[48] S.Quillard, G.Louarn, S.Lefrant, A.G.MacDiarmid; Phys.Rev., **B50**, 12496 **(1994)**.

[49] J.Laska, J.Widlarz; Polymer, **46**, 1485 **(2005)**.

[50] M.I.Boyer, S.Quillard, E.Rebourt, G.Louarn, J.P.Buisson, A.Monkman, S.Lefrant; J.Phys.Chem., **B102**, 7382 **(1998)**.

[51] R.M.Silverstein, G.C.Bassler, T.C.Morrill; Spectrometric Identification of Organic Compounds, 5th Edition J.Wiley, New York, **(1991)**.

[52] W.Yin, E.Ruckenstein; Synth.Met., **108**, 39 **(2000)**.

[53] J.Huang, S.Virji, B.H.Weiller, R.B.Kaner; J.Am.Chem.Soc., **125**, 314 **(2003)**.

[54] X.Zhang, C.Y.K.Roch, A.Jose, S.K.Manohar; Synth.Met., **145**, 23 **(2004)**.

[55] A.I.Gopalan, K.P.Lee, P.Santhosh, K.S.Kim, Y.C.Nho; Comp.Sci.Tech., **67**, 900 **(2007)**.

[56] M.Cochet, W.K.Maser, A.M.Benito, M.A.Callejas, M.T.Martinez, J.M.Benoit, J.Schreiber, O.Chauevt; Chem.Commun., **11450**, 1451 **(2000)**.

[57] X.Hesheng, Q.Wang; Chem.Mater., **14**, 2158 **(2002)**.

[58] L.Mazerolles, S.Folch, P.Colomban; Macromolecules, **32**, 8504 **(1999)**.

[59] X.Zhang, H.S.Kolla, X.Wang, K.Raja, S.K.Manohar; Adv.Funct.Mater., **16**, 1145 **(2006)**.

[60] D.Zhang, Y.Wang; Mater.Sci.Eng., **B134**, 9 **(2006)**.

[61] P.Adams, A.Monkman; Synth.Met., **87**, 165 **(1997)**.