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Surface Functionalized TiO_2 Nanoparticle Designed for the Preparation of Chiral Poly(amide-imide) Bionanocomposites Containing Phenylalanine Linkage

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Abstract

The surface of titanium dioxide (TiO_2) nanoparticles was treated with a silane coupling agent of γ-aminopropyl-triethoxy silane. An optically active poly(amide-imide) (PAI) was synthesized by the indirect polycondensation reaction of the L-phenylalanine based diacid chloride and 4,4′-diaminodiphenylether in the presence of triethylamine in *N*-methyl-2-pyrrolidone. Then PAI and surface modified TiO_2 nanoparticles were used to produce a polymer based bionanocomposites (BNC)s via ultrasonic irradiation process. The obtained BNCs were characterized by means of X-ray diffraction, electron microscopy and thermogravimetric analysis techniques. The results showed that the nanoparticles are homogeneously dispersed in PAI matrix with particle size ranging 30-50 nm.

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Keywords TiO_2 nanoparticles; ultrasonic irradiation; electron microscopy; thermal stability; bionanocomposite

INTRODUCTION

Combination of optically activity character and beneficial of thermally stable polymer properties caused to generate a new class of materials with functional potential for separation sciences.[1] Recently, synthesis of polymers by incorporation of optically active parts such as amino acids in backbone structure showed an important field in macromolecular science.[2] These polymers such as polyimides, polyamides and poly(amide-imides) (PAI) find a wide range of potential applications based on their chiral structures.[3]

Aromatic polyimides are well-known polymers that have attractive characteristics such as high thermal stability and excellent physical properties as well as outstanding chemical resistance.[4-7] They have high-performance properties but the major disadvantage of these compounds is insolubility and unprocessability after conversion from the poly(amic-acid) to form the polyimide.[8] PAI contains both amide and heterocyclic imides structures along the polymer backbone and possesses high thermal stability, good chemical resistance, excellent mechanical properties and processability. These properties in addition to different possible physical and chemical interactions, being promising matrix candidate for hybrid materials.[9,10]

In recent years, organic and inorganic nanoparticles (NP)s have attracted great attention. Among the different kinds of, titanium dioxide (TiO_2) is one of the most potential materials, nontoxicity and chemical inertness that cause wide applications in the fields of electronic and photonic.[11,12] TiO_2 has three crystalline polymorphs: rutile, anatase and brookite .The most common form of bare TiO_2 crystal that used in many industries such as paints and cosmetics is rutile that stable at high temperatures. The anatase to rutile transition is an irreversible procedure and usually generated within a temperature range of 500-1000°C.[13-15] TiO_2 nanocomposites have many applications especially in medicine, cleaning machining, jointing and chemistry industry.[16-20] Other application fields of them are ultraviolet light, absorbent coating, interference filter, antireflective coating, and optical waveguides.[21-24]

In this study we wish to report the synthesis and characterization of optically active PAI by polycondensation reaction of *N,N′*-(pyromellitoyl)-bis-phenylalanine diacid chloride 5 and 4,4′-diaminodiphenylether 6, in the present of triethylamine (Et_3N) at low temperature. The TiO_2 NPs were treated with coupling agent of γ-aminopropyl-triethoxysilane (KH550) to introduce organic functional groups on to the surface of TiO_2. Then optically active PAI/TiO_2 bionanocomposites (BNC)s were synthesized under ultrasonic irradiation conditions. The resulting novel BNCs are characterized by Fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and their surface morphology were investigated by scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) analysis.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. Pyromellitic dianhydride (benzen-1,2,4,5-tetracarboxylic dianhydride) (from Merck Chemical CO., Germany) and 4,4′-diaminodiphenylether were used as obtained without further purification. *N*-Methyl-2-pyrrolidone (NMP) was dried over BaO, by fractional distillation. L-Phenylalanine was used as obtained without further purification. Nanosized TiO_2 powder was purchased from nanosabz Co. with average particle sizes of 30-50 nm. Coupling agent KH550 obtained from Merck Chemical Co.

Synthesis of Optically Active Diacid Monomer

N,N´-(Pyromellitoyl)-bis-L-phenylalanine diacid chloride 5 was prepared according to a typical reported procedure (Scheme 1).[25,26]

Synthesis of Polymer

The chiral PAI was prepared was synthesizes according to our previous study.[27]

Preparation of PAI/TiO_2 BNCs

0.3 g of TiO_2 NPs was suspended into 10 mL acetone and was added to 10 weight percentage of silane coupling agent (KH550), which was dissolved in 10 mL H_2O. Then the mixture of TiO_2/KH550 was sonicated for 30 min at room temperature. Subsequently the solvent was removed and dried. Finally different amounts of modified TiO_2 NPs (5, 10, 15 and 20 wt.%) were added to the novel PAI and the mixture was dispersed in 20 mL of absolute ethanol and sonicated for 4 h. The solvent was removed and the precipitate was dried in vacuum at 80°C for 2 h.

Specimens Characterization Techniques

Proton nuclear magnetic resonance (^1H NMR, 400 MHz) spectrum was recorded by Bruker (Germany) advance 400 instrument, at room temperature (RT) in DMSO-d_6 solution. Multiplicities of proton resonance were chosen as singlet (s) and multiplet (m). Specific rotations were determined by a Jasco Polarimeter (Japan). Inherent viscosities were measured by a standard procedure using a Cannon-Fenske routine viscometer (Germany) at the concentration of 0.5 g/dL at 25ºC. The FTIR adsorption spectra were recorded on a Jasco-680, Japan IR spectrophotometer with KBr pallets. The band intensities are categorized as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). UV-Vis absorption of PAI/TiO_2 BNCs was measured by UV-Vis spectrometer, JASCO V-750 in the spectral range between 200 and 800 nm. Thermogravimetric analysis (TGA) data is performed with STA503 winTA instrument in nitrogen atmosphere at a heating rate of 10ºC/min from 25ºC to 800ºC. The XRD patterns of the polymer and BNCs were recorded by Philips X'PERT MPD, that were measured for 2θ, using Cu Kα incident beam (λ = 1.51418Å) in the range of 10-80o at the speed of 0.05o/min. FESEM, (Hitachi, S-4160), SEM, (XL30, Philips) and TEM, (Philips, CM 120) images were investigated the morphology of dispersion of NPs on PAI matrix. Formation of PAI/TiO_2 BNCs was occurred on a MISONIX ultrasonic liquid processor, XL-2000 Series by wave of frequency 2.25 × 104 Hz and power 100 W.

RESULTS AND DISCUSSION

Surface Modification of TiO_2 NPs

The major aim for surface modification of TiO_2 NPs is to prevent the agglomeration of NPs in polymer matrix. The surface of TiO_2 NPs was modified by KH550 coupling agent. The reaction mechanism indicate that the hydroxyl groups on the surface of TiO_2 NPs were reacted with ethoxyl groups of the KH550 reagent [27,28] and this cause to formation of Ti-O-Si bonds on the surface of TiO_2 NPs.

For the investigation of organic part in the structure of TiO_2 NP, FTIR spectroscopy is a powerful technique. Broad bands at 3500 and 3422 cm^{-1} were attributed to interactions between hydroxyl groups on TiO_2 and a broad peak at 500-800 cm-1 is belonged to the Ti-O-Ti stretching band. There is a peak around 2870-2928 cm-1 for TiO_2 modified by KH550 that is attributed to CH stretching band of KH550. Obtained results confirmed the formation of surface modified TiO_2 (Figure 1a and 1b).

Synthesis and Characterization of Monomer and Polymer

The FTIR spectrum of compound 4 (Scheme 1) showed a broad and strong peak at 2354-3463 cm^{-1}, which was assigned to the COOH groups. Also peaks around 1766, 1720 cm^{-1}, belong to carbonyl stretching of imide rings and C-N bonds.[28] Absorptions at 1382 and 727 cm^{-1} were related to the presence of the imide ring. Compound 5 was prepared from the reaction of molecule 4 with thionyl chloride.[26]

Polycondensation reaction of compound 5 with aromatic diamine 6 in NMP at room temperature provided an optically active PAI 7 (Scheme 2). Due to the presence of amino acid linkages in the structure of polymer, this PAI is optical activity. The specific rotation of this polymer is =-178.8 (0.05 g in 10 mL of DMF)

The FTIR spectrum of PAI showed a broad and strong peak at 3379 cm–1, which was assigned to the N-H group and two absorption bands at 1776 and 1725 cm–1 due to the symmetrical and asymmetrical imides carbonyl stretching vibrations (Figure 1c). Absorptions at 1382 and 727 cm-1 were related to the presence of the imide ring.

Preparation of PAI/TiO_2 BNCs

The procedure for the preparation of PAI/TiO_2 BNCs is demonstrated in Scheme 3. PAI was dispersed in absolute ethanol. A uniform colloidal dispersion was obtained after sonicated at room temperature. The suspension was mixed with the appropriate amount of TiO_2/KH550 powder to produce 5, 10, 15 and 20 wt.% based on the PAI content.

FTIR Spectra PAI/TiO_2 BNCs

Figure (2a-2d) exhibited the FTIR spectrum of PAI/TiO_2 BNCs (5, 10, 15 and 20 wt.%). All of these figures show a broad and strong peak at 3379 cm^{-1}, which was assigned to the N-H group and two absorption bands at 1775 and 1723 cm^{-1} due to the symmetrical and asymmetrical imides carbonyl stretching vibrations. The spectra of BNCs show a broad absorption peak at 500-800 cm^{-1} that is belonged to the Ti-O-Ti stretching band. There are two peaks at 2928 and 2870 cm^{-1} that is attributed to CH stretching band of KH550. In these BNCs the peaks intensity related to Ti-O-Ti bond were enhanced with increasing in TiO_2 contents.

XRD patterns of PAI/TiO_2 BNCs

The structure and crystalline phase of BNCs were studied by XRD analysis. Figure 3 (a-c) shows the XRD patterns of the PAI, TiO_2 and PAI/TiO_2 BNC 10 wt.%, respectively. The XRD of BNC 10 wt.% revealed three main peaks at 2θ values 25°, 36° and 48°, corresponding to the characteristic absorption peaks of the anatase titania phase (101, 004 and 200) and 2θ values 27°, absorption peak of the rutile titania phase (110). These results indicated that titania particles did not change after reacting with the KH550 coupling agent.[28] The XRD pattern in Figure 3a shows that the pure PAI has amorphous nature.

Figure 3b shows the existence of anatase and rutile phase for bare TiO_2 NPs. Also Figure 3c shows the presence of anatase and rutile crystalline phase of TiO_2 NPs are distinguishable in

BNC structure. According to Figure 3, there was no morphological change that has been detected during the process of BNC preparations related to TiO_2 NPs.

The average crystallite size of TiO_2 NPs in the BNCs were calculated by the Debye-Scherrer equation, $(D = K\lambda / \beta\cos\theta$). Where D is the crystallite size β is the full width at half maximum, λ is wavelength of the radiation, K is the Scherrer constant and θ is the Bragg's angle.[29]

Morphology Analysis

Figure 4 shows SEM micrograph of pure PAI and PAI/TiO_2 BNC with different magnifications, which indicates good homogeneous distribution of NPs in the polymer matrix.

Figure 5 shows the FESEM micrograph of pure PAI and PAI/TiO_2 BNC that has a homogeneous microstructure and dispersed as global beads. From this data it can be concluded that the average crystallite size for PAI is 58 nm and for TiO_2 NPs in polymer matrix is 65 nm.

Figure 6 shows the TEM micrographs of PAI/TiO_2 (10 wt.%) BNC. The TiO_2 NPs are well dispersed in the polymer matrix and average particle size distribution are remain a diameter size from 30 nm to 50 nm, representing that the KH550 coupling agent cooperate an important role in dispersion of the NPs. In modified TiO_2 the organic chains of KH550 can perform steric hindrance between inorganic NPs and avoid their aggregation.

Thermogravimetric analysis

The thermal properties of the PAI and PAI/TiO2 BNCs were assessed by TGA at a heating rate of 10oC/min, under a nitrogen atmosphere (Figure 7). Table 1 shows the values of the thermal degradation of the pure PAI and TiO2/PAI BNCs, including the temperature at which 5% (T_5) and 10% (T_{10}) degradation occurs, char yield at 800 ^oC and also limiting oxygen index (LOI) .[30]

$$\text{LOI} = 17.5 + 0.4 \text{ char yield}$$

From these data it is clear that the PAI had a high decomposition temperature of about 380^{o}C, which was further improved when TiO_2 was introduced. The char yield of pure PAI at 800^{o}C is 52%, and for those of the BNCs (PAI/TiO2 5, 10, 15, 20wt%) at 800^{o}C are in the range of 52-72%, they were enhanced with an increase of TiO_2 NPs content in the PAI.

UV-vis Absorption

The UV-Vis absorption spectra of pure PAI and PAI/TiO_2 BNCs are shown in Figure 8. The maximum absorption peaks of pure PAI and TiO_2 appeared at 339 nm, however the maximum of PAI/TiO_2 BNCs is red shifted to 355 nm. The observed absorption is around the UV region representative that this type of composite could be used as a paint-on or spray-on coating to shield against UV light.

CONCLUSIONS

In the present study, a high performance, thermally stable optically active PAI was successfully prepared by indirect polycondensation technique. The polymerization was carried out by reaction of natural amino acid based L-phenylalanine diacid chloride and 4,4′-diaminodiphenylether using NMP/Et_3N as a solvent system. This synthetic polymer is supposed to be biodegradable [31-33] due to the presence of amino acid in the polymer structure. KH550 was modified to introduce organic functional groups on the surface of TiO_2 which cause to improved compatibility and led to better dispersion of TiO_2 NPs in the polymer matrix. The morphology study of synthesized nanocomposites by TEM exhibited the TiO_2 NPs are well dispersed in the polymer matrix and average particle size distribution are remain a diameter size from 30 nm to 50 nm. FESEM show average crystallite size for PAI is 58 nm and for TiO_2 NPs in the polymer matrix is 65 nm, respectively.

Acknowledgments

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Reference

1. Mallakpour S, Dinari M, *J. Macromol. Sci. Part A: Pure Appl. Chem,* **2011**; *48*, 644-652.

2. Mallakpour S, Zadehnazari A, *Express Polym. Lett,* **2011**; *5*, 142-146.

3. Mallakpour S, Rafiee Z, *Iran. Polym. J,* **2008**; *17*, 907-915.

4. Ree M, *Macromol. Res*, **2006**; *14*, 1-10.

5. Seckin T, Koytepe S, Ozdemir I, Cetinkaya B, *J. Inorg. Organomet. Polym,* **2003**; *13*, 9-15.

6. Liu X, Xu W, Ye G, Gu Y, *Polym. Eng. Sci.,* **2006**; *46*, 123-136.

7. Kong Y, Du H, Yang J, Shi D, Wang Y, Zhang Y. Xin W, *Desalination*, 2002; *146*, 49-54.

8. Mallakpour S, *Amino Acids*, **2011**; *40*, 487-492.

9. Yamazaki N, Matsumoto M, Higashi F, *J. Polym. Sci. Polym. Chem. Ed.,* **1975**; *13*, 1373-1386.

10. Jonquieres A, Clement R, Lochon P, *Eur. Polym. J,* **2005**; *41*, 783-791.

11. Phang S.W, Kuramoto N, *Polym. Composites,* **2009**; *30*, 970-981.

12. Peining Z, Nair A.S, Shengyuan Y, Ramakrishna S, *Mater. Res. Bull,* **2011**; *46*, 588-593.

13. Dzunuzovic E, Marinovic Cincovic M, Vukovic J, Jeremic K, Nedeljkovic J. M, *Polym. Composites*, **2009**; *30*, 737-743.

14. Sawada H, Sawada E, Kakehi H, Kariya T, Mugisawa M, Chounan Y, Miura M, *N. Isu, Polym. Composites*, **2009**; *30*, 1848-1852.

15. Nie X, Zhuo S, Maeng G, Sohlberg K, *Int. J. Photoenergy*, **2009**; *2009*, 1-8.

16. Ray S. S, *Mater. Res. Bull*, **2002**; *37*, 813-822.

17. Price G.J, Lenz E.J, Ansell C.W.G, *Eur. Polym. J*, **2002**; *38*, 1531-1540.

18. Mohammed Bahadur N, Furusawa T, Sato M, Kurayama F, Suzuki N, *Mater. Res. Bull*, **2010**; *45*, 1383-1394.

19. Tolke T, Kriltz A, Rechtenbach A, *Thin. Solid. Films*, **2010**; *518*, 4242-4251.

20. Yang S, Tang W, Ishikawa Y, Feng Q, *Mater. Res. Bull*, **2011**; *46*, 531-540.

21. Munoz O, Volten H, Hovenier J.W, Min M, Shkuratov Y.G, Jalava J.P, van der Zande W.J, Waters L.B.F.M, *Astron. Astrophys*, **2006**; *446*, 525-536.

22. Devore J.R, *J. Opt. Soc. Am,* **1951**; *41*, 416-422.

23. Li H, Jiang B, Schaller R, Wu J, Jiao J, *J. Phys. Chem. C.,* **2010**; *114*, 11375-11384.

24. Que W, Zhou Y, Lam Y.L, Chan Y.C, Kam C.H, *Thin. Solid. Films.,* **2000**; *16*, 358-364.

25. Mallakpour S, Tirgir F, Sabzalian M.R, *J. Polym. Res.,* **2011**; *18*, 373-382.

26. Mallakpour S.E, Hajipour A.R, Habibi S, *J. Appl. Polym. Sci.,* **2002**; *86*, 2211-2223.

27. Mallakpour S, Dinari M, *J. Inorg. Organomet. Polym.,* **2012**; *22*, 929–937.

28. Chen J, Zhou Y.M, Nan Q.L, Ye X.Y, Sun Y.Q, Wang Z.Q, Zhang S.M, *Appl. Surf. Sci.,* **2008**; *255*, 2244-2253.

29. Nakayama N, Hayashi T, *Polym. Degrad. Stabil.*, **2007**; *92*, 1255-1264.

30. Krevelen D.V, Hoftyzer P, *Properties of polymers, Third ed., Elsevier, Amsterdam*, **1976**.

31. Mallakpour S, Dinari M, *Polymer* **2011**; *52*, 2514-2525.

32. Mallakpour S, Tirgir F, Sabzalian M.R, *J. Polym. Environ* **2010**; *18*, 685-695.

33. Mallakpour S, Asadi P, Sabzalian M.R, *Amino Acids* **2011**; *41*, 1-8.

Table 1 Thermal properties of the PAI and PAI/TiO_2 BNC

Polymer	T_5 (°C)[a]	T_{10} (°C)[b]	Char Yield(%)[c]	LOI[d]
PAI	352	382	52	38.3
PAI/TiO_2 (5 wt%)	370	391	57	40.3
PAI/TiO_2 (10wt%)	377	396	60	41.5
PAI/TiO_2 (15 wt%)	383	404	63	42.7
PAI/TiO_2 (20 wt%)	390	410	67	44.3

[a] Temperature at which 5 and 10% weight loss was recorded by TGA at heating rate of 20ºC min^{-1} in N_2 atmosphere.

[b] Weight percent of the material left undecomposed after TGA at maximum temperature 800°C in N_2 atmosphere.

[c] Limiting oxygen index (LOI) evaluated at char yield at 800°C.

Caption for Schemes

Scheme 1. Synthesis of monomer 5.

Scheme 2. Polycondensation reactions of monomer 5 with aromatic diamine 6.

Scheme 3. Preparation of PAI/TiO_2 BNCs.

Legend for Figures

Figure 1. The FTIR spectra of TiO_2 NPs (a), TiO_2 / KH550 (b) and PAI (c).

Figure 2. The FTIR spectra of PAI/TiO_2 (5 wt.%) (a), PAI/TiO_2 (10 wt.%) (b), PAI/TiO_2 (15 wt.%) (c) and PAI/TiO_2 (20 wt.%) (d).

Figure 3. The XRD patterns of PAI (a), bare TiO_2 (b) and PAI/TiO_2 (10 wt%) (c).

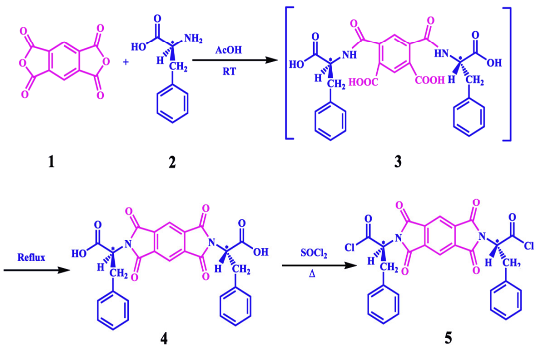
Figure 4. The SEM micrograph of pure PAI and PAI/TiO_2 (10 wt.%) BNCs.

Figure 5. The FESEM micrograph of pure PAI and TiO_2/PAI (10 wt.%) BNCs.

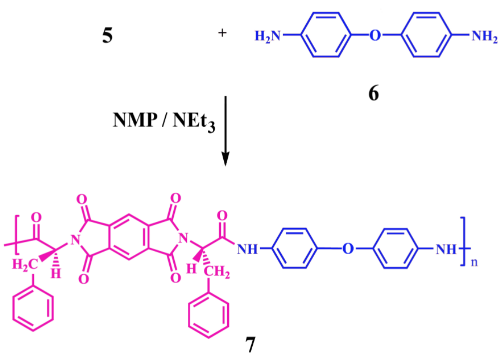
Figure 6. The TEM micrograph of PAI/TiO_2 (10 wt%) BNCs.

Figure 7. TGA thermograms of PAI and PAI/ZnO BNCs with different ZnO content.

Figure 8. The UV-Vis spectra of pure PAI (a), PAI/TiO_2 (5 wt.%) (b), PAI/TiO_2 (10 wt.%) (c), PAI/TiO_2 (15 wt.%) (d) and PAI/TiO_2 (20 wt.%) (e).



Scheme 1



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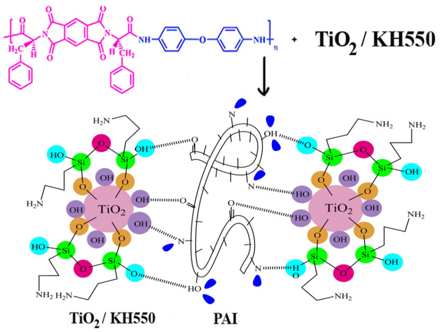

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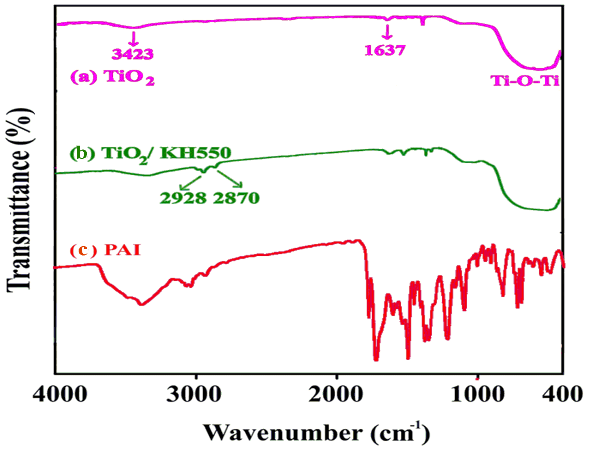

Figure 1

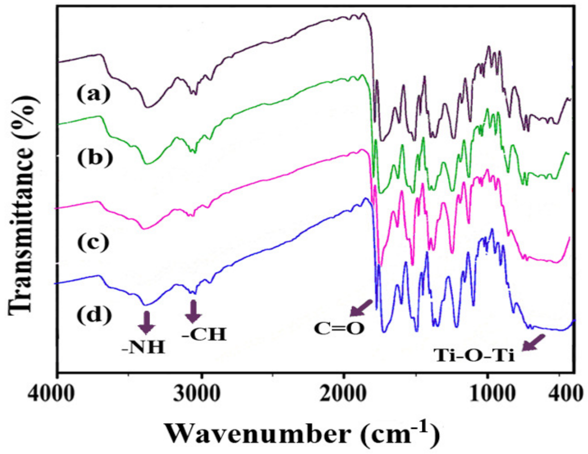

Figure 2

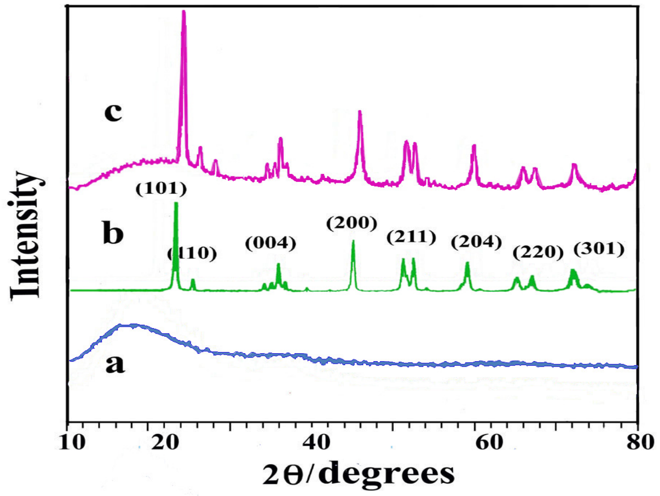

Figure 3

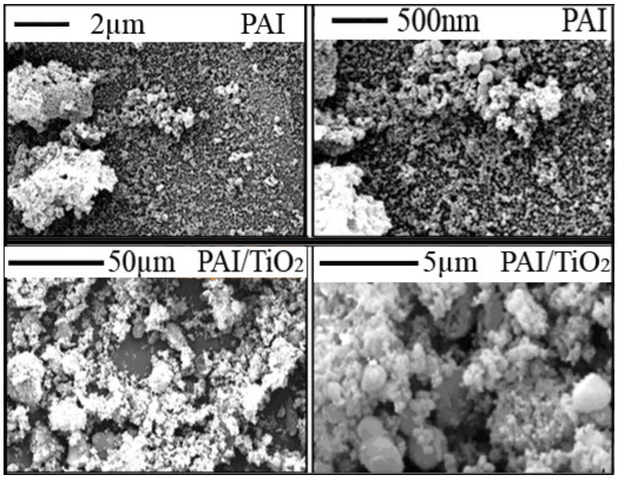

Figure 4

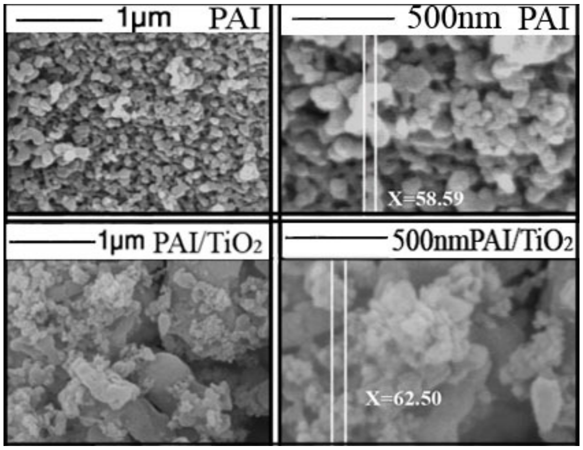

Figure 5

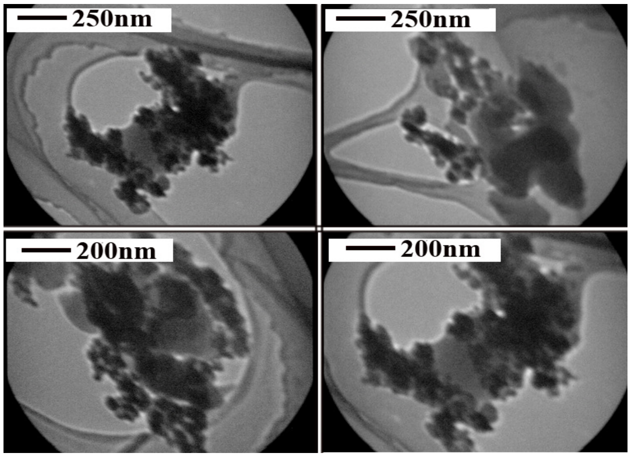

Figure 6

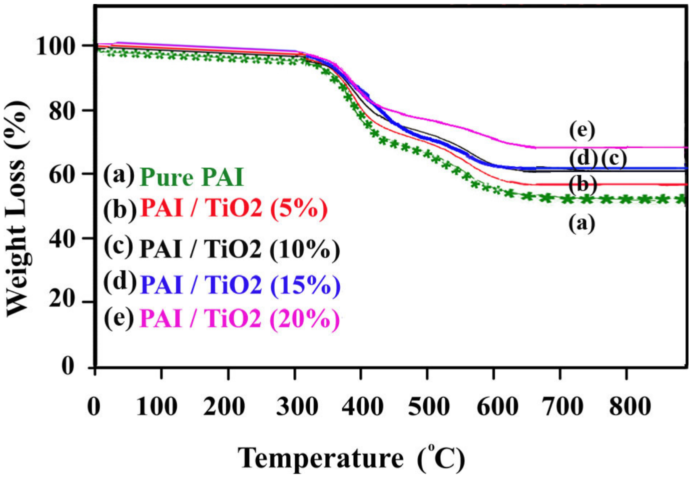

Figure 7

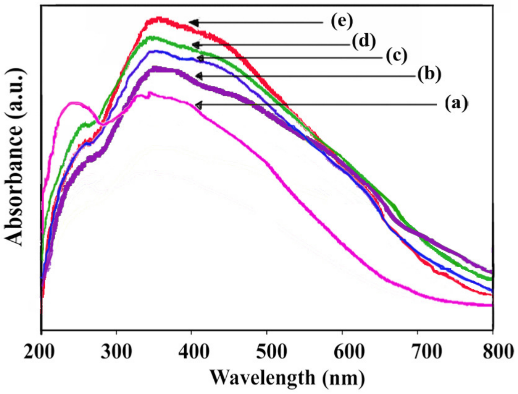

Figure 8