Synthesis of conductive PSt-g-PANI/TiO₂ nanocomposites by metal catalyzed and chemical oxidative polymerization

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ABSTRACT
Well-defined polymer-TiO₂ nanocomposites of core–shell structure were prepared by two-steps, surface-initiated atom transfer radical polymerization (ATRP) of styrene and in situ chemical oxidative polymerization of aniline monomers from the surfaces of the TiO₂ nanoparticles. The methods used include the following: initially, the ATRP initiator was covalently attached to the surface of TiO₂ nanoparticles by esterification of 2-bromo-2-methyl propionic acid with hydroxyl group. The metal-catalyzed radical polymerization of styrene with modified TiO₂ nanoparticles was performed using a copper catalyst system to give the TiO₂-based core hybrids linking PSt segments (TiO₂-PSt hybrids). Next, the TiO₂-PSt reacted with HNO₃/H₂SO₄ to produce a nitro group containing polystyrene to form TiO₂-PSt-NO₂, and obtained TiO₂-PSt-NO₂ was treated with hydrochloric acid/SnCl₂, and converted to an amine group containing polystyrene (TiO₂–PSt-NH₂). Finally, surface oxidative graft copolymerization of aniline, using the –NH₂ moieties of TiO₂/PSt-NH₂ as the anchoring sites. Characterization of these well-defined nanocomposites included FTIR, thermogravimetric analysis, transmission electron microscopy, and X-ray diffraction.

Abbreviations: TiO₂: titanium dioxide nanoparticles; TiO₂-PSt: polystyrene grafted onto titanium dioxide; Br-MPA: 2-bromo-2-methyl propionic acid; PANi: polyaniline; PSt: polystyrene; XRD: X-ray diffraction; TGA: thermogravimetric analysis; SFRP: stable free radical polymerization; ATRP: atom transfer radical polymerization; Bpy: 2,2′-bipyridine; AN: acrylonitrile; APS: ammonium persulfate; CuCl: copper chloride; FT-IR: Fourier-transform infrared; EDX: energy-dispersive X-ray; THF: tetrahydrofuran; SEM: scanning electron microscopy; TEM: transmission electron microscopy; PPy: polypyrrole; PTP: polythiophene; PNVC: poly (N-vinylcarbazole); CPs: conducting polymers; CB: carbon black; Al₂O₃: aluminium oxide; SiO₂: silica; DCC: dicyclohexylcarbodiimide; DMAP: 4-dimethylaminopyridine

INTRODUCTION

Conducting polymers (CPs) such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) are important due to their relatively easy processability, thermal and environmental stabilities, and tunable electrical conductivities.[1,2] CPs offer potential applications in the domain of composite materials, separation membranes, tissue engineering, actuator, super capacitor, molecular motors, electronic, and electro-optic devices.[3,4] Among the conductive polymers, Polyaniline (PANI) has been widely investigated because of its unique electrical, optical and electro-optical properties, and its potential applications. However, like many other conducting polymers, unsubstituted PANI is intractable and suffers from poor process ability, mainly because of its rigid and highly conjugated backbone. Several methods have been adopted to overcome their poor process ability. For example, the preparation of conventional thermoplastic-electro conductive polymer composites is a successful approach to achieve unique properties and applications of the resultant materials.[5,6] A current challenge in the field of nanotechnology is the ability to synthesize small enough monodispersed CPs nanostructures, and their composites with metal nanoparticles that have multifunctional properties. These composites are attractive because they can combine with the properties of other compounds, and the composites of PANI with graphite,[7,8] carbon nanotubes[9] and carbon black (CB) have been accepted to effectively improve the electric conductivity. As well as, encapsulation of metal nanoparticles into CPs results in hybrid organic–inorganic nanocomposites that exhibit enhanced thermal stability, electrochemical, catalytic, magnetic, mechanical,
optical, dielectrical, and electro-rheological properties.\[10–13\]

Also, recent studies have shown experimentally that the introduction of the metal or metal oxide nanoparticles in conducting polymeric matrices allow for the development of materials in various applications in the field of electrocatalysis, sensors, microelectronics, and magnetism. The unique properties of such polymer-coated metal composite materials are strongly dependent on their size and shape.\[14\]

Since, nanocrystal semiconductor TiO\(_2\) nanoparticles are attention due to their unique properties and several potential technological applications such as photocatalysis, sensors, solar cells and memory devices.\[15–18\]

Titanium dioxide (TiO\(_2\)) has many common uses, and continues to be vastly studied because of potential applications in catalysis, photovoltaics,\[19\] and heat, and photo-stabilization.\[20\] TiO\(_2\) is thermally stable, inexpensive, has a high refractive index, nontoxic, and a lack of absorbance of visible light. These properties give TiO\(_2\) a good, practical use in many nanotechnologies. However, the surface chemistry of TiO\(_2\) is rather complex,\[21\] and as such there have been far fewer publications \[22–25\] on treatment with polymer grafting to the surface of TiO\(_2\) nanoparticles, especially when compared with grafting onto silica particles.

Due to their very large surface to volume ratio of nanoparticles, nanoparticles tend to strongly agglomerate, therefore decreasing the yield mechanical properties of the nanocomposite materials.\[26\] Many works have been taken in order to overcome this problem and to enhance the filler–matrix interaction. One approach is breaking down the agglomerated nanoparticles using a mechanical method such as ultrasonic irradiation, which has been explored for dispersion of SiO\(_2\), TiO\(_2\), and Al\(_2\)O\(_3\) nanoparticles during the synthesis of inorganic/polymer nanocomposite materials.\[27–29\] However, this technique is restricted because of the limited interaction between the inorganic fillers and the organic matrix, compared with the very strong interaction between nanoparticles. An improved way is modifying the surface of the inorganic filler and covalent coupling of polymer chains to minimize agglomeration and increase interaction between the nanofiller and polymer matrix, as illustrated schematically in Scheme 1.\[30,31\]

In recent years, there have been increasing research activities in the use of various polymerization methods to grow polymer chains on the nanoparticles’ surface. These methods include anionic polymerization,\[32\] cationic polymerization,\[33\] ring opening polymerization,\[34\] and radical polymerization.\[35\] In the past few years, two new methods to realize living radical polymerization techniques were reported; these are stable free radical polymerization, using stable nitroxide radicals such as TEMPO,\[36–44\] and atom transfer radical polymerization (ATRP).\[45–53\] Because ATRP allows better control over the molecular weight and distribution of the target polymer, much attention has been paid to the use of this polymerization method in the synthesis of polymer brushes from a surface. ATRP catalyzed by copper halide complexes with 2,2’-bi pyridine (bpy) derivatives for the polymerization of various monomers, such as styrene, methacrylates, acrylates, dienes, and acrylonitrile (AN), has been developed in our laboratory and other laboratories.\[54–58\]

As part of our ongoing interest in developing strategies for the preparation of well-defined polymer-TiO\(_2\) nanocomposites, we now report on a new synthetic route by ATRP of styrene and \textit{in situ} chemical oxidating of aniline from the surfaces of the TiO\(_2\) nanoparticles (Scheme 2).

Characterization of these well-defined nanocomposites included FTIR, thermogravimetric analysis, energy-dispersive X-ray (EDX), analysis transmission electron microscopy, and X-ray diffraction.
Experimental

Materials

Aniline monomer (Merck) was distilled under reduced pressure and stored below 0 °C, 2,2′-bipyridine (bpy) was purchased from Merck. Ammonium persulfate, sulfuric acid, nitric acid, and dichloromethane (DCM), were purchased from Merck. All chemicals were used as supplied without further purification. 2-Bromo-2-methyl propionic acid (Br-MPA) and TiO2 nanoparticles, dicyclohexylcarbodiimide (DCC), and 4-dimethylaminopyridine (DMAP) were obtained from Aldrich, styrene (Merck) was purified by distillation under the reduced pressure. Copper chloride (CuCl) (Merck) was stirred overnight in acetic acid, filtered, washed with absolute ethanol, and then dried overnight under vacuum at 60 °C. Methanol (Merck), Tin(II) chloride dehydrate, SnCl2·2H2O, (Merck) was used as supplied without further purification.

Instrumentation

FTIR spectra were recorded using Shimadzu FT-IR-8101M. The samples were prepared by grinding the dry powders with KBr and compressing the mixture to form disks. The disks were stored in a desiccator to avoid moisture absorption. Spectra were recorded at room temperature. The thermal properties of TiO2/PSt-g-PANI nanocomposite were assessed with a TGA-PL (England). A sample of about 10 mg were heated from 50 to 850 °C at a rate of 10 °C min⁻¹ under nitrogen flow. XRD spectra were obtained using a Siemens D 5000, X-ray generator (CuKα radiation with λ = 1.5406 Å) with a 2θ scan range of 2–70° at room temperature. The size and morphologies of the products were examined by transmission electron microscopy (TEM; PHILIPS CM10 TEM EPSON HP8300) and scanning electron microscopy (SEM; Cam Scan MV 2300).

Preparation of polyaniline

Polyaniline was synthesized by oxidative polymerization of aniline according to the method reported in the literature.[56] Thus, 0.1 mol of aniline was dissolved in 123 mL of 1.7 M HCl. The solution was kept at 0 °C under an argon atmosphere. A prechilled solution of 0.1 mol of ammonium persulfate in 134 mL of 1.7 M HCl was added slowly with vigorous stirring. The reaction mixture was agitated continuously for another 5 h. The precipitate was subsequently filtered, washed several times with methanol, and finally a colorless filtrate was obtained. The collected green–black polyaniline salts were added into ammonia solution (1.7 M) and stirred for 2 h. The undoped polyaniline was filtered and washed several times with water. The resulting powder was dried at 50 °C under reduced pressure.

Preparation of ATRP initiator onto TiO2 nanoparticles

Br-MPA, 2.5 mL and 1.5 g of TiO2 nanoparticles were dispersed in 35 mL DCM. Then, DCC (0.01 mol) and DMAP (0.001 mol) were added into the solution, and stirred for 18 h at room temperature under the protection of nitrogen. The resulting white powder was separated using a centrifuge and washed with CH2Cl2. This process was repeated once to remove the excess initiators (Scheme 3).

Metal-catalyzed radical polymerization of styrene with modified TiO2 nanoparticles

In the ATRP reaction, Br-MPA functionalized nanoparticles (50 mg) were dried under vacuum, followed by mixing with toluene/styrene monomer (5 mL) (1:3). This mixture was purged with nitrogen for 10 min and then transferred into a flask with CuCl (9.8 mg) and 2,2′-bipyridine (38 mg). This reaction solution was heated to 120 °C and stirred for 24 h under the protection of nitrogen. After the reaction was complete, the mixture was diluted with tetrahydrofuran (THF) at a solution/THF volume ratio of 1:10. The final products were precipitated with methanol. The precipitates were separated and dissolved in toluene that was used for further characterizations (Scheme 4).

Preparation of TiO2-PSt-NO2

A total of 1.3 g TiO2/PSt was suspended in 30 mL of strong nitric acid in a 250-mL round-bottomed flask, which was placed in ice-water bath. With mechanical stirring, 45 mL of strong sulfuric acid was slowly added, and then the
Solved in 20 mL of 1.0 M HCl. The oxidant solution was injected into the TiO2/PSt-NH2 and aniline reaction mixture at 0 °C. The oxidative graft copolymerization was carried out for 8 h. The aniline moiety of the PSt-NH2 units was used as the anchoring and initiation sites for the oxidative graft copolymerization of aniline (Scheme 2). The product was redispersed into 1-methyl-2-pyrrolidone (NMP, a good solvent for ES), and centrifuged to remove the adsorbed PANi homopolymer in its ES (emeraldine salt (ES)) form. The process was repeated several times until no PANi homopolymer was found in the NMP solutions (Scheme 5).

Results and discussion
Preparation and surface modification of the TiO2 nanoparticles

The titanium surface was modified by using Br-MPA as a ATRP agent, which was used not only as a stabilizer to disperse TiO2 nanoparticles in organic solvent, but also as a source of reactive sites to initiate chain extension with styrene monomers by the ATRP method. The XRD spectra of TiO2 are shown in Figure 1(a) with higher and narrower diffraction peaks implied a good crystallization of TiO2. Also, No peaks due to impurity was observed, which indicate that high purity TiO2 nanoparticles were achieved. The average size of the TiO2 nanoparticles was concluded to be 25 nm from the peak width at half maximum and Debye–Sherrer’s formula.

Preparation of poly(p-aminostyrene)-grafted onto TiO2 (TiO2/PSt-NH2)

A total of 1.1 g TiO2/PS-NO2 was suspended in 30 mL hydrochloric acid 6 M and 42 mL absolute ethanol in a 250-mL round-bottomed flask, and then 2.8 g of SnCl2·2H2O was added. Subsequently, the temperature was raised to 75 °C and maintained for 12 h. After the reaction, the product was sequentially washed by distilled water, 10% NaOH solution, distilled water, and absolute ethanol. Then it was moved to a Soxhlet’s extraction apparatus for reflux-extraction in absolute ethanol for 9 h. Finally, the product was dried under vacuum at 40 °C for 48 h (Scheme 4).

Preparation of TiO2-g-polystyrene-g-poly aniline well-defined copolymer nanocomposite by in situ chemical oxidative polymerization

Polyaniline was synthesized by oxidative polymerization of aniline. About 0.1 g of the TiO2/PSt-NH2 nanospheres, and 1 mL of aniline were injected slowly into 30 mL of 1.0 M HCl under magnetic stirring. About 0.6 g of (NH4)2S2O8 was solved in 20 mL of 1.0 M HCl. The oxidant solution was injected into the TiO2/PSt-NH2 and aniline reaction mixture at 0 °C. The oxidative graft copolymerization was carried out for 8 h. The aniline moiety of the PSt-NH2 units was used as the anchoring and initiation sites for the oxidative graft copolymerization of aniline (Scheme 2). The product was redispersed into 1-methyl-2-pyrrolidone (NMP, a good solvent for ES), and centrifuged to remove the adsorbed PANi homopolymer in its ES (emeraldine salt (ES)) form. The process was repeated several times until no PANi homopolymer was found in the NMP solutions (Scheme 5).
EDX analysis spectra of TiO$_2$/Br-MPA are shown in figure 3 and Table 1. The presence C, O, Ti, and Br signals indicated that nanoparticles surface is modified by Br-MPA.

**Metal-catalyzed radical polymerization of styrene with modified TiO$_2$ nanoparticles**

To successfully carry out this polymerization, it was necessary to show that at this reaction temperature, no spontaneous thermal polymerization occurred and that, in this reaction condition, the polymerization is living. For comparison, a blank experiment was done in the absence of CuCl/Bpy on modified TiO$_2$. In this condition, no homo polystyrene was formed in the absence of the macro-initiator under identical ATRP conditions. This suggests that the formation of homopolymer in the grafting reaction can be excluded and that the polymerization is living.

FTIR and SEM prove that the ‘grafting from’ reaction proceeds successfully. Figure 1(c) shows the FTIR spectra of TiO$_2$ nanoparticles grafted by polystyrene. It is found that the TiO$_2$ nanoparticle grafted by polystyrene is characterized by the C–H aromatic stretching vibration at 3042 and 3026 cm$^{-1}$, the C–H aliphatic stretching vibration at 2920 and 2852 cm$^{-1}$, the phenyl ring stretching vibration at 1490, 1511, and 1600 cm$^{-1}$, the ring in phase C–H stretching vibration at 1026 cm$^{-1}$, and the ring out of-plane bend at 698 cm$^{-1}$, where the typical absorption bands for polystyrene are clearly seen, indicating the existence of polystyrene on the particle surface.

The morphologies of pure TiO$_2$ nanoparticles and TiO$_2$-g-PS were investigated using SEM (Figure 4). Figure 4(a) revealed that pure TiO$_2$ nanoparticles are spherical and having a uniform size about 25 nm. The modified TiO$_2$ nanoparticles were used as macro-initiators in the ATRP reaction. Therefore, much larger particles are obtained when the polymer chains grow from the TiO$_2$ surface. Figure 4(b) presents the more converted sample. The compacted and large amounts of polymer chains ‘clothe’ the TiO$_2$ nanoparticles and become bulk materials. As expected, the bulk materials chemically bonded between organic and inorganic have better properties than traditional composites.
This shows that the polymer has an amorphous structure. The pattern of the TiO$_2$-g-PSt nano-composite also has characteristic peak at 2$\theta$ = 25.5°, that is attributed to the presence of TiO$_2$ nanoparticles.

**Organic/water partitioning study**

In addition to FTIR, the resulting materials were studied by organic phase/water partitioning experiments. As one would expect after functionalization by an organic group, n-TiO$_2$'s hydrophilicity changes. The n-TiO$_2$ dispersed
Preparation of TiO2-polystyrene-g-polyaniline nanocomposite

Figure 6 shows the FTIR spectra of the PANi (a) and TiO2–PSt-g-PANi (b). The FTIR spectra of PANI show the C=N in the quinoidal units which appears at 1587 cm$^{-1}$, the benzenoid stretches at 1490 cm$^{-1}$, and the N–H stretches at 3379 cm$^{-1}$. The FTIR spectra of TiO2–PSt-g-PANi show characteristic absorption band of polyaniline, the C 1601 cm$^{-1}$, the benzenoid stretching band at 1498 cm$^{-1}$, the N–H stretches at 3512 cm$^{-1}$, and the aromatic C–H stretches at 3123 cm$^{-1}$ were observed. The absorption peak at 1153 cm$^{-1}$ is characteristic of electron-like absorption of the N=Q=N vibration (where Q denotes the quinoid ring) and characteristic peaks at 2921 and 2853 cm$^{-1}$ are attributed to aliphatic C–H stretching.

Figure 1(c), displays the X-ray diffraction pattern for the TiO2–PSt-g-PANi nanocomposite. This is characterized by the appearance of peaks extending over the 2θ range.
5°–30°. This shows that the polymer has an amorphous structure which surrounds the TiO$_2$ nanoparticles. The pattern of the TiO$_2$-PSt-g-PANi nanocomposite also has characteristic peak at 2θ = 25.5°, that is attributed to the presence of TiO$_2$ nanoparticles.

The morphologies of TiO$_2$-PSt-g-PANI were investigated using SEM (Figure 7). Much larger particles are obtained when the polymer chains grow from the TiO$_2$-PSt surface. The compacted and large amounts of polyaniline chains ‘clothe’ the TiO$_2$-PSt nanocomposite and become bulk materials.

The amount of organics on the surface-modified TiO$_2$ was characterized with the aid of TGA. By comparing the percent weight loss of TiO$_2$ (8(a)) and the modified TiO$_2$ with ATRP agent (8(b)), a percent weight of organics attached to the surface of TiO$_2$ can be found. Figure 8 shows TGA plots comparing unmodified and modified TiO$_2$. As expected, the sample of crude TiO$_2$ gave no apparent weight loss below 700 °C. On the contrary, the sample of ATRP agent coordinated to TiO$_2$ displayed a weight loss of 4.6%, which was removed during heating in the range of 150–450 °C.

The thermogravimetric analysis of TiO$_2$, TiO$_2$-PSt and TiO$_2$-PSt-g-PANI nanocomposite synthesized is shown in (Figure 9). Figure 9 also shows that the temperature scale for the measurement is from 50 to 800 °C. Figure 9(b) is the TG curve of PSt-grafted TiO$_2$ nanoparticles and reveals that about 62% of the total weight of PSt-grafted TiO$_2$ nanoparticles is reserved. For PSt-grafted TiO$_2$ nanoparticles, the weight loss resulted from the evaporation of adsorbed water and the burn-up of grafted polystyrene; while the TiO$_2$-PSt-g-PANI nanocomposite shows almost 40% weight loss which is shown in Figure 9(c). The initial weight loss of about 3.6% in this case, at 127 °C can be assigned to the decomposition of solvent molecules trapped between the polymer chains, and the rapid weight decrease in the second region, (the onset at ~380 °C) can be attributed to the decomposition of PANi.

The morphology and mean size distribution of TiO$_2$ nanoparticles were determined by TEM. Figure 9(a) presents the TiO$_2$ particles that show low dispersion with high aggregation that is due to large specific surface area and high surface energy, some nanoparticles aggregate. The aggregation occurred probably during the process of drying. The TEM image in Figure 9(b) shows TiO$_2$-PSt-g-PANI nanocomposite, illustrating that aggregation decreased and dispersion improved and polyaniline makes them bigger and ‘cloth’ them.

**Conductivity measurement**

Conductivity measurements were carried out by a four-point probe method. The blends of PANi nanocomposites were compacted into pellets for measurements. The reported conductivity values were the averages of four pairs of readings at different parts on both sides of the pellets. All measurements were done in air at room temperature and converted to conductivity by the following equation:

$$\rho = \frac{1}{\delta} = \frac{V}{I \omega \pi / \ln 2}$$
Conclusion

Immobilization of an ATRP initiator on the TiO$_2$ surface via esterification of Br-MPA with hydroxyl group allowed the subsequent surface-initiated ATRP to produce polystyrene-grafted polymers. Then, functionalization of polystyrene grafted to amino group was done. The resulting macro-initiator (TiO$_2$-PSt-NH$_2$) was used for in situ chemical oxidative of aniline with ammonium persulfate. Macro-initiator TiO$_2$-Br-MPA could initiates ‘living’ free radical polymerization of styrene monomers to yield the controlled graft copolymer TiO$_2$-graft-polystyrene. TGA results indicated that no polymers adsorbed noncovalently onto the surface of TiO$_2$ nanoparticles. Also FTIR spectroscopy and SEM and TEM images investigation provided direct and clear evidence for the presence of polystyrene and polyaniline shell on nano-TiO$_2$ core particle. Significantly, this procedure can be extendable to any polymer that can be grafted from an initiator bound to inorganic materials.

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Disclosure statement

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where $\rho$ is the resistivity (Ω cm), $\delta$ is the conductivity (s/cm), $V$ is the potential difference (mV), $I$ is the applied constant current (mA), and $\omega$ is the thickness (cm). The conductivity of the nanocomposite was low compared to that of PANi. The main reason seemed to be stereo chemical differences between these two conducting polymers. Oxidized PANi had an almost planar structure with a low ionization potential due to strong delocalization of the electrons. The conductivity values of the pure PANi and TiO$_2$-polystyrene-g-polyaniline nanocomposite after 8 h polymerization were 1.25 and 0.98 S cm$^{-1}$, respectively (Table 2).

![Image](image.png)

**Figure 10.** Transmission electron microscopy (TEM) images of (a) TiO$_2$ nanoparticles (b) TiO$_2$-PSt-g-PANI nanocomposite.

**Table 2.** Characteristics of the conductive nanocomposite by four-point probe method and particle size obtained from TEM.

| Sample       | Polymerization time (h) | Particle size (nm) | Shell thickness (nm) | Conductivity (σ(S/cm)) |
|--------------|-------------------------|--------------------|----------------------|------------------------|
| TiO$_2$      | 40–90                   | 60–140             | 20–30                | 0.98                   |
| TiO$_2$-PSt-g-PANI | 8                      |                   |                      |                        |

Table 2. Characteristics of the conductive nanocomposite by four-point probe method and particle size obtained from TEM.
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