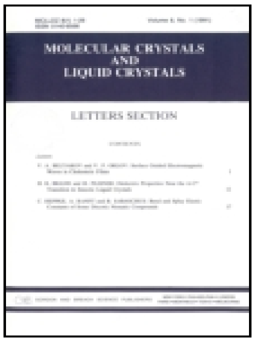

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ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Long Giang Bach, Xuan Thang Cao, Van Thi Thanh Ho, Md. Rafiqul Islam & Kwon Taek Lim (2015) A Facile Route Towards the Synthesis of Nanocomposites for the Application as Solid Electrolytes via Grafting Polymer from TiO_2 Nanoparticles, Molecular Crystals and Liquid Crystals, 618:1, 120-128, DOI: 10.1080/15421406.2015.1076315

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1076315

Mol. Crys. Liq. Cryst., Vol. 618: pp. 120–128, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1076315

A Facile Route Towards the Synthesis of Nanocomposites for the Application as Solid Electrolytes *via* Grafting Polymer from TiO_2 Nanoparticles

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Poly(acrylic acid)/TiO_2 (PAA-g-TiO_2) nanocomposites were synthesized by the surface thiol-lactam initiated radical polymerization (TLIRP) technique. The synthetic strategy involved the modification of $TiO_2$by a one-step direct anchoring of thiol groups via *reaction between the hydroxyl groups on the surface of TiO_2 and triethoxysilane groups of (3-mercapto)propyltrimethoxysilane (MPTMS). The modified TiO_2nanoparticles (NPs) were dispersed in acrylic acid monomers and subsequently polymerized by TLIRP to yield PAA-g-TiO_2nanocomposites. FT-IR spectra, XPS, EDS, UV-Vis spectroscopy and SEM images provided direct and clear evidence for the coordination of MPTMS and the presence of PAA on TiO_2 NPs. The immobilization of PAA onto TiO_2 NPs significantly improved their dispersibility in organic solvents. Additionally, laser diffraction spectroscopy of the TiO_2 NPs was examined in order to get the size distribution of nanocomposites.*

1. Introduction

The development of inorganic/polymer hybrid materials have many attractive features and now have become a new hotspot in material science. [1–3] They combine the advantages of polymers (flexibility, ductility, and processibility, elasticity, transparency, or dielectric properties) and inorganic nanoparticles (rigidity, high thermal stability, specific absorption of light, magnetoresistance effects, chemical activity, and catalysis etc.). These hybrid materials are potentially applied in diverse fields such as mechanism, optics, electronics, separation, catalysis, and biology. [4,5] Among previously reported numerous examples of

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hybrid nanoparticles, titanium dioxide (TiO_2) /polymer hybrids have been most extensively studied and successfully applied in the areas of catalysis, electrochemistry, photoluminescence, electronic ink based flexible display, and dye-sensitized solar cells. [6–10]

Due to the strong tendency of nanoparticles to agglomerate, homogeneous dispersion of these materials in a polymeric matrix is extremely challenging. [11–14] We have recently reported a simple *grafting from* protocol for the synthesis of inorganic/polymer nanocomposites materials *via*the surface thiol-lactam initiated radical polymerization (TLIRP) technique using surface bonded thiol functionalized nanoparticles and butyrolactam (BL). [15–18] Because of its tolerance to a wide range of reaction conditions, the TLIRP protocol could be thought as a simple and efficient operational method for the surface modification of nanoparticles.

In this study, we aimed to develop a method to synthesis reactive TiO_2 nanoparticles(NPs) tailored for surface grafting polymerization of a model monomer, acrylic acid (AA) by TLIRP, which are materials of interest for their potential application for the solid electrolytes in dye-sensitized solar cells. Grafting polymerization of polymer chains on TiO_2 NPs was performed following a two-step synthetic procedure: in-situ synthesis of TiO_2NPs with surface thiol (–SH) groups and subsequent grafting polymerization of AA on TiO_2 based on chain transfer to thiol groups on TiO_2 surfaces and BL (Scheme 1). The surface modification reaction and the modulated properties of surface-modified TiO_2 nanoparticles were characterized by fouriertransformed infrared spectrophotometry (FT-IR), X-ray diffraction (XRD), energy dispersive X-Ray (EDX), X-ray photoelectron spectroscopy (XPS), laser diffraction spectroscopy (LDS) and field emission scanning electron microscopy (FE-SEM). The mechanism of surface modification and the effect of grafted-PAA on the colloidal and dispersion properties of TiO_2 NPs were also described.

2. Experimental Details

Materials

AA was distilled under reduced pressure prior to polymerization. (3-mercaptopropyl) trimethoxysilane (MPTMS), BL, TiO_2 were purchased from Sigma-Aldrich and used without further purification. All other chemical reagents purchased from Sigma Aldrich were of analytical grade and used as received.

In-situ Synthesis of TiO_2(TiO_2-SH) with Surface Thiol Groups

The introduction of thiol groups onto the surface of TiO_2 NPs was achieved through the reaction between triethoxysilane groups of MPTMS and the hydroxyl groups on the surface of TiO_2. Typically, dispersing 10 g of TiO_2 NPs in 200 mL of toluene, an excess amount of MPTMS was added and the resulting solution was stirred for 24 h under argon atmosphere. Afterwards, modified TiO_2 was isolated by centrifugation and washed repeatedly with toluene to remove unreacted MPTMS. The resulting nanoparticles were dried under vacuum for 24 h.

Surface Grafting Polymerization of Acrylic Acid on TiO_2NPs

The grafting polymerization was performed by TLIRP. A typical procedure was as follows:AA monomer of 0.6 g, 0.2 g of TiO_2-SH and 0.4 g of BL were dispersed in 4 ml

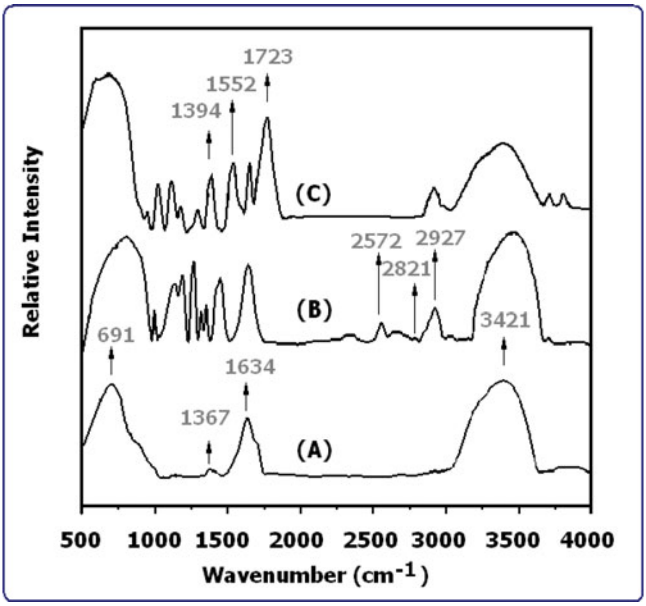


Figure 1. FT-IR spectra of (A) TiO_2 NPs, (B) TiO_2-SH and (C) PAA-g-TiO_2 nanocomposites.

methanol with the aid of ultrasonication and a Teflon-coated stir bar were placed in a 25 mL round flask equipped with a reflux condenser. The flask was purged with nitrogen, heated to 80°C and kept stirring. At the end of the reaction, the viscosity increased dramatically. After the desired time, the flask was cooled to room temperature and the reaction mixture was precipitated in diethyether and the polymer was separated by centrifuging.The product was rinsed with methanol several times and centrifuged to collect the TiO_2-PAA. The resulting solid product was obtained and dried in a vacuum oven overnight at room temperature.

Instrumentation

The changes in the surface chemical bonding of nanocomposites were captured by FT-IR using a BOMEM Hartman & Braun FT-IR Spectrometer in the frequency range of 4000–400 cm^{-1}. Surface composition was investigated using XPS (Thermo VG Multilab 2000) in ultra high vacuum with Al Kα radiation.The crystallographic state of functionalized TiO_2 NPswas determined by a Philips X'pert-MPD system diffractometer (Netherlands) with Cu Kα radiation. The morphology and elemental analysis of the hybrids were carried out by using FE-SEM images equipped with an EDX spectrometer (HitachiJEOL- JSM-6700F system, Japan). The hydrodynamic size of the PHEMA-*g*-TiO_2nanocomposites was determined by LDS (Horiba LA-950V2). The dispersibility of samples was evaluated using a Shimadzu UV-1800 Ultraviolet–visible Spectrophotometer.

3. Result and Discussion

The surface initiated grafting polymerization of AA from TiO_2NPs was carried out in the presence of TiO_2-SH and BL to afford PAA-*g*-TiO_2nanocomposite. Fig. 1 shows typical FT-IR spectra of TiO_2 NPs, TiO_2-SH and PAA-g-TiO_2nanocomposites, respectively. In the spectrum of TiO_2 NPs (Fig. 1A), the appearance of strong broad absorption peaks at

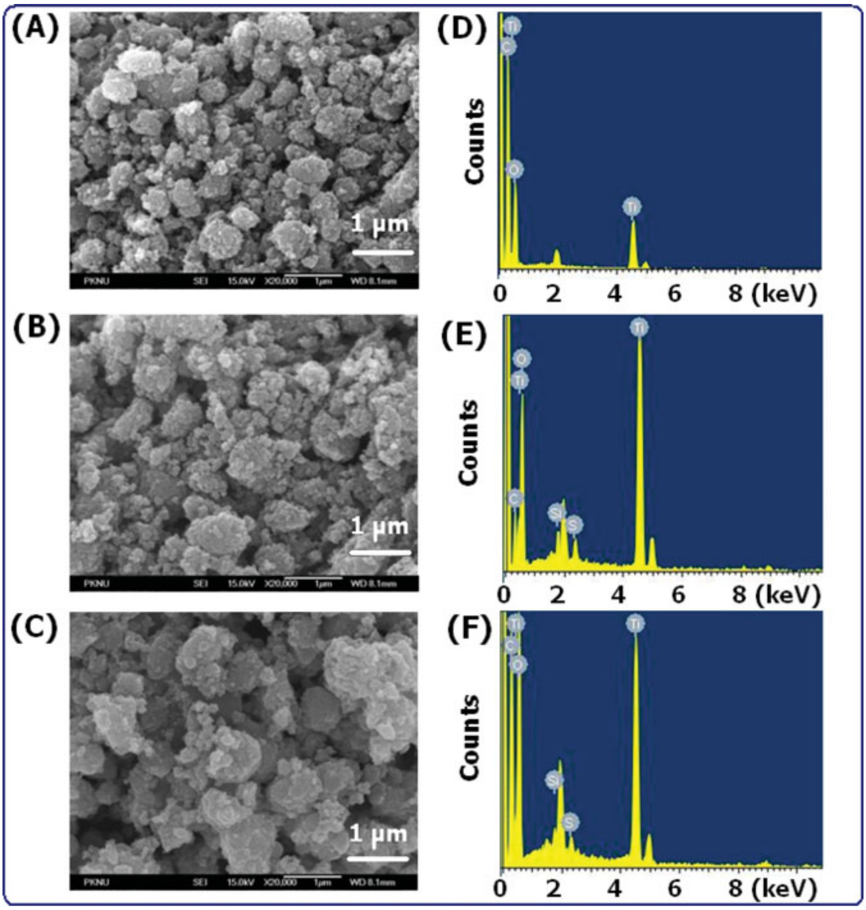


Figure 2. (A, B, C) FE-SEM images; (D, E, F) EDX spectrometric analysis of (A, D) TiO_2, (B, E) TiO_2-SH and (C, F) PAA-*g*-TiO_2 nanocomposites.

around 3421 and 1634 cm^{-1} indicates the presence of the –OH stretching vibrations and H–O–H bending vibrations on TiO_2 NPs. [19] The FT-IR spectrum of TiO_2-SH shows the characteristic absorptions at 2821and 2927 cm^{-1} due to the aliphatic C–H stretching of the coupling agent (Fig. 1A). Stretching vibration bands for Si–O–Si and Si–C bonds at 1194 and 1252 cm^{-1} are attributed to silane groups. The spectrum of TiO_2-SH has a weak but visible band at 2572 cm^{-1}, which can be assigned to the S-H stretching of MPTMS. [15,20] Figure 1C shows the FT-IR spectrums of the PAA-g-TiO_2, the strong absorption bands of 1723 cm^{-1} should belong to C=O stretching vibration while the peak at 1552 and 1394 cm^{-1} are characteristics corresponding to COO-. [21] The FT-IR data confirm that the PAA chains were anchored on the TiO_2 surface via TLIRP.

In order to examine the microstructure and nanofiller distribution within the polymer matrix, FE-SEM equipped with EDS were used. FE-SEM was used to study the morphology of TiO_2 NPs before and after functionalization, as well as the polymer nanocomposites. Fig. 3 A shows the FE-SEM image of the commercial TiO_2 NPs consisting of agglomerated spherical particles, whereas Fig. 2B shows the TiO_2 after functionalization. No obvious morphology change can be observed from the functionalization step. Compared to TiO_2

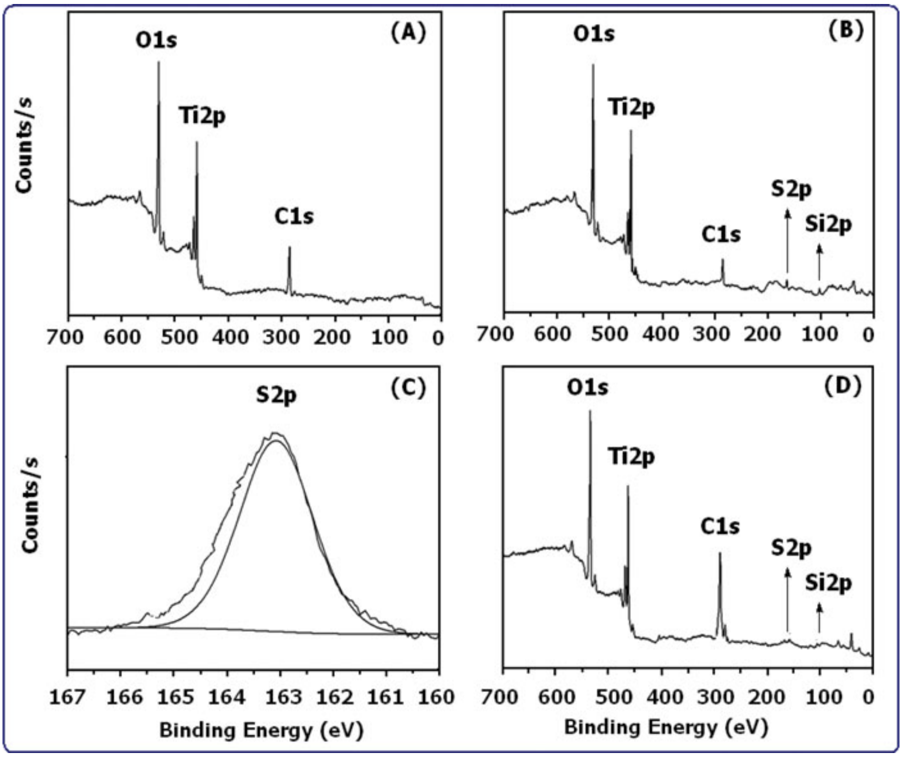


Figure 3. XPS spectra of wide-scan (A) TiO_2 NPs, (B) TiO_2-SH NPs, (C) S2p core-level spectra of TiO_2-SH surfaces and wide-scan (D) PAA-*g*-TiO_2.

NPs, the images of PAA-g-TiO_2nanocomposites (Fig. 2C) demonstrate relatively spherical shape having the polymer layer, and it is observed that TiO_2 NPs are embedded in the polymer beads. The EDX analyses suggested the presence of Ti and O elements in TiO_2 NPs as shown in Fig. 2D. The EDX analysis of TiO_2-SH NPs shows a small but detectable signal ascribed to the sulfur atoms on their surfaces (Fig. 2E). Furthermore, the EDX scan of PAA-*g*-TiO_2 _nanocomposites reveals the characteristic peaks of Ti, C, O, S, and Si as shown in the Fig. 2F.

XPS is a surface analytical technique that can provide useful information on the nature of the functional groups and also on the chemical composition of surfaces. The XPS analyses suggested the presence of Ti and O elements in TiO_2NPs as shown in Fig. 3A. To verify the presence of thiol groups on TiO_2, the XPS experiment was carried out for TiO_2-SH (Fig. 3B). As expected, significant peaks for oxygen, titanium, carbon, sulfur, and silicon were observed. It is noteworthy that the characteristic S2p peak of the S—H bond is observed at 163.2 eV, which confirms the presence of active thiol groups on TiO_2 surfaces (Fig. 3C). The XPS spectrum of PAA-*g*-TiO_2 nanocomposites is fully consistent with what is expected from a monolayer of PAA. After grafting of PAA, the C1s peak with high intensity slightly shifted to a higher binding energy (BE) (Fig. 3D) than un-grafted TiO_2 NPs, indicating that the polymeric chains were directly grafted from the surfaces of TiO_2NPs.

XRD is an effective method to investigate the interlayer changes and the crystalline properties of the synthesized material. The XRD patterns of pristine TiO_2 NPs, TiO_2-SH

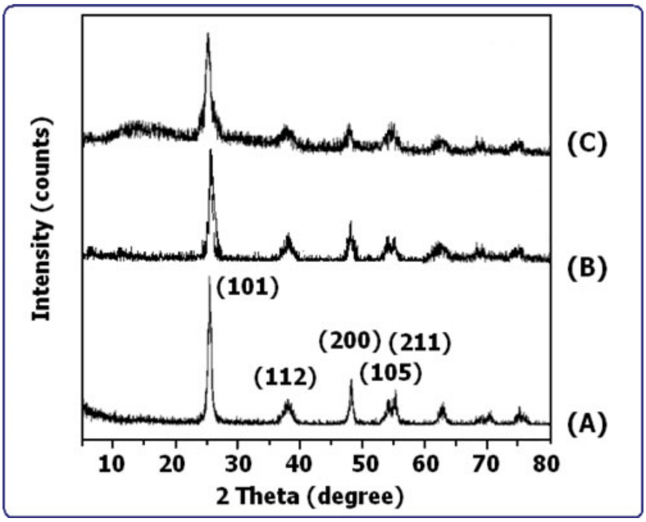


Figure 4. XRD patterns of (A) pristine TiO_2 NPs, (B) TiO_2-SH and (C) PAA-*g*-TiO_2 nanocomposites.

and PAA-*g*-TiO_2 nanocompositesin the 2θ range 5–80° are represented in Fig. 4. The pristine TiO_2 NPs exhibited several sharp peaks centered at $2\theta = 25.46$, 37.89, 48.18, and 55.18, which correspond to the (101), (112), (200), and (211) reflections, respectively, of the anatase form of TiO_2 as shown in Fig. 4A. Upon modification, the characteristic peaks of PAA-*g*-TiO_2nanocomposites were almost resembled with those of TiO_2 NPs, suggesting that the grafting polymerization did not alter the crystalline structure of TiO_2 NPs.

The resulting materials were studied by organic phase/water partitioning experiments. As expected after functionalization by an organic group, TiO_2's hydrophilicity changes. Fig. 5A shows TiO_2 NPs dispersed in ethyl acetate/water bilayers, where TiO_2 NPs is suspended in the water phase (lower phase), indicating that it is hydrophilic. TiO_2 NPs

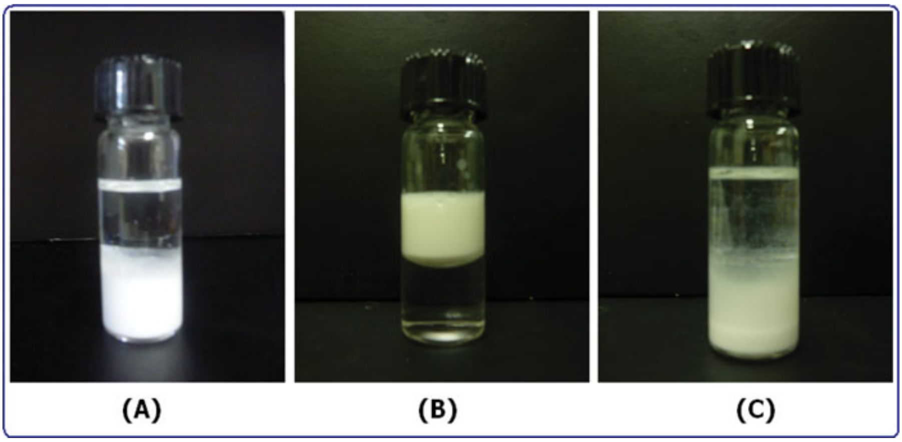


Figure 5. In the vials, the upper layer is ethyl acetate and the lower layer is water. (A) TiO_2 NPs is well dispersed in the water phase; (B) TiO_2-SH is suspended in ethyl acetate and (C) PAA-*g*-TiO_2 nanocomposite stays in the water phase.

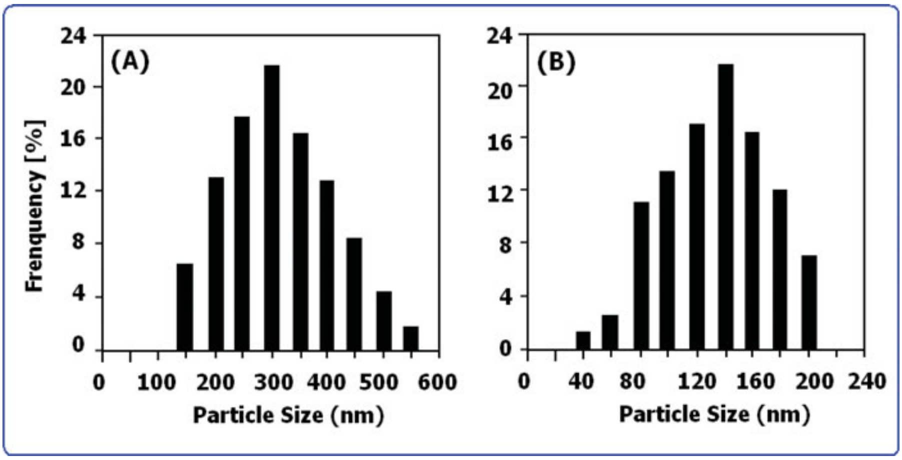


Figure 6. Size distribution of (A) TiO_2 NPs and (B) PAA-*g*-TiO_2nanocomposites.

functionalized with MPTMS, however, partitions into the organic phase (upper), due to the existence of the organic moiety (Fig. 5B). Due to many carboxylic groups in the PAA molecules, the PAA-g-TiO_2nanocomposite is mainly hydrophilic in nature, as evidenced by partitioning into the water phase (Fig. 5C).

The size distribution of TiO_2 NPs and PAA-*g*-TiO_2 nanocomposites is shown in Fig. 6. It is clearly observed that the mean size of bare TiO_2 NPs is larger than that of PAA-*g*-TiO_2nanocopmposites. A clear picture of aggregations in the unmodified TiO_2 NPs in aqueous system was visualized, so that the mean size reflected the agglomeration of several TiO_2 NPs. On the contrary, Fig. 6B shows the size distribution of homogeneous nanoparticles. The hydrodynamic diameter of PAA-*g*-TiO_2 nanocomposites in methanol was measured to be 160 ± 13 nm. It infers that PAA interferes with the aggregation of TiO_2

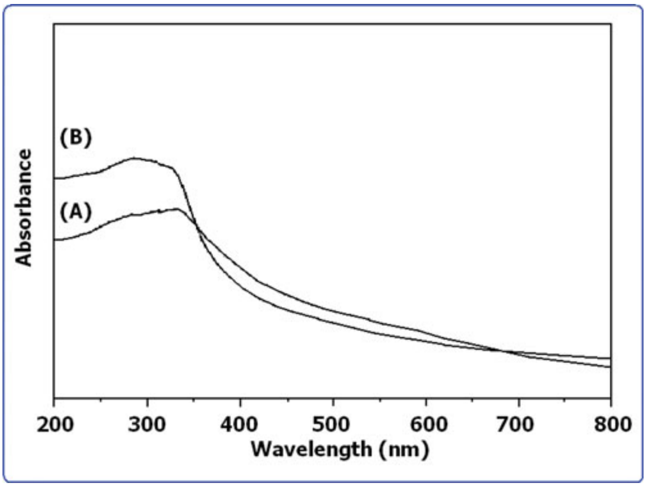
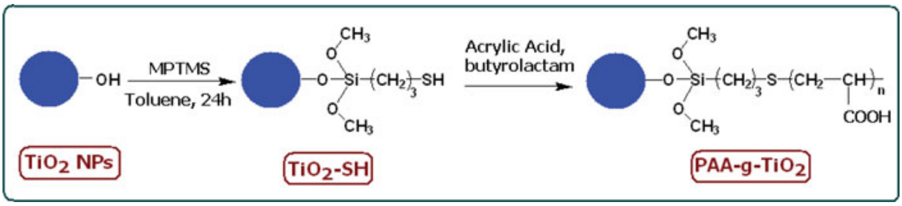


Figure 7. UV–Vis spectra of (A) pristine TiO_2 NPs and (B) PAA-*g*-TiO_2 nanocomposites.

NPs. Above results illustrate that PAA have an important role in the dispersion of TiO_2 NPs.



Scheme 1. Schematic illustration for the preparation of PAA-*g*-TiO-$_2$ nanocomposites through TLIRP protocol.

UV–Vis absorption measurements were performed to investigate the modification effects on the colloidal dispersion and optical properties of PAA-*g*-TiO_2 nanocomposites. Fig. 7 shows the UV-Vis spectra of pristine TiO_2 NPs and PAA-*g*-TiO_2nanocomposites at wavelengths between 200 and 800 nm. It is well known that photoabsorption depends on the structure and grain size of NPs. [22] The pristine TiO_2 NPs exhibited a strong UV absorption at 320 nm, assigned to the typical absorption edge of TiO_2 NPs. [23] PAA-*g*-TiO_2nanocomposites showed absorption in shorter wavelength region than the pristine TiO_2 NPs. This is presumably due to the decrease in particle size resulting from steric repulsive forces between TiO_2 NPs at the interfaces of each nanoparticle, [19] leading to an increase in the bandgap energy (Eg).

4. Conclusions

The grafting polymerization of acrylic acid on the surface of TiO_2 NPs afforded PAA-*g*-TiO_2 nanocompositesby using the simple surface TLIRP technique *via* functionalized TiO_2 NPs with MPTMS. The FT-IR, XPS, UV-Vis spectroscopy and EDX analyses provided the evidence of the surface functionalization of TiO_2 NPs by PAA chains. FE-SEM images revealed the growth of the “graft-from” polymers around TiO_2 NPs. The organic phase/water phase partitioning studies clearly provided the evidence of the functionalization of TiO_2 NPs with MPTMS and PAA. The dispersibility of TiO_2 NPs was observed to be significantly improved upon functionalization with PAA brushes as studied by LDS.

Acknowledgment

This work was supported by the the BK21 Plus program.

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