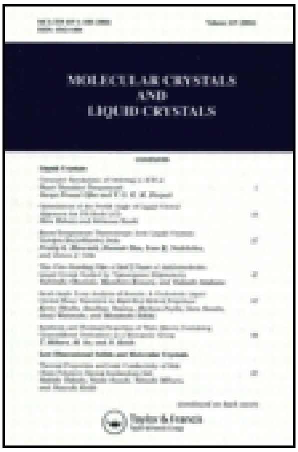

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Synthesis and Characterization of Poly(oxyethylene methacrylate) Coated TiO_2 Nanoparticles via Surface Thiol-Lactam Initiated Radical Polymerization

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Synthesis and Characterization of Poly(oxyethylene methacrylate) Coated TiO_2 Nanoparticles *via* Surface Thiol-Lactam Initiated Radical Polymerization

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Poly(oxyethylene methacrylate) (POEM) anchored TiO_2 nanoparticles were synthesized via *the surface thiol-lactam initiated radical polymerization of POEM in the presence of thiol functionalized TiO_2 nanoparticles. The grafting of POEM onto the surface of TiO_2 nanoparticles was investigated by FT-IR, XPS, EDX, TGA, XRD, and TEM analyses. The experimental findings suggested that a strong interaction prevailed between grafted POEM and TiO_2 nanoparticles. The TEM image of POEM-*g*-TiO_2 showed that the agglomeration propensity of TiO_2 nanoparticles was reduced significantly upon the functionalization of POEM. Moreover, an improved thermal property of the POEM in the POEM-*g*-TiO_2 nanocomposites was observed by TGA.*

Keywords TiO_2 nanoparticles; POEM; polymer brush; POEM-*g*-TiO_2; core-shell structure; surface initiated polymerization

Introduction

Chemical or physical surface treatments of nano-structured materials have currently been widely used to improve their colloidal stability and processibility in solutions, and adhesion with a polymer matrix in organic–inorganic hybrids. Nanocomposites can create unique properties having excellent optical, electrical, thermal, mechanical, electro-optical, magnetic and catalytic properties [1–4]. Among many classes of inorganic compounds, titanium oxide (TiO_2) is a wide band gap semiconductor and a photo catalyst with stable

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physical and chemical properties. Especially, surface modification of the TiO_2 particles by coating with polymeric materials have been studied and successfully applied in the areas of catalysis, electrochemistry, photoluminescence, electronic ink based flexible display, and solar cells [5–8].

Tethering of polymer brushes on a solid substrate is considered to be an effective method of modifying the surface properties of the substrate. Moreover, polymers provide better chemical resistance and dispersion stability for the inorganic materials. Based on this idea, a series of composites of nanoparticles with polymers have been prepared *via* several polymerization methods [9–13]. Recently poly(oxyethylene methacrylate) (POEM) encapsulated TiO_2 nanoparticles was synthesized by atom transfer radical polymerization, which are promising materials for dye-sensitized solar cell applications [14,15].

The present work reports a facile method to synthesize chemically bonded hydrophilic POEM polymer on TiO_2 nanoparticles *via* surface thiol-lactam initiated radical polymerization (TLIRP). In this method, thiol groups can initiate polymerization with the aid of butyrolactam (BL) [16,17]. The advantages of this method include one-step direct anchoring of initiator moiety and do not require any metal catalyst. At first, TiO_2 nanoparticles were immobilized with thiol groups and subsequently the grafting polymerization of POEM was accomplished from the surface of the thiol functionalized TiO_2 nanoparticles (TiO_2-SH). The surface composition and properties of POEM-*g*-TiO_2 nanocomposites was also investigated.

Experimental

Materials

3-mercaptopropyl-trimethoxysilane (MPTMS), BL, TiO_2 nanoparticles (anatase), POEM, dimethyl sulfoxide (DMSO) were purchased from Aldrich and used as received.

Grafting of MPTMS onto TiO_2 nanoparticles

TiO_2 nanoparticles were reacted with MPTMS to obtain TiO_2-SH. In a typical procedure, 5 g of TiO_2 nanoparticles was taken in 100 mL of toluene, an excess amount of MPTMS was added and the resulting solution was stirred for 24 h under argon atmosphere. TiO_2-SH was isolated by centrifugation and washed repeatedly with toluene. Finally, it was dried at 40°C under vacuum for 24 h.

Synthesis of POEM grafted TiO_2 nanoparticles via TLIRP (POEM-g-TiO_2)

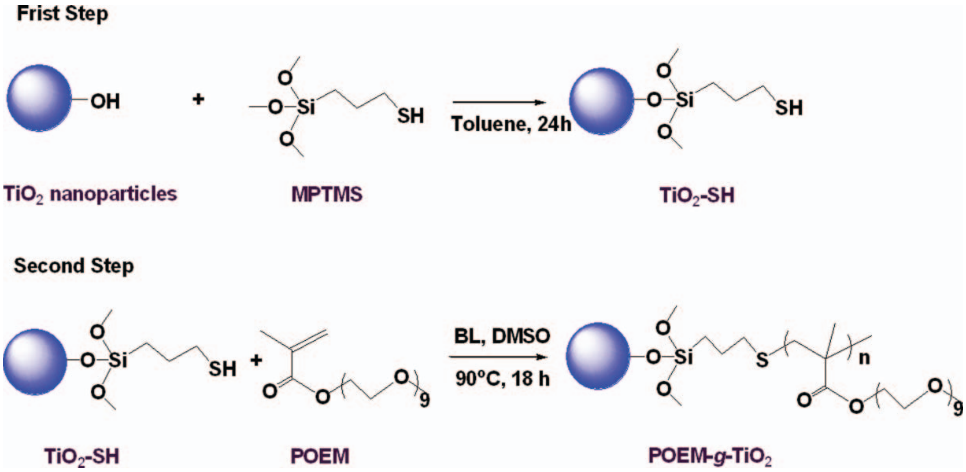
A typical procedure for synthesizing POEM-*g*-TiO_2 by TLIRP is as follows: 2.5 g of POEM, 0.5 g of TiO_2-SH, 1 g of BL, 10 mL of DMSO and a Teflon-coated stir bar were placed in a 100 mL round flask equipped with a reflux condenser. The flask was purged with nitrogen for 30 min. The mixture was placed in an oil bath at 90°C for 18 h and kept stirring. By the end of the reaction, the viscosity increased dramatically. After the reaction, the flask was cooled to room temperature and the reaction mixture was precipitated in methanol, and POEM-*g*-TiO_2 nanocomposites were separated by centrifuging. The product was washed with methanol several times to remove impurities. Finally, the nanocomposites were dried in a vacuum oven overnight at room temperature.

Characterization

The changes in the surface chemical bonding of TiO_2 nanoparticles, TiO_2-SH, and POEM-*g*-TiO_2 hybrid nanoparticles were captured by Fourier Transformed Infrared Spectrophotometry (FT-IR) using a BOMEM Hartman & Braun FT-IR Spectrometer in the frequency range of 4000–400 cm^{-1}. Surface composition was investigated using X-ray Photoelectron Spectroscopy (XPS) (Thermo VG Multilab 2000) in ultra high vacuum with Al $K\alpha$ radiation. Thermogravimetric analysis (TGA) was conducted with Perkin-Elmer Pyris 1 analyzer (USA). Before the test, all the samples were carefully grinded into fine powder. The samples were scanned within the temperature range of 50–800°C at a heating rate of 10°C min^{-1} under continuous nitrogen flow. The XRD patterns of the polymer and composites were collected on a powder X-ray diffractometer (Philips, X'Pert-MPD) with Cu Ka radiation. Transmission Electron Microscopy (TEM) images were recorded using a Hitachi H-7500 instrument operated at 80 kV. A drop of the sample dispersed in distilled ethanol was placed on a copper grid and drying. The elemental analysis of the hybrids was carried out by using a Field Emission Scanning Electron Microscopy (FE-SEM) equipped with an Energy Dispersive X-Ray (EDX) spectrometer (HitachiJEOL-JSM-6700F system, Japan).

Results and Discussion

The reaction scheme for the graft polymerization of POEM from TiO_2 nanoparticles *via* TLIRP, is illustrated in Scheme 1. Inorganic TiO_2 nanoparticles were organically modified by grafting polymer POEM *via* a two-step synthetic approach. To carry out TLIRP of POEM on TiO_2 surface, MPTMS was chosen as silane coupling agent which was immobilized onto TiO_2 nanoparticles *via* ligand-exchanging reaction between the hydroxyl groups on the surface of TiO_2 and triethoxyliane groups of MPTMS. The reaction resulted in the chemically bonded (Ti-O-Si bond) MPTMS onto the TiO_2 nanoparticle surface. The immobilization of the MPTMS onto the TiO_2 surface was investigated by FT-IR, XPS,



Scheme 1. The reaction scheme for the graft polymerization of POEM from TiO_2 nanoparticles via TLIRP technique.

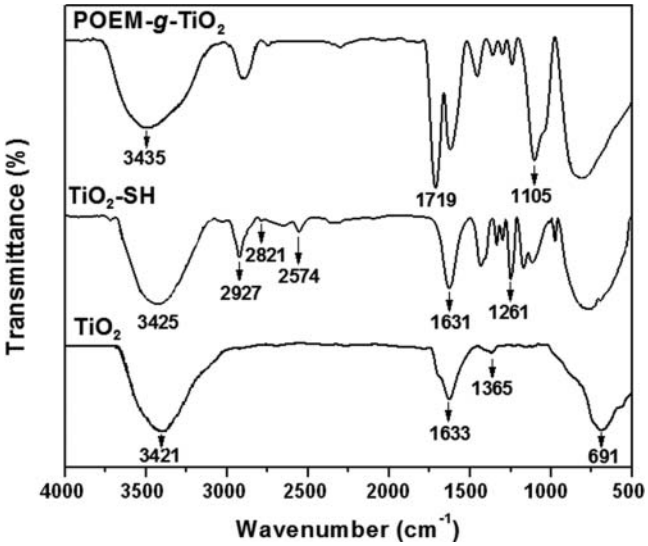


Figure 1. FT-IR spectra of pristine TiO_2 nanoparticles, TiO_2-SH and POEM-*g*-TiO_2 nanocomposites.

and TGA analyses. The resulting TiO_2-SH nanoparticles were used as initiators for TLIRP, where BL was used as a radical generating agent for the polymerization. The synthesized PHEMA-*g*-TiO_2 nanocomposites were investigated by FT-IR, XPS, EDX, TGA, XRD, TEM and SEM to get more insight of the polymerization process and nanocomposites properties.

FT-IR analyses of surface functionalization of TiO_2 and POEM-g-TiO_2 nanocomposites

The chemical composition of the pristine TiO_2, MPTMS immobilized nanoparticles (TiO_2-SH) and TiO_2 nanoparticles modified with POEM (POEM-*g*-TiO_2) were analyzed by the FT-IR (Fig. 1). The FT-IR spectrum of the pristine TiO_2 nanoparticles exhibits strong broad absorption bands at around 3421 and 1633 cm^{-1} those are attributable to the -OH stretching vibrations and H-O-H bending vibrations originating from adsorbed water on the surface of TiO_2 nanoparticles, respectively. The absorption bands between 500 and 800 cm^{-1} are assigned to the vibrations of Ti-O and Ti-O-Ti framework bonds. For MPTMS modified TiO_2 surface, characteristic absorption bands at 2822 and 2928 cm^{-1} are assigned to -CH_2 groups of the coupling agent. The TiO_2–SH gave a weak but visible absorption band at 2574 cm^{-1} assigning for the S-H stretch band, which is not be observed in the absorption spectrum of pristine TiO_2 nanoparticles, indicating chemically immobilized MPTMS onto TiO_2 nanoparticles was successfully occurred. From the above observations, it can be deduced that the MPTMS coupling agent was grafted on the surface of TiO_2 nanoparticles through the formation of chemical bonds. Upon the graft polymerization of POEM from TiO_2 nanoparticles, the strong absorption band appeared at a higher wavenumber of 3435 cm^{-1} for POEM-*g*-TiO_2. This new broad absorption band is attributed to the water molecules bound to hydrophilic polymeric chains. In the graft polymerization of POEM, two absorption bands at 1719 and 1105 cm^{-1} are appeared, attributed to the stretching vibrations of carbonyl oxygen ($C = O$) and ether oxygen (C–O–C), respectively. These FT-IR spectroscopic results demonstrate the successful of POEM via TLIRP from the TiO_2 nanoparticles surface.

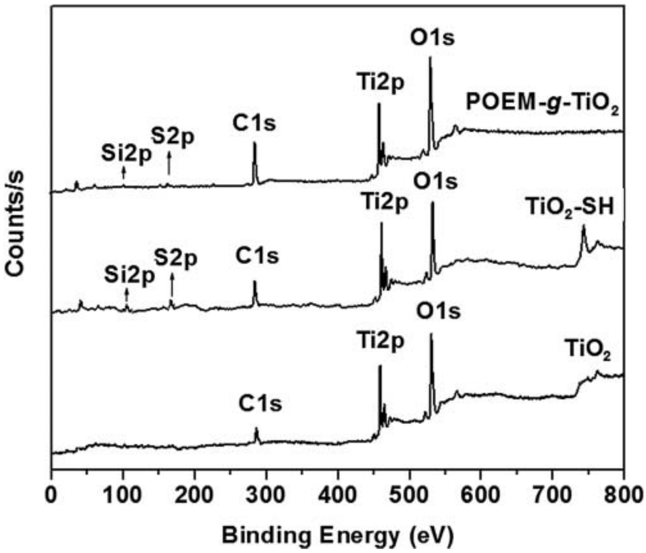


Figure 2. Wide-scan spectra of pristine TiO_2 nanoparticles, TiO_2-SH nanoparticles and POEM-*g*-TiO_2 nanocomposites.

XPS and EDX analysis

XPS was used to further examination of the surface chemical composition of TiO_2, TiO_2-SH and POEM-*g*-TiO_2 nanoparticles. The wide spectra of TiO_2, TiO_2-SH and POEM-*g*-TiO_2 nanoparticles are shown in Fig. 2. XPS spectrum of the TiO_2 surface was dominated by signals attributable to O, Ti, and C. The characteristic signals for oxygen (O1s at 530.8 eV), titanium (Ti2p at 458.1 eV), carbon (C1s at 285.2 eV), sulfur (S2p at 163.1 eV) and silicon (Si2p at 102.2 eV) are clearly observed in the wide scan XPS spectrum of TiO_2-SH. Silane coupling agent immobilized on surface of TiO_2 nanoparticles might proceeded through condensation reaction with MPTMS to produce a stable initiator monolayer which is consistent with the appearance of the Si, S core-level signals in the wide-scan spectrum of TiO_2-SH surface (Fig. 3). The XPS results confirm the success of the formation of

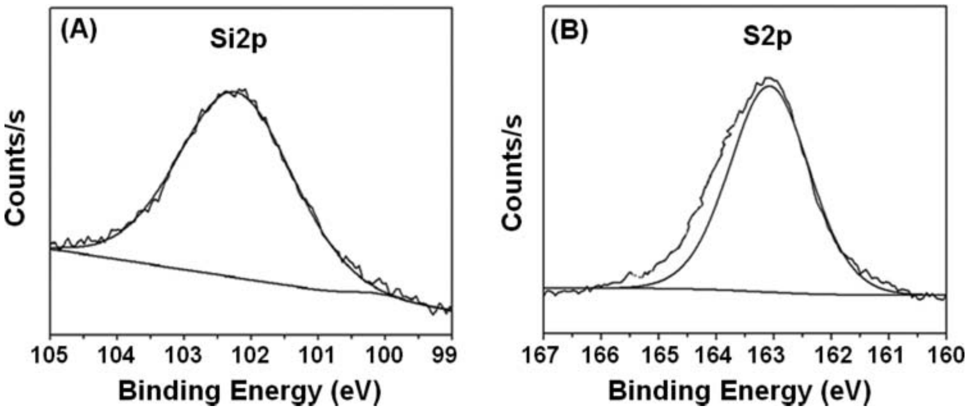


Figure 3. (A) Si2p and (B) S2p core-level spectra of the functionalized TiO_2-SH surfaces.

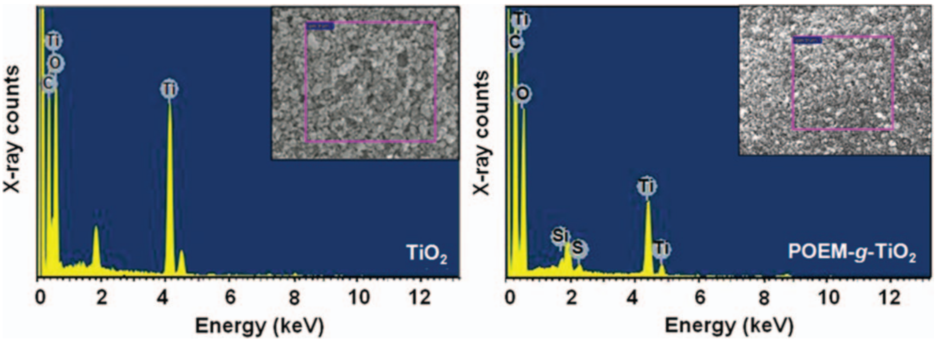


Figure 4. EDX spectrometric analysis of pristine TiO_2 nanoparticles and POEM-*g*-TiO_2 nanocomposites.

TiO_2-SH nanoparticles, that is, the immobilization of the surface-initiator. After grafting of POEM onto TiO2 nanoparticles, the XPS scan of POEM-*g*-TiO2 shows that the C1s peak with high intensity slightly shifted to a higher binding energ, indicating that the polymeric chains were directly grafted from the surfaces of TiO_2 nanoparticles.

The elemental mapping analysis of TiO_2 and POEM-*g*-TiO_2 nanocomposites is shown in Fig. 4, as captured by EDX. The characteristic peaks ascribed for titanium, silica, carbon, oxygen and sulfur elements are present in the EDX spectrum of POEM-*g*-TiO_2 which unanimously suggests that the POEM was grafted onto the surface of TiO_2 nanoparticles.

Thermo-gravimetric analysis of POEM-g-TiO_2

To examine the composition effecton the thermal degradation of the POEM-*g*-TiO_2 nanocomposites, TGA analyses were performed for all the samples at the temperature range of 50 to 800°C. Figure 5 shows the thermal decomposition behaviors of pure TiO_2, TiO_2-SH and POEM-*g*-TiO_2 nanocomposites. The weight loss of pure TiO_2 was found to

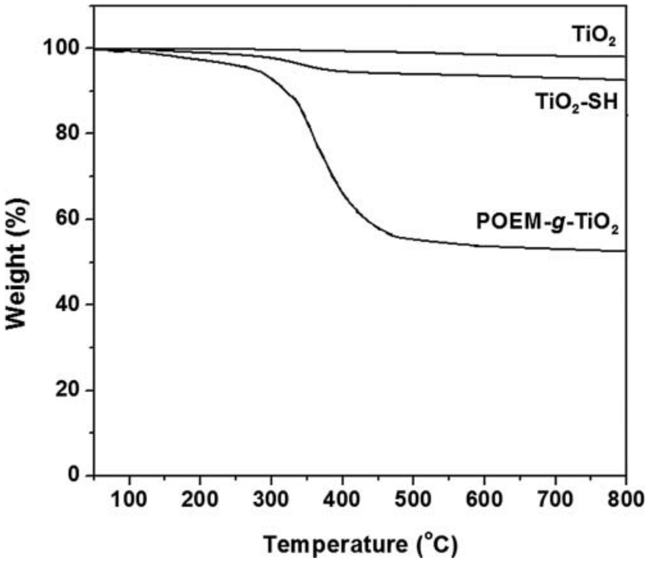


Figure 5. TGA spectra of pristine TiO_2 nanoparticles, TiO_2-SH and POEM-*g*-TiO_2 nanocomposites.

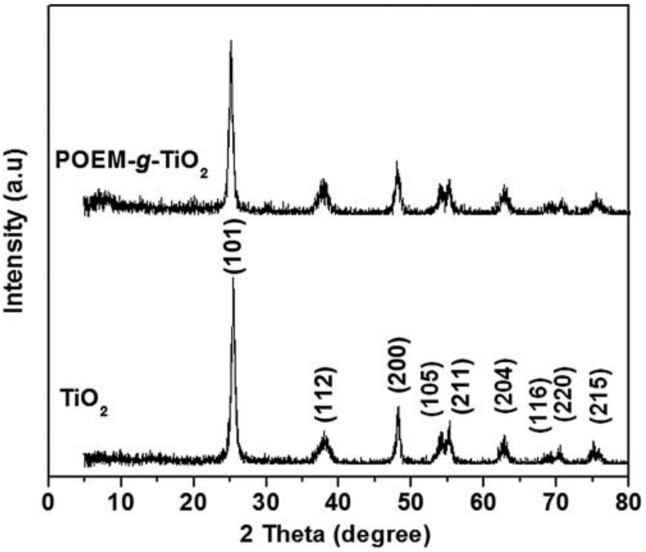


Figure 6. XRD patterns of pristine TiO$_2$ nanoparticles and POEM-*g*-TiO$_2$ nanocomposites.

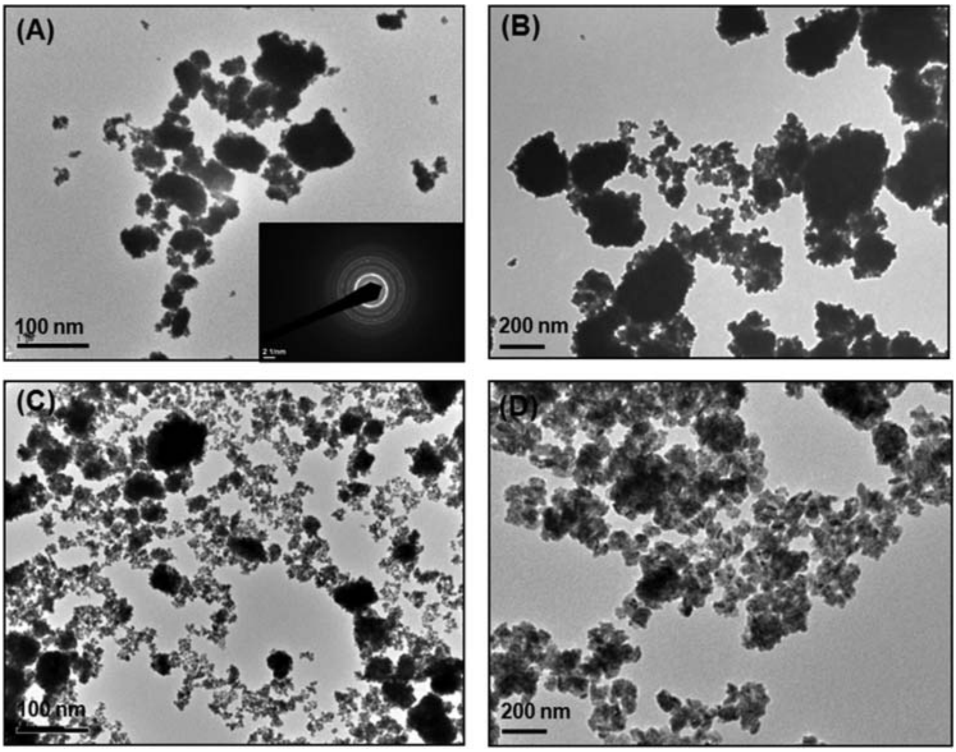


Figure 7. TEM pictures of (A) pristine TiO$_2$ nanoparticles and (C) POEM-*g*-TiO$_2$ nanocomposites. Pictures (B) and (D) are different magnifications of (A) and (C).

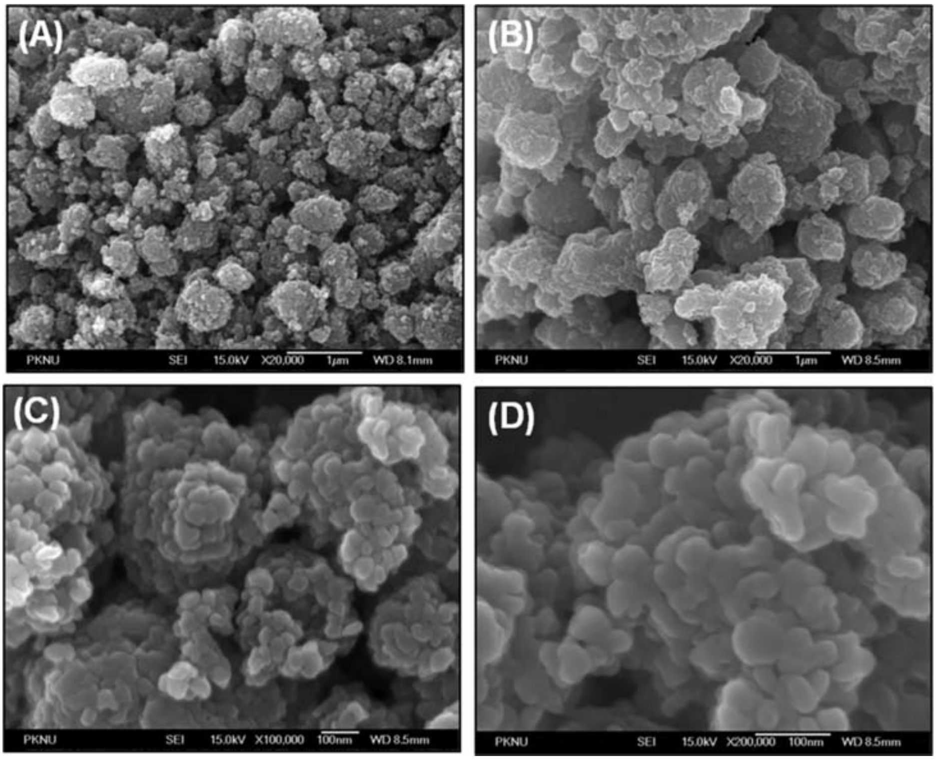


Figure 8. SEM images of (A) pristine TiO_2 nanoparticles, and (B, C, D) POEM-*g*-TiO_2 nanocomposites.

be ca. 2.1% when heated from room temperature to 800°C, which may be assigned to the weight loss of the hydroxyl groups or adsorbed matters on TiO_2 nanoparticles. The weight loss of TiO_2-SH between 50°C and 800°C was ca. 6.5%. For the as prepared POEM-*g*-TiO_2 nanocomposites, thermal decomposition was observed at temperature range from 270 to 350°C, which is due to the decomposition of grafted POEM. The weight fractions of organic moieties were found to be 54.5% for POEM-*g*-TiO_2 nanocomposites.

Physical structure and morphology nanocomposites

The structural changes of TiO_2 nanoparticles upon grafting of POEM were also investigated using XRD analysis. The XRD patterns of pristine TiO_2 and POEM-*g*-TiO_2 nanocomposites (in the 2θ range 5–80°) are presented in Fig. 6. The pristine TiO_2 nanoparticles exhibited several sharp peaks centered at $2\theta = 25.46$, 37.89, 48.18, 54.10, 55.18, 62.77, 69.04, 70.28 and 76.47, which correspond to the (101), (112), (200), (105), (211), (204), (116), (220) and (215) reflections, respectively, the anatase form of TiO_2. For POEM-*g*-TiO_2 nanocomposites, the hollows appeared in the region of $2\theta = 7.5$ in XRD curve suggests that POEM prepared in the absence of TiO_2 nanoparticles is amorphous. The main peaks of POEM-*g*-TiO_2 nanocomposites are similar to those of TiO_2 nanoparticles. The broad weak diffraction peak of POEM still exists, but its intensity significantly decreases. It indicates that the composite sample has a more ordered arrangement than the neat polymer owing to the inclusion of TiO_2 nanoparticles. All these results suggest that the incorporation of TiO_2 does not affect the crystalline behavior of TiO_2 nanoparticles and the grafted POEM polymer did not alter the crystalline structure of the TiO_2 nanoparticles significantly.

The effect of POEM polymer grafting on the dispersion property of TiO_2 nanoparticles was investigated by TEM analysis. Figure 7 shows the TEM images of pristine TiO_2 and POEM-*g*-TiO_2 nanocomposites. The pristine TiO_2 nanoparticles showed aggregation of TiO_2 nanoparticles and the electron diffraction pattern (inset Fig. 7A) consisting of rings indicates the good crystal structure of the TiO_2 nanoparticles. Whereas, the POEM-*g*-TiO_2 nanocomposites synthesized by using MPTMS modified TiO_2 nanoparticles show an image of TiO_2 nanoparticles in the polymer matrix. The agglomeration might be due to the fact that the smaller sizes of TiO_2 nanoparticles tend to agglomerate easily. The grafted POEM chains on TiO_2 nanoparticles resulted in steric repulsive forces between particles, which eventually interfere with the aggregation of each nanoparticle. It is thus concluded that the nanoparticles modified by hydrophilic POEM polymeric chains had a better dispersion property than the bare TiO_2 nanoparticles.

The SEM images of pristine TiO_2 nanoparticles and POEM-*g*-TiO_2 nanocomposites are shown in Fig. 8. Compared to pristine TiO_2 nanoparticles (Fig. 8), the images of nanocomposites (Fig. 8B–D) demonstrate uniform spherical shape and it is observed that TiO_2 nanoparticles are embedded in the polymer beads. However, the nanoparticles are also remained agglomerated in the case of synthesized nanocomposites. Several large particles are visualized, which is likely that pre-aggregation of nanoparticles was predominant.

Conclusions

Chemically anchored POEM onto the surface of TiO_2 nanoparticles was synthesized *via* a simple TLIRP technique with TiO_2-SH and BL. FT-IR, XPS, EDX and TGA investigations gave a direct and clear evidence of the presence of POEM on the surface of TiO_2 nanoparticles. In addition, TEM and SEM images revealed the growth of POEM grafting from the surface of TiO_2 nanoparticles. The thermal property of the POEM-*g*-TiO_2 nanocomposites was found to be superior to neat POEM, as evidenced by TGA.

Acknowledgments

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References

[1] Hao, R., Xing, R., Xu, Z., Hou, Y., Gao, S., & Sun, S. (2010). *Adv. Mater.*, *22*, 2729.
[2] Zou, H., Wu, S. J., & Shen, (2008). *Chem. Rev. 108*, 3893.
[3] Yuvaraj, H., Park, E. J., Gal, Y. S., & Lim, K. T. (2008). *Coll. and Sur. A: Physicochem. Eng. Aspects*, *313–314*, 300.
[4] Kim, J. S., Yun, J. H., Kim, I., & Shim, S. E., (2011). *J. Ind. Eng. Chem.*, *17*, 325.
[5] Badila, M., Brochon, C., Hebraud, A., & Hadziioannou, G. (2008). *Polymer*, *49*, 4529.
[6] Kong, H. Y., Song, J. Y., & Jang, J. S. (2010). *Environ. Sci. Technol.*, *44*, 5672.
[7] Park, J. H., Lee, M. A., Park, B. J., & Choi, H. J. (2007). *Curr. Appl. Phys.*, *7*, 349.
[8] Lee, J. Y., Sung, J. H., Jang, I. B., Park, B. J., & Choi, H. J. (2005). *Synth. Met.*, *153*, 221.
[9] Matsuno, R.; Otsuka, H., & Takahara A. (2006). *Soft Matter*, *2*, 415.
[10] Park, J. T., Koh, J. H., Koh, J. K., & Kim, J. H. (2009). *Appl. Sur. Sci.*, *255*, 3739.
[11] Barbey, R., Lavanant, L., Paripovic, D., Schuwer, N., Sugnaux, C., Tugulu, S., & Klok, H. A. (2009). *Chem. Rev.*, *109*, 5437.
[12] Park, J. T., Seo, J. A., Ahn, S. H., Kim, J. H., & Kang, S. W. (2010). *J. Ind. Eng. Chem*, *16*, 517.

[13] Hojjati, B., & Charpentier, P. A. (2008). *J. of Polym. Sci.: Part A: Polym. Chem.*, *46*, 3926.

[14] Park, J. T., Roh, D. K., Patel, R., Kim, E, Ryu, D. Y, & Kim, J. H. (2010). *J. Mater. Chem.*, *20*, 8521.

[15] Park, J. T., Koh, J. H., Koh, J. K., & Kim, J. H. (2009). *App. Sur. Sci.*, *255*, 3739.

[16] Hwang, H. S., Bae, J. H., Kim, H. G., & Lim, K. T. (2010). *Eur. Polym. J.*, *46*, 1654.

[17] Rashid, M. H., Bae, J. H., Park, C., Lim, & K. T. (2010). *Mol. Cryst. Liq. Cryst.*, *532*, 514.