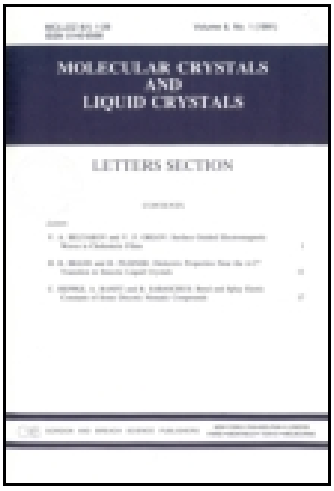

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Synthesis and Characterization of Poly(Oligoethyleneglycol Methacrylate)-g-TiO_2 Nanocomposites via Surface-Initiated ARGET ATRP

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Synthesis and Characterization of Poly(Oligoethyleneglycol Methacrylate)-g-TiO_2 Nanocomposites *via* Surface-Initiated ARGET ATRP

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Poly(oligoethyleneglycol methacrylate) (POEGMA) covalently attached to TiO_2 nanoparticles (NPs) were synthesized by the surface-initiated ARGET ATRP. The growth of polymer chains from the surface of ATRP-initiator functionalized nanoparticles was achieved under mild condition by using copper (II) as a catalyst and zerovalent copper (Cu^0) or L-ascorbic acid (AsAc) as reducing agents. The as-synthesized nanocomposites were characterized by FT-IR, TGA, FE-SEM and TEM analyses. FT-IR results suggested the formation of polymer chains covalently attached to the TiO_2 nanoparticles. The nanoparticles were found to be imbedded in polymer matrices as revealed by TEM and FE-SEM images. TGA curves demonstrated that AsAc afforded the faster grafting rate over Cu^0.

Keywords TiO_2 nanoparticles; ARGET ATRP; POEGMA-g-TiO_2; surface-initiated polymerization; nanocomposites; L-ascorbic acid

Introduction

Polymer/inorganic hybrid nanocomposites have attracted considerable attention due to their excellent optical, electronic, magnetic, mechanical, catalytic properties and their potential application as advanced functional materials [1–4]. By covalent grafting of polymers on inorganic nanoparticles, the hybrid nanocomposites can exhibit possibly intriguing properties, which cannot be obtained by simple co-mixing of the polymeric component with the inorganic phase [1, 5]. Moreover, it is also well known that the thermal and mechanical properties of polymers could be significantly improved with appropriate nano-fillers such as SiO_2, multi-wall carbon nanotube (MWNT), Au and so on [6, 7]. Therefore, a variety of methods for preparing polymer-coated nanoparticles and surface functionalization by grafting of polymers have been developed in order to obtain new hybrid materials with distinctive and desired properties [8, 9].

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Polymeric nanocomposites can be prepared by either physical adsorption or covalent grafting technique including so called "grafting to" or "grafting from" approach. Compared to the "grafting to" method, the "grafting from" method offers better control over the thickness of grafted polymers and surface grafting density because the polymerization was grown from the initiating site on the surface of initiator-immobilized particles. The surface-initiated Atom Transfer Radical Polymerization (ATRP) technique is a robust approach and has been used successfully in many nanoparticle polymer core-shell structures [10]. However, catalyst removal is still a notorious bottleneck of conventional ATRP. Alternatively, a new process called Activator ReGenerated by Electron Transfer (ARGET) ATRP has been discovered and proved to be a powerful method for preparation of polymeric nanocomposites [11, 12].

Among various classes of inorganic compounds, TiO_2 nanoparticles have become one of the most important semiconductor materials because of its promising applications in solar energy conversion and photocatalyst [13–15]. Especially, the polymeric nanocomposites of TiO_2 have been intensively studied and successfully applied for high performance catalysts, electrochemistry processes, electronic ink based flexible display, and solar cell devices [16, 17]. Recently, poly(oligoethylene methacrylate) (POEGMA) encapsulated TiO_2 nanoparticles was synthesized and utilized as a candidate for dye-sensitized solar cell applications [18, 19].

In this report, we demonstrated a facile method to synthesize chemically bonded hydrophilic POEGMA on TiO_2 nanoparticles by surface initiated ARGET ATRP. Initially, TiO_2 NPs were treated with the silane agent modified with an ATRP-initiator to introduce the initiating site on the TiO_2 surface. Subsequently, the polymerization was performed by using 100 ppm of copper (II) (Cu^{2+}) under the presence of L-ascorbic acid or zerovalent copper as a reducing agent. The method was found to be simple and environment friendly compare to conventional ATRP because they employed the ppm level of Cu^{2+} as a stable catalyst against oxygen.

Experimental

Materials

2-bromo-2-methyl-N- [3-(trimethoxysilyl)propyl] propanamide (BrTMSPA) was synthesized according to the literature procedure [20]. Oligoethyleneglycol methacrylate (OEGMA) from Aldrich was passed through an activated alumina column to remove the inhibitor. $CuBr_2$, Cu^0, L-Ascorbic Acid (AsAc), *N*,*N*,*N*′,*N*″,*N*‴-Pentamethyldiethylenetriamine (PMDETA), and solvents were supplied from commercial sources and used as received. TiO_2 nanoparticles (anatase, <25 nm) was supplied from Aldrich and stored under vacuum prior to use.

Immobilization of the ATRP-initiator on the TiO_2 Surface

TiO_2 NPs (3 g) were dispersed into the solution of 2-propanol (IPA) (100 ml) and BrTMSPA (3 g). After ultrasonication for 30 min, the stirring of the mixture was prolonged for 24 h at room temperature. The product, TiO_2-Br was washed with an excess amount of IPA to remove the free initiator and dried overnight under vacuum at 40°C.

Synthesis of POEGMA Grafted TiO_2 Nanoparticles by Surface-initiated ARGET ATRP

The surface-initiated ARGET ATRP was used to synthesize POEGMA-g-TiO_2. In an actual process, 3.6 g of POEGMA, 0.2 g of TiO_2-Br, 10 mL of dimethylformamide (DMF), 1.76 mg

of AsAc (or 5 mg Cu^0 powder) and a Teflon-coated stir bar were placed in a 30 mL open-cap vial. The vial was purged with nitrogen for 30 min. To this vial, a degassed catalyst solution containing 0.223 mg of $CuBr_2$, 0.52 mg of PMDETA and 1 mL of DMF was injected. The mixture was kept stirring at room temperature for 6h. By the end of the reaction, the mixture was poured into methanol, the Cu^0 was removed by decantation, and POEGMA-g-TiO_2 nanocomposites were collected by centrifuging. The product was washed with methanol thoroughly to remove impurities. Finally, the product was dried in a vacuum oven overnight at room temperature until constant weight.

Measurements

The Fourier Transformed Infrared Spectrophotometry (FT-IR) recorded by a BOMEM Hartman & Braun FT-IR Spectrometer was used to investigate the changes in the surface chemical bonding of pristine TiO_2 nanoparticles, TiO_2-Br, and POEGMA-g-TiO_2 hybrid nanoparticles. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer Pyris 1analyzer (USA) under nitrogen flow. Transmission Electron Microscopy (TEM) images were captured using a JOEL instrument operated at 80 kV. A drop of the sample dispersed in distilled methanol was placed on a carbon-coated copper grid and drying by simple evaporation. The surface morphology of the nanoparticles upon the grafting process were recorded by a Field-Emission Scanning Electron Microscopy (FE-SEM) (JOEL2010).

Results and Discussion

The synthetic strategy for the graft polymerization of POEGMA from TiO_2 nanoparticles by ARGET ATRP is showed in Fig. 1. Initially, the immobilization of the ATRP initiator on the surface of TiO_2 NPs was conducted by taking advantage of the ligand-exchanging reaction between the hydroxyl groups on the surface of TiO_2 and trimethoxysilane groups of BrTMSPA. By formation of chemical bond (Ti-O-Si bond) of BrTMSPA and TiO_2 NPs, the pseudo bromide could be introduced to TiO_2 NPs and play the role of an initiating site. Subsequently, the polymeric nanocomposites were successfully synthesized *via* robust surface-initiated ARGET ATRP.

The success of the different functionalization processes at different stages was confirmed by using FT-IR spectroscopy. In Fig. 2, the FT-IR spectra of pristine TiO_2 NPs (Fig. 2a), ATRP-initiator modified TiO_2 (Fig. 2b) and POEGMA-g-TiO_2 (Fig. 2c) are depicted. The broad absorption bands around 450 to 800 cm^{-1} assigned to stretching vibrations of the Ti-O-Ti framework was recorded for all samples. For the pristine TiO_2, the

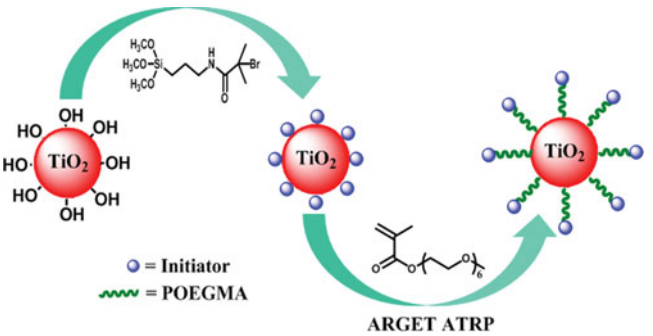

Figure 1. Synthetic approach for POEGMA-g-TiO_2 nanocomposites by ARGET ATRP.

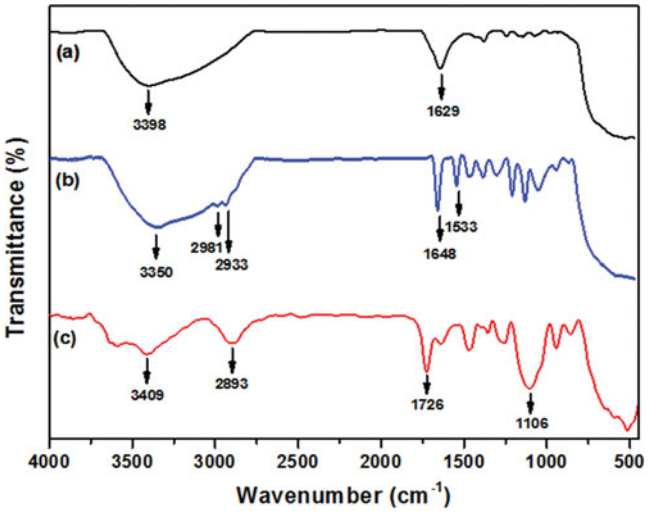

Figure 2. FT-IR spectra of pristine TiO_2 (a), TiO_2-Br and POEGMA-g-TiO_2.

peak observed at about 3398 cm^{-1} and 1629 cm^{-1} indicated the stretching vibration of hydroxyl group on the surface of the particles and bending vibration of physically adsorbed water, respectively. The success of the immobilization of the ATRP-initiator on TiO_2 was confirmed by the appearance of the characteristic adsorption bands of amide groups at 1648 cm^{-1} (stretching of C═O) and 1533 cm^{-1} (bending of N—H). The TiO_2-Br was used as a macro-initiator for the preparation of POEGMA-g-TiO_2 nanocomposites. As observed in Fig. 2c, the formation of polymer brushes has caused the emergence of a strong peak at 1726 cm−1 which could be ascribed to the carbonyl groups on the polymer backbone.

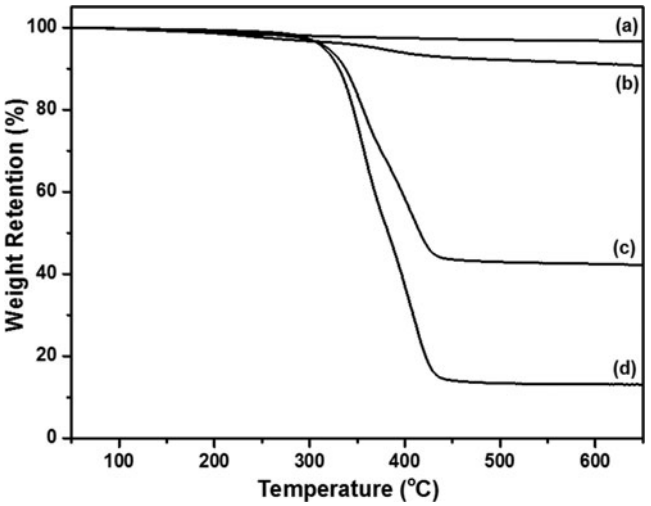

Figure 3. TGA curves of pristine TiO_2 (a), TiO_2-Br (b) and POEGMA-g-TiO_2 prepared with AsAc for 3 h (c) and 6 h (d).

Table 1. Weight loss of experimental samples

Sample	Reaction time (h)	Reducing agent	Weight loss (%)
Pristine TiO_2			3.44
TiO_2-Br			10.00
POEGMA-g-TiO_2 AsAc1	3	Ascorbic Acid	58.10
POEGMA-g-TiO_2 AsAc2	6	Ascorbic Acid	86.93
POEGMA-g-TiO_2 Cu1	12	Copper (0)	52.34
POEGMA-g-TiO_2 Cu2	24	Copper (0)	89.05

In addition, the adsorption band at 1106 cm^{-1} due to the ether linkage (C—O—C) of oligoethyleneglycol moieties suggested the successful surface-initiated polymerization.

TGA was used to study the immobilization process of the ATRP-initiator on TiO_2 as well as the grafting amount of the polymer upon the modification. The TGA data was summarized into Table 1. TGA curves of TiO_2 NPs and TiO_2-Br were shown in Fig. 3 and Fig. 4. The weight loss of 3.44% for the pristine TiO_2 may be due to the detachment of physically absorbed water, whereas the amount of the ATRP initiator was estimated to be 5.56% by comparing Fig. 3a with Fig. 3b (or Fig. 4a with Fig. 4b). The main weight loss at the range from 300°C to 430°C for POEGMA-g-TiO_2 samples could be assigned to the existence of combustible polymer brushes on TiO_2. In order to evaluate the effect of the reducing agent to the grafting process, L-ascorbic acid and zerovalent copper were used as homogenous and heterogeneous reducing agents, respectively. As observed in Fig. 3(c, d) and Fig. 4(c, d), the amount of the polymer grafted to TiO_2 NPs was found to be 48.10% after 3 h and up to 76.93% after 6 h of reaction in the case of L-ascorbic acid while zerovalent copper provided slower grafting rate which led to 42.34% after 12 h and 79.05% after 24 h. Since L-ascorbic acid was a strong reducing agent and soluble in DMF, the electron transfer from Cu^{2+} to L-ascorbic acid to regenerate the Cu^{+} activators may proceed quickly and

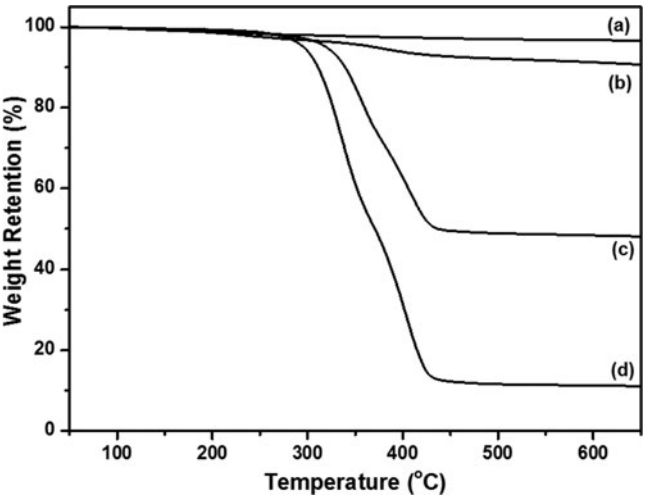

Figure 4. TGA curves of pristine TiO_2 (a), TiO_2-Br (b) and POEGMA-g-TiO_2 prepared with Cu^0 for 12 h (c) and 24 h (d).

most of Cu^{2+} deactivators were consumed. Therefore, the initiation process was induced rapidly and the high rate of surface-initiated polymerization was obtained as a consequence [21]. However, the exhausted consumption of deactivators may lead to conceivable loss of control manner [21]. In addition, it is worthy to note that the control of grafting density on time could be achieved by using either AsAc or Cu^0 as reducing agents.

The FE-SEM analysis was employed to explore the surface morphology of as-synthesized nanocomposites. Fig. 5 display the FE-SEM micrographs of TiO_2 (a, b), POEGMA-g-TiO_2 after 6 h with AsAc (c) and 24 h with Cu^0 (d). The pristine TiO_2 NPs exhibited severe agglomeration due to the high surface energy of individual particles. Comparing to the pristine TiO_2, the images of nanocomposites showed quite different morphology due to the formation of polymer brushes on TiO_2. However, it should be noted that the surface morphology looked similar despite of different reducing agents used. Additionally, the TiO_2 nanoparticles were embedded in the polymer, which was indicated by the existence of the polymer layer around the inorganic nanofiller.

For the deeper study on the morphology, the TEM analysis of the pristine TiO_2, TiO_2-Br and POEGMA-g-TiO_2 was performed. Fig. 6a shows an overview of the pristine TiO_2, clearly illustrating the agglomerated state of TiO_2NPs. Upon the modification with POEGMA, the severe macro-aggregation of the particles has changed dramatically as shown in Fig 6b. Compare to the pristine TiO_2, the functionalized TiO_2 exhibited sufficient colloidal stability due to the existence of the polymer shell. Fig. 6c and 6d revealed high magnification images of the as-synthesizedPOEGMA-g-TiO_2 prepared with AsAc for 6h

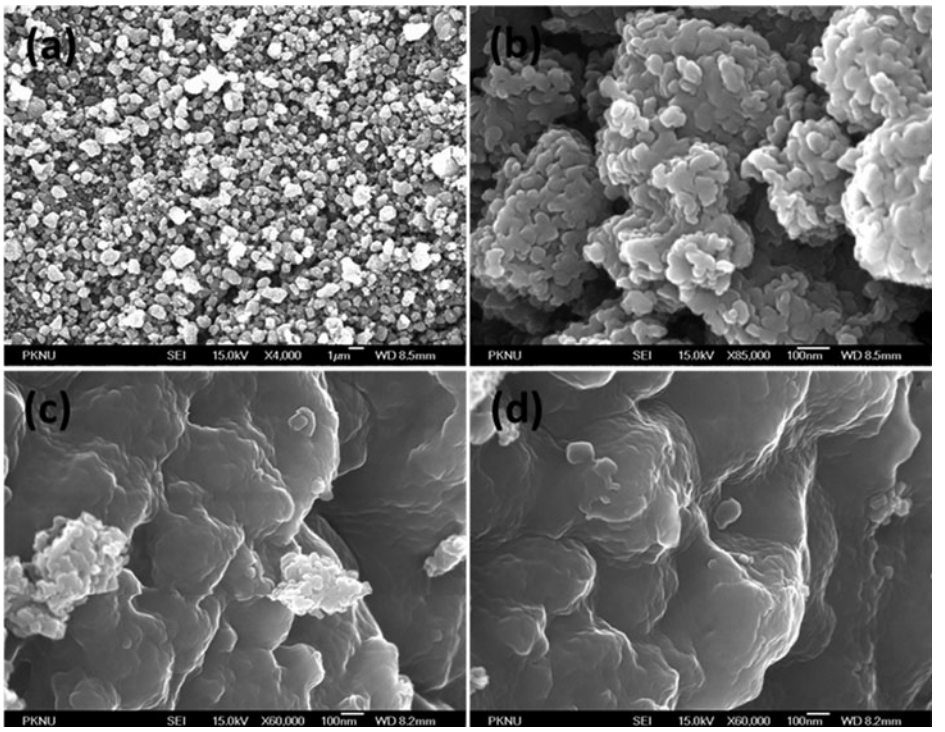

Figure 5. FE-SEM images of TiO_2 (a, b), POEGMA-g-TiO_2 prepared with AsAc for 6 h (c) and Cu^0 for 24 h (d).

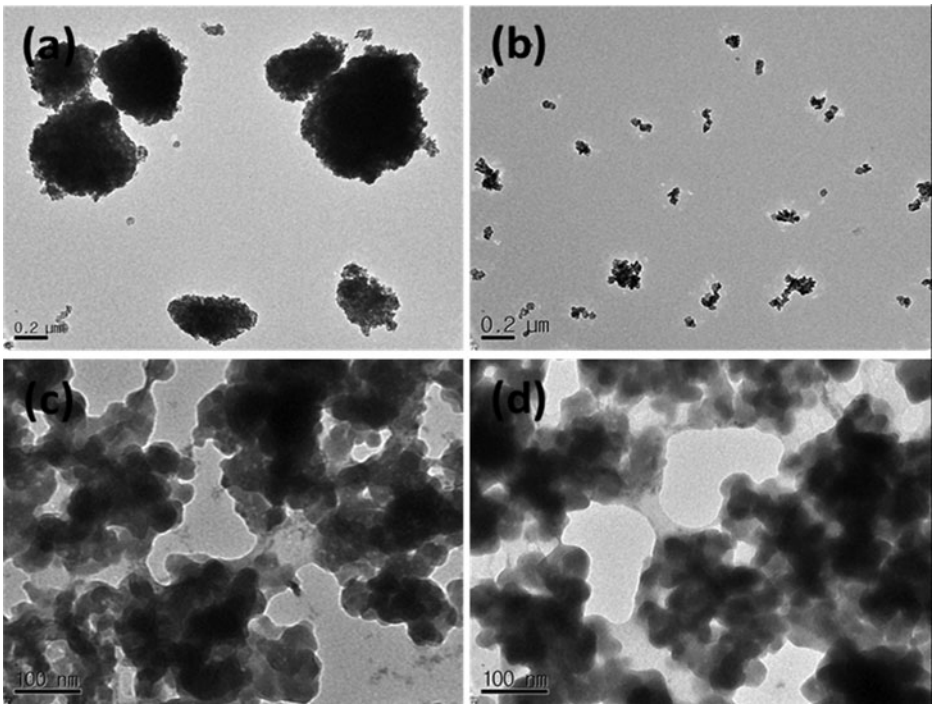

Figure 6. TEM micrographs of TiO_2 (a), POEGMA-g-TiO_2 prepared with AsAc for 6 h (low magnification) (b), POEGMA-g-TiO_2 prepared with AsAc for 6 h (high magnification) (c) and by Cu^0 for 24 h (d).

and Cu^0 for 24 h, respectively. Well-defined nanocomposites were readily observed with light contrast shells of the polymers and dark contrast cores of TiO_2. It was clearly evident that TiO_2 cores were surrounded by the polymer shell even though the individual particles were connected to each other forming the nano-cluster.

Conclusion

Covalently anchored POEGMA onto the surface of TiO_2 NPs was achieved by the robust surface-initiated ARGET ATRP under ambient temperature. The zerovalent copper and L-ascorbic Acid were used as reducing agents for the regeneration of the activators. The as-synthesized nanocomposites were characterized by means of FT-IR, TGA, FE-SEM and TEM analyses. TEM and SEM images sufficiently demonstrated the existence of the polymer shell on the surface of TiO_2 NPs upon the modification. With the control of grafting amount of polymer brushes over reaction time, the grafting rate in the case of L-ascorbic Acid was found to be superior to zerovalent copper as indicated by TGA.

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