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Surface initiated graft polymerization from carbon-doped TiO_2 nanoparticles under sunlight illumination

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Abstract

A simple and efficient method is presented for the preparation of polymer-grafted TiO_2 by a photocatalytic polymerization. PMMA chains are directly grafted from the surface of the TiO_2 nanoparticles in water under sunlight illumination. FT-IR and TEM results demonstrate that there existed strong chemical bonding at the interface of TiO_2 nanoparticles and PMMA chains. The thermal stabilities of the grafted polymer are dramatically elevated relative to that of pure PMMA according to TGA results. Moreover, the resulted polymer exhibits much higher melting temperature compared with traditional stereoregular PMMA by controlling the conformation of polymer chains growing in the highly restricted space on the surface of nanoparticles.

Keywords: Carbon-doped TiO_2; Graft polymerization; Poly(methyl methacrylate) (PMMA)

1. Introduction

TiO_2 is a very promising material for various properties such as UV light shielding, high refractive index [1], and photocatalytic activity [2] and has a large number of applications in catalysis [3], solar cells [4], and pigment industries [5]. However, a smaller number of papers reported about the use of semiconductor TiO_2 to initiate polymerization reactions [6–10].

TiO_2 semiconductor material only absorbs the UV light which accounts for merely ~5% of the solar spectrum because of the large band gap of 3.0 or 3.2 eV in the rutile or anatase crystalline phase, respectively. Therefore, there have been many efforts to extend activity of TiO_2 into the visible region to improve its utilization efficiency. The doping of TiO_2 is currently attracted considerable interest as a promising route to extend the optical response to visible region, which would allow the use of sunlight in photochemistry and photocatalysis. Carbon-doped TiO_2 has received steadily growing attention [11–20], because incorporation of carbon atoms into TiO_2 can be easily achieved with excellent reproducibility and great applicability [12]. Moreover a carbon-doped powder recently was reported to be five times more active than nitrogen-doped TiO_2 in the degradation of 4-chlorophenol by artificial light [12]. It has been proved by some experimental results [12,13] and theoretical analyses [18,19] that the photocatalytic activity of carbon-doped TiO_2 under visible-light illumination is ascribed to the formation of localized midgap states. Therefore, the state of photogenerated charges in carbon-doped TiO_2 and the photochemical reactivities may be dramatically different from that in undoped TiO_2. And subsequently, the mechanism of the chemical reactions is also probably affected by doping with carbon atoms. Up to now, the photochemical reactions induced by photogenerated charges in carbon-doped TiO_2 have seldom been reported [6].

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Grafting polymer onto the surface of inorganic particles is attracting a great deal of interests because of the diverse applicability of these particles in the polymer/inorganic composition [21–25]. In general, graft polymerization was carried out via two general routes. One method is the "grafting from" – grafting of polymer chains is initiated by introducing the initiating groups onto the particles' surfaces [22–24] and another method is the "grafting to" – propagating polymer radicals are trapped by the particles' surfaces during polymerization, initiated by a conventional radical initiation [25]. However, these methods all need to introduce functional groups onto the particles' surfaces and the progresses are relatively inconvenient.

In this communication, we have presented a simple and efficient approach to prepare PMMA-grafted TiO_2. We do not need to introduce any groups onto surface of carbon-doped TiO_2 nanoparticles and direct polymerization of monomers from the surface of the nanoparticles is achieved under indoor sunlight illumination at ambient condition. It is found that, compared with traditional PMMA, the structure and properties of the resulted polymer have great differences because of the highly restricted space on the surface of nanoparticles for the growth of polymer chains. We believe that this convenient method opens up the possibility to define new ways to obtain polymers with novel properties.

2. Experimental part

2.1. Materials

Titanium(IV) chloride ($TiCl_4$, chemical reagent grade), ethanol (EtOH, analytical reagent grade), methyl methacrylate (MMA, analytical reagent grade) and tetrahydrofuran (THF, analytical reagent grade) were purchased from Shanghai Chemical Reagent Company. MMA was purified by distillation. $TiCl_4$, EtOH and THF were used without further purification. Deionized water was used in the experiments.

2.2. Synthesis of carbon-doped TiO_2 nanoparticles

The carbon-doped TiO_2 nanoparticles were prepared according to the procedure described in another paper [26]. Briefly, the $TiCl_4$ solution was slowly added to anhydrous ethanol under vigorous stirring and stirred at room temperature for 12 h. This solution was dried at 100 °C for 12 h, and then calcined at about 400 °C for 1 h in air in a muffle furnace without gas flow. Dark brown carbon-doped TiO_2 nanoparticles were obtained.

2.3. Synthesis of PMMA-grafted TiO_2 nanoparticles

In a typical preparation, 25 g purified MMA, 1 g TiO_2 powders and 100 g deionized water were taken in a flask. Polymerization was carried out by exposing the flask to the diffuse radiation arriving through the window with continuous stirring for 20 and 50 h at room temperature from 7:00 to 17:00. The product was dried at 80 °C for 12 h and then washed with a good solvent of PMMA (THF) for three times to remove the free polymer chains if they had formed in the experimental procedure. However, there were almost no free polymer chains dissolved in THF after careful rinsing. So we considered that the grafting efficiency was close to 100%. The precipitation was dried at 60 °C under vacuum for 12 h to obtain PMMA-grafted TiO_2 nanoparticles.

2.4. Preparation of PMMA homopolymer

For comparison, PMMA was also prepared via a conventional free radical polymerization described as follows. The monomers MMA and the initiator AIBN (0.2 wt.% in the monomers) were added to a reaction flask and were polymerized at 70 °C under nitrogen atmosphere for 12 h. The resulting polymer was purified by precipitating in methanol and then dried *in vacuo* at room temperature. The M_w of PMMA was $\sim 120\,000$ and its polydispersity (D) was 1.8.

2.5. Characterization

FT-IR spectroscopy was performed on a Nicolet Nexus-470 spectrometer with KBr beam-splitter. Spectra were collected with a resolution of 4 cm^{-1} by using 64 scans. Transmission electron microscopic (TEM) investigations were performed on a JEOL JEM-2010 microscope. The samples for TEM were prepared by adding 1–2 drops of an ethanol–TiO_2 solution onto lacey carbon copper grids. The DSC measurements were carried out on a Perkin–Elmer DSC-7 apparatus by heating 7–10 mg sample from 50 to 350 °C at a heating rate of 10 °C/min followed by cooling to 50 °C at the same rate under a nitrogen atmosphere. Thermogravimetric analyses (TGAs) were performed using a Perkin–Elmer Pyris 1 thermogravimetric analyzer with a heating rate of 10 °C/min in air. The X-ray powder diffraction (XRD) patterns were measured on an X'Pert PRO (PANalytical) diffractometer at room temperature with Cu Kα radiation. XRD diagrams were obtained in the range $2\theta = 5°–80°$ by step scanning with a step size of 0.017°. Gel permeation chromatographic (GPC, Agilent 1100, USA) analysis was carried out at 30 °C at a flow rate of 1 ml/min using THF as solvent. The instrument was calibrated using polystyrene as standard.

3. Results and discussion

Polymerization of monomers was confirmed by the precipitation of the polymer, together with TiO_2 nanoparticles. For clarifying whether PMMA grafted from the surface of TiO_2 particles, the chemical structures of TiO_2 and polymer after rinsing were characterized with FT-IR spectroscopy as shown in Fig. 1. It is well known that the grafted PMMA on the surface of TiO_2 particles cannot be extracted by the good solvent for PMMA, whereas the non-grafted polymer is easily removed. Compared with the spectrum of the TiO_2 particles, the characteristic absorption peaks of PMMA are clearly identified from Fig. 1b, the characteristic peaks at about 2860 and 2925 cm^{-1} are corresponding to the stretching vibrations of

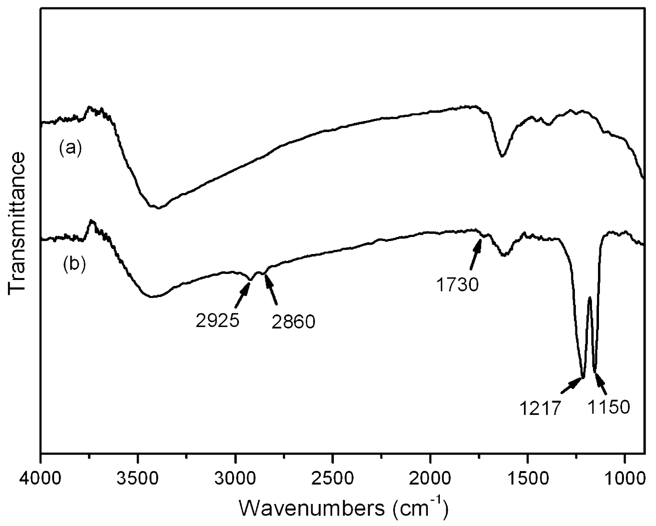

Fig. 1. FT-IR spectra of (a) TiO_2 and (b) PMMA-grafted TiO_2 after polymerization for 20 h.

the C—H bond [27]. The weak peak at about 1730 cm^{-1} is assigned to the stretching vibration of the carbonyl groups [28,29]. Its intensity is relatively weaker as compared with that of pure PMMA, which may be attributed to the interaction of carbonyl groups in PMMA with titanium centers. The strong peaks at about 1217 and 1150 cm^{-1} are assigned to C—O stretching and C—H bending, respectively [29,30]. These experimental results of FT-IR spectra indicate that MMA monomers have been successfully photo-initiated by carbon-doped TiO_2 and grown from the surface of nanoparticles. Consequently, the polymer chains are well grafted on the nanoparticles' surface via firm chemical bonds or at least some other kinds of strong interactions. Very recently, Ni and coworkers [31] carried out the photopolymerization of MMA initiated by undoped TiO_2 nanoparticles under UV irradiation. They found that the polymer component did not show any strong interactions with nanoparticles and could well dissolve in acetone. The great difference between the resulted polymer initiated by undoped and carbon-doped TiO_2 may come from the band-gap level and reactivity of photogenerated charges.

The successful grafting of PMMA is also observed by TEM images displayed in Fig. 2. It is clearly found that there is polymer formation on the surface of TiO_2 nanoparticles as shown in Fig. 2b and some of the TiO_2 nanoparticles were indicated by arrows. After polymerization for 20 h, the TiO_2 particles are wrapped within PMMA matrices even after they have been rinsed with THF and their size keeps almost unchanged (about 10 nm) compared with original nanoparticles. Both the FT-IR spectrum and the TEM image of PMMA-grafted TiO_2 nanoparticles suggest the successful photocatalytic polymerization of the monomers. The conformation of the polymer chains may have been greatly affected because the polymerization reaction was conducted in a restricted space on the nanoparticles' surface.

TGA is used to estimate the content of the PMMA grafted on the TiO_2 particles' surface. Fig. 3 shows the thermal decomposition behaviors of traditional pure PMMA, TiO_2 and PMMA-grafted TiO_2 after 20 and 50 h polymerization. The total weight loss for TiO_2 is about 4.2 wt.% when heated from 50 to 550 °C, which is mainly induced by the volatilization of the absorbed water. The weight loss of traditional PMMA ($M_w \sim 120\,000$, M_w/M_n 1.8) prepared via a conventional free radical polymerization is close to 100 wt.% and shows significant decomposition from about 290 to 400 °C. Compared with the traditional PMMA, it is obviously seen that

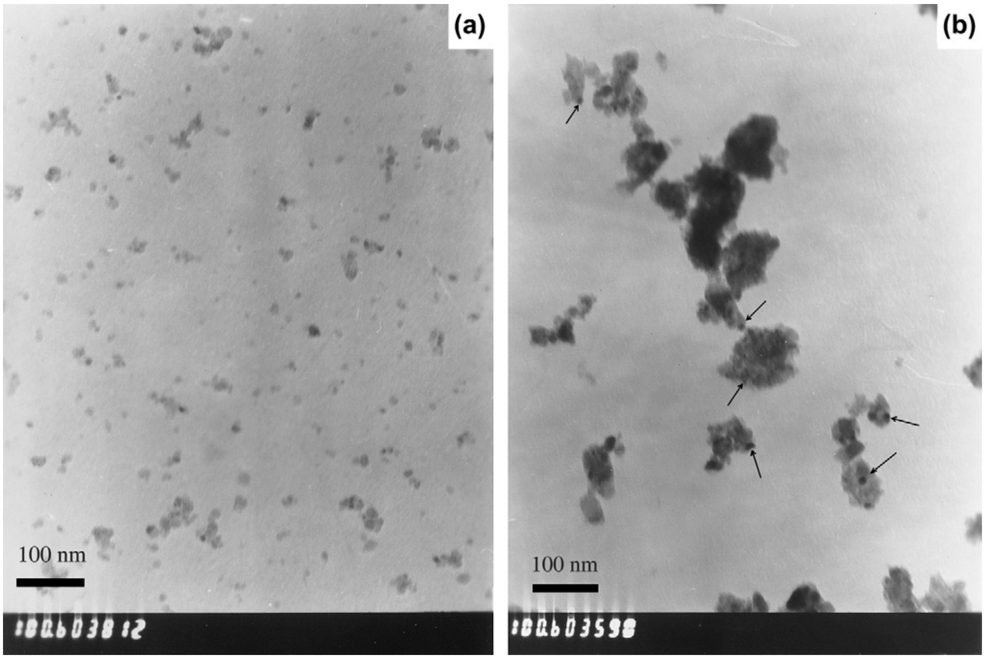

Fig. 2. TEM images of (a) TiO_2 and (b) PMMA-grafted TiO_2 after polymerization for 20 h.

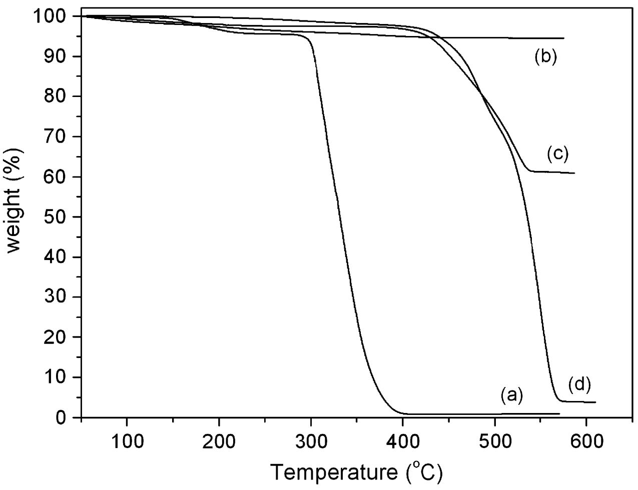

Fig. 3. TGA curves of (a) pure PMMA, (b) TiO_2, and PMMA-grafted TiO_2 after polymerization for (c) 20 and (d) 50 h.

there is a remarkable difference in thermal behaviors for PMMA grafted on the surface of TiO_2 nanoparticles. The thermal decomposition of those grafted PMMA (from about 420 to 540 °C) shifts toward the much higher temperature than that of traditional PMMA, which further verifies the presence of strong interactions between PMMA chains and TiO_2 nanoparticles. In addition, the weight loss of PMMA-grafted TiO_2 after 20 (Fig. 3c) and 50 h (Fig. 3d) polymerization are about 36 and 92 wt.%, respectively. It is confirmed that the percentage of grafted polymer increases with the reaction time. That is to say, it is possible to better control the content of the polymer chains grafted from surface of inorganic nanoparticles by varying the polymerization time. Furthermore, the feeding MMA (about 96 wt.% in the system) is almost completely consumed after 50 h polymerization. Our previous report had proved that the thermo-oxidative stability of PMMA could be enhanced about 60–70 °C by the addition of TiO_2 nanoparticles [32]. So this much more dramatic improvement of the thermal decomposition temperature about 130 °C is mainly caused by the grafting of polymer chains onto the inorganic nanoparticles.

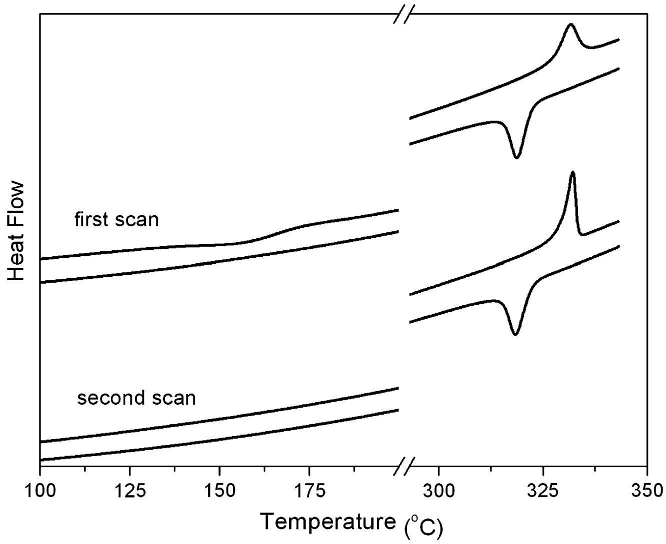

Fig. 4. DSC curves of the PMMA-grafted TiO_2 after polymerization for 20 h.

Fig. 4 shows the representative DSC curves of the PMMA-grafted TiO_2 after 20 h polymerization. From the curve, an exothermic transition at about 157 °C is found in the first scan and it disappears in the subsequent scan after cooling to the ambient temperature. This indicates that at least some of the polymer chains distort during the polymerization reaction because of the restricted volume on the surface of TiO_2 nanoparticles for the growth of polymer chains and the incompatibility between the growing polymer chains and water. So the exothermic peak at about 157 °C is correlative with the arrangement of PMMA chains to lower their potential energy. In both of DSC running cycles, the endothermic peaks at about 331 °C are clearly found in the heating process and the exothermic transitions are at about 318 °C in the cooling step, corresponding to the melting and crystallizing of the polymer, respectively. The melting temperature of the polymer growing from the carbon-doped TiO_2 nanoparticles is much higher than the value of 203 °C for traditional syndiotactic PMMA [33]. The elevated melting point of the resulted polymer may result from the orientation of PMMA chains because the monomers have to grow in the highly restricted space. Moreover, the orientation of polymer chains may also be induced by their incompatibility with water and therefore, the growing polymer chains cannot be well entangled. The glass transition of PMMA is not clearly found from these DSC curves, which is caused by the high crystallizability of the original polymer chains. The XRD patterns shown in Fig. 5 are used to further confirm the DSC results. It has been reported that there were at least three diffractive peaks in the syndiotactic PMMA at $2\theta = 10.9°$, 13.2° and 17.4° [34]. The PMMA chains grafted on the surface of TiO_2 nanoparticles do not show clear peaks where syndiotactic PMMA did, but they show peaks at 18.3°, 31.8°, 41.7° and 73.0°, which indicate that there were some ordered regions in PMMA grafted from the surface of TiO_2

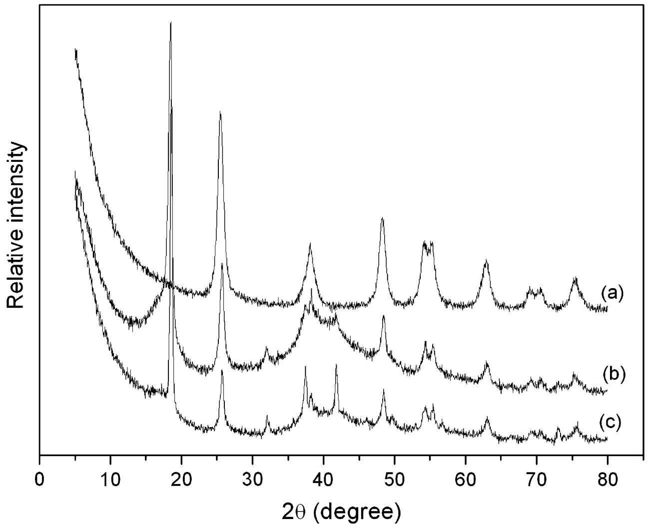

Fig. 5. XRD patterns of (a) TiO_2, (b) PMMA-grafted TiO_2, and (c) PMMA-grafted TiO_2 after DSC test.

nanoparticles. Furthermore, after DSC running, the diffractive peaks became much sharper, revealing the formation of the more ordered structure in the polymer, which proves the high crystallizability of grafted polymer chains.

4. Conclusion

We have presented a simple and efficient method to prepare polymers by a photo-initiated polymerization on the surface of carbon-doped TiO_2. Based on the FT-IR and TEM results, it is indicated that PMMA is directly grafted from the surface of carbon-doped TiO_2 by photocatalytic polymerization under sunlight illumination. Furthermore, the thermal stabilities of the grafted polymer were dramatically elevated relative to that of pure PMMA according to TGA results. DSC results demonstrate that the PMMA-grafted TiO_2 exhibited much higher melting temperature compared with traditional stereoregular PMMA. Above all, this versatile approach can be applied to graft other polymers, and may open a new route to control the structures and properties of polymers. Further work on the mechanism of photopolymerization initiated by the photogenerated charges in carbon-doped TiO_2 particles is currently in progress.

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