Surface Modification of TiO2 Particles Induced by γ Irradiation (Postprint)

Authors: LI Zhi, QI Xiangzhi, GE Xueping, YANG Cunzhong, FANG Bin, ZHANG Weidong, YANG Xiangmin

Date: 2023-06-18T00:00:00+00:00

Abstract

The surface of anatase TiO2 was modified by maleic andydride (MAH) γ radiation. The properties of surface modified TiO2 were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT IR), X-ray photoelectron spectrum (XPS), thermal gravimetric analysis (TGA), as well as transmission electron microscopy (TEM). The results suggest that the MAH anchored on the surface of TiO2 through chemical bonding and the grafting ratio was approximately 2.7%. TEM image revealed that the modified particles had good dispersibility and compatibility with N,N-Dimethylformamide(DMF), which facilitated to hinder the aggregation of TiO2 particles.

Full Text

Preamble

Surface Modification of TiO_2 Particles Induced by γ Irradiation

LI Zhi*, QI Xiangzhi, GE Xueping, YANG Cunzhong, FANG Bin, ZHANG Weidong, YANG Xiangmin

Institute of Nuclear Radiation Application, School of Science, East China University of Science and Technology, Shanghai 200237, China

Abstract

The surface of anatase TiO_2 was modified by maleic anhydride (MAH) through γ radiation. The properties of surface-modified TiO_2 were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), and transmission electron microscopy (TEM). The results suggest that MAH anchored onto the surface of TiO_2 through chemical bonding, with a grafting ratio of approximately 2.7%. TEM images revealed that the modified particles exhibited good dispersibility and compatibility with N,N-Dimethylformamide (DMF), which helped hinder the aggregation of TiO_2 particles.

Key words
Modification, γ irradiation, TiO_2

Introduction

Titanium dioxide (TiO_2) is one of the most important materials for many applications such as catalysts, UV-protective coatings, chemical sensors, solar cells, and luminescent devices. However, TiO_2 particles are difficult to disperse stably in non-polar solvents due to their strong tendency to agglomerate, and they exhibit weak combination with polymer matrices because of poor interfacial interaction. Surface modification of TiO_2, using methods such as coupling agents, sol-gel blending techniques, in situ polymerization processes, and polymer grafting from the surface of inorganic particles, is considered an effective way to improve its dispersion in solvents or polymer matrices. Among these approaches, graft polymerization of polymer onto the surface of TiO_2 particles has made considerable progress.

Traditional graft polymerizations are relatively fussy and easily introduce low molecular weight compounds. Ionizing radiation is a direct, effective, and attractive method for contacting inorganic/organic material interfaces and modifying surfaces of inorganic materials. Many studies have focused on changes in physical properties and photocatalytic effects of modified TiO_2 using laser, UV-Vis light, electron beam, and γ radiation as indirect radiation methods. In recent years, X.T. Zu and coworkers carried out modification of TiO_2 with methyl methacrylate (MMA) induced by electron beam radiation and ^{60}Co γ irradiation [1,2]. Xiuyuan Ni et al. investigated PMMA grafting onto TiO_2 under UV irradiation [3]. Shaofeng Zhong studied "graft from" polymerization of MMA by N_2 plasma [4]. However, research on grafting monomers onto TiO_2 with direct radiation remains relatively limited. Although some mechanisms of graft polymerizations induced by ionizing irradiation are still obscure, many studies apply free radical theory for interpretation. The oxygen on anatase TiO_2 surfaces can initiate graft polymerization during radiation. The radiation produces δ anion radicals on TiO_2 nanoparticle surfaces with high activation [3]. These radicals can only change the surface properties of the materials rather than the bulk properties [4].

In this article, we report the surface modification of anatase TiO_2 with MAH through γ radiation. The surface-modified TiO_2 was investigated by FTIR, XRD, XPS, TGA, and TEM.

2.1 Chemicals

Titanium dioxide (TiO_2) powder was obtained from Sinopharm Chemical Reagent Co. Ltd (China) and used without any pretreatment. Maleic anhydride (MAH), xylene, and N,N-Dimethylformamide (DMF) were all purchased from Shanghai Chemical Works "Ling-feng", China. Other reagents were of analytical grade and used without further purification.

2.2 Modification of TiO_2 Particles Induced by γ Irradiation

In a glass shallow container, 4.0 g MAH was dissolved in 16.0 g xylene solution at 80°C. Then 2.0 g TiO_2 powder was dispersed in the above mixture, followed by ultrasonication for 30 min. The container was degassed and then filled with dry nitrogen at room temperature. The samples were irradiated with 60 kGy doses from a ^{60}Co source at ambient temperature.

After irradiation, the resulting suspension was separated by centrifugation at 3500 rpm for 5 min. The obtained powder was re-dispersed in excess xylene and centrifuged again. The cycle of "dispersion-centrifugation" was repeated at least 5 times to completely remove the unreacted MAH on the surface of TiO_2 particles. The samples, designated as g-TiO_2, were dried in vacuum at 70°C for 12 h.

2.3 Materials Characterization

X-ray diffraction (XRD) experiments were conducted using an X-ray diffractometer (RIGAKU, D/max 2550VB/PC, Japan) equipped with a graphite monochromator and Cu Kα radiation. The generator was operated at 40 kV and 100 mA. The samples were scanned at diffraction angles from 10–80° at a rate of 0.02°/s.

X-ray photoelectron spectroscopy (XPS) experiments were carried out in ultra-high vacuum using a spectrometer (PHI 5000C, ESCA, Japan) with Mg Kα radiation at 14.0 kV and 25 mA.

Fourier transform infrared (FTIR) spectra were obtained on a spectrometer (Nicolet-550, USA) with a scanning range of 400–4000 cm^{-1} under ambient conditions using KBr pellets.

Thermal gravimetric analysis (TGA) was performed using a thermal analyzer (PerkinElmer Inc). Samples were heated from room temperature to 700°C at a rate of 10°C/min under air atmosphere.

The morphology analysis was performed using a transmission electron microscope (TEM) analyzer (JEM-2100F, Japan). The TEM specimens were prepared by dispersing the g-TiO_2 particles in absolute DMF by ultrasonication for 30 min and then depositing a small droplet onto a copper grid covered with carbon film, evaporating the solvent completely at room temperature.

3.1 Modification of TiO_2 (g-TiO_2)

As shown in Fig.1, TiO_2 possessed peaks at 2 = 25.4°, 37.8°, 48.2°, 55.2°, and 62.8°, corresponding to the anatase crystalline form [5]. After reaction with

MAH, these peaks remained with unchanged intensity, but a new signal appeared at 28.1°, which should correspond to MAH. In other words, there was no obvious change in the XRD patterns after radiation-induced modification, indicating that the modification did not significantly affect the crystalline structure of TiO_2 and that the MAH segments had not entered the crystal lattice of the titanium dioxide. The grafted MAH chains only covered the surface of the titanium dioxide powder. These results were similar to those in references [4,6].

The FTIR spectra of bare TiO_2 and TiO_2 after grafting with MAH are shown in Fig.2. The bare TiO_2 showed a broad band between 3500 cm^{-1} and 3000 cm^{-1}, indicating the presence of -OH groups on the surface of the titania. A weak band at approximately 1630 cm^{-1} was attributed to adsorbed oxygen species (Ti-O-C), which showed that MAH was successfully grafted onto the surface of the titanium dioxide powder [4]. The infrared absorption bands between 400 cm^{-1} and 800 cm^{-1} should be assigned to the vibrations of Ti-O and Ti-O-Ti framework bonds [7].

After surface grafting modification, new absorption bands appeared at 1706 cm^{-1}, 1636 cm^{-1} (C=O stretching vibration mode), and 1300–1200 cm^{-1} (C-O stretching vibration mode) [8], which could originate from the polymerization of MAH onto the surface of TiO_2 particles. Moreover, it could be found that the peak of modified TiO_2 particles at 400–800 cm^{-1} shifted to higher wavenumbers. However, -OH absorption bands remained slightly after grafting modification, indicating that the surface groups of TiO_2 had changed mostly from Ti-OH to Ti-O-C.

Further characterization of surface-modified TiO_2 was conducted by XPS analysis. Fig.3 presents the XPS spectra of modified TiO_2 in the C 1s region and O 1s region. The C 1s peak at 284.86 eV was probably associated with the adsorption of carbon dioxide (CO_2) on the surface of TiO_2 or trace amounts of hydrocarbon contaminants when air-exposed samples were introduced into XPS chambers. Two other peak components at about 285.56 eV and 288.89 eV were assigned to carbon adjacent to an anhydride (C-C-O(=O)) and anhydride groups (O=C-O-C=O) of MAH units. The O 1s region was decomposed into five contributions. The peaks at 530.0 eV and 530.7 eV corresponded to Ti-O and the hydroxyl groups (-OH) in TiO_2, respectively. The peak at a binding energy of 532.2 eV corresponded to the carbonyl oxygen (C=O) of the maleic anhydride unit, whereas the peak at 532.70 eV arose from the ether oxygen C-O-C. Other C 1s and O 1s peak-fitting results were according to Beamson [9].

Thermal stability of TiO_2 and modified TiO_2 was measured by dynamic thermogravimetric analysis (TGA) as shown in Fig.4. The thermal decomposition of native TiO_2 began at about 40°C and continuous mass loss could be seen from 40°C to 800°C. It was found that ungrafted TiO_2 displayed nearly 1.7% weight loss below 800°C, which was attributed to water absorbed by TiO_2. The decomposition range of grafted TiO_2 was clearly divided into three stages. Weight loss from 40°C to 120°C could be attributed to the loss of physically adsorbed water on the surface of TiO_2. Weight loss from 120°C to 150°C resulted from the degradation of MAH chains, while weight loss from 150°C to 800°C resulted from removal of chemically bound water (hydroxyl groups) from the powder surface [10].

TGA was also used to determine the amount of grafted MAH on the TiO_2 particles. The grafting ratio was calculated as follows [11]:

Grafting ratio = Weight loss% (g-TiO_2) - Weight loss% (TiO_2)

It was concluded that 2.65% of MAH was grafted onto TiO_2 particles under γ irradiation. According to the results of TGA, FTIR, and XPS, MAH was successfully grafted onto the TiO_2 surface with a low grafting ratio. One possible reason was due to the low polymerization ability of MAH, which might form a monolayer of MAH onto TiO_2 by the irradiation method.

Transmission electron microscopy images of TiO_2 and modified TiO_2 dispersed in DMF are shown in Fig.5. In the prepared samples, small size TiO_2 particles existed in the upper layer. Obvious agglomeration could be seen in the images of untreated TiO_2, while homogeneous dispersion could be seen in the images of modified TiO_2 and the agglomerations had been reduced. From Fig.5(c), MAH layers coated on the surface of TiO_2 particles were clearly shown as gray areas. This suggested that MAH introduced onto the surface of TiO_2 not only provided functional groups anchoring TiO_2 but also made the particles disperse compatibly in organic solvents. The molecular chains grafted on the surface of TiO_2 bring mutual exclusion and steric hindrance effects, while the surface free energy had been reduced and agglomeration controlled [8].

References

1. Wang Z G, Zu X T, Yu H J, et al. Nucl Inst Meth Phys Res B, 2006, 250:196–200.
2. Jiang Bo, Zu X T, Tang F Y, et al. J Appl Polym Sci, 2006, 100: 3510–3518.
3. Ni X, Ye J, Dong C. J Photochem Photobiol A: Chem, 2006, 181: 19-27.
4. Zhong S F, Meng Y D, Qu Q R, et al. J Appl Polym Sci, 2005, 97: 2112–2117.
5. Wang Z G, Zu X T, Zhu S, et al. Phys Lett A. 2006, 350: 81–92.
6. Luo Y B, Wang H L, Xu D Y, et al. Appl Surface Sci, 2009, 255: 6795–6801.
7. Heng Z, Chen H. Appl Surface Sci, 2010, 256: 41.
8. Tai Y, Qian J, Zhang Y, et al. Chem Eng J, 2008, 41.
9. Beamson G, Briggs, D. High resolution XPS of organic polymer: The Scienta ESCA300 Database; Wiley: Chichester, UK, 1992.
10. Lu X, Lv X, Sun Z, et al. European Polym J, 2008, 44.
11. (Reference incomplete in original)

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv — Machine translation. Verify with original.