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Organic modification on TiO_2 nanoparticles by grafting polymer

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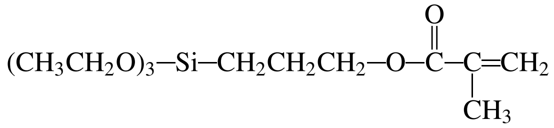
Recently, TiO_2 nanoparticles are attracting more and more interests in cosmetic, catalysis, and pigment industries, for the great improvement in physical and chemical properties the nanosize materials may bring about [1, 2]. Due to the high surface area and high polarity, TiO_2 nanoparticles flocculate spontaneously in a low polarity dispersion medium. The application of nanoparticles in a low polarity dispersion medium is thus seriously obstructed. To disperse nanoparticles into a low polarity medium remains a challenge for the nanoparticles application.

With little or no contribution of electrical charges to the interaction of particles in a non-aqueous system, the steric hindrance of the grafted polymer plays a major role in the dispersion stability of nanoparticles in an organic medium [3]. Caris *et al.* [4] modified TiO_2 by the titanate coupling agent, then dispersed these particles into an emulsion. By means of the emulsion polymerization process, several types of particles with the core-shell morphology (TiO_2 core and polymer shell) can be obtained. The polymer shell provides adequate steric hindrance to TiO_2 particles, nevertheless, the surfactant adsorbed onto the surface of composite particles is too difficult to elute, causing unnecessary trouble for some applications of nanosized TiO_2, for example, when used as optical nano-composite. Tsubokawa *et al.* [5–7] introduced azo groups onto the surface of TiO_2, and radicals formed by the decomposition of azo groups initiated the polymerization of vinyl monomers. During the polymerization, the polymer was effectively grafted onto the surface of the particles. Laible *et al.* [3] synthesized a kind of polymer, which had siloxanes groups at the end of the polymer chain, these polymer chains then grafted onto the surface of TiO_2. All these methods can graft polymer onto the surface of TiO_2, however, due to the high chemical activity of azo and other similar groups, the grafting reaction should be carried out under very strict conditions. If the dispersion stability of nanoparticles in organic medium is the only purpose, these methods are somehow overplayed.

In this paper, a simpler method is introduced to graft polymers onto the surface of TiO_2 nanoparticles. One kind of silicone coupling agent WD-70 (Wuhan University Chemical & New Material Co., Ltd.) is used to co-polymerize with styrene and connected copolymer to the surface of TiO_2 (Rutile TiO_2, primary particle size in the range of 60–80 nm, prepared in the present laboratory [8]). The molecular formula of agent WD-70 is



$$(CH_3CH_2O)_3\text{–Si–}CH_2CH_2CH_2\text{–O–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2$$

The grafting process is as follows: dissolve 5×10^{-6} m^3 WD-70 in 125×10^{-6} m^3 isopropanol, add and disperse 50 g TiO_2 (dried at 120 °C for 2 h.) into the solution with the help of ultrasonic vibration for 20 min. This suspension is transferred in a Wolff bottle. Keep stirring at 35 °C for 2 h. Then 25×10^{-6} m^3 styrene, in which 0.2 g AIBN (2,2′-Azo-bis-iso-butyronitrile, Shanghai Chemical Reagent Co., Ltd.) had been dissolved, is added into the Wolff bottle. The mixture is then refluxed with stirring at 80 °C for 20 h under the flow of nitrogen. After the reaction, the mixture is centrifuged. The grafted TiO_2 can be extracted with toluene and three cycles are necessary to remove the polymers adsorbed on its surface. The extracted grafted- TiO_2(G-TiO_2) should be dried in vacuum at 110 °C and then stored at room temperature in a dark place.

In this process, a random copolymerization between WD-70 and styrene was carried out on the solid surface. At the same time a bridging reaction between WD-70 and the surface hydroxyl of TiO_2 was carried too. As a result, a kind of polymer with random framework was grafted onto the solid surface, as shown in Fig.1. It is much easier to obtain a random framework of polymer than a regular framework, and the random copolymer provides the same hindrance effect. Therefore, this process is simple and convenient compared to other grafting methods.

G-TiO_2, prepared by this process, has been first examined by infra-red spectrum (JA.Transform Nicolet FT-170SX). The IR spectra of G-TiO_2 after extraction by toluene and untreated TiO_2 particles, is shown in Fig. 2. The broad peak at 3400 cm^{-1} corresponds to stretching motions of the surface hydroxyl or the adsorption water; the peak at 1630 cm^{-1} corresponds to the flexural vibration of the H—O—H bonds of the adsorbed water. The peak at 1106 cm^{-1} corresponds to Si—O stretching motions, and the peak at 1713 cm^{-1} corresponds to >C=O stretching motions. The strong peak at 1375 cm^{-1} and the weak peaks at 2924 cm^{-1}, 2860 cm^{-1} correspond to CH_3, CH_2 stretching motions respectively. There are a series of peaks in the

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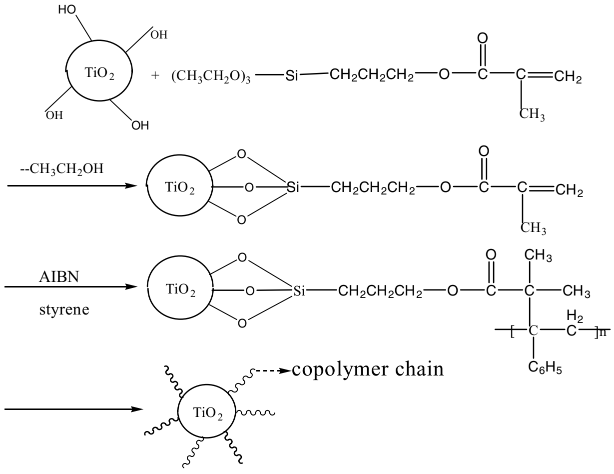


Figure 1 The progress of random co-polymerization on the TiO_2 surface.

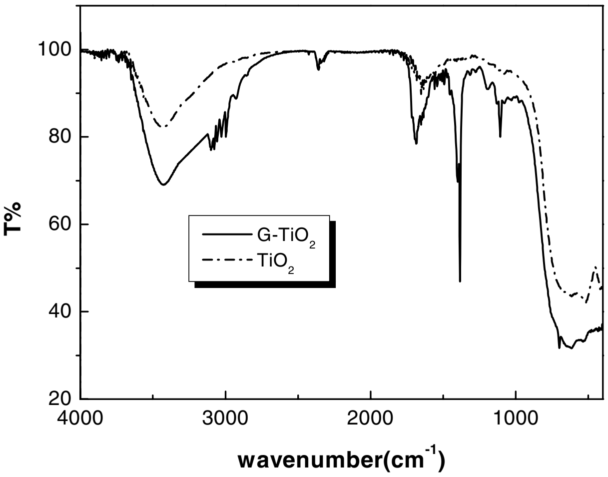


Figure 2 IR spectra of the pure TiO_2 and G-TiO_2 after extraction.

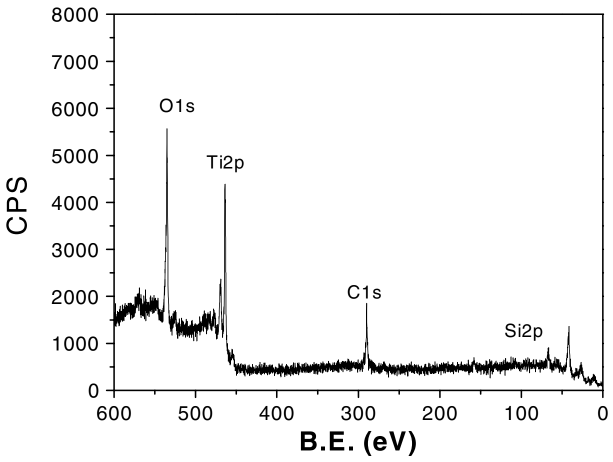


Figure 3 XPS survey of G-TiO_2 after extraction.

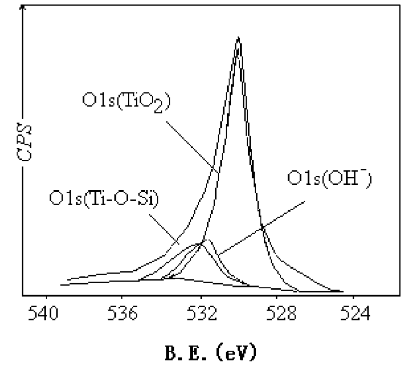


Figure 4 High-resolution XPS spectra of the O1s region of the G-TiO_2 after extraction.

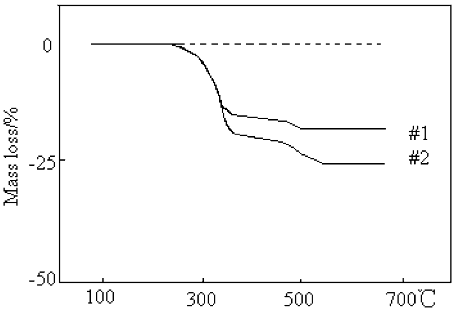
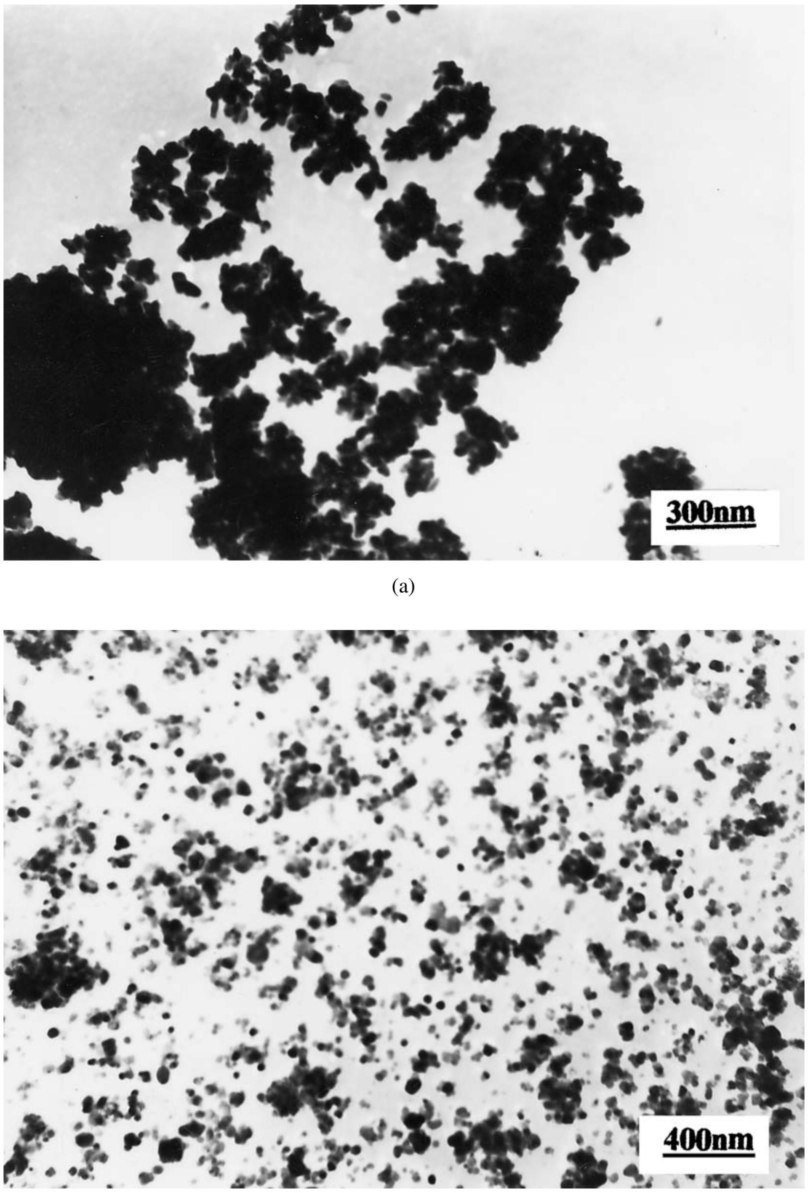


Figure 5 TGA profile: #1: G-TiO_2 after extraction by toluene; #2: G-TiO_2 before extraction by toluene.

region 3000–3100 cm^{-1}, which is the diagnostic adsorption of phenyl. The strong and broad peak in the region 700–400 cm^{-1} belongs to the IR active mode of TiO_2 nano-particles. All this information indicated the presence of silicone coupling agent and the polymer chains in the $GTiO_2$ nano-particles. According to Hamann [3], polystyrene that is adsorbed on TiO_2 by physical adsorption can be completely desorbed from the its surface by long time solvent extraction, leaving only grafted polystyrene unaffected. Therefore, the copolymer on the surface is in connection with TiO_2 via chemical bonds.

The properties of the TiO_2 surface were further investigated by X-ray photoelectron spectroscopy (XPS, PHI 5300, Al K_α). Fig. 3 is the survey spectrum of G-TiO_2 after toluene extraction. It contains C1s and Si2p peaks in addition to the Ti2p and O1s peaks, confirming the presence of the polymer in the sample. Fig.4 shows the high-resolution XPS spectra of O1s peaks of G-TiO_2 after extraction. The O1s region is decomposed into three contributions. The peaks at 530.0 and 531.5 eV correspond to Ti—O in TiO_2 and hydroxyl groups (OH^-), respectively. The peak at binding energy of 532.2 eV corresponds the oxygen species Ti—O—Si, according to Erdem *et al.* [9]. The chemical bond Ti—O—Si is exactly what is considered to bind the copolymer and the surface of TiO_2, as discussed above.

Thermo-gravimetric analysis (TGA, Shimadzu DT-40, 20–800 °C) was applied to estimate the quantity of polymer on the TiO_2 surface. Fig. 5 demonstrates the TGA profiles of grafted TiO_2 before and after toluene extraction. The polymer began to decompose at 280 °C and had decomposed completely at 600 °C. The weight loss of sample #1 is obviously lower than that of sample #2. This suggests there are two different statuses of polymer on the TiO_2 surface, A: one is the copolymer grafted on the solid surface by chemical bond, which is unaffected by solvent extraction. Its quantity can be determined by the weight loss of sample #1 (treated by solvent extraction) at 800 °C; B: another is the copolymer absorbed on the solid surface by physical adsorption,



(a)

(b)

Figure 6 (a) TEM photograph of ungrafted TiO_2 particles dispersed in toluene. (b) TEM photograph of G-TiO_2 particles dispersed in toluene.

which desorbs from the surface by solvent extraction. The total quantity of these two kinds of polymer can be determined by the weight loss of sample #2 (not treated by solvent extraction) at 800 °C. The difference in weight loss of these two samples reflects the quantity of physically adsorbed polymer on the TiO_2 surface.

The sedimentation behavior of grafted TiO_2 was studied by a sedimentation test. G-TiO_2 (0.2 g) was dispersed into 20×10^{-6} m^3 toluene in comparison tubes. The height of the clear layer on the top of the tubes was recorded after different times. It has been observed that once the amount of grafted polymer reaches 150 mg/g (TiO_2), the TiO_2 nanoparticles would be stable when dispersed in toluene. The height of the clear layer on the top of the comparison tubes was only 5 mm after 7 days' sedimentation. As a comparison, the untreated TiO_2 particles would completely settle in toluene in only 5 min. The quantity of chemically grafted copolymers is affected by many conditions, such as reaction temperature, amount of reacted monomer, and coupling agent etc. This influences the stability of TiO_2 nanoparticles in an organic medium to a great extent, and the details on this issue will be discussed elsewhere.

The sedimentation behavior of grafted TiO_2 nanoparticles in toluene shows their excellent macroscopic dispersion stability. The transmission electron microscopy (TEM) images, Fig. 6a and b, demonstrate the uniform dispersion of G-TiO_2 nanoparticles in microdimensions. Ungrafted TiO_2 particles cannot be dispersed in toluene and aggregated. G-TiO_2 particles are well dispersed owing to the steric hindrance, provided by the copolymers on their surface.

In summary, polymer grafted TiO_2 particles can be prepared via co-polymerizing of styrene monomer and silicone coupling agent in the TiO_2-isopropanol system. It is the chemical bond Ti—O—Si which connects the grafted polymer and the surface of TiO_2. G-TiO_2 nanoparticles can be readily dispersed in toluene, thanks to the steric hindrance effect provided by the polymer on the surface of TiO_2. The suspension solution of G-TiO_2 nanoparticles so prepared, has demonstrated a high stability. This simple grafting process may also be applied to prepare different types of grafted TiO_2 nanoparticles, by changing the coupling agent and monomer precursors.

References

1. GUO-CAI XU and LI-DE ZHANG, "Nano-Composite Materials [M]" Chemical Industry Press., Beijing, 2002) p. 83c.
2. M. R. HOFFMANN, S. T. MARTIN and D. W. BAHNEMANN, *Chem. Review* **95** (1995) 69.
3. R. LAIBLE and K. HAMANN, *Adv. In Coll. Int. Sci.* **13** (1980) 65.
4. C. H. M. CARIS, LOUISA P. M. VAN ELVEN and ALEX M. VAN HERK, *British Polym. J.* **21** (1989) 133.
5. YUKIO SHIRAI and NORIO TSUBOKAWA, *React. Funct. Polym.* **32** (1997) 153.
6. YUKIO SHIRAI, KAZUE KAWATSURA and NORIO TSUBOKAWA, *Prog. Org. Coating* **36** (1999) 217.
7. NORIO TSUBOKAWA and A. KOGURE, *J. Polym. Sci., Part A: Polym. Chem.* **29** (1991) 697.
8. LING ZAN, JIACHENG ZHONG and QIRONG LUO, *J. Inorg. Mater. (in Chinese)* **14** (1999) 264.
9. ERDEM BEDRI, R. A. HUNSICKER, G. W. SIMMONS, E. D. SUDOL, V. L. DIMONIE and EL-AASSER, *Langmuir* **17** (2001) 2664.

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