

Research on surface-modification of Nano-TiO₂ by span 60

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Nano-TiO₂ is likely to agglomerate easily because of its high surface energy, which decreases its photocatalytic activity. Also the hydrophilic nature of the TiO₂ restricts its usefulness in organic materials and in solution. Nano-TiO₂ particles were modified by Span 60 in anhydrous ethanol in this paper. The powders were characterized by Fourier transform infrared (FT-IR) and transmission electron microscopy (TEM). The results showed that there were characteristic absorption peaks of Span 60 from the surface of TiO₂ nanoparticles and the degree of aggregation of TiO₂ particles has been decreased effectively after modification. The surface of TiO₂ changed from hydrophilic to hydrophobic.

Key words: Nano-TiO₂, Surface modification, Span 60, Hydrophobicity; Anhydrous ethanol.

Introduction

Titanium dioxide (TiO₂) has received great attention as a photocatalyst because of its photochemical stability, non-toxic and low-cost [1]. Nano-TiO₂ particles have been introduced into photocatalysts [2], structural ceramics [3], semiconductor technology [4], and other scientific fields [5]. However, nano-TiO₂ particles show a great tendency to aggregate due to their high specific surface area and the hydroxyl groups on the TiO₂ surface, which not only decrease its photocatalytic activity, but also impede their application in organic systems because of the hydrophilic nature of TiO₂ caused by hydroxyl groups. So it is necessary to modify the surface of TiO₂ from hydrophilic to hydrophobic. Various methods have been employed to stabilize TiO₂ particles, such as Langmuir-Boldgett films [6], vesicles [7], surfactant and silane coupling agent coatings [8, 9].

In a previous paper, Arellano et al. [10] modified TiO₂ using sodium di(2-ethyl hexyl)sulfosuccionate (AOT), sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulfate (SDS). The results showed that modified TiO₂ particles had a less hydrophilic nature and a greater stability in non-polar media than that of unmodified TiO₂. Xue et al. [11] synthesized a 2-ethyl hexoic acid surface modified TiO₂ nanoparticle which was applied as a lubricating oil additive. Wu et al. [12] prepared titanium dioxide nanoparticles capped with stearate by a sol-gel process. However, nonionic surfactant modified TiO₂ has rarely been reported. In this paper, nano-TiO₂ particles were modified by span-60 in anhydrous ethanol. The organo-capped layer can not only prevent particle

aggregation, but can also allow the particles to form a stable dispersion in an organic solvent.

Experimental Procedure

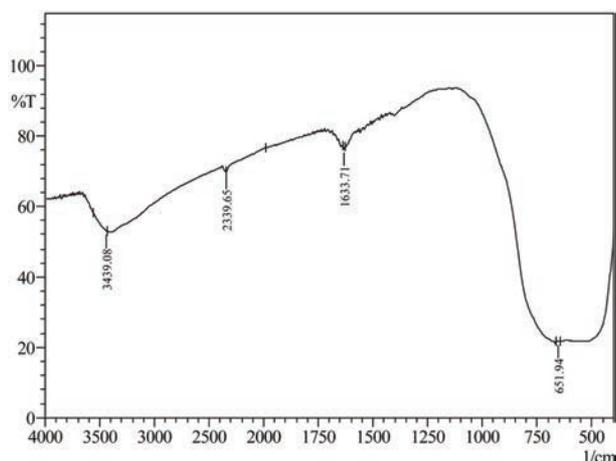
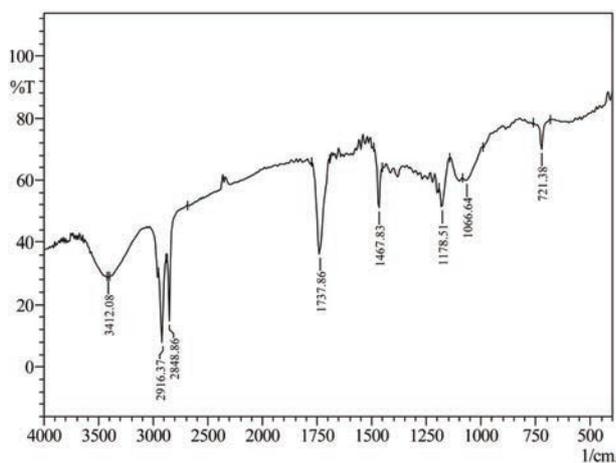
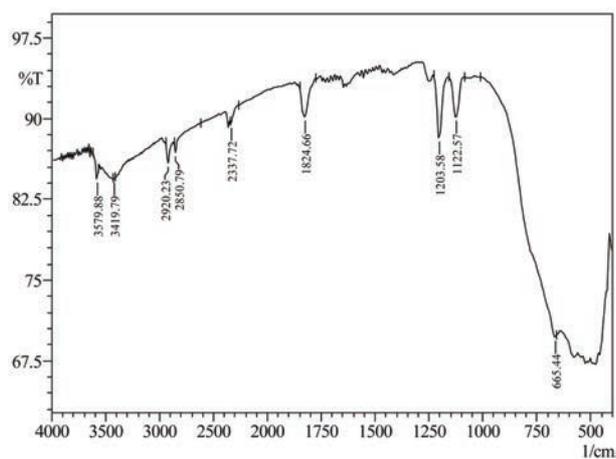
0.5 g TiO₂ was added into 50 ml anhydrous ethanol containing 0.2 g Span 60 and stirred for 1 h at room temperature. Then the modified TiO₂ particles were collected by centrifugation and subsequently washed with anhydrous ethanol followed by hexane three times to wash away the residual Span 60. The particles obtained were dried in a vacuum oven at 60 °C for 2 h. The powders were characterized by Fourier transform infrared spectroscopy (FT-IR; SHIMADZU IRPrestige-21, Japan) and transmission electron microscopy (TEM; HITACH H7500, Japan).

Results and Discussion

The FT-IR spectrum of non-modified TiO₂ is exhibited in Fig. 1. As shown in Fig. 1, the strong and wide peak at 3439.08 cm⁻¹ and peak at 1633.71 cm⁻¹ are due to the hydroxyl groups of Ti-OH with which physisorbed water molecules are bound by weak hydrogen bonds [13, 14]. The strong absorption centered at 651.94 cm⁻¹ is the typical Ti-O-Ti vibration [15]. The absorption at 2339.65 cm⁻¹ is attributed to the CO₂ in air.

Figure 2 and Fig. 3 show the FT-IR spectra of the Span 60 and Span 60 modified TiO₂ respectively. In Fig. 2, the strong peaks at 2848.86 and 2916.37 cm⁻¹ can be assigned to the symmetric and asymmetric vibrations of -CH₂- and -CH₃ groups, respectively. The sharp peak at 1467.83 cm⁻¹ is due to the scissoring of -CH₂- or the symmetric deformation of the -CH₃ group. The 721.38 cm⁻¹ signal represents the vibration energy of -(CH₂)-*n* where *n* is equal to or greater than 4. All absorption bands above are attributed to long-chain aliphatic groups [16], which are the nonpolar parts of Span 60. As for the polar groups of

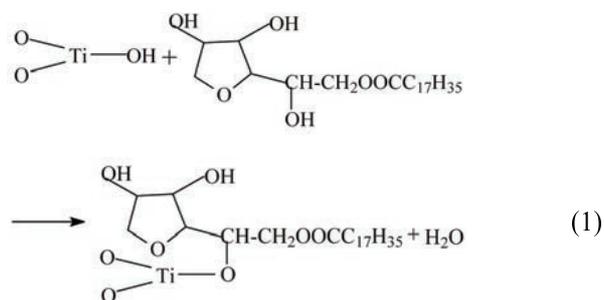
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Fig. 1. FT-IR spectrum of unmodified TiO₂.

Fig. 2. FT-IR spectrum of Span 60.

Fig. 3. FT-IR spectrum of TiO₂ modified by Span 60.

Span 60, the strong peak at 1737.86 cm⁻¹ is due to the stretching vibration of the C = O bond. The peaks at 1178.51 and 1066.64 cm⁻¹ are from the skeletal vibration of -C-CO-O- and -C-O-H, respectively [17]. Compared with the spectrum of non-modified TiO₂, the FT-IR spectrum of the Span 60 modified sample exhibits characteristic

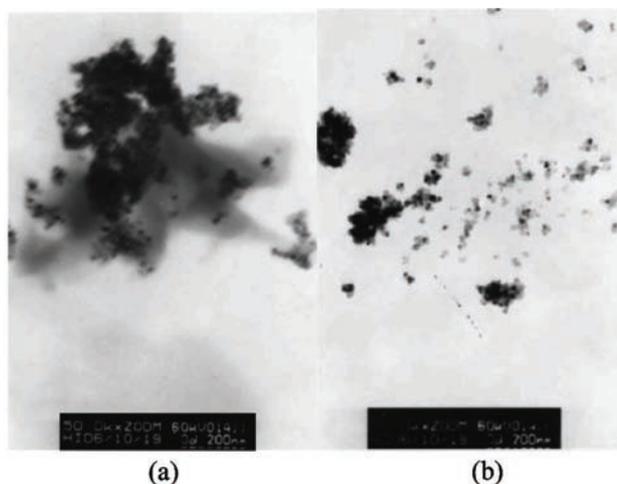
absorption peaks of Span 60 at 2920.23, 2850.79, 1203.58 and 1122.57 cm⁻¹, and the latter two are shifted from 1178.51 and 1066.64 cm⁻¹, respectively, suggesting that Span 60 molecules have been grafted onto TiO₂ particles. Compared with Fig. 2, peaks at 1737.86, 1467.83, 721.38 cm⁻¹ disappear and new peaks at 1824.66 and 3579.88 cm⁻¹ appear, which illustrates that there is no free Span 60 molecules on it, providing evidence that an esterification reaction between Span 60 and TiO₂ has been occurred.

From the FT-IR spectrum and the molecular structure of Span 60 and TiO₂, a mechanism of formation of the organic-capped TiO₂ is proposed as equation (1):



There are three hydroxyls on a Span 60 molecule which can all react with the hydroxyl groups of TiO₂. The reaction may occur on the carbon chain because the hydroxyl on the carbon chain of Span 60 has a lower steric hindrance than that of others.

It is considered that the surfactant has two functions, that is, dispersion of TiO₂ particles and inhibition of their agglomeration. Fig. 4 displays TEM images of unmodified and modified samples. It can be observed that the particles stick together with massive or small particles, becoming larger agglomerates in the case of the unmodified TiO₂, whereas, the quantity and size of all the agglomerates decrease in case of modified TiO₂ powders. The observations show that surface modification with Span 60 may increase dispersity and decrease agglomeration of


Fig. 4. TEM images of TiO₂ (a) unmodified (b) modified by Span 60.

TiO₂ powders. The difference of particle size between the modified and unmodified samples is small, which suggests that there is a small effect of surface modification on the size of TiO₂ powders.

Conclusions

From the foregoing, Span 60 modified TiO₂ was prepared by an organic reaction between Span 60 molecules and the hydroxyl groups on the TiO₂ surface. Compared with the unmodified TiO₂, the modified TiO₂ shows higher dispersity and lower agglomeration. The surface of TiO₂ changed from a hydrophilic to a hydrophobic nature.

Acknowledgments

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