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The Synthesis of Solvent-Free TiO_2 Nanofluids through Surface Modification

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ABSTRACT

TiO_2 nanoparticles with surface hydroxyl groups are treated by trimethoxysilane $(CH_3O)_3Si(CH_2)_3O(CH_2CH_2O)_{6–9}CH_3$ and a inorganic core/organic shell hybridmaterials, which shows itself a yellow viscous fluid, is obtained. We call it solvent-free TiO_2 nanofliuds. Transmission electron microscopy (TEM), Fourier transform infrared spectrum (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and rheometer are adopted to characterize the product. As a result, the content of TiO_2 nanoparticles in the nanofliuds is about 5.5wt%, the functionalized TiO_2 nanoparticles possess better dispersion, very low viscosity and an obvious liquid-like behavior at room temperature in absence of solvent.

***Keywords*:** *Solvent-Free, Nanofulids, TiO_2 Nanoparticles, Liquid-Like Behave*

1. Introduction

Nanoparticles have many unique mechanical, magnetic, thermal, optical, catalytic properties, but its agglomeration due to high surface energy and surface activity hinders their application [1,2].

A method for solving this problem is to disperse nanoparticles in a base fluid, known as nanofluids, is studied for many years. The nanofluids is composed of two parts, including solvents and nanoparticles. The solvents of nanofluids are always water, oil, acetone, decene and ethylene glycol, and the nanoparticles used are usually metallic particles [3,4], metallic and nonmetallic oxides [5-7], carbon nanotube [8], etc. These conventional nanofluids improve the dispersion of nanoparticles to a certain extent, but the system is a kind of suspension and unstable, nanoparticles in the nanofluids may aggregate and settle down [9]. The factors influencing the stability and properties of nanofluids include the nanoparticle's concentration, dispersant, viscosity of system [10], moreover, the variety, diameter [11,12], density of nanoparticle and ultrasonic vibration are not be ignored [13].

Recently, some researchers synthesize a new series of nanofluids which can flow at low temperature in absence of solvent (liquid) by surface modification. These solvent-free nanofluids involve SiO_2 [14,15], TiO_2 [16], $CaCO_3$, C_{60} [17], ZnO [18], carbon naotube [19-21], etc. By the chemical reactions between active groups on the nanoparticles' surface (always hydroxyl groups) and the organic modifier, an organic soft shell forms on the surface of nanoparticles, it can not only reduce the agglomeration of nanoparticles, but also impart new properties to them.

Actually, another method is to introduce the nanoparticle into block copolymer nanostructures. Prof. Ruckenstein and co-worker have been identified it [22,23].

In this paper, we select the organic reagent $(CH_3O)_3Si(CH_2)_3O(CH_2CH_2O)_{6–9}CH_3$ to modify TiO_2 nanoparticles, which is synthesized by sol-gel method. The silanol groups in the modifier can interact with hydroxyl groups on the surface of nanostructures, after a long reaction process, TiO_2 nanoparticles are coated by a mass of organic molecular and a core-shell structure forms. The new system possesses much better dispersion and can flow at the room temperature.

2. Materials and Methods

2.1. Raw Materials

Tetra-n-butyl titanate was purchased from TianJing Ke-Miou Chemical Company. Methanol (CH_3OH, 99.5%), ethanol, HCl (36% - 38%), ammonia(NH_4OH) and tetrahydrofuran were purchased as analytical grade reagents from Fuchen Chemical Ind., Ltd., and used without further purification. Deionized water was made in lab. $(CH_3O)_3Si(CH_2)_3N^+(CH_3)(C_{10}H_{21})_2Cl^-$ in methanol (40%) was from Gelest. C_9H_{19}-C_6H_4-$(OCH_2$-$CH_2)_{20}(CH_2)_3SO_3^- K^+$ was from Sigma-aldrich.

2.2. Synthesis of TiO_2 Nanoparticles

TiO_2 nanoparticles were prepared by a sol-gel method through Tetrabutyl titanate hydrolysis. 17mL of Tetrabutyl titanate was mixed with 15mL of ethanol. The mixture was called as solution A. Solution B was prepared by mixing 15mL of ethanol, 2 mL of 5.5 mol/L hydrochloric acid solution, and1mL of deionized water. Then trickled solution B slowly to solution A with stiring constantly, and stop the experiment after the formation of gel. The gel was aged for 6 h at room temperature and carefully grinded after drying at 65˚C.

2.3. Synthesis of TiO_2 Nanofluids

For the TiO_2 nanofluids, 0.5 g of TiO_2 powder was dispersed in 10mL of ammonia (pH 10), the suspension was treated with ultrasonic for 30 min, then 2.5 g $(CH_3O)_3Si(CH_2)_3O(CH_2CH_2O)_{6–9}CH_3$ was added. The mixture was placed in a sealed single-mouth flask and treated at 70˚C for 24 h. The final solution was extracted with toluene three times, the aqueous layer was collected and dried at 65˚C. The dried material was dispersed in 20mL of deionized water and extracted with toluene three times again. After collecting the aqueous layer, the solution was dried at 65˚C. Subsequently, the material was dispersed in 20 mL of the acetone, after centrifugation, the transparent sol was dried at 65˚C. The product is a yellow transparent liquid.

2.4. Characterizations

The structure of the TiO_2 nanofluids was investigated by Fourier transform-infrared (FTIR) spectrometer analysis (WQF-310, Beijing Second Optical Instruments Factory) using KBr pellets. Transmission electron microscope (TEM) images were obtained on a Hitachi H-800 instrument at an accelerating voltage of 200 kV, placing a few drops of the dispersion on a copper grid, and evaporating them prior to observation. The thermogravimeric analysis (TGA) measurements were taken under N_2 flow by using TA TGAQ50 instrument. Differential scanning calorimetry (DSC) traces were recorded collected on a TA Q1000 Instruments, heating rate of 10˚C/min, from −60˚C to 60˚C. Rheological properties were studied by using the rheometer of TA AR-G2 instrument, heating rate of 5˚C/min.

3. Results and Discussion

The FTIR spectra of the TiO_2 nanofluids are presented in **Figure 1**. The figure shows that they all have peak(s) at 450 cm^{-1} - 700 cm^{-1} which is the location of characteristic peaks of titania. The TiO_2 nanofluids also have many new absorption peaks of organic groups compared with pure TiO_2 nanoparticles. In theory, the reaction between TiO_2 nanoparticles and $(CH_3O)_3Si(CH_2)_3O(CH_2CH_2O)_{6–9}CH_3$ can yield Ti-O-Si, Si-O-Si bonds, from the spectra, their peaks are found at 944 cm^{-1} and 1110 cm^{-1} respectively [24]. In addition, the peak of stretching vibration of polyoxyethene is also observed at 1110 cm^{-1} overlapping with Si-O-Si. The strong peak at 3459 cm^{-1} is attributed to the presence of remaining hydroxyl groups on the TiO_2 nanoparticles. The results prove that the modifier has been grafted on the surface of TiO_2 nanoparticles.

The microstructure of the pure TiO_2 nanoparticals and TiO_2 nanofluids could be clearly observed from the TEM images (**Figure 2**). As shown in **Figure 2**, the pure TiO_2 nanoparticals have serious phenomenon of agglomeration, its dispersion is significantly improved after modification. The modifier protects TiO_2 nanoparticles from agglomeration and probably can improve its compatibility with organic materials.

Figure 3 is the DSC curve of the modifier $(CH_3O)_3Si(CH_2)_3O(CH_2CH_2O)_{6–9}CH_3$ and the TiO_2 nanofluids. In the heating process, both the modifier and TiO_2 nanofluids show a second order transition at −50˚C, corresponding to the glass transition temperature (T_g). The first order transition of the modifier occurs at −0.4˚C, corresponding to the melting temperature (T_m). Differently, the TiO_2 nanofluids has two first order transition at −27˚C and −3.6˚C, this may be the result of oligomeric siloxane of different molecular weight produced during the modification [22]. The two possess the same T_g (−50˚C), the

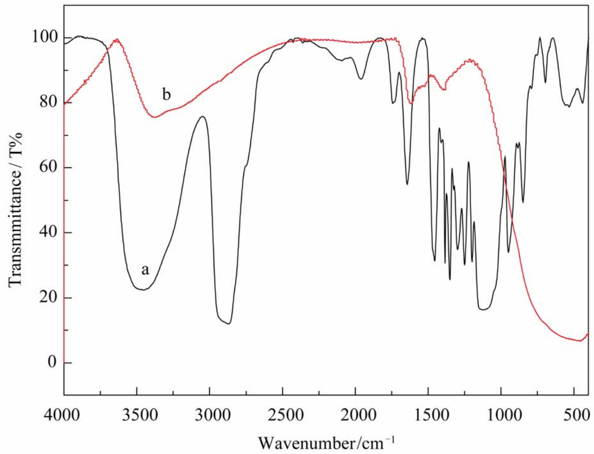
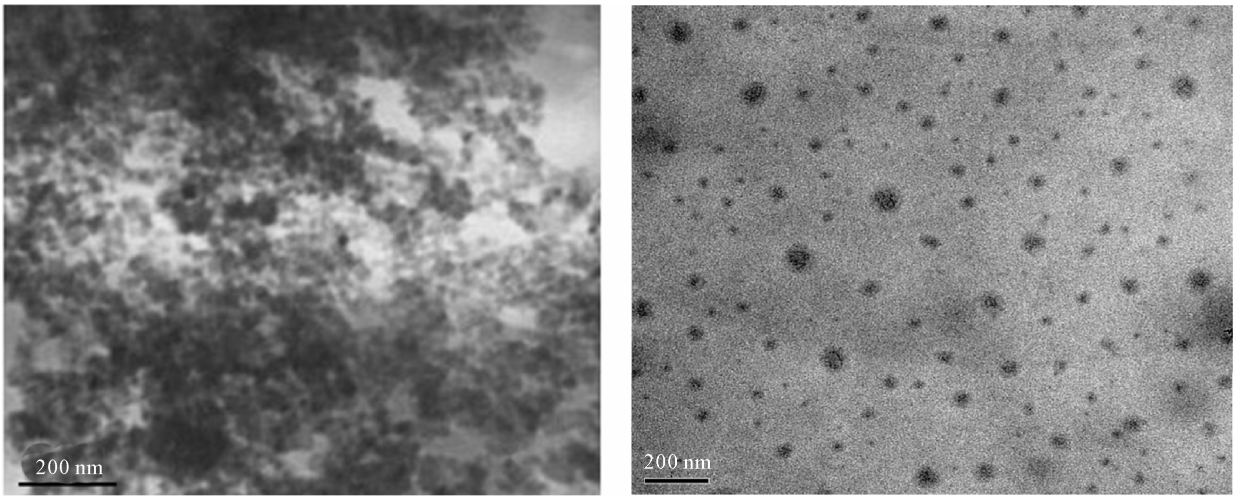
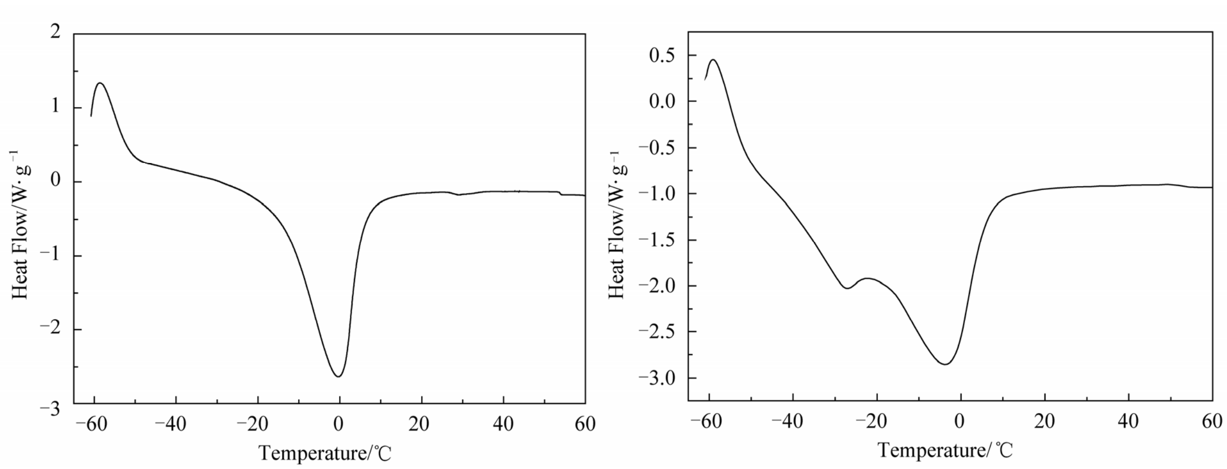


Figure 1. The FTIR spectra of (a) TiO_2-ionic liquid nanofluid and (b) pure TiO_2.



(a) (b)

Figure 2. The TEM photos of (a) pure TiO_2 nanoparticals and (b) TiO_2 nanofluids.



(a) (b)

Figure 3. The DSC curve of (a) modifier $(CH_3O)_3Si(CH_2)_3O(CH_2CH_2O)_{6\text{–}9}CH_3$ and (b) TiO_2 nanofluid.

similar T_m (−0.4˚C, −3.6˚C), this indicated that the modifier is coated on the surface of nanoparticles.

The organic canopy content of the TiO_2 nanofluid influence the properties of inorganic-organic hybridmaterial. The TGA was carried out to confirm the thermal stability (see **Figure 4**). The decomposition temperature is above 200˚C and the weight loss is only 29 wt% at 357˚C, these results indicate that the product has a good heat-resistance property. In addition, the content of the TiO_2 nanoparticles and the modifier can be obtained from the curve, they are 5.5 wt% and 94.5 wt%, respectively. The low inorganic content may be improved by reducing the quantity of the modifier during the modification process.

In the rheological theory, the loss shear modulus G" reflects the energy loss for irreversible deformations of

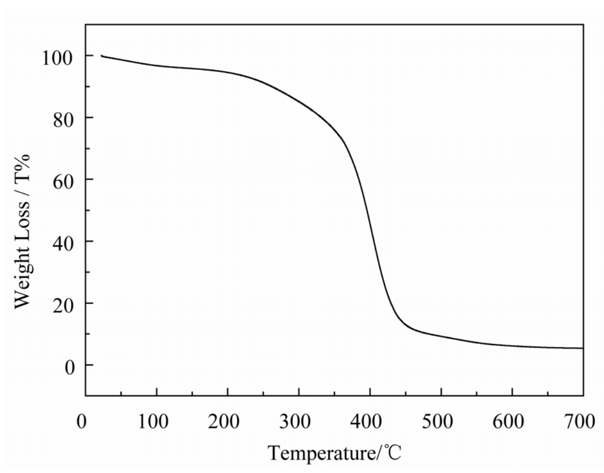
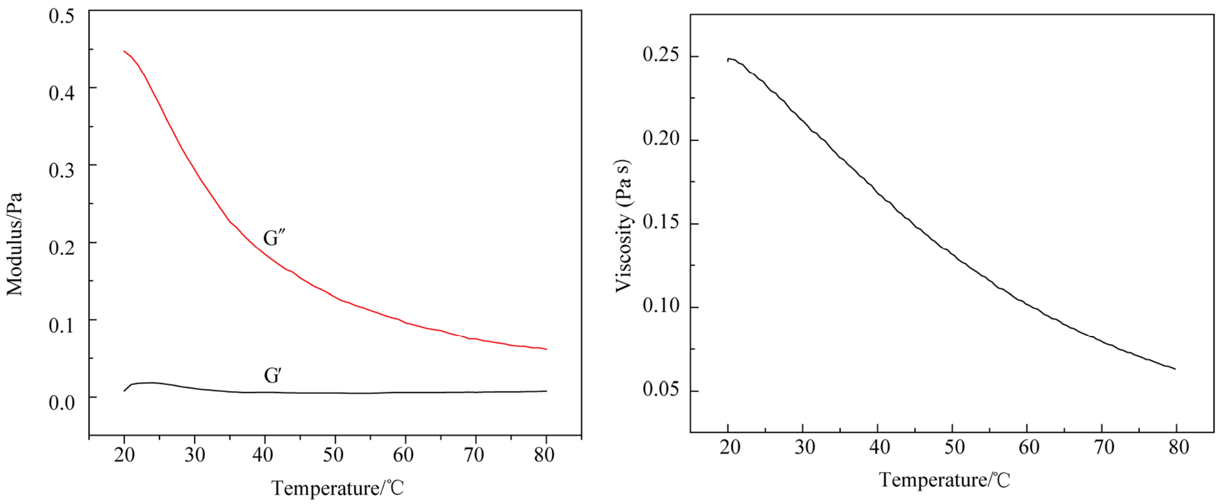


Figure 4. The TGA curve of TiO_2 nanofluid.



(a) (b)

Figure 5. The rheological behavior of TiO_2 nanofluid.

materials, and the storage shear modulus G′ embodies the energy storage for reversible deformations of materials. When G" is higher than G', the material has a characteristic of a fluid. The rheological behavior of the TiO_2 nanofluids is presented in **Figure 5(a)**.

It is clear that the G", which decreases with the temperature increasing, is higher than the G'.

At the measurement stage, G' is almost constant. The result indicates obviously that the TiO_2 nanofluids has a typical liquid-like behavior. Actually, the product can flow at room temperature without any solvent. In the **Figure 5(b)**, the viscosity of TiO_2 nanofluids decreases with the increasing temperature and becomes 0.06 Pa·s at 80˚C.

4. Conclusion

The TiO_2 nanofluids was prepared successfully by using the modifier $(CH_3O)_3Si(CH_2)_3O\text{-}(CH_2CH_2O)_{6\text{–}9}CH_3$. The product shows itself a yellow viscous liquid and can flow at room temperature in absence of solvent. TiO_2 nanoparticles are coated by organic canopy and have better dispersion after modification. The content of TiO_2 nanoparticles in the nanofluids is about 5.5wt%. This kind of inorganic-organic hybridmaterials which probably possess better compatibility with organic materials will have potential application in nano-composite materials.

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