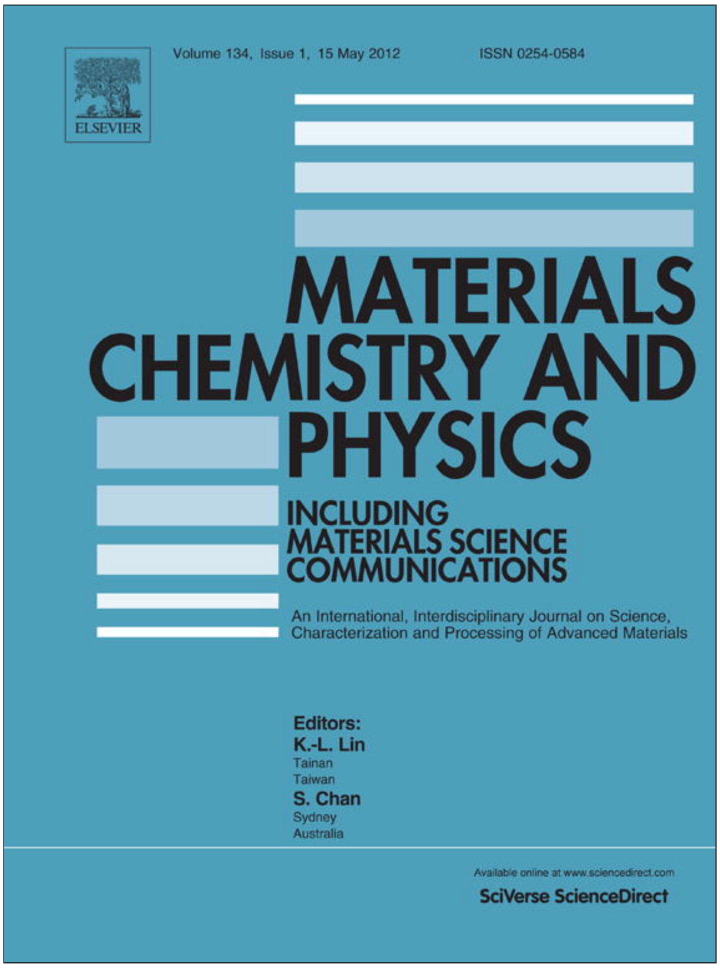

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A new method for surface modification of TiO_2/Al_2O_3 nanocomposites with enhanced anti-friction properties

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ABSTRACT

In this paper, the TiO_2/Al_2O_3 composite nanoparticles were prepared by a hydrothermal method and *in situ* modified with acrylic acid. It was found that the mean particle size of modified TiO_2/Al_2O_3 composite nanoparticles was about 80 nm with a uniform distribution by the particle size analysis. The modified TiO_2/Al_2O_3 composite nanoparticles can disperse in lubricating oil homogenously for several weeks. The dispersion stabilization of modified TiO_2/Al_2O_3 composite nanoparticles in lubricating oil was significantly improved in comparison with the as-prepared nanoparticles, which was due to the introduction of grafted polymers by surface modification. The formation of covalent bands was identified by Fourier transform infrared spectrum. Under an optimized concentration of 0.1 wt%, the averaged friction coefficient was reduced by 14.75%, when the modified TiO_2/Al_2O_3 composite nanoparticles were used as lubricating oil additivities.

1. Introduction

Nanoparticles are very important functional inorganic fillers that are widely used in plastics, rubber, magnetic, paint and paper industries [1–8]. Nanoparticles as lubricating oil additives are one of the most important applications. It is reported that when some nanoparticles were added into the lubricating oil, their lubrication properties can be effectively improved [9,10], which is better than the traditional solid lubricant additives. So, functional nanoparticles have become a promising new lubricating material. However, they tend to agglomerate due to the small particle size and high surface energy. The surface of most inorganic nanoparticles is hydrophilic. So the affinity with the organic medium is poor, which limits their application as additives in lubricating oil. Therefore, many studies have been reported on surface modification of nanoparticles [11–19]. For example, tercopolymer BA-MAA-AN [20], tercopolymer BA-MMAVTES [21], and tercopolymer were synthesized and used to modify nanoparticles surfaces, which was applied to prepare nanoparticles/rubber composites. Due to the strong interface action, these nanocomposites exhibit unique hybrid properties including lubrication performance, good heat-resistance, good wear-resistance and good dynamic mechanical properties [22].

Now, there are several methods to modify the surface of nanoparticles reported in literatures. Swihart and coworkers [23,24] grafted octadecyltri methoxy silane, octadecene or undecylenicacid onto the surface of silicon nanoparticles, and scanning electron micrograph (SEM), Fourier transform infrared spectra (FT-IR), and photoluminescence measurements were used to discuss the results. Xu and coworkers [25] used covalent graft polymerization and block copolymerization to modify the chlorinated SiO_2 (SiO_2-Cl) by atom transfer radical polymerization (ATRP). Kang and coworkers prepared SiO_2 nanoparticles by sol–gel approaches and used oleic acid to modify SiO_2 nanoparticles [26]. More importantly, when modified SiO_2 nanoparticles were used as oil additives, it exhibited better tribological property in load-carrying capacity, anti-wear, and friction reduction.

In this paper, TiO_2/Al_2O_3 composite nanoparticles were prepared by a hydrothermal method and *in situ* modified with acrylic acid. Such modified TiO_2/Al_2O_3 nanoparticles showed good dispersion stability in lubricating oil. The dispersion of modified TiO_2/Al_2O_3 nanoparticles as well as the mechanism of stable colloidal dispersion was discussed in lubricating oil, whose polar was quite low. The using efficiency of acrylic acid as a modifier was also studied. The friction coefficient was tested by a four-ball tester. The fraction properties of TiO_2/Al_2O_3 composite nanoparticles as additives in lubricating oil under variable concentration were evaluated.

2. Experimental

2.1. *The synthesis and surface modification of TiO_2/Al_2O_3 composite nanoparticles*

For clarity, the experimental method was described with nine steps as follows. (1) 10 mL tetra-n-butyl titanate ($1\,g\,mL^{-1}$) was

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dissolved in alcohol (70 mL) at room temperature and then 1 g polyethylene glycol was added to the solution. After ultrasonic dispersion for 10 min, the solution was then magnetically stirred for 15 min (Solution A). (2) 10 mL distilled water and 2 mL ice acetic were dropped into 100 mL beaker filled with 35 mL alcohol. The pH value of solution was adjusted at 1–2 by dropping strong nitric acid then we got Solution B. (3) The Solution A was put into burette and dripped into Solution B at the rate of 3 mL min^{-1} and then magnetically stirred for 30 min (Solution C). (4) The pH value of Solution C was adjusted at 8–10 by ammonia water dropping and then the TiO_2 precursor was prepared. (5) 13 g of aluminum nitrate was dissolved in alcohol (95%, 40 mL) and then 1 g polyethylene glycol was added (Solution D). (6) The pH value of solution D was set at 8–10 by ammonia water dropping and then the Al_2O_3 precursor was prepared. (7) The TiO_2 precursor and Al_2O_3 precursor were mixed in a 250 mL beaker to get the TiO_2/Al_2O_3 precursor. (8) After the TiO_2/Al_2O_3 precursor washed three times with alcohol, 1 g acrylic acid was added and kept at room temperature for 1.5 h. (9) The TiO_2/Al_2O_3 precursor was put into the autoclave and the reaction temperature were set as 240 °C under an pressure of 4.0 MPa. The reaction time is 2 h. Finally, the modified TiO_2/Al_2O_3 composite nanoparticles were prepared. Similarly, the unmodified TiO_2/Al_2O_3 composite nanoparticles were prepared without the Step 8. The TiO_2/Al_2O_3 composite nanoparticles were modified with acrylic acid. In comparison with the traditional method for nanoparticles surface modification, the applied process has two advantages. First, the preparation and modification of nanoparticles were finished in one-step. Second, the process was easier for large scale synthesis because the experimental apparatus were simple with low cost.

2.2. Material characterizations

The diameters of TiO_2/Al_2O_3 composite nanoparticles were analyzed by laser particle size analyzer (LS 13320; BECKMAN) and zeta-potential analyzer (Zeta PALS; Phase Analysis Light Scattering; BIC). Through scanning electron micrograph (SEM, QUANTA FEG 250; FEI) observation, the dispensability of TiO_2/Al_2O_3 composite nanoparticles was investigated. The formation of covalent bands was testified by Fourier transform infrared spectra (FT-IR, FIS-165; DBio-Rod). The anti-friction properties were tested by a four balls tester (MMU-10G, Jinan). Finally, the anti-friction property of TiO_2/Al_2O_3 composite nanoparticles as additives in lubricating oil was studied.

2.3. Friction test

The anti-friction properties were tested by a four-ball tester (MMU-10G, Jinan). The modified TiO_2/Al_2O_3 composite nanoparticles were added into lubricating oil (20#, Great Wall, Sinopec) that is a typical kind of mineral lubricating. The mass concentrations of particles added were 0 wt%, 0.05 wt%, 0.1 wt%, 0.5 wt%, and 1 wt%. The oil solution was firstly dispersed with ultrasonic irradiation for 30 min and then kept at room temperature for 48 h before friction tests to ensure that nanoparticles were fully dispersed in the lubricating oil. The experimental data were acquired with a computer automatically. In the friction process, test parameters were set as follows, temperature at 75 °C, speed of 1200 rpm, load at 200 N, time for 30 min. For each concentration, the friction coefficients were measured five times and then averaged to ensure the data accuracy.

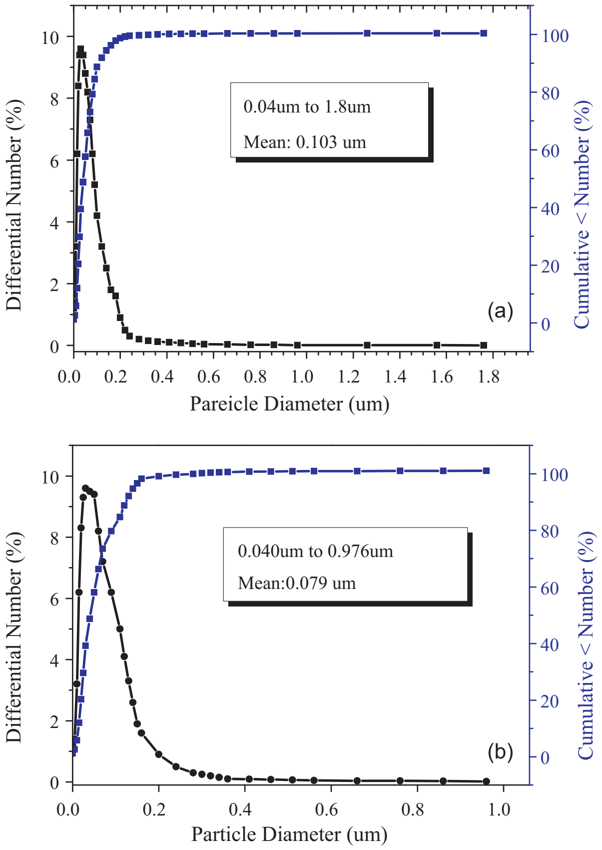

Fig. 1. The particle size distribution of TiO_2/Al_2O_3 composite nanoparticles: (a) native TiO_2/Al_2O_3 composite nanoparticles and (b) modified TiO_2/Al_2O_3 composite nanoparticles.

3. Results and discussion

3.1. Particle size of TiO_2/Al_2O_3 composite nanoparticles

The TiO_2/Al_2O_3 composite nanoparticles were dispersed into alcohol and measured with a laser particle size analyzer, as shown in Fig. 1. The average diameter of native TiO_2/Al_2O_3 composite nanoparticles is 103 nm while that of modified nanoparticles is 79 nm. So, compared with the native particles, the particle size of TiO_2/Al_2O_3 composite nanoparticles modified with acrylic acid is smaller and more uniform. Because of the formation of new chemical bond between acrylic acid and TiO_2/Al_2O_3 composite nanoparticles, the interaction among nanoparticles is broken down and the agglomeration is controlled effectively.

3.2. Decentralized stability of TiO_2/Al_2O_3 composite nanoparticles

The agglomeration between nanoparticles was characterized by Zeta potential measurement. The bigger the Zeta potential value, the slighter the nanoparticles agglomeration. Zeta potential absolute value of nanoparticles were measured six times and then averaged to ensure the data accuracy. The Zeta potential absolute value of TiO_2/Al_2O_3 composite nanoparticles is shown in Table 1. As shown in Table 1, the Zeta potential absolute

Table 1
The absolute value of TiO_2/Al_2O_3 composite nanoparticles Zeta potential.

Number	1	2	3	4	5	6	Mean
Native nanoparticle	4.8	4.6	5.1	5.0	5.3	5.1	5.0
Modified nanoparticle	7.9	8.2	7.8	8.2	8	8.3	8.1

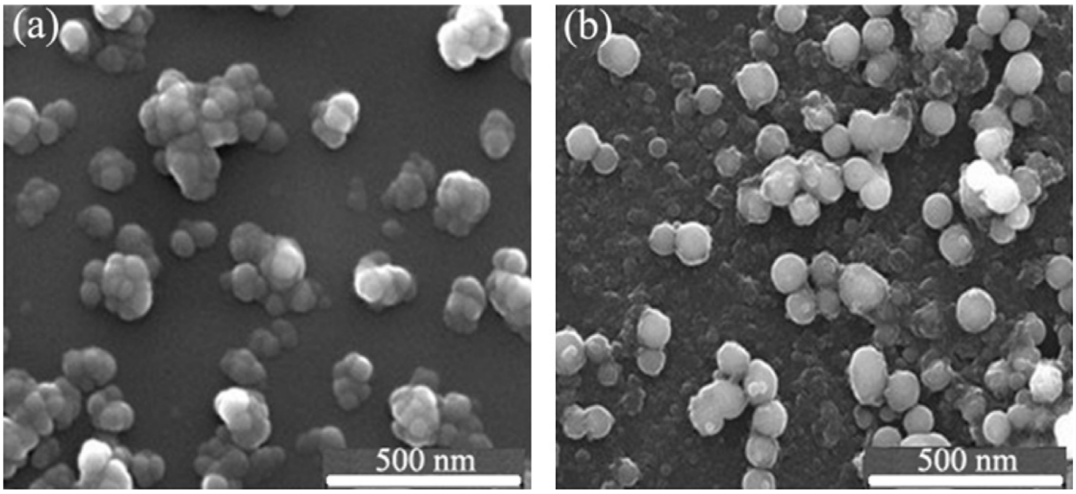

Fig. 2. The SEM images of TiO_2/Al_2O_3 composite nanoparticles: (a) native TiO_2/Al_2O_3 nanoparticles and (b) modified TiO_2/Al_2O_3 nanoparticles.

value of modified TiO_2/Al_2O_3 composite nanoparticles is bigger than native TiO_2/Al_2O_3 composite nanoparticles. These indicate that static repellency of modified TiO_2/Al_2O_3 composite nanoparticles becomes stronger than native TiO_2/Al_2O_3 nanoparticles, which means the dispersibility of modified TiO_2/Al_2O_3 composite nanoparticles is better than native TiO_2/Al_2O_3 composite nanoparticles.

3.3. Morphology of TiO_2/Al_2O_3 nanoparticles

In order to represent detailed morphological information of the specimens, the SEM images of native TiO_2/Al_2O_3 composite nanoparticles and modified TiO_2/Al_2O_3 composite nanoparticles were shown in Fig. 2. The obvious agglomeration can be seen in the images of native TiO_2/Al_2O_3 composite nanoparticles (Fig. 2(a)) and the dispersion of modified TiO_2/Al_2O_3 composite nanoparticles was found to be more homogeneous (Fig. 2(b)). The reason is that acrylic acid layers were coated on the surface of TiO_2/Al_2O_3 composite nanoparticles. This indicates that chemical bonding or physical bonding occurs between the polarity bonds of acrylic acid and hydroxide group. The macromolecular chains grafted on the surface of TiO_2/Al_2O_3 composite nanoparticles bring mutual exclusion and steric hindrance effect, thus the surface free energy has been reduced correspondingly and the agglomeration is controlled. All the results above further illustrate that acrylic acid has played an important role in the dispersion of TiO_2/Al_2O_3 composite nanoparticles.

3.4. FT-IR analysis

Fig. 3 shows typical FT-IR spectra of native TiO_2/Al_2O_3 composite nanoparticles and the modified TiO_2/Al_2O_3 composite nanoparticles, respectively. For the FT-IR spectra of native TiO_2/Al_2O_3 composite nanoparticles, the peak at 3459 cm^{-1} attributed to hydroxyl (—OH) stretching mode were observed. For the FT-IR spectra of modified TiO_2/Al_2O_3 composite nanoparticles, the absorption peak at 1737 cm^{-1} correspond to the carbonyl group [—(C=O)—]. At the same time, the peak near 1439 cm^{-1} corresponds to the carbon p-bond (—CH=CH_2) of acrylic acid. This is due to the esterification reaction happened between Ti/Ai–OH groups and acrylic acid.

Moreover, the hydroxyl groups (—OH) of native TiO_2/Al_2O_3 composite nanoparticles disappear. This further explains that the hydroxyl groups (—OH) from TiO_2/Al_2O_3 composite nanoparticles interacted with acrylic acid to form complex on the surface of TiO_2/Al_2O_3 composite nanoparticles. So, a simple schematic representation of the one-step procedure for attaching an acrylic acid to a TiO_2/Al_2O_3 composite nanoparticles surface is shown in Fig. 4. Accordingly, the surface structure of modified TiO_2/Al_2O_3 composite nanoparticles is shown in Fig. 5.

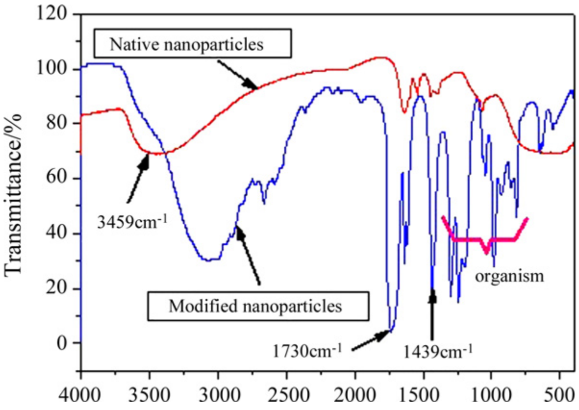

Fig. 3. The infrared spectrum of TiO_2/Al_2O_3 composite nanoparticles.

3.5. Dispersion stability test in lubricating oil

The dispersion stability of modified TiO_2/Al_2O_3 composite nanoparticles in lubricating oil is compared with native TiO_2/Al_2O_3 composite nanoparticles as shown in Fig. 6. The TiO_2/Al_2O_3 composite nanoparticles were added into the lubricating oil. The absorbency of lubricating oil with nanoparticles was measured by

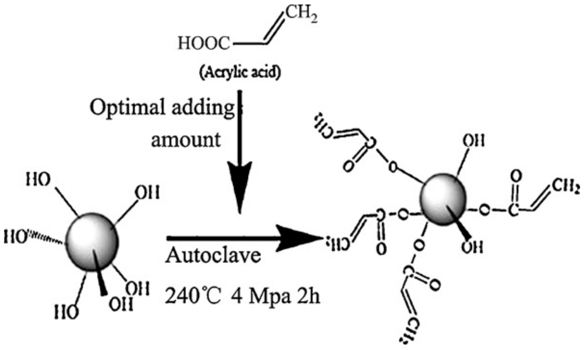

Fig. 4. Schematic representation for the modification of TiO_2/Al_2O_3 composite nanoparticles with acrylic acid.

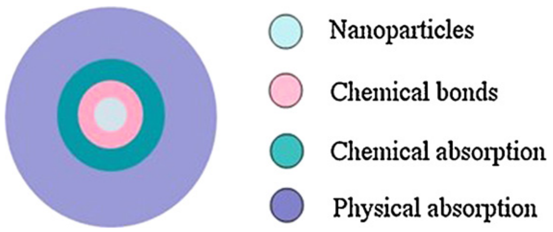

Fig. 5. The proposed surface structure of the modified TiO_2/Al_2O_3 composite nanoparticles.

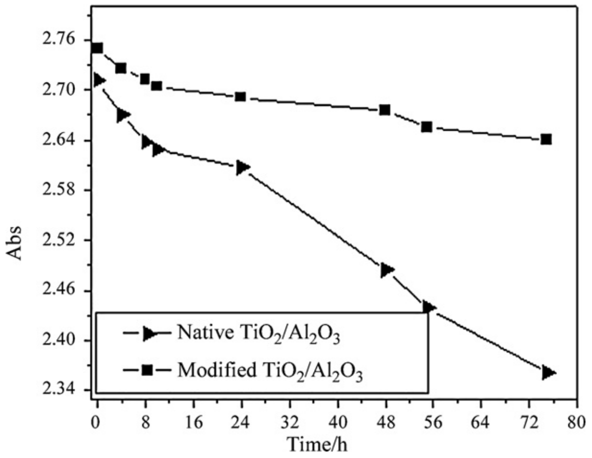

Fig. 6. The absorbency curve of nano-lubricating oil with time after adding TiO_2/Al_2O_3 composite nanoparticles.

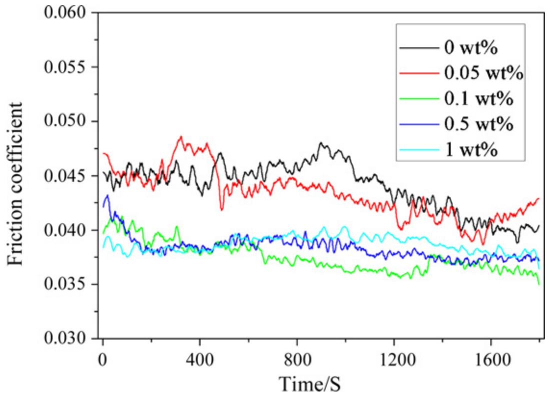

Fig. 8. The friction coefficient variation with times for lubricating oil with different concentration of nanoparticles.

Table 2
The mean of friction coefficient and the corresponding reduction ratio relative to that of pure lubricating oil.

Concentration	0 wt%	0.05 wt%	0.1 wt%	0.5 wt%	1 wt%
Friction coefficient	0.0440	0.0433	0.0375	0.0384	0.0387
Friction reduction (%)	–	1.59	14.75	12.73	12.04

UV spectrophotometer (λ = 190 nm). The higher absorbency reflects the better dispersibility of nanoparticles in lubricating oil. As shown in Fig. 6, after 56 h, the absorbency of nano-oil with modified TiO_2/Al_2O_3 composite nanoparticles is stable. But the absorbency of nano-oil with unmodified TiO_2/Al_2O_3 composite nanoparticles still decreases. This indicates that modified TiO_2/Al_2O_3 composite nanoparticles can steadily exist in lubricating oil.

The oil was kept at room temperature and the results of sedimentation tests of TiO_2/Al_2O_3 composite nanoparticles suspended in lubricating oil were shown in Fig. 7. For unmodified TiO_2/Al_2O_3 composite nanoparticles, the sedimentation mainly occurred by flocculation. The suspensions separated very quickly into sediments and a clear supernatant on top of the sediment was observed. The separation interfaces between the sediment and the supernatant were sharp and moved downward with time. This sedimentation behavior is typical of flocculated suspensions. For modified TiO_2/Al_2O_3 composite nanoparticles, solution exhibits good turbidity. This behavior is typical of well-dispersed suspensions and smaller particles have much slower deposition rates, which might be counter balanced by Brownian motion. Even after 10 days, the solution containing modified TiO_2/Al_2O_3 composite nanoparticles remained turbid. It indicates that acrylic acid modification can increase the stability of nanoparticles in non-polar organic media.

3.6. Friction test

Fig. 8 showed variation of friction coefficient with times, when the concentration fraction of TiO_2/Al_2O_3 composite nanoparticles is different in lubricant oil. Friction time is 1800 s, and friction coefficient was recorded every second with a computer automatically. Table 2 lists the mean of friction coefficient when the concentration fraction of nanoparticles is different. From Fig. 8, we can see that the friction coefficient decreased with the TiO_2/Al_2O_3 composite nanoparticles concentration increased when the concentration was smaller than 0.1 wt%. However, the friction coefficient began to increase when the additive concentration was bigger than 0.1 wt%, as shown in Fig. 8. So, only when the amounts of nanoparticles were added in an optimal concentration range, the friction-reduction effect is better. From Table 2, we can see that the friction-reduction

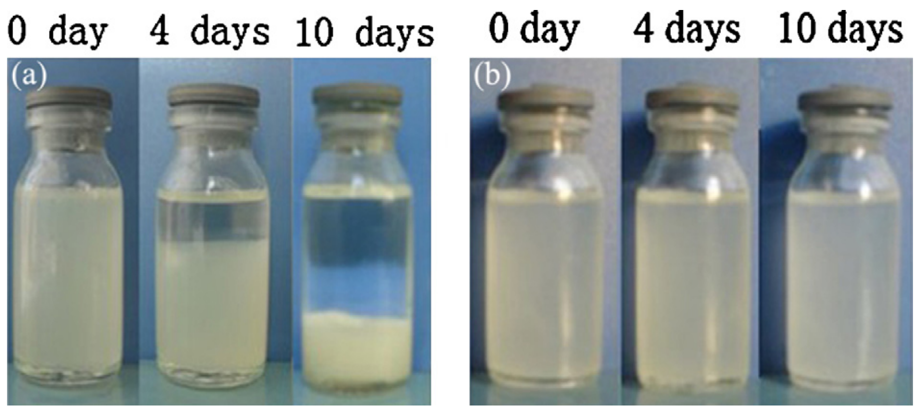

Fig. 7. The images of lubricating oil with different nanoparticles: (a) native nanoparticles and (b) modified nanoparticles.

effect was more effective at the additivities concentration of 0.1 wt% with an average friction coefficient decreasing of 14.75%. The influence of the nanoparticle additivities concentration in lubricating oil on its friction properties was discussed in our former paper [27–29].

4. Conclusion

In this paper, the preparation and surface modification of TiO_2/Al_2O_3 composite nanoparticles are finished by a hydrothermal method in one-step. It was found that acrylic acid was anchored on the surface of TiO_2/Al_2O_3 composite nanoparticles. Therefore, the modified TiO_2/Al_2O_3 composite nanoparticles exhibited a more stable colloidal dispersion in lubricating oil than that of native TiO_2/Al_2O_3 composite nanoparticles. Then the modified TiO_2/Al_2O_3 composite nanoparticles were added into the lubricating oil. Under an optimized concentration of 0.1 wt%, the average friction coefficient was reduced by 14.75%.

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