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Preparation of ZnO Nanoparticles with Enhanced Antifriction Properties

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In this paper, the ZnO nanoparticles were prepared by a non-hydrolytic sol method. It was found that the mean particle size of ZnO nanoparticles was about 80 nm with a uniform distribution by the particle size analysis. The prepared ZnO nanoparticles can disperse in lubricating oil homogenously for several weeks. The reason is that the grafted polymers are introduced by non-hydrolytic sol method. The formation of covalent bands was identified by Fourier transform infrared spectrum. Under an optimized concentration of 1.5 wt %, the averaged friction coefficient was reduced by 8.42 %, when the ZnO nanoparticles sol was used as lubricating oil additives.

Key Words: ZnO nanoparticles, Non-hydrolytic sol method, Additive, Antifriction.

INTRODUCTION

The surface modification of inorganic nanoparticles is an area of increasing research activity because the resulting organic-inorganic composite particles offer many potential applications in areas as diverse as photocatalysis[1], lithography[2], optics[3], biotechnology[4] and lubricant additives[5].

It is reported that when some nanoparticles were added into the lubricating oil, their lubrication properties can be effectively improved[6,7], which is better than the traditional solid lubricant additives and becomes a promising new lubricating material. A previous study revealed that nano-lubricant, which was a mixture of nanoparticles and lubricating oil increased the extreme pressure of the lubricant and reduced the friction coefficient, which could make the bearing more durable[8,9]. But the nanoparticles are inorganic and are easy to agglomerate due to the drawbacks of traditional method of preparation. For example of hydrolytic sol-gel method, the reason is that, in the absence of sulfate ions, the precursor consists of fine particles that have been joined together by hydroxyls to form a network structure similar to a gel, so that the precursor is not only difficult to wash, but even after washing and filtration much water is still retained in fine channels of the network. Fig. 1, contains a schematic diagram of this network structure[10]. So the surface modification of nanoparticles is a necessary work for the well dispersion of nanoparticles in lubricating oil.

There are several methods to modify the surface of nanoparticles in literatures[11,12]. The chemical treatment and functionalization of the nanoparticles surface can be used to enhance the nanoparticles' overall properties for targeted applications. In pervious work[13], the nanoparticles were modified with aluminum zirconium coupling agent and the modified nanoparticles can steadily exist in lubricating oil. This is because that the hydroxyl groups (-OH) from nanoparticles can interacted with hydroxyl groups from aluminum zirconium coupling agent to form complex on the surface of nanoparticles. Finally, the surface of nanoparticles changed from inorganic phase to organic phase.

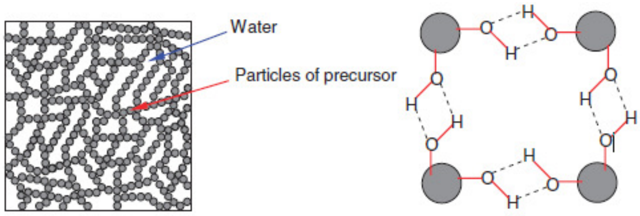

Fig. 1. Schematic diagram of the structure of the precursor in the absence of sulfate ions

In this work, ZnO nanoparticles were prepared with non-hydrolytic sol method. This method shows many advantages in the preparation of nonmaterial[14-16] compared to the traditional method of preparation. In this method, the precursor solutions of nanomaterials are prepared through the reactions between organic solvents used as oxygen donors and metal chlorides. The applied process has mainly two advantages. First, the preparation and modification of nanoparticles were finished in one-step[17]. Second, the process was easier for large scale synthesis because the experimental apparatus were simple with low cost. Main reaction process as follows. M refers to metal elements and R or R refers to organic groups[18]:

$$\text{M-Cl} + \text{ROH} \rightarrow \text{M-OR} + \text{HCl} \quad (1)$$

$$\text{H-OOC-R'} + \text{M-Cl} \rightarrow \text{M-OOC-R'} + \text{HCl} \quad (2)$$

$$\text{M-OOC-R'} + \text{R-O-M} \rightarrow \text{M-O-M} + \text{R-OOC-R'} \quad (3)$$

Such prepared ZnO nanoparticles showed good dispersion stability in lubricating oil. The friction coefficient was tested by a four-ball tester. The fraction properties of ZnO nanoparticles as additives in lubricating oil under variable concentration were evaluated.

EXPERIMENTAL

Preparation of ZnO nanoparticles: For clarity, the experimental method was described in four steps as follows: (1) 1 g of zinc chloride was dissolved in alcohol (50 mL) at 75 ºC. At the same time, the solution was magnetically stirred for 6 h (solution A). (2) 1 g of zinc chloride was dissolved in oleic acid (50 mL) at 75 ºC. The solution was also magnetically stirred for 6 h (solution B). (3) The solution A was put into burette and dripped into solution B at the rate of 3 mL/min and then magnetically stirred for 2 min at 135 ºC (solution C). (4) The solution C was put into the autoclave and the reaction temperature were set as 150 ºC. The reaction time is 5 h. Finally, the ZnO nanoparticles sol, which contacts 3 wt % ZnO nanoparticles was prepared.

Characterizations of ZnO nanoparticles: The crystal form of ZnO nanoparticles was analyzed by X-ray diffraction analyzer (XRD, D8 Advance, Bruker). The diameters of ZnO nanoparticles were analyzed by laser particle size analyzer (LS 13320;Beckman Coulter Inc.). Through scanning electron micrograph (SEM, QUANTAFEG 250;FEI) observation, the dispensability of ZnO 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 antifriction property of ZnO nanoparticles as additives in lubricating oil was studied.

Friction test: The best prepared ZnO nanoparticles sol is dispersed stability in lubricating oil. The antifriction properties were tested by a four-ball tester (MMU-10G, Jinan). The best prepared ZnO nanoparticles sol were added into lubricating oil (20 #) with different mass concentrations of 0, 1.5, 3, 15 and 30 wt %. For each concentration, the fraction coefficients were measured five times and then averaged to ensure the data accuracy. The oil solution was dispersed with ultrasonic for 0.5 h and then was ready for test. Then the nanoparticles were homogenously dispersed in the lubricating oil. The oil was kept at room temperature for 48 h before friction tests. The experimental data was recorded and the test data were acquired with a computer automatically. In the friction process, test parameters were set as follows, temperature (75 ºC), speed (1200 rpm), load (200 N), time (0.5 h).

RESULTS AND DISCUSSION

X-Ray diffraction analysis: The organic solvent with ZnO nanoparticles was calcined at 800 ºC for 2 h. X-Ray diffraction pattern (Fig. 2) of the powders obtained by calcination. From the pattern, it is observed that the powders' crystal structure was wurtzite of ZnO. This shows that ZnO nanoparticles were prepared successfully in this work.

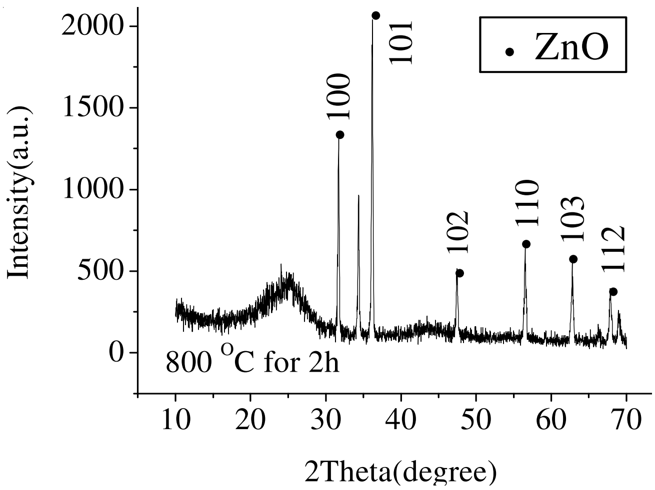

Fig. 2. X-ray diffraction pattern of the ZnO nanoparticles by calcinations test at 800 ºC for 2 h

Particle size analysis: The organic solvent with ZnO nanoparticles were diluted with alcohol and its particle size was measured with a laser particle size analyzer (Fig. 3). The mean diameter of ZnO nanoparticles is 80 nm. In addition, from Table-1, we can see that most particles size is less than 100 nm. These show that prepared ZnO nanoparticles has uniform particle size distribution.

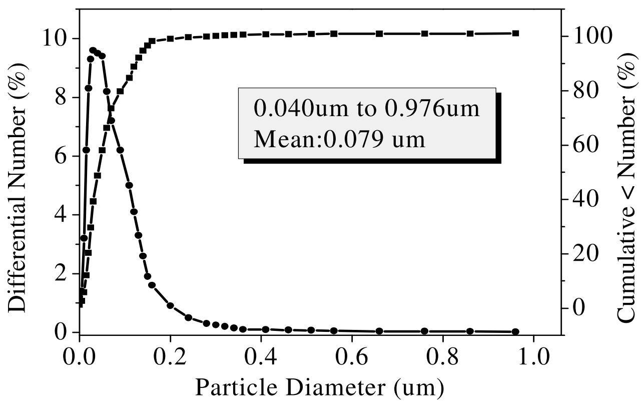

Fig. 3. Particle size distribution of ZnO nanoparticles

TABLE-1
DIVISION STATISTICS VALUE OF ZNO NANOPARTICLES

Particle Size/nm	57	69	78	95	126	80
Accumulative (%)	<10	<25	<50	<75	<90	Mean

Morphology of ZnO nanoparticles sol: In order to represent morphological information of the specimens, the ZnO nanoparticles sol were diluted with alcohol and the SEM images of ZnO nanoparticles were shown in Fig. 4. The dispersion of ZnO nanoparticles was found to be homogeneous and it is no agglomeration. The reason is that oleic acid layers or ethanol layers were coated on the surface of ZnO nanoparticles. The macromolecular chains grafted on the surface of ZnO 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

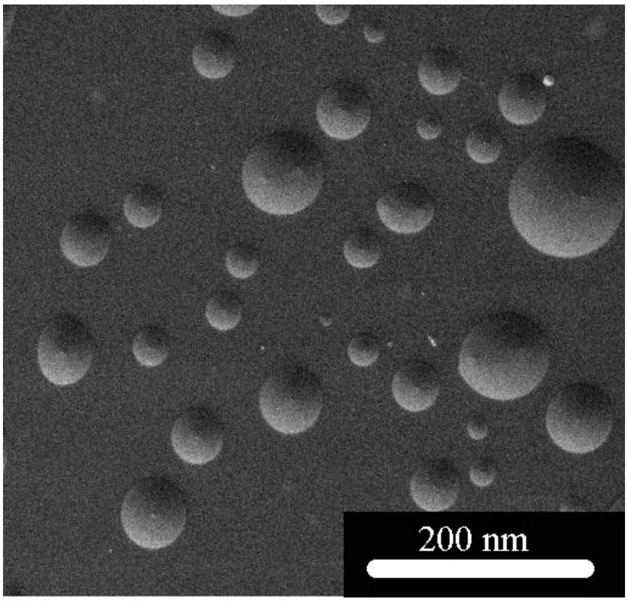

Fig. 4. SEM images of ZnO nanoparticles

further illustrate that prepared ZnO nanoparticles by non-hydrolytic sol method shows good dispersion and stability.

FT-IR analysis: Fig. 5 shows typical FT-IR spectra of oleic acid and ZnO nanoparticles. For the FT-IR spectra of oleic acid, the peak at 3006 cm^{-1} attributed to hydroxyl (-OH) stretching mode were observed. But for the FT-IR spectra of ZnO nanoparticles, the peak at 3006 cm^{-1} disappears. The reason is that the hydroxyl groups (-OH) from oleic acid interacted with metal chlorides. And the absorption peak at 1030 cm^{-1} corresponds to the ether [-(C-O-C)-]. This is due to the esterification reaction happened between oleic acid aluminum and alcohol aluminum. The absorption peak at 1640, 1593 and 1030 cm^{-1} was attributed to the side effects.

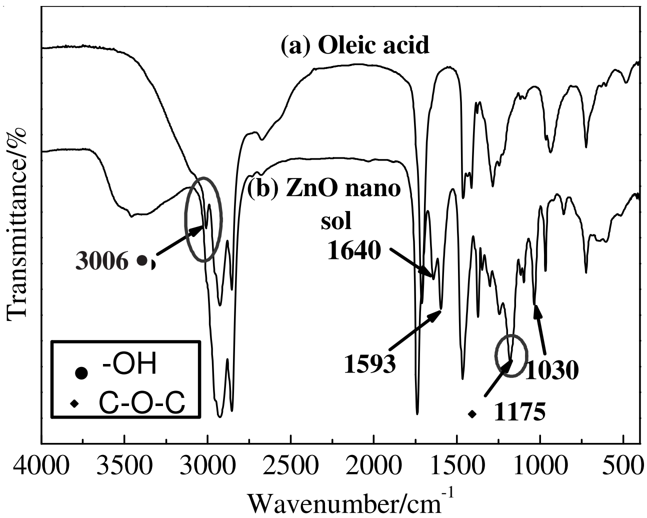

Fig. 5. Infrared spectrum of oleic acid and ZnO nanoparticles sol

Dispersion stability test in lubricating oil: The nano-oil is put aside at room temperature for 60 days and the results of sedimentation tests of ZnO nanoparticles suspended in lubricating oil are shown in Fig. 6. For sample native ZnO nanoparticles, the sedimentation mainly occurred by flocculation mechanism. The suspensions separated quickly into sediments and a clear supernatant on top of the sediment was observed. For samples modified ZnO nanoparticles, solution exhibits the most turbidity. This behaviour is typical of well-dispersed suspensions and smaller particles have much slower settling rates, which might be counter balanced by Brownian motion, they will remain in the supernatant for long times. It indicates that ZnO nanoparticles prepared by non-hydrolytic sol method can lead to increase stability of nanoparticles in non-polar organic media.

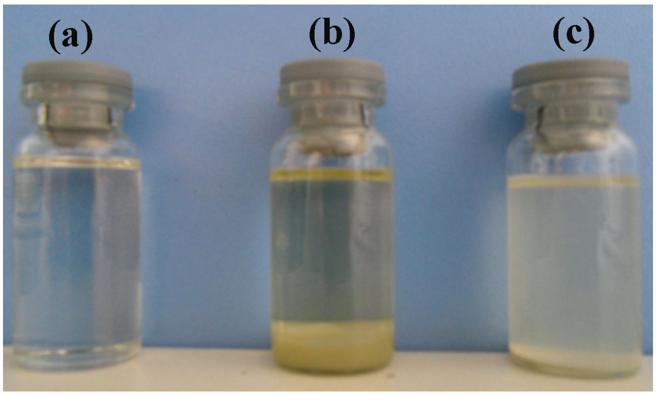

Fig. 6. Image of oil-soluble about nano-oil with nanoparticles (a) Base oil (b) Native nanoparticles (c) Modified nanoparticles

Friction test: Fig. 7 showed friction coefficient changes with the concentration fraction of ZnO nanoparticles sol in lubricant oil. The friction coefficient decreased with the ZnO nanoparticles sol concentration increased when the concentration was smaller than 1.5 wt %. However, the friction coefficient began to increase when the additive concentration was bigger than 1.5 wt % (Fig. 7). So, only when the amounts of nanoparticles were added in an optimal concentration range, the friction-reducing effect is better. For ZnO nanoparticles sol, the friction-reducing effect was more effective at the adding concentration of 1.5 wt % with an average friction coefficient decreasing of 8.42 %. The influence of the nanoparticles adding concentration in lubricating oil on its friction properties was discussed in previous work[19,20].

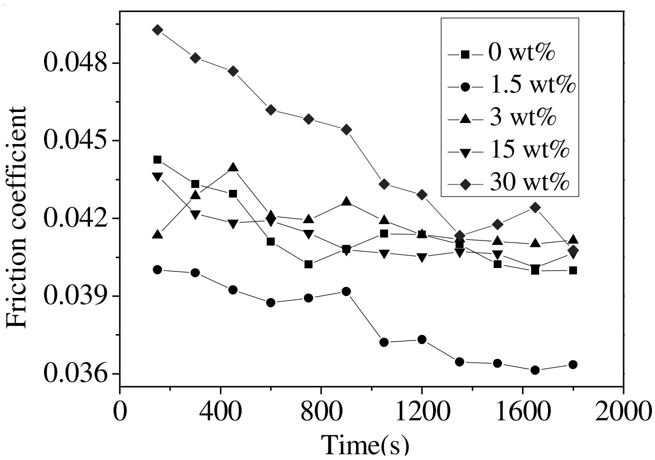

Fig. 7. Friction coefficient variation with times for lubricating oil with different concentration of nanoparticles sol

Conclusion

In this paper, the preparation of ZnO nanoparticles is finished by a non-hydrolytic sol method in one-step. It was found that the dispersion of ZnO nanoparticles was very homogeneous and it shows good stability in the lubricating oil. Then the prepared ZnO nanoparticles sol was added into the lubricating oil. Under an optimized concentration of 1.5 wt %, the average friction coefficient was reduced by 8.42 %.

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