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Preparation and Surface Modification of ZnO/Al_2O_3 Nanocomposites

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In this work, the ZnO/Al_2O_3 nanocomposites are prepared by *situ*-modified method and the ZnO/Al_2O_3 nanocomposites are modified by silane coupling agent. By using the particle size analysis, it is confirmed that the mean particle size of modified ZnO/Al_2O_3 nanocomposites is 68 nm and its distribution is uniform. The dispersion of modified ZnO/Al_2O_3 nanocomposites is analyzed by the absolute value of ZnO/Al_2O_3 nanocomposites zeta potential. Through scanning electron microscope studies, it is found that the silane coupling agent improve the dispersibility of ZnO/Al_2O_3 nanocomposites. The hydroxyl groups on the surface of ZnO/Al_2O_3 nanocomposites can interact with hydroxyl groups of silane coupling agent and an organic coating layer is formed. The formed covalent bands are testified by Fourier transform infrared spectra (FT-IR). The dispersion stabilization of modified ZnO/Al_2O_3 nanocomposites is significantly improved due to the introduction of grafted polymers on the surface of nanoparticles. In addition, their surfaces become organic phase from inorganic phase.

Key Words: Preparation, Surface modification: ZnO/Al_2O_3 nanocomposites, Lubricants.

INTRODUCTION

Nanoparticles with functional properties have been extensively used in a wide range of bioapplications[1,2]: for example, drug and gene delivery, cell and tissue engineering and medical imaging, for diagnostic and therapeutic purposes. Nanoparticles as lubricating oil additives are one of the most important researches. It is reported that when some nanoparticles were added into the lubricating oil, their lubrication properties can be effectively improved[3-6]. Ming *et al.*[7] reported that using $CaCO_3$ nanoparticles as PAO base oil additives can dramatically improve the load-carrying capacity, as well as the antiwear and friction-reduction properties of PAO base oil. In addition, higher applied load, moderate frequency, longer duration time and lower temperatures were beneficial to the deposition of $CaCO_3$ nanoparticles accumulating on rubbing surfaces. It is also found that there are different interactions when two or more nanoparticles lubricant additives are added, such as adduct effect, synergy and antagonism effects[8]. In previous papers[9,10], we have reported the tribology properties of two oxide nanoparticles used as an additive for lubricating oil and found that it exhibit good lubrication performance.

But nanoparticles have a strong tendency to agglomerate due to its high surface energy and have weak combination with the polymer matrix because of badly consistent interface[11,12]. So the surface modification of nanoparticles is a difficult task. The crux lies in the fact how to well disperse inorganic nanoparticles in lubricating oil and how to improve their interfacial interaction. This has been the critical procedure to prepare high-performance nanocomposites.

In this paper, ZnO/Al_2O_3 nanocomposites were prepared with *situ*-modified method and surface was modified by silane coupling agent. Such modified ZnO/Al_2O_3 nanocomposites showed good dispersion stability in lubricating oil. The dispersion of modified ZnO/Al_2O_3 nanocomposites as well as the mechanism of stable colloidal dispersion was discussed in lubricating oil, whose polar is quite low. The using efficiency of silane coupling agent as a modifier was also studied.

EXPERIMENTAL

Superficial modification of ZnO/Al_2O_3 nanocomposites: For clarity, the experimental method was described with seven steps as follows. (1) 15 g of aluminum vitriolic was dissolved in alcohol (95 %, 60 mL) and then 1 g polyethylene glycol was added (solution A). (2) The pH value of solution A was adjusted at 8-10 by ammonia water dropping and then the Al_2O_3 precursor was prepared. (3) 13 g of zinc nitrate was dissolved in alcohol (95 %, 40 mL) and then 1 g polyethylene glycol was added (solution B). (4) The pH value of solution B was set at 8-10 by ammonia water dropping and then the ZnO precursor was prepared. (5) The Al_2O_3 precursor and ZnO precursor were mixed in a 250 mL beaker to get the ZnO/Al_2O_3 precursor. (6) After the ZnO/Al_2O_3 precursor washed three times with alcohol, 1 g silane coupling agent was added and kept at room temperature for 1.5 h. Fig. 1 is the molecular structure of silane coupling agent after hydrolysis reaction. (7) The ZnO/Al_2O_3 precursor was put into the autoclave and the reaction temperature was set as 240 ºC under a pressure of 4.0 Mpa. The reaction time is 2 h. Finally, the modified ZnO/Al_2O_3 nanocomposites were prepared. Similarly, the unmodified ZnO/Al_2O_3 nanocomposites were prepared without the step 6. 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.

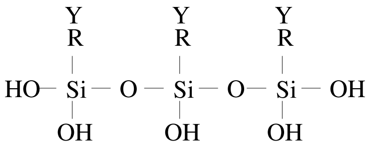
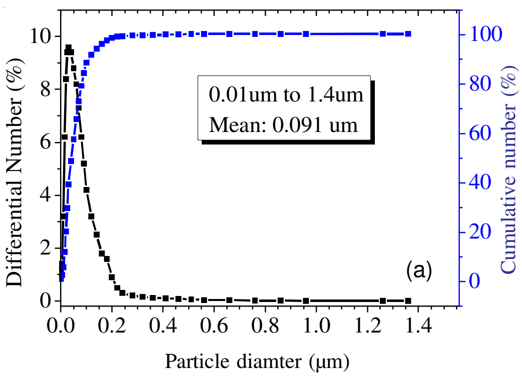


Fig. 1. Molecular structure of silane coupling agent after hydrolysis reaction

Material characterizations: The diameters of ZnO/Al_2O_3 nanocomposites were analyzed by laser particle size analyzer (LS 13320; Beckman Coulter Inc.) and zeta-potential analyzer (Zeta PALS; Phase Analysis Light Scattering;BIC). Through scanning electron micrograph (SEM, Quantafeg 250;FEI) observation, the dispensability of ZnO/Al_2O_3 nanocomposites was investigated. The formation of covalent bands was testified by Fourier transform infrared spectra (FT-IR, FIS-165; DBio-Rod).

RESULTS AND DISCUSSION

Particle size analyses: The ZnO/Al_2O_3 nanocomposites were dispersed into alcohol and measured with a laser particle size analyzer (Fig. 2). The average diameter of native ZnO/Al_2O_3 nanocomposites is 91 nm while that of modified nanoparticles is 68 nm. So, compared with the native particles, the particle size of ZnO/Al_2O_3 nanocomposites modified with silane coupling agent is smaller but more uniform. Because of the formation of new chemical bond between silane coupling agent and ZnO/Al_2O_3 nanocomposites, the interaction among nanoparticles is broken down and the agglomeration controlled effectively.



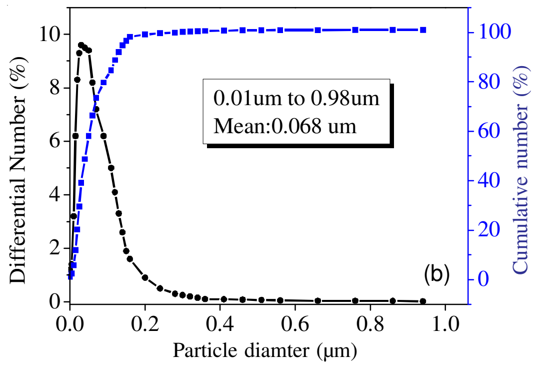


Fig. 2. Particle size distribution of ZnO/Al_2O_3 nanocomposites (a) native ZnO/Al_2O_3 nanocomposites (b) modified ZnO/Al_2O_3 nanocomposites

Decentralized stability analysis: Zeta potential absolute value of nanoparticles were measured six times and then averaged to ensure the data accuracy. The zeta potential absolute value of ZnO/Al_2O_3 nanocomposites is shown in Table-1. The zeta potential value is bigger, the nanoparticles agglomeration is slighter. As shown in Table-1, the zeta potential absolute value of modified ZnO/Al_2O_3 nanocomposites is bigger than native ZnO/Al_2O_3 nanocomposites. These indicate that static repellency of modified ZnO/Al_2O_3 nanocomposites becomes stronger than native ZnO/Al_2O_3 nanocomposites, which means the dispersibility of modified ZnO/Al_2O_3 nanocomposites is better than native ZnO/Al_2O_3 nanocomposites.

TABLE-1
ABSOLUTE VALUE OF ZnO/Al_2O_3
NANOCOMPOSITES ZETA POTENTIAL

Number	1	2	3	4	5	6	Mean
Native nanoparticle (mV)	5.9	5.5	5.4	5.6	5.5	5.8	5.6
Modified nanoparticle (mV)	8.1	8.2	7.8	7.9	8	8.2	8.0

SEM analysis: In order to represent detailed morphological information of the specimens, the SEM images of native ZnO/Al_2O_3 nanocomposites and modified ZnO/Al_2O_3 nanocomposites were shown in Fig. 3. The obvious agglomeration can be seen in the images of native ZnO/Al_2O_3 nanocomposites (Fig. 3a) and the dispersion of modified ZnO/Al_2O_3 nanocomposites was found to be more homogeneous (Fig. 2b). The reason is that silane coupling agent layers were coated on the surface of ZnO/Al_2O_3 nanocomposites. This indicates that chemical bonding or physical bonding occurs between the polarity bonds of silane coupling agent and hydroxide group. The macromolecular chains grafted on the surface of ZnO/Al_2O_3 nanocomposites bring mutual exclusion and steric hindrance effect, thus the surface free energy has been reduced correspondingly and the agglomeration is controlled.

FT-IR analysis: Fig. 4 shows typical FT-IR spectra of native ZnO/Al_2O_3 nanocomposites and the modified ZnO/Al_2O_3 nanocomposites, respectively. For the FT-IR spectra of modified ZnO/Al_2O_3 nanocomposites, the absorption peak at 2160 cm^{-1} corresponds to the alkynes group. At the same time, the peak near 2376 cm^{-1} corresponds to the TBDMS of silane coupling agent. This is due to the hydroxyl groups (-OH) from ZnO/Al_2O_3 nanocomposites interacted with silane coupling agent to form complex on the surface of ZnO/Al_2O_3 nanocomposites.

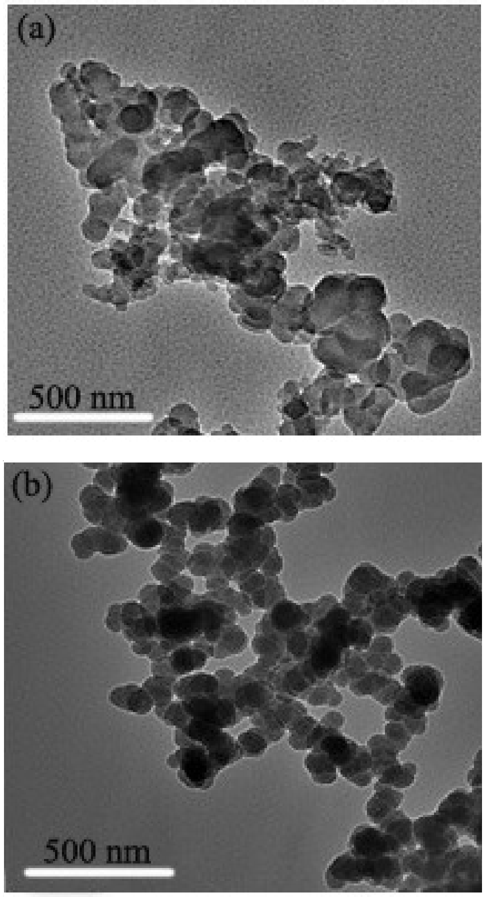


Fig. 3. SEM images of ZnO/Al_2O_3 nanocomposites (a) native (b) modified

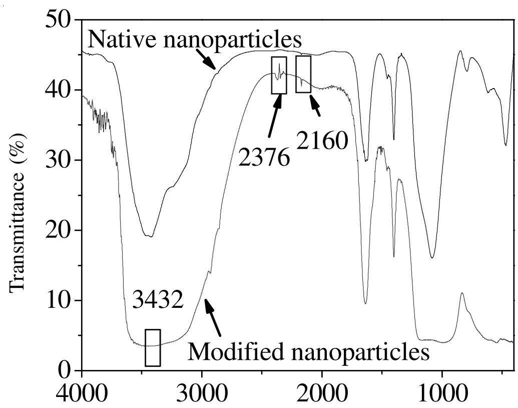


Fig. 4. Infrared spectrum of ZnO/Al_2O_3 nanocomposites

Oil-soluble analysis: The ZnO/Al_2O_3 nanocomposites are added into lubricating oil to form the nano-oil and then the nano-oil is put aside at room temperature for 56 h. The image of oil-soluble about nano-oil with nanoparticles is shown in Fig. 5. As can be seen from Fig. 5, native ZrO_2/SiO_2 nanoparticles are insoluble in oil. However, the modified ZrO_2/SiO_2 nanoparticles are soluble in oil. This because that the surface of nanoparticles changed from inorganic phase to organic phase.

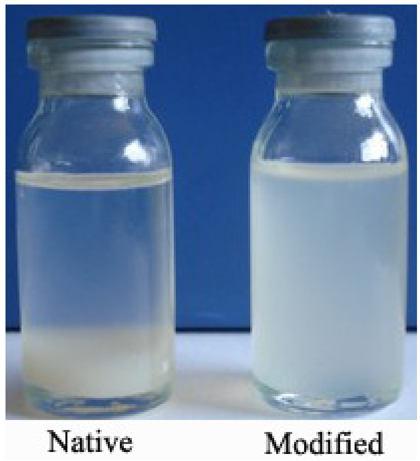


Fig. 5. Image of oil-soluble about nano-oil with nanoparticles

The hydroxyl groups (-OH) from ZnO/Al_2O_3 nanocomposites can interacted with hydroxyl groups from silane coupling agent to form complex on the surface of ZnO/Al_2O_3 nanocomposites. Consequently, no matter what reaction occurred, the graft copolymers are initially grafted or anchored on the surface of the particles at one or several spots. The other terminal of silane coupling agent is organic polymer chain, which fulfills steric hindrance between inorganic nanoparticles. All above factors give rise to the homogeneous dispersion of ZnO/Al_2O_3 nanocomposites in lubricating oil and maintain a stable colloidal dispersion for a long time. We can more intuitionistic see from Fig. 5. They are the photographs of dispersion stabilized of ZnO/Al_2O_3 nanocomposites in lubricating oil with time.

Conclusion

ZnO/Al_2O_3 nanocomposites are modified by silane coupling agent. The results show that the silane coupling agent has been anchored on the surface of ZnO/Al_2O_3 nanocomposites, the modified ZnO/Al_2O_3 nanocomposites present a more stable colloidal dispersion in lubricating oil than that of native ZnO/Al_2O_3 nanocomposites.

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