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Synthesis and characterization of DDP-coated PbO nanoparticles

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Di-*n*-hexadecyldithiophosphate (DDP) coated PbO nanoparticles have been chemically synthesized and characterized using infrared spectroscopy (IR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). The antiwear ability of the DDP-coated PbO nanoparticles as an additive in liquid paraffin was evaluated on a four-ball machine. Results show that DDP-coated PbO nanoparticles, with an average diameter of about 5 nm, are able to prevent water adsorption and are capable of being dispersed stably in organic solvents or mineral oil. Thermal stability of DDP coating on PbO nanoparticles is superior to that of pyridinium di-*n*-hexadecyldithiophosphate (PyDDP). Meanwhile, DDP-coated PbO nanoparticles can improve the antiwear ability of liquid paraffin even at an extremely low concentration.

Introduction

Nano-sized particles have received considerable attention in recent years because of their special physical and chemical properties. Research has been focused on preparing nanoparticles and evaluating their properties recently.[1–5] However, relatively limited attention has been paid to their tribological properties, especially as additives in lubricating oils. The insolubility and dispersion difficulties of inorganic powders limit their applications in lubricating oils. Hence, research in this area is urgently needed to resolve these difficulties. The above problems could be resolved by using some special preparation technique, for example, preparation of the nanoparticles using a surface modifications method.[6–9] If the surface modification agents are high-weight hydrocarbons, the nanoparticles thus prepared will have good dispersion capacity in lubrication oils.

Zinc dialkyldithiophosphate (ZDDP) is a commonly used oil additive for its good antiwear ability. Hoping that the prepared coated nanoparticles may also exhibit good antiwear ability as oil additives, we choose DDP as the modification agent. This paper deals with the preparation process of DDP-coated PbO nanoparticles, and the characterization of the prepared product with a variety of methods including infrared spectroscopy (IR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). The antiwear properties of DDP-coated PbO nanoparticles as an additive in liquid paraffin are also studied on a four-ball machine.

Experimental

Synthesis of PbO nanoparticles

Analytically pure lead acetate [$Pb(Ac)_2{\cdot}3H_2O$] and aqueous ammonia ($NH_3{\cdot}H_2O$) were used as the raw materials for synthesis. Pyridinium di-*n*-hexadecyldithiophosphate (PyDDP) as modification agent was synthesized according to the literature.[10] Its structure is shown in Fig. 1a. Analytically pure ethanol and distilled water were used as solvents.

The main preparation process was as follows. 0.66 g (1 mmol) PyDDP crystals were added to 150 ml of an ethanol–water mixed solvent, and the mixture was heated to 328 K with stirring. After PyDDP was completely dissolved, an excess of $NH_3{\cdot}H_2O$ was added, and finally a solution of 0.38 g (1 mmol) $Pb(Ac)_2{\cdot}3H_2O$ in distilled water was added dropwise, upon which a white precipitate appeared immediately. Three hours after the precipitate was formed, it was filtered and washed before being dried in a degassed desiccator. This the final product, the white powder obtained, was the expected DDP-coated PbO nanoparticles. PbO nanoparticles without surface modification were prepared by the same procedure, except that no PyDDP was added.

Dispersion capacity

The prepared DDP-coated PbO nanoparticles could be dispersed in several organic solvents, including chloroform, benzene, toluene, and liquid paraffin (bp > 573 K), whereas bare PbO nanoparticles cannot be dispersed in these solvents. It

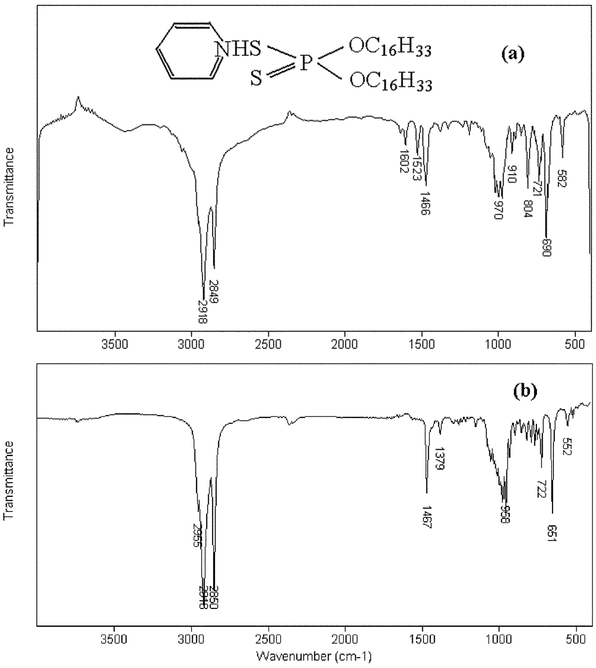

Fig. 1 IR spectra of (a) PyDDP and (b) DDP-coated PbO nanoparticles.

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is therefore concluded that after surface modification with DDP, the dispersion capability of nano-sized PbO is improved. The improvement in the dispersion capability enables the DDP-coated PbO nanoparticles to be used as an additive in lubricating oils.

Characterization

IR spectra were taken on a Bio-Rad FTS-165 IR spectrometer, which operated from 4000 to 500 cm^{-1}, to characterize the structure of the PbO nanoparticle surface. Elemental analyses (EA) were conducted on an Italian 1106 elemental analyzer. A JEM-1200 EX/S transmission electron microscope was used to examine the morphology and size of PbO nanoparticles. XPS analysis was performed on a PHI-5702 photoelectron spectrometer using a pass energy of 29.35 eV and a MgKα line excitation source with the reference of C 1s at 284.6 eV. Because a monochromator was used, the resolution for binding energy reached 0.3 eV. TGA was conducted in a nitrogen atmosphere on a Perkin-Elmer TGA-7 at a scanning rate of 10 K min^{-1}.

The antiwear ability of DDP-coated PbO nanoparticles as an additive in liquid paraffin was evaluated on a four-ball machine under a rotating speed of 1450 rpm at ambient conditions, and the test duration was 30 min.

Results and discussion

Fig. 1 shows the IR transmission spectra of PyDDP, and DDP-coated PbO nanoparticles, respectively. The structure of the modification agent PyDDP is also shown in Fig. 1a. The band assignments of IR spectra are listed in Table 1. Characteristics of PyDDP related to the long alkyl chain and the double bond between the P atom and the S atom can be clearly seen. In Fig. 1a, the spectrum reveals the C–H stretching vibration bands at around 2900 cm^{-1}, the C–H bend modes at 1466 cm^{-1}, and the relatively weak methylene rocking vibration at 721 cm^{-1}. The vibration at 721 cm^{-1} is characteristic of a minimum of four methylene groups, $(CH_2)_{n\,>\,4}$, in a row and assigned to the methylene rocking vibration.[11] So it is concluded that the long alkyl chain does exist in PyDDP. The sharp peak at 804 cm^{-1} in Fig. 1a corresponds to the P=S stretching band.[12] This result indicates that the phosphorus atom is double-bonded to the sulfur atom in PyDDP. The broad P–O–CH$_2$ vibration peak at 920–980 cm^{-1}, and the ring structure vibrations of pyridine[13] at 1602 and 1523 cm^{-1} all support the structure of PyDDP. The EA results for PyDDP shown in Table 2 are in good agreement with theoretical values. In combination with the results of IR analyses, it can be concluded that the modification agent PyDDP was successfully prepared in this work. After the modification reaction, as shown in Fig. 1b, the IR transmission spectrum of DDP-coated PbO nanoparticles displays marked changes from what is shown in Fig. 1a. The most obvious changes are the disappearance of the P=S stretching vibration at 804 cm^{-1}, the disappearance of the ring structure vibrations at 1602 and 1523 cm^{-1} and the shifting of wavenumber from 690 to 651 cm^{-1}. The disappearance of the peak at 804 cm^{-1} after the modification agent PyDDP reacted with PbO nanoparticles (comparing spectra 1a and 1b) gives strong evidence that the phosphorus atom is not double-bonded to the sulfur atom any more. In other words, a chemical reaction occurred between the polar radical in the PyDDP molecule and the Pb moiety during the synthesis process of DDP-coated PbO nanoparticles. The disappearance of the peaks at 1602 and 1523 cm^{-1}, which are assigned to the ring structure vibration, lead to the conclusion that the pyridine ring does not exist in the DDP-coated PbO nanoparticles. The sharp peaks of C–H vibrations at 2900, 1467, and 722 cm^{-1}, and the broad peak of P–O–CH$_2$ at 920–980 cm^{-1}, which are observed in both PyDDP (Fig. 1a) and DDP-coated PbO nanoparticles (Fig. 1b), indicate that the long alkyl chain in the backbone of DDP did not dissociate after the reaction of PyDDP with PbO nanoparticles. The shifting of wavenumber from 690 to 651 cm^{-1} can be related to the conjugate structure between DDP and the Pb moiety on the surface. No peak near 3400 cm^{-1} is found in Fig. 1b, indicating that the surface modification layer can effectively prevent the adsorption of water on the surface of PbO nanoparticles.

Table 1 Assignments of the IR peaks shown in Fig. 1

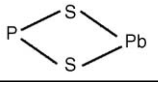
Peak position/cm^{-1}	Assignment
2918, 2850	C–H stretching vibration
1602, 1523	C=C and C=N in plane vibration (ring structure vibration)
1466	C–H bending vibration
ca. 920–980	P–O–CH$_2$ stretching vibration
804	P=S stretching vibration
721	$(CH_2)_{n\,>\,4}$ rocking vibration
690	P–S vibration
650	 vibration

Table 2 Elemental analysis of PyDDP

		Found (Calc.) (%)		
Sample	Chemical formula	C	H	N
PyDDP	$(C_{16}H_{33}O)_2PSSHNC_5H_5$	67.16 (67.53)	10.03 (11.03)	2.19 (2.13)

Fig. 2 shows the TEM images of non-coated PbO nanoparticles and DDP-coated PbO nanoparticles. It is found that non-coated PbO nanoparticles tend to agglomerate and that they are rod-shaped owing to the high surface energy of the nanoparticles.[1,2] Inversely, DDP-coated PbO nanoparticles distribute uniformly and have an average diameter of *ca.* 5 nm. This indicates that the existence of the surface modification layer effectively prevents agglomeration among PbO nanoparticles and leads to the formation of very fine nanoparticles.

XPS is very sensitive to the chemical composition and environment of the elements in a material, so it was used to evaluate the chemical composition of the prepared PbO nanoparticles. The XPS spectra of DDP-coated PbO nanoparticles are shown in Fig. 3. Because there are a large number of CH$_2$ groups in the nanoparticles, the binding energy of C 1s in polyethylene at 284.6 eV is used as the reference. The XPS analysis results of DDP-coated PbO nanoparticles show that the binding energy of Pb4f7/2 is at 138.8 eV, and O1s at 531.9 eV illustrates the existence of PbO.[14]

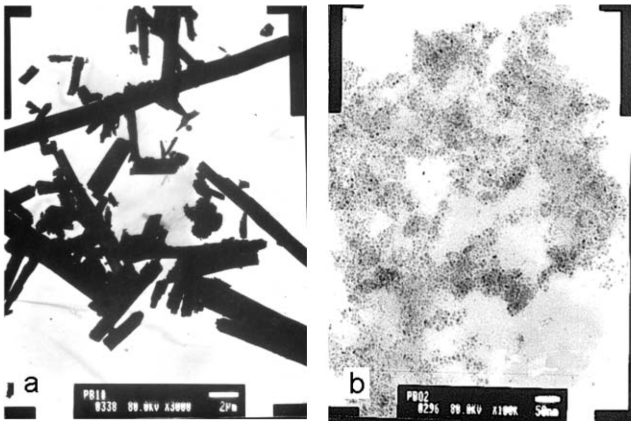


Fig. 2 TEM images of (a) non-coated PbO nanoparticles (× 3000) and (b) DDP-coated PbO nanoparticles (× 100 000).

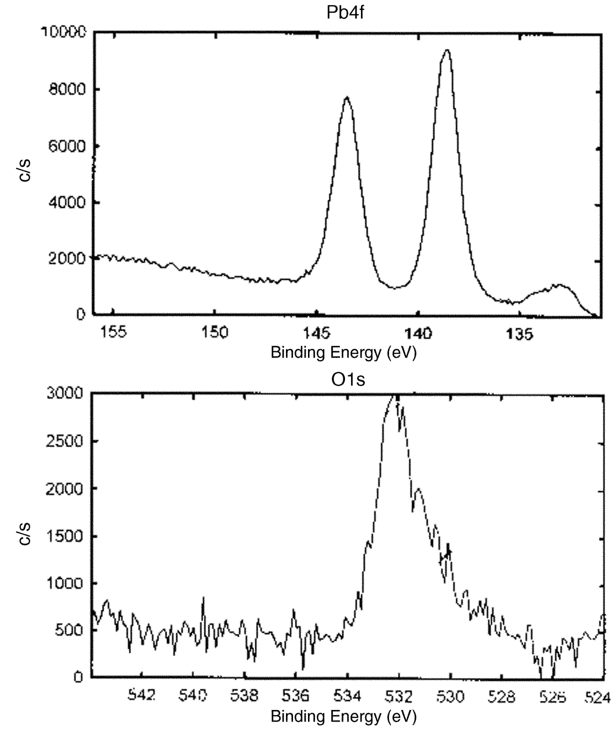


Fig. 3 XPS spectra of DDP-coated PbO nanoparticles.

Fig. 4 shows the TGA curves of (a) PyDDP and (b) DDP-coated PbO nanoparticles. It is found that PyDDP loses weight at 385 and 523 K, relating to the loss of the adsorbed water and the decomposition of the compound, respectively. On the other hand, Fig. 4b shows that DDP-coated PbO nanoparticles begin to lose weight at 548 K and suffer no weight loss at a temperature lower than 473 K. This result indicates that DDP-coated PbO nanoparticles have no surface-adsorbed water (having been confirmed in the IR analysis in Fig. 1b). Comparing the decomposition temperatures of PyDDP and the DDP coating on the PbO nanoparticles, it is seen that the latter possesses a higher decomposition temperature (*ca.* 548 K) than the former (*ca.* 523 K). It is therefore concluded that the existence of the surface modification layer could prevent the adsorption of water on the surface of the coated nanoparticles and could improve the thermal stability of the modification layer. The results of the TGA experiments also confirm that DDP attaches to the surface of the PbO nanoparticles by chemical bond, not by surface adsorption. This has also been proved by the IR analyses.

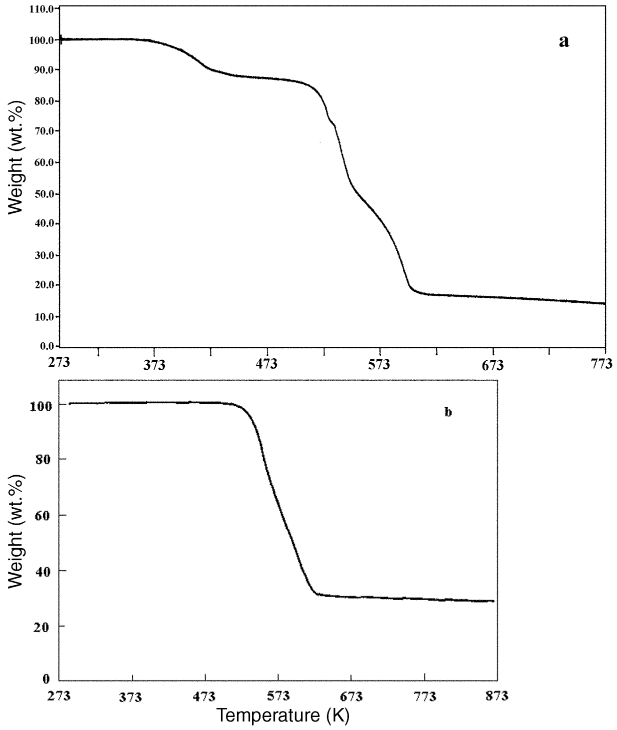


Fig. 4 TGA curve of (a) PyDDP and (b) DDP-coated PbO nanoparticles.

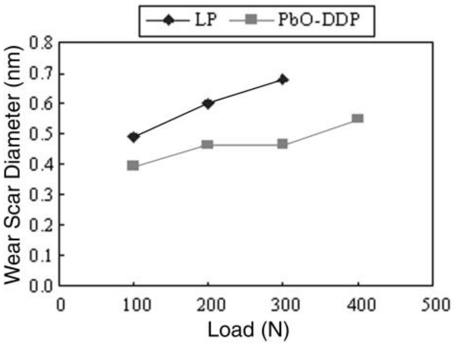


Fig. 5 Wear scar diameter as a function of applied load with the lubrication of liquid paraffin alone and that containing 0.05 wt.% DDP-coated PbO nanoparticles (four-ball machine, 1450 rpm, 30 min).

Fig. 5 shows the variation of wear scar diameter with different loads for liquid paraffin alone and for liquid paraffin containing 0.05 wt.% DDP-coated PbO nanoparticles. With liquid paraffin alone, the wear scar diameter is relatively large, and at a load higher than 300 N, scuffing took place. On the contrary, the wear scar diameter is smaller with lubrication of liquid paraffin containing 0.05 wt.% DDP-coated PbO nanoparticles, especially at higher loads, which exhibits the higher load-carrying capacity and good antiwear ability as compared with liquid paraffin alone.

Conclusions

DDP-coated PbO nanoparticles were successfully prepared by a chemical surface modification method. The synthesized nanoparticles could be well dispersed in several organic solvents and in liquid paraffin, which enabled the synthesized particles to be used as additives in lubricating oils. Because of the existence of the DDP coating on the surface of the PbO nanoparticles, water adsorption and agglomeration of nanoparticles were effectively prevented. DDP reacted chemically with PbO nanoparticles, which enhanced the thermal stability of the DDP coating. DDP-coated PbO nanoparticles used as an additive in liquid paraffin could effectively improve the antiwear properties of the base oil at low concentration.

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