Applied Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Preparation of surface–modified lanthanum fluoride–graphene oxide nanohybrids and evaluation of their tribological properties as lubricant additive in liquid paraffin

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ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form 6 November 2015
Accepted 6 November 2015
Available online xxx

Keywords:
Surface modification
Lanthanum trifluoride
Graphene oxide
Nanohybrids
Tribological properties

ABSTRACT

Oleic acid surface–modified Lanthanum trifluoride–graphene oxide (OA–LaF_3–GO) nanohybrids were successfully prepared by surface modification technology. The morphology and phase structure of as-prepared samples were analyzed by means of X-ray diffraction and transmission electron microscopy, Fourier transform infrared spectrometry, Raman spectrometry and thermogravimetry. The results revealed that OA were bonded onto the surface of LaF_3–GO nanohybrids. Subsequently, the tribological properties of OA–LaF_3–GO nanohybrids as lubricant additive in liquid paraffin were evaluated with a four-ball machine, and the morphology and elemental composition of worn steel surfaces were examined on a scanning electron microscope with an energy dispersive spectrometer. Tribological results showed that OA–LaF_3–GO nanohybrids had excellent friction reduction and antiwear ability at the loading of 0.5 wt.% OA–LaF_3–GO nanohybrids, compared to liquid paraffin alone. The results of energy dispersive spectrometer revealed that improved tribological properties resulted from OA–LaF_3–GO could transfer to the rubbed steel surface and decompose to form protective layers, which help to improve tribological properties.

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1. Introduction

Conservation of materials and energy is becoming a very important global issue. There are increasingly stringent regulations to reduce energy consumption and avoid energy loss. However, energy loss in passenger cars is estimated to be 28% of the fuel energy to overcome friction in the engine, transmission, tires, and brakes [1]. Thus, a number of attempts have been made to introduce various kinds of methods to overcome friction. As it is well known, lubrication is one of the most effective approaches to reduce friction and wear, which mostly affected by lubricating additive. Nowadays, there has been growing concern about the use of nanomaterials as lubricating additive to improve tribological properties of lubrication due to their special properties [2–5].

Recently with the discovery of graphene, some remarkable progresses have been made in the development of graphene materials and it has attracted considerable attention because of their excellent properties [6–9]. These excellent properties of graphene enable it become bright prospects in various applications for many fields, e.g., field effect devices, transparent electrodes, practical sensors, solar cells, nanocomposites, etc [10,11]. Besides, graphene has been found to have outstanding tribological properties and it has been considered as an excellent candidate for reducing friction, adhesion, and wear [12–15]. For instance, Ou et al. found that reduced graphene oxide obtains a good friction reduction and antiwear ability on silicon wafers [14]; Lin et al. pointed out that the tribological behavior of the lubricating oil was greatly improved only with 0.075 wt.% of modified graphene nanosheets [15]. Very recently, many efforts have been making to achieve the fabrication of various graphene-based composites as additives in tribology in aspect of synergistic effects of two or more components, which may produce excellent tribological properties [16–21]. For example, Song et al. investigated the tribological behaviors of a-Fe_2O_3 nanorod/GO composites, the result showed that a-Fe_2O_3 nanorod/GO composites possessed good antiwear and friction reduction properties as well as load-carrying capacity [20]; Li et al. synthesized $MoSe_2$/reduced graphene oxide composites and use as oil-based additives, which improve the friction reduction and antiwear properties in comparison with the oil mixed with $MoSe_2$ nanoflowers and pure paraffin oil [21]. Therefore, graphene-based composites have great potential as lubricant additives and are worth carrying out further study.

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http://dx.doi.org/10.1016/j.apsusc.2015.11.067
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Please cite this article in press as: C. Yang, et al., Preparation of surface–modified lanthanum fluoride–graphene oxide nanohybrids and evaluation of their tribological properties as lubricant additive in liquid paraffin, Appl. Surf. Sci. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.11.067

In our previous study, we revealed that LaF_3–GO nanohybrids can effectively improve the tribological properties of distilled water based on the synergistic effect of LaF_3 and GO [22]. However, LaF_3–GO nanohybrids have poor dispersion and stability in base oil which have restrained their wide application. To address this shortcoming, surface modification is necessary to improve the dispersion and control the interfacial structure [4,5]. To our best knowledge, there are various surface modifiers, such as sodium dodecyl benzene sulfonate, stearic acid, dodecyl trimethyl ammonium chloride, oleic acid(OA), sorbitan monooleate, as well as polysorbate and others. Considering that sulfur-containing modifiers may cause environmental pollution and do bad to the engine. we choose OA as the modifier to surface modify LaF_3–GO nanohybrids because OA provides low friction, low wear and is also friendly to the environment. If that can be accomplished, then it may be possible to obtain uniform dispersion as a result of the similarity and intermiscibility of OA and base oil.

In this study, the LaF_3–GO nanohybrids capped with OA were successfully synthesized by a simple chemical method. Subsequently, we used the as-synthesized OA–LaF_3–GO composites as paraffin oil additive for lubrication to evaluate its tribological properties.

2. Experimental

2.1. Materials

Ammonium fluoride, absolute ethanol, oleic acid were purchased from Tianjin Kermel Chemical Reagent Company (Tianjin, China). Lanthanum nitrate was purchased from Tianjin Institute of Fine Chemicals Retrocession (Tianjin, China). GO nanosheets were prepared through a modified Hummers method [23]. All the reagents used are of analytical purity and used without further purification. Distilled water was used throughout the experiment.

2.2. Preparation of OA–LaF_3–GO nanohybrids

Briefly, Ammonium fluoride and GO nanosheets were added into an water and ethanol mixed solution. Subsequently, lanthanum nitrate solution was dropwise added to the flask at 70 °C. After approximately 3 h, 120 ml absolute ethanol (containing 4 ml oleic acid) was added to the flask. After another 3 h, the products were cooled to ambient temperature and isolated by filtration, repeatedly washed with distilled water and absolute ethanol several times. In the next step, as-prepared products were dried in an air atmosphere at 80 °C for 12 h.

2.3. Apparatus and experimental method

X-ray powder diffraction (XRD) patterns were collected on a X' Pert Pro diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm). Transmission electron microscopy (TEM) images were obtained on a JEM-2010 microscope. Raman scattering spectra were measured with a confocal microscopic Raman spectrometer (RM-1000, Renishaw) using a 632.8 nm laser as the excitation source. Fourier transform infrared (FTIR) spectra were measured on an AVATAR360 FT-IR spectrometer using KBr pellet. Background correction was made using a reference blank KBr pellet. Thermo gravity (TG) and differential thermal analysis (DTA) were conducted on a DSC6200 thermal analyzer at the scanning rate of 10 °C/min in an air flow.

The tribological properties of as-prepared samples as a lubricating additive in liquid paraffin were investigated using a MSR-10A four-ball apparatus made by Jinan Testing Machine Factory (Jinan, China). The friction and wear tests were conducted at a rotary speed of 1450 rev/min and ambient temperature of about 25 °C for 30 min. The friction and wear test under each preset condition was repeated three times so as to minimize data scattering. At the end of each test, the wear scar diameter (WSD) on the three lower balls was measured using an optical microscope with an accuracy of 0.01 mm. The average wear scar diameter of three lower balls is calculated and reported in this paper. The elemental distribution of the boundary film and the morphology of worn steel surfaces were observed on a Nova Nano SEM 450 scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS).

3. Results and discussion

3.1. Analyses of OA–LaF_3–GO nanohybrids

The XRD patterns are shown in Fig. 1, which depicts the crystal structure of GO and OA–LaF_3–GO. For GO, there are two obvious characteristic diffraction peaks of GO. The sharp diffraction peak and the weak peak are assigned to the (0 0 1) and (1 0 0) reflection of GO, respectively. However, as for OA–LaF_3–GO, there are only the diffraction peaks of the hexagonal structure phase of LaF_3 (JCPDS no. 32-0483) and no signal for any other phases of GO. The main reason for the disappearance of diffraction peaks of GO may be the destruction of the regular layer stacking of GO by the crystal growth of LaF_3 between the interlayer of GO. Besides, LaF_3 possessing good crystallinity provides strong reflections to cover the GO signal in OA–LaF_3–GO nanohybrids was another reason. These results indicate OA–LaF_3–GO nanohybrids were successfully prepared.

To further confirm the structure of OA–LaF_3–GO nanohybrids, Raman scattering and TEM were used to document the existence of GO in OA–LaF_3–GO nanohybrids, and TEM was also used to observe the morphology of OA–LaF_3–GO nanohybrids. Fig. 2a exhibits Raman spectra of OA–LaF_3–GO nanohybrids and GO nanosheets. It is clear that both samples possess two obvious Raman featured peaks, D band (1350 cm^{-1}) and G band (1576 cm^{-1}) of GO, indicating there is the existence of GO in the structure of the OA–LaF_3–GO nanohybrids. Fig. 2b shows a typical TEM image of GO nanosheets, which presents highly transparent films. TEM image (Fig. 2c) of OA–LaF_3–GO nanohybrids reveal that LaF_3 nanoparticles combined on the surface of GO nanosheets formed the structure of the LaF_3–GO nanohybrids.

FTIR was used to reveal whether OA modified on the surface of LaF_3–GO nanohybrids. FTIR spectra of OA–LaF_3–GO nanohybrids and GO nanosheets are shown in Fig. 3. GO shows a peak around 1622 cm^{-1} and it corresponds to the C=C vibration, the one at 1395 cm^{-1} is assigned to the tertiary C—OH group, and those at 1261 cm^{-1} and 1067 cm^{-1} are attributed to the C—O stretching vibrations of —COOH and C—OH groups situated at the edges of the GO nanosheets. As for OA–LaF_3–GO nanohybrids, it retains the stretching vibration bands of the —COOH and C—OH groups at the edges of GO nanosheets, and it exhibits an additional stretching vibration band of a La—F bond around 546 cm^{-1}. Furthermore, the absorption peak of OA–LaF_3–GO nanohybrids at 2924 cm^{-1} and 2853 cm^{-1} are features of CH_2 and CH_3 groups, suggesting the presence of long alkyl chains in the OA–LaF_3–GO nanohybrids. Besides, the band at 1709 cm^{-1} corresponds to the functional group C=O and the bands below 1500 cm^{-1} come from the group C—H. All these results indicate that OA modified on the surface of LaF_3–GO nanohybrids. Combined with the XRD, Raman and TEM results of OA–LaF_3–GO nanohybrids, this further proves that OA–LaF_3–GO nanohybrids were successfully prepared.

TG curves of OA–LaF_3–GO nanohybrids, LaF_3–GO nanohybrids and GO nanosheets are shown in Fig. 4. For GO, the mass loss of 6% below 100° C is mainly due to the disappearance of adsorbed water; the main mass loss (32%) at the ranges of 100–300° C is attributed to the decomposition of labile oxygen functional groups; and steady

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