Synthesis and tribological properties of the novel tubular MoS_2/GR nanocomposite

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This study used a simple one-step hydrothermal method to synthesize the MoS_2/GR composites with a new morphology composed of graphene nanotubes and ultra-thin molybdenum disulfide with the help of sodium chloride. The composites were characterized by XRD, XPS, SEM, TEM, and a series of characterization methods. Meanwhile, the tribological properties of the composites were studied. The results show that the addition of 1% MoS_2/GR composite nanotubes has excellent tribological properties. In addition, the structure and excellent tribological properties of MoS_2-C- nanocomposite lubrication materials will be conducive to designing new nanomaterials with 2D/3D structures, enhancing the anti-friction and anti-wear properties, and expanding their practical applications in industrial and agricultural fields.

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1. Introduction

Laminated materials such as graphite and MoS_2 have long been considered the most effective lubricating materials, either as solid wetting materials, coated on solid material surfaces, or as lubricant additives to enhance the performance of lubricants when they are not suitable for use. Graphite has better frictional properties under air conditions and poor lubrication under vacuum or dry conditions. MoS_2, on the other hand, has uniformly better lubrication under air and vacuum conditions, while the friction coefficient is lower under vacuum conditions, which may be due to partial oxidation in humid air[1-4]. Therefore, the development of lubricating materials with better frictional properties is a focus of current tribological research.

Recently, the development of 2D layered materials, especially the increasing maturity of techniques for synthesizing single- or multilayer 2D layered materials, has made the research about their tribological properties a current hot topic[5-9]. Since graphene materials have been successfully prepared, surprisingly, they have many unique electronic and mechanical properties, such as high electron transport rate, high specific surface area, and low friction coefficient. Based on its unique structure and properties, graphene has a broad potential for applications in material compounding, energy storage, electronic components, mechanical devices, and friction and lubrication. Numerous studies have shown that single or multilayer graphene's tribological properties are better than graphite-lubricated materials. Berman et al[10]. investigated the friction and wear properties of graphene-lubricated 440 c steel counter-abrasion under dry N_2 conditions and showed that the addition of graphene significantly reduced the friction coefficient and reduced the wear of 440 c steel discs. Similarly, MoS_2 nanomaterials, especially MoS_2 ultrathin nanosheets can provide good friction and wear reduction. Wu et al[11]. investigated the tribological properties of MoS_2 nanosheets synthesized by microdomain reaction using an MRS-10A four-ball friction tester, and the results showed that the nanosheets can be uniformly dispersed onto the substrate surface and also strongly adhere to the substrate, effectively increasing the tribological properties. Kogovšek et al[12]. studied the tribological properties of different lubricant additives on base oil poly-α-olefin (PAO), here the additives were mainly MoS_2 nanotubes, MoS_2 nanosheets, WS_2 nanotubes, WS_2 fullerene nanoparticles, graphite flakes, and C nanotubes. The results of friction experiments show that MoS_2 nanomaterials have the best tribological properties, especially since the friction coefficient of MoS_2

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nanosheets is slightly lower than that of nanotubes. Therefore, it is of great practical importance to develop a 2D composite lubricating material with a graphene structure, and MoS_2/GR composite nanomaterials have unparalleled advantages in terms of structure and performance.

However, recent studies on graphene and MoS_2 composites have focused more on their energy conversion and storage applications, such as lithium batteries, photocatalytic hydrogen production, solar cells, and supercapacitors. For example, Zhou et al[13]. synthesized graphene-MoS_2 composite nanosheets by liquid-phase embedded lithium exfoliation with a hydrazine hydrate vapor reduction process, and the results showed that graphene-MoS_2 composite nanosheets effectively enhanced the performance of lithium batteries and improved the cycle life (>700) of lithium batteries. At present, there are almost no reports on the tribological properties of MoS_2/GR composite nanomaterials. Therefore, in this chapter, a new tubular structure MoS_2/GR nanocomposite was synthesized by hydrothermal method assisted by sodium chloride, and its tribological properties were studied. Through the tribological property test and wear trace analysis, it can be determined that MoS_2/GR nano-composite has excellent lubrication performance as a solid lubrication additive.

2. Experimental

2.1. Synthesis of MoS_2/GR composite nanomaterials

2.1.1 Preparation of Graphene Oxide (GO)

The GO was prepared by the modified Hummers method with the following experimental procedure: 1 g of graphite powder was dispersed into 25 mL of concentrated sulfuric acid under the condition of an ice bath and stirred continuously for 2 h to make the solution well mixed. The reaction system was then transferred to a water bath at 30 °C, and 50 mL of deionized water was added and stirred magnetically for 0.5 h. After that, 10 mL of 30% hydrogen peroxide was added and stirred for 12 h. The products were separated by centrifugation and washed several times with 5% HCl solution, deionized water, and acetone by mass. The above products were separated by centrifugation, washed several times with 5% HCl solution, deionized water, and acetone, and finally dried under vacuum at 60 °C for 12 h to obtain GO nanosheets.

2.1.2 Preparation of MoS_2/GR nanotubes

The synthesis of MoS_2/GR nanotubes was performed by NaCl-assisted hydrothermal synthesis. The experimental procedure was as follows: 0.1 g of graphite powder prepared was dispersed into 50 mL of deionized water, followed by 0.88 g of Na_2MoO_4, 0.8 g of CH_4N_2S and 0.6 g of NaCl dissolved in the above solution, and the pH of the solution was adjusted to about 2 with 2 mol/L HCl. The above solution was stirred magnetically for 1 h and then transferred to a 100 mL hydrothermal reactor and placed in an oven at 200 °C for 48 h. The reaction was then cooled naturally to room temperature. The black products obtained from the reaction were separated by centrifugation, washed several times with anhydrous ethanol and deionized water, and finally dried at 60 °C for 12 h under a vacuum to obtain the hydrothermal synthesis MoS_2/GR nanotubes.

2.2. Characterization

XRD (Bruker-AXS), XPS (Thermo Scientific K-Alpha+ system)0, SEM (JEOL JXA-840A), and TEM analysis (JEOL JEM-2100) are performed to investigate the phase compositions, chemical states, and microstructure of the as-prepared products.

2.3. Tribological test

The tribological properties of the synthesized samples were determined using the UMT-2 multi-purpose tribometer from CETR, USA. The friction experiment was conducted using ball-disc friction, and the upper specimen was a 440 C stainless steel ball with a diameter of 10 mm and material hardness of HRC 62; the lower specimen was a 45# steel disc with a diameter of Ø40 mm × 3 mm. The improvement effect of MoS_2 nanoparticles as lubricant additives on the friction reduction performance of the base oil was evaluated by testing the friction coefficient of the steel ball-steel disc friction substrate under lubricant flow conditions to assess its friction reduction performance. The mixed oil samples were made by mixing the prepared MoS_2 samples with the base oil in a certain ratio and ultrasonically dispersed for 60 min. The base oil was paraffin, HVI1500, and vegetable oil. The friction and wear conditions were 50-300 rpm, 5-30 N load, and 1 h. The abrasion marks were observed by HITACHI S-3400N electron microscope, and the non-contact optical profiler PS50 of Nanovea, USA, was used to measure the abrasion marks. The three-dimensional profile of the abrasion marks and the width of the abrasion marks were measured by a Nanovea PS50 non-contact optical profiler.

3. Results and discussion

3.1. Characterization of MoS_2/GR nanotubes

The phase composition of MoS_2/GR nanocomposites was determined by an X-ray diffractometer (XRD). Fig. 1 shows the XRD patterns of RGO, MoS_2/GR, and the MoS_2 standard card MoS_2. The XRD diffraction peaks of the synthesized product MoS_2/GR are all consistent with the MoS_2 standard pattern of the hexagonal phase (JCPDS No. 37-1492). The absence of obvious RGO peaks in the plots may be related to the amount of RGO added. This is because the relatively low content in the composites makes them correspond to lower diffraction intensities.

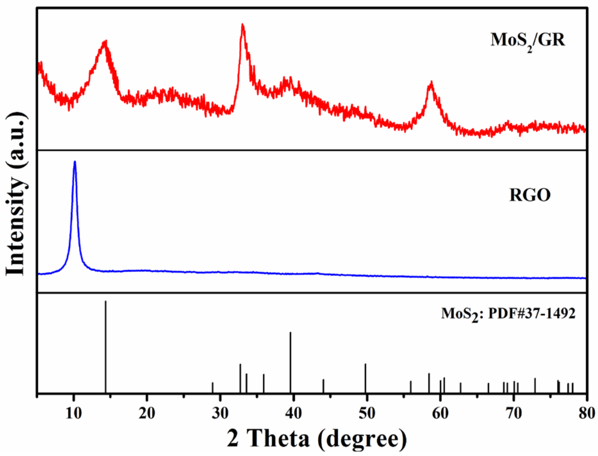

Fig. 1. XRD pattern of the as-prepared MoS_2/GR.

The elements and their valence states in the MoS_2/GR nanocomposites were analyzed by X-ray photoelectron spectroscopy (XPS) (Fig. 2). Fig. 2a shows the full spectrum of the XPS detection of MoS_2/GR, which shows that the synthesized product is mainly composed of Mo, S and C elements, where the molar ratio of Mo and S elements is 1:1.98, which is consistent with the MoS_2 stoichiometric ratio. Fig. 2b shows two stronger characteristic peaks of Mo 3d at 229.3 eV and 232.5 eV, corresponding to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ signal peaks, which are typical of the Mo^{4+} valence state in MoS_2. And the S 2p double peaks are located at 162.1 eV and 163.3 eV (Fig. 2c), corresponding to the S $2p_{3/2}$ and S $2p_{1/2}$ binding energies, respectively, which indicate the presence of the S^{2-} valence state in MoS_2[7]. The above results confirm the presence of MoS_2 in MoS_2/GR nanocomposites. Fig. 3d shows the C 1s spectrum of GO, which can be decomposed into three small peaks corresponding to the C-C bond (284.6 eV), C=O double build (286.8 eV) and O-C-O bond (288.8 eV), while it can be seen that the C=O peak is stronger, indicating the presence of oxygen in GO. On the contrary, the XPS pattern of MoS_2/GR composite nanotubes C 1s showed a significantly lower intensity of the C=O peak of the functional group, indicating that GO was reduced to graphene during the hydrothermal process (Fig. 2e).

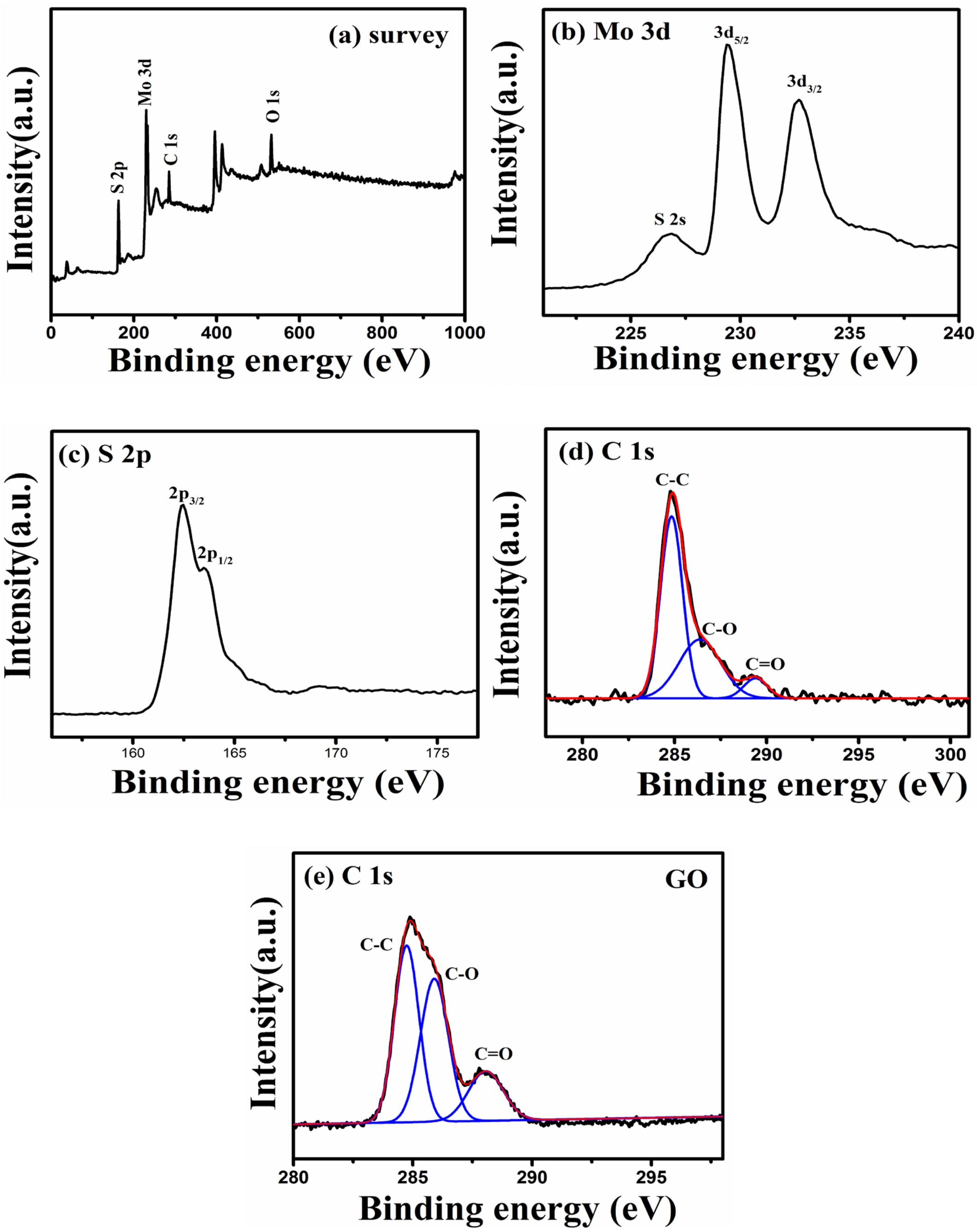

Fig. 2. XPS spectra of MoS_2/GR composite: (a) survey spectrum, (b) Mo 3d, (c) S 2ps, (d) C 1s, and (e) C 1s of GO.

To further determine the structure and morphology of the MoS_2/GR nanocomposites, the prepared MoS_2/GR samples were tested by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 3a shows the SEM images of the sample MoS_2/GR nanotubes, it can be seen that the prepared samples are mainly MoS_2/GR nanotubes of about 1-2 μm in length with very uniform distribution, and the surface of MoS_2/GR nanotubes can be seen to be flower-like structure. Fig. 3b is a high-magnification SEM image, from which it can be seen that the inner diameter of the nanotubes is about 200 nm, and the flower-like structure on the surface is more obvious. Fig. 3c and d show the TEM and HRTEM images of the product MoS_2. Fig. 3c shows the TEM of the surface of MoS_2/GR nanotubes, and irregular nanosheets can be encapsulated on the nanotubes' outer wall. The tubular structure inside the MoS_2/GR nanostructures is probably made of graphene convolutions, and the flower-like nanosheets grown or encapsulated on the surface are MoS_2. Fig. 3d shows the HRTEM image of the nanosheets on the surface of the product, and the lattice spacing of its product can be measured from the Fig. is about 0.63 nm, which is consistent with the theoretical value of the MoS_2 hexagonal structure (002) surface, further indicating that the flower-like nanosheets on the surface of MoS_2/GR nanotubes are MoS_2.

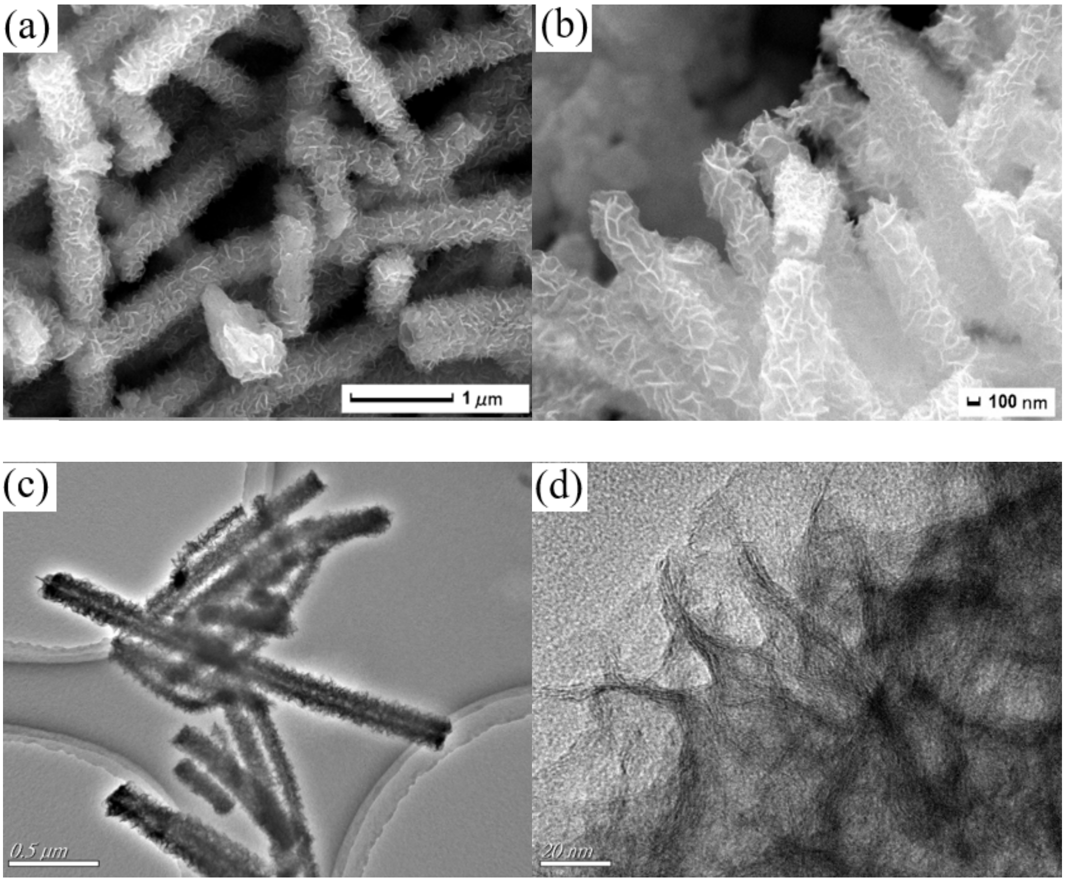

Fig. 3. SEM (a, b) images of the as-prepared MoS_2/GR nanotubes; TEM (c) and HRTEM (d) images of the as-prepared MoS_2/GR nanotubes.

3.2. Tribological properties study

First, we explored the effect of MoS_2/GR addition on the tribological properties of the base oil, specifically, a mixed oil sample was made by adding 0.5%~5% MoS_2/GR heterojunction structure by mass to the base oil paraffin, and its tribological properties were tested on a UMT-2 multi-purpose tribometer under the following experimental conditions. Load 10 N, speed 100 rpm, and the experimental conditions were as follows: load 10 N, speed 100 rpm, time 1 h, and paraffin wax as the base oil. Fig. 4a shows the friction curves of different concentrations with time under the above experimental conditions. From the figure, it can be seen that the friction curves of the base oil increased with time and fluctuated greatly, while the friction coefficients of all the mixed oil samples with MoS_2/GR nanotubes were significantly lower than those of the pure oil, especially the lowest friction coefficient with 1.0 wt% MoS_2/GR nanotubes. Then, we tested pure graphene and MoS_2 under the same friction experimental conditions (Fig. 4b), and the results showed that compared with pure oil, consistent with those reported in the literature, both graphene and MoS_2 as lubricant additives could reduce the friction coefficient of pure oil to some extent, but both were higher than that of MoS_2/GR composite nanotubes. These indicate that the synergistic effect of the composite nanosheet structure formed by MoS_2 and GR can effectively improve the tribological properties of the base oil.

Finally, we examined the pure paraffin oil friction coefficients and the mixed oil samples with 1.0% MoS_2/GR compound nanotubes under the same speed with different loads and the same speed with different loads, respectively. Under the conditions of maintaining the speed of 100 rpm and varying the load friction experiment for 1 h, the friction coefficient of the blended oil sample with 1.0 wt.% MoS_2/GR was lower than that of the pure base oil and more stable under high load, with the friction coefficient ranging from 0.07 to 0.11 (Fig. 4c). Fig. 4d shows the friction coefficients of the pure base oil and the mixed oil samples with 1.0 wt.% MoS_2/GR at constant load (10 N) for 1 h. The friction coefficients of the base oil decreased as the speed increased, while the friction coefficients of the mixed oil samples with MoS_2/GR heterojunction nanoflakes were lower and more stable than those of the pure oil. It further indicates that the addition of MoS_2/GR can effectively improve the tribological performance of base oil.

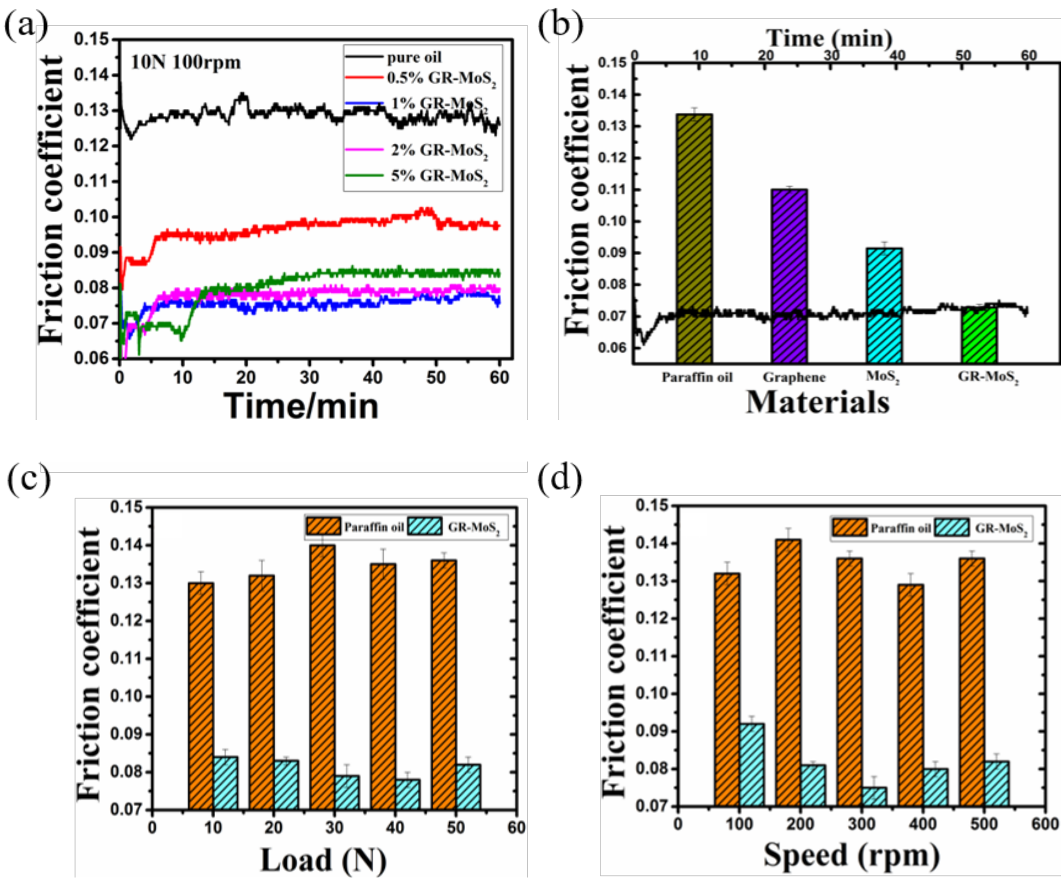

Fig. 4. (a) Friction coefficient curves of the oil with different MoS_2/GR contents (0.5 wt.% ~ 5.0 wt.%) at the speed of 100 r/min; (b) Mean friction coefficients of steel/steel contacts lubricated with paraffin, paraffin with 1% MoS_2, Graphene and MoS_2/GR; Variations of friction coefficient of lubricant with increasing load (c) and under diverse speeds (d).

To further investigate the effect of the addition of MoS_2/GR composite nanotubes on the anti-wear performance of the base oil, we conducted SEM tests on the abrasion marks formed by friction experiments with pure paraffin wax and the addition of 1 wt.% MoS_2/GR composite nanotubes at a speed of 100 rpm and a load of 10 N (Fig. 5a and b). From the SEM image, it can be seen that the abrasion marks of pure base oil (paraffin) are deep and wide, with obvious furrows and scratches, and the wear of the friction substrate on the surface of the steel disc is also large. In contrast, the abrasion marks formed by the sample with MoS_2/GR were shallower and relatively narrower in width than those of the friction experiment with a base oil, the friction surface was smoother and there were no obvious furrows and scratches.

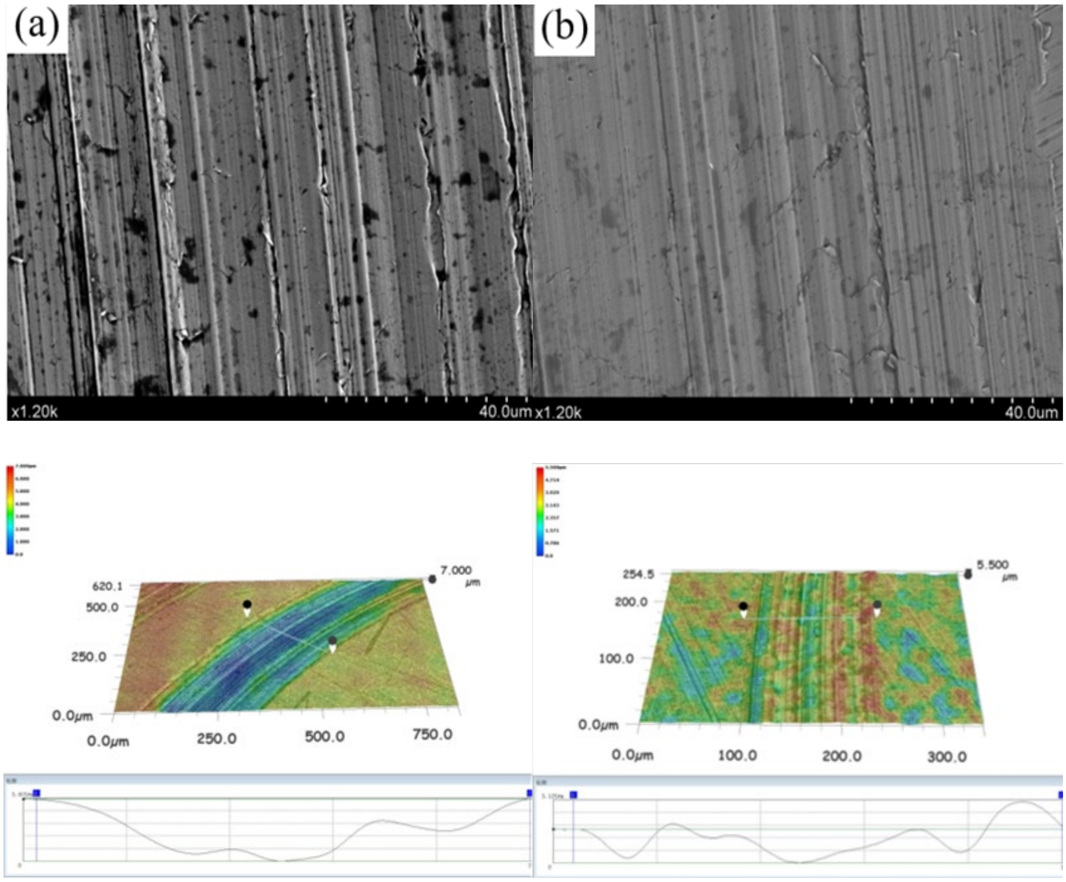

Fig. 5. SEM images of abrasion marks: (a) base oil HVI500, (b) oil blend with 1.0 wt.% MoS_2/GR; Non-contact optical profile testing instrument images of wear scar: (c) Pure base oil, (d) 1 wt% MoS_2/GR nanosheets + base oil.

To more clearly illustrate the effect of the addition of MoS_2/GR nanotubes on the anti-wear performance of the base oil, we tested the wear surface of the experimental friction sub-material (45# steel disc) using a non-contact optical profile tester (VEECO WYKO NT1100), as shown in Fig. 5c and d. The figure clearly shows that the wear marks formed by adding GR-MoS_2 nanotubes are all shallower than those formed by pure oil, which is consistent with the SEM results. From the profilometer analysis graph, we can see that the depth and width of the wear marks of the mixed oil samples with 1.0 wt% MoS_2/GR nanotubes are about 1.67 µm and 139 µm, while the depth and width of the wear marks with pure base oil are about 3.7 µm and 278 µm. Based on the above results and analysis, MoS_2/GR nanotubes as lubricant additives can effectively increase the base oil the anti-wear performance is mainly attributed to the MoS_2/GR nanostructures, and the graphene-curled nanotubes are conducive to the conversion of sliding friction into rolling friction during friction, which is beneficial to the reduction of wear. At the same time, the surface of the tubular structure is a MoS_2 flower-like lamellar structure, which can easily transfer to the surface of abrasion marks with the flow of lubricant and play a certain repairing role, while the lubricating film formed with base oil has a certain bearing effect, so the nanostructures of MoS_2/GR nanotubes can play a synergistic role to further improve the lubricating performance of base oil.

4. Conclusions

In summary, MoS_2/GR composite nanotubes were prepared by sodium chloride-assisted hydrothermal synthesis. We investigated the effects of GO and NaCl concentrations on the products' morphology, and the results showed that the appropriate amounts of GO and NaCl contributed to the formation of MoS_2/GR composite nanotubes. In addition, we investigated the tribological properties of MoS_2/GR composite nanotubes synthesized by hydrothermal method as base oil (paraffin) additives, and the results showed that the friction coefficients of all oil samples mixed with MoS_2/GR composite nanotubes were reduced, especially the oil samples with 1% MoS_2/GR composite nanotubes had better tribological properties. It is shown that the MoS_2/GR composite nanotubes can effectively improve the tribological properties of paraffin and reduce the wear of the material.

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