

Ionic Liquids Based on Chromotropic Acid: Excellent Lubricating Additives for Aqueous System

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Abstract

In this paper, four ionic liquids based on chromotropate (CAILs) were prepared and applied to heighten the tribological performance of aqueous system on different metal friction contacts. Taking for the potential choice for water-based lubricating additive, CAILs exhibited excellent water solubility and corrosion resistance. Tribological results showed that the CAILs, especially the phenolic hydroxyl group decorated samples (TsnN₄₄₄₄ and TsnP₄₄₄₄), demonstrated extremely effective lubricating properties with the efficient friction and wear descent (69% and 83% for Fe, 47% and 94% for Cu, 74% and 69% for Al, respectively). Especially, the excellent load-carrying capacity was also presented with the highest P_B (833N) and P_D (1568N) values for TsnP₄₄₄₄. It is speculated that the CAIL molecular adsorption on the interface and further generation of tribochemical films are beneficial for their lubricating effects. Resulting from the systematic discussion and analysis of CA, QCM, SEM, XPS, and FIB-TEM tests. However, TsnN₄₄₄₄ and TsnP₄₄₄₄ showed less effective lubricating performances and poor load-carrying capacities due to tribocorrosion of hydroxyl groups at the interface.

1. Introduction

Friction is widespread in the world, which will not only cause more accidents, but also consume more energy if it can't be effectively inhibited.[1] Thus, different kinds of lubricants have been used to reduce friction.[2] PBLs are always used to make industrial equipment run orderly, aiming to save energy and avoid accidents. However, many drawbacks are obvious as for PBLs, such as inefficient cooling ability, flammability, poor biodegradability, and severe pollution, etc., which limit their application in many special fields.[3] Therefore, developing novel lubricants to replace PBLs, which can avoid these drawbacks, is still desired.

WBLs have been studied by many researchers in recently years.[4–11] Compared with PBLs, WBLs can avoid the above drawbacks and own many distinctive advantages, such as good thermal conductivity, low price, environmental friendliness, etc., which make them emerge actively in the field of metal cutting fluids.[12–14] However, the viscosity-pressure coefficient of water is very low, so it is hard to shape a useful tribofilm on friction surfaces, resulting in its ineffective lubricating property for most friction contacts. Additionally, the poor carrying capacity of water may also limit its application in many complex industries. Thus, using powerful additives to improve the lubricating performance of water is highly demanded.

ILs have become the research hotspot in lubricating field since they were firstly applied as lubricant by Liu et al. in 2001.[15] A wide range of ILs have been developed and used as lubricants[16–20] or lubricating additives[21–24] attributed to their peculiar physicochemical properties, including low volatility, wide range of liquid temperature, high viscosity, etc.[25–31] Previously, conventional halogen-containing ILs have been widely and systematically studied. For example, ILs containing BF₄⁻ [32] and PF₆⁻ [33] anions assuredly have excellent lubricating performances, but corrosion initiated by the halogen-containing anions may not be avoided. Therefore, halogen-free ILs have been widely studied by many researchers in

recent years. But the research of halogen-free ILs as additives in water-based lubricating systems is still in the preliminary stage. Wang [34] et al studied the synergistic effect of lithium salt and non-ionic surfactant with a certain proportion in aqueous system. It was found that the lubricating performance of the aqueous system was improved, but the corrosion problem still exists. Therefore, it is desirable to develop novel IL additives with stable hydrolysis, excellent corrosion resistance and anti-friction and anti-wear effect. Our group have been endeavoring to design and explore new halogen-free IL water-based lubricating additives. Samples like naphthalene dicarboxylate ILs [5] and in-situ type benzotriazole ILs (N_{4444} BTA and P_{4444} BTA) [4] were developed, and they were found to possess less corrosion and excellent lubricating properties. For further researching whether the tribological properties of IL lubricating additives can be improved by modifying the anion structure, novel ILs that anions possess large conjugated system were prepared, the physicochemical and lubricating properties of the ILs were systematically evaluated.

2. Experimental Section

2.1. Materials

The major raw materials used in the CAILs preparation are as follows: chromotropic acid (99%), N_{4444} Br (99%) and P_{4444} Br (98%) were purchased from Energy Chemical Scientific Ltd. N_{4444} OH (40% aqueous solution) was purchased from J&K Scientific Ltd. P_{4444} OH (40% aqueous solution) and *p*-toluenesulfonyl chloride (99%) were purchased from Aladdin Scientific Ltd.

2.2. Synthesis and characterization

To synthesis the TsN_{4444} and TsP_{4444} , 0.01 mol of chromotropic acid was firstly mixed with 0.02 mol of N_{4444} OH or P_{4444} OH at ambient temperature for 24 h. After vacuum distillation and drying, the ultimate products of TsN_{4444} and TsP_{4444} were obtained, respectively. As far as the $TsnN_{4444}$ and $TsnP_{4444}$, the intermediate was synthesized firstly according to the reported method. [35] And then 0.01 mol of the intermediate and 0.02 mol of N_{4444} Br or P_{4444} Br were added into 100 mL deionized water. The solution was stirred at ambient temperature for 24 h. Then, it was extracted twice with 100 mL dichloromethane, the obtained extract was washed twice with 100 mL deionized water and dried with anhydrous Na_2SO_4 . [36] After removal of the solvent, the targeted ILs were dried at 150°C for 24 h to get ultimate products. The CAILs were characterized by NMR and HRMS. The chemical structures of the CAILs were shown in Figure 1 and the detailed NMR and HRMS data were shown in the Support Information.

2.3. Viscosity, pH and corrosion tests

The KVs (at 25°C) of the samples were tested through a SYP1003-III kinematic viscometer. The pH data was tested using accurate pH test paper. For the corrosion test, GB 6144-2010 procedure was applied.

2.4. Contact angle and QCM tests

The optical contact angle tester produced by Swedish Biolin Scientific was selected to evaluate the wettability of the samples on the corresponding baseplates. The sample (3 μL) was placed on a polished baseplate, and then the CA can be successfully measured by the instrument after 10 s. Tests were repeated three times to avoid accidental. The QCM-D produced by Swedish Biolin Scientific was selected to judge the amount of adsorbed CAILs according to frequency-changing (Δf), and which should be carried out under the following conditions: the tested temperature was $25 \pm 1^\circ\text{C}$, the flow rate should be kept at 200 $\mu\text{L}/\text{min}$. Ultimately, the Δf was recorded automatically by the QCM-D equipment which was equipped with gold-plated quartz crystal sensors (Qsx-301, Q-Sense).

2.5. Tribological tests

The lubricating performances of all the samples were assessed with an Optimol SRV-V oscillating reciprocating friction and wear instrument under conditions of 100 N, 25°C , 25 Hz, 1 mm, 30 min and the comparative humidity was 20-50%. According to the analysis of antifriction and antiwear properties, the optimal additive concentration (0.5%) for CAILs was obtained with above tested conditions to achieve best tribological performance, so all physicochemical, adsorption and tribological experiments are based on the addition of 0.5%. After the experiments, the worn volumes of the baseplates were estimated with a 3D profiler (BRUKER-NPFLEX). The above tests must be conducted three times and then figured out the average value to ensure the authenticity of the data. The load increasing rate of the variable load test was 50 N/2 min, and the frequency increasing speed of the frequency-changing test was 10 Hz/6 min. The detail parameters of the used friction pairs were represented as follows: a steel ball (hardness=700-800 HV and diameter=10 mm) was selected to move against an AISI 52100 bearing steel (ϕ 24 mm \times 7.9 mm), ZQSn663 copper or 2024 aluminum alloy baseplate. The hardness of the baseplates is 850-920 HV, 90-120 HV and 140-165 HV, respectively. Before these tests, the baseplates must be polished by sandpaper. The extreme pressure properties of the lubricants were further explored by a four-ball friction tester (SETA 19900-2, UK), which can successfully evaluate the P_B and P_D values in accordance with standard method of GB/T 3142-1982.

2.6. SEM and XPS tests

The morphologies of the worn baseplates were measured with a SEM (Quanta 250 EFG) made by FEI company in United States, and the magnifications was 100 \times , 1500 \times , respectively. An XPS spectrometer made by Kratos Analytical company of England was used to analysis the ingredients and chemical states of the lubricated metal surfaces after the friction experiment, according to the following conditions: the power=225 W, the exciting source of Al-K α radiation=1486.6 eV, the voltage=15 kV, the output angle=0 degrees and the resolution= ± 0.3 eV. Additionally, it is necessary to clean the worn metal surfaces through ultrasonic in acetone for 5 min firstly, and then the data was finally gotten based on the standard binding energy of C1s peak (284.8 eV).

2.7. TEM and FIB tests

The tribofilm was detected by TEM (FEI, Tecnai, G2 TF20 S-TWIN). With the help of FIB milling, TEM micrographs and EDS element diagrams of the cross section were gotten.

3. Results And Discussion

3.1. Viscosity, pH and corrosion analysis

The corrosive properties of the aqueous systems with the best adding concentration (0.5%) of the CAILs were further tested, and their pH and KVs were also measured. The detailed data were presented in Figure 2 and Table 1. As shown, the KVs of water containing the CAILs were slightly higher than water, indicating that the CAILs could mildly enhance the KV of water, which might be beneficial to heighten the tribological performances of water. The corrosion test results and the corresponding SEM figures were shown in Figure 2. These figures intuitively illustrated that all the CAILs could greatly reduce the corrosion initiated by the reaction between water and cast iron, suggesting that the CAILs displayed excellent anti-corrosion properties. Besides, 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄ showed slight better anti-corrosion property than 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄, respectively. This might be owing to the adsorption of the CAILs on the cast iron surface, which prevented the direct contact between water and the cast iron. EDS was served to further explore the element content on the cast iron surface after corrosion. As shown in Figure 2 and Table 2, compared with other samples, water showed the highest content of C, O elements and the lowest content of Fe element, demonstrating that severe reaction did occur between water and the cast iron. At the same time, 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄ presented higher C, O elements and lower Fe element than the CAILs modified by *p*-toluenesulfonyl group (0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄), which proved that 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄ had better anti-corrosion properties than 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄. From what is mentioned above, we may conclude that the CAILs, especially the phenolic hydroxyl group decorated samples can exhibit good anti-corrosion properties as water based lubricating additives.

Table 1
The KVs and pH of all the samples (at 25°C).

Samples	KV (mm ² /s)	pH
Water	0.9979	7.0-7.5
0.5% TsN ₄₄₄₄	1.029	6.0-6.5
0.5% TsP ₄₄₄₄	1.014	6.0-6.5
0.5% TsN ₄₄₄₄	1.164	6.5-7.0
0.5% TsP ₄₄₄₄	1.054	6.5-7.0

Table 2
The element content on the cast iron surface before and after corrosion (wt %).

Samples	C	O	Fe
Blank	3.22	1.52	95.26
Water	6.77	3.00	90.23
0.5% TsN ₄₄₄₄	3.36	2.16	94.48
0.5% TsP ₄₄₄₄	2.92	2.46	94.62
0.5% TsnN ₄₄₄₄	2.12	2.03	95.55
0.5% TsnP ₄₄₄₄	2.31	1.92	95.77

3.2. Friction and wear analysis

To explore appropriate addition of the CAILs that they can achieve the best tribological performances, the lubricating properties of water with different concentrations of TsN₄₄₄₄ were evaluated. From Figure S1, we can see that the aqueous systems with different concentrations of TsN₄₄₄₄ displayed obvious lower COFs and wear volumes than neat water on steel/steel friction contacts. Particularly, just adding extreme low concentration of TsN₄₄₄₄ (0.5%) could effectively heighten the tribological performance of water. The COF decreased from 0.36 to about 0.10-0.13 and the wear volume reduced by 81%. Consequently, the following friction tests were all carried out at the concentration of 0.5%. As shown in Figure 3a and 3b, 0.5% TsN₄₄₄₄ showed the best performance compared to other samples, which reduced the COF to 0.11-0.12 and decreased the wear volume by 83%, while 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄ gave the relative inferior results. The horizontal profiles of all the worn scars were also an intuitive way to reflect the property of anti-wear. It is seen from Figure 3c that the depth of the wear scars lubricated with all the WBLs was obvious shallower than that of water, which was in accord with the results of wear volume tests. Figure 3d further showed the tribological performances of the WBLs tested under different loads. What we could clearly see was that the wear volume increased for all the samples with the increase of load. Apparently, no matter what load was applied, water presented the biggest growth rate in wear volume. At the same time, 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄ showed higher growth rate than 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄. These outcomes also demonstrated that 0.5%TsN₄₄₄₄ and 0.5%TsnP₄₄₄₄ did have better load carrying capacity than 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄. To further explore the load carrying capacity of the CAILs, their P_B and P_D were measured using a four-ball tester. The P_B and P_D data of all samples were shown in Figure 4, and the minimum P_B value (98 N) and P_D value (314 N) were presented by water. However, obvious improvement of P_B and P_D values were achieved when the CAILs were added. Particularly, the addition of 0.5% TsnP₄₄₄₄ showed the maximum P_B value (833 N) and P_D value (1568 N).

The CAILs also showed excellent tribological properties under increasing load and frequency conditions. Figure 5a revealed the results of variable load test. Good extreme pressure performance was exhibited

when the CAILs were added into water. Especially, as for 0.5% TsnP₄₄₄₄, the extreme pressure could reach up to 850 N, which was far higher than water (100 N). In addition, the COF of 0.5% TsnP₄₄₄₄ was kept at lower level at about 0.10-0.12 during the whole tested process compared with the higher COF value for 0.5% TsP₄₄₄₄. During the frequency-changing tests, the COF of water continuously increased with the increase of frequency. Contrast to water, the COFs of 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄ were much lower and more stable. Particularly, the COFs of 0.5% TsN₄₄₄₄ and 0.5% TsnP₄₄₄₄ kept at a very low and stable level (0.11-0.15) in the whole tested duration (Figure 5b).

3.3. The contact angle and QCM analysis

From what is mentioned above, we may conclude that the CAILs, especially TsN₄₄₄₄ and TsnP₄₄₄₄ do have superior tribological properties as adding to aqueous system. It is speculated that their lubricating performances are related to the physical adsorption or friction chemical reaction of the CAIL molecules on/with the sliding surfaces, resulting in the generation of physical adsorption/chemical reaction protecting films on the surfaces. In order to verify these speculations, the wettability of the WBLs were evaluated. CA is always used to evaluate the wettability of lubricants. Generally, smaller CA means better wettability and good spread ability.[37] The CAs of the WBLs and water on the used contact surfaces were showed in Figure 6a, 6b and 6c. As shown, the CA of water was bigger than the aqueous systems with the CAILs on different contact surfaces. In addition, the CAs of 0.5% TsN₄₄₄₄ and 0.5% TsnP₄₄₄₄ were much smaller than water. It indicated that 0.5% TsN₄₄₄₄ and 0.5% TsnP₄₄₄₄ had better wettability than water on the contact surfaces, which might be beneficial for their physical adsorption and further friction chemical reaction on/with the metal surfaces. Moreover, aiming to further research the action of how much the CAILs adsorbed on the metal surface, frequency-changing measured on a QCM-D was selected to evaluate the amount of the adsorbed additives.[38] The bigger value of the Δf , the thicker and more stable physical adsorption tribofilm formed, resulting in more effective protective film formation to protect substrates from wear, to decrease the friction coefficient and wear volume. What we could see from Figure 6d was that 0.5% TsN₄₄₄₄ and 0.5% TsnP₄₄₄₄ presented higher Δf value than that of 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄, respectively, signifying that the thicker and more stable physico-chemical adsorption films were formed by 0.5% TsN₄₄₄₄ and 0.5% TsnP₄₄₄₄. From the analysis of CA and QCM, it can be concluded that thicker physical adsorption films generated by 0.5% TsN₄₄₄₄ and 0.5% TsnP₄₄₄₄ on the sliding surfaces may have a significant impact for the ILs to show better tribological properties.

3.4. XPS and SEM analysis

For further researching the reducing-friction and anti-wear mechanism of the CAILs, the element chemical states on the lubricated steel surface were tested using XPS. The XPS spectra were shown in Figure 7. As seen in Figure 8a, the XPS spectra of Fe2p for new polished steel surface was different from those surfaces lubricated by the CAILs, implying that some new compounds formed on the surfaces. On the Fe2p spectra, characteristic peaks appeared at about 711.2eV and 724.8eV. Combined with the peak of O1s at about 530.5 eV and 532.1 eV, it could be concluded that oxide compounds of Fe₂O₃, FeOOH, FeO, Fe₃O₄, or Fe(OH)O formed on the lubricated steel surface.[3] From the peaks of Fe2p located at 706.6-

707.3 eV and the peaks of S2p at 161.3 eV-162.7 eV, it could be conjectured that FeS₂ might be generated in the process of rubbing. As for 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄, obvious N1s peaks were observed at about 399.9-400.4 eV, which might be attributed to complicated nitrogen oxides, Fe(NO) and/or Fe(NO₂) formed.[2] Based the above data, what we could primarily conclude was that friction chemical reaction did have occurred between the lubricants and the friction contacts. From the spectra, it could also be seen that the peaks formed by 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄ were much obvious than those formed by 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄, indicating that more stable and denser tribochemical films were generated. However, the aqueous systems with 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄ presented worse tribological properties than those with 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄. The comparison showed the formed tribochemical reaction films might not be the main reason for 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄ to present superior tribological properties. Correspondingly, the physico-chemical adsorption films shaped by the CAIL molecules on the metal surfaces were conjectured to be the biggest contributor.

Commonly, the CAIL molecules were easily to adsorb on the metal surfaces through electrostatic interaction between the sulfonic anions and the exoelectronic surfaces. The physico-chemical adsorption films formed by TsN₄₄₄₄ and TsP₄₄₄₄ were much thicker than those formed by TsN₄₄₄₄ and TsP₄₄₄₄ attributed to the substitution of the phenolic hydroxyl groups with p-toluenesulfonyl groups. As a result, 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄ could show better reducing-friction and anti-wear performances than 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄. Additionally, hydrogen ions might be generated from the phenolic hydroxyl groups in the aqueous solution of 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄, which made the solution more acidic and corrosive. It is speculated that the high corrosion of the 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄ solution led them to exhibit worse tribological properties than 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄. These speculations were proved by measuring the pH value of the aqueous systems and scanning the worn morphologies. The pH values of the 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄ solutions were found to be lower than those of 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄ (Table 1). So, the 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄ solutions might present more serious corrosion than 0.5%TsN₄₄₄₄ and 0.5%TsP₄₄₄₄.

The pH tested result was validated by the results of the scanning electron microscope images (Figure 8). It clearly showed that the scar lubricated by water was wide and rough, which was also accompanied with severe corrosion Figure (8a and 8a₁). Meanwhile, the narrower scars were presented by 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄ compared with water, but severe corrosion still existed after rubbing (Figure 8b, 8c, 8b₁ and 8c₁). However, in contrast to the worn morphologies of water, 0.5% TsN₄₄₄₄ and 0.5% TsP₄₄₄₄ exhibited no corrosion and smoother morphologies (Figure 8d, 8e, 8d₁ and 8e₁). From what is mentioned above, we may conclude that physico-chemical adsorption films shaped by the CAILs on the metal surfaces are conjectured to be the main reason for them to present good tribological properties as lubricating additives for water. Among the CAILs, TsN₄₄₄₄ and TsP₄₄₄₄ showed less effective lubricating performances due to their higher corrosion initiated by the H⁺ generation through the effect of conjugation between phenolic hydroxyl and the naphthalene ring. Furthermore, in terms of the friction contacts of copper/steel and aluminum/steel, it is also could be seen that excellent tribological

performances were presented by the CAILs, especially TsnN_{4444} and TsnP_{4444} (Figure S2, S3 and S4). It proves that the CAILs are excellent lubricating additives for aqueous system.

3.5. FIB- TEM analysis

To further investigate the formation of tribofilms on the friction contacts, the surfaces of the grinding spots after the lubricating effect of H_2O , TsP_{4444} and TsnP_{4444} were treated with FIB. Then the morphologies were observed from TEM, which were shown in Figure 9 (H_2O), Figure 10 (TsP_{4444}) and Figure 11 (TsnP_{4444}), respectively. From the figures, it is seen protective films with varying thickness and unevenness were generated on the surfaces (marked by the yellow dashed line). For the surface after the action of pure water, the overall formation of the film was relatively thin with high content of iron oxide. While in a relatively thick region, there were some fragments of iron mixed in it, which might be mainly because the oxide film formed on the surface lubricated by pure water was not solid enough, the substrate will be partially stripped and then involved in its tribo-film under the action of mechanical shear. For the surface after lubrication with the synthesized ILs (TsP_{4444}), the similar boundary film was detected with thicker and thinner portions. It still contained a large amount of nano metallic iron oxides in the film, while the distribution of active elements P and S contributed by the CAILs could be seen in combination with the results of elemental line scan and EDS (Figure 10g and 10f), indicating the occurrence of chemical reaction on the sliding surface. Comparatively speaking, for TsnP_{4444} , its tribo-film formed at the sliding surface was thicker. As mentioned above, TsnP_{4444} exhibited a good chemisorption on the iron substrate and it also underwent chemical reaction at the interface. The dual role made the lubrication effect of TsnP_{4444} excellent. As seen in the Figure 11f, there were two layers of film appeared on the surface, the layer immediately next to the iron substrate was full of the elements of S, O, Fe, and further up showed higher content of element C, O, P. It is implied that the presence of oxide layer and the extreme pressure layer containing sulfur and phosphorus elements was obvious, which could well resist the high stress during sliding. This could well explain the excellent extreme pressure of TsnP_{4444} . Immediately after, the corresponding confirmation from the line-scan and EDS data (Figure 11g and 11h), the increase in carbon content compared to that of TsP_{4444} , also indicated the positive effect of the rigid ring in the molecular structure on the load-bearing properties.

4. Conclusion

Four chromotropic acid based ILs were obtained and applied as water-based lubricating additives. The CAILs, especially the phenolic hydroxyl group decorated samples showed excellent tribological properties on different friction contacts. These results demonstrated that the anions in the CAILs molecules assuredly determined their tribological properties. According to the results of corrosion degree, CA, QCM, XPS, SEM, TEM and FIB analysis, it is easy to conclude that physical adsorption and chemical reaction films shaped by the CAILs on the metal surfaces are the most important contributor for the decorated CAILs (TsnN_{4444} and TsnP_{4444}) to present excellent tribological properties and good extreme pressure. Among the CAILs, Tsn_{4444} and TsP_{4444} showed less effective lubricating performances due to their

higher corrosion initiated by the H⁺ generation through the effect of conjugation between phenolic hydroxyl and the naphthalene ring. In conclusion, it is expected that the decorated CAILs may have a dramatic potential application in the field of water-based lubricating additives.

Abbreviations

Full name	Abbreviation
Friction coefficient	COF
Chromotropate ionic liquids	CAILs
Petroleum-based lubricants	PBLs
Water-based lubricants	WBLs
Ionic liquids	ILs
Tetrabutylammonium hydroxide	N ₄₄₄₄ OH
Tetrabutyl phosphorus hydroxide	P ₄₄₄₄ OH
Tetrabutylamine bromide	N ₄₄₄₄ Br
Tetrabutylphosphorus bromide	P ₄₄₄₄ Br
Disodium4,5-Ditosyloxynaphthalene-2,7-disulfonate	intermediate
Nuclear Magnetic Resonance	NMR
High-resolution mass spectra	HRMS
Kinematic viscosity	KV
Contact angle	CA
Maximum non-seizure loads	P _B
Sintering loads	P _D
Scanning electron microscope	SEM
X-ray photoelectron spectroscopy	XPS
Focused ion beam	FIB
Transmission electron microscope	TEM

Declarations

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Author Contributions

All authors conceived of the study and analyzed the results. **Peng Wang**: Designed and carried out all measurements and fitted the data. **Peng Gao**: Participated in all the arrangement and writing. **Lin Ma**: Data analysis and result discussion. **Ping Wen**: Guided experiment and participated in the discussion of the theory. **Yunyan Han**: Data analysis and result discussion. **Rui Dong**: Conceived the research and writing - review & editing. **Mingjin Fan**: Funding acquisition, coordinated the project and writing - review & editing.

Declaration of Competing Interest

The authors declare no competing financial interest.

References

1. Yang, Z., Sun, C., Zhang, C., Zhao, S., Cai, M., Liu, Z., et al.: Amino acid ionic liquids as anticorrosive and lubricating additives for water and their environmental impact. *Tribol Int.* **153**, 106663 (2021)
2. Dong, R., Yu, Q., Bai, Y., Wu, Y., Ma, Z., Zhang, J., et al.: Towards superior lubricity and anticorrosion performances of proton-type ionic liquids additives for water-based lubricating fluids. *Chem. Eng. J.* **383**, 123201 (2020)
3. Wang, Y., Yu, Q., Ma, Z., Huang, G., Cai, M., Zhou, F., et al.: Significant enhancement of anti-friction capability of cationic surfactant by phosphonate functionality as additive in water. *Tribol Int.* **112**, 86–93 (2017)
4. Fan, M., Du, X., Ma, L., Wen, P., Zhang, S., Dong, R., et al.: In situ preparation of multifunctional additives in water. *Tribol Int.* **130**, 317–323 (2019)
5. Yang, D., Du, X., Li, W., Han, Y., Ma, L., Fan, M., et al.: Facile Preparation and Tribological Properties of Water-Based Naphthalene Dicarboxylate Ionic Liquid Lubricating Additives. *Tribol Lett.* **68**, 84 (2020)
6. Phillips, B.S., Zabinski, J.S.: Ionic Liquid Lubrication Effects on Ceramics in a Water Environment. *Tribol Lett.* **17**(3), 533–541 (2004)
7. Tomala, A., Karpinska, A., Werner, W.S.M., Olver, A., Störi, H.: Tribological properties of additives for water-based lubricants. *Wear.* **269**(11-12), 804–810 (2010)
8. Guo, P., Chen, L., Wang, J., Geng, Z., Lu, Z., Zhang, G.: Enhanced Tribological Performance of Aminated Nano-Silica Modified Graphene Oxide as Water-Based Lubricant Additive. *ACS Appl. Nano Mater.* **1**(11), 6444–6453 (2018)

9. Del Sol, I., Gámez, A.J., Rivero, A., Iglesias, P.: Tribological performance of ionic liquids as additives of water-based cutting fluids. *Wear*. **426-427**(Part A), 845–52 (2019)
10. Arcifa, A., Rossi, A., Ramakrishna, S.N., Espinosa-Marzal, R., Sheehan, A., Spencer, N.D.: Lubrication of Si-Based Tribopairs with a Hydrophobic Ionic Liquid: The Multiscale Influence of Water. *J. Phys. Chem. C* **122**(13), 7331–7343 (2018)
11. Wen, P., Lei, Y., Li, W., Fan, M.: Synergy between Covalent Organic Frameworks and Surfactants to Promote Water-Based Lubrication and Corrosion Resistance. *ACS Appl. Nano Mater.* **3**(2), 1400–1411 (2020)
12. Davis, B., Schueller, J.K., Huang, Y.: Study of ionic liquid as effective additive for minimum quantity lubrication during titanium machining. *MFGLET*. **5**, 1–6 (2015)
13. Pham, M.-Q., Yoon, H.-S., Khare, V., Ahn, S.-H.: Evaluation of ionic liquids as lubricants in micro milling – process capability and sustainability. *J. Clean. Prod.* **76**, 167–173 (2014)
14. Kajdas, C.: Additives for metalworking lubricants - a review. *Lubr Sci.* **1**(4), 385–409 (1989)
15. Ye, C., Liu, W., Chen, Y., Yu, L.: Room-temperature ionic liquids: a novel versatile lubricant. *Chem Comm.* 2244–2245 (2001)
16. Jiménez, A.E., Bermúdez, M.D., Iglesias, P., Carrión, F.J., Martínez-Nicolás, G.: 1-N-alkyl -3-methylimidazolium ionic liquids as neat lubricants and lubricant additives in steel–aluminium contacts. *Wear*. **260**(7-8), 766–782 (2006)
17. Amiril, S.A.S., Rahim, E.A., Syahrullail, S.: A review on ionic liquids as sustainable lubricants in manufacturing and engineering: Recent research, performance, and applications. *J. Clean. Prod.* **168**, 1571–1589 (2017)
18. Bermúdez, M.-D., Jiménez, A.-E., Sanes, J., Carrión, F.-J.: Ionic Liquids as Advanced Lubricant Fluids. *Molecules*. **14**(8), 2888–2908 (2009)
19. Cooper, P.K., Wear, C.J., Li, H., Atkin, R.: Ionic Liquid Lubrication of Stainless Steel: Friction is Inversely Correlated with Interfacial Liquid Nanostructure. *ACS Sustain. Chem. Eng.* **5**(12), 11737–11743 (2017)
20. Zhou, F., Liang, Y., Liu, W.: Ionic liquid lubricants: designed chemistry for engineering applications. *Chem. Soc. Rev.* **38**(9), 2590–2599 (2009)
21. Mu, L., Shi, Y., Guo, X., Wu, J., Ji, T., Chen, L., et al.: Enriching Heteroelements in Lignin as Lubricating Additives for Bioionic Liquids. *ACS Sustain. Chem. Eng.* **4**(7), 3877–3887 (2016)
22. Pejaković, V., Tomastik, C., Dörr, N., Kalin, M.: Influence of concentration and anion alkyl chain length on tribological properties of imidazolium sulfate ionic liquids as additives to glycerol in steel–steel contact lubrication. *Tribol Int.* **97**, 234–243 (2016)
23. Cai, M., Liang, Y., Zhou, F., Liu, W.: A novel imidazolium salt with antioxidation and anticorrosion dual functionalities as the additive in poly(ethylene glycol) for steel/steel contacts. *Wear*. **306**(1-2), 197–208 (2013)

24. Barnhill, W.C., Qu, J., Luo, H., Meyer, H.M., Ma, C., Chi, M., et al.: Phosphonium-Organophosphate Ionic Liquids as Lubricant Additives: Effects of Cation Structure on Physicochemical and Tribological Characteristics. *ACS Appl. Mater. Interfaces*. **6**(24), 22585–22593 (2014)
25. Stump, B.C., Zhou, Y., Luo, H., Leonard, D.N., Viola, M.B., Qu, J.: New Functionality of Ionic Liquids as Lubricant Additives: Mitigating Rolling Contact Fatigue. *ACS Appl. Mater. Interfaces*. **11**(33), 30484–30492 (2019)
26. Naveed, T., Zahid, R., Mufti, R.A., Waqas, M., Hanif, M.T.. A review on tribological performance of ionic liquids as additives to bio lubricants. *Proceedings of the Institution of Mechanical Engineers, P I Mech Eng J-J Eng*. **235**(9), 1782-1806: (2020)
27. Dong, R., Wen, P., Zhang, S., Zhang, C., Sun, W., Fan, M., et al.: The synthesis and tribological properties of dicarboxylic acid ionic liquids. *Tribol Int*. **114**, 132–140 (2017)
28. Zheng, G., Zhang, G., Ding, T., Xiang, X., Li, F., Ren, T., et al.: Tribological properties and surface interaction of novel water-soluble ionic liquid in water-glycol. *Tribol Int*. **116**, 440–448 (2017)
29. Khanmohammadi, H., Wijanarko, W., Espallargas, N.: Ionic Liquids as Additives in Water-Based Lubricants: From Surface Adsorption to Tribofilm Formation. *Tribol Lett*. **68**(4), 130 (2020)
30. Li, Y., Zhang, S., Ding, Q., Feng, D., Qin, B., Hu, L.: The corrosion and lubrication properties of 2-Mercaptobenzothiazole functionalized ionic liquids for bronze. *Tribol Int*. **114**, 121–131 (2017)
31. Espinosa, T., Jiménez, M., Sanes, J., Jiménez, A.-E., Iglesias, M., Bermúdez, M.-D.: Ultra-Low Friction with a Protic Ionic Liquid Boundary Film at the Water-Lubricated Sapphire–Stainless Steel Interface. *Tribol Lett*. **53**(1), 1–9 (2014)
32. Liu, W., Ye, C., Gong, Q., et al.: Tribological performance of room-temperature ionic liquids as lubricant. *Tribol Lett*. **13**(2), 81–85 (2002)
33. Wang, H., Lu, Q., Ye, C., et al.: Friction and wear behaviors of ionic liquid of alkyimidazolium hexafluorophosphates as lubricants for steel/steel contact. *Wear*. **256**(1-2), 44–48 (2004)
34. Wang, Y., Yu, Q., Cai, M., Shi, L., Zhou, F., Liu, W.: Synergy of lithium salt and non-ionic surfactant for significantly improved tribological properties of water-based fluids. *Tribol Int*. **113**, 58–64 (2017)
35. Paruch, K., Vyklický, L., Katz, T.J., Incarvito, C.D., Rheingold, A.L.: Expedient Procedure To Synthesize Ethers and Esters of Tri- and Tetrahydroxy[6]helicenebisquinones from the Dye-Intermediates Disodium 4-Hydroxy- and 4,5-Dihydroxynaphthalene-2,7-disulfonates. *J. Org. Chem*. **65**(25), 8774–8782 (2000)
36. Gusain, R., Bakshi, P.S., Panda, S., Sharma, O.P., Gardas, R., Khatri, O.P.: Physicochemical and tribophysical properties of trioctylalkylammonium bis(salicylato)borate (N888n-BScB) ionic liquids: effect of alkyl chain length. *Phys. Chem. Chem. Phys*. **19**(9), 6433–6442 (2017)
37. Matos, M., Lobo, A., Benito, J.M., Coca, J., Pazos, C.: Extending the Useful Life of Metalworking Fluids in a Copper Wire Drawing Industry by Monitoring Their Functional Properties. *Tribol T*. **55**(5), 685–692 (2012)
38. Huang, G., Yu, Q., Cai, M., Zhou, F., Liu, W.: Highlighting the Effect of Interfacial Interaction on Tribological Properties of Supramolecular Gel Lubricants. *Adv. Mater. Interfaces*. **3**(3), 1500489

(2016)

Figures

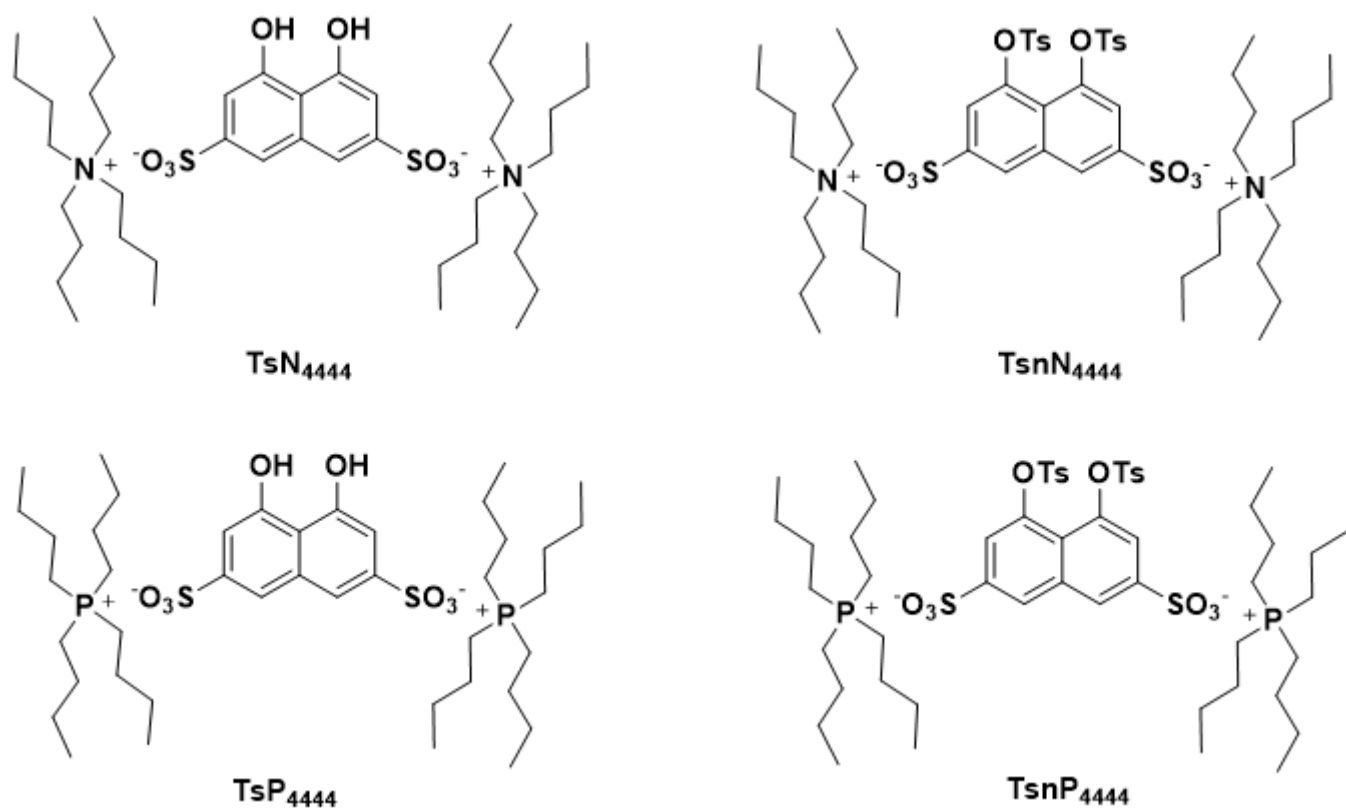


Figure 1

Chemical structures of the synthesized CAILs.

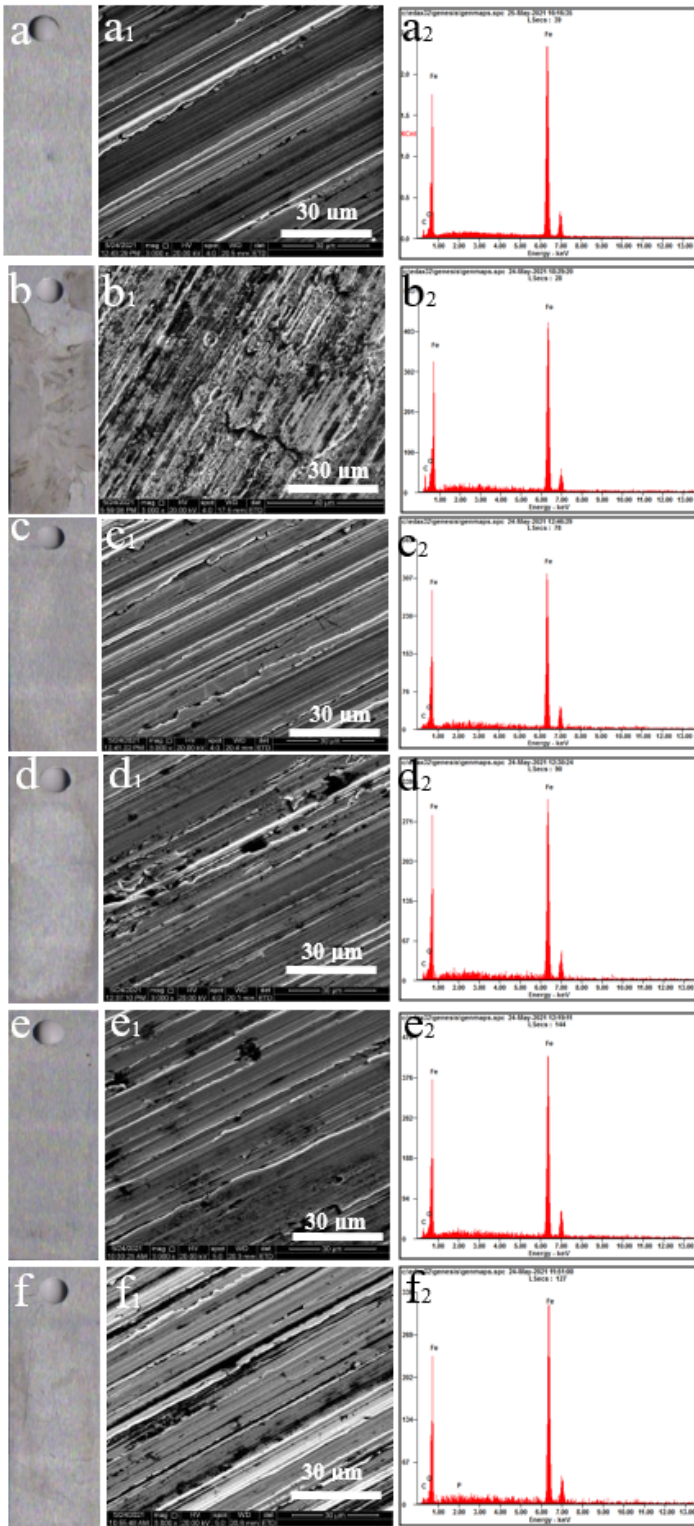


Figure 2

The figures of the cast iron bars (x), The SEM figures (x_1) and the EDS (x_2) of all the samples before and after corrosion, figure a, a_1 and a_2 (blank), figure b, b_1 and b_2 (H_2O), figure c, c_1 and c_2 (0.5% TsN_{4444}), figure d, d_1 and d_2 (0.5% TsP_{4444}), figure e, e_1 and e_2 (0.5% TsN_{4444}), figure f, f_1 and f_2 (0.5% TsN_{4444}), magnification is $\times 3000$ for SEM test.

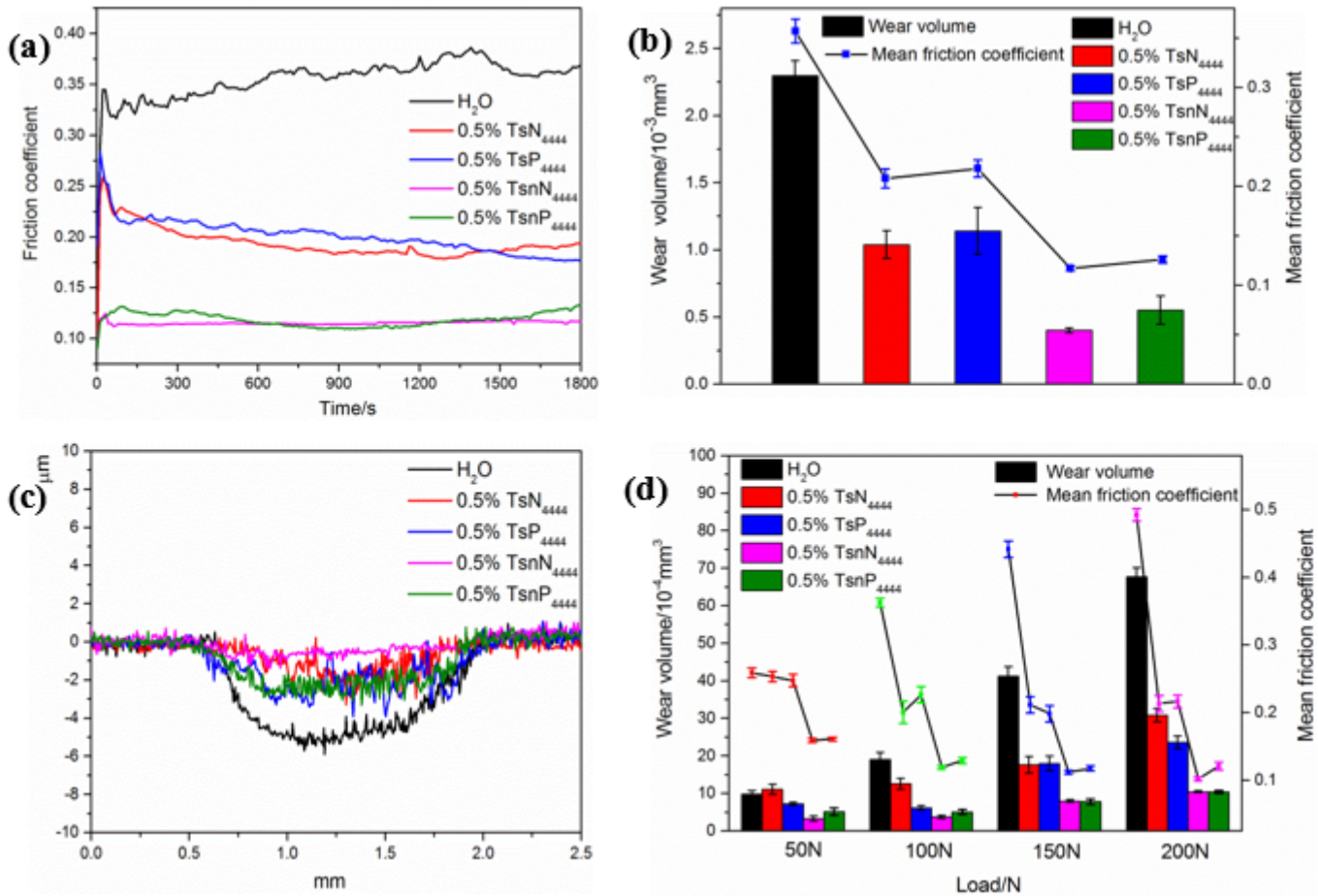


Figure 3

The COF curves (a), the wear volumes accompanied with mean COFs (b), the corresponding worn horizontal profiles (c) and the tribological properties measured under different loads (d) of all the samples for steel/steel friction contacts.

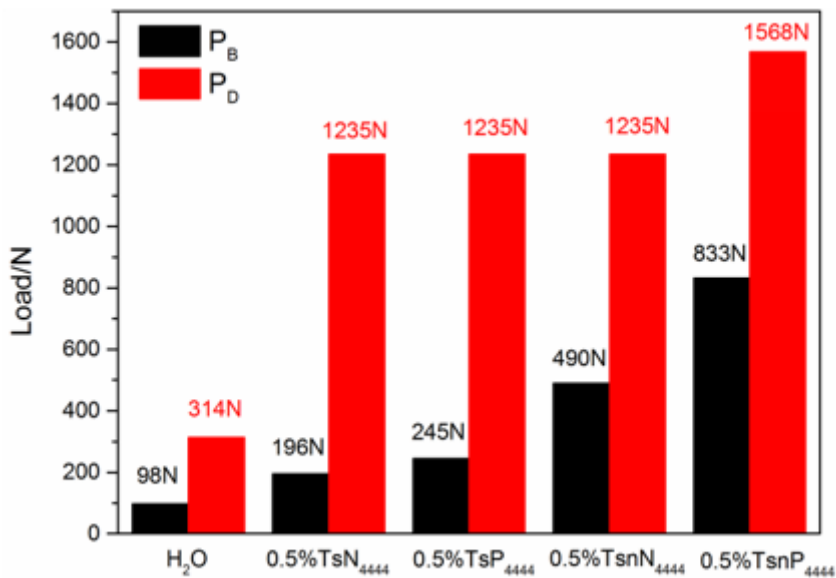


Figure 4

The P_B values and P_D values of all the samples

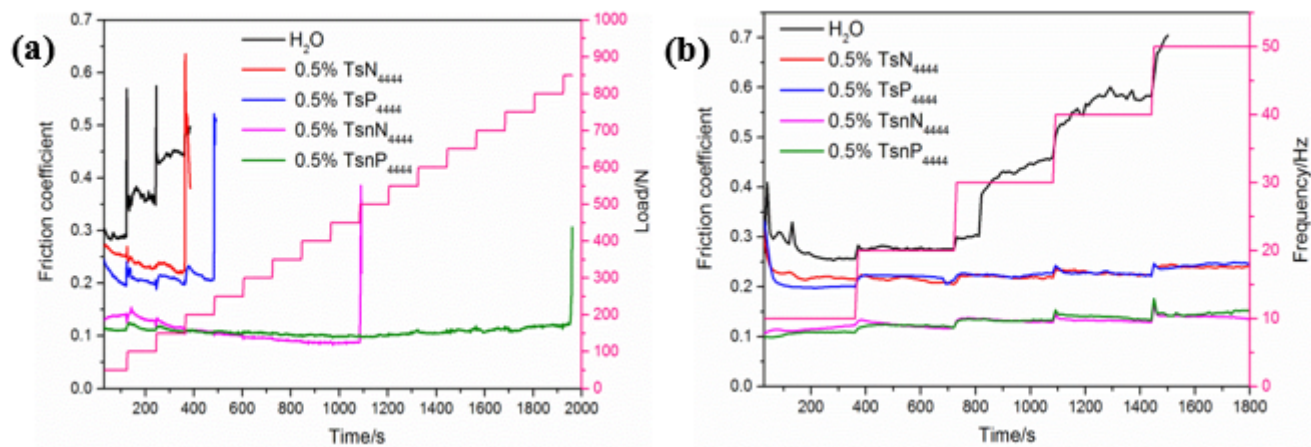


Figure 5

The COF of all the samples measured under increasing load (a) and increasing frequency conditions (b).

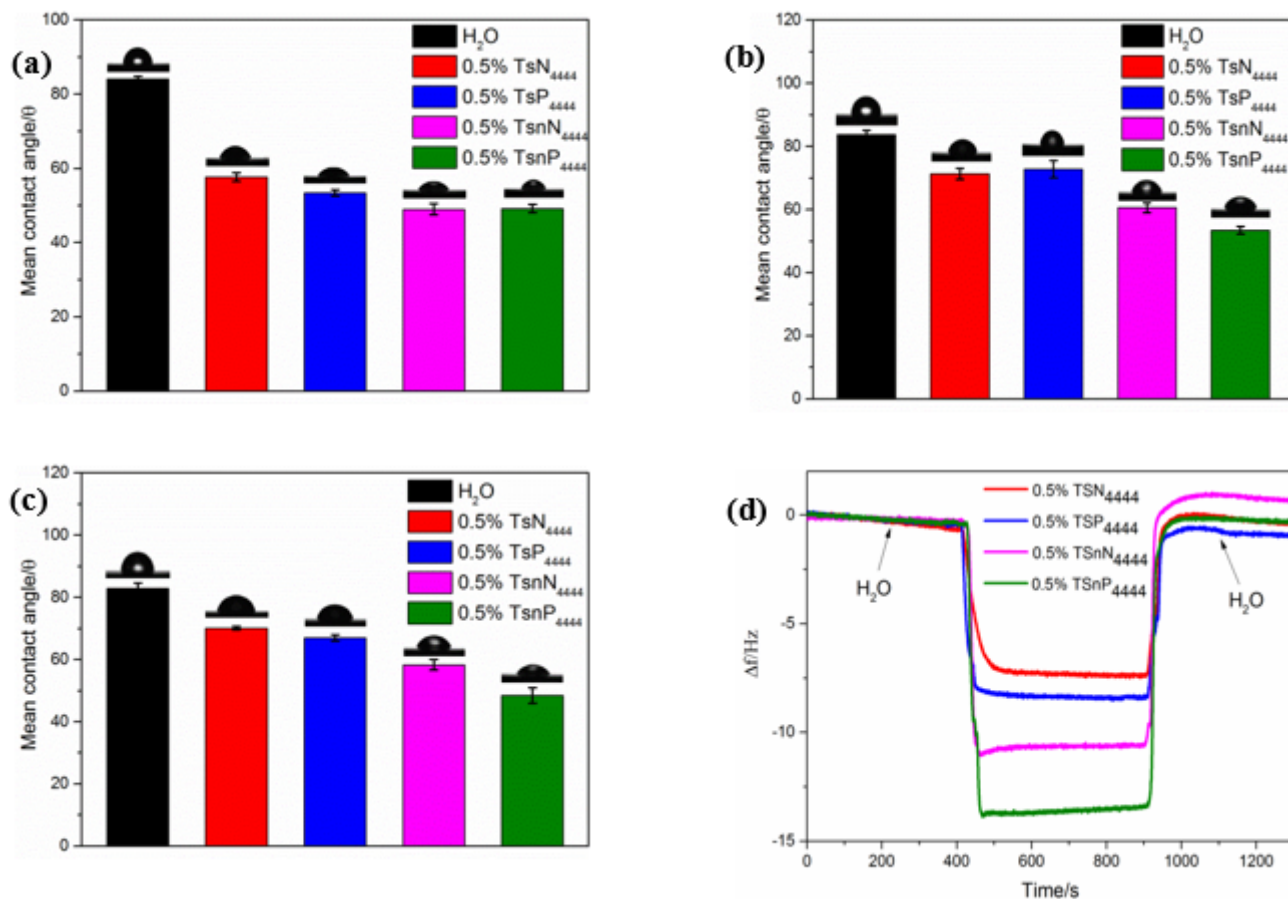


Figure 6

The mean CAs of all the samples on polished steel (a), copper (b) and aluminum (c) surfaces and the frequency-changing data of all the samples tested on gold sheets (d).

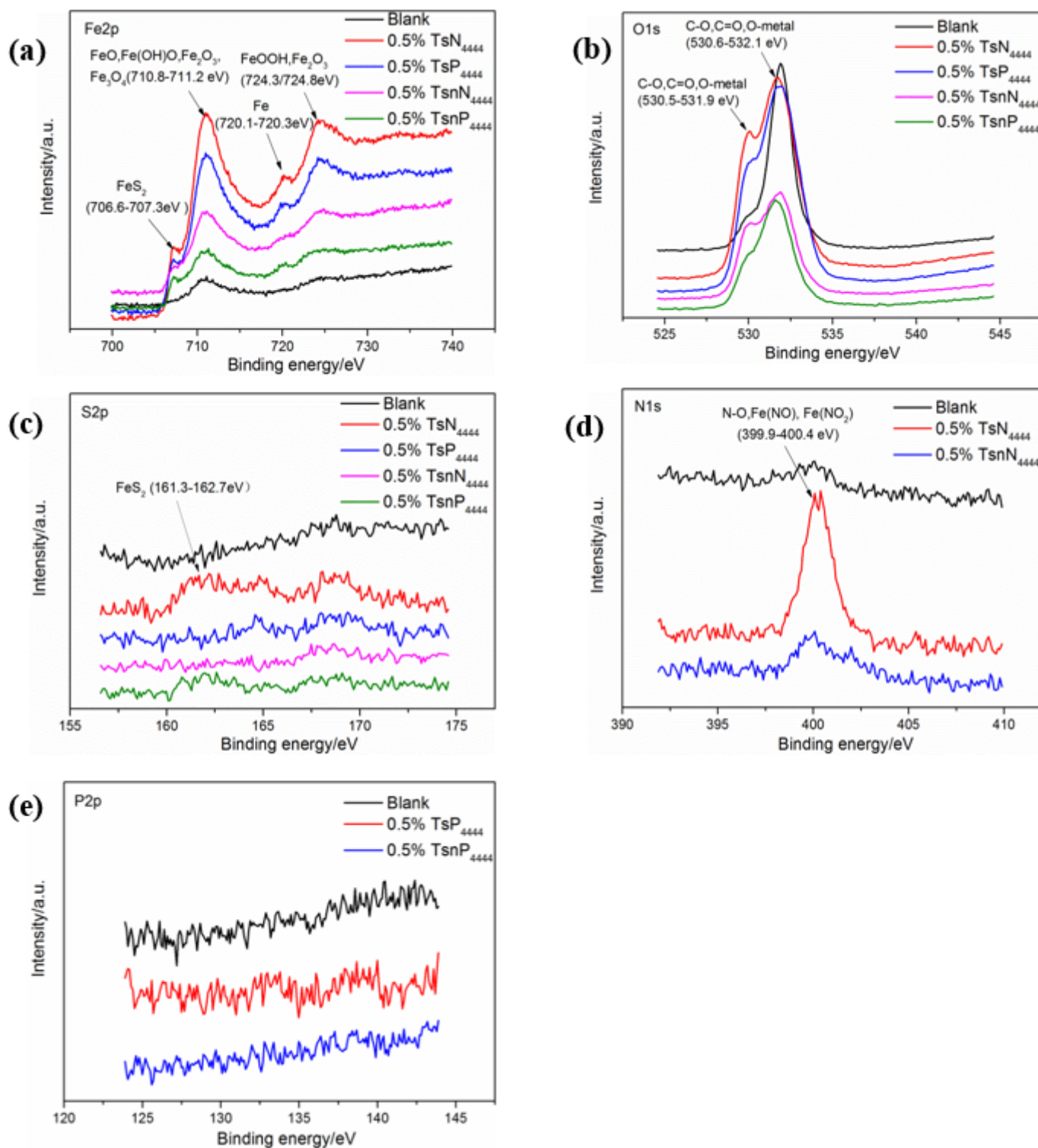


Figure 7

The XPS spectra of the lubricated steel surfaces.

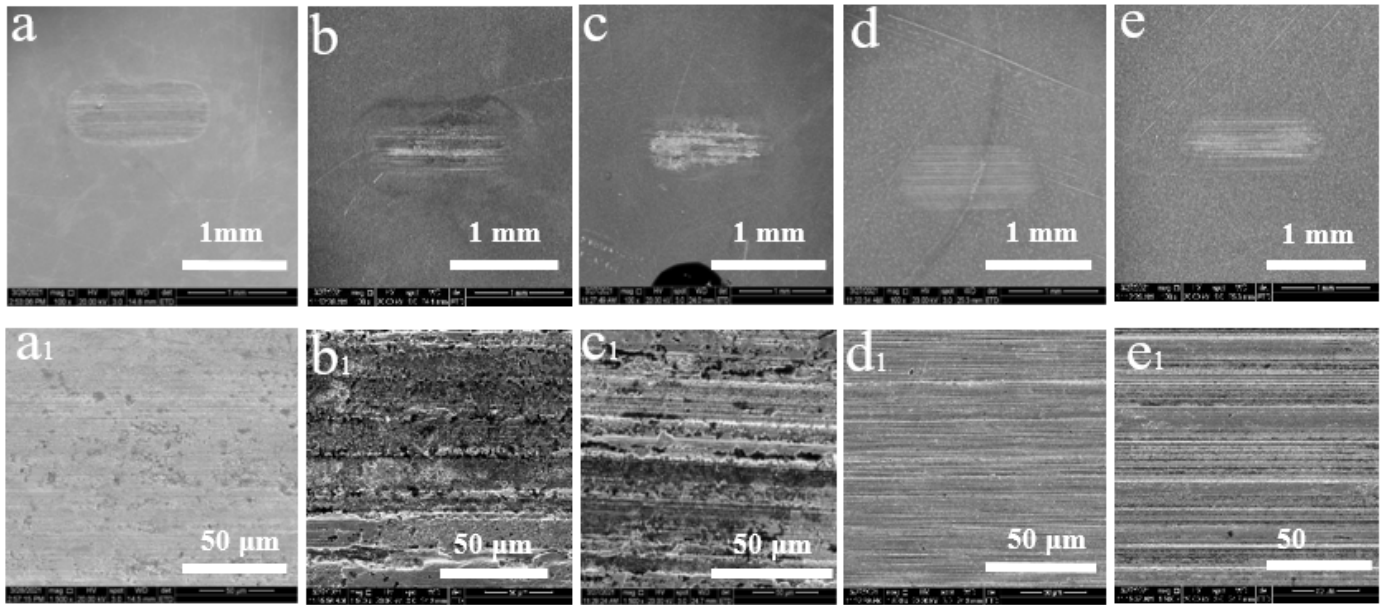


Figure 8

The SEM morphologies of the lubricated steel surfaces (above: magnification of 100×, and below: magnification of 1500×). figure a and a1 (H₂O), figure b and b1 (0.5%TsN4444), figure c and c1 (0.5%TsP4444), figure d and d1 (0.5%TsnN4444), figure e and e1 (0.5%TsnP4444).

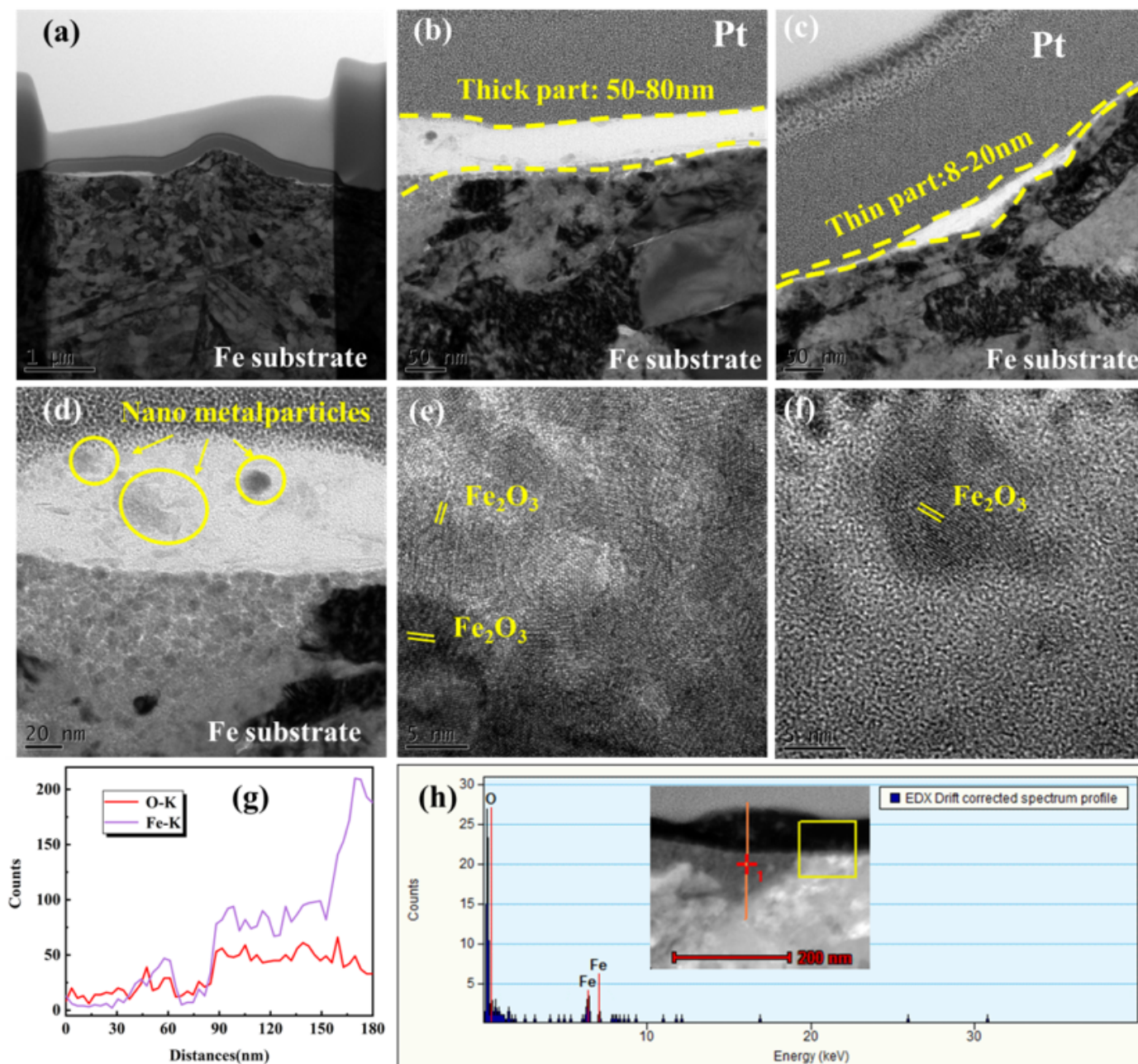


Figure 9

The morphological and elemental analysis results of tribo-film on the surface (after the lubrication of H₂O) with FIB treatment. (a) Overall shape of tribo-film, (b) (c) (d) (e) (f) the partial enlargement from (a), (g) (h) the line-scan and EDS result, the positions marked by straight lines (origin) and boxes (yellow) are the selected positions on the tribo-film for the line scan and EDS in the set-in picture, respectively.

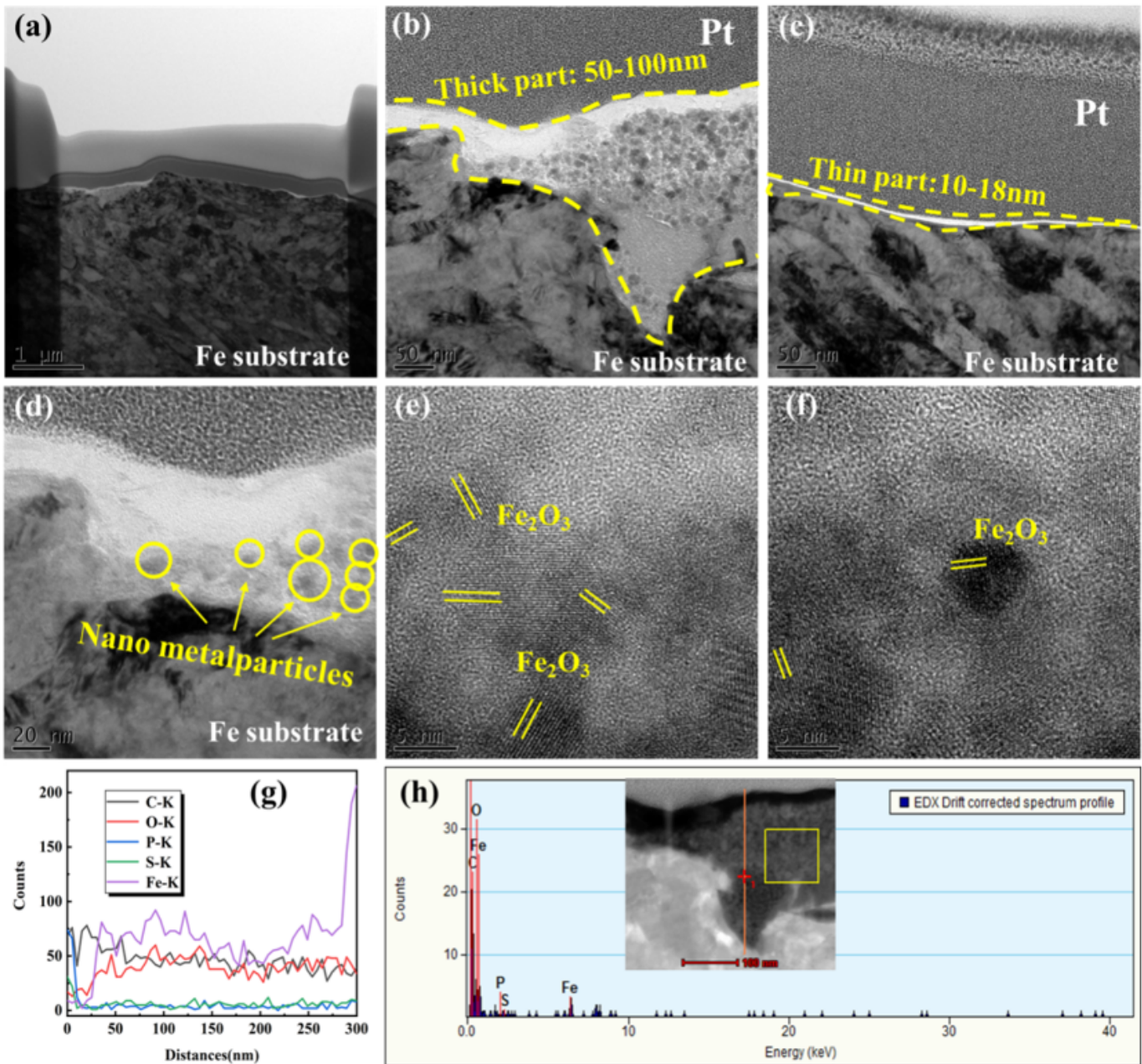


Figure 10

The morphological and elemental analysis results of the tribo-film on the surface (after the lubrication of 0.5% TsP4444) with FIB treatment. (a) Overall shape of tribo-film, (b) (c) (d) (e) (f) the partial enlargement from (a), (g) (h) the line-scan and EDS result, the positions marked by straight lines (origin) and boxes (yellow) are the selected positions on the tribo-film for the line scan and EDS in the set-in picture, respectively.

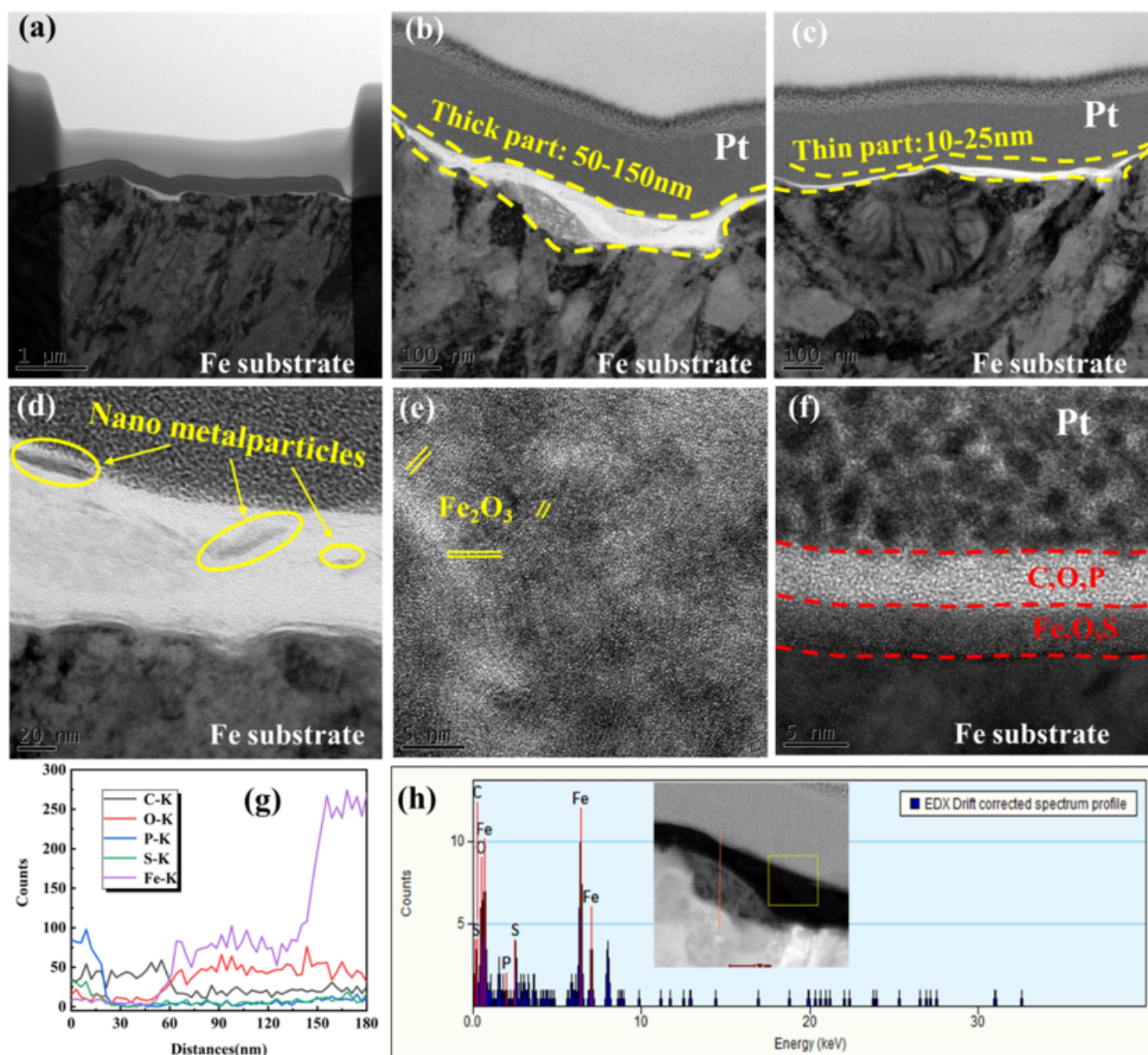


Figure 11

The morphological and elemental analysis results of tribo-film on the surface (after the lubrication of 0.5% TsnP4444 with FIB treatment). (a) Overall shape of tribo-film, (b) (c) (d) (e) (f) the partial enlargement from (a), (g) (h) the line-scan and EDS result, the positions marked by straight lines (origin) and boxes (yellow) are the selected positions on the tribo-film for the line scan and EDS in the set-in picture, respectively.

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