Grafting Heteroelement-Rich Groups on Graphene Oxide: Tuning Polarity and Molecular Interaction with Bio-Ionic Liquid for Enhanced Lubrication

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ABSTRACT

Two different heteroelement-rich molecules have been successfully grafted on graphene oxide (GO) sheets which were then used as lubricant additives in bio-ionic liquid. The grafting was processed with reactions between GO sheets and synthesized heteroelement-rich molecules (Imidazol-1-yl phosphonic dichloride and 1H-1,2,4-triazol-1-yl phosphonic dichloride, respectively). The modified GO (m-GO) was added into [Choline][Proline] ([CH][P]) bio-ionic liquid, and has been demonstrated effective additive in promoting lubrication. Different characterization techniques have been utilized to study the reaction between GO and the two modifiers. The effect of molecular structure of the modifiers on the rheological and tribological properties of m-GO/[CH][P] lubricants was systematically investigated. Both theoretical calculation and experimental results demonstrated that the introduced heteroelement-rich groups are beneficial to increase the robustness of lubrication film by intensified hydrogen bonding and enhance the lubricant/friction surface adhesion by increased polarity of the m-GO. As a result, the interfacial lubrication could be significantly improved by these newly developed m-GO/[CH][P] lubricants.

Keywords: Graphene oxide, hetero-element, hydrogen bonding, lubrication, ionic liquids

1. Introduction

Energy and environmental challenges are the major themes of this century. About 100 million terajoules of energy is consumed annually to overcome friction and that is one fifth of the total energy produced every year.[1] Lubrication techniques are developed to reduce friction, wear and energy loss in many industrial and transportation processes.[2, 3] The continuous increase of lubricant consumption over past decade (>36 million tons in 2014) and the discharge of huge amount of lubricants into environment has caused a series of problems such as soil contamination, water pollution and others. In 2011, US Environmental Protection Agency published a memo on “Environmentally acceptable lubricants” for regulating the use and disposal of synthetic lubricants.[4]

Ionic liquids (ILs), defined as molten salts those are entirely ionic in nature, comprising both cationic and anionic species with a melting point below 100 °C,[5] have attracted great interests as synthetic lubricants since 2001.[6] The major advantages of ILs over petroleum oil based lubricants are their distinct physicochemical properties, such as negligible vapour pressure, high polarity and non-flammability.[3, 6, 7] The bio-ILs, with both cation and anion extracted from renewable bio-resources,[8] have attracted tremendous interests in the fields of biomass pre-treatment and lubrication[9, 10] due to their distinct advantages of biodegradability, non-toxicity, and environmentally benign feature.[11, 12] Pure bio-ILs have relatively higher friction coefficient and wear rate, especially in severe conditions such as high vacuum and high pressure.[10, 13, 14] Therefore, additives such as carbon nanotubes, graphene, lignin and *etc.* are often added into bio-ILs for enhanced lubrication properties.[15-17]

Graphene is a two-dimensional single sheet of carbon atoms arranged in a hexagonal network.[18, 19] It shows unique friction and wear properties those are not seen in conventional

materials.[20] The chemical inertness, excellent mechanical strength, and easy shear capability on its densely packed and atomically smooth surface are the major advantages that contribute to its impressive tribological behavior as solid or colloidal liquid lubricant.[21, 22] In previous study, graphene has been demonstrated a promising additive to improve the tribological properties of various polymers including but not limited to polyetheretherketone,[23] polytetrafluoroethylene,[24] poly(methyl methacrylate),[25] bismaleimide resins.[26] More than that, graphene can be used as effective lubricant additive in wide range of liquid bases including oil,[20, 27] water,[28, 29] grease,[30] and ILs[13, 31, 32].

In liquid lubricants, dispersion of graphene seems the major challenge in practical applications,[20, 33, 34] which can be addressed by tuning the interfacial compatibility and interfacial bonding. Among the different approaches, graphene dispersion can be greatly improved with the aid of surfactant or by chemical functionalization.[34-36] For example, Om P. Khatri introduced long alkyl chains at the defect edges of reduced graphene oxide sheets through amide linkage, which facilitates a stable dispersion and increases its compatibility with lube oil.[37] Another way is using graphene oxide (GO) instead of graphene. GO, an oxidized form of graphene, can be synthesized from natural graphite flakes by chemical oxidation method.[38] It acquires the similar material structure as graphene but it shows excellent dispersibility in polar solvents, which makes it an attractive candidate as solid lubricant or additive in liquid lubricant.[39, 40] Because of the presence of epoxy, hydroxyl, and carboxyl functional groups on GO's basal plane and edge area, it can be easily reacted with functional chemicals to improve GO dispersion, compatibility and functionality.[25] For example, Wu et.al[41] grafted tree-like polymeric phosphate esters onto GO nanosheets, which exhibited good dispersion in polyalkylene glycols and excellent tribological properties at elevated temperatures. Prasad et.

al[42] treated GO with [Choline][Formate] and [Choline][Caproate] and the products can be dispersed and stabilized in water for more than a year. Self-assembling of reduced GO (rGO) on silicon surface reduced friction coefficient from 0.6 (bare silicon) to 0.12–0.15.[43] Nitrogen element is often introduced to strengthen the interaction between lubricant base and additive through internal hydrogen bonding, which seems an effective approach to improve the compatibility and the overall lubrication performance.[10, 44] Besides, researchers have demonstrated that nitrogen and phosphorus hetero-elements are helpful to form a robust protective surface film on the metal surface, and thus enhancing the load-carrying capacity and improving the lubrication properties.[45-48]

In this work, two different heteroelement-rich groups were grafted on GO sheets through covalent bonding. The modified GO sheets were added in [Choline][Proline] IL as lubricant additive and its effectiveness in promoting lubrication was evaluated. The rheological and tribological properties of the [Choline][Proline]/GO lubricants were systematically investigated. The molecular interaction between GO (and modified GO) and ionic liquids as well as its effect on the resulting lubrication properties are discussed from both theoretical calculation and experimental approaches.

2. Experimental

2.1. Materials

Choline hydroxide aqueous solution (48-50 wt% in water) was purchased from Tokyo Chemical Industry. Graphite (99.99%) was purchased from Bay Carbon Inc. L-proline ($\geq 99\%$), imidazole ($\geq 99\%$), 1,2,4-1H-triazole (98%), phosphoryl chloride (POCl_3 , 99%), triethylamine (Et_3N , $>99\%$), dimethylformamide (DMF, $\geq 99.8\%$), potassium permanganate (KMnO_4 , $\geq 99\%$), sulfuric acid (H_2SO_4 , 95-98%), hydrochloric acid (HCl,

36.5–38.0%), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, $\geq 99.0\%$), phosphorus pentoxide (P_2O_5 , $\geq 98.0\%$), H_2O_2 solution (PERDROGEN[®] 30% H_2O_2 (w/w)), and polyvinylidene difluoride (PVDF) membrane filter (Durapore PVDF) were purchased from Sigma Aldrich. Deionized water was purified using a Milli-Q Direct 8 Ultrapure Water system (Millipore, Billerica, MA) with a minimum resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$. All chemicals were used as received without further treatment.

2.2. Graphene Oxide (GO) modification

Graphene oxide was prepared by modified Hummers method, which includes pre-oxidation and oxidation steps.[38, 49] The detailed preparation method refers to our previous publications.[50, 51] For GO modification, 0.002 M imidazole (or 1,2,4-1H-triazole) and 0.008 M Et_3N were firstly dissolved in 20 mL DMF. After heating the mixture to 60 °C, 0.002 M POCl_3 was added dropwise into the mixture with continuous magnetic stirring under nitrogen protection. By completing the addition of POCl_3 , the solution was heated up to 80 °C and refluxed for 6 h. Two intermediate products were formed, *i. e.* (Imidazol-1-yl)phosphonic dichloride ($\text{POCl}_2\text{-Im}$) and (1H-1,2,4-triazol-1-yl)phosphonic dichloride ($\text{POCl}_2\text{-Tr}$). Then, GO/DMF solution (0.25 g/50 mL) was added into the mixture. The reaction temperature was further heated to 95 °C and maintained for another 12 h. By the completion of reaction, the products were centrifuged at 6000 rpm, washed with deionized water 3 times and dried at 100 °C for 24 hours. The products were named as following: GO represents the as-synthesized GO, GO-Im and GO-Tr are GO modified by (Imidazol-1-yl)phosphonic dichloride and (1H-1,2,4-triazol-1-yl)phosphonic dichloride.

2.3. Synthesis of [Choline][L-proline]([CH])[P]) ionic liquid

Choline hydroxide aqueous solution was added dropwise to equimolar glycine with ice cooling. Then, the mixture was magnetically stirred at room temperature for 48 h. After reaction, the water in the mixture was removed using a rotary evaporator at 60 °C. Finally, the [CH][P] was dried *in vacuo* for 48 h at 70 °C.[10, 15]

2.4. Preparation of lubricants

To determine the loading of GO and GO-Im/Tr in [CH][P] ionic liquids, 1, 5, 10 and 30 mg GO (or GO-Im/Tr) was added to a glass vial containing 1.0 g [CH][P] and stirred at 90 °C for 24 hours with N₂ protection. The dispersion can be visually checked by observing whether the solution contains undissolved solids. The maximum loading is determined until the mixture cannot disperse any more solid and also the mixture solution keeps homogeneous for at least 24 hours. The maximum GO loading in [CH][P] is 1 wt%, which increases to 3 wt% for GO-Im/Tr. That is, GO modification increases its dispersibility in ionic liquid. The dispersibility of GO and m-GO is rechecked after 6 months and the mixture remained uniform without noticeable solid precipitates. The [CH][P] based lubricants were also prepared by incorporating 0.1, 0.5 and 1.0 wt% GO and denoted product name as [CH][P]-0.1, [CH][P]-0.5 and [CH][P]-1.0. The GO-Tr/Im (0.1, 0.5, 1.0 and 3.0 wt%)/[CH][P] lubricants are denoted as [CH][P]-0.1-Tr/Im, [CH][P]-0.5-Tr/Im, [CH][P]-1.0-Tr/Im and [CH][P]-3.0-Tr/Im. In this work, the weight percentage is calculated with [CH][P] as basis instead of the mixture.

2.5. Characterization

The thermal decomposition temperature (T_d) of the lubricants was determined by thermogravimetric analysis (TGA, TA instrument Q500) in N₂ atmosphere from 20 to 600 °C with a heating rate of 10 °C/min. The average viscosity of the lubricants within a range of shear

rate from 50 to 300 s⁻¹ was reported using a Bohlin CVO 100 rheometer at 25 °C. A cone-on-plate geometry was used with a 1° cone angle and 20 mm cone diameter. The lower plate has a diameter of 60 mm. The lubricant samples were dried in vacuo for 24 h at 70 °C before the viscosity test. The water content in the lubricant samples is lower than 1%. X-ray photoelectron spectra (XPS) was used to characterize the elemental species in GO, GO-Tr and GO-Im by using a PHI VersaProbe II Scanning XPS Microprobe with Al-K α line excitation source. An Optimol SRV-III oscillating friction and wear tester was used to evaluate tribological properties of the lubricants under lubrication conditions based on ASTM D 6425 protocol. During the test, the upper steel ball (52100 bearing steel, diameter 10 mm, surface roughness (R_a) 20 nm) slides under reciprocating motion against a stationary steel disc (100CR6 ESU hardened, Ø24 mm×7.9 mm, and surface roughness (R_a) 120 nm). The disc was supplied by Optimol Instruments Prüftechnik GmbH, Germany. The ball was provided by SKF, Sweden. Before each test the device and specimens were cleaned with acetone and ethanol. Then 0.5 mL lubricants were applied on the steel disc uniformly using the glass rod. All tests were conducted under the load of 258 N (3 GPa Maximum Hertzian pressure) at room temperature (25 °C), a sliding frequency of 50 Hz, and an amplitude of 1 mm. The temperature was measured and controlled by a cooling/heating device under the steel disc which was served as the sample holder for the disc. The temperature variation range is $\pm 1^\circ\text{C}$. The friction coefficient curves were recorded automatically with a data acquiring system linked to the SRV-III tester. After the tests the wear volumes of the lower discs and wear diameter of the balls were determined using an optical profiling system (Zygo 7300). Three duplicate friction and wear tests were carried out to minimize the experimental error.

2.6. Theoretical calculation

The calculations of optimized geometries and single point energies of GO, m-GO were performed using Gaussian 09 C1 suite of programs[52] by the density functional theory (DFT) with the Becke's three-parameter hybrid (B3LYP) functional.[53, 54] The 6-31G(d) basis set was employed for the geometry optimization. Harmonic vibrational frequencies were calculated to confirm the optimized structures as the local minima on the potential energy surfaces. The single-point calculations at the optimized geometries were conducted with the 6-311++G(d,p) basis set. Chemical descriptors such as ionization potentials (I), electron affinities (A), dipole momentum (μ_D) were calculated as indicators of the capability to form molecular interactions.

The I and A were calculated by using Equations (1) and (2):

$$I = E_c^{N-1} - E_o^N \quad (1)$$

$$A = E_o^N - E_a^{N+1} \quad (2)$$

where E_c^{N-1} is the energy of GO or m-GO after losing one electron (cation), E_o^N is the basal state energy (neutral) and E_a^{N+1} is the energy of GO or m-GO after gaining one electron (anion). Two descriptors, ω^- and ω^+ , were calculated as well according to Equations (3) and (4),[55] which relate to the capability of the molecule in donating and accepting electrons, respectively.

$$\omega^- = \frac{(3I+A)^2}{16(I-A)} \quad (3)$$

$$\omega^+ = \frac{(I+3A)^2}{16(I-A)} \quad (4)$$

3. Results and discussion

The reaction pathways of GO modification are provided in Figure 1. Firstly, heteroelement-rich groups, POCl₂-Im and POCl₂-Tr, were synthesized from an equimolar reaction of POCl₃ and imidazole (or 1,2,4-1H-triazole) reactants. The reaction is performed in DMF solvent with Et₃N catalyst, yielding hydrogen chloride as side product. With the addition of GO sheets in the system, the intermediate molecules (POCl₂-Im and POCl₂-Tr) further react with

the hydroxyl groups on GO sheet. Eventually, the functional molecules can be successfully grafted on GO sheet and form the desired products of GO-Im and GO-Tr.

Figure 1. Reaction pathway of GO modification with heteroatom-rich modifiers.

FT-IR spectrum was used to confirm the reaction occurred between GO and the two chemical modifiers. Figure 2(a) gives the typical GO adsorption spectrum. The peaks at 3140, 1730, 1051 cm⁻¹ are attributed to the O-H, C=O and C-O stretching vibration of GO, respectively.[56, 57] Within the range of 2500-3000 cm⁻¹, additional peaks circled in Figure 2(b&c) feature the presence of triazole and imidazole groups.[58, 59] Additional peaks were also observed at 985/976 and 800 cm⁻¹ in GO-Im or GO-Tr corresponding to the P-O-C and P-N vibration modes, Figure 2 (b1&c1).[60, 61] The P-N vibration peak confirms the successful reaction between POCl₃ and imidazole (or 1,2,4-1H-triazole). And the occurrence of the P-O-C

peak reveals the reaction between the hydroxyl group in GO and (Imidazol-1-yl)phosphonic dichloride and (1H-1,2,4-triazol-1-yl)phosphonic dichloride.

Figure 2. (a)-(c) FT-IR of GO, GO-Im and GO-Tr. (a1), (b1) and (c1) represent the enlarged IR spectrums within 700-1100 cm^{-1} . (d) XPS spectra of GO and GO-Tr/Im.

Realizing that the reaction yield could not be hundred percent, it is important to know how much modifier has actually been reacted with GO. The elemental analysis of the GO and GO-Tr/Im was conducted by XPS as seen in Figure 2(d) and the quantitative results were summarized in the inserted table in Figure 2(d). It is obvious that C and O elements present in all the samples. After reaction with the two modifiers, the characteristic peaks of N elements appeared in the XPS spectrum of GO-Tr/Im. However, the P element is not observed in GO-Tr/Im, which might be due to the low P element content in the GO-Im/Tr. In this work, the weight percent of the grafted modifiers in GO-Im/Tr was calculated based on the atomic percentage of N element from XPS analysis. The mass ratio of modifiers is then calculated as 12.4 and 20.7% and the reaction yields are determined as 23.2 and 38.5% for GO-Tr and GO-Im, respectively.

TGA and derivative thermogravimetry (DTG) of GO, GO-Im and GO-Tr under N₂ atmosphere were conducted to further confirm the weight ratio of the heteroelement modifiers in the GO-Im/Tr, Figure 3. The weight loss follows GO-Im > GO-Tr > GO over the entire temperature range, which indicates that the content of modifier in GO-Im is larger than that of GO-Tr. The difference in residue percentage at 600 °C is 24.3% between GO and GO-Im and 29.0% between GO and GO-Tr. Considering the remained weight percentage of GO itself (56%) at 600 °C, the weight percentage of the modifiers in GO can be further calculated as 13.6 and 16.2%, respectively. Figure 3(b) gives one broad degradation peaks centered at 200 °C, which corresponds well to the depletion of oxygen-containing groups from GO sheet and the decomposition of heteroelement modifiers.[62]

Figure 3. (a) TGA and (b) DTG curves of GO, GO-Im and GO-Tr under N₂ atmosphere.

Table 1 summarizes the viscosity of [CH][P] based lubricants. Pure [CH][P] show relatively lower viscosity of 0.22 Pa.s. Generally, viscosity increases after incorporating GO and m-GO in [CH][P] ILs. Larger mass fraction of GO (m-GO) in ILs leads to higher viscosity. At the same loading, the enhancement of viscosity is relatively higher by adding m-GO compared to GO. The weak interaction between GO and [CH][P] could be the major reason for its relatively

lower viscosity. The viscosity of [CH][P] filled with GO-Tr is higher than that of GO-Im at the same loading, which could be attributed to the stronger hydrogen bonding between GO-Tr and [CH][P]. The bonding strength among the different components can be elucidated from a DFT calculation study. The details of the DFT calculation results are summarized in Table 2. Such intensified hydrogen bonding is beneficial to improve the overall mechanical strength of the lubrication film. The viscosity was also measured from the samples with 3.0 wt% m-GO and it was found that the viscosity of [CH][P]-3.0-GO-Tr is more than doubled as compared to the sample with 1.0 wt% GO loading. Even though larger viscosity could be beneficial in certain circumstances by providing robust lubricating film,[63] it could be detrimental as well since larger viscosity of lubricant would generate and accumulate large amount of friction heat.[64] In this study, all of the prepared lubricants were tested to investigate the effects of GO loading and modification on lubrication.

Table 1. Viscosity of [CH][P] based lubricants in Pa·s.

Samples	Filler loading (wt%)				
	0	0.1	0.5	1.0	3.0
[CH][P]	0.22	-	-	-	-
[CH][P]-GO	-	0.24	0.33	0.37	NA
[CH][P]-GO-Im	-	0.31	0.36	0.40	0.99
[CH][P]-GO-Tr	-	0.34	0.40	0.51	1.07

Figure 4 shows the friction coefficient (μ) evolution during one-hour friction test with the presence of [CH][P] based lubricants at 3.0 GPa pressure. Apparently, unstable friction coefficient was observed by using pure [CH][P] as evidenced by the sharp jump of friction coefficient at about 1050 and 2600 s, Figure 4(a). The addition of GO helps to decrease the

fluctuation of friction coefficient, but still unsteady friction could be observed during the test, Figure 4(b-d). The average friction coefficient of [CH][P] was reduced by about 10% with the addition of 0.1 wt% GO. By testing the lubricants with 0.1 wt% GO-Im/Tr, it seems that such small fraction of GO-Im/Tr does not help to promote lubrication as evidenced by the unstable friction coefficient, Figure 4(e & i). However, larger fraction of GO-Im/Tr could improve the lubrication significantly. By adding 0.5, 1.0 and 3.0 wt% of GO-Im/Tr, the friction coefficient of the lubricants could be stabilized at below 0.1. With the addition of GO-Im/Tr in [CH][P], the average friction coefficient decreases slightly and reaches the lowest at 1.0 wt% loading. Further increasing filler loading to 3 wt% leads to a slight increase of friction coefficient. It is believed that the grafted heteroelement modifier incorporates additional sites with larger polarity (evidenced by the higher dipole moment μ_D in Table 2) that tends to form a stronger adhesion layer with metal surface and thus reduces the friction coefficient.

Figure 4. Friction coefficient of [CH][P] based lubricants. Load: 3.0 GPa, testing duration: 1 h, room temperature. (a) [CH][P], (b) [CH][P]-0.1, (c) [CH][P]-0.5, (d) [CH][P]-1.0, (e) [CH][P]-0.1-Im, (f) [CH][P]-0.5-Im, (g) [CH][P]-1.0-Im, (h) [CH][P]-3.0-Im, (i) [CH][P]-0.1-Tr, (j) [CH][P]-0.5-Tr, (k) [CH][P]-1.0-Tr and (l) [CH][P]-3.0-Tr.

Figure 5 shows the wear volume loss of the discs lubricated by different [CH][P] based lubricants. The wear volume loss with [CH][P]-0.1/0.5/1.0 is apparently lower than the one lubricated by pure [CH][P], which indicates the positive contribution of GO in promoting anti-wear property of lubricant. It is also observed that the wear volume loss decreases continuously with increasing GO fraction in the [CH][P]. Specifically, the wear volume of the disc by [CH][P]-1.0 is only 48 % of the one lubricated by pure [CH][P]. In addition, the wear volume loss decreases continuously with increasing GO-Im/Tr loading and reaches the lowest value at 1.0 wt%. The wear volume loss of the disc can be reduced by 73% by using [CH][P]-1.0-Im lubricant compared to pure [CH][P]. Moreover, the positive contribution of heteroelement groups is revealed by the 73% wear loss reduction in [CH][P]-1.0-Tr compared to its corresponding compound [CH][P]-1.0. These results demonstrate the positive contribution of the grafted heteroelement-rich groups in GO to promote anti-wear capability of the lubricants.

Figure 5. Disc wear volume of steel disc lubricated by [CH][P] based lubricants. Load: 3.0 GPa, testing duration: 1 h, room temperature.

To understand how the grafted heteroatom-containing groups in GO interacts with [CH][P] and helps to improve lubrication property, DFT calculation study was also involved to analyse the capability of donating/accepting electrons (ω^-/ω^+) and dipole moment (μ_D) of GO and m-GO. The results are summarized in Table 2. The dipole moment of m-GO is obviously larger than GO, which indicates that the grafted groups in GO enhances its polarity. The larger μ_D of m-GO favours a stronger adhesion on metal surface.[65] Therefore, a better protection by m-GO on the friction surface could be expected and thus facilitates the interfacial lubrication. On the other side, the larger ω^- and ω^+ values from m-GO than GO imply a more favourable hydrogen bonding interaction between m-GO and [CH][P]. The hydrogen bonding would strengthen the interaction between m-GO and [CH][P] and improve the mechanical strength of the lubrication film. Comparing the tribological property of GO-Tr/Im filled lubricants, the better anti-wear property of GO-Tr could be attributed to its stronger lubricating film (evidenced by viscosity in Table 1).

Table 2. Descriptors calculated with B3LYP/6-311++G** for GO and m-GO.

Molecule	$I(\text{eV})$	$A(\text{eV})$	$\omega^- (\text{eV})$	$\omega^+ (\text{eV})$	μ_D (Debye)
GO	2.755	1.159	3.480	1.522	1.370
GO-Im	2.826	1.252	3.760	1.720	7.093
GO-Tr	2.819	1.244	3.735	1.703	5.688

Figure 6 shows the three-dimensional (3D) surface profiles of the wear tracks on disc. The wear track with [CH][P] is obviously deeper than the tracks with GO reinforced lubricants. The optimal lubrication was achieved at 1 wt% GO and m-GO loading, which is confirmed by the shallower wear tracks observed in [CH][P]-1.0 and [CH][P]-1.0-

Im/Tr, Figure 6(d, g & k). Comparing the 3D images from second and third rows of Figure 6, the [CH][P] based lubricants filled with GO-Im give relatively larger and deeper wear tracks than that of GO-Tr. Overall, the addition of GO increases the load-bearing capability of [CH][P]. Grafting heteroelement-rich groups on GO further strengthens its lubrication property in [CH][P].

Figure 6. 3D surface profile of the wear tracks on disc by using different [CH][P] based lubricants. Load: 3.0 GPa, testing duration: 1 h, room temperature. (a) [CH][P], (b) [CH][P]-0.1, (c) [CH][P]-0.5, (d) [CH][P]-1.0, (e) [CH][P]-0.1-Im, (f) [CH][P]-0.5-Im, (g) [CH][P]-1.0-Im, (h) [CH][P]-3.0-Im, (i) [CH][P]-0.1-Tr, (j) [CH][P]-0.5-Tr, (k) [CH][P]-1.0-Tr, (l) [CH][P]-3.0-Tr.

To illustrate the effectiveness of the modified GO in promoting lubrication, the friction coefficient and wear loss reduction have been compared with literature reports. By introducing GO, rGO or graphene in different lubricant bases, improved tribological properties have been observed. For example, rGO/PEG (50% wear and 70% friction reduction),[66] oleic acid-modified graphene/polyalphaolefin (~16% wear and 16% friction reduction),[27] microwave-synthesized rGO/paraffin oil (~64% wear and 3% friction reduction),[67] graphene/1-Butyl-3-

methylimidazolium tetrafluoroborate ILs (~45% wear and 24% friction reduction),[31] graphene/bentone lubricating grease (~55% wear and 10% friction reduction),[30] modified GO/oil-in-water emulsion (~27% wear and 18% friction reduction).[68] In this work, the wear loss and average friction coefficient are reduced by 87% and 9% after adding 1% GO-Tr in [CH][P]. Comparing with the GO or graphene based lubricants from literature reports, modified GO has the capability to reduce average friction coefficient, stabilize friction fluctuation and improve wear resistance simultaneously. It is worth mentioning simultaneous reduction of friction coefficient and stabilization of friction fluctuation is difficult to achieve in most cases. For example, the largest friction reduction of 70% in rGO/PEG leads to fluctuation of friction coefficient.[66] The outstanding tribological properties of the [CH][P]/m-GO system are most likely attributed to the formation of lubrication films during the friction process. The enhanced lubrication property of the [CH][P]/m-GO system could be attributed to two main factors. Firstly, the introduced hetero-elements would increase the dipole moment of the m-GO and thus lead to large polarity, which facilitates its adhesion on metal surface that prevents the direct metal/metal contacts and thus promotes interfacial lubrication.[69] Secondly, the introduced heteroatoms are able to offer additional electrons in the modified GO, which could form intensified hydrogen bond interactions with [CH][P]. Such additional hydrogen bonding would favour a stronger [CH][P]/m-GO interaction, and thus strengthen the lubrication film between metal/metal contact.

4. Conclusions

GO modification with heteroatom-containing molecules has been carried out for the development of new lubricant additives. Two heteroelement-rich modifiers, imidazol-1-yl phosphonic dichloride and 1H-1,2,4-triazol-1-yl phosphonic dichloride, were synthesized to react

with GO in this work. Results show that the introduced hetero-elements in GO could help to promoted lubrication when added into [CH][P] bio-ionic liquid. The positive effect of heteroatom groups is revealed by the 73% wear loss reduction in [CH][P]-1.0-Tr compared to its corresponding compound [CH][P]-1.0. The positive contribution of heteroatoms in lubrication can be attributed to two factors: intensified hydrogen bonding between m-GO and [CH][P] that strengthens the lubrication film; increased polarity of m-GO that facilitates its strong adhesion with metal surface. These two factors have been verified by theoretical calculation where m-GO shows larger polarity and better capability to form hydrogen bonding than that of GO. This work offers a new approach for GO functionalization and its promising application in advanced lubrication systems.

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Graphical abstract

Grafting Heteroelement-Rich Groups on Graphene Oxide: Tuning Polarity and Molecular Interaction with Bio-Ionic Liquid for Enhanced Lubrication

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Heteroelement-rich groups on GO favors strong surface adhesion and promotes hydrogen bonding in bulk lubricant that synergistically improve lubrication.