

Novel concept of nano-additive design: PTFE@silica Janus nanoparticles for water lubrication

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Abstract: Polytetrafluoroethylene (PTFE) has been widely used as a lubrication additive for reducing friction and wear; however, the hydrophobic nature of PTFE restricts its application in eco-friendly water-based lubrication systems. In this study, for the first time, we designed novel PTFE@silica Janus nanoparticles (JNs) to meet the requirement for additives in water-based lubricants, which have excellent dispersion stability in water attributed to the unique amphiphilic structure. By introducing the lubrication of the aqueous dispersion of the JNs with a concentration of 0.5 wt%, the coefficient of friction (COF) and wear volume were reduced by 63.8% and 94.2%, respectively, comparing to those with the lubrication of pure water. Meanwhile, the JNs suspension also exhibits better lubrication and wear-resistance performances comparing to commercial silica and PTFE suspensions. The excellent tribological behaviors of PTFE@silica JNs as nano-additives could be attributed to the synergetic effect of the two components, where the PTFE provided lubrication through the formed tribofilms on the friction pairs, and the rigid silica further enhanced the wear-resistance performance. Most importantly, the unique structure of JNs makes it possible to use PTFE as an additive in water-lubrication systems. Our study shed light on the design and application of novel JNs nanomaterials as additives to meet the requirements of future industrial applications.

Keywords: Janus nanoparticles (JNs); polytetrafluoroethylene (PTFE); nano-additives; friction; lubrication

1 Introduction

Friction between machine pairs usually causes significant energy losses and carbon emissions, whereas machine wear leads to equipment failures for industrial applications. Traditional oil-based lubricants are harmful to the environment. Developing advanced lubrication technologies is of vital significance as they throttle the comprehensive ecological improvement and sustainable development of human society [1, 2].

Under such a background, water-based lubricants have attracted significant attention as they exhibit potential in various industrial applications [3–7]. However, the lubrication performance of pure water is difficult to meet the needs for engineering applications. Hence, additives are critical to enhancing the tribological performance of water-based lubricants.

Recently, it was found that the nanomaterials, including two-dimensional materials [8–12], nanodiamonds [13], metals or metal oxides [14], and

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organic nanoparticles [15], exhibited excellent practical prospect as nano-additives due to the small size, regulatable chemical and physical structures, and the excellent lubrication and wear-resistance performance [13]. Polytetrafluoroethylene (PTFE), as an important engineering material, has been widely used as a solid lubricant or additive owing to its unique chemical and physical properties. When rubbed by hard surfaces, scission between PTFE chains can effectively reduce the shear strength. The tribochemical reaction between PTFE and counterfaces leads to the formation of a coherent transfer film, providing excellent lubrication and corrosion-resistance properties [16–18]. It was found that even a low concentration of PTFE particles can lead to a significantly reduced coefficient of friction (COF) of oil-based lubricant in rolling and sliding contacts [19, 20], but the wear-resistance behavior of PTFE particles is usually unsatisfactory. To overcome this limitation, Qu et al. [21] have found that the wear-reduction property of PTFE particles can be improved by embedding hard particles such as Cu or silica into the PTFE outer shell. PTFE has been widely used as nano-additive for oil-based lubricants [22–27]. However, achieving long-term stability of PTFE as nano-additive for water-based lubricants remains a great challenge due to its hydrophobic nature. The development of PTFE-based nano-additive with excellent lubrication, wear-resistance, and dispersion stability is important for advanced water-based lubrication systems.

Targeted structural design of nanomaterials is an effective mean to improving its performance. Janus is the name of the god in Roman mythology, who has double faces for the past and the future. In 1991, Pierre Gilles de Gennes [28] first used “Janus” to describe partitioned particles with dual properties on the same particle in his Nobel speech, which can simultaneously have two different or even opposite properties: From the perspective of morphology, the structural asymmetry gives Janus special steric effect. Janus materials with different components can simultaneously exhibit the hydrophilic/hydrophobic, positive/negative charges, and polar/nonpolar to give the material versatility [29–31]. Therefore, Janus materials can adjust the functionality of materials based on the use environment to meet the use requirements

in complex conditions. In this study, novel PTFE@silica Janus nanoparticles (JNs) were designed to apply hydrophobic PTFE as the additive for water-based lubricant for the first time, which have excellent dispersibility in pure water owing to their unique hydrophilic/hydrophobic structure. The water suspension of PTFE@silica JNs exhibits excellent tribological performance, effectively reducing the friction and wear of steel counterparts. Meanwhile, the lubrication mechanisms governed by the structural conversation and synergetic between the rigid silica particles and flexible PTFE at the sliding interface were studied in detail, which provide a new pathway to designing high-performance nano-additives for future lubrication systems.

2 Experimental

2.1 Materials

A PTFE dispersion (DISP 30) with a solid content of 60 wt% was provided by DuPont Co., USA, which was used as the seed spheres. The silica lobes of the JNs were produced using 3-methacryloxypropyltrimethoxysilane (MPS), sodium dodecyl benzenesulfonate (SDS), azobisisobutyronitrile (AIBN), and potassium peroxydisulfate (KPS). The MPS was provided by Tokyo Chemical Industry Co. Ltd., Japan, and the SDS, AIBN, and KPS were provided by Sinopharm Chemical Reagent Co. Ltd., China.

2.2 Synthesis of PTFE@silica JNs

Typical JNs with a silica monomer (MPS)/PTFE seed mass ratio of 2.0 were prepared as follows. The latex of the PTFE seed particles (1.67 g, containing 1 g of solid particles) was suspended in deionized water (50 g). Subsequently, 1 wt% of KPS aqueous solution (2 g) and MPS (2 g) were added into deionized water (10 g) containing SDS (0.06 g), followed by 5 min of ultrasonication to form the emulsion of the MPS monomer. The prepared emulsion was then added into the PTFE seed dispersion, stirring for 6 h at 300 r/min. After that, the mixture was kept at 70 °C for 24 h with mechanical stirring for the reaction. At last, PTFE@silica JNs were obtained after centrifugation, and the product was washed by pure water.

2.3 Characterization of JNs

The Fourier transform infrared (FTIR) spectrometer (IRTracer-100, Shimadzu, Japan) was used to investigate the chemical structures and compositions of the JNs. The scanning electron microscope (SEM; JSM-7900F, JEOL, Japan; at 5 kV) and high-resolution transmission electron microscope (HRTEM; JEM-2100F, JEOL, Japan; at 200 kV) were used to observe the morphologies of the JNs.

2.4 Friction tests

The JNs were dispersed in pure water to prepare water suspension with a concentration of 0.1–10 wt% as lubricants for the friction tests. Water suspension of silica nanoparticles (XFNano, China) with a concentration of 0.5 wt% was also prepared for comparison. The macroscale tribological behavior of the JNs water suspension as a lubricant was investigated using ball-on-disk friction tests in a rotating mode (universal micro-tribometer; UMT-3, Bruker, USA). Commercially available American Iron and Steel Institute (AISI) 52100 steel plates and bearing balls with a diameter of 4 mm were used as friction pairs. The steel plates and bearing balls have surface roughness of $S_a = 14$ and 7 nm, respectively, and a hardness of approximately 700 HV [32, 33], and were used as the counterparts (Fig. S1 in the Electronic Supplementary Material (ESM)), which were firstly washed with acetone and ethanol by bath sonication for 30 min to eliminate residual contaminants. Before each friction test, 160 μL of the JNs water suspension was supplied between the counterparts. The radius, rotation speed, and applied normal load of the friction tests were set as 4 mm, 180 r/min, and 2 N, respectively. The corresponding sliding velocity and initial Hertzian contact pressure were 0.075 m/s and approximately 1.1 GPa, respectively. To ensure the reproducibility, the friction tests were conducted at least 3 times (25 ± 1 °C, relative humidity in the range of 10%–12%).

2.5 Surface characterization

The wear region morphologies of the counterparts were measured using a three-dimensional (3D) white light interferometer (Nexview, ZYGO Lamda, USA)

and a field-emission scanning electron microscopy (FESEM; SU8220, Hitachi, Japan; accelerating voltage of 10 kV under high-vacuum conditions) to investigate the anti-wear performance of the JNs as additives in pure water. The elemental distributions in the wear regions were obtained by the energy-dispersive X-ray spectroscopy (EDS) equipped on the FESEM. The chemical compositions after 10 min of friction tests were characterized by the X-ray photoelectron spectroscopy (XPS; PHI Quantera II, ULVAC-PHI, Japan) to investigate the potential tribochemical reaction during the friction tests. Lamellar samples were prepared using a focused ion beam (FIB; Helios G4 UC, Thermo Fisher Scientific, USA) from the wear surfaces of the counterparts for further HRTEM investigations. A Cr layer and a Pt layer were deposited on top of the wear regions as protecting layers. The microstructures and the chemical compositions of the wear surfaces were further investigated using the HRTEM equipped with the EDS.

3 Results and discussion

3.1 Characterization of JNs

The morphologies and chemical compositions of the synthesized JNs were firstly investigated. PTFE@silica JNs were prepared using the seed-swell emulsion polymerization method (Fig. 1 and Figs. S2 and S3 in the ESM). Commercial PTFE particles were used as seeds to grow silica bulbs. A silica hemisphere was formed on one side of the PTFE seed after polymerization owing to the phase separation between silica and the PTFE polymer (Fig. 2(a)). From the FTIR results (Fig. 2(b)), the characteristic peaks of PTFE@silica JNs appear at 697 cm^{-1} , 816, 908, and 1,720 cm^{-1} , demonstrating the presence of the Si–C group and C=O group, further indicating the formation of a silica lobe on the PTFE seed particles.

The silica lobe formed on one side of the JNs was also confirmed by the HRTEM–EDS line scanning image (Fig. 2(c)) and mapping images (Figs. 2(d)–2(h)). The results show that Si and O were enriched at one side of the JNs, while a high concentration of F was mostly enriched at the other side of the JNs of the PTFE seed owing to the silica lobe separating well from the PTFE seed. The unique structure of the JNs

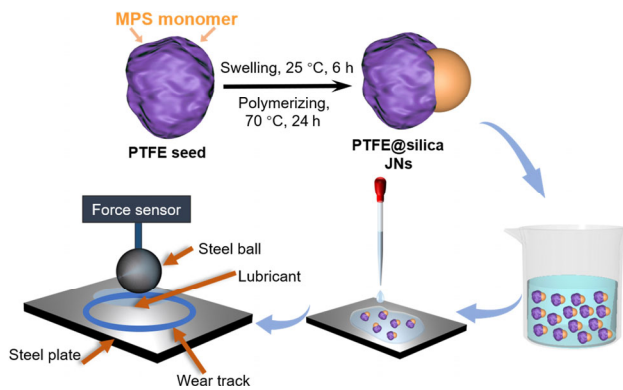


Fig. 1 Schematic of preparing process of JNs and friction tests.

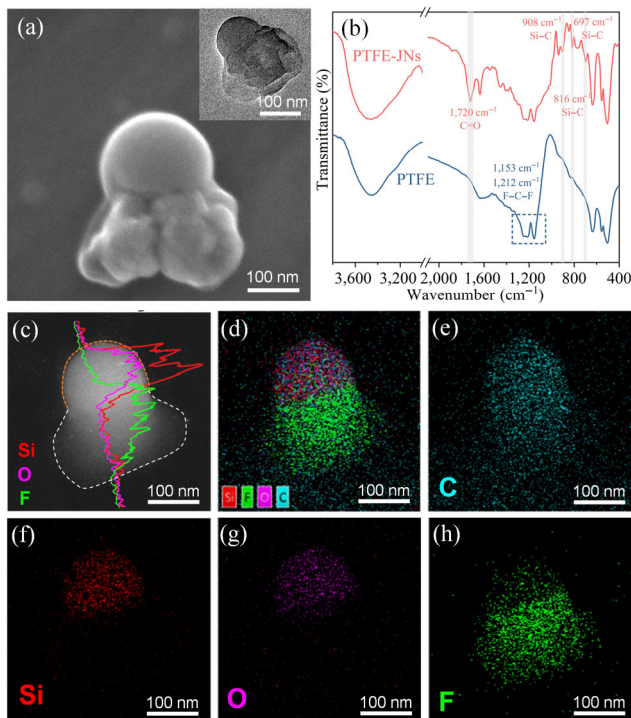


Fig. 2 Characterization of PTFE@silica JNs. (a) SEM image and TEM image (the inset) of JNs. (b) FTIR spectra of JNs and PTFE particles, where the peaks of F–C–F for PTFE and the peaks of silica can be observed. (c) TEM image of JNs, where the inset is the EDS line scanning results of JNs. EDS mapping results for (d) mixture of different elements and single elements of (e) C, (f) Si, (g) O, and (h) F. Those results indicate that the two sides of the JNs are composed by PTFE and silica.

with hydrophilic silica attached to the hydrophobic PTFE led to the excellent dispersion stability of JNs in pure water (Fig. S4 in the ESM).

3.2 Lubrication performance of JNs as additives

Aqueous suspension of JNs was used as a lubricant for the friction test to study the lubrication

performance of JNs as additives. The lubrication and anti-wear performances were investigated through macroscale friction tests (2 N and 0.075 m/s) (Fig. 3). The COF with pure water as a lubricant was firstly measured for comparison (Fig. 3(a)). The COF was maintained at high values of approximately 0.30–0.37 with significant fluctuation during the entire friction test with pure water lubrication. The COFs with the lubrication of water suspensions with JNs as additives were then measured (Figs. 3(a) and 3(c)). Friction tests with the lubrication of the JNs water suspension were conducted in a wide range of JNs concentrations from 0.1 to 10 wt%. A significantly small amount of JNs (0.1 wt%) added to pure water can lead to a significant reduction in the COF, from an average COF of 0.330 to approximately 0.105 (reduced by 68.2%). However, it should be noted that the lubrication behaviors with different concentrations of JNs are not the same. Evident fluctuations can be observed from the COF curve with the lubrication of water suspension with 0.1 wt% JNs. A stable COF after the running-in process can be obtained by increasing the JNs concentration to 2 wt%. However, although lower average COFs in the friction process can be obtained with a further increasing JNs concentration to 5 wt%, the stability of the COF during the friction process with high JNs concentrations of 5 and 10 wt% is unsatisfactory compared to that with moderate JNs concentrations from 0.2 to 2 wt%. The average COFs of independent friction tests indicate that the average COFs gradually decrease from 0.105 to 0.072 with the increasing JNs concentration from 0.1 to 5 wt%, but the average COF increased to 0.087 with a further increase in the concentration of JNs to 10 wt%. The lowest COF was obtained with a JNs concentration of 5 wt%, which was 78.2% lower than that of pure water. The lubrication behavior of PTFE@silica JNs was also compared with that of commercial silica nanoparticles as additives. The PTFE@silica JNs suspension exhibits better lubrication performance at both a low concentration of 0.5 wt% (reduction of 63.8%) and a high concentration of 5 wt% (reduction of 66.5%) compared to silica suspension (Fig. 3(b)). Only PTFE nanoparticles cannot be dispersed in pure water owing to their hydrophobic nature, so it is difficult to evaluate the lubrication performance of PTFE nanoparticles using its pure

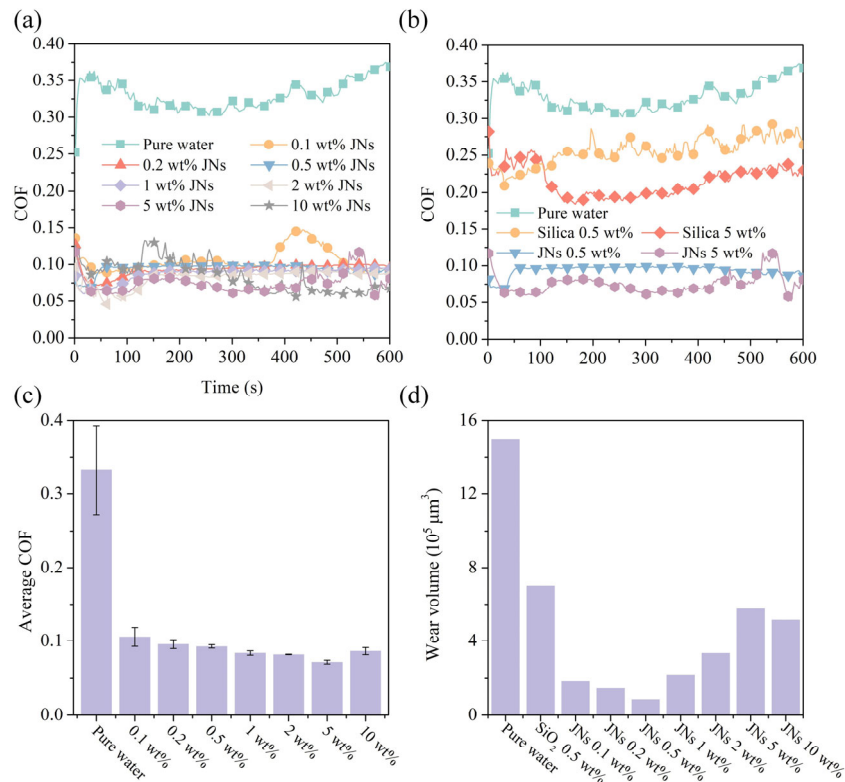


Fig. 3 Lubrication performance with JNs as additives. (a) COF vs. time with the lubrication of pure water and JNs suspensions with different concentrations (2 N and 0.075 m/s). (b) COF vs. time curves with the lubrication of pure water, silica suspension, and JNs suspension (2 N and 0.075 m/s). (c) Average COFs of independent friction tests with the lubrication of JNs suspensions with different concentrations (2 N and 0.075 m/s), where the error bars indicate the standard deviations of the COF data. (d) Wear volumes of steel balls after the friction tests with different lubricants (2 N, 0.075 m/s, and 600 s).

water suspension. Hence, the lubrication behaviors of diluted commercial PTFE suspension (DISP 30) were studied as comparison (Fig. S5 in the ESM) [34]. Differently, with a moderate concentration of 0.5 wt%, the average COF with the lubrication of PTFE suspension (0.118) is only slightly higher than that with the lubrication of JNs suspension (0.093), but having more obvious fluctuation. With a high concentration of 5 wt%, the average COF with the lubrication of PTFE suspension (0.234) is much higher than that with the lubrication of JNs (0.072), which might attribute to the poor dispersibility of PTFE nanoparticles. Those results indicate that the PTFE exhibits a dominant role for the lubrication performance of the PTFE@silica JNs as additives.

Moreover, the 3D white light interferometry was used to obtain the morphologies of the wear regions (Fig. S6 in the ESM). With pure water lubrication, a large wear scar with a diameter of approximately 498 μm was observed on the steel ball, indicating that

severe wear is induced by rubbing. The wear-track region of the steel plate was higher than the unworn region, which could be attributed to severe material transfer and oxidation induced by rubbing. With JNs concentration in the range of 0.1 to 2 wt%, the wear tracks on the steel plates were hard to be observed (Fig. S6 in the ESM). However, more severe wear of both friction pairs was observed with a further increase in the concentration of JNs as additives. The wear volumes (Fig. 3(d)) and diameters of the wear scar (Fig. S7 in the ESM) on the steel balls with different lubricants were used to evaluate the anti-wear performance of the JNs. The obtained 3D morphology was first flattened to a plane, and the volume of the wear scar region below the unworn region as the reference plane was automatically obtained using the software (MetroproX, Zygo, USA). With only 0.1 wt% of the JNs as additives, the wear volume was significantly reduced by 87.67% compared to that of pure water alone. The wear volume of steel balls can be further

decreased by increasing the content of JNs, obtaining the lowest wear volume with 0.5 wt% JNs concentration, which is reduced by 94.22% compared to that of pure water alone. However, a further increase in the concentration of JNs leads to a significant increase in the wear volume of steel balls. The morphologies of the friction pairs with the lubrication of commercial silica (Fig. S8 in the ESM) and PTFE (Fig. S9 in the ESM) nanoparticles and the corresponding wear volumes (Fig. S10 in the ESM) are also obtained for comparison, indicating that the JNs exhibit better wear-reduction performance than silica and PTFE suspensions. The excellent lubrication and wear-reduction performances

of the JNs as additives are due to the synergetic effect of silica and PTFE.

3.3 Surface characterization

Various surface characterization techniques were conducted on the friction pairs to reveal the functional mechanism of JNs as nano-additives. The counterparts were immediately rinsed with pure water after the friction test to eliminate contaminants on the friction pairs. The surface morphologies of the friction pairs and corresponding elemental distributions of the contact regions were observed using the FESEM equipped with the EDS (Fig. 4). After the friction test

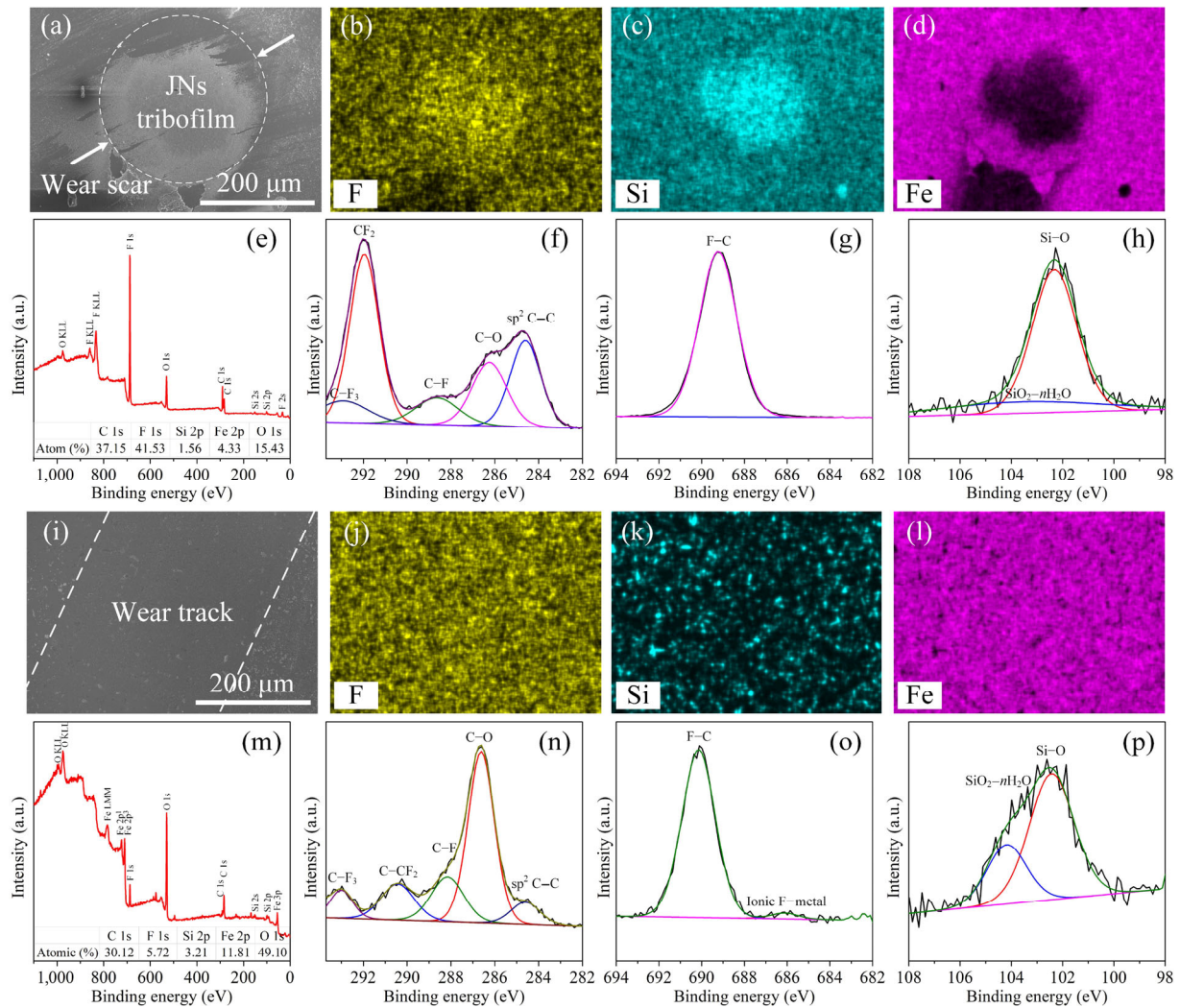


Fig. 4 Characterization of wear surfaces of counterparts after friction test with the lubrication of 0.5 wt% JNs suspension (2 N, 0.075 m/s, and 600 s). (a) SEM image of wear scar surface of steel ball and elemental distributions of (b) F, (c) Si, and (d) Fe. Corresponding XPS: (e) full spectrum and high-resolution spectra of (f) C, (g) F, and (h) Si on wear scar surface. (i) SEM image of wear-track surface of steel plate and elemental distributions of (j) F, (k) Si, and (l) Fe. Corresponding XPS: (m) full spectrum and high-resolution spectra of (n) C, (o) F, and (p) Si on wear-track surface.

with the lubrication of the JNs suspension, a tribofilm was clearly observed at the center of the wear scar surface of the steel ball (Fig. 4(a)), which is different from the wear regions of the friction pairs without JNs as additives (Fig. S11 in the ESM). The tribofilm had high concentrations of F (Fig. 4(b)) and Si (Fig. 4(c)), indicating that the tribofilm was composed of PTFE and silica. Furthermore, a high concentration of Fe was observed at the edge of the wear scar (Fig. 4(d)), which corresponds to the accumulation of wear debris.

The chemical compositions and structures of the wear regions were investigated by the XPS spectra, revealing the potential tribochemical reaction. The full spectrum of the tribofilm had a high F 1s peak but a small Si 2p peak (Fig. 4(e)), indicating the high concentrated F and relatively low concentrated Si. The semi-quantitative results show that the atomic concentrations of C, F, Si, Fe, and O in the tribofilm were 37.15%, 41.53%, 1.56%, 4.33%, and 15.43%, respectively. The high-resolution XPS spectra were obtained to further elucidate the chemical structure of the tribofilm. All the XPS spectra results were processed with Lorentzian–Gaussian fitting, and the obtained results were calibrated by C 1s at 284.6 eV. For the tribofilm on the wear surface of steel ball lubricated using JNs suspension, there were five peaks centered at 284.6, 286.3, 288.6, 291.9, and 292.8 eV with area ratios of 23.13%, 17.39%, 10.12%, 39.70%, and 9.66%, respectively, in the C 1s XPS spectra (Fig. 4(f)), which can be indexed to the sp^2 C–C, C–O, C–F, CF_2 , and CF_3 chemical bonds [35], respectively. Meanwhile, the only peak in the F 1s spectrum is centered at 689.2 eV (Fig. 4(g)), which can be indexed to the F–C chemical bonds [36]. Furthermore, two peaks centered at 102.2 and 103.6 eV with area ratios of 77.45% and 22.55%, respectively, can be observed in the Si 2p XPS spectra (Fig. 4(h)), corresponding to the Si–O chemical bonds and SiO_2-nH_2O [37], respectively, which indicates that the structure of silica was slightly changed by rubbing in water environment.

For the steel plate with the lubrication of the JNs suspension, the wear of the contact surface was difficult to be observed (Fig. 4(i)), which is in accordance with the results obtained using a 3D white light interferometer (Fig. S6 in the ESM). The EDS mapping

results indicate that F is more uniformly distributed in the wear-track region than Si (Figs. 4(j) and 4(k)). In contrast to the wear scar on the steel ball, the Fe signal was strong in the wear-track region (Fig. 4(l)), which could be attributed to the small thickness of tribofilm on the wear-track surface of the steel plate.

The XPS spectra were also obtained for the wear track of the steel plate. Small peaks for F 1s and Si 2p were observed in the full spectrum of the wear track (Fig. 4(m)), whereas a high O 1s peak was clearly observed. The atomic concentrations of C, F, Si, Fe, and O in the tribofilm were 30.12%, 5.72%, 3.21%, 11.81%, and 49.10%, respectively. The wear-track surface of the steel ball lubricated by the JNs suspension showed five peaks centered at 284.6, 286.6, 288.2, 290.4, and 293.0 eV in the C 1s spectra (Fig. 4(n)), which can be indexed to the sp^2 C–C, C–O, C–F, $C-CF_2$, and $C-F_3$ chemical bonds [35, 38, 39], respectively. In addition to the peak corresponding to the F–C chemical bonds, a less intense peak was observed in the F 1s spectra (Fig. 4(o)), which can be attributed to the formation of ionic F–metal chemical bonds [40]. Moreover, for the Si 2p spectra, two peaks centered at 102.4 and 104.2 eV with area ratios of 70.45% and 29.55%, respectively, can be observed (Fig. 4(p)).

From the results with the lubrication of the JNs suspension, clearly, the tribofilm with PTFE and silica can be formed both on the surfaces of the steel ball and steel plate, where the different distributions of PTFE and silica arise from the detachment of the two components of the JNs. However, the tribofilm can be more easily formed on the surface of the steel ball, which can be attributed to the fact that the ball surface is constantly in contact, whereas the plane surface is only periodically in contact, leading to different surface structures of the friction pair surfaces. Comparing the XPS results obtained from the wear regions of the friction pairs, the area ratio of the peak for the C–O chemical bonds on the steel plate was higher than that on the steel ball (Figs. 4(f) and 4(n)), indicating that the PTFE in the tribofilm on the steel plate suffered more severe degradation induced by rubbing. A small peak corresponding to ionic metal–F chemical bonds was observed in the high-resolution F 1s spectrum on the wear-track surface of the steel plate (Fig. 4(o)), but it was not observed on the steel ball

(Fig. 4(g)). It is widely accepted that tribofilm formation on friction pairs is an important mechanism for the lubrication performance of PTFE [16, 18], which is also observed for the friction pairs lubricated by PTFE suspension (Fig. S12 in the ESM). The formation of metal–F chemical bonds is a key factor in the formation of tribofilms on metal counterparts [17]. The peak for the metal–F chemical bonds on the steel ball surface was absent, which could be attributed to the fact that the interfacial chemical structure between the tribofilm and the steel ball surface is difficult to obtain using the XPS because of the relatively large thickness of the tribofilm.

After the friction test lubricated by JNs suspension (0.5 wt%), the cross-sectional lamellar samples are extracted from the center of the wear scar (Fig. 5) and wear track (Fig. 6) by the FIB for the HRTEM characterization. For the wear surface of the steel ball (Fig. 5(a)), a tribofilm of approximately 400–600 nm was observed (Fig. 5(b)). The high-resolution image (Fig. 5(c)) and the corresponding EDS mapping results (Figs. 5(d)–5(h)) are obtained to investigate the morphology and elemental compositions of the tribofilm. The tribofilm on the steel ball has a porous structure (the dark regions in the EDS mapping correspond to the pores). In contrast to that of the

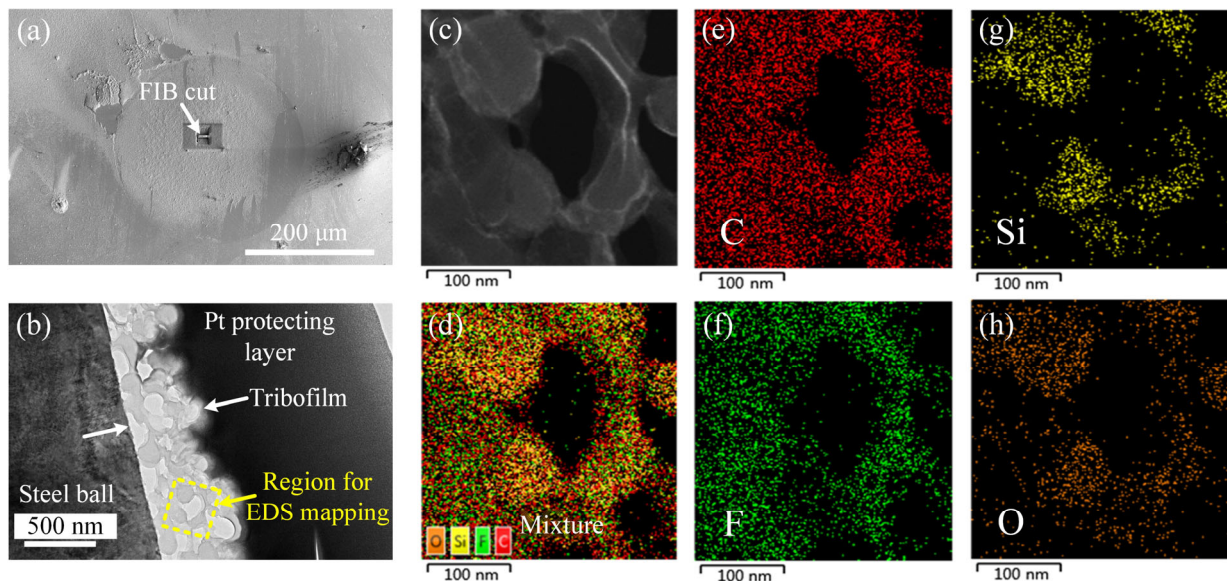


Fig. 5 Cross-sectional investigation of tribofilm on steel ball after friction test (2 N, 10 min, and 0.075 m/s) lubricated using JNs suspension with a concentration of 0.5 wt%. (a) Location of lamellar sample for the HRTEM; (b) cross-sectional morphology of tribofilm on steel ball; (c) high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image of tribofilm; and corresponding EDS mapping results for (d) mixture of different elements and single elements of (e) C, (f) F, (g) Si, and (h) O, where the region for the EDS mapping is marked in (b).

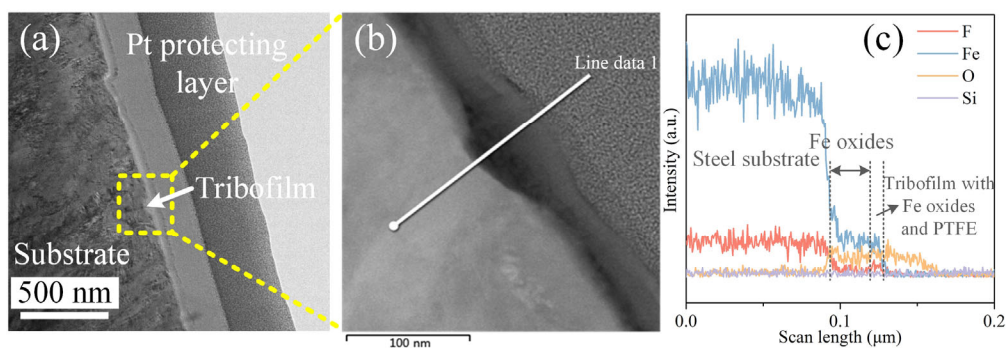


Fig. 6 Cross-sectional investigation of steel plate surface lubricated using JNs suspension (0.5 wt%). (a) HRTEM image of lamellar sample. (b) HAADF-STEM image of tribofilm and (c) corresponding EDS line scanning results for different elements, where the location of the HAADF-STEM image is marked in (a).

original JNs (Fig. 2(a)), the structure of the JNs could not be observed in the tribofilm (Fig. 5(c)). The cross-sectional EDS mapping results showed that F was homogeneously distributed throughout the tribofilm without pores (Fig. 5(f)). To the contrary, bright regions are observed in the EDS mapping results for Si (Fig. 5(g)) and O (Fig. 5(h)), corresponding to the silica nanoparticles in the tribofilm. Combining the results obtained by the TEM–EDS, it can be concluded that the tribofilm on the steel ball surface was composed of PTFE embedded with randomly distributed silica nanoparticles, where the structure of the original JNs was destroyed by rubbing. The lamellar sample on the steel plate was extracted from the center of the wear track for the TEM–EDS investigation (Fig. 6). A thin tribofilm with a thickness of ~5–20 nm between the Cr protecting layer and steel substrate was observed (Figs. 6(a) and 6(b)). The EDS line scanning results indicate that the thin tribofilm was composed of Fe oxides and PTFE; however, the signal for Si was not detected (Fig. 6(c)).

3.4 Lubrication mechanisms of JNs as additives

The nanostructure design of materials provides great opportunities for the achievement of new properties [41]. In this study, novel PTFE@silica JNs were designed for future eco-friendly water-based lubrication systems (Figs. S13 and S14 in the ESM). Conventional PTFE nanoparticles are commonly used as additives for oil-based lubricants [24]; however, they are difficult to be applied in water-based lubrication systems because of their hydrophobic nature. With the composition of silica forming a unique nanostructure, stable water suspensions of JNs can be obtained. A low COF of 0.093 can be achieved by JNs suspension with a concentration of 0.5 wt%, which is reduced by 72.07%, 63.82%, and 21.19% compared to those of pure water, silica, and PTFE suspensions, respectively. In addition, the wear volume of the steel ball can be also reduced by 94.22%, 87.66%, and 74.71% compared to those of pure water, silica, and PTFE suspensions, respectively. From the SEM–EDS and cross-sectional TEM–EDS results, it can be concluded that tribofilms can be formed on the wear regions of the counterparts, which dominates the lubrication and anti-wear

performances. However, the distributions of PTFE and silica are not the same. The presence of silica nanoparticles can be observed in the tribofilm on steel ball, but difficult to be found in the tribofilm on steel plate. Conversely, PTFE was homogeneously distributed on the wear regions of its counterparts. These results indicate that the two components of the JNs can be detached by rubbing, where PTFE and silica exhibit different performances during the friction process. For PTFE, which is a widely used lubricating material, a transfer film was formed on metal friction pairs during friction. The formation of the PTFE tribofilm can be attributed to the easy deformation between the molecular chains of PTFE and the formation of Fe–C and Fe–F chemical bonds between the friction pairs and the PTFE transfer film, induced by the tribochemical reaction [42]. The PTFE tribofilm was anchored on its counterparts by interfacial chemical bonds, and the re-orientation of the molecular chains also occurred, enhancing the lubrication performance. In this study, a thick tribofilm (with thickness of ~400–600 nm) containing PTFE was formed on the surface of steel ball, whereas a thin tribofilm (with thickness of ~5–20 nm) was formed on the surface of steel plate. The difference between the tribofilms on their counterparts can be attributed to that the steel ball surface was constantly in contact, while the steel plate was only periodically in contact. The formation of F–Fe chemical bonds on the surface of steel plate is verified by the XPS results (Fig. 4(o)), but not observed from the results on the surface of the steel ball (Fig. 4(g)), because of the large tribofilm thickness on the wear scar surface of the steel ball. Moreover, shear-induced degradation and oxidation of PTFE occurred owing to rubbing (Figs. 4(f) and 4(n)), which is in accordance with the molecular dynamics simulation results presented in Ref. [18]. Degradation induced by the tribochemical reaction was also observed during the friction process with carbon fluoride as lubricants [43–45]. The F content of the tribofilm on the steel plate was lower than that on the steel ball, while the area ratio bonds of the tribofilm C–O chemical on the steel plate surface was higher than that on the steel ball, indicating that the degradation of the PTFE tribofilm on the steel plate surface suffered more severe defluorination and oxidation than that on the steel

ball. Silica nanoparticles are also used as additives for water lubrication to reduce friction and wear, and these mechanisms can be attributed to the rolling bearing effect and formation of a tribofilm with nanoparticles [46]. However, the friction results show that the lubrication and wear-reduction performances of silica suspension are limited compared to those of JNs suspension, which can be attributed to the fact that the aggregates of silica nanoparticles lead to plough wear and additional frictional energy dissipation [47]. The aggregation of silica nanoparticles could be the reason for the increased wear volume at a relatively high concentration of JNs. By lubrication using JNs as additives (0.5 wt%), the tribofilm on the wear scar of ball is composed of PTFE and silica (Fig. 5), where the silica nanoparticles are embedded into the PTFE. Harris et al. [48] have investigated the tribological behavior of PTFE embedded with rigid nanoparticles. It was determined that PTFE embedded with rigid nanoparticles exhibited a lower wear rate than bulk PTFE, which can be attributed to the enhanced load-bearing capacity and reinforcement of rigid nanoparticles.

Based on the above discussion, lubrication and wear-reduction mechanisms were proposed. During the friction process, the two components of the JNs were detached through rubbing. Plastic deformation of PTFE occurred during the friction process, forming a thin tribofilm (with thickness of ~5–20 nm) on the steel substrate and thick tribofilm (with thickness of ~400–600 nm) on the steel ball as a counterpart. Rigid silica nanoparticles were embedded into the thick tribofilm on the steel ball, which enhanced the load-carrying capacity and wear resistance of the tribofilm. With the targeted design of the structure of nanomaterials, excellent dispersity, lubrication, and wear-resistance performances were achieved using JNs as additives simultaneously through the synergetic effect between the two components. This study provides a new strategy for designing novel JNs with unique structures for the use as lubrication additives. Moreover, it is suggested that the concept of the JNs structure can be applied to design nano-additives with high performance, high stability, and high environmental adaptivity to meet future industrial applications.

4 Conclusions

PTFE has been widely used as a lubrication additive to reduce friction and wear; however, the hydrophobic nature of PTFE restricts its application in water-based lubrication systems. In this study, we designed novel PTFE@silica JNs to meet the requirement for additives for water-based lubricants for the first time, which have excellent dispersion in pure water because of their unique structures. With the lubrication using JNs suspension with a concentration of 0.5 wt%, the COF and wear were reduced by 63.8% and 94.2%, respectively, compared to those lubricated by pure water. Meanwhile, the JNs suspension also exhibits better lubrication and wear-resistance performances comparing to commercial silica and PTFE suspensions. The excellent tribological performance of JNs as additives can be attributed to the synergetic effect of the two components, where the PTFE dominates the lubrication performance through the formation of tribofilms on their counterparts, while the rigid silica nanoparticles can further enhance the wear-reduction performance. Our study shed light on the design and application of novel JNs as additives in future lubrication systems for industrial applications.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

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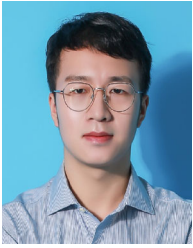
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