Supporting Information

Design of ternary solid lubricants SiO_2/Ti_3C_2/PTFE for wear-resistant, self-lubricating polyimide composites

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Materials

MAX phase (Ti_3AlC_2) was purchased from Jilin 11 Technology Co, the particle size is 5 μm. HF (AR) and Homophthalic dianhydride (PMDA, AR) were purchased from Shanghai Sarn Chemical Technology Co. 4,4'-Diaminodiphenyl ether (ODA, AR), Tetraethyl orthosilicate (TEOS, AR) and Ammonia ($NH_3 \cdot H_2O$, 25%~27%,) were provided by Anhui Zesheng Technology Co. Polytetrafluoroethylene (PTFE, 12 μm), Anhydrous ethanol (EtOH, AR) and N, N-Dimethylacetamide (DMAc, AR) were purchased from Tianjin Guang Fu Technology Development Co.

Preparation of Ti_3C_2

Ti_3AlC_2 (1 g) was added to HF (20 mL, 40 wt%) in batches, the stirring speed and temperature were set to 500 rpm and 35°C respectively. After 24 h of reaction, the mixed solution was washed with deionized water and centrifuged at 3500 rpm for 5 min. The above washing operation was repeated until the pH of the supernatant liquid surface was neutral. Finally, the precipitate was freeze-dried at -69°C for 8 h to obtain $Ti_3C_2T_x$.

Preparation of SiO_2-Ti_3C_2 (ST)

$Ti_3C_2T_x$ powder (0.20 g) was ultrasonically dispersed in a mixture of anhydrous ethanol (130 mL) and deionized water (25 mL). The above mixture was magnetically stirred in a flask and $NH_3 \cdot H_2O$ (6 mL) was added dropwise until the pH of the solution up to 10. TEOS (2 g) was dissolved in anhydrous ethanol (20 mL) and the TEOS solution was added dropwise to the $Ti_3C_2T_x$ dispersion with a dropwise acceleration of 1 drop/s. After the dropwise addition was completed, the temperature was raised to 35°C and the reaction was carried out for 4 h under magnetic stirring. When the reaction is finished, the above mixture was centrifuged several times and remove $NH_3 \cdot H_2O$ and other by-products. Eventually, the sediment was dried under 60 °C to capture the hybrids $Ti_3C_2T_x@SiO_2$.

Preparation of PAA

The $Ti_3C_2T_x$/PI composites were prepared in two steps: In the first step, ODA was pre-dried under vacuum at 80°C for 4 h. Similarly, PMDA was dried under vacuum at

100°C for 4 h. ODA (4 g) was added to DMAc (50 mL) and sonicated for 30 min until completely dissolved. Equimolar ratios of PMDA (4.36 g) were added to the ODA solution in three batches with high-speed stirring, and the addition was completed within 30 min. After the last addition, the speed was reduced to 80 rpm and the reaction was carried out under an ice-water bath for 3 h to obtain the polyamidoacetic acid (PAA) solution with 12% solid content.

Characterization

X-ray diffraction (XRD) patterns were recorded with a D8 Advance diffractometer, Cu was used as the target material with a scanning speed of 10°/min and a scanning interval of 5° to 70°. STP and transfer film were characterized with Thermo ESCALAB 250XI X-ray photoelectron spectroscopy (XPS) and LabRAM HR Evolution Raman Spectroscopy (the excitation wavelength was 633 nm). Morphology and microstructures were observed with a scanning electron microscope (SEM) (Gemini 300). Atomic force microscope (AFM) analysis of composite surface morphology using Bruker's Dimension XR model. FT-IR test was obtained from a NICOLET IS10 fourier transform infrared spectrometer (Nicolet, USA)，and the scanning range was 4000~400 cm^{-1}, the number of scans was 32, and the resolution was 4.

Tribological tests

The friction coefficient and wear rate of the samples were tested by the friction and wear tester model MS-M9000 (Lanzhou, China). Friction experiments were conducted at room temperature using a 4 mm diameter bearing steel (GCr15) ball as the upper counterpart ball, a cured PI composite as surface film, and a steel (304) disc as the underlying counter facing plate. (The rotating speed was 300 r/min, and the rotating radius was 3 mm. The normal load was 5N, and the experimental duration was 30 min).

Table S1. The mass ratio of $Ti_3C_2T_x$-SiO_2 /PTFE and samples name

mass ratio	Sample
0:5	PTFE
1:4	1T-S/4P
2:3	2T-S/3P
3:2	3T-S/2P
4:1	4T-S/1P
5:0	$Ti_3C_2T_x$-SiO_2

The mass ratios of $Ti_3C_2T_x$-SiO_2/PTFE and the corresponding sample names are listed in **Table S1**. The tribological test results of the samples are shown in **Fig.S1.** The COF of the composites increased with the decrease of the percentage of PTFE (**Fig. S1a**), and the average wear rate was the lowest at the mass ratio of Ti_3C_2Tx-SiO_2 and PTFE of 3:2, which was 0.315 × 10^{-5} mm^3/(N.m) (**Fig. S1b**). Therefore, this ratio was comprehensively selected as the optimal ratio.

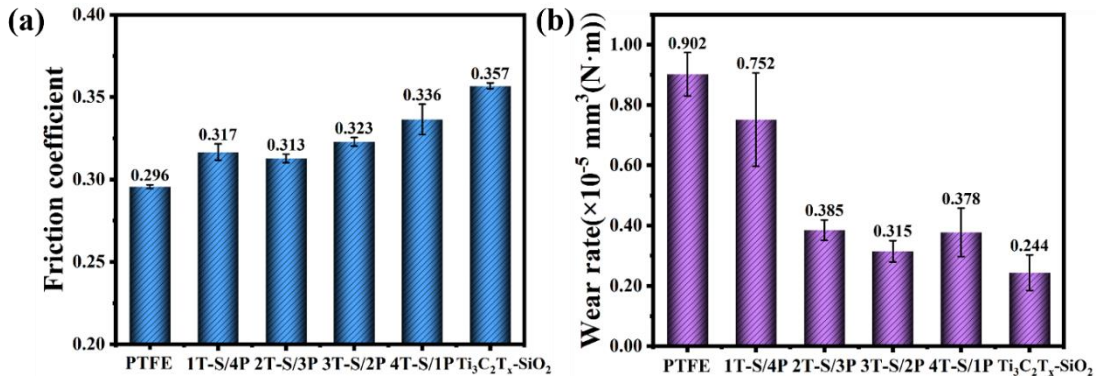

Fig. S1. Tribological properties of PI composites with different SiO_2-Ti_3C_2 and PTFE mass ratios. (a) COF; (b) wear rate.

Table S2. Roughness value of the STP/PI samples

Sample	PI	STP1	STP2	STP3	STP4	STP5	STP6
Ra	0.42	2.81	3.71	4.77	4.81	4.97	5.93
error bar	±0.03	±0.06	±0.11	±0.02	±0.08	±0.10	±0.47

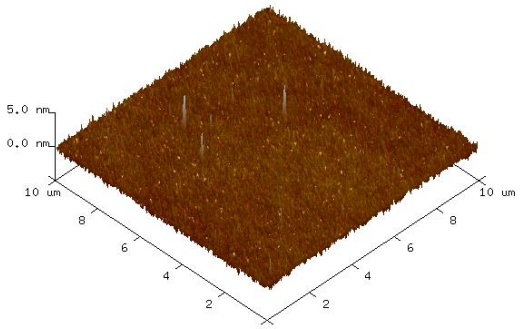

Fig. S2. AFM image of PI.

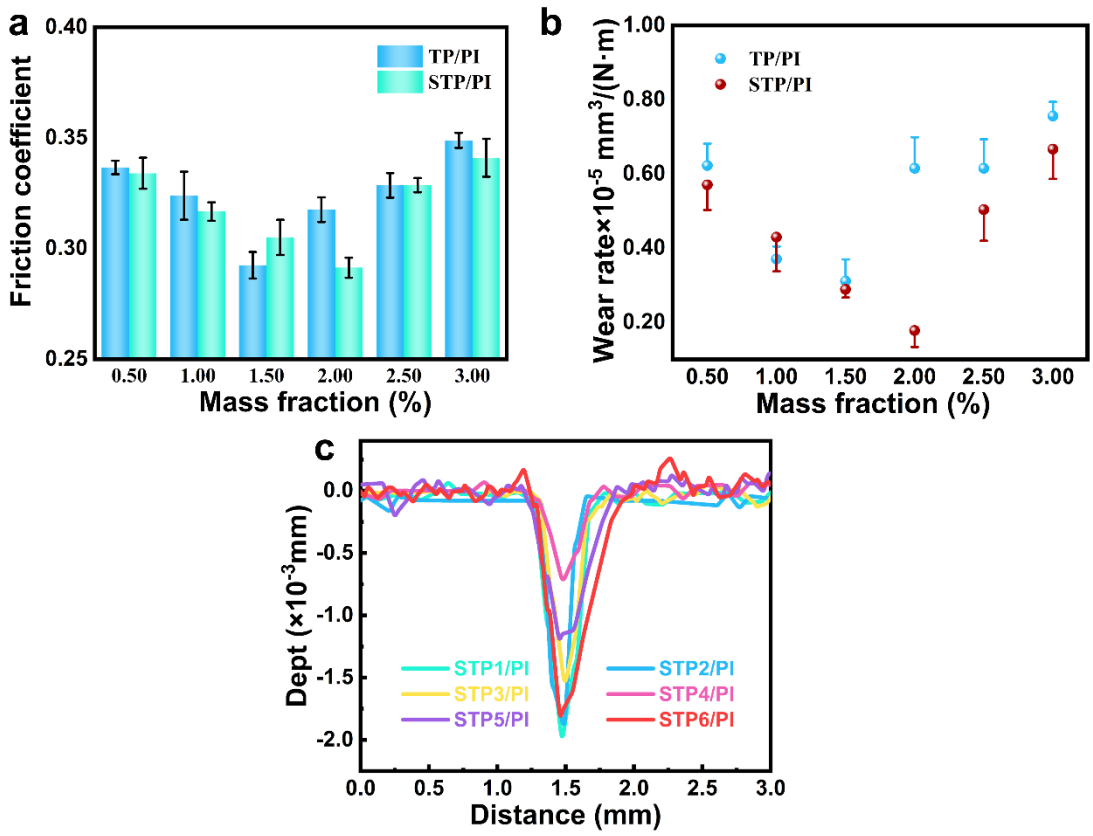

Fig.S3. Friction performance of TP/PI and STP/PI samples. (a) The COF comparison between TP/PI and STP/PI. (b) The wear rate comparison between TP/PI and STP/PI (c) Depth of the wear track of STP/PI.

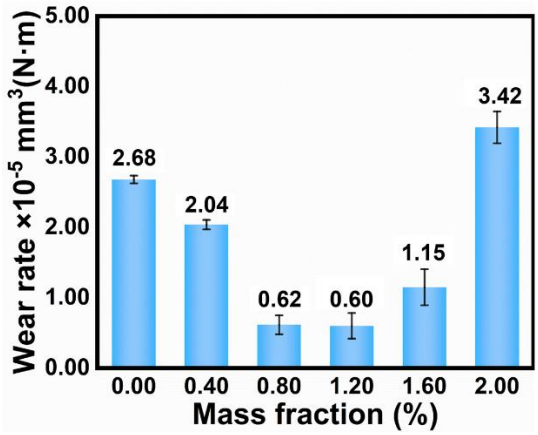

Fig. S4. Average wear rate of T/PI (Ti_3C_2/PI) with different Ti_3C_2 content

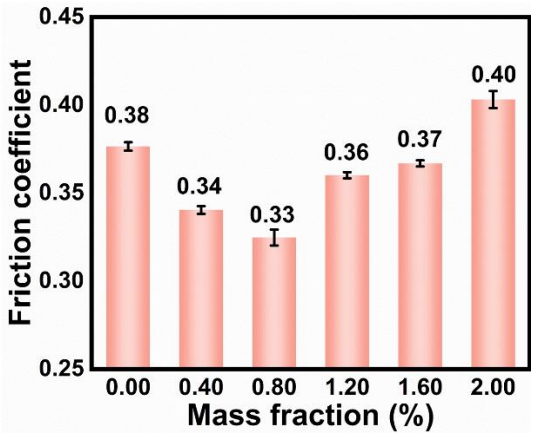

Fig. S5. Average coefficient of friction of ST/PI (Ti_3C_2@SiO_2/PI) with different Ti_3C_2@SiO_2 contents

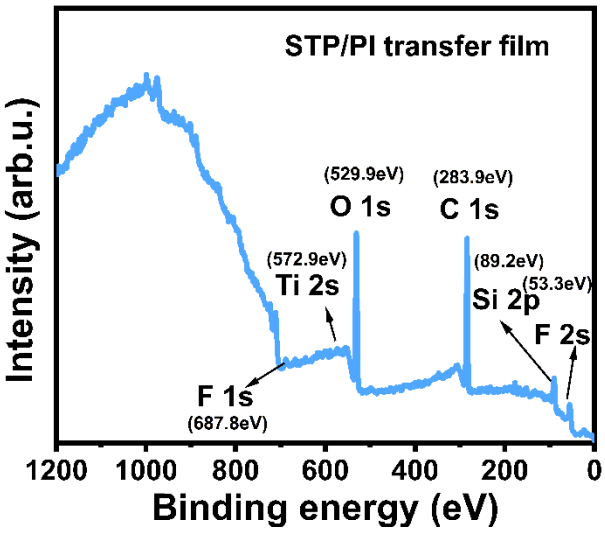

Fig. S6. XPS spectrum of transfer film on steel ball.

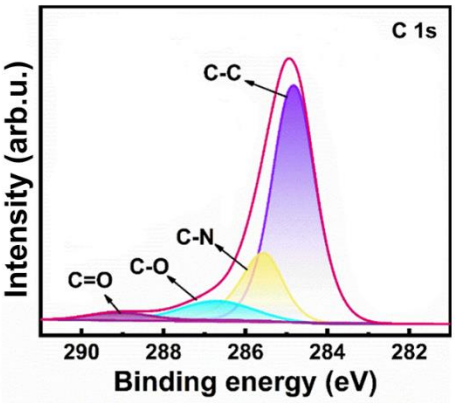

Fig. S7. XPS narrow spectrum of C1s from ST/PI transfer film

The Ti2p narrow spectrum can be divided into $Ti^{+}2p_{3/2}$ (454.7 eV), $Ti^{+}2p_{1/2}$ (461.9 eV), $Ti^{2+}2p_{3/2}$ (455.7 eV), $Ti^{2+}2p_{1/2}$ (461.4 eV), $Ti^{3+}2p_{3/2}$ (457.2 eV), $Ti^{3+}2p_{1/2}$ (464.9 eV), $Ti^{4+}2p_{3/2}$ (458.5 eV) and $Ti^{4+}2p_{1/2}$ (464.7 eV) due to energy level splitting. The peaks of Ti-O bonds are shown at 460.3 eV and 464.7 eV and the Ti-C bonds corresponds to 462.9 eV [1].

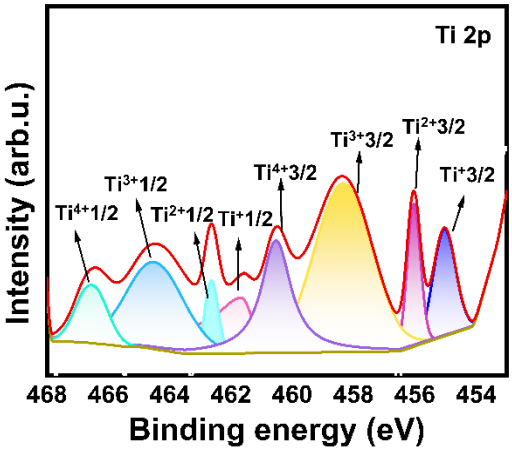

Fig. S8. XPS narrow spectrum (Ti2p) of the transfer film on steel ball

Table S3. Comparison of the tribological properties of this paper with other literatures

Ref.	[2]	[3]	[4]	[5]	[6]	[7]	This work
COF	0.27	0.51	0.31	0.31	0.32	0.33	0.29
Wear rate $\times 10^{-5}$	1.78	0.47	0.20	0.39	0.62	0.24	0.18

Compared with the work reported in recent years this study has some advantages in general, but the difference in data may be due to the difference in test loads. It is worthwhile to recognize that this work is a continuation of our group's previous work [6, 7] and is therefore comparable under the same testing conditions and sampling process. It can be seen that (**Table S3**) the tribological properties of STP as a solid lubricant are better than those of ST [7] and single MXene [6]. Therefore, this experimental data also proves that the addition of PTFE can effectively increase the interlayer movement of ST and MXene sheets.

References

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