Electronic Supporting Information

Integration of bubble phobicity, gas sensing and alleviating frication into a versatile MoS_2/SnO_2/CNF heterostructure by an impressive simple but effective method †

Fuchao Yang[#a], Caiyun Wang[#b] and Zhiguang Guo [*ac]

[a] Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, School of Materials Science & Engineering and Hubei Key Laboratory of Polymer Materials, Hubei University, Wuhan 430062, People's Republic of China

[b] Center for Nanoscale Characterization & Devices (CNCD), School of Physics & Wuhan National Laboratory for Optoelectronics (WNLO), Huazhong University of Science and Technology (HUST), Wuhan 430074, P. R. China.

[c] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

* The corresponding author: Tel: 0086-931-4968105; Fax: 0086-931-8277088; Email: zguo@licp.cas.cn.

†Electronic supplementary information (ESI) available.

# The authors contributed equally to this work.

Electronic Supporting Information

Experimental Section

1. Reagents and preparation of MoS_2/SnO_2/CNF

Carbon nanofibers (CNF, >98%) was obtained from Sigma Aldrich (Shanghai) Trading Co., Ltd. The stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) was purchased from Tianjin Damao Chemical Reagent Co. Ltd, China. Trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) was obtained from Xilong Chemical Reagent Co. Ltd, China. The sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$, >99.0%) and thiourea (CH_4N_2S, >99.0%) were provided by Shanghai Guangming Chemical Reagent Co.,Ltd and Sinopharm Chemical Reagent Co.,Ltd (China), respectively. All the chemicals were of analytical-grade and used as received without further purification.

The 20 mmol $SnCl_2 \cdot 2H_2O$ and 40 mmol $C_6H_5Na_3O_7 \cdot 2H_2O$ were dissolved in a 160 mL mixed solution of deionized water and ethanol (volume ratio, 1:1) under magnetic stirring. Next the 10 mmol carbon nanofiber was added into the above mixed solution and this system was kept stirring for 1 hour. Then it was transformed into Teflon-lined steel autoclaves. The precursor was subjected to a solvothermal process 180 ^oC for 10 h and then cooled down to the room temperature naturally. After being washed several times, the SnO_2/CNF product was collected and part of them was applied to the coming synthesis of MoS_2/SnO_2/CNF. The SnO_2/CNF with a mass of 0.65 g was added into the 80 mL mixed solution containing of 5 mmol sodium molybdate and 20 mmol thiourea under vigorous stirring. The hydrothermal procedure is also fixed at 180 ^oC for 10 h and the final product of MoS_2/SnO_2/CNF was harvested after the cooling and washing processes. These products were not subjected to thermal annealing process.

2 Materials characterizations

Surface morphologies were observed by environmental field-emission scanning electron

microscopy (EFESEM; FEI QUANTA FEG 650) and transmission electron microscopy (TEM, FEI Tecnai G20 and operating at 300 KV). The crystal structure was investigated by X-ray diffraction (XRD) using an X'PERT PRO diffractometer with Cu K_α radiation (λ = 1.5418 Å) at 2θ ranging from 10^o to 80^o. The information about specific surface area and pore diameter distribution of the products were tested by the single point Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method through nitrogen adsorption/desorption analysis (ASAP 2010, USA Micromeritics). Thermogravimetry (TG) and differential thermal analysis (DTA) measurements were performed in air or N_2 with a heating rate of 10 ^{o}C/min using a NETZSCH STA 449F3 apparatus. Raman scattering spectra of CNF, SnO_2/CNF, MoS_2/SnO_2/CNF and wear scars were carried out by LabRAM HR Evolution using 532 nm argon ion laser as the excitation source. UV–visible absorption spectra were recorded by using a Cary 60 spectrophotometer (Agilent). Chemical composition information was obtained by X-ray photoelectron spectroscopy (XPS, Thermon Scientific ESCALAB 250xi) using Al K_α radiation. The binding energies were referenced to the C 1s line at 284.8 eV. The MicroXAM-3D non-contact surface profiler was employed to obtain the wear volume and morphologies of the wear scars.

3 The preparation and details for functional test

The MoS_2/SnO_2/CNF coatings can be formed by spraying method (the concentration of dispersion: 0.05 g MoS_2/SnO_2/CNF in 50 ml anhydrous ethanol) on the following substrates: glass, silicon, sponge, AISI 52100 steel disk, copper screen, fabric, copper slice and stainless steel meshes. The spray gun was under 0.2 MPa N_2 gas flow and the distance from nozzle to substrate material is about 20 cm. The static oil (or bubble) contact angles (CA) of MoS_2/SnO_2/CNF coatings on various substrates were characterized using a JC2000D system with a 5 (or 3) μL volume. Gas sensing

apparatus applied in our experiment is WS-60A. The as-prepared MoS_2/SnO_2/CNF or SnO_2/CNF powder was mixed with a droplet (3 μL) of deionized water to form paste and then coated onto the surface of a ceramic tube on which a pair of gold electrodes was previously printed, forming current closed loops. These gas sensing materials of MoS_2/SnO_2/CNF or SnO_2/CNF were not subjected to annealing process and the operating temperature is as low as at 200 °C. Further details about the gas sensing test can be found in our previous work.[S1] The lubricating performances of MoS_2/SnO_2/CNF as annexing agent in base or commercial lubricating oil was characterized by Optimol SRV-IV oscillating reciprocating friction and wear tester. The running ball (ø = 10 mm) and stationary disk (ø = 24.0 mm × 7.9 mm) are AISI 52100 steel. The MoS_2/SnO_2/CNF or MoS_2/SnO_2/CNF was added into the Poly Alpha Olefin 4 (PAO4), CNOOC (China National Offshore Oil Corporation), Abu Dhabi 100N base oil or commercial 5W30 lubricating oil with the fixed additive amount of 0.0420 g/mL. Some key test parameters are set as Frequency = 25 Hz; Load = 100 or 250 N; Amplitude = 1 mm; Temperature = 20 °C; Time = 30 min.

Supplementary Figures

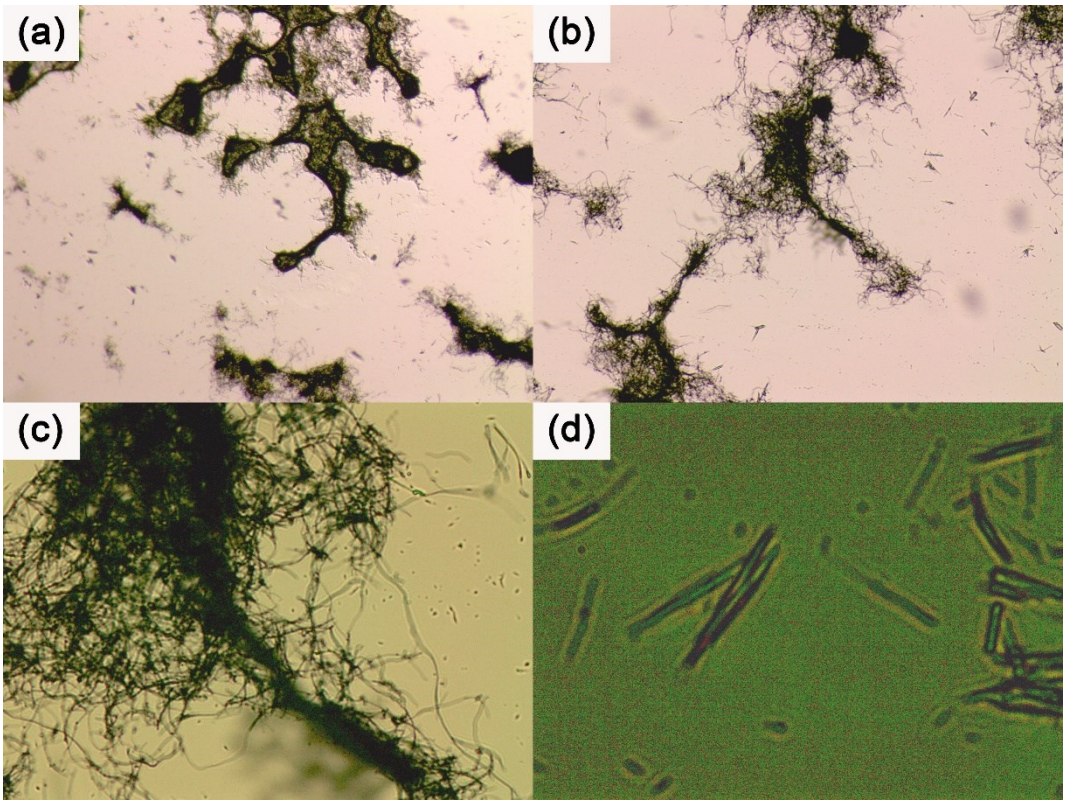

Fig.S1 The optical microscope view of CNF (a) multiply by 40 times magnification, (b) multiply by 100 times magnification, (c) multiply by 400 times magnification and (d) multiply by 1000 times magnification.

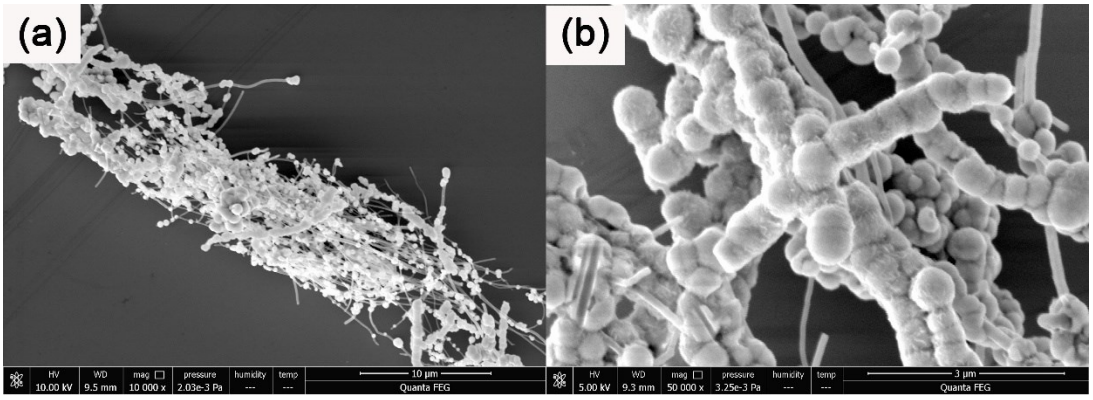

Fig.S2 The EFESEM view of SnO_2/CNF (a) multiply by 1×10^4 times magnification and (b) multiply by 5×10^4 times magnification.

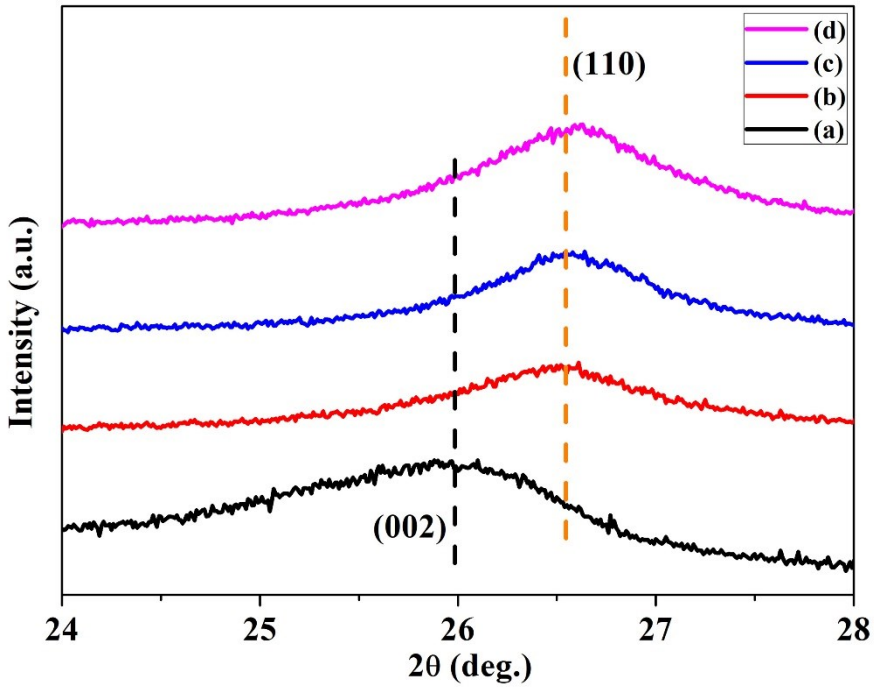

Fig.S3 The XRD pattern enlarge view of dominated reflection: (a) CNF, (b) SnO_2/CNF, (c) MoS_2/SnO_2/CNF and (d) MoS_2/SnO_2.

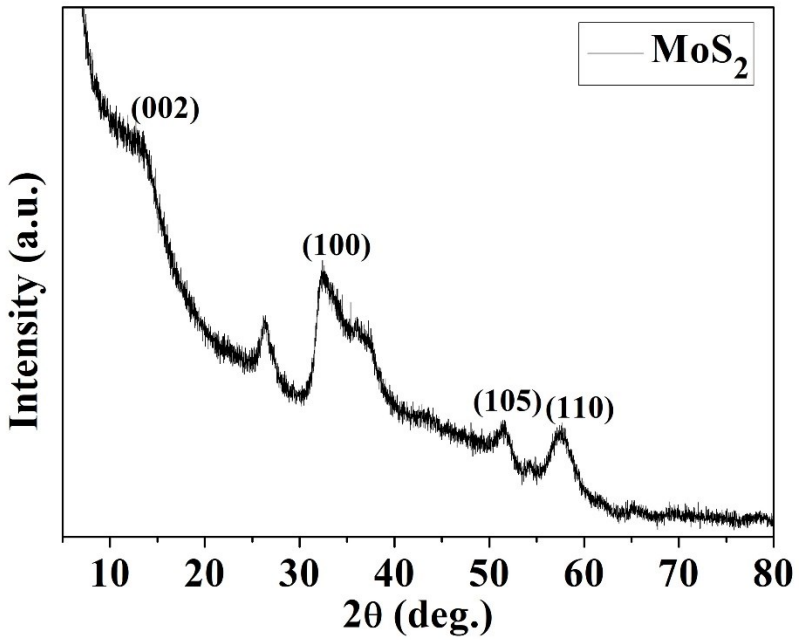

Fig.S4 The XRD pattern of MoS_2 synthesized by hydrothermal method in our experiment.

The reference PDF card of MoS_2 is ICDD No. 03-065-0160, indicating a hexagonal structure with

the space group P63/mnc.

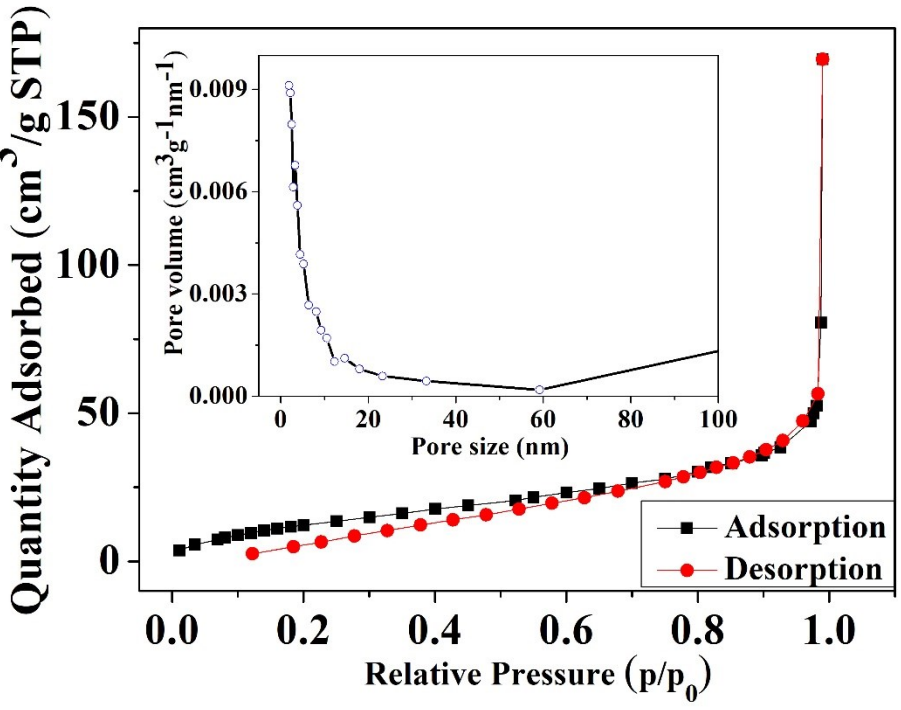

Fig.S5 The N_2 adsorption/desorption analysis of pristine CNF.

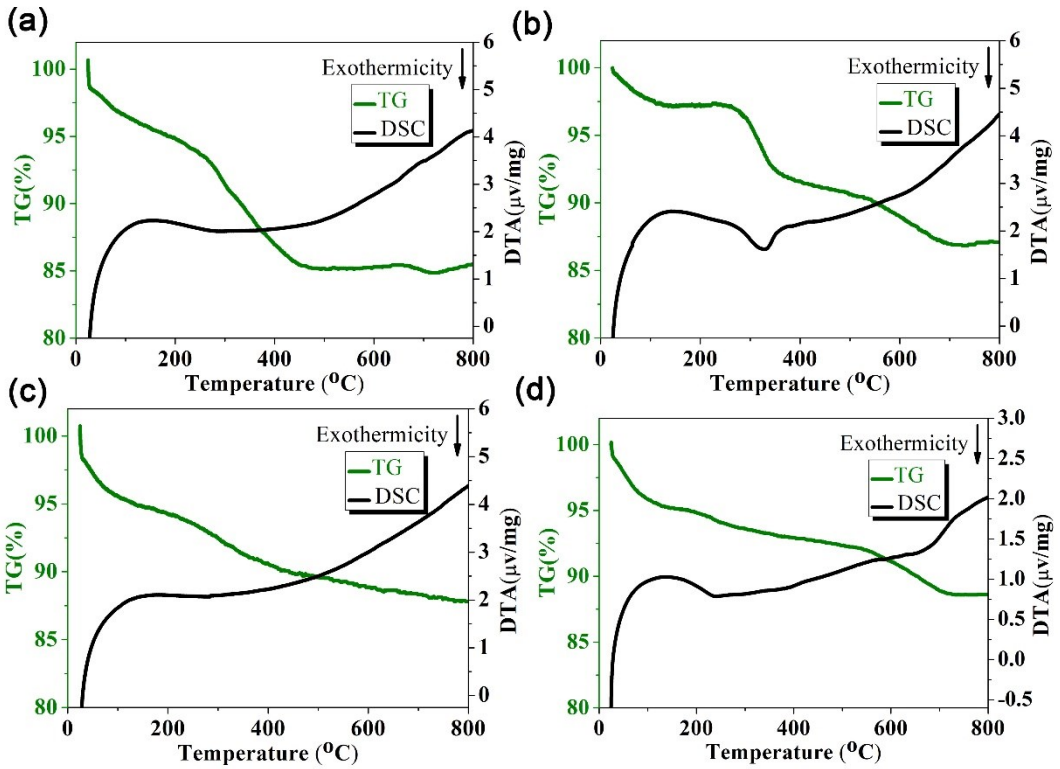

Fig.S6 The thermogravimetry (TG) and differential thermal analysis (DTA) of SnO_2/CNF (a)

under N_2 atmosphere and (b) under O_2 atmosphere, and MoS_2/SnO_2/CNF (c) under N_2 atmosphere and (d) under O_2 atmosphere.

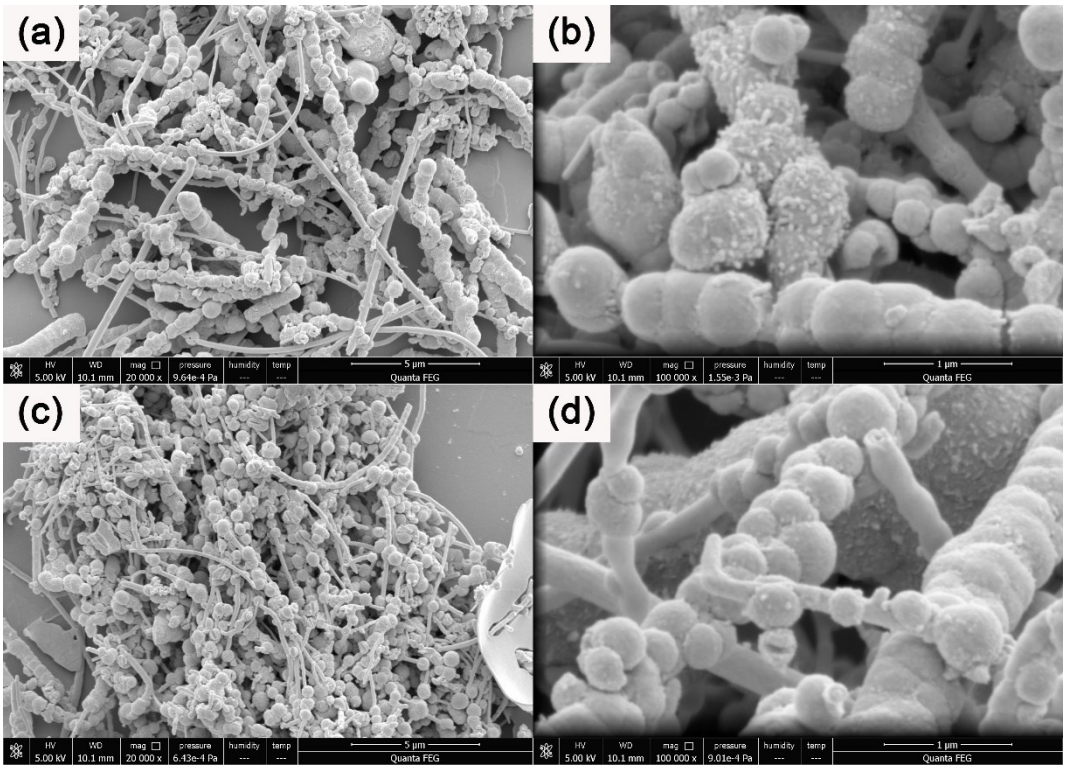

Fig.S7 The typical EFESEM images of the morphology of (a-b) SnO_2/CNF and (c-d) MoS_2/SnO_2/CNF after 500 ^oC heat treating for 2 h.

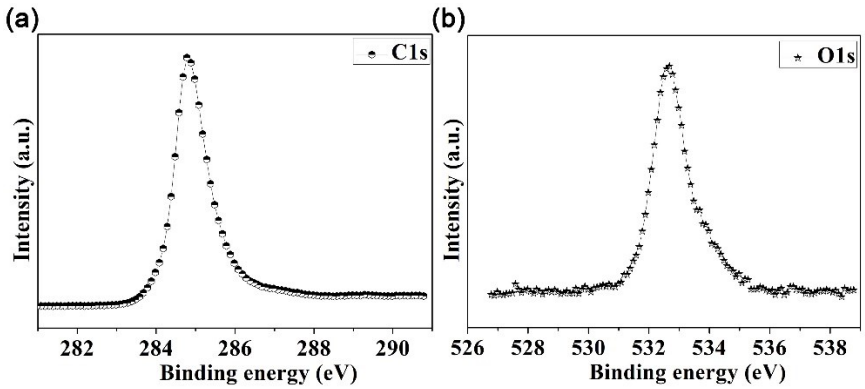

Fig.S8 The XPS fine spectra of CNF sample: (a) C1s and (b) O1s peak.

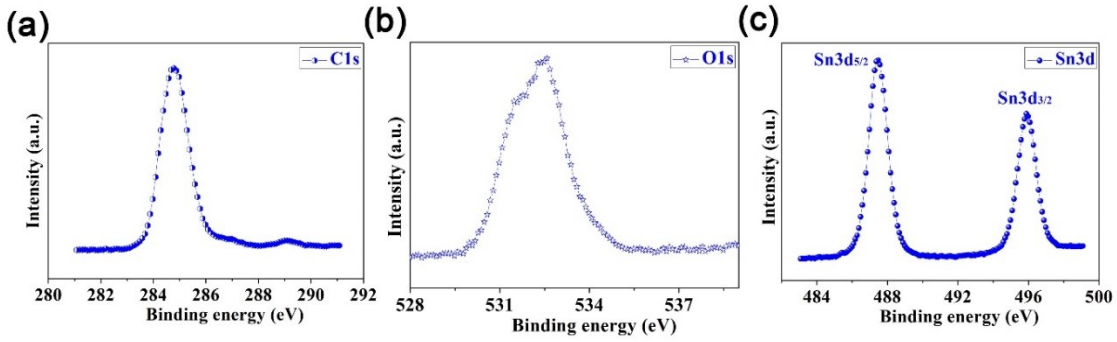

Fig.S7 The XPS fine spectra of SnO_2/CNF sample: (a) C1s, (b) O1s and (c) Sn3d peak.

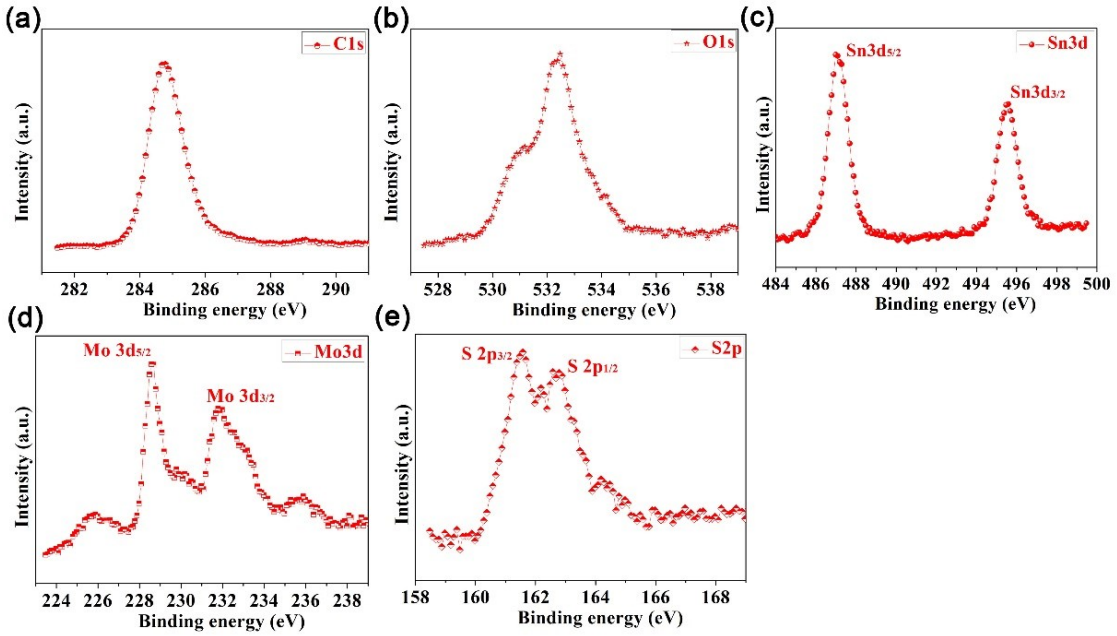

Fig.S10 The XPS fine spectra of MoS_2/SnO_2/CNF sample: (a) C1s, (b), O1s, (c) Sn3d, (d) Mo3d and (e) S2p peak.

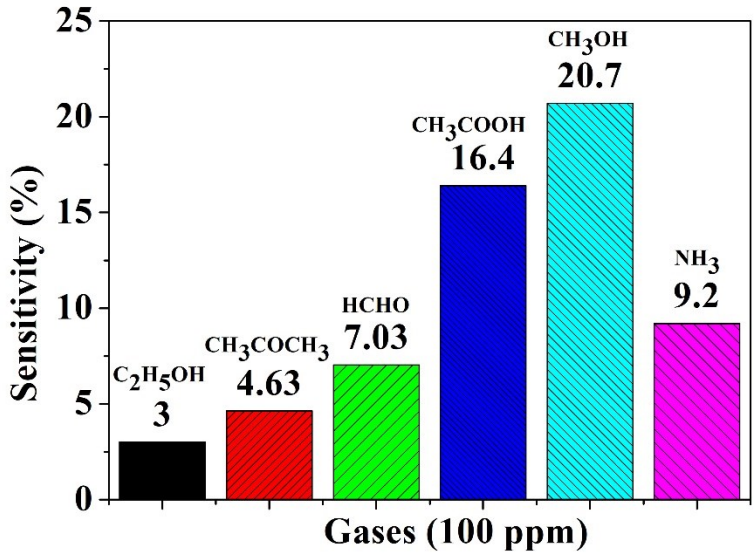

Fig.S11 The selectivity of MoS_2/SnO_2/CNF gas sensing material.

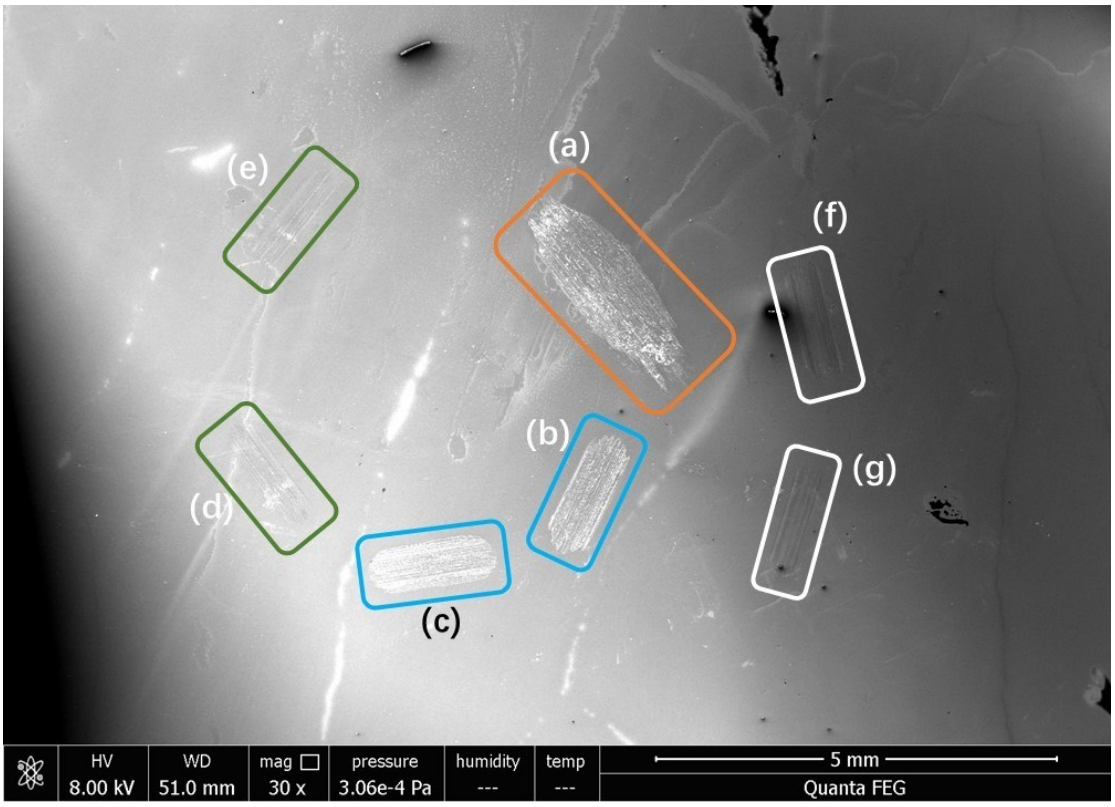

Fig.S12 The overview of worn scars on the steel disk lubricated by PAO4 and its additives.

Zone (a) is lubricated by PAO4 under 250 N loading. Zone (b-c) is lubricated by PAO4 under 100 N loading. Zone (d-e) is lubricated by PAO4 and MoS_2/SnO_2/CNF additives under 100 N

loading. Zone (f-g) is lubricated by PAO4 and MoS_2/SnO_2 additives under 100 N loading.

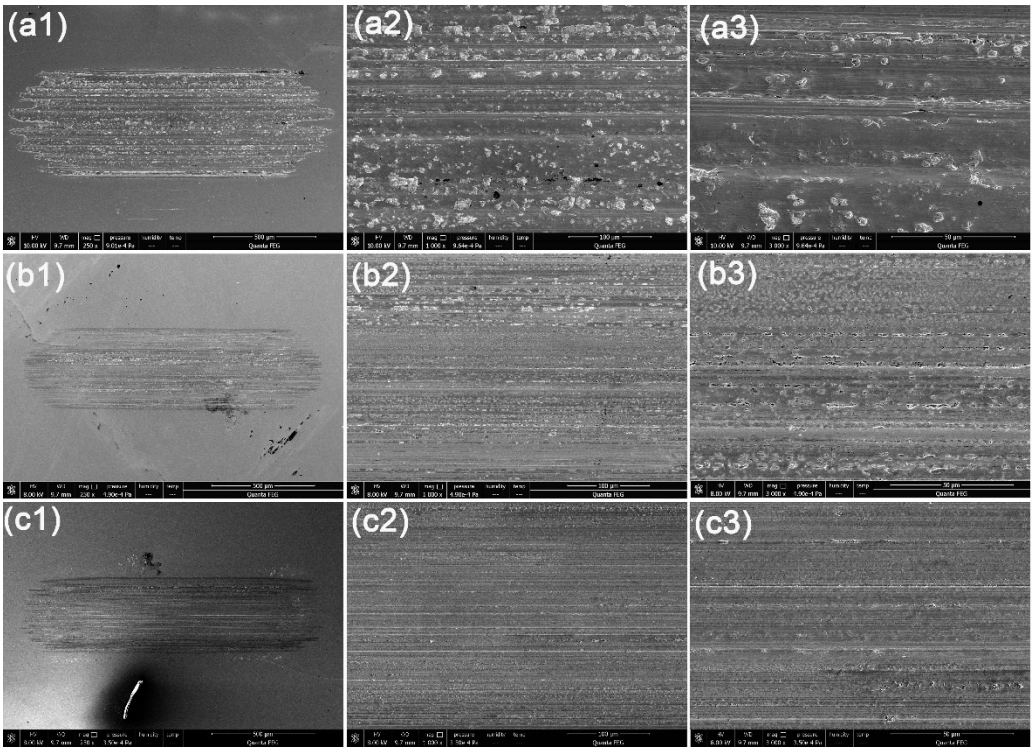

Fig.S13 The FESEM observation of worn scars on the steel disk lubricated by PAO4 (a1-a3); by PAO4-MoS_2/SnO_2/CNF additives (b1-b3); and by PAO4-MoS_2/SnO_2 additives (c1-c3).

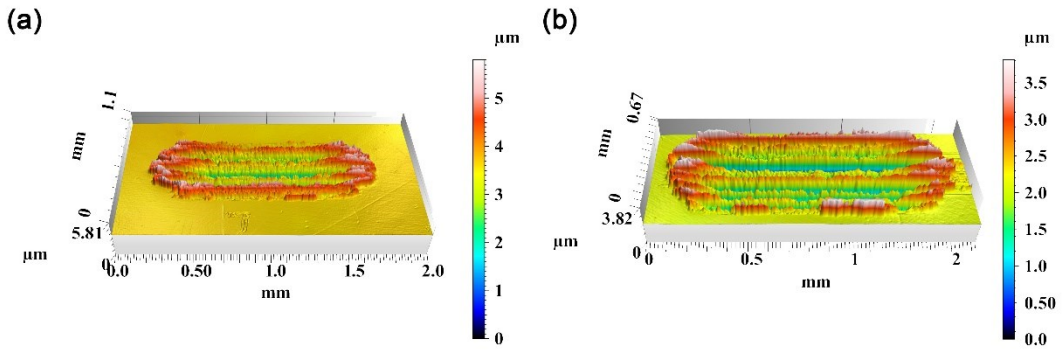

Fig.S14 The 3D profiles from (a) CNOOC 32# and (b) Abu Dhabi 100N black control friction test.

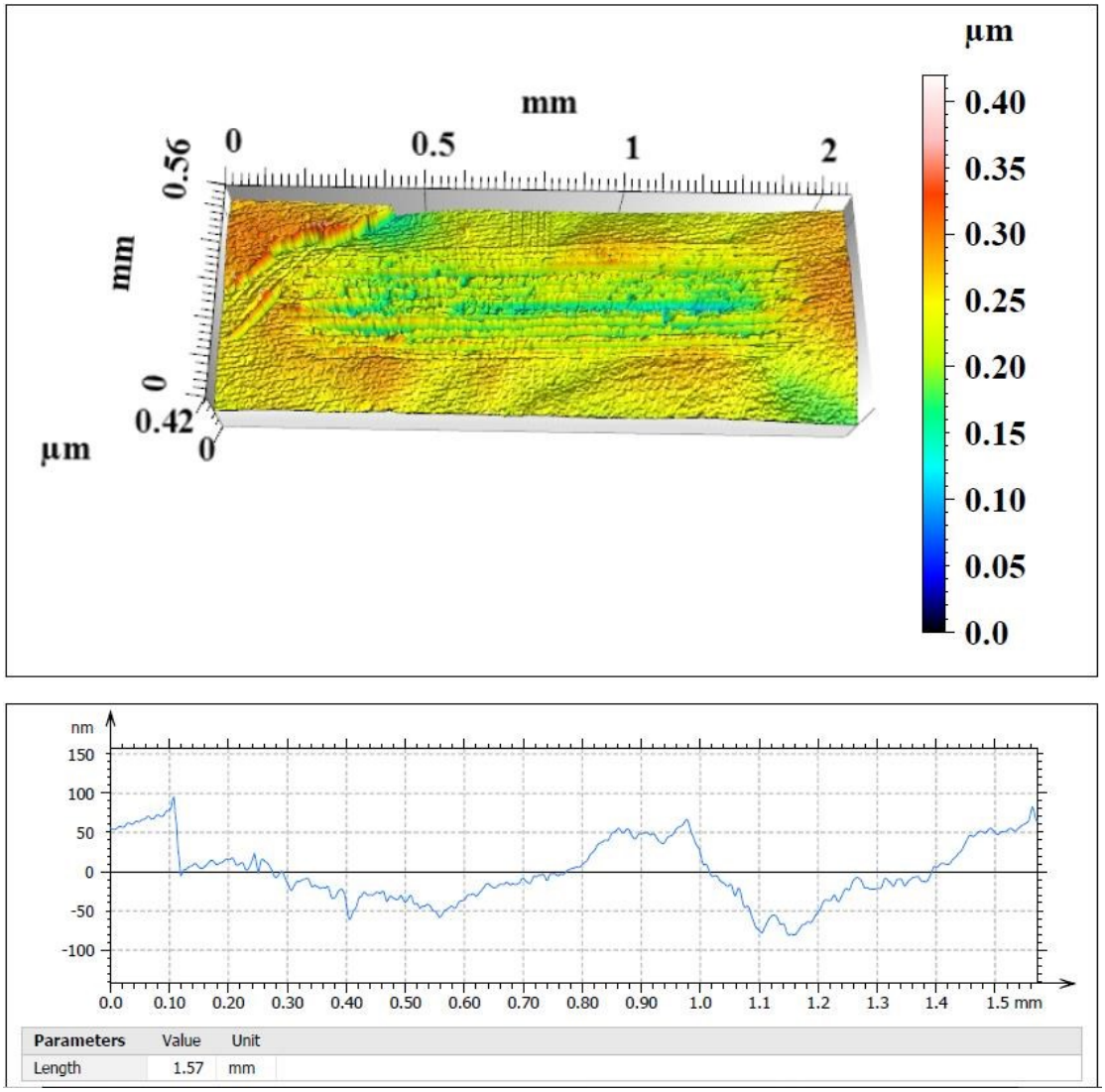

Fig.S15 The 3D profiles from commercial 5W30 lubricant oil black control friction test.

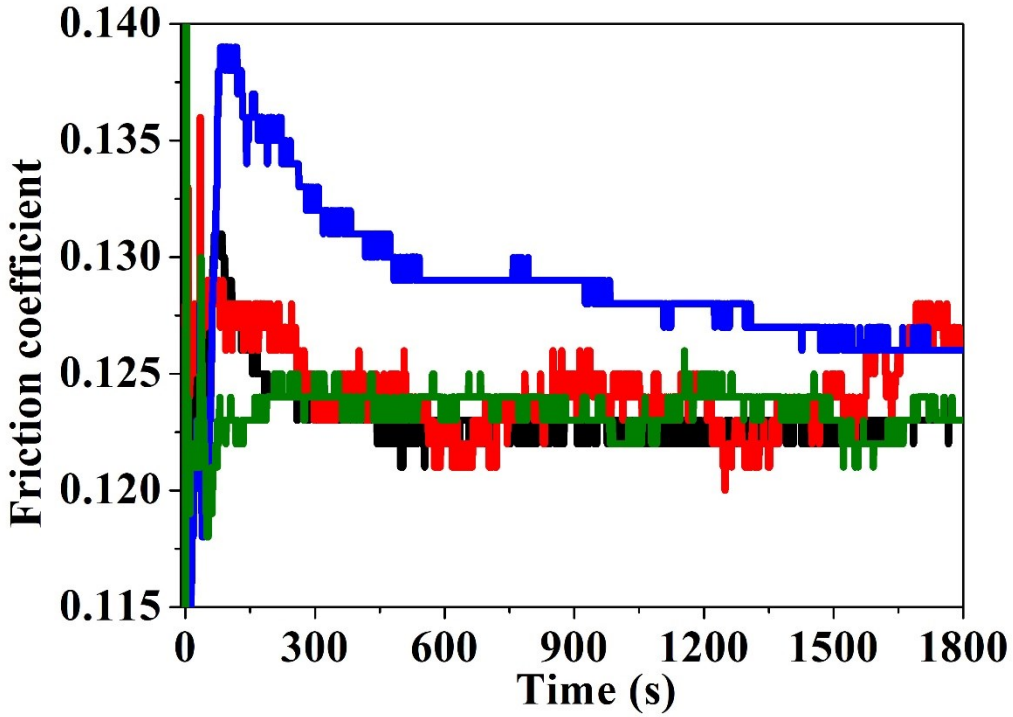

Fig.S16 The extremely enlarged view of real-time COF of MoS_2/SnO_2/CNF additive in 5W30.

Black line: 5W30, Load: 100N; **Red line**: 5W30& MoS_2/SnO_2/CNF, Load: 100N. **Blue line**: 5W30, Load: 250N; **Green line**: 5W30& MoS_2/SnO_2/CNF, Load: 250N.

Table S1. The bubble CA values on different kinds of substrates underwater and under PAO4.

	Bubble CAs underwater		Bubble CAs under PAO4	
	Neat	Coated	Neat	Coated
S1	102.5 ±2°	134±3°	139.5±3°	147±4°
S2	118.5±4°	146.5±5°	152.5±4°	145±4°
S3	136±3°	151.5±3°	135±3°	130±5°
S4	128±6°	146±8°	156±4°	144±3°
S5	123±8°	141±3°	151±4°	131±5°
S6	138±8°	146±9°	153±3°	136±4°
S7	115±3°	125±6°	149±8°	140±6°
S8	128±6°	137±3°	150±6°	143±6°

Table S2. The sensitivity (%) value to ethanol, acetone and formaldehyde with 5-1500 ppm.

(ppm)	ethanol	acetone	formaldehyde	Operating temperature
5	1.49	2.57	1.77	200 °C
10	1.98	2.71	2.32	200 °C
20	1.64	3.68	3.49	200 °C
50	2.09	3.36	7.21	200 °C
100	3.00	4.63	7.03	200 °C
200	3.84	6.21	6.01	200 °C
400	4.39	7.52	7.06	200 °C
800	5.42	9.43	6.86	200 °C
1000	7.04	14.2	7.96	200 °C
1500	9.97	21.5	12.0	200 °C

Table S3. The comparison of sensitivity (%) between this work (MoS_2/SnO_2/CNF) and similar state-of-the-art materials.

(ppm)	Acetone gas (MoS_2/SnO_2/CNF)	Gas sensing material	Targeting gas	Sensitivity	Operating temperature
5	2.57	$WO_{3\text{-}NWAs}$ [S2]	CH_3COCH_3	~30*	300 °C
10	2.71	Fe_2O_3@MoS_2[S3]	NO_2	1.25	150 °C
20	3.68	ZnO[S4]	CO	2	250 °C
50	3.36	MnO_2 [S5]	Ethylene	0.15	150 °C
100	4.63	In_2O_3-ZnO[S6]	CO	1.1	400 °C
200	6.21	SnO_2[S7]	CO	3*	300 °C
400	7.52	In_2O_3-ZnO[S6]	ethanol	7.1	400 °C
800	9.43	N/A	N/A	N/A	N/A
1000	14.2	In_2O_3[S8]	methanol	0.5	200 °C
1500	21.5	In_2O_3[S8]	CO	1.0	200 °C

The symbol "*" represents another defined method of response R_a/R_g in the references and the differences between these two ways can see our previous work [S9].

Table S4. The comparison of additives' lubrication effect between this work (MoS_2/SnO_2/CNF) and similar state-of-the-art materials.

Additives	Structures	Amount	Base oil	f_1	f_2	load	Reference
MoS_2/SnO_2/CNF	necklace	0.042 g/mL	PAO4	0.247	0.126	100 N	This work
MoS_2/SnO_2/CNF	necklace	0.042 g/mL	CNOOC 32#	0.236	0.129	100 N	This work
h-BN&Graphene	2D&3D	0.2 wt%	PAO4	0.09	0.06	100 N	Qi et al.[46]
MoS_2/SnO_2/CNF	necklace	0.042 g/mL	Abu Dhabi 100N	0.239	0.132	100 N	This work
Modified TiO_2	nanoparticles	0.5%	PAO10	~0.2	~0.06	200 N	Zhang et al.[S10]
Carbon/polymer	nanofiber	1:4 (wt)	BPETPP-E	0.9	0.3	0.74 N	Chen etal.[56]
graphene	sheets	0.3 wt%	hydraulic oil	~0.22	~0.10	8 N	Mao et al. [S11]
Modified CuS	nanoparticles	0.8 wt%	water	~0.55	~0.18	1 N	Zhao et al.[S12]
WS_2	nanosheets	1%	PAO8	~0.24	~0.10	200 N	Zhang et al.[57]
MoS_2	nanoparticles	1 wt %	PAO	N/A	Reduce ~ 20%	5.4 N	Jazaa et al. [S13]

The f_1 or f_2 represent the friction coefficient before or after the utilizing of lubricant additives.

References

[S1] F. Yang and Z. Guo, *J. Colloid Interface Sci.*, **2015**, *448*, 265-274.

[S2] Y. Ren, Y. Zou, Y. Liu, X. Zhou, J. Ma, D. Zhao, G. Wei, Y. Ai, S. Xi, Y. Deng, *Nat. Mater.*, **2020**, 19, 203-211.

[S3] M. Yin, Y. Wang, L. Yu, H. Wang, Y. Zhu, C. Li, *J. Alloys Compd.*, **2020**, 829, 154471.

[S4] G. E. Buono-Core, A. H. Klahn, G. Cabello, L. Lillo, *Polyhedron* **2013,** *62*, 1-6.

[S5] L. Bigiani, D. Zappa, E. Comini, C. Maccato, A. Gasparotto, D. Barreca, *J. Nanosci. Nanotechnol.* **2020,** *20*, 3025-3030.

[S6] N. Singh, A. Ponzoni, R. K. Gupta, P. S. Lee, E. Comini, *Sens. Actuators, B* **2011,** *160*, 1346-1351.

[S7] C. Li, M. Lv, J. Zuo, X. Huang, *Sensors* **2015,** *15*, 3789-3800.

[S8] A. Salehi, *Sens. Actuators, B* **2003,** *94*, 184-188.

[S9] F. Yang, F. Wang, Z. Guo, *J. Colloid Interface Sci.* **2018,** *524*, 32-41.

[S10] R. Zhang, D. Qiao, X. Liu, Z. Guo, L. Hu, L. Shi, *Ind. Eng. Chem. Res.* **2018**, *57*, 10379−10390.

[S11] J. Mao, G. Chen, J. Zhao, Y. He, J. Luo, *Friction* **2020**, DOI: 10.1007/s40544-019-0327-x.

[S12] J. Zhao, G. Yang, Y. Zhang, S. Zhang, P. Zhang, *Tribol. Lett.* **2019**, *67*, 88 (No.).

[S13] Y. Jazaa , T. Lan, S. Padalkar, S. Sundararajan, Lubricants **2018**, *6*, 106 (No.).