

Supporting information

Tribological gain enabled by synergy of copper nanoparticles and friction induced in-situ tribo-click reaction

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1. Experimental section

The synthesis of 1-(2-propynyl)-3-methyl-imidazolium trifluoromethanesulfonate ([PMIM]OTf): [PMIM]OTf was synthesized according to the previous works with some modifications¹. 3-Bromopropyne (4.926 g, 60 mmol, 1.2 equiv) was dissolved in toluene (50 mL). 1-Methylimidazole (5.948 g, 50 mmol, 1 equiv) was dropped into the solution at 0 °C. The solution was stirred overnight, and the temperature gradually returned to room temperature. Remove the solvent in vacuo to obtain 77% [PMIM]Br (3-methyl-1-propargylimidazolium bromide). Subsequently, the [PMIM]Br was dissolved in water, and then the equivalent Silver(I) trifluoromethanesulfonate was added into the solution at 50 °C according to the previous works with some modifications. After filtering out the solid, remove the solvent in vacuo to obtain 90% [PMIM]OTf.

([PMIM]OTf): ¹H NMR (400 MHz, DMSO-d₆) δ 9.19 (d, *J* = 1.8 Hz, 1H), 7.78 (t, *J* = 1.9 Hz, 1H), 7.74 (t, *J* = 1.8 Hz, 1H), 5.19 (d, *J* = 2.6 Hz, 2H), 3.88 (s, 3H), 3.83 (t, *J* = 2.6 Hz, 1H).

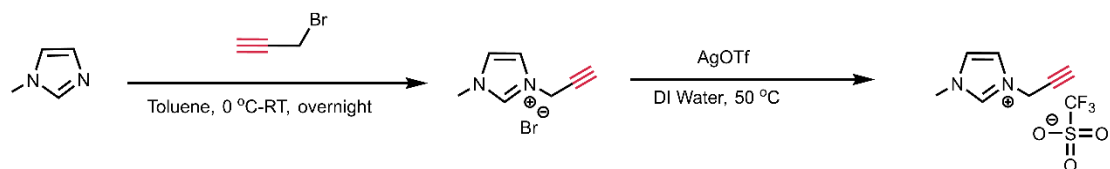


Fig. S1 The synthesis of [PMIM]OTf.

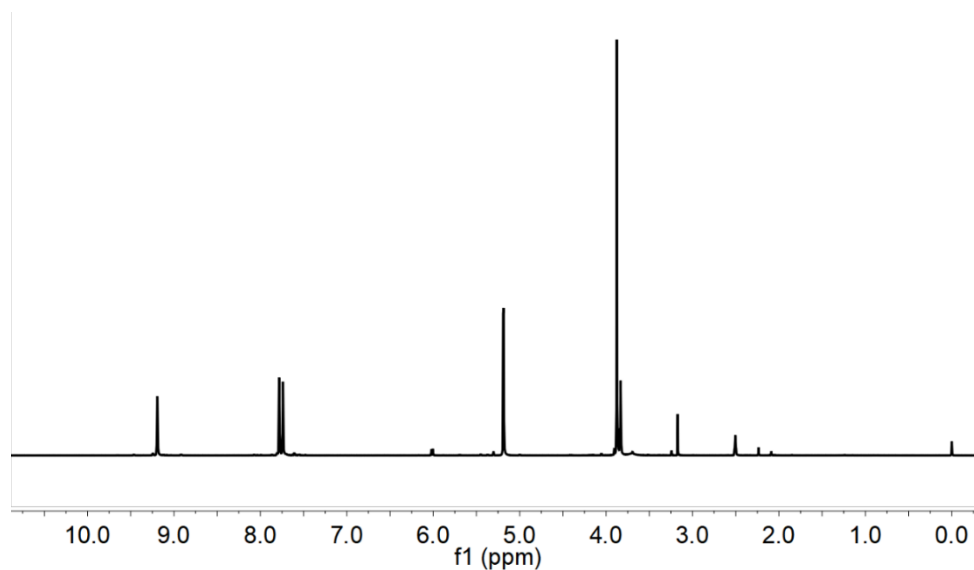


Fig. S2 The ^1H NMR spectra of [PMIM]OTf.

The synthesis of 1-azidododecane: Sodium azides (1.561 g, 24 mmol, 1.2 equiv) and 1-bromododecane (4.962 g, 20 mmol, 1 equiv) was dissolved in DMSO (50 mL). After stirring 12 h at 60 °C, the solution was washed by water and then extracted with methylene chloride, and 1-azidododecane was given by removing the solvent in vacuo. The yields of 1-azidododecane were 90 %.

1-azidododecane: ^1H NMR (400 MHz, Chloroform-d) δ 3.25 (t, $J = 7.0$ Hz, 2H), 1.60 (p, $J = 7.0$ Hz, 2H), 1.40 – 1.20 (m, 18H), 0.93 – 0.83 (m, 3H).

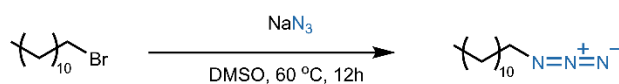


Fig. S3 The synthesis of 1-azidododecane.

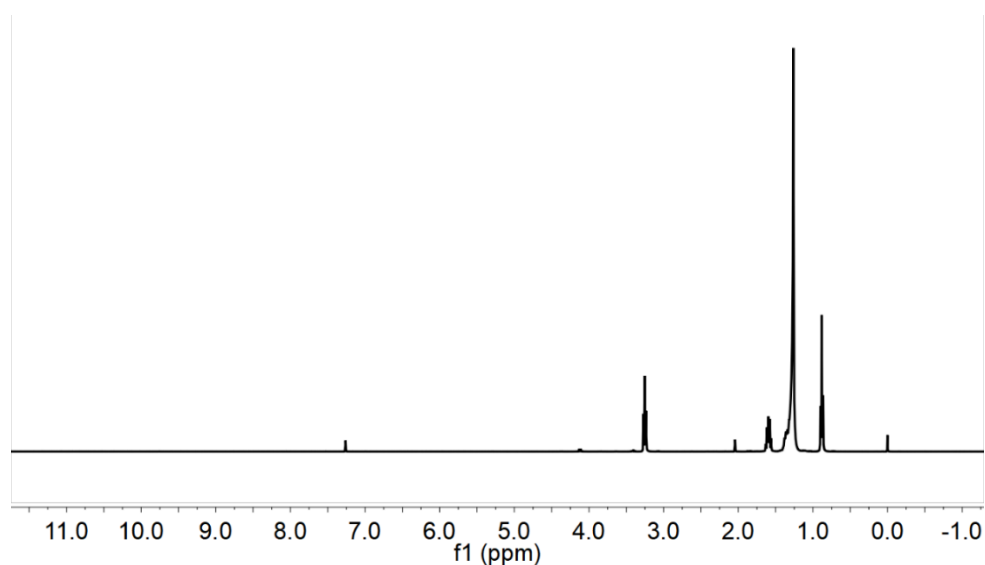


Fig. S4 The ^1H NMR spectra of 1-azidododecane.

The synthesis of 3-Azido-7-hydroxycoumarin: 3-Azido-7-hydroxycoumarin was synthesized according to the previous works with some modifications². A mixture of 2,4-dihydroxy benzaldehyde (2.76 g, 20 mmol), *N*-acetylglycine (2.34 g, 20 mmol), anhydrous sodium acetate (60 mmol) in acetic anhydride (100 mL) was refluxed under stirring for 4 h. The reaction mixture was poured onto ice to give a yellow precipitate. After filtration, the yellow solid was washed by ice water before it was refluxed in a solution of conc. HCl and ethanol (2:1, 30 mL) for 1 hour, then ice water (40 mL) was added to dilute the solution. The solution was then cooled in an ice bath and NaNO_2 (40 mmol) was added. The mixture was stirred for 5-10 minutes and NaN_3 (60 mmol) was added in portions. After stirring for another 15 minutes, the resulting precipitate was filtered off, washed with water, and dried under reduced pressure to afford a brown solid; 1.75 g (43% overall yield). The product was pure enough for further reactions.

3-Azido-7-hydroxycoumarin: ^1H NMR (400 MHz, DMSO- d_6) δ 10.54 (s, 1H), 7.59 (s, 1H), 7.48 (d, $J = 8.6$ Hz, 1H), 6.81 (dd, $J = 8.5, 2.3$ Hz, 1H), 6.76 (d, $J = 2.3$ Hz, 1H).

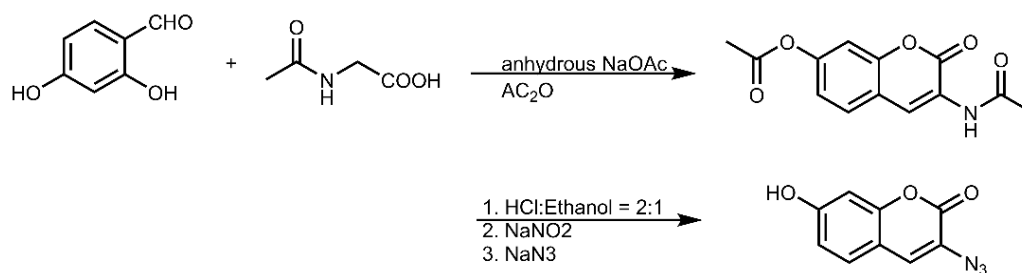


Fig. S5 The synthesis of 3-Azido-7-hydroxycoumarin.

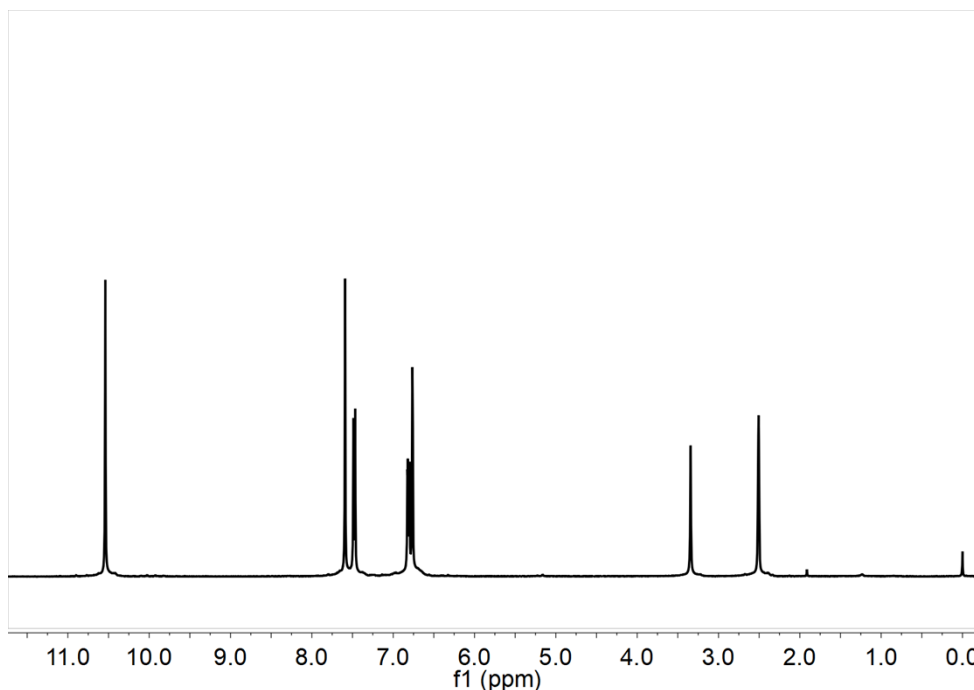


Fig. S6 The ^1H NMR spectra of 3-Azido-7-hydroxycoumarin.

The synthesis of 3-((1-dodecyl-1H-1,2,3-triazol-4-yl) methyl)-1-methyl-1H-imidazol-3-ium trifluoromethanesulfonate ([DTYIm]OTf): [PMIM]OTf (3.242 g, 10 mmol, 1.2 equiv) and 1-azidododecane (1,663 g, 10 mmol 1 equiv) were dissolved in DMSO (50 mL), After stirring 6 h at 50 °C, the solution was washed by water and then extracted with methylene chloride. After filtering out the solid, remove the solvent in vacuo to obtain 68% product.

[DTYIm]OTf: ^1H NMR (400 MHz, DMSO- d_6) δ 9.18 (d, $J = 1.8$ Hz, 1H), 8.24 (s, 1H), 7.75 (d, $J = 1.8$ Hz, 1H), 7.71 (t, $J = 1.8$ Hz, 1H), 5.52 (s, 2H), 4.36 (t, $J = 7.1$ Hz,

2H), 3.86 (s, 3H), 1.80 (p, $J = 7.2$ Hz, 2H), 1.24 (d, $J = 4.6$ Hz, 18H), 0.88 – 0.83 (m, 3H).

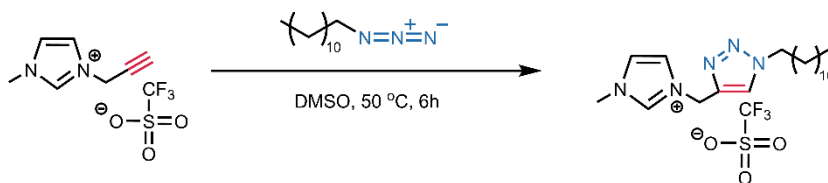


Fig. S7 The synthesis of [PMIM]OTf.

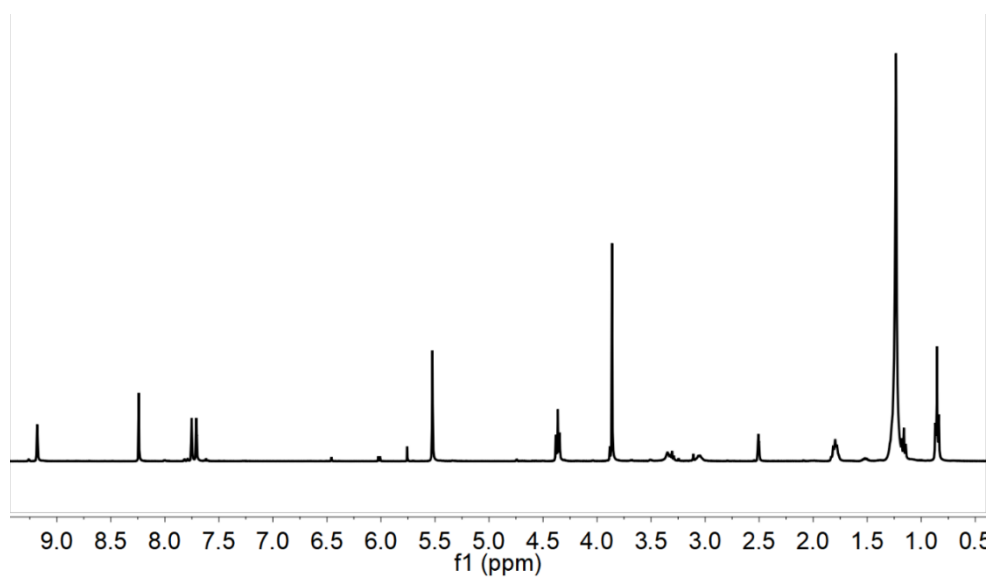


Fig. S8 The ^1H NMR spectra of [PMIM]OTf.

2. Coefficient of Friction for different variables in the in-situ tribo-click system

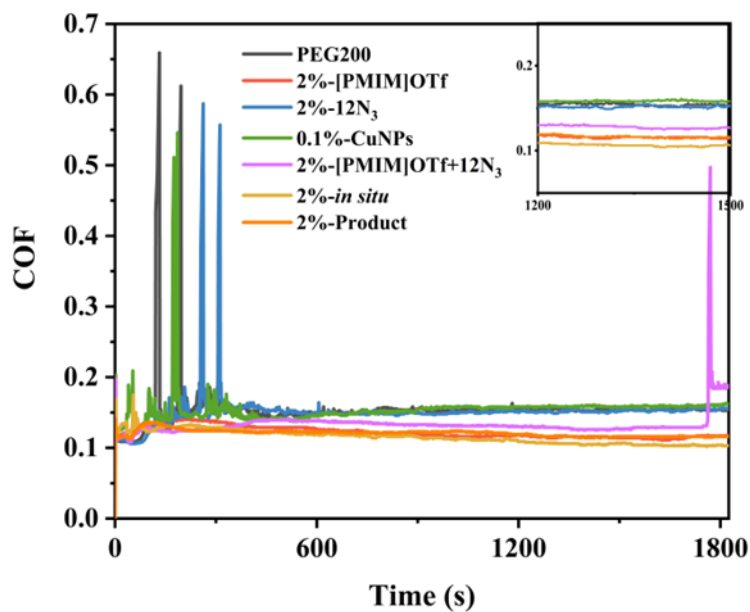


Fig. S9 COF curves of the in-situ tribo-click system in PEG200 (The mini-figure is an enlargement of the corresponding position).

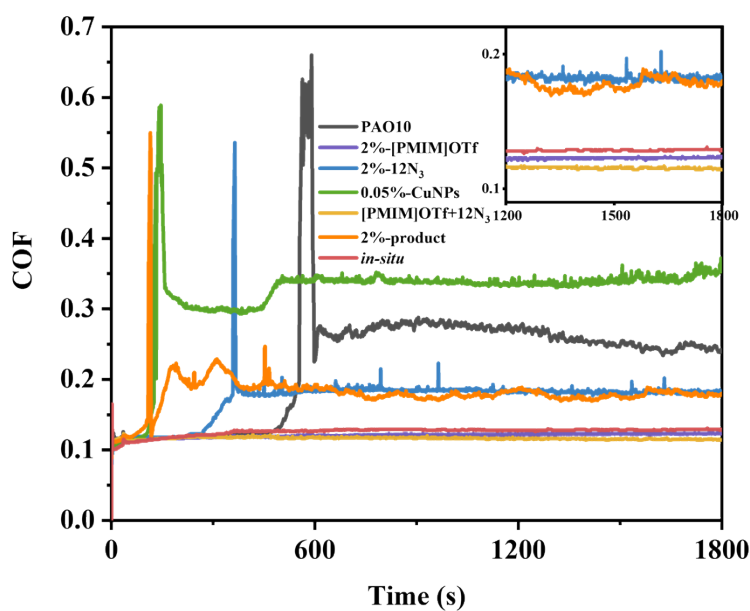


Fig. S10 COF curves of the in-situ tribo-click system in PAO10 (The mini-figure is an enlargement of the corresponding position).

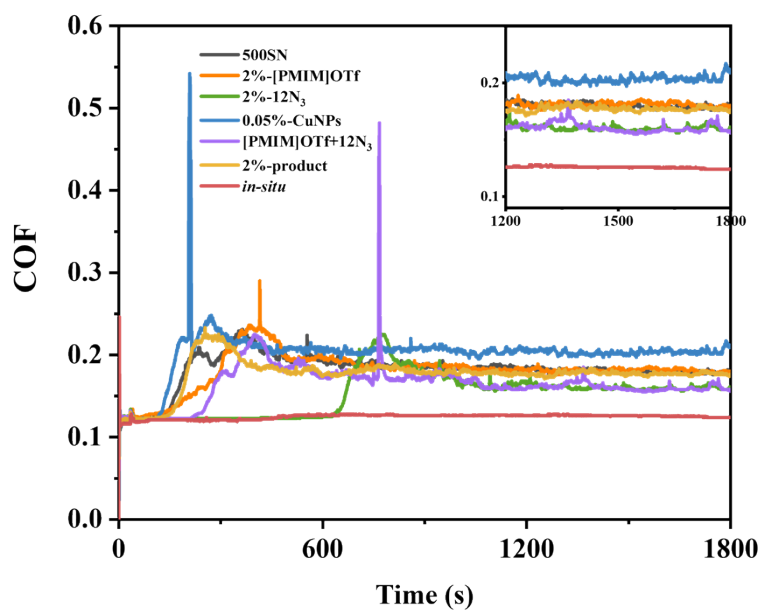


Fig. S11 COF curves of the in-situ tribo-click system in 500SN (The mini-figure is an enlargement of the corresponding position).

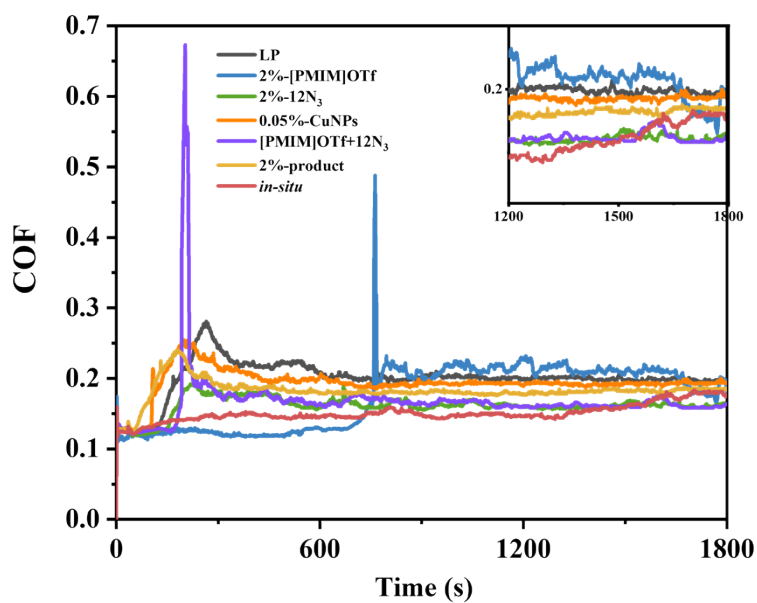


Fig. S12 COF curves of the in-situ tribo-click system in liquid paraffin (The mini-figure is an enlargement of the corresponding position).

3. 3D morphologies of worn scars for different variables in the in-situ tribo-click system

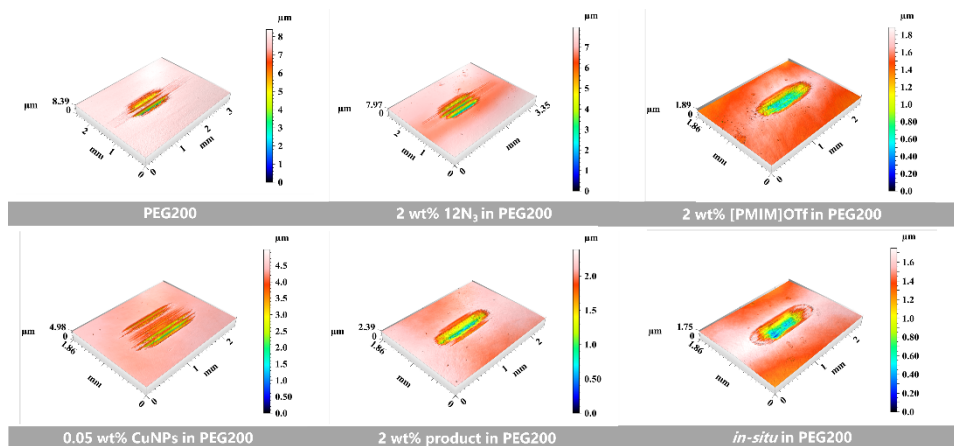


Fig. S13 3D morphologies of worn scars for different variables in the in-situ tribo-click system with the base oil PEG200.

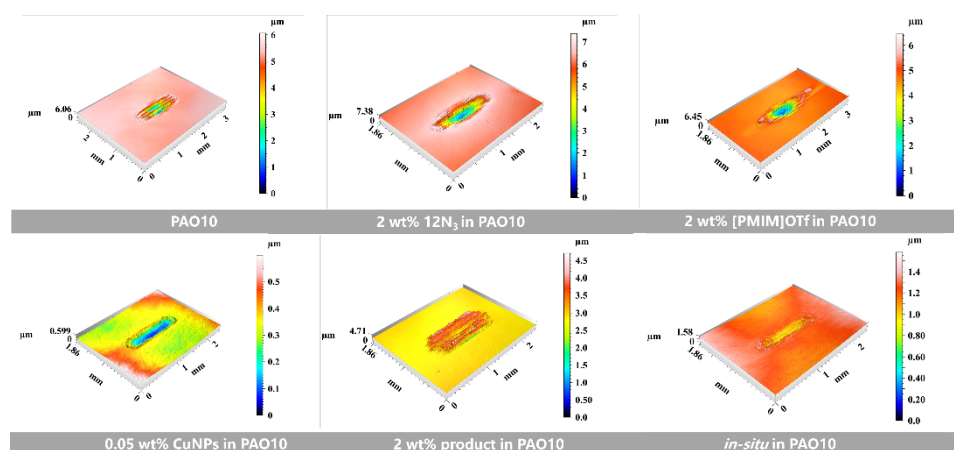


Fig. S14 3D morphologies of worn scars for different variables in the in-situ tribo-click system with the base oil PAO10.

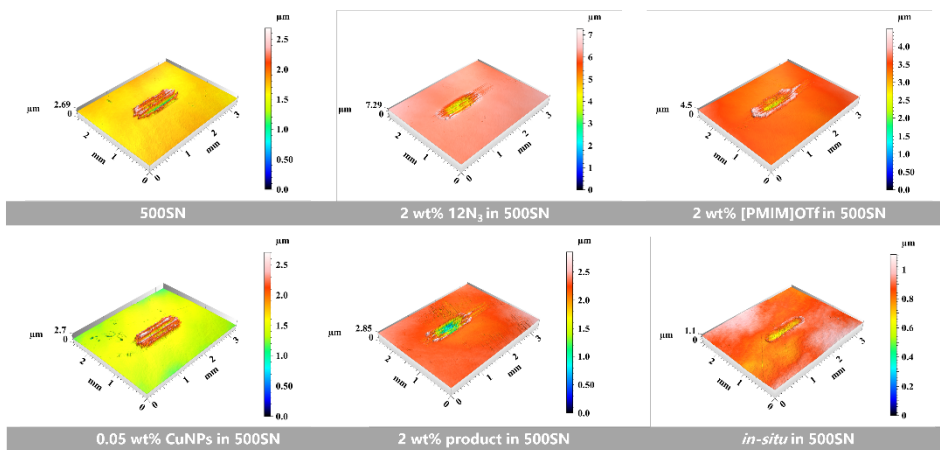


Fig. S15 3D morphologies of worn scars for different variables in the in-situ tribo-click system with the base oil 500SN.

4. The XPS survey spectra of in-situ tribo-click system:

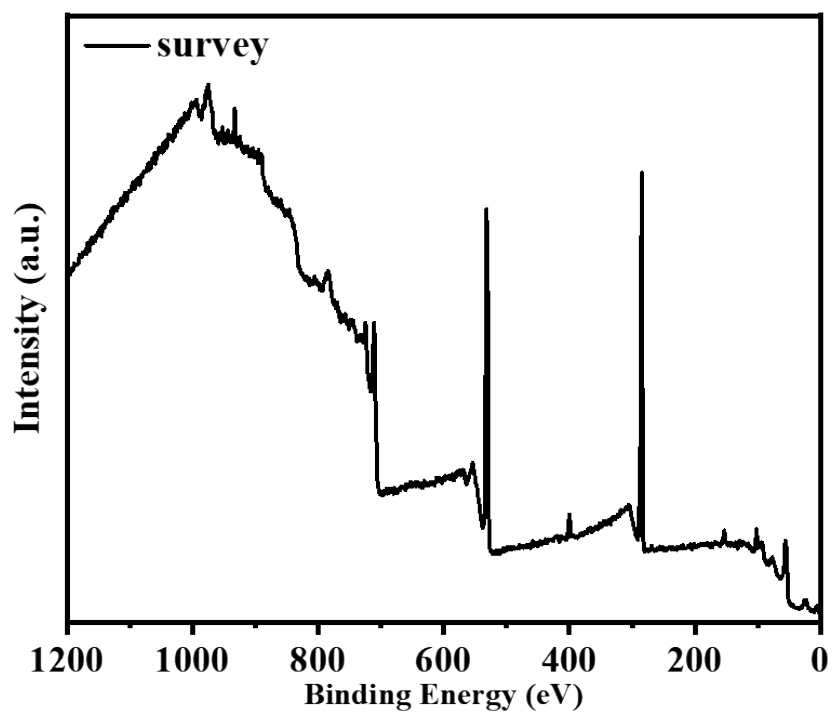


Fig. S16 The XPS survey spectra of in-situ tribo-click system.

5. The EDS linear scanning spectra: C, Pt, S

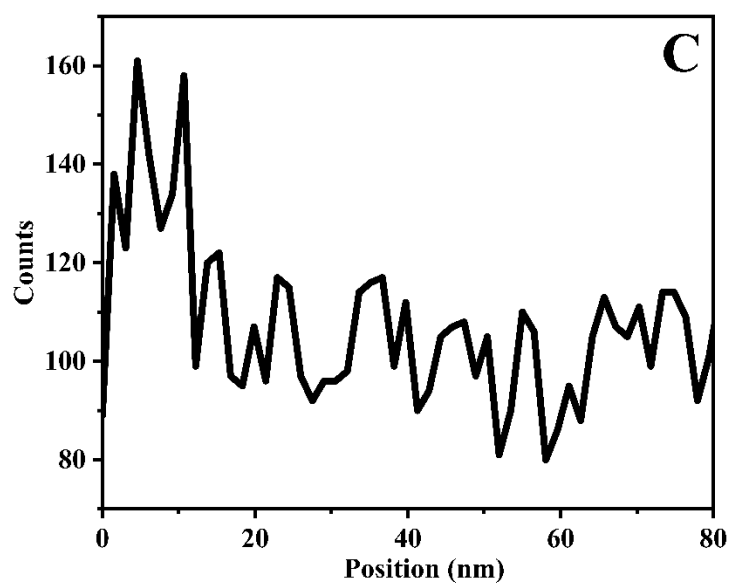


Fig. S17 The EDS linear scanning spectra of C.

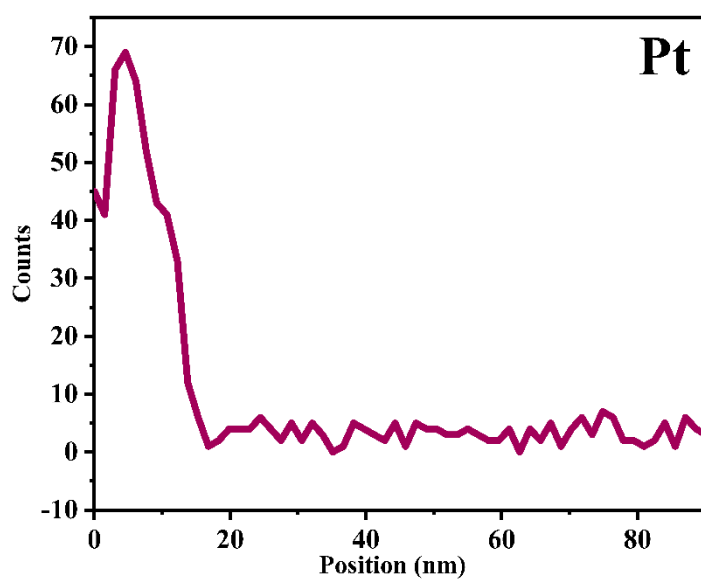


Fig. S18 The EDS linear scanning spectra of Pt.

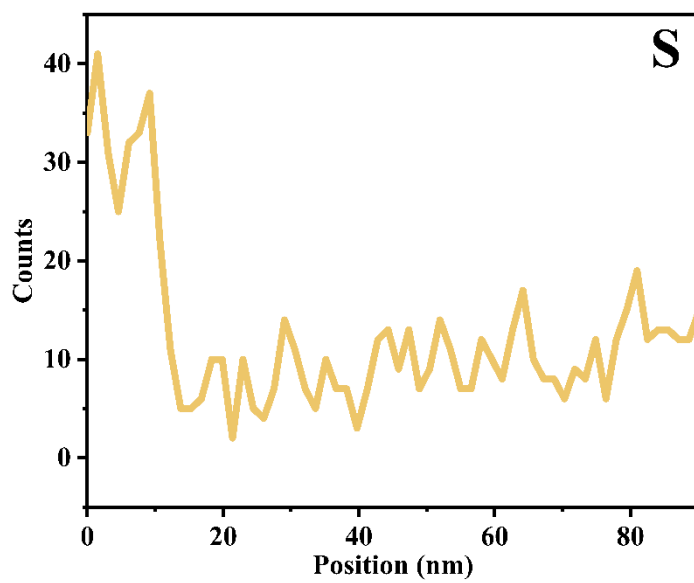


Fig. S19 The EDS linear scanning spectra of S.

6. The morphology of copper nanoparticles

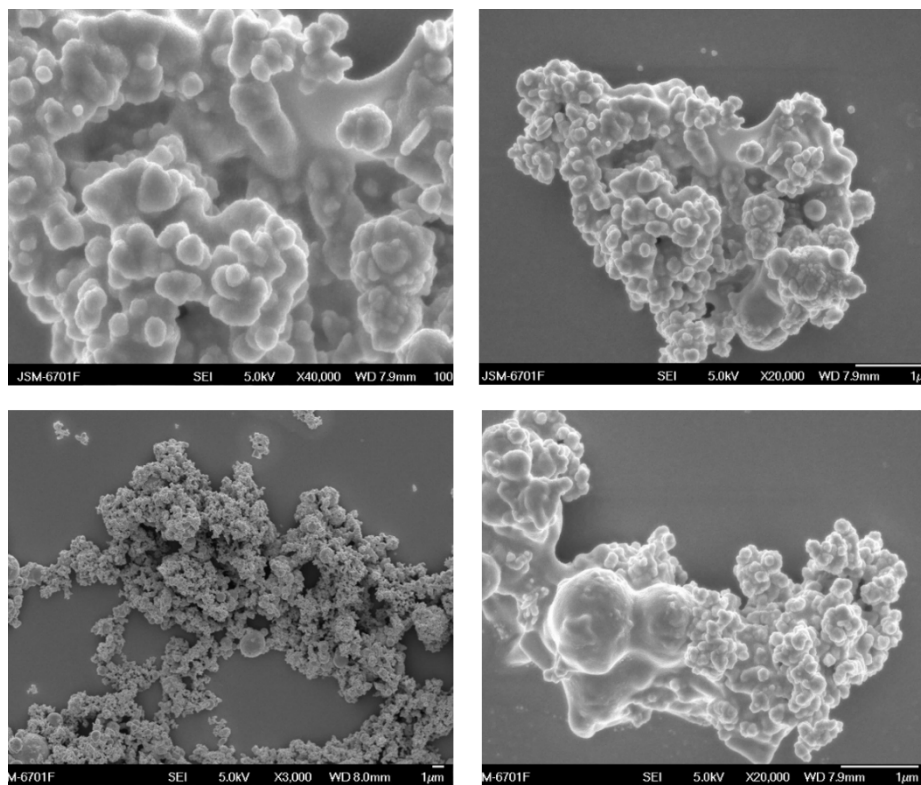


Fig. S20 SEM images of Copper Nanoparticles at different magnifications.

7. The XPS spectra of copper nanoparticles

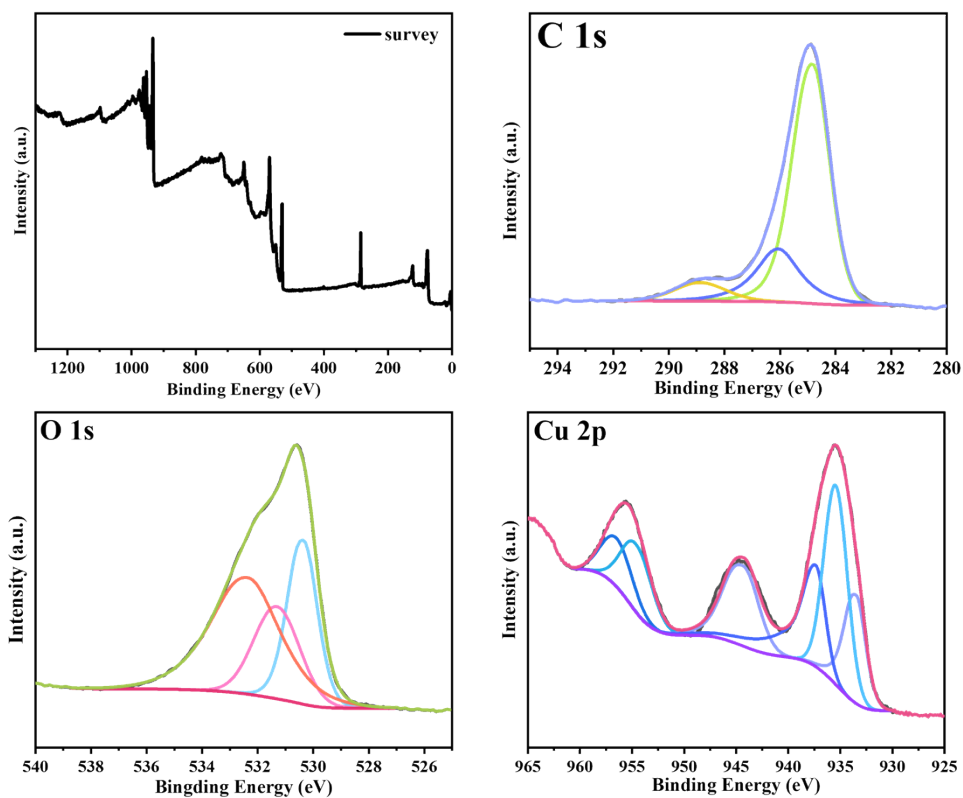


Fig. S21 XPS spectra of Copper Nanoparticles.

References

1. S. Ravula, N. E. Larm, Y. Liu, J. L. Atwood, S. N. Baker and G. A. Baker, *New Journal of Chemistry*, 2018, **42**, 1979-1986.
2. K. Sivakumar, F. Xie, B. M. Cash, S. Long, H. N. Barnhill and Q. Wang, *Organic Letters*, 2004, **6**, 4603-4606.