Supporting information

Smooth and solid WS_2 submicrospheres grown by a new laser fragmentation and reshaping process with enhanced tribology properties

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1, Experimental details

Preparation of spherical WS_2 particles

Smooth and solid WS_2 submicrospheres were prepared with pulse laser irradiation in liquid. Fig. 1a depicted the experimental step for laser irradiation in liquid. Raw commercial WS_2 powder (99.5%) with size distribution of 0.5-13 μm (measured by laser particle size analyzer, LS-13320, Beckman), were dispersed in ethanol at a mass concentration of 15 gL^{-1} to form a colloidal solution. A KrF excimer laser (10 Hz, 25 ns, Coherent, CompexPro 205) was used as the light source. The laser beam was focused on the colloidal solution through a convex lens with a focal length of 150 mm. Laser irradiation of bulk WS_2 slices were performed with different growth time and different energy fluence (300, 500, 700 and 1000 mJ $pulse^{-1}$ cm^{-1}), which were determined by a laser energy/power meter (FieldMaxII, Coherent). The raw WS_2 colloidal solution was continuously stirred during laser irradiation to prevent gravitational sedimentation. After laser irradiation, all prepared colloidal suspensions were centrifuged at 7000 rpm for 10 min and dried at 30 ^oC to obtain power products for further characterizations. The relative centrifugation force (RCF) was calculated according to

$$RCF=1.118\times10^{-5}\times R\times n^2, \quad (1)$$

where R is the radius of rotation (cm) and n is the speed of centrifuge rotor (r/min), respectively. The calculated number is 2739 g.

Material Characterizations

The morphology of different samples was observed by scanning electron microscope (SEM, FEI Quanta 250 FEG). The X-ray diffraction pattern (2θ=10-80^o) was investigated with an X-ray diffraction (XRD, D8-Advance, Bruker), operated at 40 kV and 40 mA using a Cu-Kαline (λ=0.154184 nm). Microstructural examination was characterized by transmission electron microscopy (TEM, JEM-2100F) with a 200 kV acceleration voltage, by dispersing the powders in ethanol and dropping a drop onto a carbon-coated Cu grid. Raman spectrometer equipped with a 532 nm laser (LabRAM HR Evolution, HORIBA) was used for recording the Raman spectra of different WS_2 samples. The binding energies of W and S in different WS_2 samples were detected by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, with an Al Kα X-ray source).

Tribology study

The tribology properties of bulk slices and solid spheres as additives in lubricating oil were measured with a four-ball tribology tester (MMU-10G, Sinomach-Jinan) in terms of the friction coefficient (FC) and wear scar diameter (WSD). The tester was operated with one steel ball under load rotating against three steel balls held stationary in the form of a cradle, as shown in Fig. S1. The steel balls with a hardness of 64–66 HRC were selected according to the National Standard of China (G20, GB/T308-2002). Paraffin liquid (PL) (Q/CYDZ352-2007, China) was used as a reference lubricant for tribology measurements. Different WS_2 powder was ultrasonically dispersed (10 min) in the PL at different 0.5, 1.5, 2.0 and 3.0 wt% concentrations. Control experiments were performed by measuring the tribological properties of raw WS_2 slices and smooth WS_2 spheres. Detailed experimental conditions of the four-ball test were set as follows: rotation speed at 1450 rpm, load of 392 N, totally time of 30 min, temperature at 40 °C and 75°C, respectively. The friction coefficient was recorded in situ and the test data were acquired

automatically with a computer. The WSDs were measured with a metallographic microscope. After washing with petroleum ether and acetone, the wear scar morphology was observed by SEM.

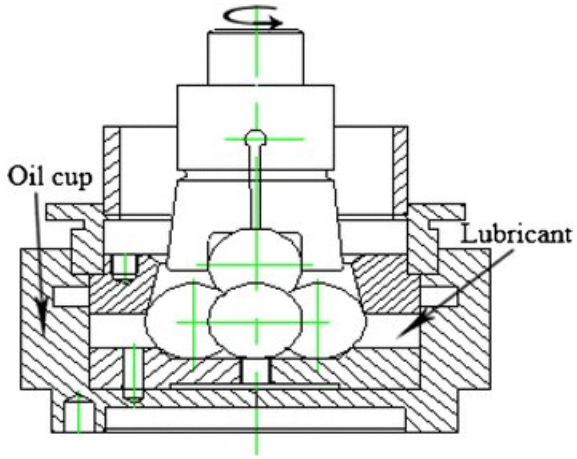

Fig. S1 Structure sketch map of the four-ball tribology tester

2, Additional results and discussions

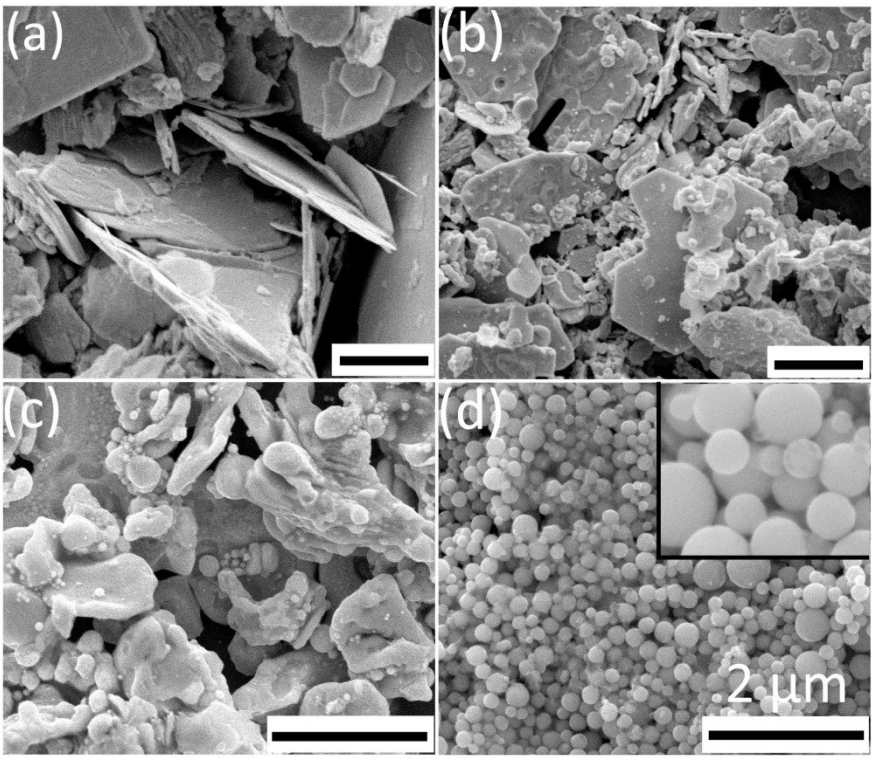

Fig. S2 SEM images of raw-bulk WS_2 slices irradiated with different laser energy fluence for 30 min. (a) Raw WS_2 slices, (b ~ d) Laser fluence is 300, 500, and 700 mJ pulse^{-1} cm^{-2}, respectively.

Fig. S2(a ~ d) show the SEM images of the prepared WS_2 particles by using different laser fluence. When the laser fluence is as low as 300 mJ pulse^{-1} cm^{-2}, only inconspicuous size reduction and small sized particles melting are observed because the pulse laser cannot produce enough energy to smash or melt big WS_2 particles (Fig. S2b). When the laser fluence increases to 500 mJ pulse cm^{-2}, all WS_2 particles lose their sharp edges and present a round shape trend (Fig. S2c). When the laser energy density further is increased to 700 mJ pulse^{-1} cm^{-2}, perfectly solid WS_2 submicrospheres with smooth surface are obtained, as shown in Fig. S2d. In such high laser energy density of 700 mJ pulse^{-1} cm^{-2}, a considerable particle-size reduction of WS_2 spheres due to laser fragmentation.

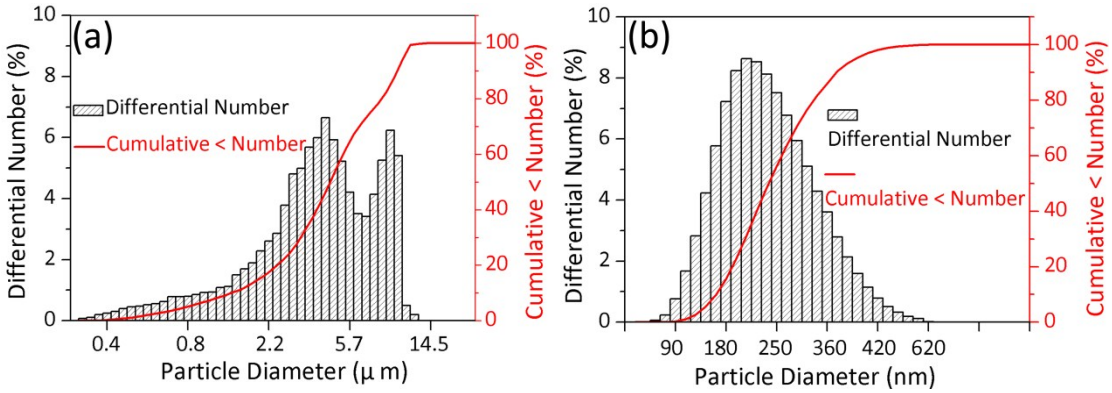

Fig. S3 (a ~ b) Size distribution histograms of raw-bulk WS_2 slices and WS_2 spheres after laser irradiation with pulse of 700mJ pulse^{-1} cm^{-1}, respectively.

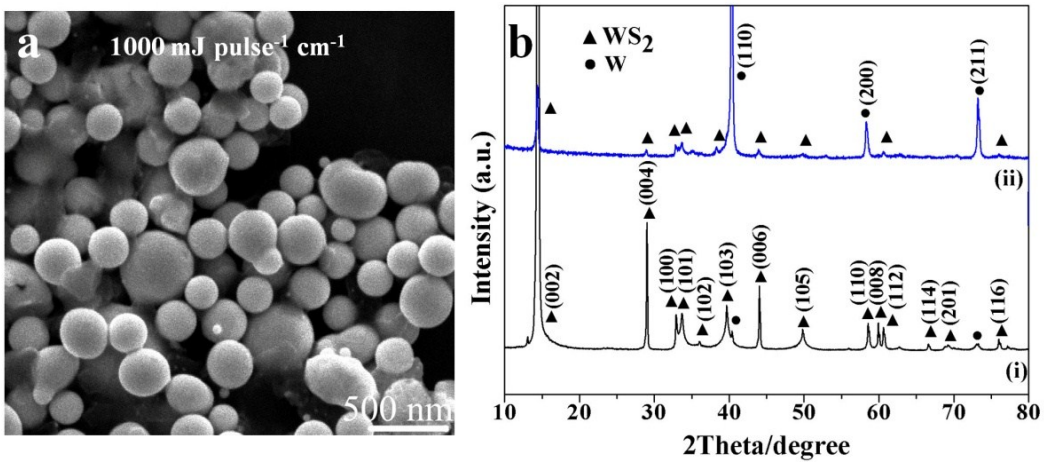

Fig. S4 (a) SEM image of WS_2 submicroparticles irradiated with laser energy fluence of 1000 mJ pulse^{-1} cm^{-1}. XRD patterns: (i) raw slices, (ii) 1000 mJ pulse^{-1} cm^{-1}.

Fig. S4 show the SEM images and XRD pattern of the WS_2 particles prepared using laser fluence as high as 1000 mJ pulse^{-1} cm^{-1}. The spherical morphology can still retain. But, after high energy laser irradiation, stronger W peaks in comparison with the raw commercial WS_2 slice samples were observed from the submicrosphere samples indicating a reduction effect during the laser irradiation process, which is similar to our former report.[13c]

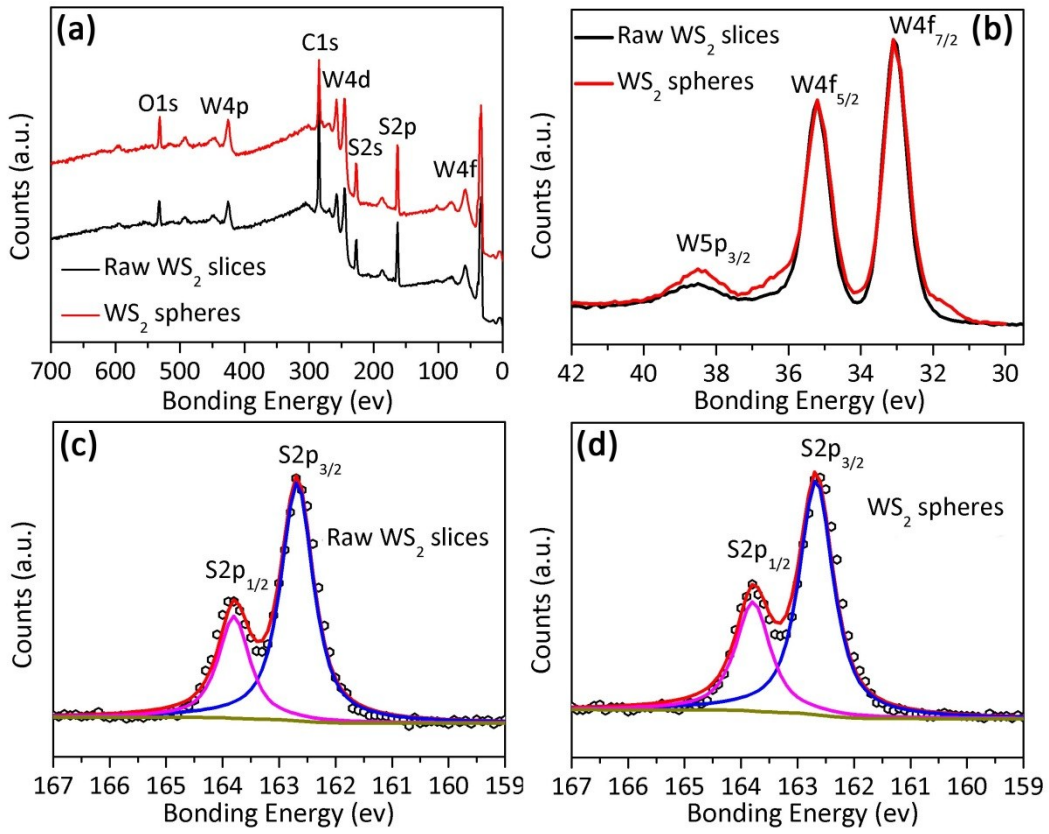

Fig. S5 XPS analysis of raw WS_2 slices and WS_2 spheres induced by LFR: (a) general spectra; (b) W4f and W5p peaks; (c~d) S2p peaks and the fitting result.

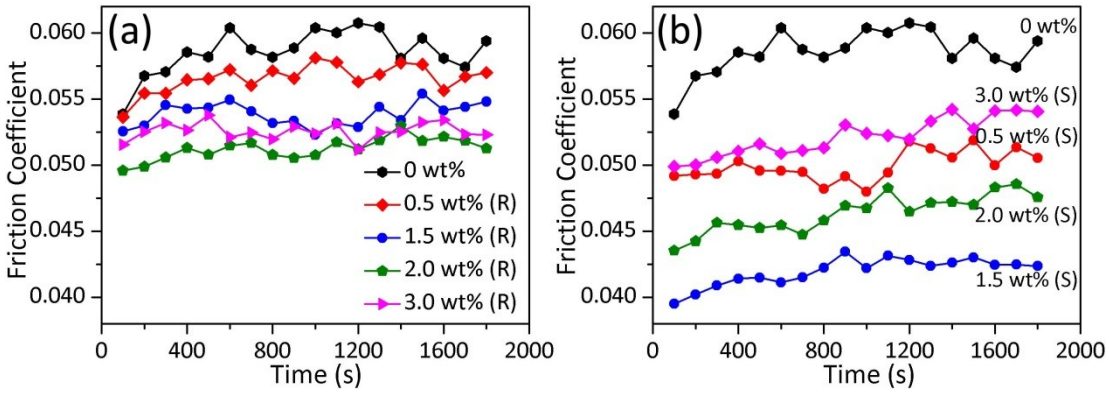

Fig. S6 Friction coefficients variation with time under temperature of 40 °C for PL with different concentrations of raw WS_2 slices (R) and smooth WS_2 spheres(S).

Tab. S1 Average WSDs on the testing balls lubricated by PL with different mass concentrations of raw WS_2 slices (R) and smooth WS_2 spheres (S).

Concn. (wt%)	0	0.5 R	1.5 R	2.0 R	3.0 R	0.5 S	1.5 S	2.0 S	3.0 S
Avg. WSD (μm) With error ± 2	603	590	564	520	549	499	437	475	517
Reduction (%)		2.1	6.4	13.7	8.9	17.3	27. 5	21.2	14.3