

Supporting Information

Efficient generation of sulfate radicals in Fe (II)/S (IV) system induced by WS₂ nanosheets and examined by its intrinsic chemiluminescence

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Chemicals and Reagents. WS₂ powders, sodium sulfate (Na₂SO₃), ferrous sulfate (FeSO₄·7H₂O), 1,10-Phenanthroline, rhodamine B (RhB) were of analytical grade (AR) and were purchased from Adamas Reagent Co., Ltd. N,N-dimethylformamide (DMF) was obtained from Chengdu chemical reagent Co., Ltd. 5,5-dimethyl-1-pyrroline-oxide (DMPO) and nitrotetrazolium blue chloride (NBT) were supplied from Sigma-Aldrich chemical Co. (St. Louis, MO, USA). All the extra chemical reagents were of analytical grade and bought from Chengdu United Institute of Chemical & Reagent. The used ultrapure water in all experiments was prepared by a Mili-Q ultrapure system and the conductivity was 18.2 MΩ/cm.

Synthesis of WS₂ nanosheets. WS₂ nanosheets were prepared by solvent exfoliation method. Firstly, 100 mg WS₂ powder was added in 100 mL DMF and kept sonication for 6 h below 30°C. Then the dispersion was settled for 6 h. Afterwards, the resulting suspensions were transferred into flask and kept vigorous stirring for 12h at 140°C. The mixture was cooled down to ambient temperature naturally and centrifuged for 20 min at 2000 rpm to remove the bulk WS₂. The supernatant was centrifuged for 20 min at 6000 rpm to obtain the sediments (WS₂ nanosheets 1). Then the remaining supernatant was centrifuged again at 10000 rpm to obtain the sediments (WS₂ nanosheets 2). Finally, the surplus solution was evaporated to eliminate DMF via rotary evaporation method and obtain the products (WS₂ nanosheets 3). WS₂ nanosheets 1, 2 and 3 were washed with absolute ethyl alcohol and pure water for further purification, then dried and preserved in vacuum bags.

Instruments. JME-2010 microscope (JEOL Co., Japan) was applied to obtain transmission electron microscopy (TEM) images and high-resolution TEM images, setting the accelerating voltage as 200 kV. Atomic Force Microscope (AFM) images were obtained by Scanning Probe Microscope (Cypher VRS, Oxford, UK). The Philips X'Pert Pro X-ray diffractometer with Cu Kα radiation (λ=1.5406 Å) was employed to collect X-ray diffraction (XRD) patterns over the range of 10° to 50°. The X-ray photoelectron spectrum (XPS) was recorded by an ESCA Lab 250Xi

(Thermo Scientific, USA). All fluorescence spectra were investigated with F-7000 fluorescence spectrophotometer (Hitachi, Japan). The UV-vis spectra were scanned by UV-2910 UV-Vis photometer (Hitachi, Japan). Electron paramagnetic resonance (EPR) spectra for reactive species were measured on Bruker E-500. The size distribution of the products was characterized by Zeta sizer Nano ZS (Malvern Co., UK).

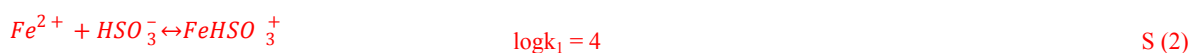
The degradation of RhB. All the degradation experiments were carried out at near neutral and the detail condition were 1.4 mM Na₂SO₃, 0.1 mg/mL WS₂ nanosheets, 0.14 mM Fe²⁺, a certain concentration of RhB. In order to evaluate the efficiency of degeneration, the absorbance of the samples at set intervals was measured by UV-Vis spectrometer at 554 nm.

Chemiluminescence analysis. The CL experiments were carried out through the Ultra Weak Luminescence Analyzer (BPCL-2-TGC), which was supported by Institute of Biophysics, Chinese Academy of Sciences, Beijing. When the CL spectrum was measured on the BPCL luminescence analyser, the high-energy optical filters from 400 to 640 nm were settled between the CL cell and the PMT. The testing condition of PMT was voltage 0.875 Kv, time interval 0.1 s. The injection order effect was measured at this condition: 10 μL of 10 mM FeSO₄, 100 μL of 10 mM Na₂SO₃, 200 μL of 0.1 mg/mL WS₂ nanosheets and 400 μL of 10 mM PBS.

Detection of Fe²⁺. To evaluate the conversion of the cycle of Fe³⁺/Fe²⁺, 1,10-phenan-throline monohydrate (5 mg/mL) was used as the colour-developing agent. The sample was mixed with 1,10-phenan-throline monohydrate and set aside for several minutes. The absorbance spectrum was measured by UV-Vis spectrometer at 510 nm.

The chromogenic reaction of superoxide anion (O₂⁻) with NBT. To demonstrate the existent of O₂⁻ in Fe²⁺-SO₃²⁻ with the addition of WS₂ nanosheets, O₂⁻ can be scavenged by NBT and the absorbance was obtained on UV-Vis spectrometer. Note: 10 μL of 10 mM FeSO₄, 100 μL of 10 mM Na₂SO₃, 200 μL of WS₂ nanosheets 2.

Eqn S(1)–(8) in Fe²⁺-SO₃²⁻ system.



(6)



Fig. S1 the AFM images of the WS₂ nanosheets 1 (A), 2 (B) and 3 (C).

Fig. S1

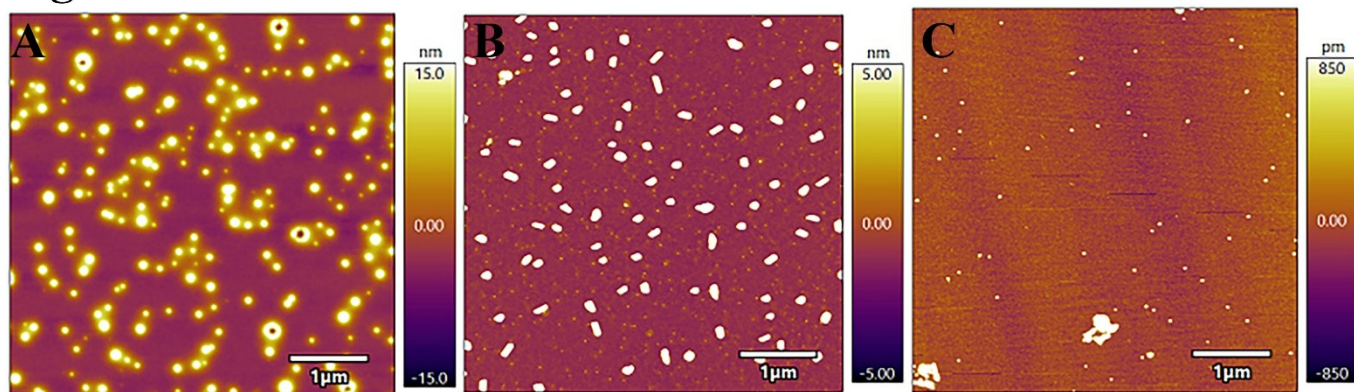


Fig. S2 The relationship between the thin WS₂ and RhB degradation in Fe²⁺-SO₃²⁻ system. Legend: 1.4 mM Na₂SO₃, 0.1 mg/mL WS₂ nanosheets, 0.14 mM Fe²⁺, 5 μg/mL RhB, the solution pH was neutral.

Fig. S2

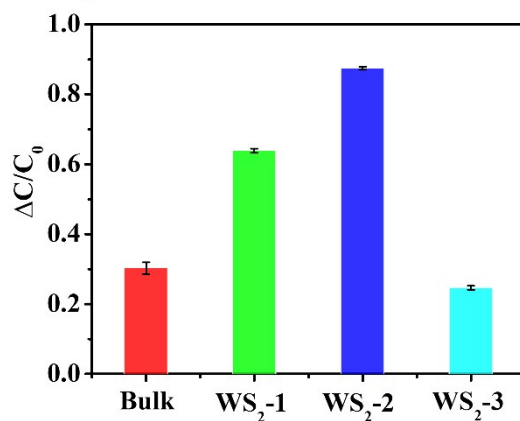
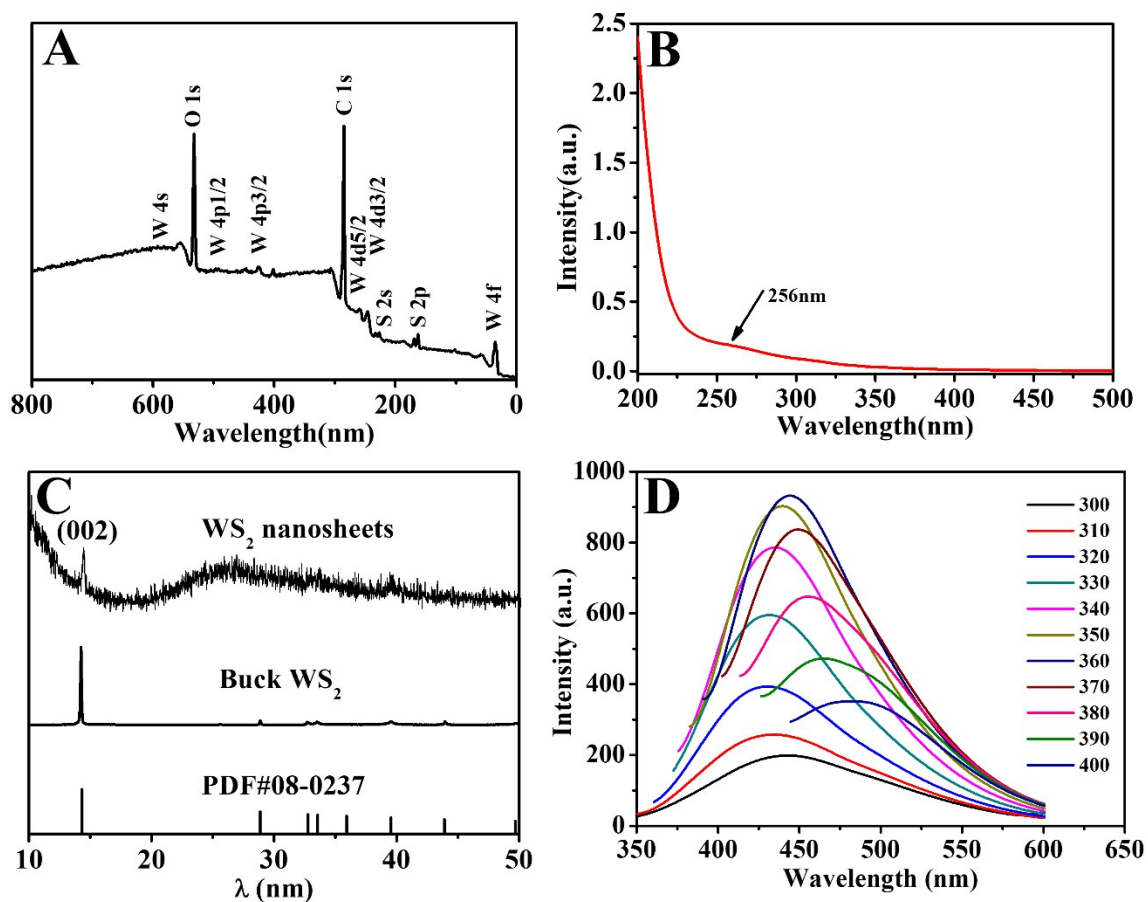


Fig. S3 (A) the full XPS spectrum and (B) UV-vis of WS₂ nanosheets; (C) XRD pattern of WS₂ nanosheets, bulk WS₂ and JCPDF (08-0237); (D) FL spectra of WS₂ nanosheets. Note: The indicated C and O elements might be originated from light oxidation and the adsorption of CO₂ on the surface of WS₂ nanosheets.

Fig. S3



The acquired X-ray diffraction (XRD) pattern of the WS₂ nanosheets showed a very strong peak at $2\theta = 14.4^\circ$ and two lower peaks at $2\theta = 28.9^\circ$ and $2\theta = 39.6^\circ$ (Fig. S3C, ESI[†]), which were assigned to the (002), (004), (103) faces, respectively (PDF # 08-0237). However, the signal of (002) reflection was weakened and other peaks were broadened or insignificant compared with the bulk pattern, indicating bulk WS₂ was exfoliated successfully to few-layer nanosheets, quite consistent with the AFM images (Fig. S1B, ESI[†]). Additionally, its peak fluorescence (Fig. S3D, ESI[†]) shifted from 430 to 480 nm when the excitation wavelength (λ_{ex}) was changed from 300 to 400 nm. The strongest emission was observed at about 440 nm when λ_{ex} was 360 nm. The intensity of fluorescence first ascended and then decreased as λ_{ex} was increased from 300 to 400 nm. This dependency of fluorescence on wavelength may have resulted from the size and layer distribution of the WS₂ nanosheets.

Fig. S4 Transformation of free radical (C) WS_2 nanosheets- $\text{Fe}^{2+}\text{-SO}_3^{2-}$ system and (D) $\text{Fe}^{2+}\text{-SO}_3^{2-}$ system at different time. (◆ stands for $\text{DMPO}\text{-SO}_3^{\cdot -}$ adduct, ▼ stands for $\text{DMPO}\text{-SO}_4^{\cdot -}$ adduct, ◇ stands for the coexisting $\text{DMPO}\text{-SO}_3^{\cdot -}$ and $\text{DMPO}\text{-OH}$ adduct, ★ stands for $\text{DMPO}\text{-OH}$ adduct). **Note: at 10 min, -OH was also observed in these two systems. In addition, the concentration of radicals in the WS_2 nanosheets- $\text{Fe}^{2+}\text{-SO}_3^{2-}$ system was much higher than that in the $\text{Fe}^{2+}\text{-SO}_3^{2-}$ system.**

Fig. S4

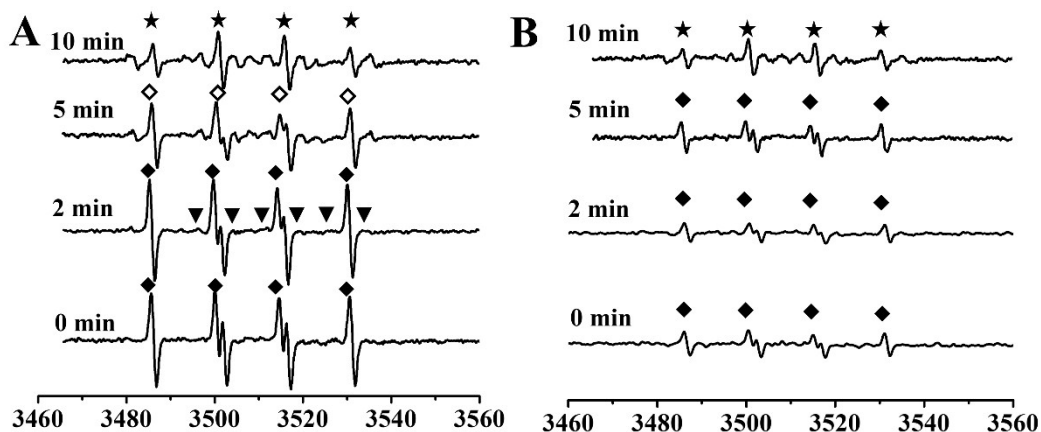
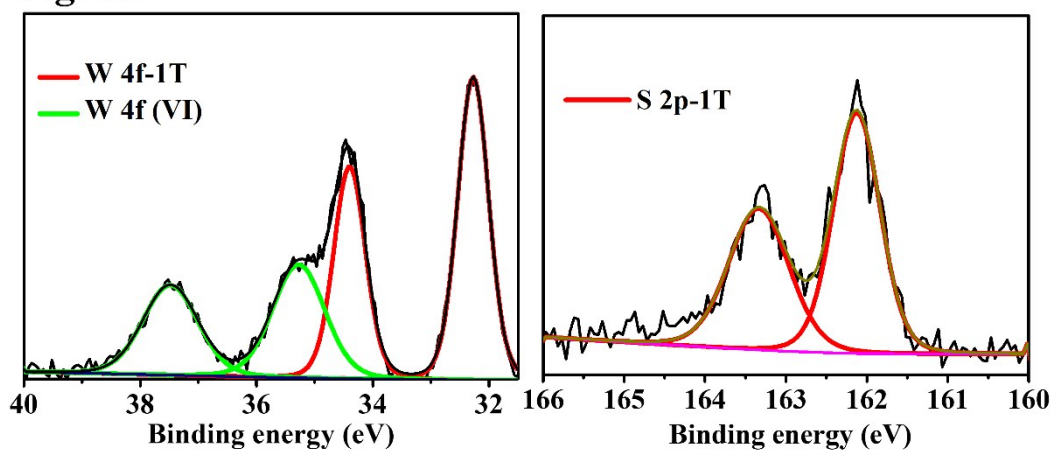


Fig. S5 the XPS spectra of the WS_2 nanosheets after SR-AOP.

Fig. S5



Tab. S1 The ratio of W^{4+} to W^{6+} of WS_2 nanosheets before and after SR-AOP

	W^{4+}		W^{6+}		W^{4+}/W^{6+}
Peak (eV)	32.5	34.6	35.5	37.7	
Before reaction					
Area (a.u.)	1901.8	1051.8	1850.5	1203.4	0.9672
After reaction					
Area (a.u.)	539.4	749.7	477.0	406.3	1.459

Fig. S6 Effects of (A) pH, (B) the concentration of WS_2 nanosheets, (C) the ratio of $FeSO_4/Na_2SO_3$, and (D) the concentration of PBS on the relative CL intensity (High voltage: 875 V; interval time was set for 0.1 s).

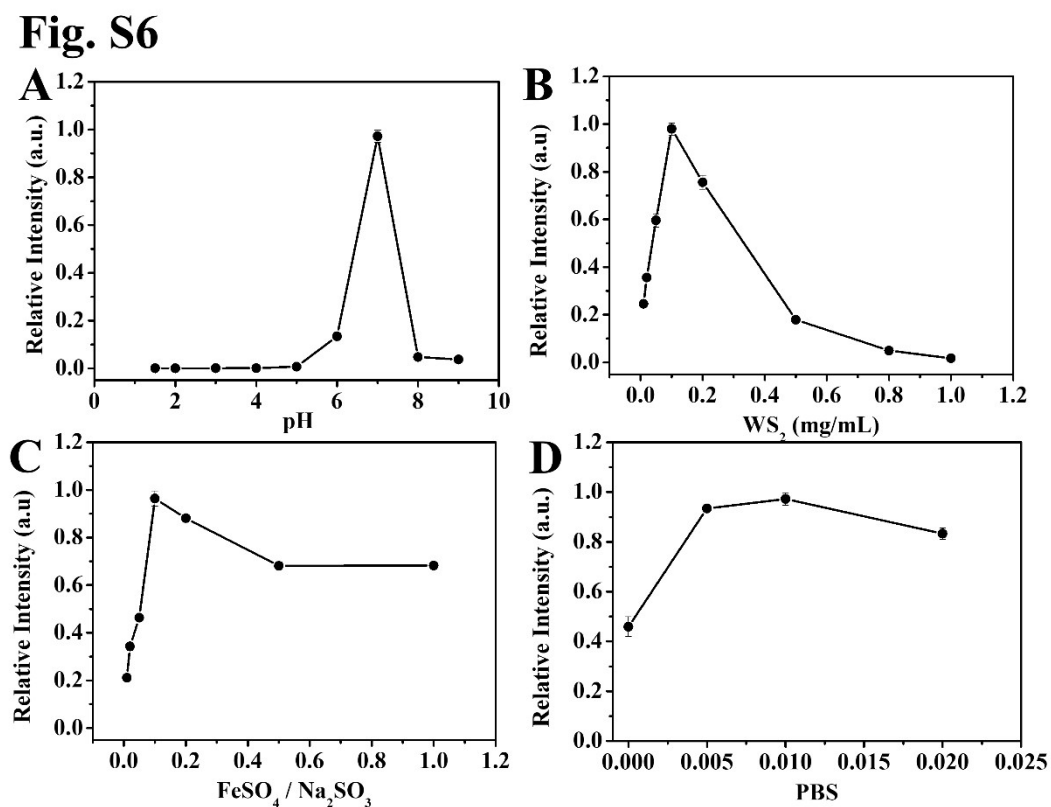


Fig. S7 Effect of oxygen on the CL intensity of WS_2 nanosheets– $FeSO_4$ – Na_2SO_3 system. (a) the chemiluminescence intensity without bubbling; (b) all solutions were bubbled with N_2 for 30 min; (c) all solutions were bubbled with O_2 for 30 min. Condition: 10 μ L of 10 mM $FeSO_4$, 100 μ L of 10 mM Na_2SO_3 , 200 μ L of 0.1mg / mL WS_2 nanosheets; 400 μ L of 10 mM PBS.

Fig. S7

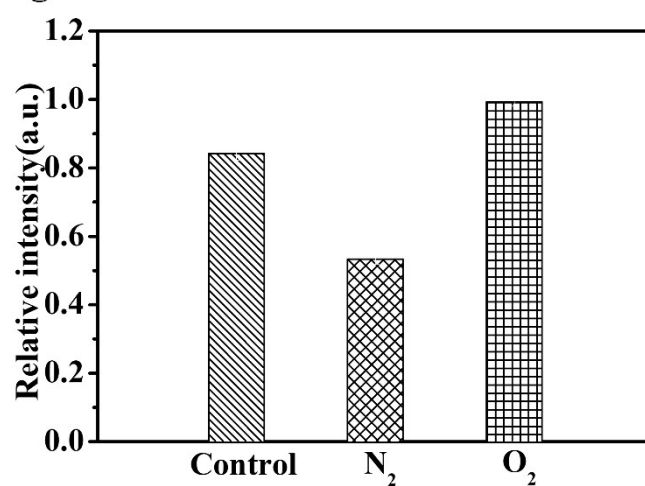


Fig. S8 Effects of 6 scavengers on the CL intensity in WS₂-FeSO₄-Na₂SO₃ system. Condition: 10 μL of 10 mM Fe²⁺, 100 μL of 10 mM Na₂SO₃, 200 μL of 0.1 mg/mL WS₂ nanosheets and 400 μL of 10 mM PBS (pH=7). Note : NaN₃, NBT, thiourea and Ascorbic Acid (AA) are applied to quench ¹O₂, O₂^{•-}, ·OH and all radicals, respectively. TBA and EtOH were used as the effective quenching agents for ·OH and SO₄^{•-}.

Fig. S8

