Electronic Supplementary Information (ESI)

A WS_2 nanosheet based chemiluminescence resonance energy transfer platform for sensing biomolecules

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1. Experimental section

Materials: All DNA and RNA oligonucleotides were obtained from Takara Biotech Co., Ltd. (Dalian, China). The sequences of these miRNAs and DNA probe are given in Table S1. The tungsten disulfide (WS_2) nanosheet was purchased from Nanjing XFNano Material Tech Co., Ltd. (Nanjing, China). 5-Amino-2,3-dihydro- 1,4-phthalazinedione (luminol), hemin and H_2O_2 were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Other chemicals used in this work were of analytical grade and directly used without further purification. The solutions used in all experiments were prepared using DEPC treated water.

Table S1. Sequences of DNA probe and micorRNAs used in this work

Name	Sequence (5′ to 3′)
DNA probe	GGGTTGGGCGGGATGGGTTTTTCAACAGTCTGATAAGCTA
miR-21	UAGCUUAUCAGACUGAUGUUGA
miR-141	UAACACUGUCUGGUAAAGATGG
miR-143	UGAGAUGAAGCACUGTAGCUCA
Let-7d	AGAGGUAGUAGGUUGCAUAGUU

Apparatus: CL spectra were measured with a LS-55 luminescence spectrometer (Perkin-Elmer, USA). UV-visible spectra were measured with a Cray 60 UV−visible spectrophotometer (Agilent Technologies).

Cell culture and sample preparation. Human breast cancer cell lines (MCF-7) were cultured in RPMI 1640 medium (Thermo Scientific Hyclone) supplemented with 10% fetal bovine serum, 10 U/mL penicillin and 10 μg/mL streptomycin. These cells were cultured at 37 °C in a humidified atmosphere containing 5% CO_2 for 24 h. Cells

(1×10^6) were dispensed in an RNase-free 1.5 mL centrifuge tube, washed twice with PBS (137 mM NaCl, 2.7 mM KCl, 10 mM phosphate, pH 7.4) at 2000 rpm for 3min, and then suspended in 10 mM Tris-HCl with pH 7.4. The suspended cells were sonicated with an ultrasonicator for 10 min on ice, and then centrifuged at 12000 rpm for 20 min at 4 °C. The extract was used immediately for miRNA assay or stored at -80 °C.

Detection of miR-21 with WS_2 nanosheet based CRET platform. In a typical experiment, 20 μL of 5.0 μM DNA probe solution (HEPES-NH_4OH, pH=7.4) first was incubated at 90 ^oC for 10 min. Then, this solution was mixed with 5 μL miR-21 solutions with different concentrations. The mixture was incubated at room temperature for 1 h. Subsequently, 25 μL of hemin solution (final concentration was 5.0 μM) was added, and the mixture was incubated at room temperature for 2 h. Then, 40 μL of WS_2 nanosheet solution (final concentration was 100 μg/mL) and 110 μL HEPES-NH_4OH buffer (pH 7.4) solution were added, and the mixture was kept at room temperature for 6 min. The resultant mixture was transfered into a 1 cm path length quartz cell. Then, 8 μL of luminol (final concentration: 6.0 mM) and 400 μL pH 9.0 of HEPES-NH_4OH buffer solution (containing 1.7 mM H_2O_2) were poured to the quartz cell, and CL spectrum was recorded immediately with a LS-55 luminescence spectrometer. The relative luminescence intensity ($I-I_0$, where I and I_0 are the CL intensities in the presence or absence of target respectively) at 425 nm was used for quantification of miR-21.

2. Supporting Figures

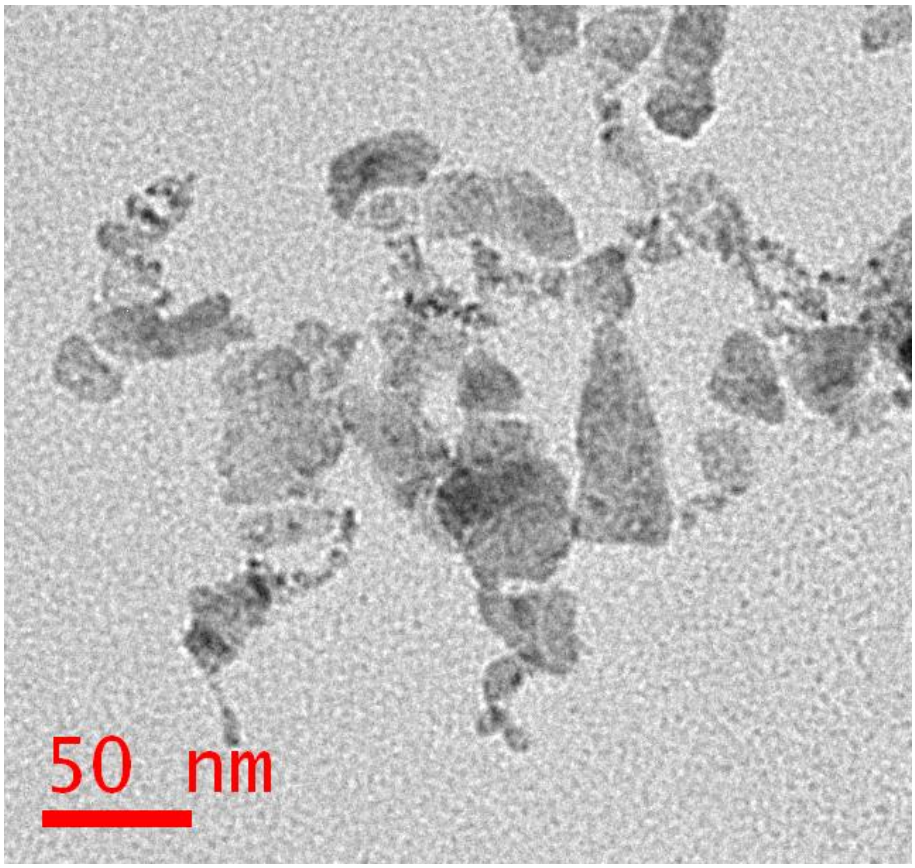

Fig. S1 TEM image of the used WS_2 nanosheet.

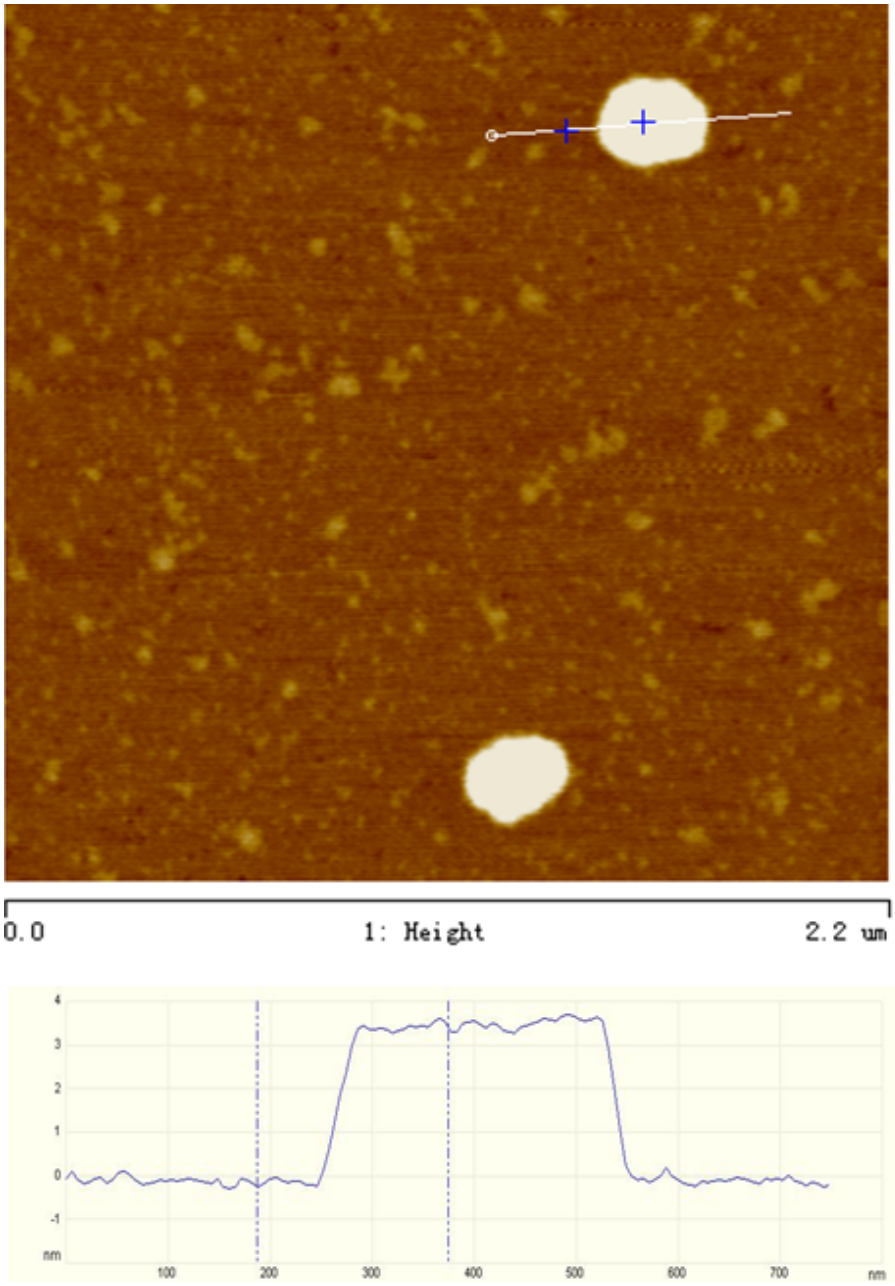

Fig. S2 AFM image and height profile of the used WS_2 nanosheet.

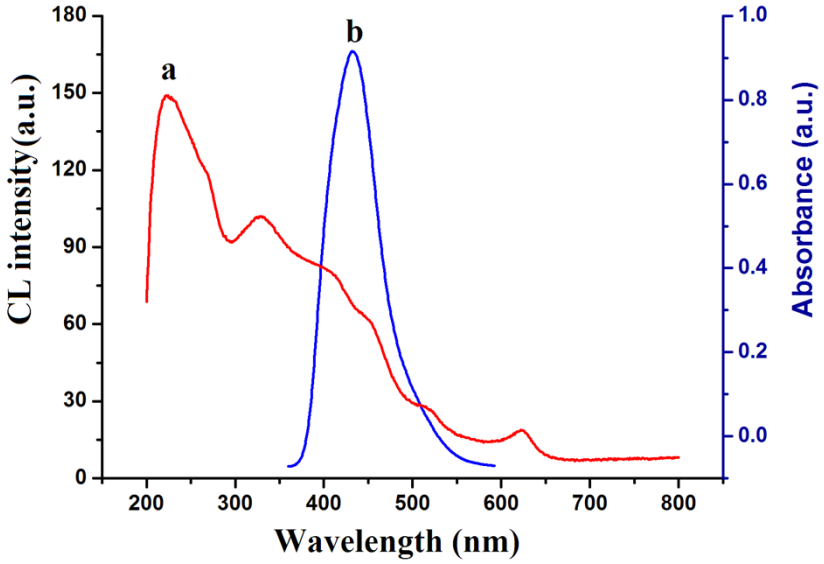

Fig. S3 UV-visible absorption spectrum of WS_2 nanosheet solution (a) and CL spectrum of luminol (b).

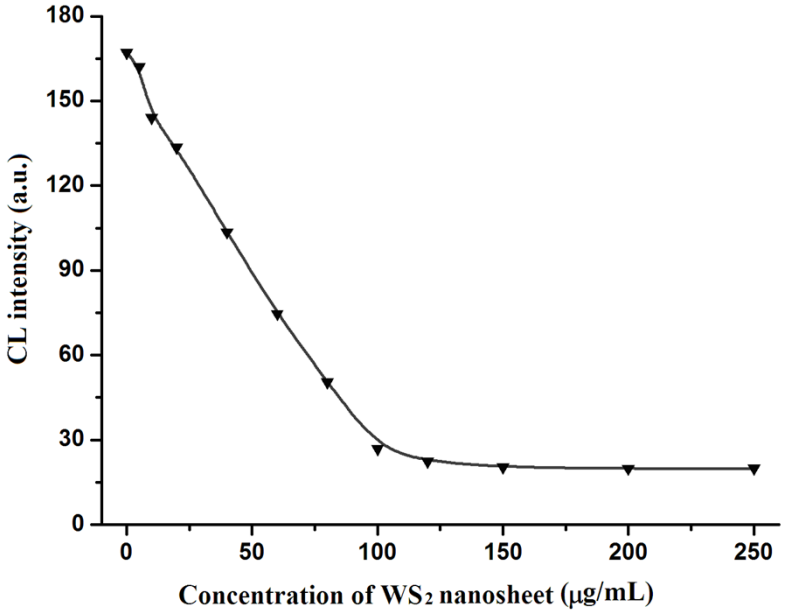

Fig. S4 The effect of WS_2 nanosheet concentration on the CL intensity at 425 nm. The concentrations of DNA probe, luminol and H_2O_2 were 0.5 μM, 8 mM and 20 mM, respectively.

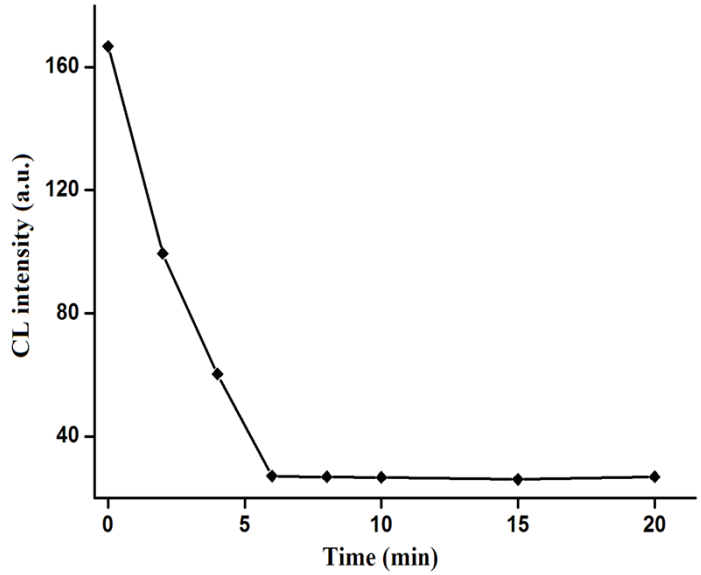

Fig. S5 The effect of the incubation time of DNA probe and WS_2 nanosheet on the CL quenching. The concentrations of DNA probe, WS_2 nanosheet, luminol and H_2O_2 were 0.5 μM, 100 μg/mL, 8 mM and 20 mM, respectively.

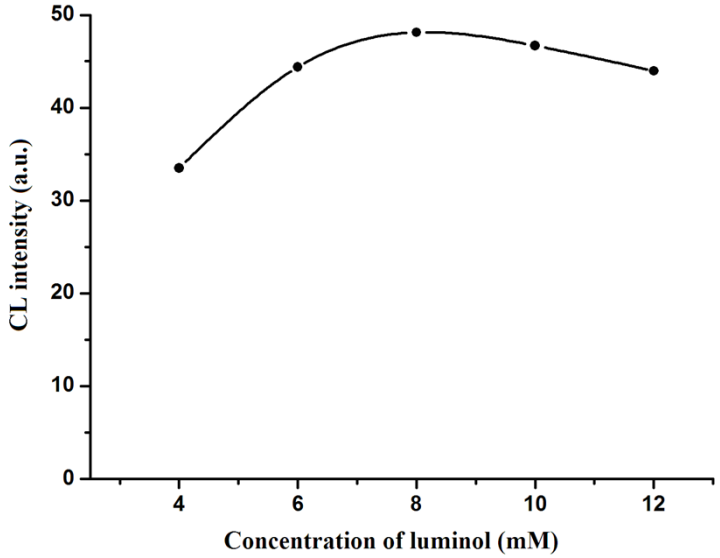

Fig. S6 The effect of luminol concentration on the CL recovery in the presence of 5.0 nM target miR-21. The concentrations of DNA probe, WS_2 nanosheet and H_2O_2 were 0.5 μM, 100 μg/mL and 20 mM, respectively.

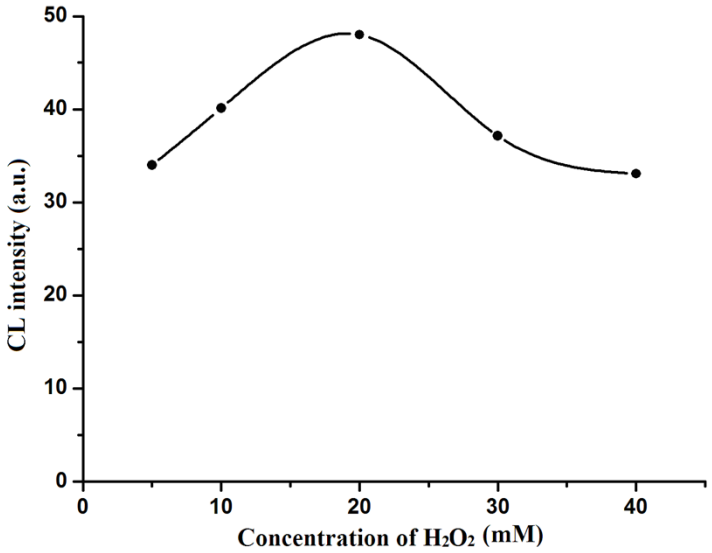

Fig. S7 The effect of H_2O_2 concentration on the CL recovery in the presence of 5.0 nM target miR-21. The concentrations of DNA probe, WS_2 nanosheet and luminol were 0.5 μM, 100 μg/mL and 8 mM, respectively.

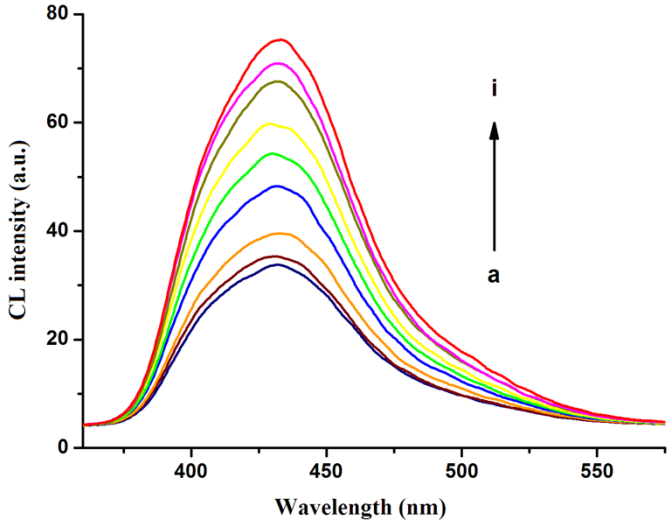

Fig. S8 CL spectra of the developed platform in the presence of miR-21 with different concentrations. The concentrations of miR-21 from a to i are 0, 0.5, 2.0, 5.0, 8.0, 10, 25, 50 and 100 nM, respectively.

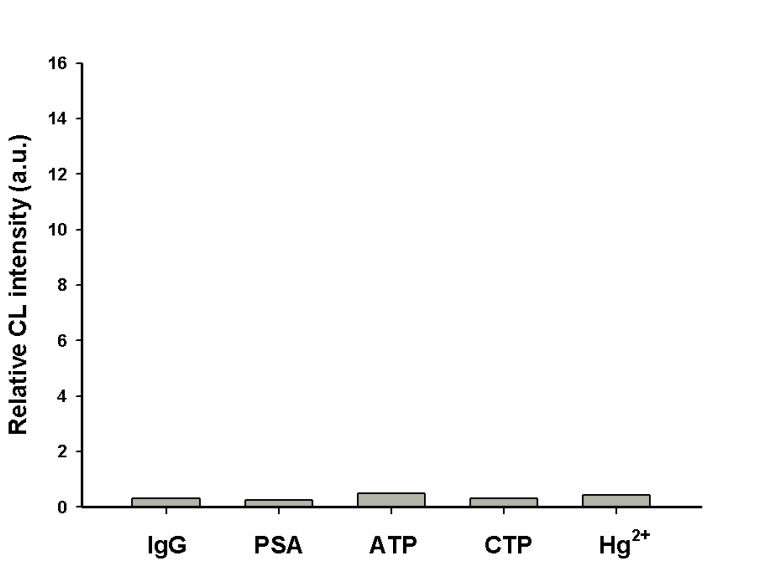

Fig. S9 The CL response of other control species. The concentrations of immunoglobulin G (IgG), prostate specific antigen (PSA), adenosine triphosphate (ATP), cytidine triphosphate (CTP) and Hg^{2+} were 20 ng/mL, 20 ng/mL, 50 μM, 50 μM and 100 nM, respectively.