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SUPPORTING INFORMATION

A facile and one-step ethanol-thermal synthesis of MoS_2 quantum dots for two-photon fluorescence imaging

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EXPERIMENTAL SECTION

Reagents and Chemicals

Bulk molybdenum (IV) disulfide (MoS_2 powder, 99.5%), quinine sulfate dehydrate (99.0%), propidium iodide (PI, 94.0%) and bisBenzimide H 33342 trihydrochloride (Hoechst 33342, 98%) were commercially available from Aladdin Industrial Co. Ltd. (Shanghai, China). 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was obtained from Amresco (USA). Ethanol, sodium phosphate monobasic dihydrate ($NaH_2PO_4 \cdot 2H_2O$), sodium phosphate dibasic dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$), sodium chloride (NaCl), dimethyl sulfoxide (DMSO) and sulfuric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized distilled water was used throughout.

Instruments and Measurements

Transmission electron microscope (TEM) and high solution transmission electron microscope (HR-TEM) imaging were performed using JEM-2100F transmission electron microscope (JEOM, Japan). Atomic force microscope (AFM) image was recorded with a tapping mode in air using Multimode 8 atomic force microscope (VEECO, USA). X-ray diffraction (XRD) pattern was characterized on D8 advance X-ray powder diffractometer (Bruker, Germany). Raman measurement was obtained by confocal Raman 35 microscope (CRM200, WITec) with 50× objective using excitation laser line of 532 nm. The X-ray photoelectron spectra (XPS) was detected on AXIS Ultra DLD X-ray photoelectron spectrometer (Shimadzu, Japan). UV-vis spectra was

taken using UV-2550 spectrophotometer (Shimadzu, Japan). Fluorescent spectra and fluorescence lifetime were recorded on F-7000 fluorescence spectrometer (Hitachi, Japan) and C11367 fluorescence lifetime spectrometer (Hamamatsu Photonics, Japan), respectively. The cell images were taken by TCS SP8 MP multiphoton microscope (Leica, Germany) with femtosecond laser pulse and Ti: sapphire system as the light source.

Synthesis of MoS_2 QDs

The MoS_2 QDs were synthesized through one-step solvothermal route from MoS_2 powder. In a typical procedure, 20 mg MoS_2 powder was dispersed to 40 mL ethanol and was ultrasonicated for 6 h. Then, the mixture was transferred into a 50 mL poly(tetrafluoroethlene) (Teflon) autoclave which was kept at 200 °C for 12 h, followed by cooling to room temperature. The reaction solution was filtered by the 0.22 μm microporous membrane to remove large tracts of MoS_2. The solid product can be obtained by vacuum distillation.

Cytotoxicity Assay

The cytotoxicity of MoS_2 QDs was assessed on human breast-cancer cells MDA-MB-468 by the MTT assay. The cells were cultured and maintained in Dulbecco's Modified Eagle's medium (DMEM) with fetal bovine serum (10%, v/v). Firstly, the cells were seeded in a 96-well plate at a density of 5×10^3 cells per well and cultured in an incubator at 37 °C with 5% CO_2 for 18 h. Then, the cells were incubated in the fresh culture medium containing MoS_2 QDs with different concentrations of (25, 50,

75, 100, 120, 150 μg/mL) for 24 h and washed with PBS for three times. 100μL of the new culture medium containing MTT (20 μL, 5 mg/mL) was added to each well, and followed by incubation for 4 h. Finally, the medium was replaced with 100 μL DMSO and the absorbance at 490 nm was measured on a Synergy H1 Multi-Mode Reader (BioTek, USA), the cell viability was determined by manually subtracting the blank value and normalized against the control values.

Hoechst 33342/PI staining

MDA-Mb-468 cells were planted onto 12 mm-diameter glass coverslips in a 24-well plate, and incubated for 48 h in DMEM. Then, different concentrations of MoS_2 QDs (0, 50, 100, 150 μg/mL) were added into the culture medium, followed by incubation for 24 h, respectively. After removing the DMEM medium, MDA-MB-468 cells were stained with Hoechst 33342 (5 μg/mL) for 20 min and then PI (10 μg/mL) for 15 min. Finally, the cells were washed with PBS three times and mounted by anti-fade mounting media. Fluorescence images of cells were acquired by confocal microscopy.

Two-photon Cell Imaging

MDA-MB-468 and Hela cells were placed onto 12 mm-diameter glass coverslips in a 24-well plates, and incubated for 48 h in DMEM to adhere on cover glass, respectively. MoS_2 QDs were added at the concentration of 20 μg/mL into the culture medium, and the cells were grown for another 3 h. Then, the cells on the cover slip were wash with PBS to remove free MoS_2 QDs and mounted by anti-fade mounting media. Cells were imaged on a TCS SP8 MP multiphoton microscope, and the excitation wavelength was 690 nm.

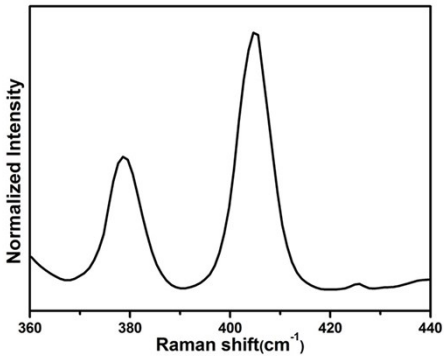

Fig. S1 Raman spectrum of the MoS_2 QDs (Ex: 532 nm).

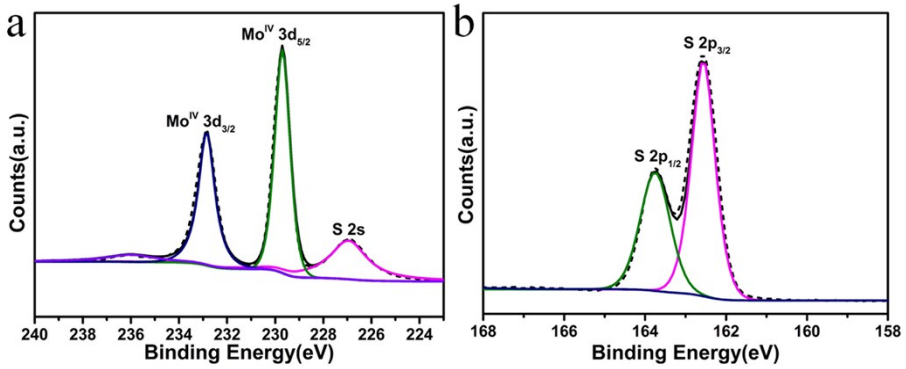

Fig. S2 XPS spectra of (a) Mo 3d and (b) S 2p regions for MoS_2 QDs.

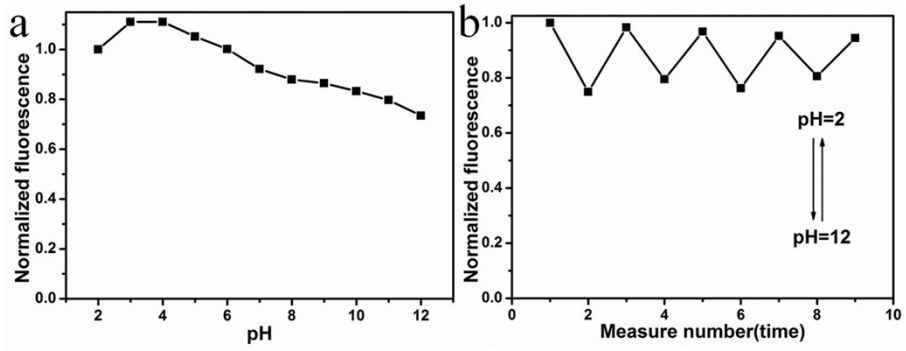

Fig. S3 (a) Effect of pH on fluorescent intensity of MoS_2 QDs, (b) reversible switching of fluorescent intensity with the change of pH between 2 and 12.

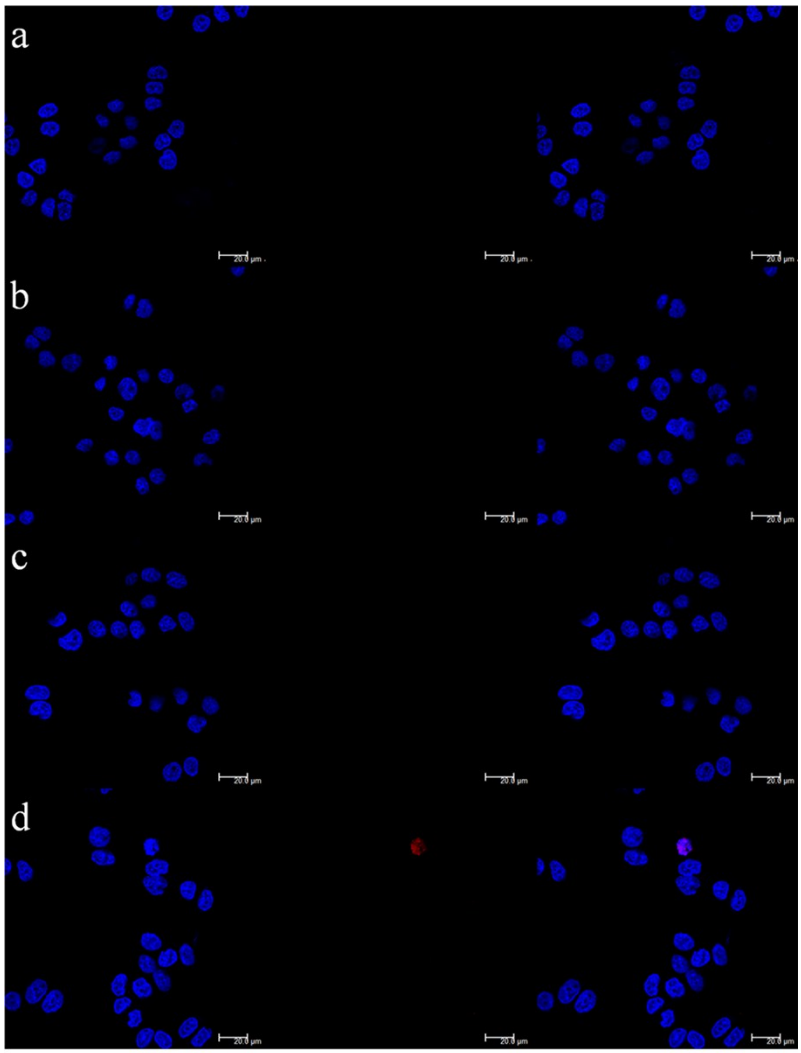

Fig. S4 Fluorescence images of MDA-MB-468 cells incubated with different concentrations of MoS_2 QDs for 24 h (a: 0 μg/mL, b: 50 μg/mL, c: 100 μg/mL, d: 150 μg/mL) followed by staining with Hoechst 33342 and PI.

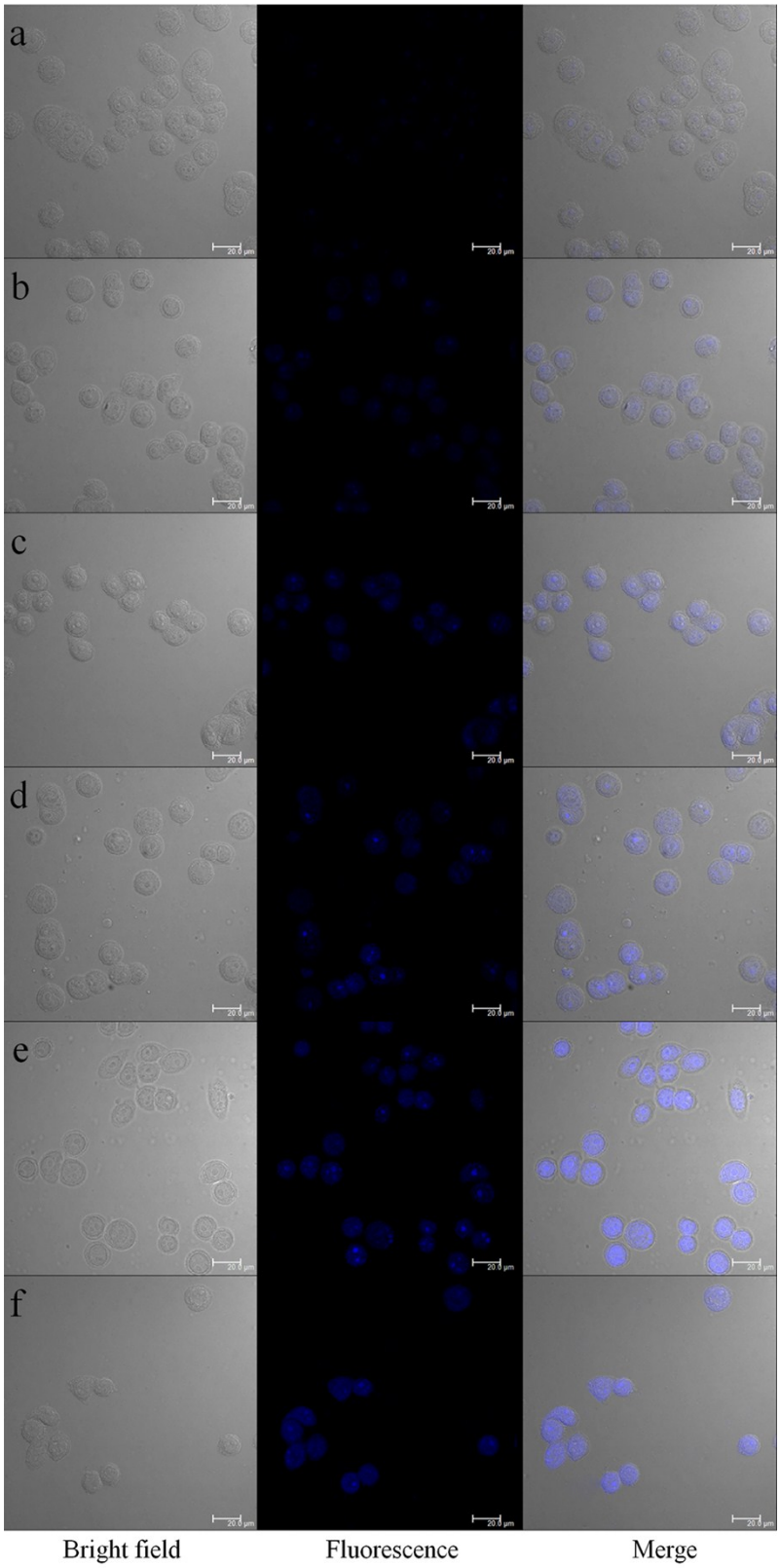

Fig. S5 TPF images of MDA-MB-468 cells incubated with MoS_2 QDs (50 μg/mL) from 0 min to 3 h. (a: 0 min, b: 10 min, c: 30 min, d: 1 h, e: 2 h, f: 3 h)

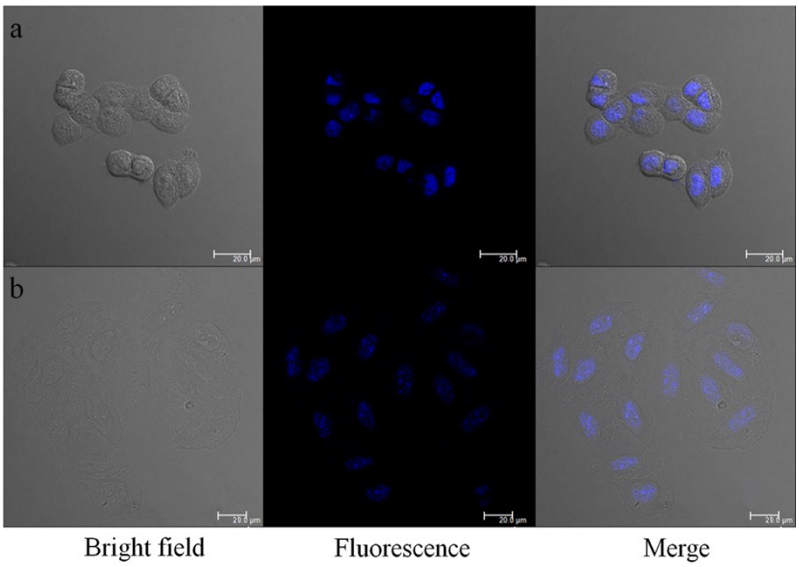

Fig. S6 TPF images of MDA-MB-468 cells (a) and Hela cells (b) incubated with MoS_2 QDs. Experiment conditions: the cells have been incubated with the MoS_2 QDs at 37 °C for 2 h.

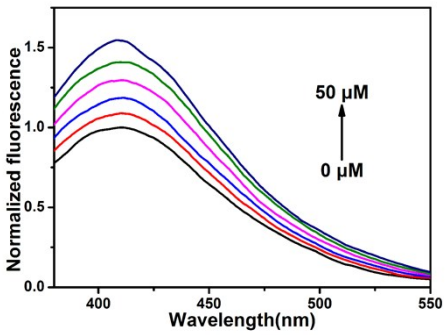

Fig. S7 Fluorescence of the aqueous solution of the MoS_2 QDs in the presence of different concentrations of DNA.

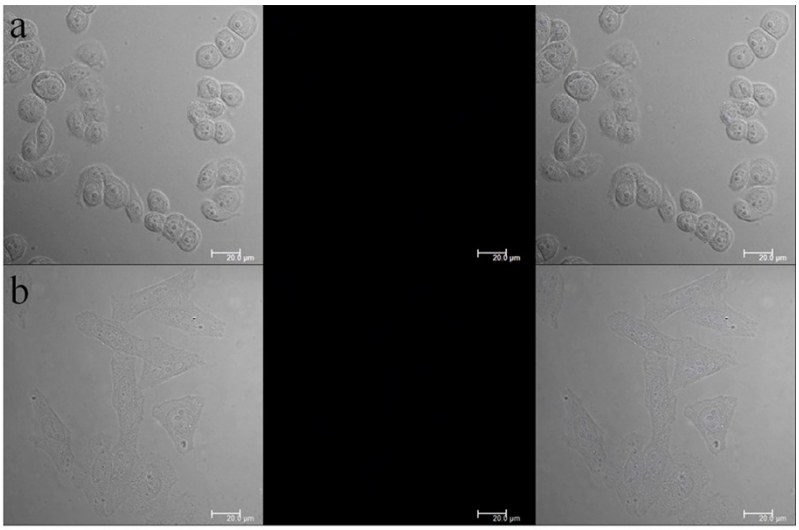

Fig. S8 TPF images in MDA-MB-468 cells (a) and Hela cells (b) without MoS_2 QDs

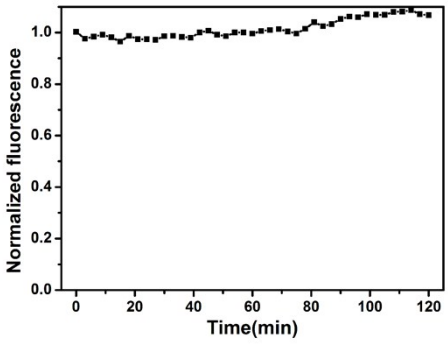

Fig. S9 Photostability of MoS_2 QDs under excitation of 690 nm within cells.