Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Rare Earth Ions Enhanced Near Infrared Fluorescence of Ag_2S Quantum Dots for the Detection of Fluoride Ions in Living Cells

Caiping Ding, Xuanyu Cao, Cuiling Zhang,*, Tangrong He, Nan Hua, Yuezhong Xian ,*

*Corresponding authors: clzhang@chem.ecnu.edu.cn; yzxian@chem.ecnu.edu.cn (Y.Z. Xian) Tel &Fax: +86-21-54340046.

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, China

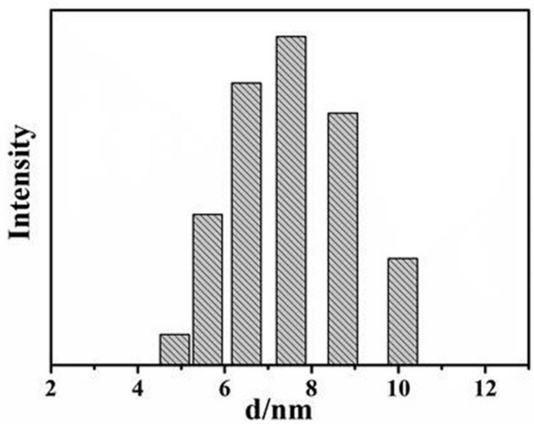

Fig. S1 The hydrodynamic size of Ag_2S QDs measured by dynamic light scattering.

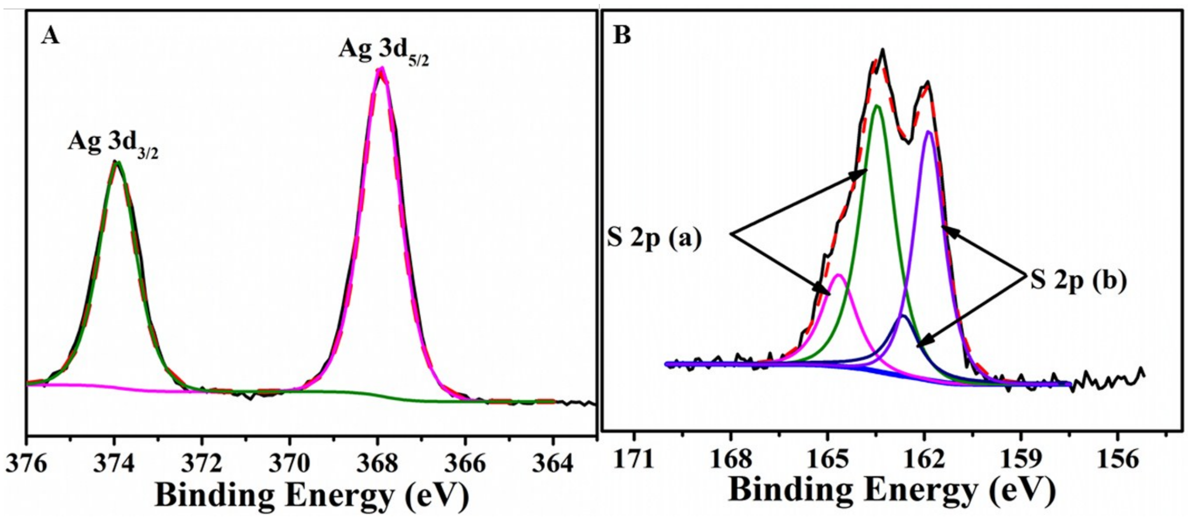

Fig. S2 XPS spectra of (A) Ag 3d and (B) S 2p for Ag_2S QDs.

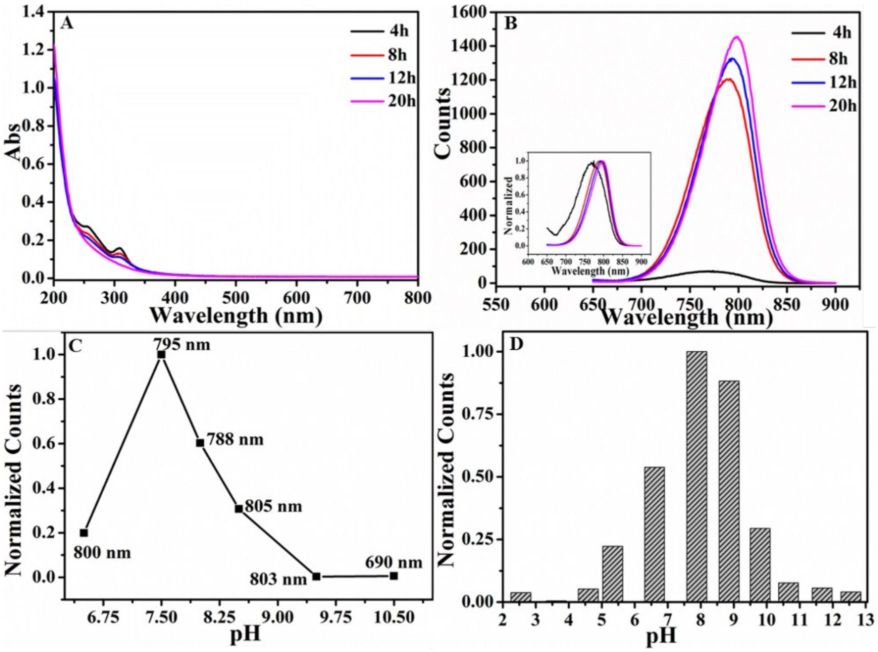

Fig. S3 Absorbance (A) and fluorescence (B) spectra of the Ag_2S QDs at different reaction time, the normalized fluorescence intensity and peak position of the Ag_2S QDs at different reaction pH value (C) and (D) the pH stability toward the Ag_2S particles. Inset of (B) is the normalized fluorescence spectra.

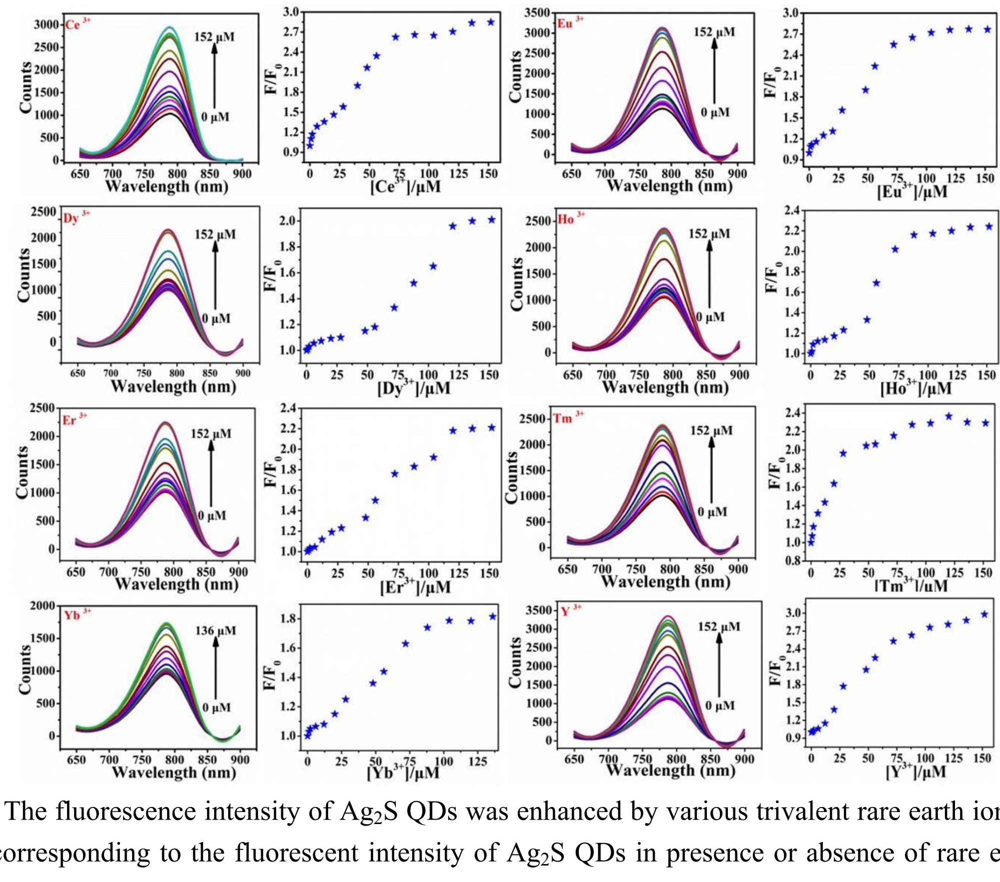

Fig. S4 The fluorescence intensity of Ag_2S QDs was enhanced by various trivalent rare earth ions. F and F_0 are corresponding to the fluorescent intensity of Ag_2S QDs in presence or absence of rare earth ion, respectively.

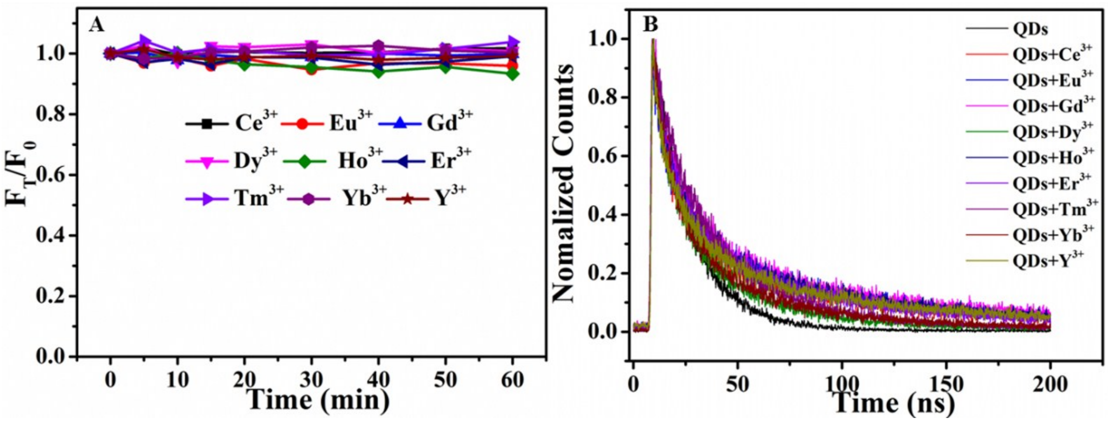

Fig. S5 Fluorescence stability of the rare earth ions conjugated Ag_2S QDs (A) and the fluorescence decay curves of QDs (B) in the absence and presence of different rare earth ions (including Ce^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} and Y^{3+}, respectively).

Table S1: Zeta potential and hydrodynamic size of the Ag_2S QDs colloidal in presence of different rare earth ions.

Cations	Zeta potential (mV)	Hydrodynamic size (nm)
H_2O	-44.6	7.5
Gd^{3+}	-15.5	167
Ce^{3+}	-18.5	158
Eu^{3+}	-23.9	142
Y^{3+}	-26.0	129
Tm^{3+}	-32.5	113
Ho^{3+}	-32.8	109
Er^{3+}	-36.5	100
Yb^{3+}	-38.1	79
Dy^{3+}	-39.7	60

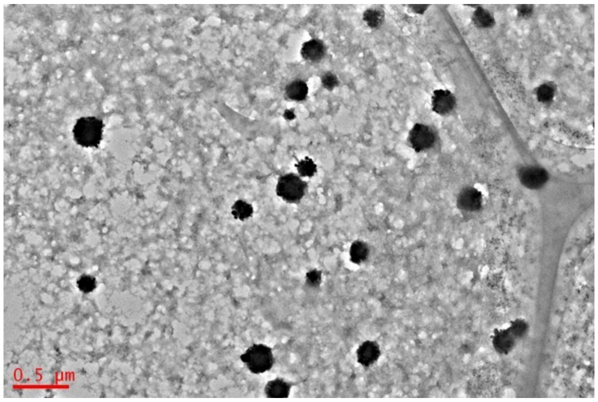

Fig. S6 TEM images of Ag_2S QDs in the presence of Gd^{3+} (185 μM).

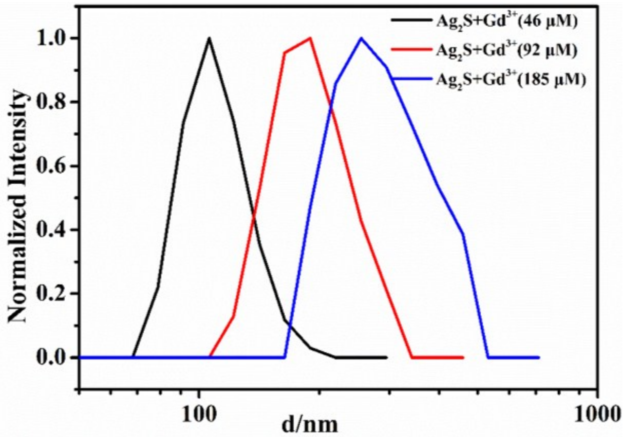

Fig. S7 The hydrodynamic size of Ag_2S QDs with increased concentration of Gd^{3+} measured by DLS.

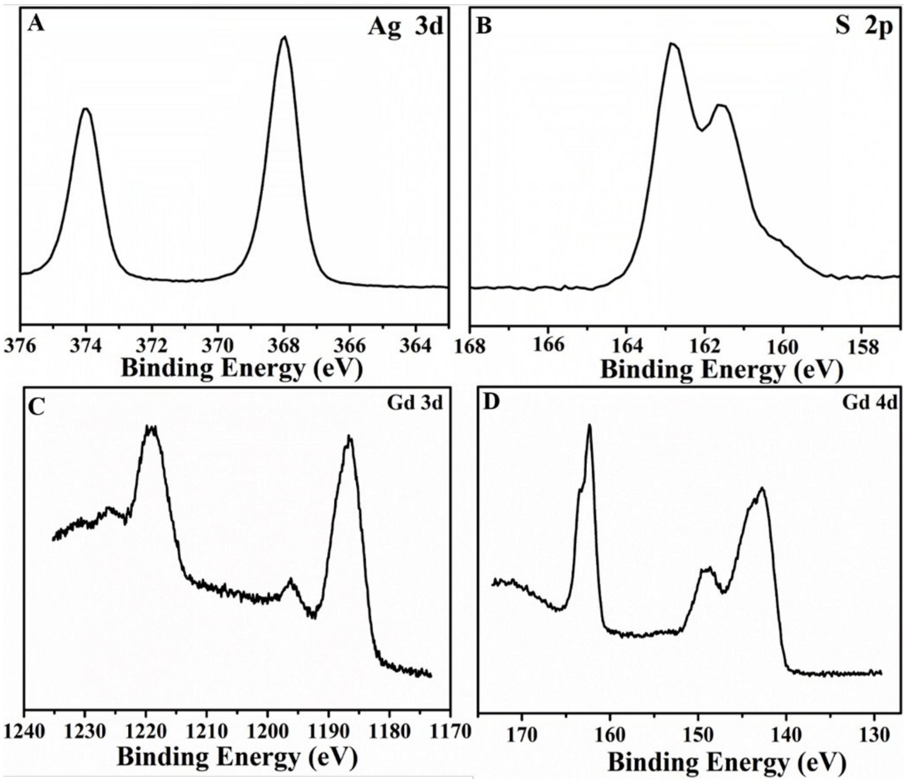

Fig. S8 XPS spectra of Gd^{3+}-Ag_2S QDs complex: (A) Ag 3d, (B) S 2p, (C) Gd 3d and Gd 4d.

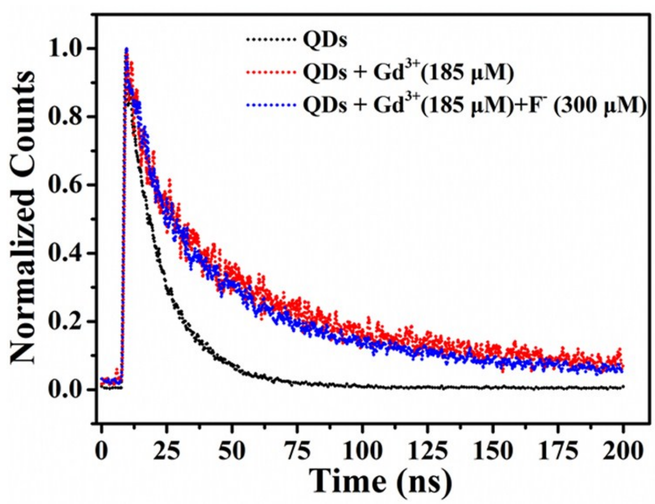

Fig. S9 The fluorescence decay curves of Ag_2S QDs, Ag_2S QDs+Gd^{3+} (185 μM), Ag_2S QDs+Gd^{3+} (185 μM) +F^- (300 μM).

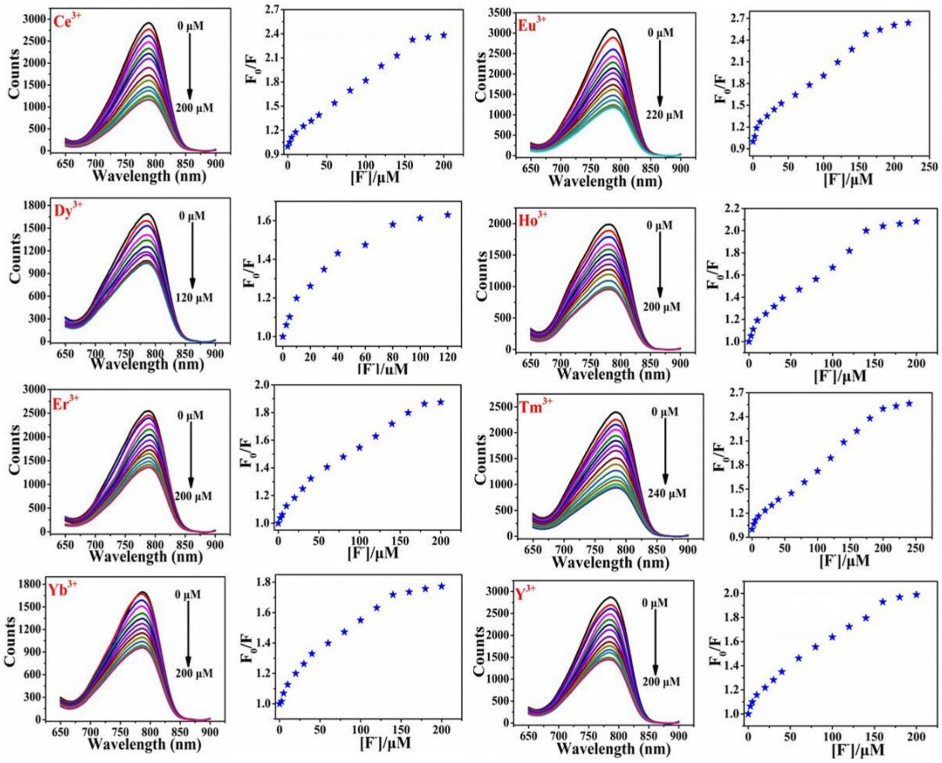

Fig. S10 The fluorescence of rare earth ions conjugated Ag_2S QDs are quenched by F^- (left) and fluorescence response of rare earth ions conjugated Ag_2S QDs for different concentration of F^- (right), (rare earth ions = Ce^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} and Y^{3+}, respectively).

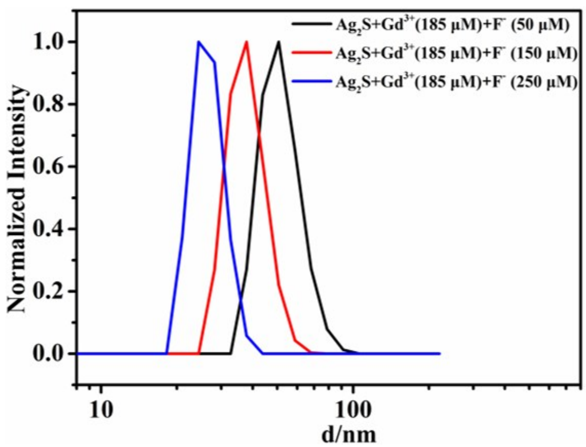

Fig. S11 The hydrodynamic size of Gd^{3+} - Ag_2S QDs with increased concentration of F^- measured by DLS.

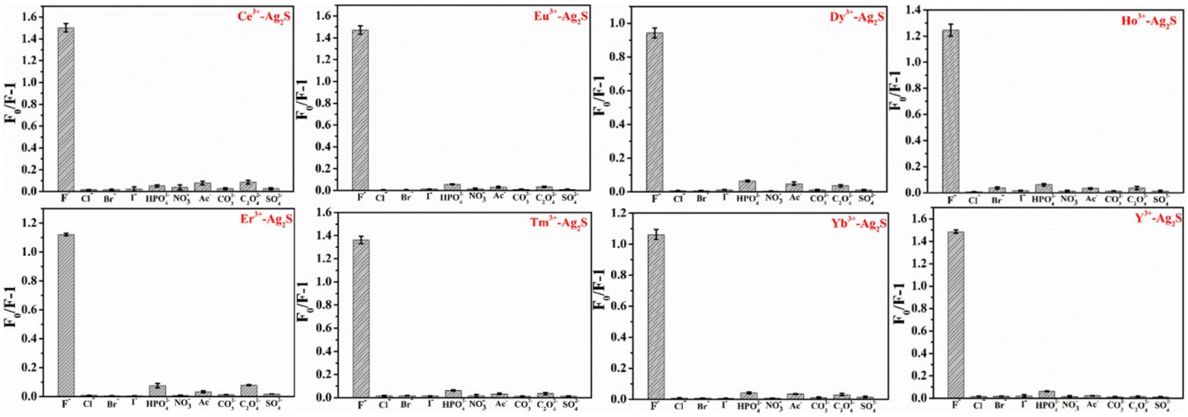

Fig. S12 The selectivity of the rare earth ions conjugated Ag_2S QDs nanoprobe for F^- detection by monitoring the emission at 795 nm. The concentration of different anions are 250 μM. F_0 and F are the fluorescence intensity in the absence and presence of anions. (rare earth ions = Ce^{3+}, Eu^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} and Y^{3+}, respectively).

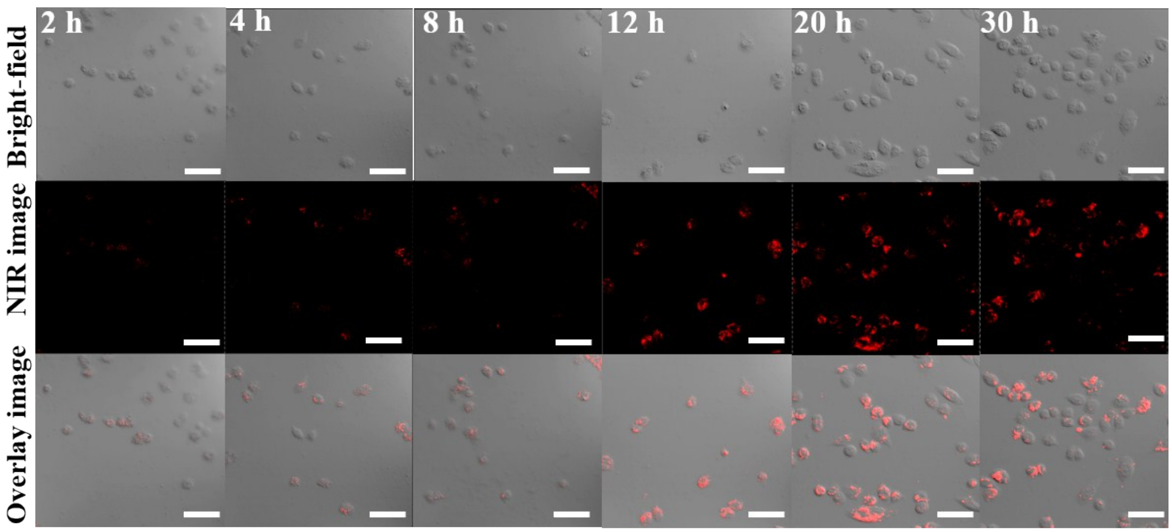

Fig. S13 Photostability of Gd^{3+}- Ag_2S complex in MDA-MB-468 cells. The scale bar is 50 μm.

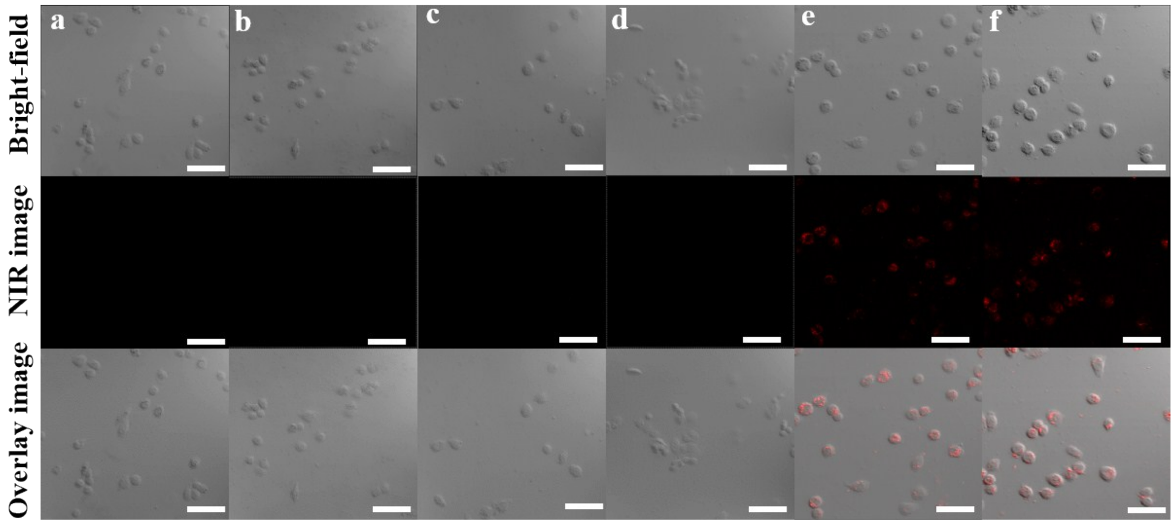

Fig. S14 Confocal images for MDA-MB-468 cells under different conditions. (a) Control, (b) NaF (800 μM), (c) NaF (1600 μM), (d) NaF (2400 μM), (e) Ag_2S QDs (150 μg/ml), (f) Ag_2S QDs (150 μg/ml) and NaF (2400 μM). The scale bar is 50 μm.

Table S2: Comparison of the sensor performance for F^- detection.

Sensor	Detection Range	Detection of limit	Ref. Our work
$CuInS_2$ QDs	0.1-700 μM	0.029 μM	[32]
Fe_3O_4@SiO_2@Carbon QD	1-20 μM	0.06 μM	[29]
GO-AgNPs	0.05-0.55 nM	9.07 pM	[30]
CdTe QDs	0-10 mM	5.0 μM	[28]
CdS/ZnS nanoparticles	300-5600 μM	74.0 μM	[27]
Ag doped CdS/ZnS nanoparticles	10-1200 μM	5.25 μM	[16]
SiNWs	0.7-1.2 μM	1 μM	[34]
rare earth ion conjugated Ag_2S QDs	5-260 μM	1.5 μM	Our work

Table S3: The detection of F^- in living cells by fluoride-ion-selective electrode (FISE) and proposed method.

	Cells Lysates	
Cultured F^-[μM]	F^-[μM] /FISE	F^-[μM] /proposed method
800	92.420±0.054	91.579±0.011
1600	153.716±0.024	149.230±0.050
2400	230.865±0.034	229.620±0.011