Supporting Information

Chemiluminescence Character of ZnS Quantum Dots with Bisulphite-Hydrogen Peroxide System in Acidic Medium

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Synthesis and Characterization of ZnS quantum dots (QDs). ZnS QDs were synthesized from alkaline solution of $ZnSO_4$ and Na_2S in one-pot at room temperature. 2-Mercaptopropanoic Acid was uses as capping agent. The sample for TEM was dialyzed before analysis to remove soluble electrolytes. Dialysis was performed by using MW cut off 3.5 kDa Biotech regenerated cellulose (RC) membrane for 12 h against distilled water under gentle stirring by replacing the distilled water after each 2 h. The sample was prepared by molding a drop of ZnS QDs on to a 300-mesh holey carbon- coated copper grid. Figure S1 showed the transmission electron microscopy (TEM) image of the as-prepared water dispersible ZnS QDs. The average particle size was about 5 nm.

Batch CL System. The CL reaction was carried out in a glass cuvette under ambient conditions by a batch method, and the detection was performed on a BPCL luminescence analyzer. First, H_2O_2, ZnS QDs and H_2SO_4 were mixed in a glass cuvette, and then $NaHSO_3$ solution was injected by a microliter syringe in different concentrations and volumes to get the optimum intensity. The CL intensity was displayed and integrated with 0.1 s intervals at 1.3 kV.

CL Spectrum Measurements. The CL spectrum was obtained with a Hitachi F-7000 spectrophotometer when the Xe lamp was turned off with a flow cell, which consisted of two peristaltic pumps, a CL detector, and a flow cell placed inside the cell holder of the fluorescence spectrophotometer. The emission slit width was 20 nm during the documentation of the CL spectrum. All optical measurements were performed at room temperature.

EPR Analysis. EPR spectra were recorded at room temperature using a JEOL JES-FA200 spectrometer. For the examination of $^1O_2$ or $^{\bullet}OH$ radicals, for that, 30 µL of each reagent i.e. $NaHSO_3$ (1.5 M), H_2O_2 (0.1M), H2SO_4 (0.1M) and ZnS QDs were mixed with 30 µL of 0.1 M DMPO (or 10% TEMP) in different orders. In a typical experiment, a final volume of 10 µL of this sample solution was loaded into a 50 µL quartz micropipette for the ESR measurement. All spectra were recorded at the appropriate time after the addition of the oxidant. The instrument was operated at microwave power of 1.0 mW and the modulation amplitude was 1.0 G.

The photoluminescent spectra of ZnS QDs after the reaction shown in Figure S2 was scanned at different excitation wavelengths. Different peaks could be found in addition to that of the ZnS QDs, which changes as the wavelength changes, indicating the different emitting species in the system. The low intensity of the peaks was due to dilution effect.

Figure S3 showed the effect of order of reagents on $NaHSO_3$-H_2O_2 system in the presence of ZnS QDs in acidic medium. The addition of acid at different position causes difference in CL

intensity. (i) $NaHSO_3$ injected to ZnS QDs−H_2O_2−H_2SO_4 (ii) $NaHSO_3$ injected to H_2SO_4−ZnS QDs−H_2O_2 (iii) $NaHSO_3$ injected to H_2O_2−H_2SO_4−ZnS QDs. When acid were added in last causes 10 time higher CL intensity compared to the other two cases, which is attributed to the decomposition of H_2O_2 on the surface of ZnS QDs without the presence of acids.

A remarkable enhancement in CL intensity of the system was observed by the addition of water. Figure S4 showed the increase in CL intensity of the system by applying different volume of water to the system.

The CL intensity was significantly decreased by the addition of different free radical scavengers. The study was carried out in the presence and absence of ZnS QDs. Figure S5 showed the effect of free radical scavengers on the CL intensity of $NaHSO_3$-H_2O_2 system in acidic medium with and without ZnS QDs. Thiourea, ascorbic acid and DMPO greatly decrease the CL intensity compared to NaN_3 and NBT. From which we can conclude that the $^{\bullet}OH$ and $HSO_3^{\bullet}$ were the main radicals produced in the system, and the system operates through radical path. The smaller decrease of NaN_3 and NBT indicate the lower quantity of $^1O_2$ and $^{\bullet}O_2^-$ in the system.

The enhancement in CL signals by water may attribute to the conversion of different tautomeric form of $NaHSO_3$ as shown in Figure S6 or to the stability of the ions produced in the system. The water enhances the CL intensity but when added in the last. The addition of water at first, results in no enhancement, when added after the addition of H_2O_2 causes a slight enhancement while its addition at last results in greater enhancement as shown in the Figure S7.

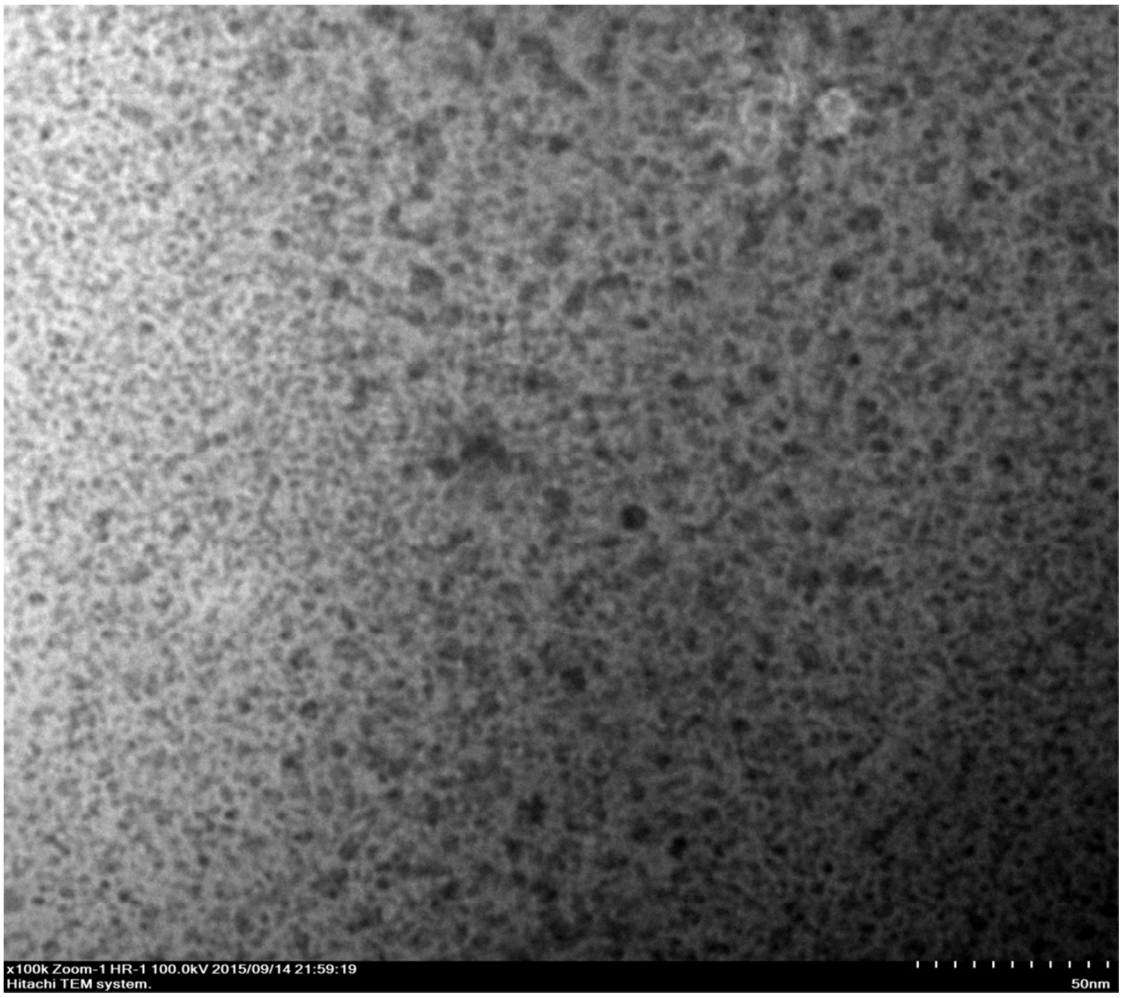

Figure S1. TEM image of water dispersible ZnS QDs, with an average size of about 5 nm. The size histogram is given aside.

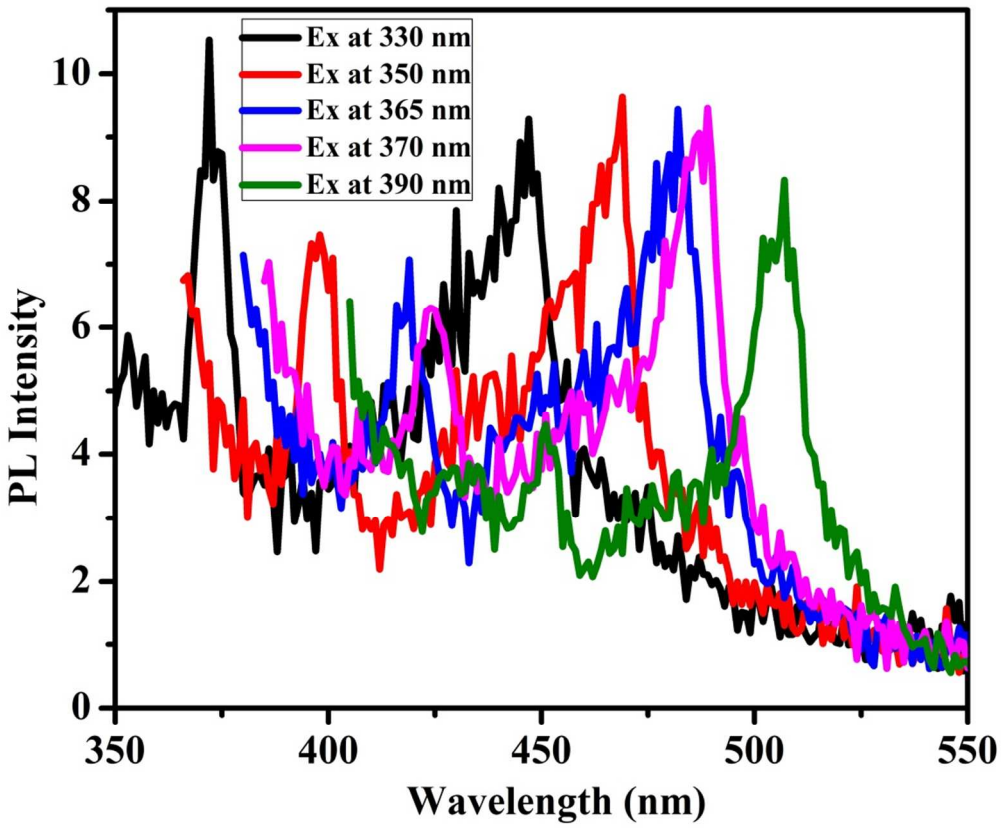

Figure S2. Photoluminescent spectra of $NaHSO_3$−ZnS QDs−H_2O_2−H_2SO_4 system, after the chemical reaction. The concentration of H_2O_2 and H_2SO_4 was 1M and that of $NaHSO_3$ was 1.5 M. The volume of each reagent used was 100 µL.

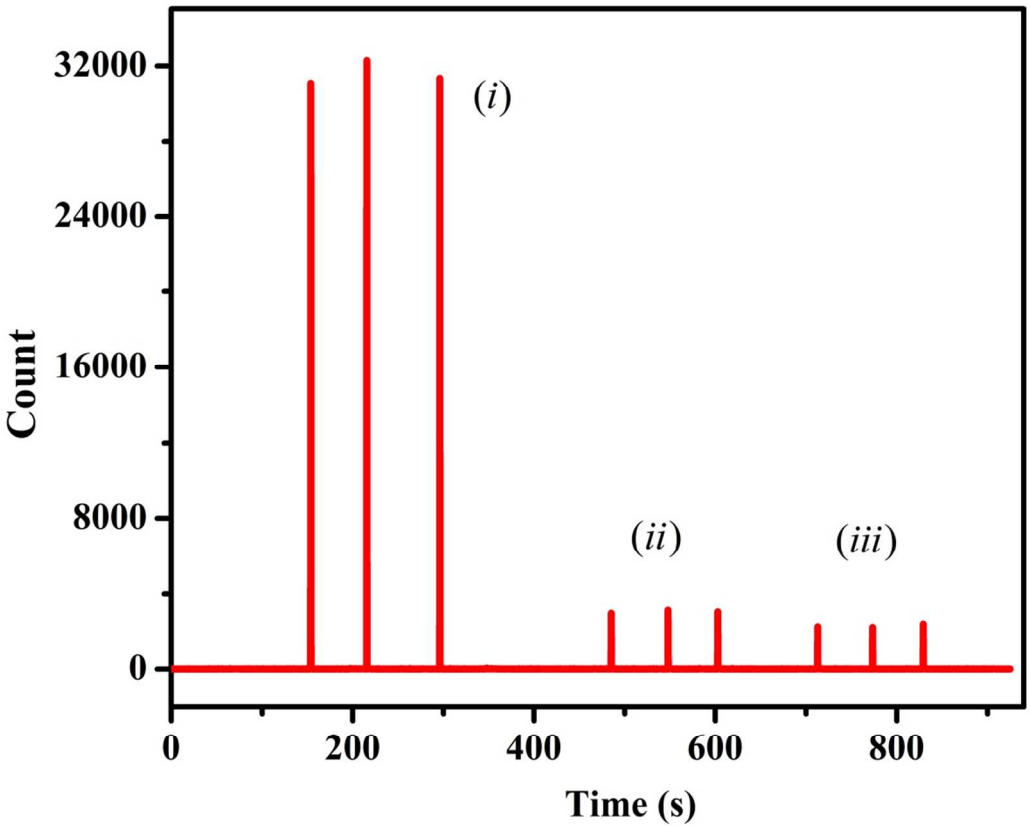

Figure S3. Effect of order of reagents on $NaHSO_3$-H_2O_2 system in the presence of ZnS QDs in acidic medium (i) $NaHSO_3$ injected to ZnS QDs−H_2O_2−H_2SO_4 (ii) $NaHSO_3$ injected to H_2SO_4−ZnS QDs−H_2O_2 (iii) $NaHSO_3$ injected to H_2O_2−H_2SO_4−ZnS QDs. The concentration of H_2SO_4 and H_2O_2 was 1M while that of $NaHSO_3$ was 1.5 M. the volume of each reagent used was 100 µL.

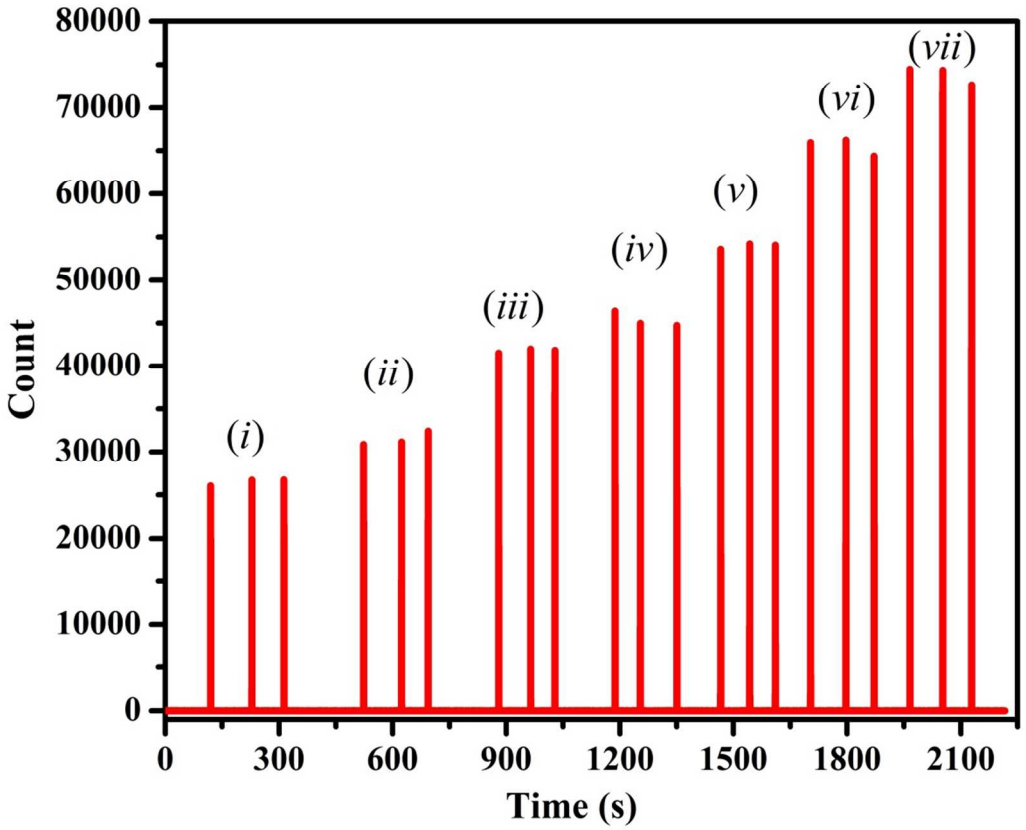

Figure S4. Consequences of addition of different volume of water to $NaHSO_3$-H_2O_2-ZnS QDs system in acidic medium. $NaHSO_3$ was injected to H_2O_2-ZnS QDs-H_2SO_4-water; the volume of added water was as mentioned. (i) 0 µL (ii) 50 µL (iii) 100 µL (iv) 150 µL (v) 200 µL (vi) 300 µL (vii) 500 µL. The concentration of H_2SO_4 and H_2O_2 were 1M while that of $NaHSO_3$ was 1.5 M. The volume of each reagent used was 100 µL.

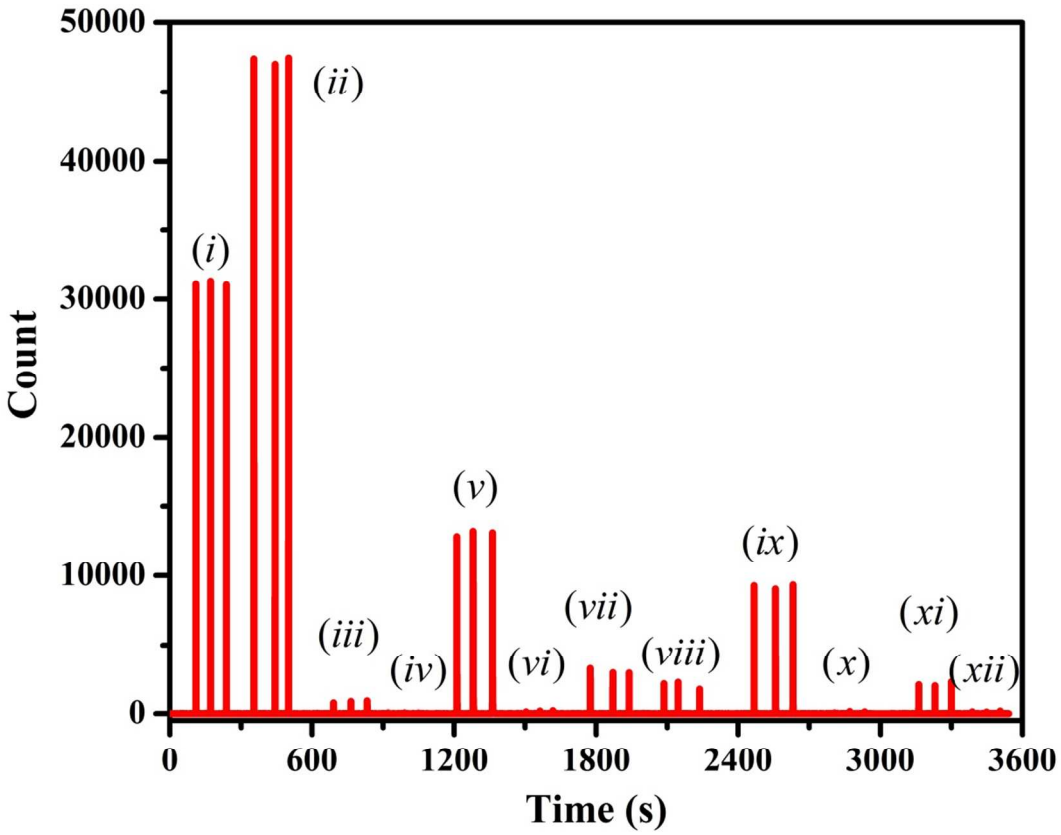

Figure S5. Effect of free radical scavengers on the CL intensity of $NaHSO_3$-H_2O_2 system in acidic medium with and without ZnS QDs. Injection of $NaHSO_3$ to H_2O_2-ZnS QDs-H_2SO_4-(-), (i) blank (ii) water (iii) thiourea (iv) the same as previous but without ZnS QDs (v) NaN_3 (vi) the same as previous but without ZnS QDs (vii) ascorbic acid (viii) the same as previous but without ZnS QDs (ix) NBT (x) the same as previous but without ZnS QDs (xi) DMPO (xii) the same as previous but without ZnS QDs. The concentration of H_2SO_4 and H_2O_2 were 1M, $NaHSO_3$ was 1.5M, NaN_3, ascorbic acid, DMPO and thiourea were 0.1M while NBT was 0.05M. The volume of each reagent used was 100 μL.

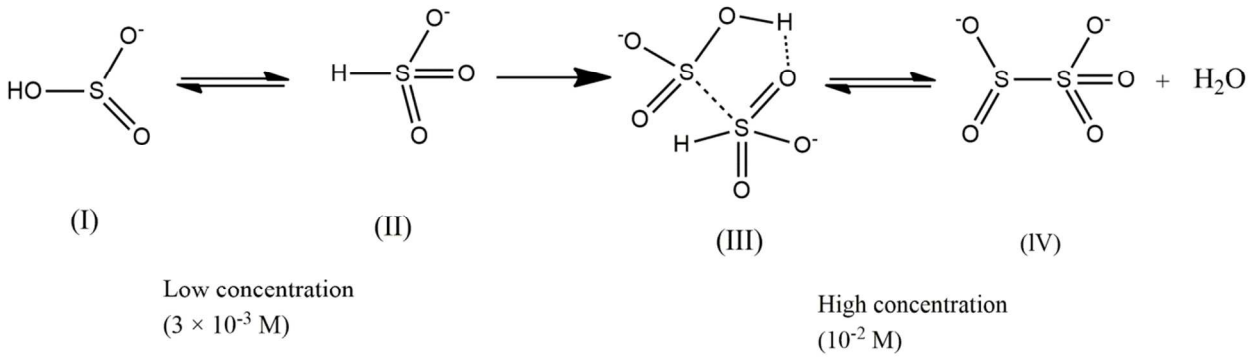

Figure S6. Scheme showing the conversion of different form of $NaHSO_3$ at different concentration and the role of water in its conversion

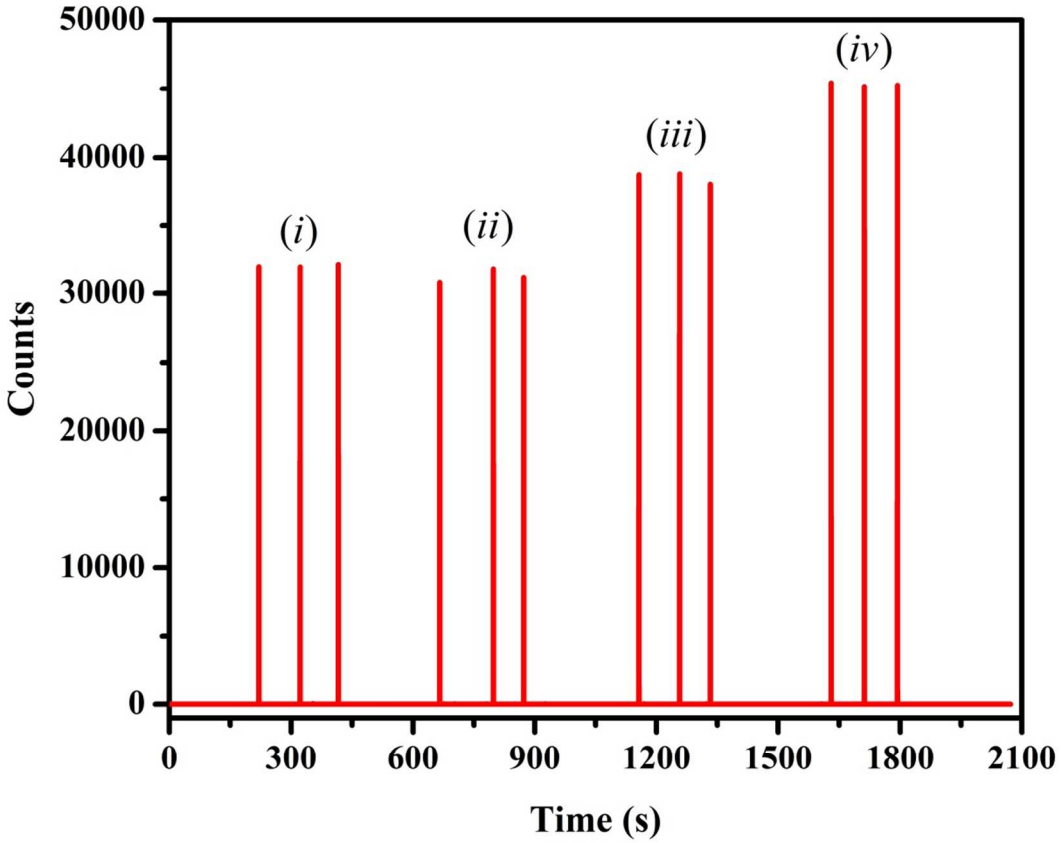

Figure S7. Effect of order of addition of water. Water was added at different position to know about the enhancement. (i) $NaHSO_3$ injected to ZnS QDs-H_2O_2-H_2SO_4 (ii) $NaHSO_3$ injected to H_2O-ZnS QDs-H_2O_2-H_2SO_4 (iii) $NaHSO_3$ injected to ZnS QDs-H_2O_2-H_2O-H_2SO_4 (iv) $NaHSO_3$ injected to ZnS QDs-H_2O_2-H_2SO_4-H_2O. The concentration of $NaHSO_3$ was 1.5 M, H_2O_2 and H_2SO_4 was 1 M. The volume of each reagent used was 100 µL.