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Synthesis and Characterization of CdTe QDs Capped with Branched 3MB3MP Ligand and Fluorescent Switching Detection of H_2O_2

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Experiments and Methods

Reagents and Materials

Cadmium chloride hydrate ($CdCl_2.H_2O$, 99.99%) was purchased from Alfa Aesar. Tellurium dioxide (TeO_2, 99.99%) powder and Glutathione were purchased from Sigma Aldrich. 3-Methoxybutyl-3-Mercaptopropionate (3MB3MP) was purchased from TCI chemicals. Sodium borohydride ($NaBH_4$, 97%) was purchased from Otto Chemicals Pvt. Ltd. Cobalt sulphate ($CoSO_4$), tin chloride ($SnCl_2$), silver nitrate ($AgNO_3$), lead nitrate [$Pb(NO_3)_2$], manganese nitrate $Mn(NO_3)_2$, ferrous sulphate ($FeSO_4$), nickel sulphate ($NiSO_4$), calcium carbonate ($CaCO_3$), aluminum nitrate [$Al(NO_3)_3$], copper sulphate ($CuSO_4$), sodium carbonate (Na_2CO_3), potassium chloride (KCl), ferric chloride ($FeCl_3$), magnesium sulphate ($MgSO_4$), barium chloride ($BaCl_2$), mercuric chloride ($HgCl_2$), hydrogen peroxide (H_2O_2), zinc Sulphate ($ZnSO_4$), sodium hydroxide (NaOH), and ascorbic acid were purchased from Merck, India.

Ultrapure water was used throughout the experiments. All chemicals were used as received without any further purification.

Characterization

UV-visible spectra were recorded using a Carry 100 UV-visible spectrometer (USA). All steady state fluorescence measurements (excitation and emission) were carried out using FluoroMax-4C Spectrofluorometer (Horiba Instruments, USA). Both excitation and emission slit widths were fixed at 2 nm with an integration time of 0.1 ns. Time resolved fluorescence measurements were performed using time-correlated single-photon counting (TCSPC). Fourier transform infrared (FTIR) analysis was performed using Spectrum 100 from Perkin Elmer FTIR spectrometer (USA) in transmission mode using KBr pellet. The transmission electron microscopy (TEM) analysis was carried out using JEM 2100, LaB_6 from Jeol (Japan). The X-ray crystallography (XRD) was carried out using Bruker AXS D8 Advance (USA). Zeta potential measurements were performed using Zetasizer Nano ZS series, Malvern Instruments, Malvern,

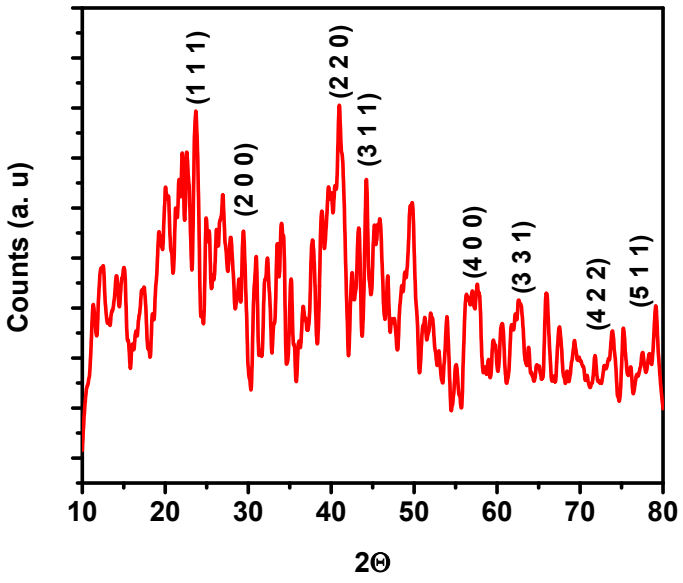
UK. Surface chemistry of CdTe@3MB3MP QDs were tested by X-ray photoelectron spectroscopy (XPS) using PHI 5000 Versa Probe II (ULVAC-PHI Inc., USA) with micro focused (15 KV) monochromatic Al-Kα X-Ray source (hv = 1486.6 eV). Both survey spectra and narrow scan (high-resolution spectra) were recorded.

Photostability experiments were carried out by irradiating aqueous solution of various QDs under 360 nm UV lamp (16 W power) and fluorescence spectra of photo-irradiated sample were recorded at specified time intervals.

Real sample preparation

For real sample detection, spiked samples were prepared by adding known concentrations of analytes (H_2O_2) into tap water and urine. Urine sample was diluted with water prior to spiking. Aliquots of these solutions were taken into a cuvette containing 2.5 mL of CdTe QD solution and mixed thoroughly. The PL emission spectra was collected at respective excitation wavelength, each time.

For a test strip assay, 10 µL of CdTe QD solutions were drop-casted on a thin layer chromatography (TLC) plate and kept for drying naturally. Various analyte solutions of different concentrations were then added drop-by-drop over these spots on the TLC plate. The response was discerned after an incubation period of 5 min, using a UV light source (365 nm, 16 W). All experiments were performed at room temperature.



2 theta peaks	Crystal Planes
23.7°	(111)
28.9	(200)
39.6°	(220)
45.8°	(311)
49.4°	(222)
57.0°	(400)
65.9°	(331)
73.9°	(422)
79.1°	(511)

Fig. S1. XRD of CdTe@3MB3MP QDs

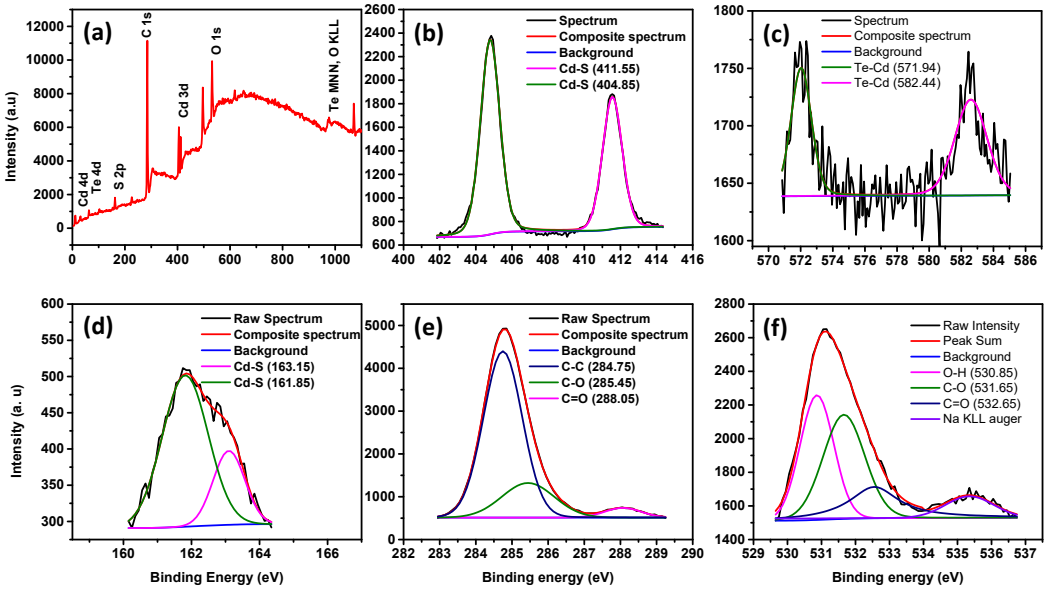


Fig. S2 a) Survey scan spectra of CdTe@3MB3MP. b-f) HRXPS spectra of Cd, Te, S, C and O respectively.

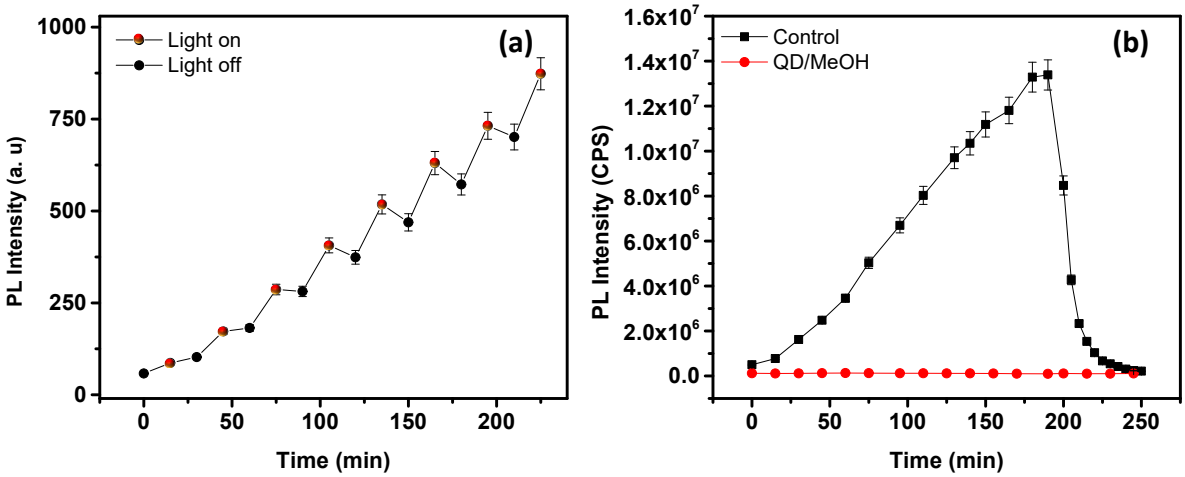


Fig. S3. a) Photoactivation study with light on and off. b) Photoactivation study using methanol as solvent

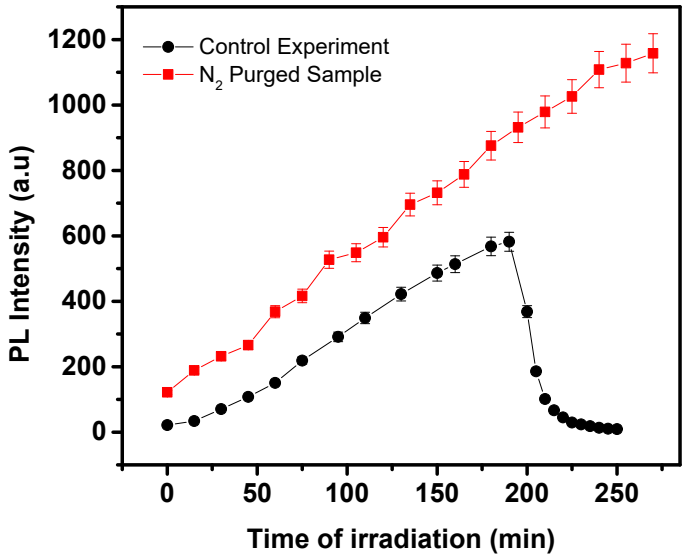


Fig. S4. Photoactivation study of the nitrogen purged sample

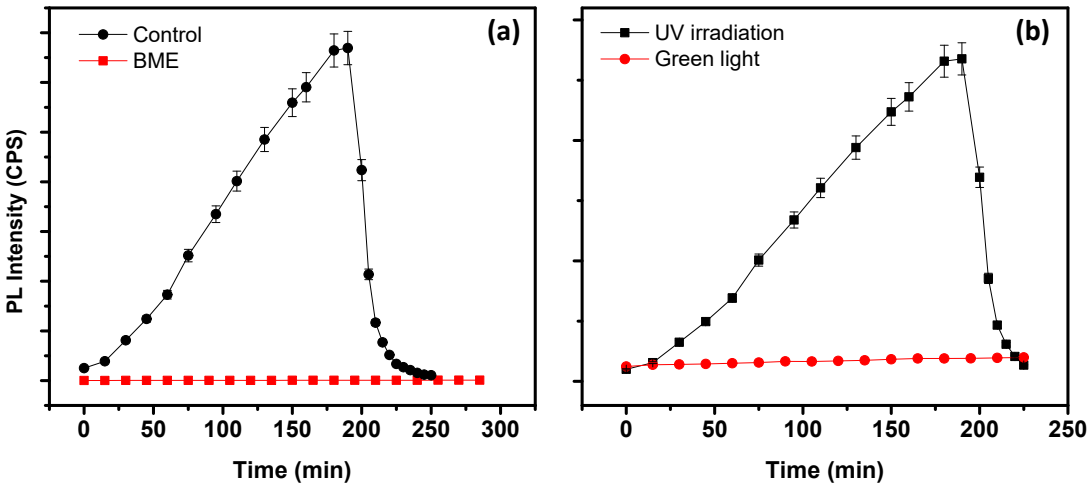


Fig. S5. a) Photoactivation of QDs in the presence of beta mercapto ethanol b) photoactivation study using green light

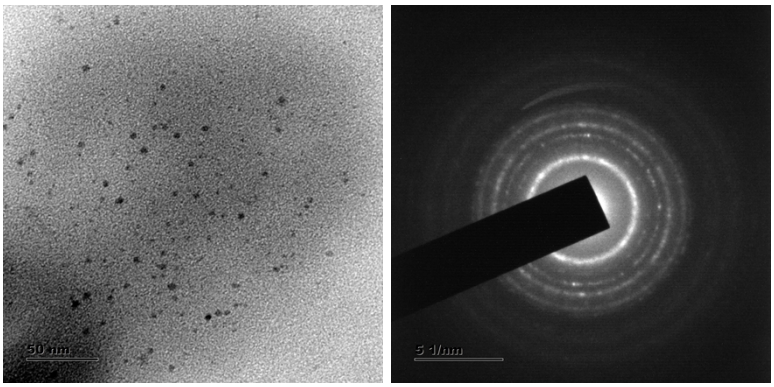


Fig. S6. TEM images of CdTe@3MB3MP after 150 minutes of UV irradiation

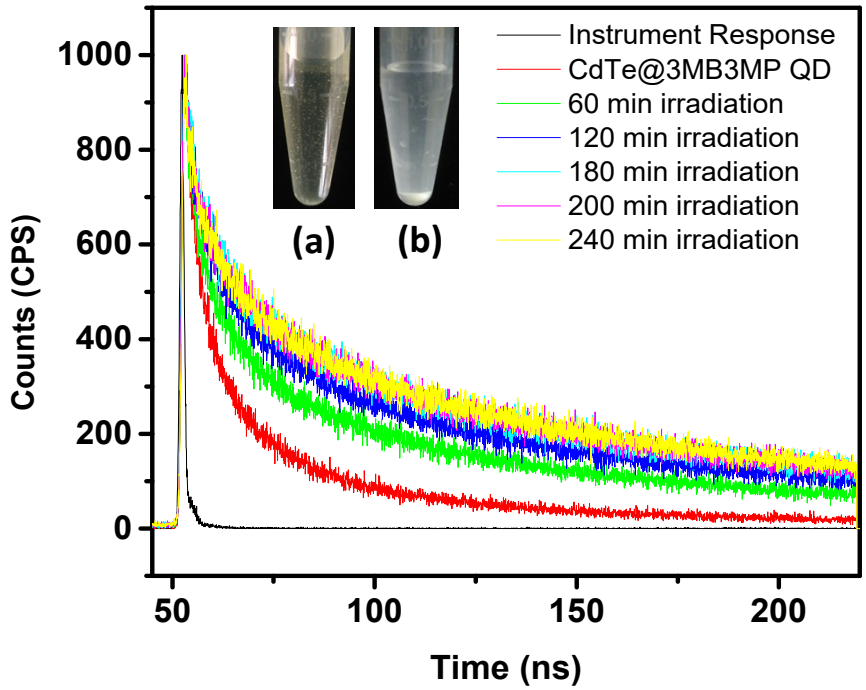


Fig. S7. Time resolved fluorescence spectra of CdTe@3MB3MP QDs at different time of irradiation. Inset shows the QD solution before (a) and after (b) the irradiation experiment

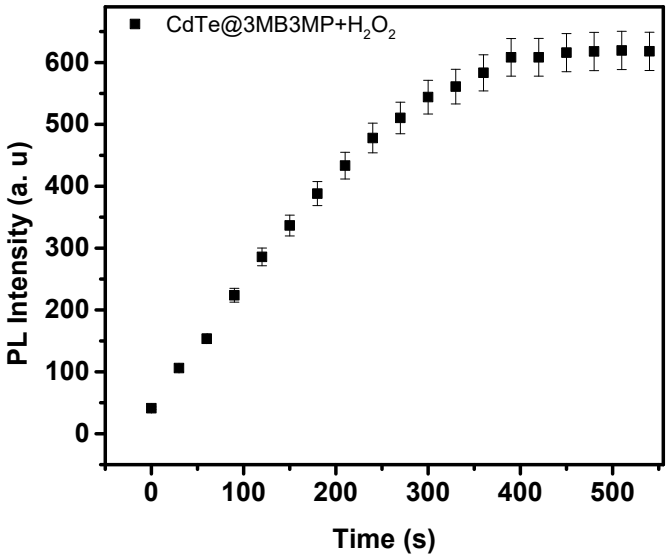


Fig. S8. Graph showing the response time of the sensor towards detection of H_2O_2

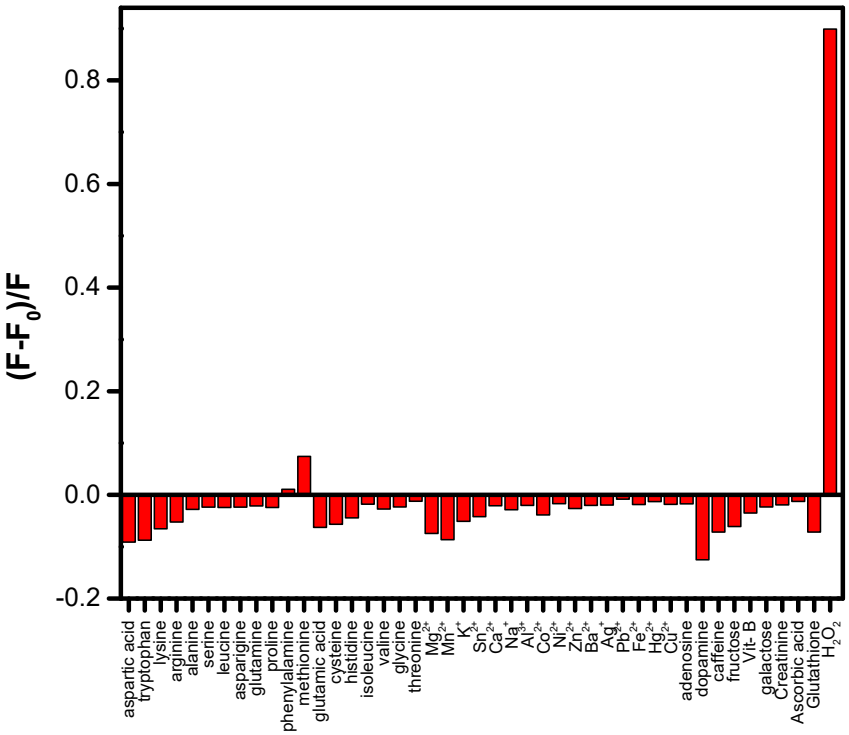


Fig. S9. Selectivity profile of CdTe@3MB3MP QDs towards H_2O_2

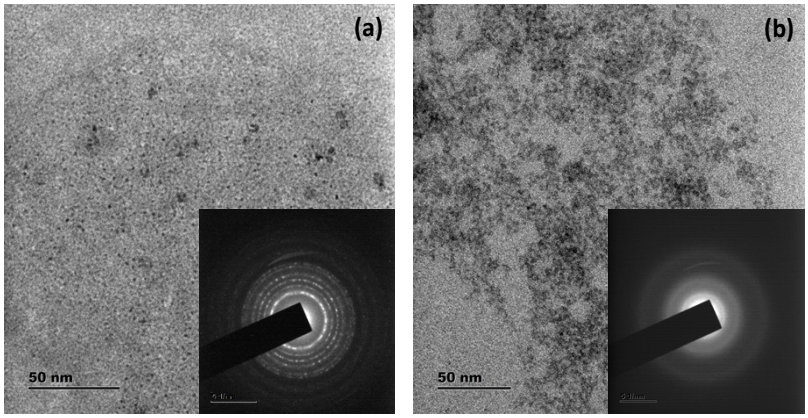


Fig. S10. TEM images of CdTe@3MB3MP QDs at 100 nM (a) and 500 nM (b) concentrations of H_2O_2

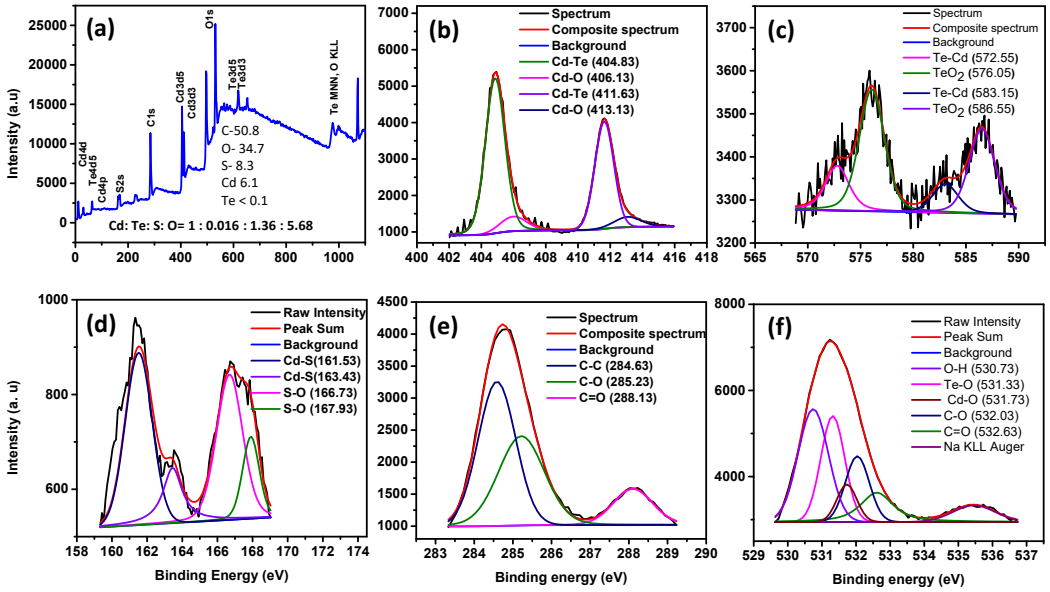


Fig. S11. a) Survey scan spectrum of CdTe@3MB3MP QDs at lower concentrations of H_2O_2. b-f) Corresponding HRXPS spectra of Cd, Te, S, C and O respectively

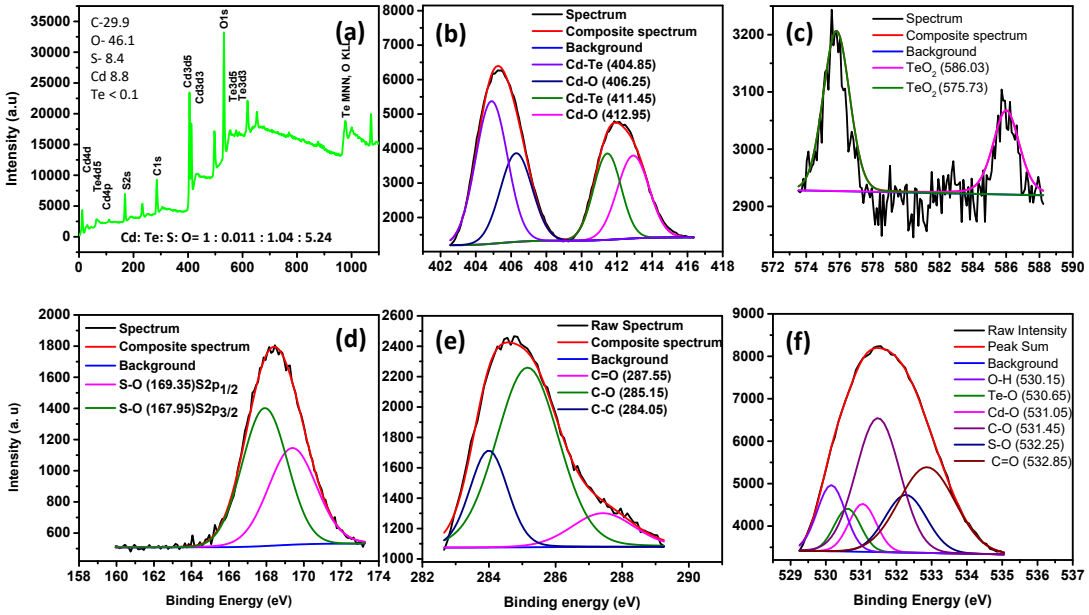
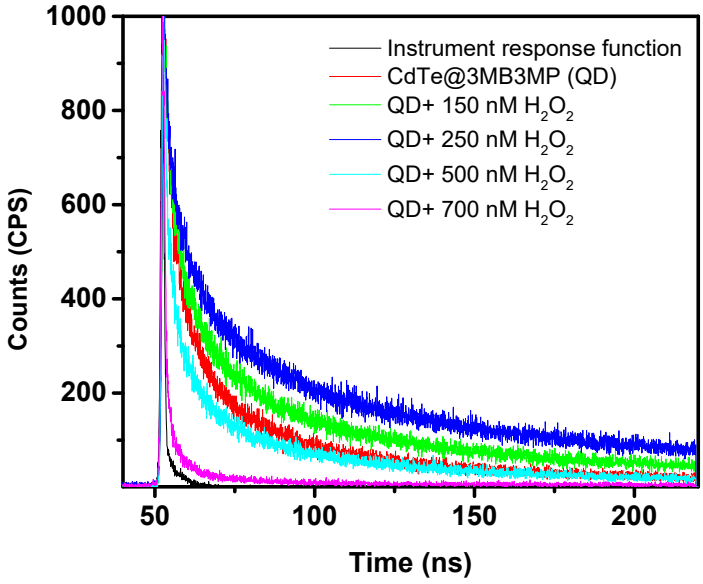


Fig. S12. a) Survey scan spectrum of CdTe@3MB3MP QDs at higher concentrations of H_2O_2. b-f) Corresponding HRXPS spectra of Cd, Te, S, C and O respectively



SYSTEM	τ_1 (ns)	a_1	τ_2 (ns)	a_2	τ_3 (ns)	a_3	<τ> (ns)	χ^2
QD	77.66	57.52	13.89	28.83	1.89	13.65	72.04	1.2
QD+150 nM	86.81	70.84	14.18	23.40	1.49	5.76	82.98	1.04
QD+ 250 nM	99.62	79.22	15.51	15.86	0.91	4.92	97.02	1.01
QD+ 500 nM	78.24	58.89	13.13	18.04	0.64	23.07	74.83	1.07

QD+ 700 nM	31.27	26.86	5.17	29.58	0.76	43.56	26.39	1.2

Fig. S13. Time resolved fluorescence spectra of QDs at different concentrations of H_2O_2

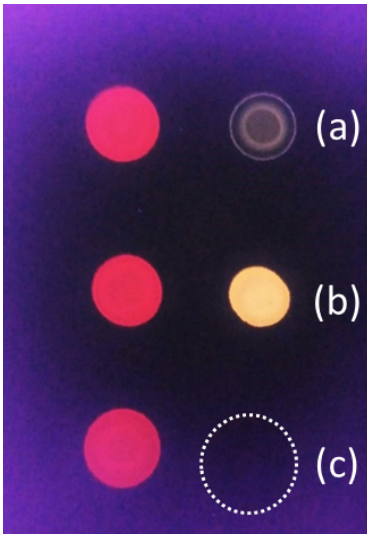


Fig. S14. Photographs of TLC plate based sensor platform. The first column represents CdTe@3MB3MP QD drop casted on TLC under UV light (red dots) and the second column represent QDs treated with a) 50 nM b) 250 nM and c) 750 nM concentrations of H_2O_2

Sample	**Zeta Value (mV)**
CdTe@3MB3MP QDs (QD)	-30.9
QDs + 50 nM of H_2O_2	-32.9
QDs + 100 nM of H_2O_2	-34.2
QDs + 150 nM of H_2O_2	-35.3
QDs + 200 nM of H_2O_2	-38.0
QDs + 250 nM of H_2O_2	-43.8
QDs + 300 nM of H_2O_2	-42.7
QDs + 350 nM of H_2O_2	-32.7
QDs + 400 nM of H_2O_2	-30.7
QDs + 450 nM of H_2O_2	-28.2

Table S1. Table showing Zeta potential values of CdTe@3MB3MP QDs at different concentrations of H_2O_2