# Electronic Supplementary Information

## Recovering Hidden Quanta of $Cu^{2+}$-doped ZnS Quantum Dots in Reductive Environment

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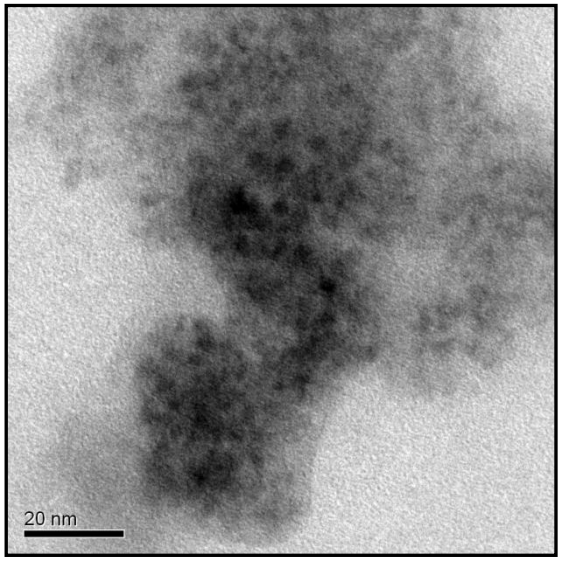


**Figure S1.** Transmission electron microscopy (TEM) image of chitosan-stabilized ZnS Qdots.

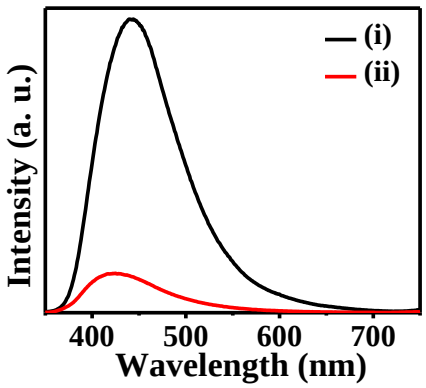


**Figure S2.** Emission spectra of chitosan-stabilized (**i**) ZnS Qdots and (**ii**) ZnS Qdots treated with 50 uL of 0.5 mM copper acetate solution.

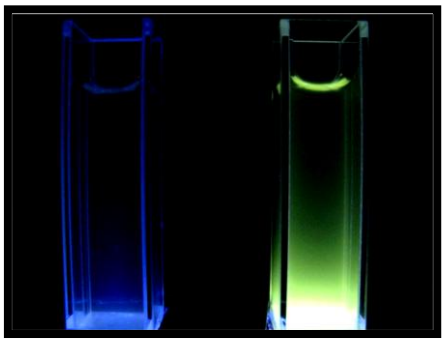

**Figure S3.** Digital images of as synthesized $Cu^{2+}$-doped ZnS Qdots (left) and those of treated with $NaBH_4$ (right). The images were recorded using UV light as the excitation source.

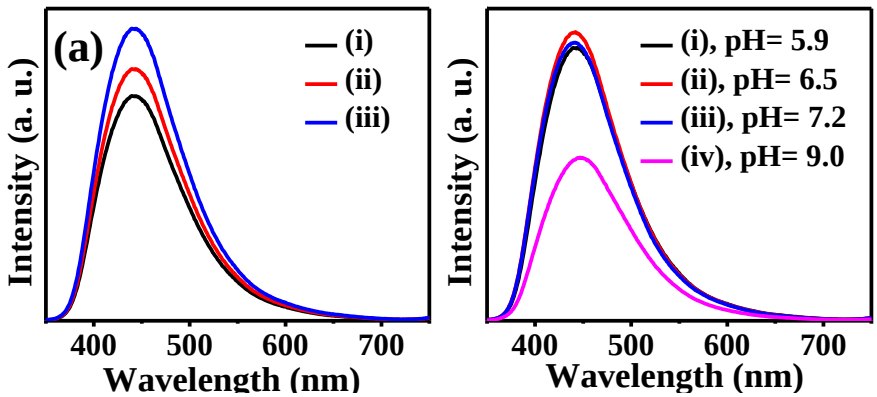


**Figure S4.** (**a**) Emission spectra of (**i**) chitosan-stabilized as synthesized ZnS Qdots;(**ii**) those treated with 12 mM $NaBH_4$ and incubated for 10 min and (**iii**) the same after 20 min. (**b**) Emission spectrum of (**i**) as-synthesized Qdots at pH 5.9; those of (**ii**) sample treated with 10 uL, (**iii**) 25 uL and (**iv**) 50 uL of dilute NaOH solutions and incubated for 1 h, respectively.

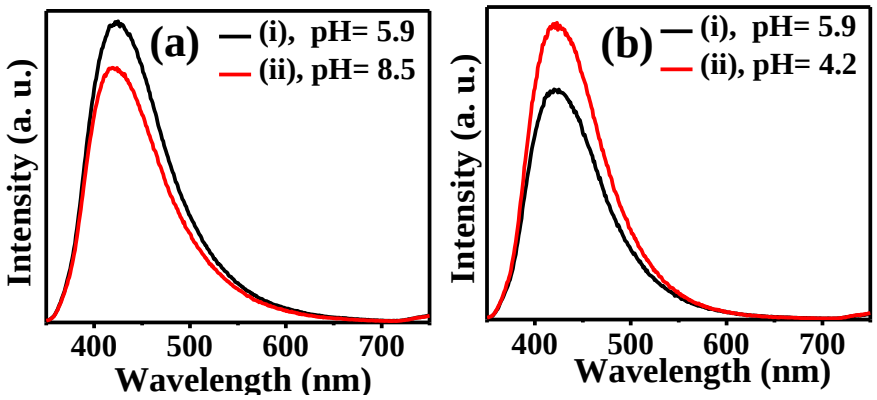


**Figure S5.** Emission spectrum of (i) as-synthesized Cu-doped ZnS Qdots at pH 5.9 those of sample treated with 25 uL of dilute (**a**) NaOH solutions and (**b**) HCl acid, also incubated for 1 h, respectively.

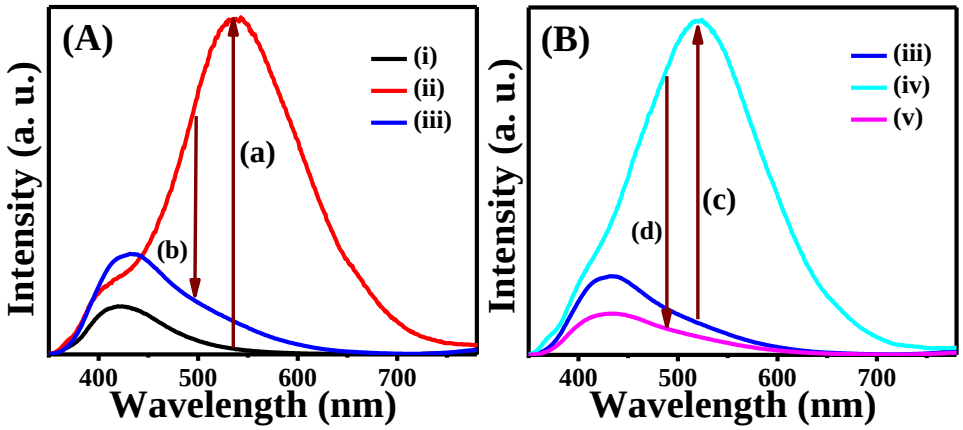


**Figure S6.** Emission spectra of **(A)** (**i**) as-synthesized Qdots, (**ii**) the Qdots following treatment with $NaBH_4$ and pH adjustment, and (**iii**) that following KPS addition. (**B**) The emission spectra of (**iii**) the same Qdot dispersion as in (**A-iii**), (**iv**) Qdots following treatment with $NaBH_4$ and pH adjustment, and (**v**) that when was again treated with KPS. Overall, the spectra revelealed reversibility of redox induced fluorescence emission changes for two consecutive cycles.

**NOTE**: We had first recorded TEM images of the sample at different locations. Then from the clearly observed spherical particles (for each image) we calculated their sizes. We had considered sizes of 100 such particles. The reported value is an average of those numbers.

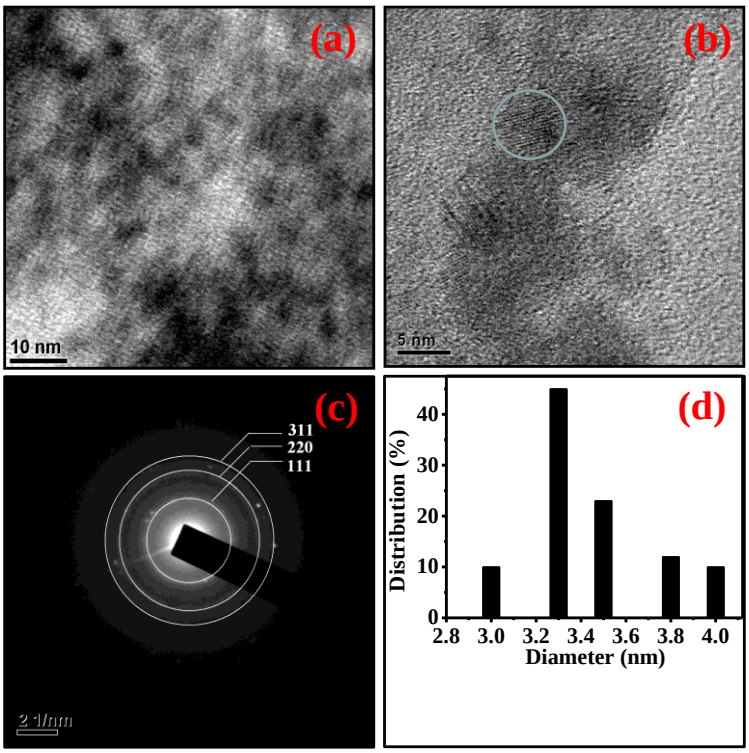


**Figure S7.** (**a**) TEM image, (**b**) high resolution TEM (HRTEM) image, (**c**) selected area electron diffraction (SAED) pattern and (**d**) particle size distribution (as calculated from (**a**)) of as-synthesized chitosan-stabilized Cu doped ZnS Qdots. The diffraction corresponding to lattice planes are identified in Figure (**c**).

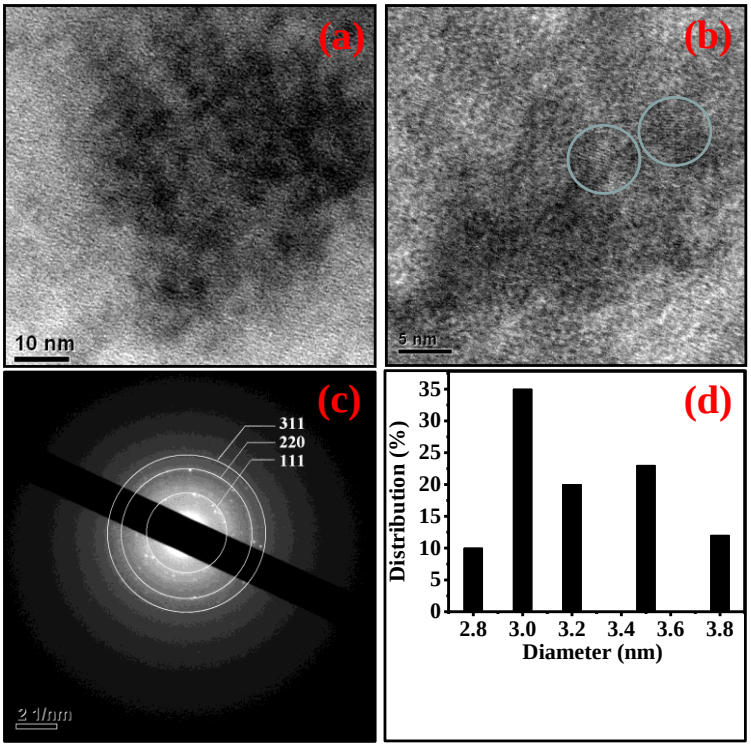


**Figure S8.** (**a**) TEM image, (**b**) HRTEM image, (**c**) selected area electron diffraction (SAED) pattern and (**d**) particle size distribution (as calculated from (**a**)) of $NaBH_4$ treated chitosan-stabilized Cu doped ZnS Qdots. The diffraction corresponding to lattice planes are identified in Figure (**c**).

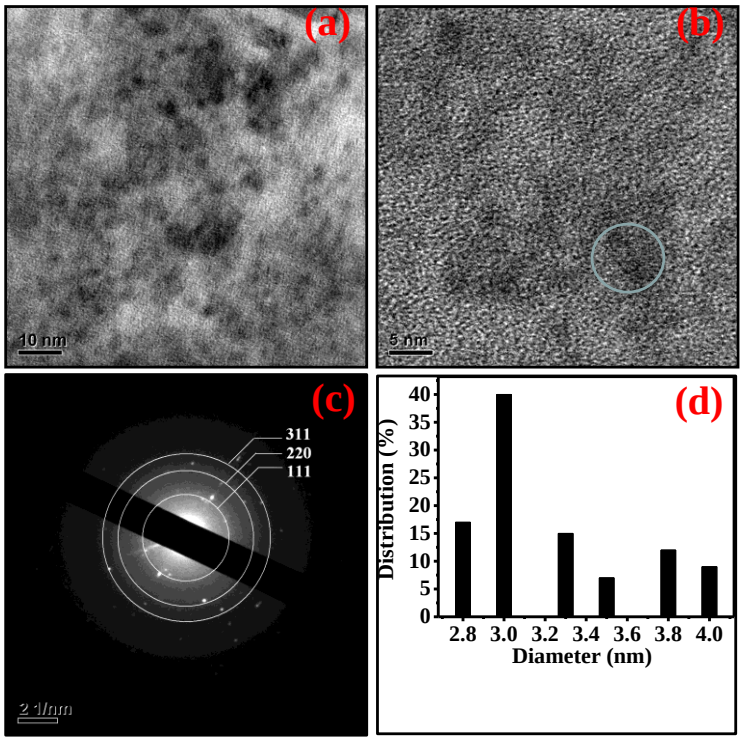


**Figure S9.** (**a**) TEM image, (**b**) HRTEM image, (**c**) selected area electron diffraction (SAED) pattern and (**d**) particle size distribution (as calculated from (**a**)) of chitosan-stabilized Cu doped ZnS Qdots, which were first treated with $NaBH_4$ and then with KPS. The diffraction corresponding to lattice planes are identified in Figure (**c**).

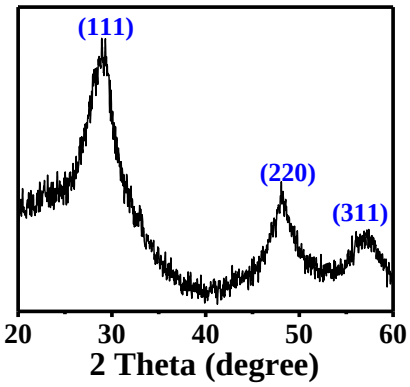


**Figure S10.** Powder X-ray diffraction pattern of as-synthesized chitosan-stabilized Cu doped ZnS Qdots.

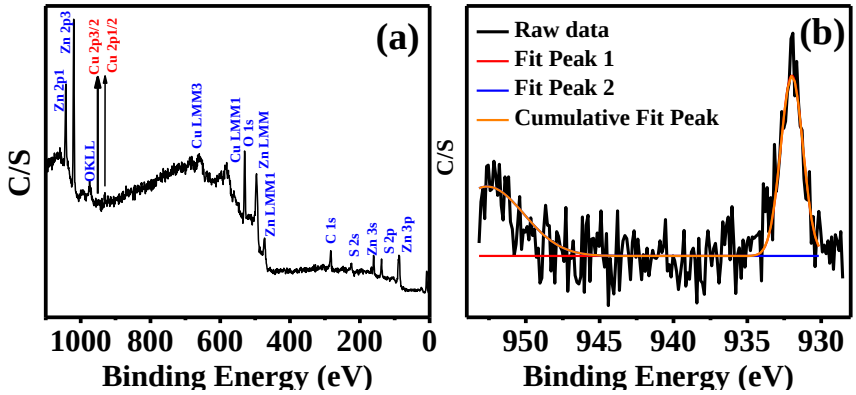


**Figure S11.** (**a**) X-ray photoelectron spectrum of as-synthesized Cu-doped ZnS Qdots. (**b**) Expanded view of the same depicting Cu- peaks. The peaks in (**b**) were fitted with Gaussian curves.

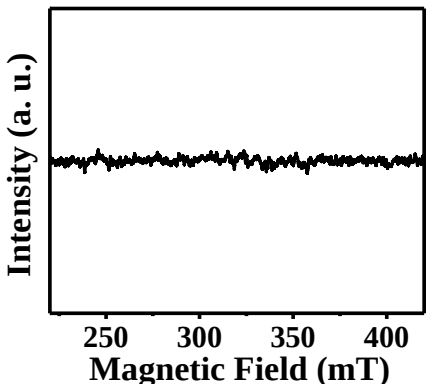


**Figure S12.** ESR spectrum of as-synthesized chitosan-stabilized ZnS Qdots.

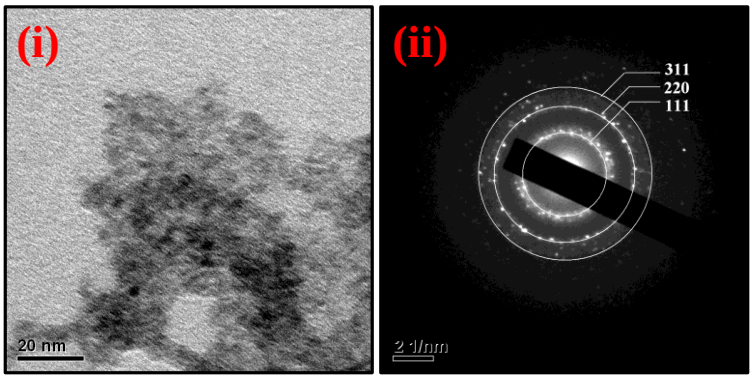


**Figure S13.** (**i**)TEM image and (**ii**) SAED pattern of $NH_4SCN$-stabilized Cu doped ZnS Qdots. The diffraction corresponding to lattice planes are identified in Figure (**ii**).

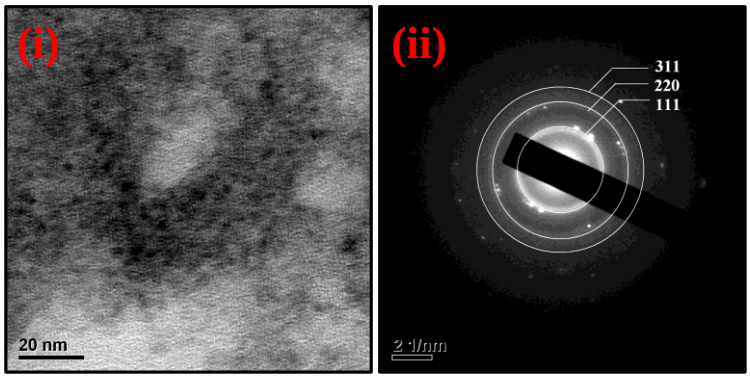


**Figure S14.** (**i**)TEM image and (**ii**) SAED patterns of trisodium Citrate stabilized Cu doped ZnS Qdots. The diffraction corresponding to lattice planes are identified in Figure (**ii**).

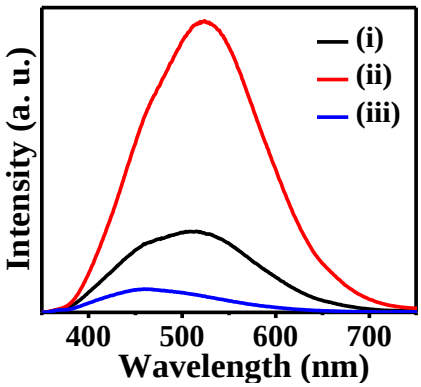


**Figure S15.** Emission spectra of (**i**) as-synthesized $NH_4SCN$ stabilized Cu-doped ZnS Qdots, (**ii**) those treated with 12 mM of $NaBH_4$ and (**iii**) those following 0.2 mM of KPS addition, subsequent to $NaBH_4$ treatment. Excitation wavelength was set at 320 nm.

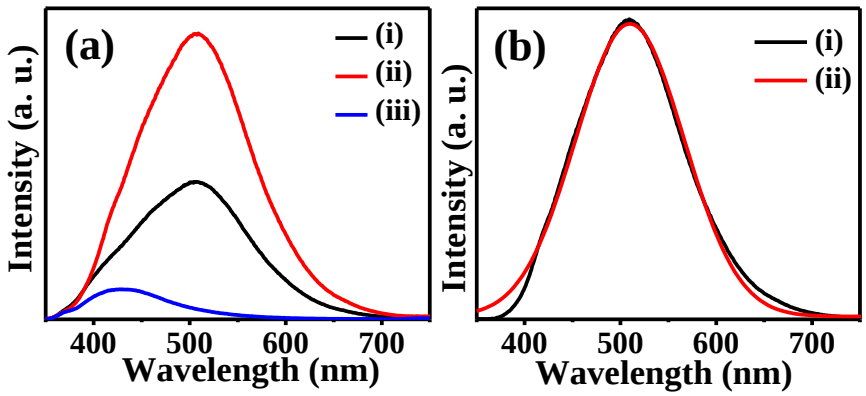


**Figure S16.** (**a**) Emission spectra of trisodium citrate-stabilized $Cu^{2+}$-doped ZnS Qdots (i), followed by treatment with ascorbic acid (**ii**), and then following addition of KPS (**b**) Single Gaussian fitting of emission spectrum of trisodium citrate stabilized Cu-doped ZnS Qdots, treated with ascorbic acid and corresponding to Figure **S15** (a-ii). Excitation wavelength was set at 320 nm.

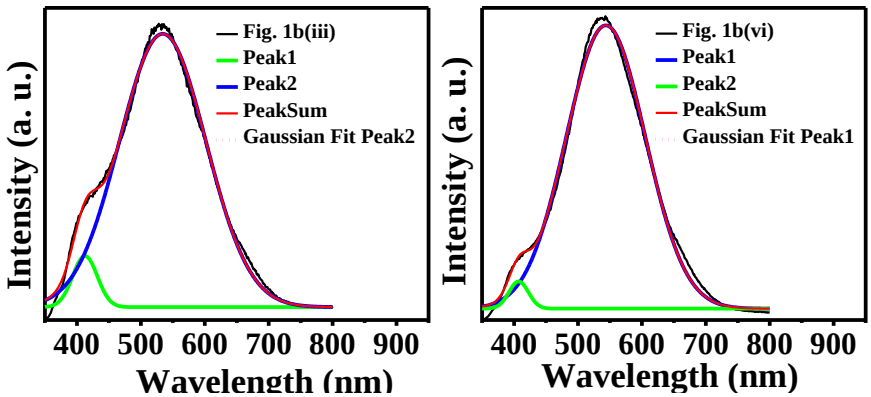


**Figure S17.** Fitting of emission spectra in Figure 1b (of the manuscript) by two Gaussian peaks. The left panel spectrum (in black) corresponds to Figure 1b (iii) of the manuscript, while that in the right panel (in black) corresponds to Figure 1b (vi) of the manuscript. Excitation wavelength was set at 320 nm.

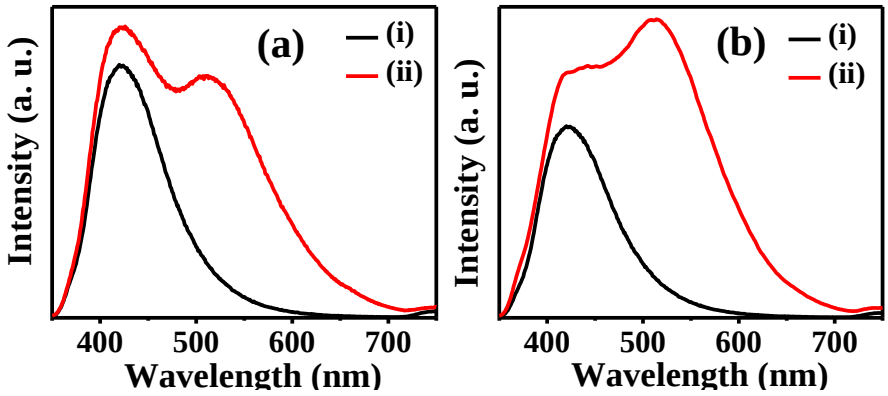


**Figure S18.** Emission spectra of (**i**) as synthesized chitosan-stabilized Cu doped ZnS Qdots –for both the panels; (**ii**) the same upon addition of (**a**) trisodium citrate or (**b**) ascorbic acid – for both the panels. Excitation wavelength was set at 320 nm.

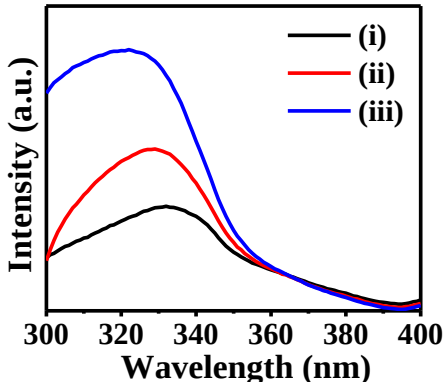


**Figure S19.** Excitation spectrum (measured without using cut on 385 filter) of (**i**) as synthesized chitosan-stabilized Cu-doped ZnS Qdots; and the same upon treatment with $NaBH_4$ and incubation for (**ii**) 30 min and (**iii**) 1 h. The emission peak was set at 540 nm.

**Quantum Yield Calculation:**

We have calculated quantum yield with respect to quinine sulphate (QS) in 0.1 M $H_2SO_4$, using the formula:

$Q_S = Q_R \times (I_S/I_R) \times (A_R/A_S) \times (\eta^2_S/\eta^2_R)$

Where,

$Q_S$ = quantum yield of sample; $Q_R$ = quantum yield of reference; $I_S$ = area under PL curve of sample; $I_R$ = area under PL curve of reference; $A_R$ = absorbance of the reference; $A_S$ = absorbance of the sample; $\eta_S$ = refractive index of sample; $\eta_R$ = refractive index of reference. Quinine sulphate in 0.1 M $H_2SO_4$ absorbs in the UV region with $\lambda_{max}$ at 347 nm; however, emission spectra were recorded using an excitation wavelength of 320 nm (near the $\lambda_{max}$ corresponding to the Qdots). Absorbance values at 320 nm were therefore considered for QS as well as for the Qdots for the determination of QY. QS (literature QY=0.54) was dissolved in 0.1M $H_2SO_4$ (refractive index ($\eta_s$) of 1.33) and the Qdots were dispersed in distilled water ($\eta_R$=1.33).

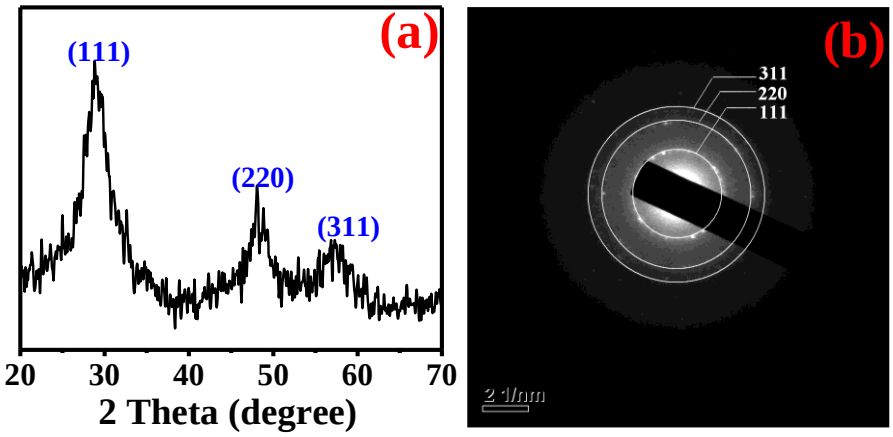


**Figure S20.** (**a**) Powder XRD patterns of as-synthesized composite NPs of chitosan and Cu doped ZnS Qdots. (**b**) SAED patterns of the sample corresponding to the sample in Figure **2a** in the manuscript. The diffraction corresponding to lattice planes are identified in Figure (**c**).

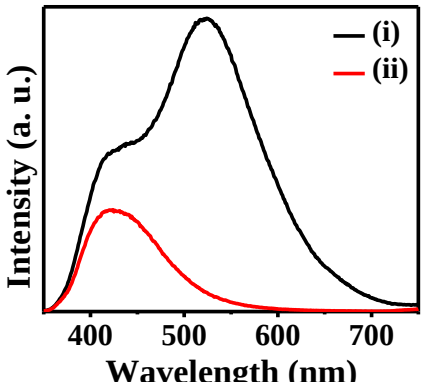


**Figure S21.** Emission spectrum of (**i**) as synthesized composite NPs of chitosan and Cu doped ZnS Qdots; (**ii**) the same upon addition of 5 mM of GSH and incubation for 1 h. Excitation wavelength was set at 320 nm.

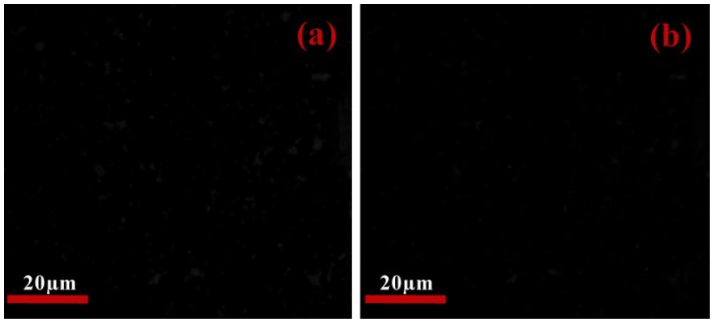


**Figure S22.** Fluorescence micrographs of composite NPs of chitosan and Cu doped ZnS Qdots. The images were captured using (**a**) blue emission filter (435-485 nm) and (**b**) green emission filter (515-555 nm); Scale bar: 20 µm.

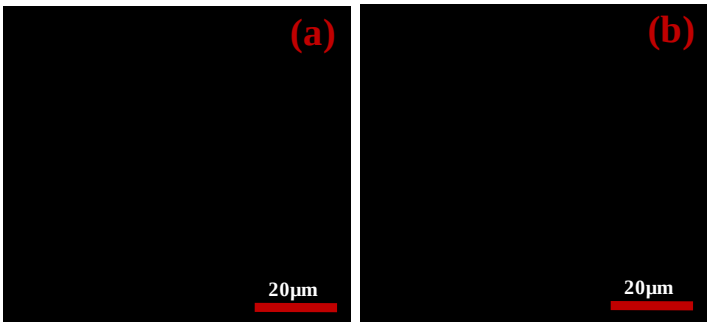


**Figure S23.** Fluorescence micrographs of composite NPs of chitosan and Cu doped ZnS Qdots treated with $NaBH_4$. The images were captured using (**a**) blue emission filter (435-485 nm) and (**b**) KPS treated sample under green emission filter (515-555 nm); Scale bar: 20 µm.

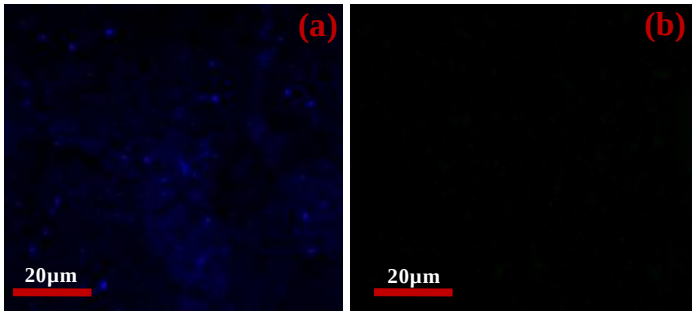


**Figure S24.** Fluorescence micrographs of composite NPs of chitosan and ZnS Qdots captured under (**a**) blue emission filter (435-485 nm) and (**b**) green emission filter (515-555 nm); Scale bar: 20 µm.

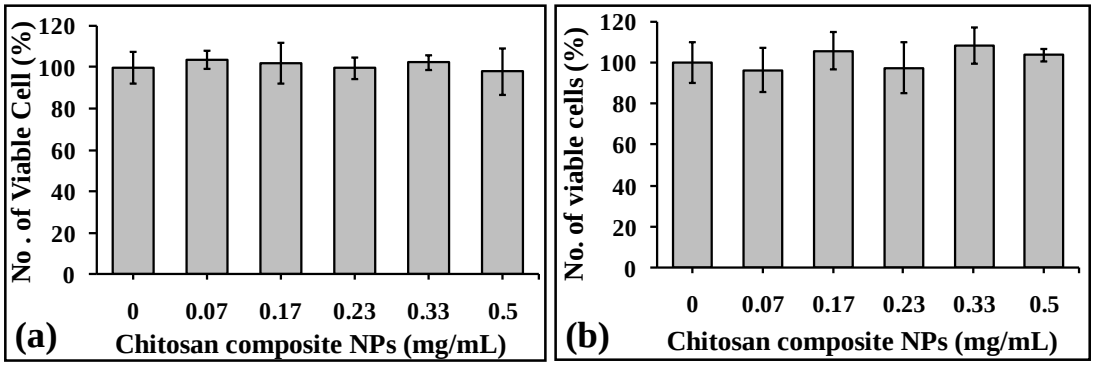


**Figure S25.** XTT based cell viability assay for (**a**) HeLa cells (**b**) HEK 293 cells at different concentrations of chitosan composite NPs. Data are presented as the mean ± SD of three individual experiments.

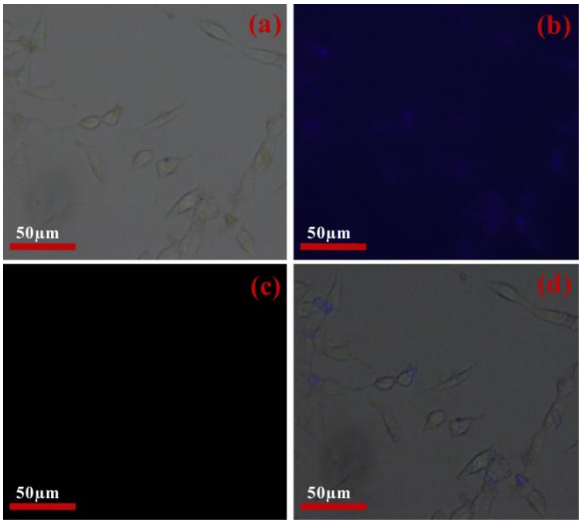


**Figure S26.** Fluorescence micrographs of HeLa cells treated with composite NPs of ZnS; captured under irradiation of (**a**) White light, (**b**) blue emission filter (435-485 nm), (**c**) using green emission filter (515-555 nm) (**d**) Merged image of (**a**) and (**b**); Scale bar: 50 µm; Magnification 20X.