Electronic Supporting Information

Cobalt substituted ZnS QDs: A diluted magnetic semiconductor and an efficient photocatalyst

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Synthesis of pure and Co doped ZnS QDs

In order to synthesize pure and cobalt-doped ZnS QDs [$Co_xZn_{1-x}S$ (x = 0.00, 0.03, 0.06 and 0.09)], the conventional chemical co-precipitation technique was utilized. We have used thioacetamide [TAA, C_2H_5NS] as the sulfur source, cobalt (II) nitrate hexahydrate [$Co(NO_3)_2.6H_2O$] as the cobalt source, zinc acetate dihydrate [$Zn(CH_3CO_2)_2.2H_2O$] as the zinc source, and polyvinyl pyrrolidone (PVP, mean molecular weight 40000) as the surface-active binding agent for preparing both the pristine and doped ZnS QDs. 200 ml of DI water and 1 g of PVP were combined at room temperature in a 1 L beaker while being vigorously stirred using a magnetic stirrer. After stirred vigorously for 30 minutes at room temperature, the zinc source in stoichiometric ratio was added to the solution. Further the sulfur source was added to

the solution, stirring continued for an additional 90 minutes at 80 °C. Afterward, the NaOH solution was gradually infused dropwise into the mixture until the pH attained 10 and complete precipitation was taken place under steady stirring condition at room temperature. The surfactant was removed once the precipitate sinks to the bottom, and the precipitate was then centrifuged and cleaned. The residue was washed with water and ethanol to bring the pH back to neutral and got rid of any contaminants. The resulting residue was collected in a petri dish and left in the oven for a day to dry at 60 ˚C temperature. The dry powder was then ground using a mortar and pestle and stored carefully.

Further we have synthesized the Co-doped ZnS QDs using the same method. The measured amounts of zinc and cobalt sources were combined depending on the desired doping level of the samples. All the prepared powder samples were ground, gathered, and indexed with Co-00 (ZnS), Co-03 (ZnS), Co-06 (ZnS), and Co-09 (ZnS) respectively as per the increasing Co content in ZnS QDs. Various physical characterizations of these prepared powder samples were further conducted.

Characterization techniques

All the physical characteristics of prepared QDs including crystallographic phase formation, microstructural, optical, dielectric and magnetic properties were investigated thoroughly using several characterization techniques. We have recorded the X-ray diffractograms (XRD) in Bruker D8 Advance powder X-ray diffractometer at room temperature using copper K_{α} radiation (1.5406 Å). The morphology of synthesized samples was recorded using HRTEM (JEM-2100F, JEOL, Japan) at an accelerating voltage of 200 kV. All the FTIR spectra of as-prepared samples were registered at room temperature using the Perkin-Elmer FTIR spectrophotometer. Room temperature photoluminescence spectra of synthesized samples were registered using Horiba (QM08075-21-C) spectrometer. All the magnetic measurements

of prepared QDs were collected using 16 T-VSM-PPMS (Quantum design). The room temperature absorption spectra together with entire photodegradation profiles of all the QD samples were registered by using UV DRS spectrometer (UV-2550, Shimadzu, USA). All the nitrogen adsorption–desorption isotherms of prepared QDs were obtained by using Brunauer–Emmett–Teller (BET) technique (Quantachrome iQ autosorb analyzer, USA). The average pore sizes of pure and doped samples were calculated as per the Barrett–Joyner–Halenda (BJH) approach. Dielectric properties of prepared QDs were measured using a LCR meter (HIOKI, IM 3536) at room temperature.

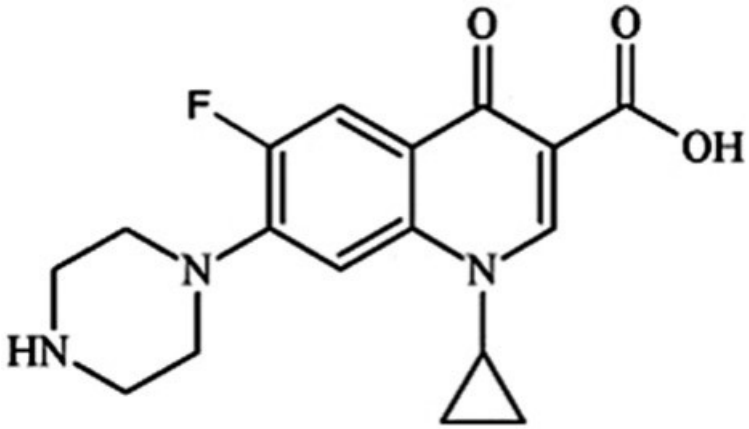
Name	Molecular Structure	M_w (g/mol)	λ_{max}	Molecular Formula
Ciprofloxacin		331.4	270 nm	$C_{17}H_{18}FN_3O_3$

Table S1: Physicochemical characteristics of Ciprofloxacin (CIP)

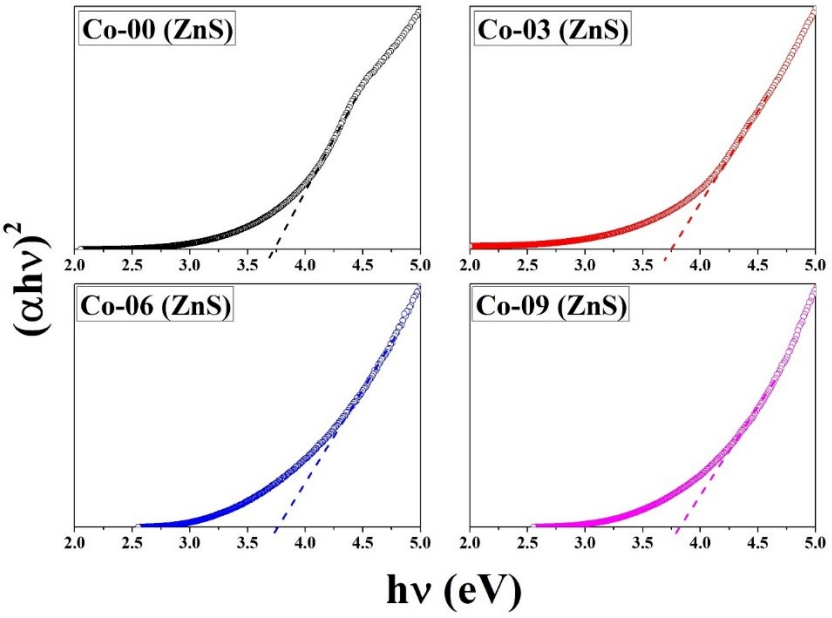


Figure S1: Tauc plots of all the QDs.

Sample Id	Bandgap (eV)
Co-00 (ZnS)	3.71
Co-03 (ZnS)	3.74
Co-06 (ZnS)	3.76
Co-09 (ZnS)	3.82

Table S2: Contains band gap of all the samples

Computational method for FDTD study

FDTD was developed by Kane Yee in 1966 to solve Maxwell's equations for materials with a definite geometrical structure. Ansys Lumerical FDTD Solutions is the software package used for simulating electromagnetic behavior in various nanostructures [http://www.lumerical.com/fdtd.php]. This software is widely utilized by researchers.[1-4] In FDTD simulations, the physical space surrounding the material is divided into small cubic cells called Yee cells. These cells form the basis for solving Maxwell's equation. The FDTD algorithm starts with the electric and magnetic field, these fields are iteratively updated by solving Maxwell's equations to obtain higher-order approximations until a convergent limit is

reached, representing the physical values of the fields. In the beginning, a ZnS quantum dot with an 8 nm diameter developed inside the FDTD simulation. The ZnS quantum dot is repeated in the x and y direction with 0.25 nm interparticle distance in order to represent the particle distribution observed in the experimental TEM image. Similarly, we have also designed Cobalt-doped ZnS QDs of 8 nm diameter and the gap between particles is 0.25 nm. The convergence of the FDTD simulation is influenced by the size of the Yee cell cube, known as the mesh size. The simulation space is defined with dimensions of 2000 nm in the x, y, and z directions, centered at the origin, and the mess size is 0.5 and the representation of the nanostructured material within a large simulation space. Symmetric, antisymmetric, and perfectly matched layers (PML) boundary conditions are considered during the FDTD simulation. These boundary conditions help to ensure accurate wave propagation in the model. Total Field Scatter Field (TFSF) is used as a light source in the simulation. TFSF involves using plane waves within a defined field contour where the nanostructured material is placed. It provides control over the incident light's propagation direction and polarization. Power monitors are strategically placed within the simulation to monitor the interaction of light with the nanostructures and measure various optical properties or scattering characteristics as shown in figure S2.

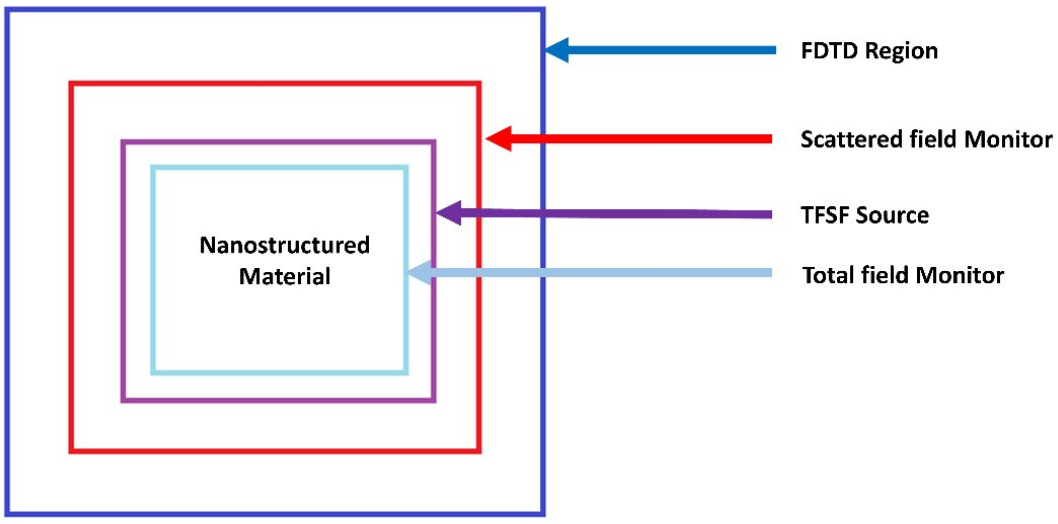


Figure S2: Schematic of simulated region.

When a material is exposed to electromagnetic radiation, the power absorbed by the material, the absorption cross-section (σ_{abs}) is generally determined by the analysis group existing inside the total field scatter field (TFSF) source. The analysis group finds out the total power flowing into the volume as well as by normalizing it to the source intensity.[5] The study covers a range of incident wavelengths from 300 nm to 600 nm, with a polarization angle of 90 degrees. The refractive index profiles of ZnS QDs and cobalt-doped ZnS QDs are obtained from a reliable source (IIT Roorkee; VASE ellipsometry) to calculate the real and imaginary parts of the permittivity values.

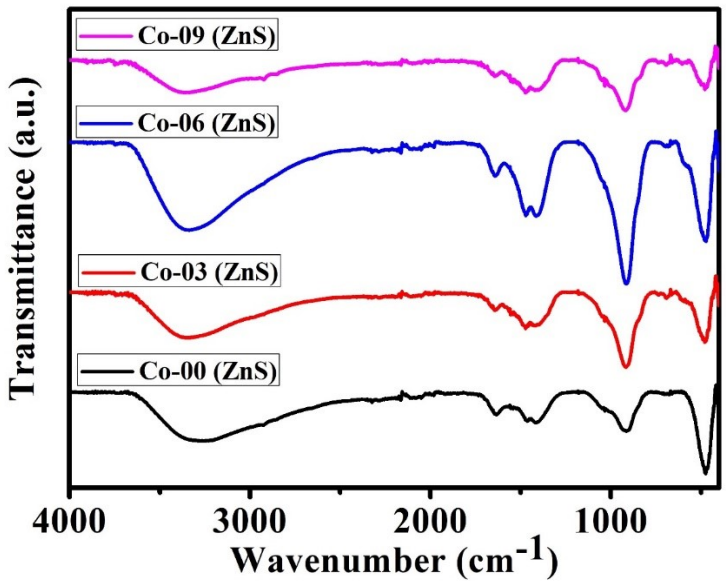


Figure S3: FTIR spectra of all the Co doped ZnS QDs.

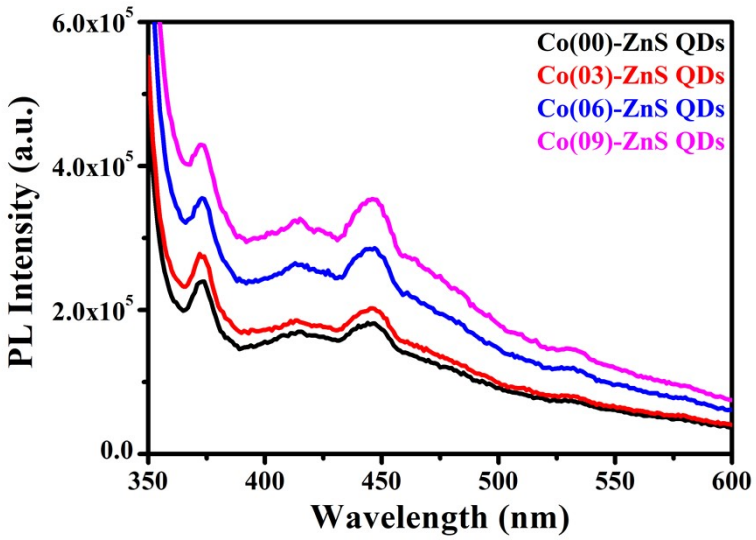


Figure S4: PL spectra of all the Co doped ZnS QDs.

Sample Id	Coercivity (Oe)	Max. magnetization at 70 kOe (emu/g)
Co-00 (ZnS)	---	-0.04
Co-03 (ZnS)	23	+0.05
Co-06 (ZnS)	57	+0.16
Co-09 (ZnS)	91	+0.35

Table S3: Represents magnetic parameters of all the samples

Computational method for DFT study

Almost all computations are performed using the Ab Initio Total Energy Program called CASTEP under Material Studio.[6] Zinc-blende (ZB) ZnS regularly shapes a structure aided by the space group F43-m, to which a 2 x 1 x 1 super-cell of ZB ZnS is made. Density functional theory (DFT) with the generalized gradient approximation (GGA) of the PBE functional is used in the computation in order to optimize the structure.[7] The same PBE functional is used by many researchers for optimizing different structures because of having surpassing ability.[8, 9] Furthermore, to increase the speed of the simulation process, ultrasoft pseudopotential is used.

In the interior space of reciprocal K, the plane wave energy cut-off is considered as 420 eV, together with the essential computation of the Brillouin zone, applying a 4 x 4 x 8 Monkhorst-Pack grid as well as an atomic force of 1 x 10-2 eV. Å. In addition to that, single atomic energy is attained at 5 x 10-6 eV, followed by internal stress organized under 2x10-2 GPa. A simulation model of a 2x1x1 super-cell of ZnS is created with a total 31 number of atoms. Then the structure is optimized and system energy converges quite well.

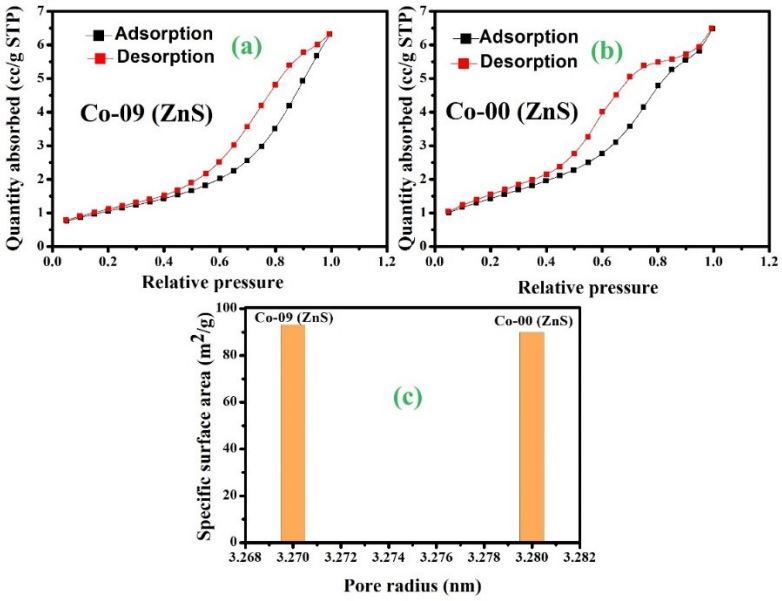


Figure S5: (a, b) N_2 gas adsorption-desorption isotherms of pure and 9% Co-ZnS QDs and (c) Graph of specific surface area vs pore radius.

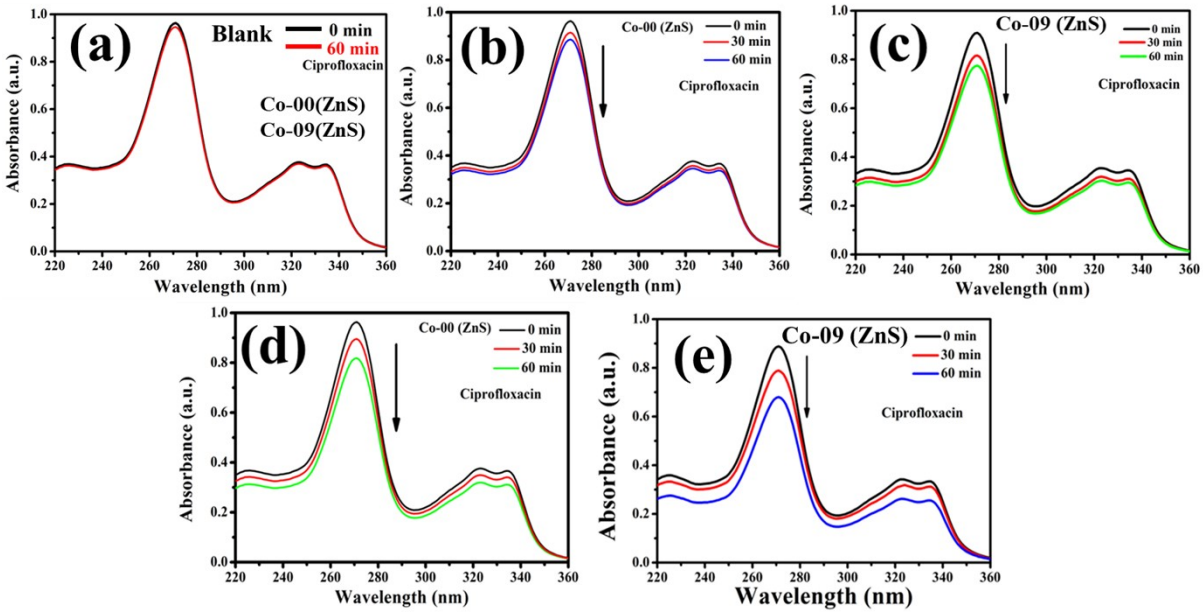


Figure S6: (a) Absorption spectrum of the solution obtained in dark mode (without light and catalyst) for Co-00 (ZnS) QDs and Co-09 (ZnS) QDs, (b, c) absorption spectrum of the solution obtained under only light exposer without catalyst of Co-00 (ZnS) and Co-09 (ZnS) QDs respectively, (d, e) absorption spectrum of the solution obtained without the presence of light with catalyst of Co-00 (ZnS) and Co-09 (ZnS) QDs

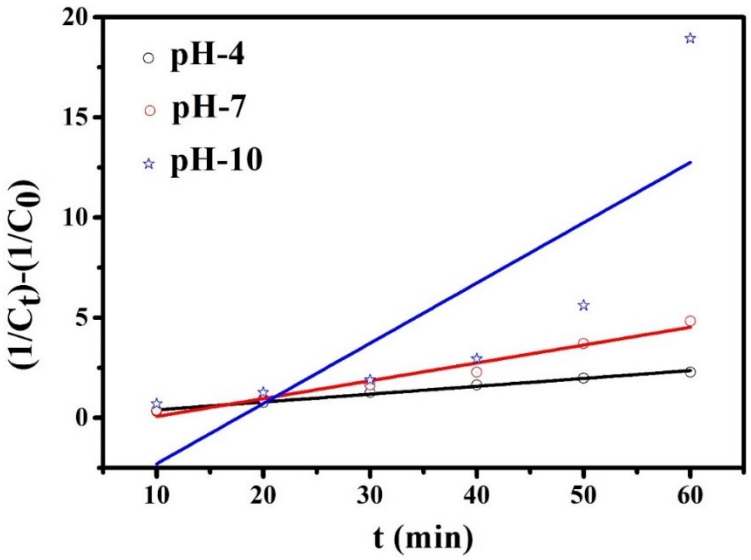


Figure S7: Plot of rate constant obtained from 2nd order kinetics

With catalyst and light				
pH values	Rate constant (min^{-1})	R^2 (I^{st} order)	R^2 (2^{nd} order)	DE (%)
(i) at pH-4	0.017	0.94	0.93	68.4
(ii) at pH-7	0.028	0.99	0.96	82.1
(iii) at pH-10	0.044	0.87	0.57	94.7
Condition	Rate constant (min^{-1})	R^2 (1^{st} order)	DE (%)	
Blank	0.0003	0.94	1.2	
Only light without catalyst	0.002	0.97	15.3	
With catalyst but without light	0.005	0.99	22.2	

Table S4: Contains rate constants, regression and degradation efficiency of doped QDs

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