Electronic Supporting Information (ESI)

Non-stoichiometric Cu$_x$In$_{1-x}$S quantum dot for Robust Photodegradation of Gemifloxacin: Influencing parameters, Intermediates, and Insights into the Mechanism

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Chemicals Requirement

Copper chloride dihydrate (CuCl$_2$·2H$_2$O, 99%), Thioglycolic acid (TGA, 79%), sodium hydroxide (NaOH, 97%), NBT (Nitro Blue Tetrazolium chloride), TA (Terephthalic Acid) Methanol, Nafion, Na$_2$SO$_4$, NaCl, NaNO$_3$, DMSO, p- Benzoquinone, iso-propyl alcohol, citric acid and Na$_2$CO$_3$ were purchased from Merck and Indium chloride (InCl$_3$, 98%), sodium sulfide nonahydrate (Na$_2$S·9H$_2$O, 58%), DMPO from Himedia chemical company. All reagents are in analytical grade and are used in reaction without further purification.

Characterization techniques

Sl. No.	Instrument	Description	Model name	Company name
1	Field Emission Scanning Electron Microscopy(FESEM)	Sample was dispersed in ethanol, coated with Au, Al foil used for deposition	FEI Quanta 400FEG_SEM	FEI
2	X-ray diffraction (XRD)	Cu Kα radiation (λ = 1.54 Å) at a 2θ range of 10-60º, 40 KV/40 mA	Rigaku-Ultima-IV	Rigaku
3	X- ray photoelectron spectroscopy (XPS)	Non-monochromatic Kα Mg X-ray, 284.8 eVbinding energy of C 1s as reference	VG MicrotechMultil abESCA 3000	VG

4	Photoluminescencespectro fluorometer (PL)	Xe- lamp as excitation source, dueterium UV lamp	JASCO-FP-8300	JASCO
5	UV- visible diffuse reflectance spectroscopy (UV – VIS DRS)	Deuterium UV lamp and Xe visible light, $BaSO_4$ as reference	JASCO-V-750	JASCO
6	Electrochemical analyser	Three electrode system such as synthesized sample as a working electrode, platinum as counter electrode and Ag/AgCl as reference electrode, 0.1 M Na_2SO_4 solution at pH of 6.8 as electrolyte	multi-channel-IVIUMpotentios tatanalyzer	IVIUM Technology
7	High resolution transmission electron microscope (HRTEM)	200kV acceleration voltage	TEM, JEOL-2100	JEOL

Gemifloxacin photodegradation experiment:

In the performed photodegradation reaction, 20 mg of catalyst was dispersed in 20 mL of 10 ppm gemifloxacin model pollutant solution (by dissolving required amount of Gemifloxacin in deionized water). Prior to photo-irradiation the above suspension was kept in dark under slow stirring for 30 min to develop adsorption-desorption equilibrium between catalyst and GMF. After that, the suspension in neutral medium was illuminated with a 20 W LED bulb for 120 min under constant stirring at room temperature. Then, the light treated solution was filtered and the absorbance of supernatant (degraded GMF) was measured using UV-Vis spectrophotometer within wavelength window of 200 to 400 nm. To figure out the intermediates/by-products of GMF degradation Liquid Chromatography (LC) (Agilent 6890)-Mass Chromatography (MS) (Agilent 5973) analysis of the supernatant is also carried out. Further, external parameters like (i) presence of anion, and (ii) pH variation is also studied. Scavenger experiment, blank reaction and degradation without catalyst are performed to trace the active species responsible for degradation

and to justify that the degradation over catalyst goes via photocatalytic pathway following our reported articles.

Preparation of working electrodes:

Dropcast method was employed to prepare the working electrodes by taking 2 mg of as prepared materials. Then the catalyst was dispersed in solution of 40 μL nafion and 1.4ml ethanol to form suspension which was sonicated for 7 min forming uniform solution and then was drop casted on 1 cm^2 area of a FTO (Fluorine Doped Tin Oxide). In order to study electrochemical analysis, the catalyst loaded area was dried at room temperature in a vacuum oven whole night.

Table. S1: Calculated compositional ratios of all the synthesized catalysts from XPS.

Catalyst	Cu	In
$Cu_{0.25}In_{0.75}S$ QD	0.24	0.76
$Cu_{0.5}In_{0.5}S$ QD	0.51	0.49
$Cu_{0.75}In_{0.25}S$ QD	0.74	0.26

Table. S2: VB, CB and E_g of all the synthesized catalysts.

Catalyst	VB vs. NHE (V)	CB vs. NHE (V)	E_g (eV)
$Cu_{0.25}In_{0.75}S$ QD	1.18	-0.65	1.84
$Cu_{0.5}In_{0.5}S$ QD	1.27	-0.75	2.03
$Cu_{0.75}In_{0.25}S$ QD	1.22	-1.01	2.24

Table. S3: Comparison Table for degradation of GMF using various photocatalysts.

S.L. No.	Photocatalyst	Reaction condition	Degradation Efficiency	Reference
1	Zn-Co-LDH @biochara	10W UV-B light, 100 min, 30 ppm	92.70%	1
2	Activated carbon@Au/ZnO	250W visible lamp, 35 min, 20 ppm	98.00%	2
3	Pt/Bi_2S_3 nanoflakes	250W and $30W/cm^2$ power density visible light, 25 min, 20 ppm	93.00%	3
4	TiO_2 / H_2O_2	6W UV lamp, 30 min, 100ppm	91.00%	4
5	$ZnFe_2O_4/WO_{3-x}$	150W Xenon lamp, 60 min, 100 ppm	95.00%	5
6	$BiVO_4@Ag@CoAl$ LDH	300W Xenon lamp, 90min, 20 ppm	89.72%	6
7	Carbon doped TiO_2 nanoparticle	LED irradiation, 60 min, Na_2S applied to cease reaction, 50 ppm	74.00%	7
8	$Cu_{0.75}In_{0.25}S$ QD	20 W LED Lamp, 2 h, 10 ppm	95.00%	This Work
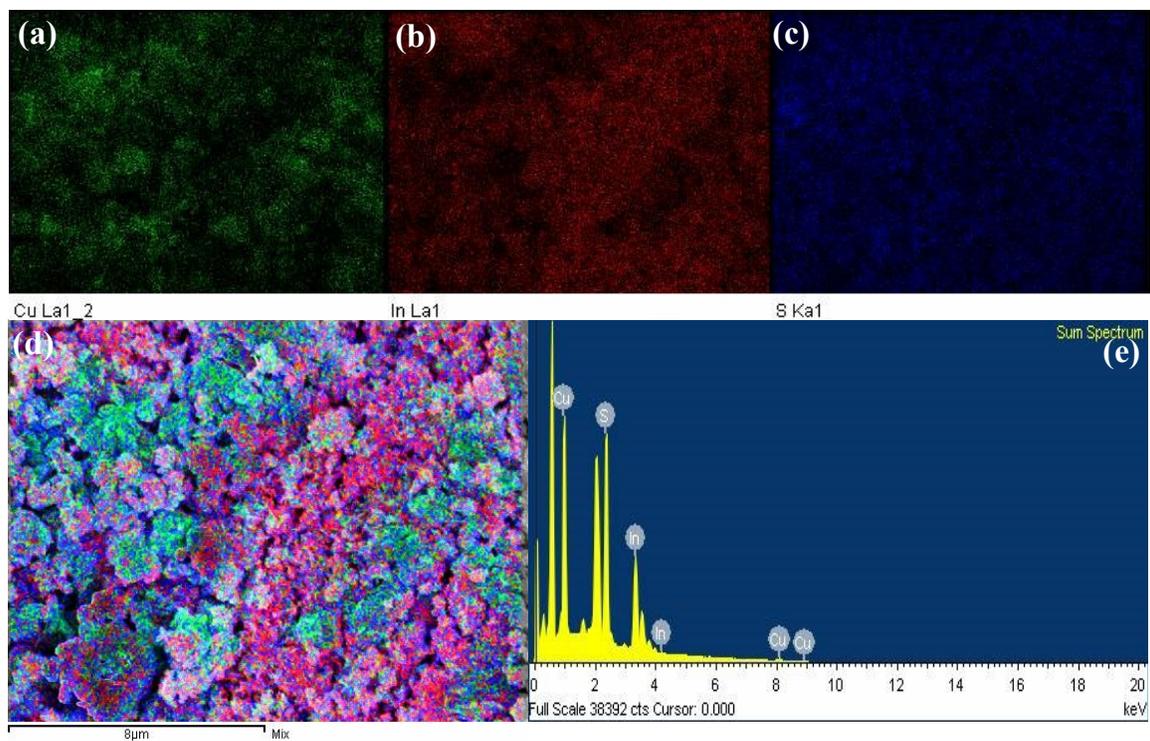
Fig. S1: Color mapping image of (a) Cu, (b) In, (c) S, and (d) $Cu_{0.75}In_{0.25}S$; (e) EDX image of $Cu_{0.75}In_{0.25}S$ QD.
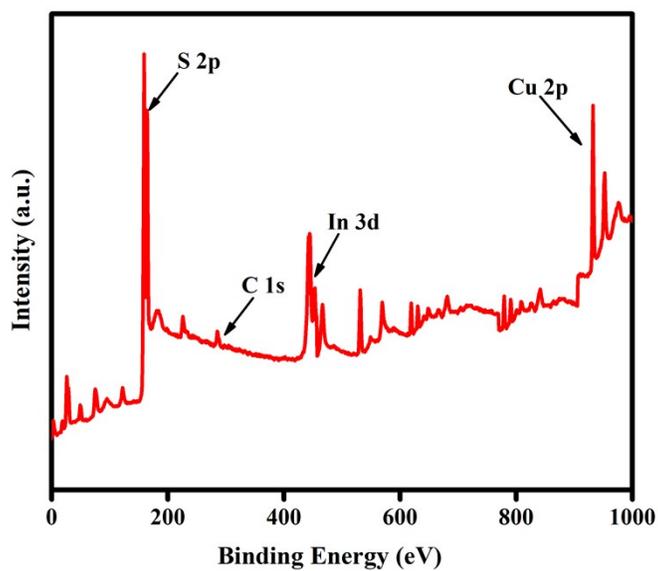
Fig. S2: XPS Survey of $Cu_{0.75}In_{0.25}S$ QD.
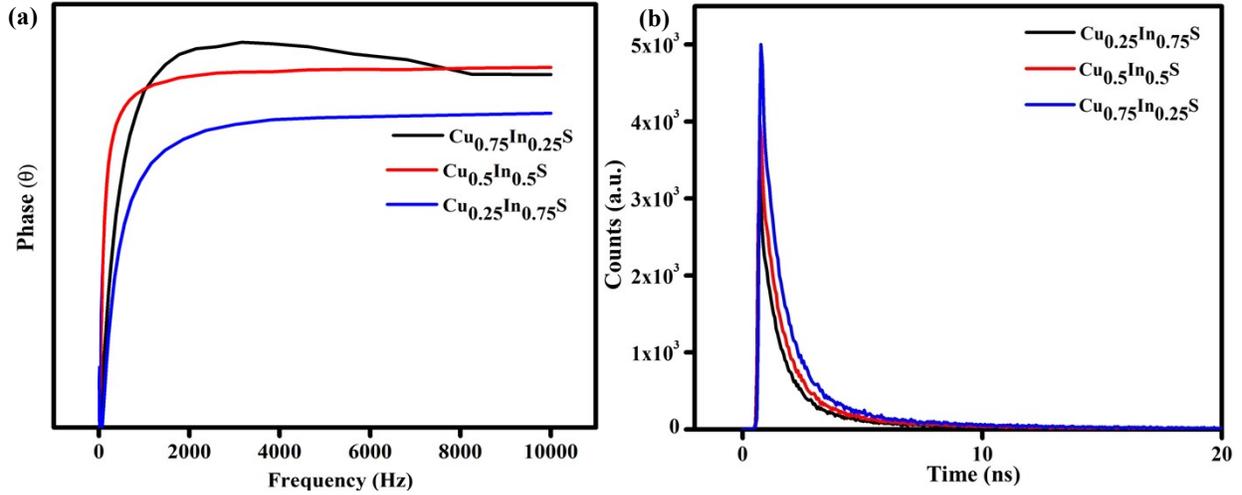
Fig. S3: (a) Bode-phase plot and (b) TR-PL plot of $Cu_{0.25}In_{0.75}S$, $Cu_{0.5}In_{0.5}S$ and $Cu_{0.75}In_{0.25}S$ QDs.

Tri-exponential function for TRPL fitting:[8]

Fit $= A + \alpha_1 \exp\{-t/\tau_1\} + \alpha_2 \exp\{-t/\tau_2\} + \alpha_3 \exp\{-t/\tau_3\}$ -------------- S1

Where A is a constant, α_1, α_2 and α_3 are relative contributions; τ_1, τ_2 and τ_3 are decay times of the compounds. The average life-times (τ_{avg}) of $Cu_{0.25}In_{0.75}S$, $Cu_{0.5}In_{0.5}S$ and $Cu_{0.75}In_{0.25}S$ QDs were estimated by following the equation below:

$$\tau_{avg} = \frac{\alpha_1\tau_1^2 + \alpha_2\tau_2^2 + \alpha_3\tau_3^2}{\alpha_1\tau_1 + \alpha_2\tau_2 + \alpha_3\tau_3}$$ -------------- S2
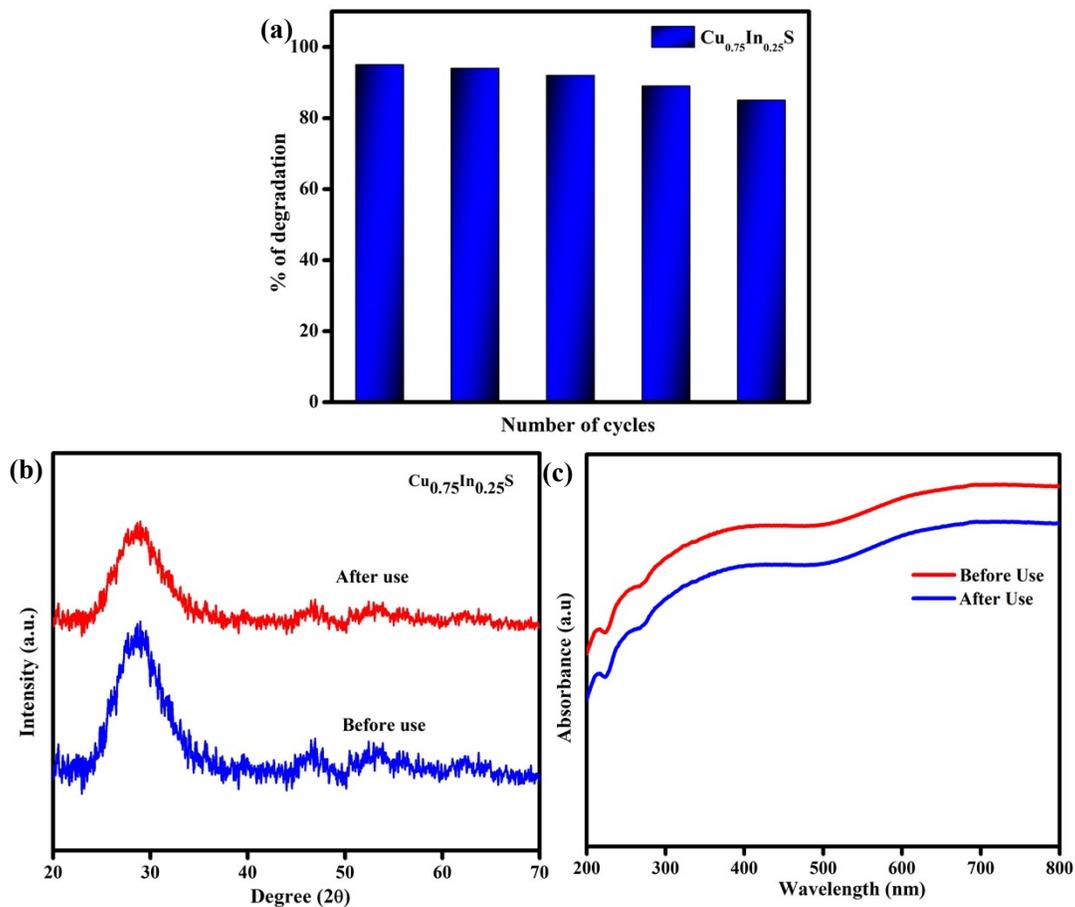
Fig. S4: (a) Degradation plot of $Cu_{0.75}In_{0.25}S$ QD for five successive times; (b) XRD plot, and (b)

UV-Vis absorbance plot of $Cu_{0.75}In_{0.25}S$ QD after and before use.
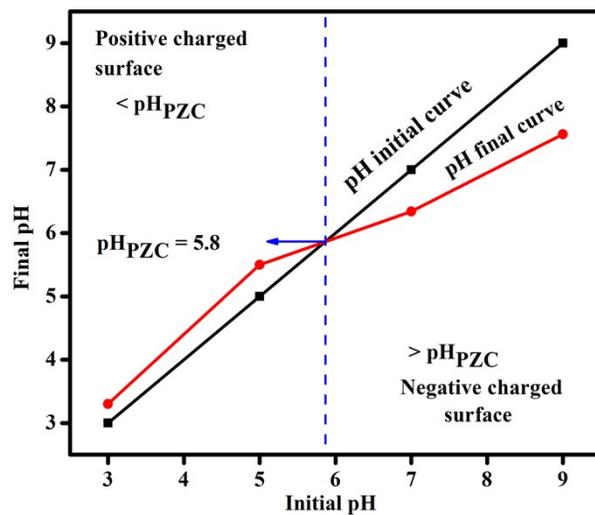
Fig. S5: PZC plot of Cu$_{0.75}$In$_{0.25}$S QD.
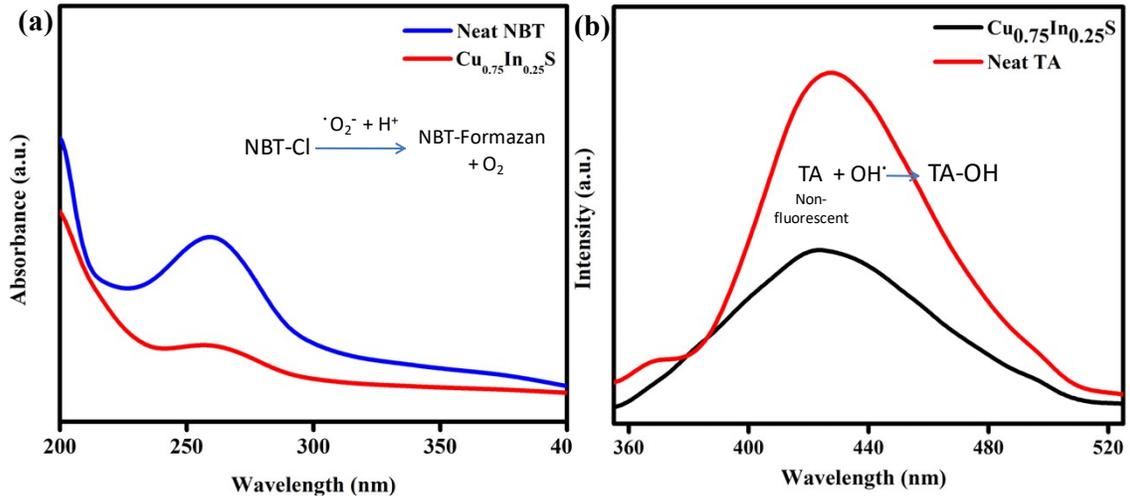
Fig. S6: (a) UV-Vis DRS spectra of neat NBT and Cu$_{0.75}$In$_{0.25}$S QD; and (b) PL-emission spectra

of neat TA and Cu$_{0.75}$In$_{0.25}$S QD.
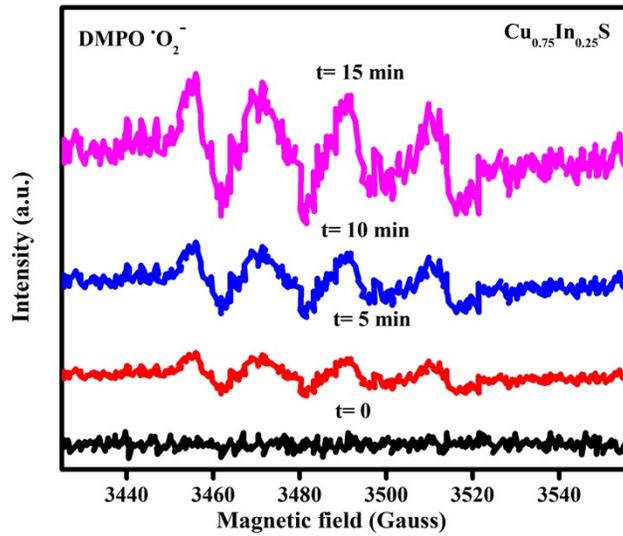
Fig. S7: ESR analysis of Cu$_{0.75}$In$_{0.25}$S QD in different time interval.
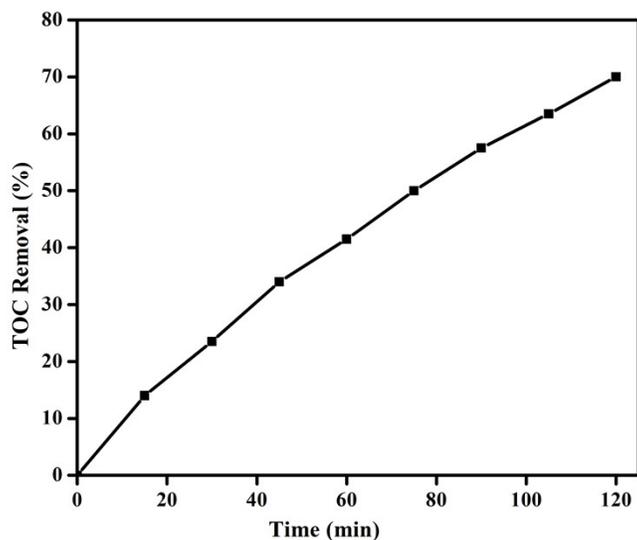
Fig. S8: Mineralization percentage of $Cu_{0.75}In_{0.25}S$ QD.

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