Supporting Information

Tuning of morphological and electronic properties of In_2S_3 nanosheets by cerium ion intercalation for optimizing photocatalytic activity

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Materials and methods

Sample synthesis: A surfactant assisted hydrothermal method has been followed to develop In_2S_3 compounds doped with cerium. 1 mmol 4-hydrated indium (III) nitrate ($In(NO_3)_3 \cdot 4H_2O$) [Sigma Aldrich, 99.99%], 0.01 mmol cerium nitrate hydrate ($Ce(NO_3)_3 \cdot H_2O$) [Sigma Aldrich, 99.99%] and 2 mmol L-Cystein [Sigma Aldrich, 97%] were dissolved in distilled water in a Teflon-lined stainless steel autoclave (50 ml volume). The hydrothermal synthesis was conducted at 160 ^{0}C for 24 hours in an electric oven. After synthesis, the autoclave was cooled to room temperature naturally. Then the sample was taken out and was rinsed thoroughly with distilled water. After repeated centrifugation, the sample was dried at 105 degree C. Thus 1 mol% Ce Doped In_2S_3 was prepared. Samples with different molar percentages of cerium were prepared by varying the amounts of 4-hydrated Indium (III) nitrate ($In(NO_3)_3 \cdot H_2O$) precursor. In this way 0.5 mol%, and 2 mol% Ce doped samples were prepared. A pristine In_2S_3 sample was also prepared without any cerium precursor to examine the effects of cerium dopant. Thus 4 samples were prepared, and they have been referred to as InS, 0.5C-InS, 1C-InS and 2C-InS.

Characterization: The crystalline structure of the developed samples was studied by obtaining X-Ray Diffractograms from a a PANanalytical diffractometer (model: PW-3050/60, UK), using Cu-Kα radiation at 40 kV and 30 mA. The powder samples were spread on a conventional glass sample holder and scanned at a 2θ range of 10° to 70°. To

study the surface morpohology, Field Emission Scanning Electron Microscope (FESEM) images of the samples were obtained from a FESEM-JEOL scanning electron microscope. The FESEM instrument was equipped with Energy dispersive X-ray (EDX) spectroscopy (Oxford, UK) to analyze atomic percentages. The nanoparticle size, orientation and lattice fringes were further studied by obtaining (High resolution Transmission Electron Microscope) HRTEM images from a JEM-2100 HRTEM (JEOL, Japan) microscope having point to point resolution of 0.194 nm and lattice resolution of 0.14 nm. Brunauer-Emmett-Teller (BET) surface areas and pore dimensions were determined from Quantrachrome (AUTOSORB1, UK) instrument by adsorption of nitrogen at 77 K after degassing at 573 K for 2 hours under high vacuum. For obtaining Fourier transform infrared spectra (FTIR) of the developed samples, the samples were first made into pellets using KBr as a binder. The FTIR spectra were obtained from a Perkin Elmer Spectrum 100 instrument. The optical properties of the samples were studied by obtaining their UV Vis absorbance spectra from a Perkin Elmer lambda 25 spectrophotometer. This spectrophotometer was also used to measure the absorbance of ciprofloxacin at a wavelength of 271 nm. Photoluminescence (PL) spectrum of the samples were recorded on a Hamamatsu R928 photomultiplier detector with He–Cd laser as the excitation source operating at 325 nm with an output power of 50 mW. The chemical states of the samples were analyzed by obtaining X-Ray Photoelectron Spectra (XPS) spectra from a ULVACPHI 5000 versaprobe II instrument with Al Kα electrode.

Photocatalytic experiment setup: The photocatalytic activity of the synthesized samples was tested on a solution of pharmaceutical drug ciprofloxacin in presence of visible light. A 20 ppm solution containing 0.6 g/L of the prepared catalysts was ultrasonicated to disperse the catalysts. This was then poured into in a 500 ml cylindrical glass reactor equipped with a CFL lamp (l>400 nm, Philips, India with a cutoff filter) which was positioned inside a centrally pivoted glass tube in the reactor, to serve as the visible light source. The reactor had been attached to a compressor which supplied air at 0.5 LPM to agitate the reaction mixture contained in the annular space. The light was turned off for the first 30 minutes, to let the reaction attain adsorption desorption equilibrium. Then the light was turned on to start the photocatalytic degradation process. To measure the change in ciprofloxacin

concentration with time, a 5 ml sample was collected at every interval of 15 minutes followed by separation of the catalysts by centrifuging at 10000 pm. Then the absorbances of the samples were checked in a UV Vis spectrophotometer at wavelength of 272 nm, which is the λ_{max} for ciprofloxacin. This was followed by determination of concentrations of the samples from a previously prepared absorbance vs concentration calibration curve.

Photoelectrochemical setup: Transient photocurrent responses and Electrochemical Impedance Spectra were obtained from a conventional 3 electrode setup connected to a CHI643B workstation using 1.0 M Na_2SO_4 as electrolyte. The working electrode was prepared by depositing the samples on ITO plates with 1 cm^2 surface area, followed by drying. The samples were ultrasonicated in a solution of 9 ml ethanol and 1 ml nafion prior to deposition. Ag/AgCl was used as reference electrode and Pt wire was chosen as counter electrode respectively. For obtaining the photocurrent responses, a 300 W Xe lamp fitted with a cutoff channel ($\lambda > 400$ nm) was used as the light source.

Computational methodology : To theoretically establish the electronic configurations of the doped and pristine In_2S_3 structures, first principals calculations were employed using Quantum ESPRESSO package. The Perdew–Burke–Ernzerhof (PBE) functional generalized gradient approximation (GGA) was employed as exchange correlation for geometric optimization. The GGA + U approach was employed to overcome the shortcomings of the GGA approach and obtain reasonably accurate electronic configurations. A value of 5 eV was chosen for the Hubbard parameter U since this value has shown accurate results in previous reports on DFT calculations on In_2S_3.[1] To describe the relations between the ionic core and valence electrons, ultrasoft pseudopotentials of the involved atoms were considered with a valence electron configuration of $4d^{10}5s^24p^1$ for In, $3s^23p^4$ for S and $4f^15d^16s^2$ for Ce respectively. The conventional unit cell of 16 formula units (80 atoms) was constructed on a 2x2x1 Monkhorst–Pack k-point grid representing the irreducible Brillouin zone. The relaxation of the atomic coordinates was achieved using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme as the minimization algorithm with an optimization threshold of 0.001 Ry/Bohr. Upon obtaining optimized crystal geometry, Self-Consistent Field (SCF) convergence was performed with a plane wave energy cutoff of 30 Ry for wavefunction and 300 Ry for charge. The SCF convergence was followed by

DOS calculations to predict the electronic configurations of the pristine In_2S_3 and doped In_2S_3 samples.

Table S1. Calculated CB and VB edge potentials of the synthesized samples

Sample	Energy gap (eV)	Conduction band (eV)	Valence band (eV)
InS	2.48	-1.03	1.45
0.5C-InS	2.34	-0.96	1.38
1C-InS	2.18	-0.88	1.3
2C-InS	2.00	-0.79	1.21

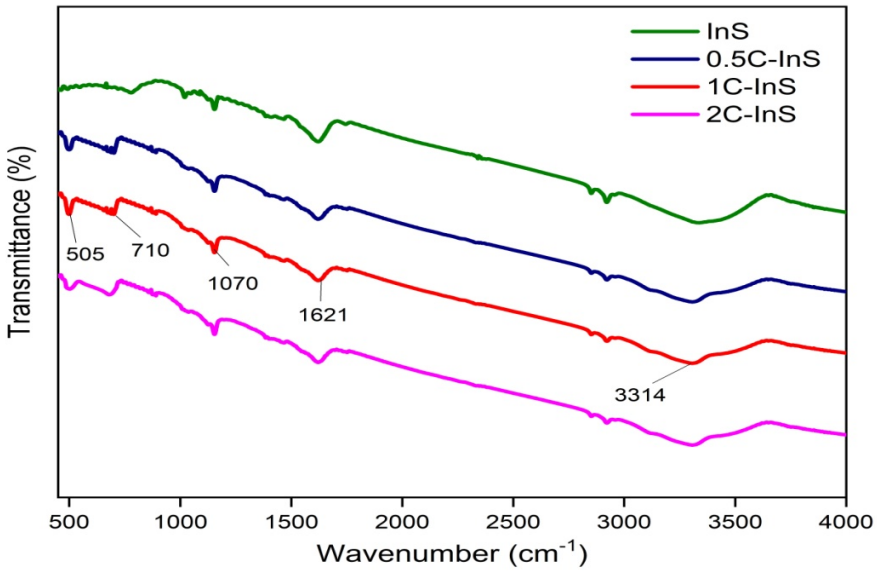

Fig. S1 FTIR Spectra of InS and 1C-InS samples

Table S2. Atomic percentages in prepared samples determined by EDX analysis

Sample	S	In	Ce
InS	57.41	42.59	0
0.5C-InS	57.38	42.18	0.44
1C-InS	57.33	41.75	0.92
2C-InS	57.32	41.20	1.48

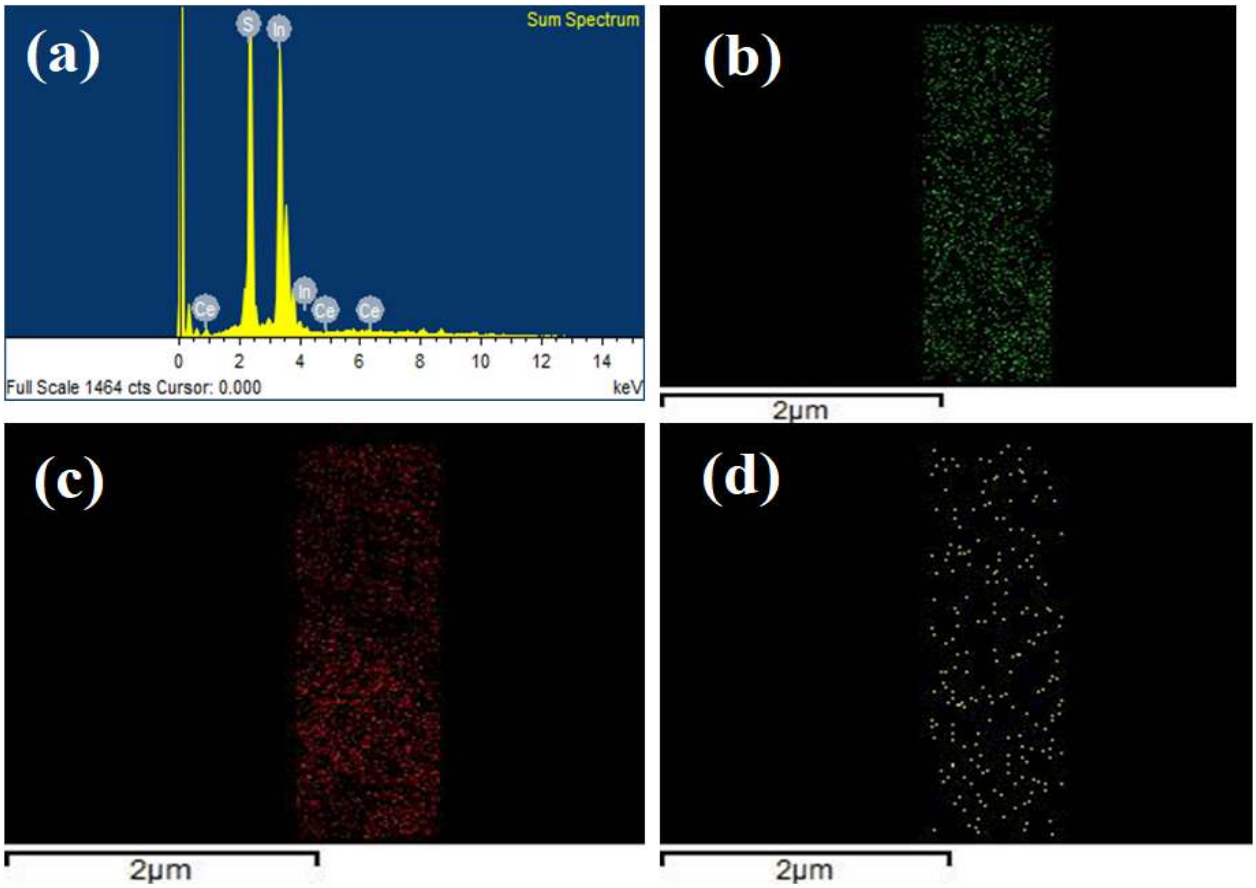

Fig. S2 (a) EDX spectrum of 1C-InS (b) Elemental mapping of In (c) S and (d) Ce in 1C-InS

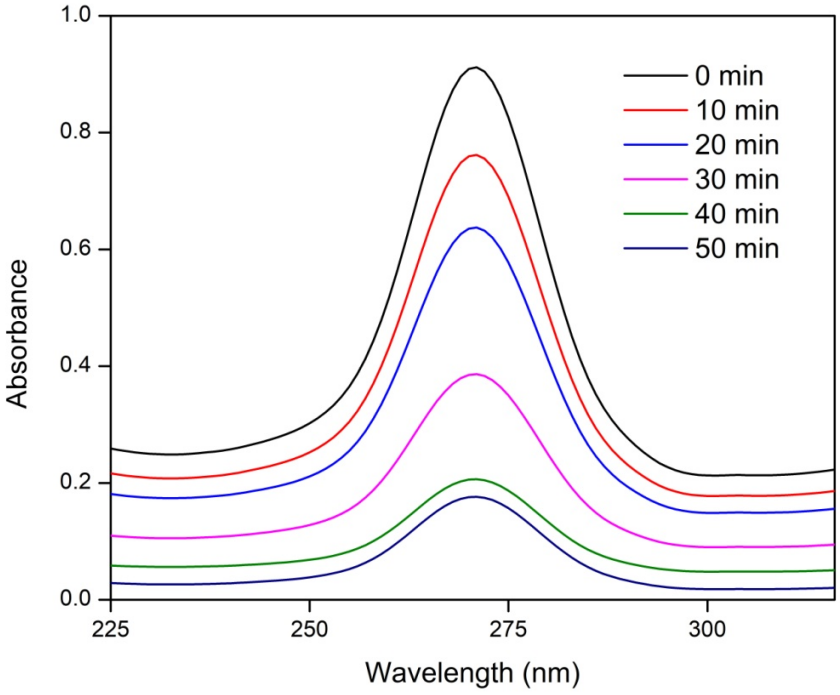

Fig. S3 Photodegradation of ciprofloxacin over time

1. Z. Zhao, Y. Cao, J. Yi, X. He, C. Ma, and J. Qiu, ChemPhysChem 2012, 13, 1551 – 1556