Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Visible light-induced hydrogen generation using colloidal $(ZnS)_{0.4}(AgInS_2)_{0.6}$ nanocrystals capped by S^{2-} ions†

Metikoti Jagadeeswararao,[a] Sunita Dey,[b] Angshuman Nag *[a] and C. N. R. Rao[b]

[a] *Department of Chemistry, Indian Institute of Science Education and Research (IISER), Pune, India – 411008.*

E-mail: angshuman@iiserpune.ac.in

[b] *Chemistry and Physics of Materials Unit, CSIR Centre of Excellence in Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, P.O., Bangalore-560064, India.*

Electronic Supplementary Information (ESI)

Chemicals:

Silver (I) nitrate (99%, Aldrich), zinc (II) nitrate hexahydrate (98%, Aldrich), indium (III) nitrate hexahydrate (99.99%, Aldrich), sodium diethyl dithiocarbamate trihydrate (Aldrich), oleylamine (70%, Aldrich), ammonium sulfide (40-48 wt% solution in water, Aldrich) formamide (99.0%, Fluka analytical), acetonitrile (dry, S D Fine chem. Ltd.), methanol (99.5%, Rankem), toluene (99.5%, Rankem).

Synthesis of Oleylamine Capped $(ZnS)_{0.4}(AgInS2)_{0.6}$ Nanocrystals (NCs):

$(ZnS)_{0.4}(AgInS2)_{0.6}$ NCs were synthesized by following ref[1] using single molecular precursor $(AgIn)_xZn_{2(1-x)}(S_2CN(C2H5)_2)_4$, where x = 0.75. The molecular precursor was prepared by mixing 50 mL aqueous solution of 0.025 mol/L metal ions ($AgNO_3$: $InNO_3$: $Zn(NO_3)_2$ = x : x : 2(1-x)) with 50 mL aqueous solution of sodium diethyl dithiocarbamate trihydrate (0.05 mol/L). The resultant precipitate was washed several times with methanol and water mixture and dried under vacuum at room temperature. 50 mg of precursor powder has been taken in a three neck round bottom flask and heated at 180 °C under Ar atmosphere for 30 minutes followed by injecting 3.0 mL of oleylamine and the reaction was continued for another 3 minutes. The obtained suspension was centrifuged at 2000 rpm for 2 minutes and the supernatant was collected by removing the larger particles. Sufficient amount of methanol was added to the supernatant containing NCs followed by centrifugation at the speed of 5000 rpm for 5min. The obtained NC precipitate can be redispersed in non-polar solvents like toluene and chloroform for further processing.

Ligand Exchange of Oleylamine Capped $(ZnS)_{0.4}(AgInS2)_{0.6}$ NCs using $(NH_4)_2S$:

ligand exchange reaction was carried out air condition at room temperature. As-prepared oleylamine capped $(ZnS)_{0.4}(AgInS2)_{0.6}$ NCs were redispersed in 3 mL toluene in a glass vial. 3 mL formamide and 130-150 µL aqueous $(NH_4)_2S$ were added to the NC dispersion and magnetically stirred for 5 min. NCs were transferred into formamide phase leaving a colorless toluene phase. The toluene phase was removed and followed addition of pure toluene and stirring. The pure toluene removes any remaining organic molecules in FA phase, and this washing was repeated thrice. The resulted NCs in formamide phase were precipitated by centrifugation after adding acetonitrile as a non-solvent. The obtained precipitate can be re-dispersed in formamide and water for studying different properties.

Characterization:

UV-visible absorption and photoluminescence (PL) spectra of $(ZnS)_{0.4}(AgInS_2)_{0.6}$ NCs were recorded using a Perkin Elmer, Lambda-45 UV/Vis spectrometer and FluoroMax-4 spectrofluoremeter (HORIBA scientific), respectively. PL decay dynamics were measured using time correlated single photon counting (TCSPC) technique set up from Horiba JobinYvon at an excitation energy of 459 nm (2.70 eV). Fourier-transform infrared (FTIR) spectra were acquired in the transmission mode using a NICOLET 6700 FTIR spectrometer (Thermo scientific). Powder XRD data were collected by using Bruker D8 Advance Powder XRD diffractometer using Cu Kα radiation (λ = 1.54Å). Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 2100F microscope operated at 200 kV.

Photocatalytic reactions: Photocatalytic H_2 evolution experiments were conducted in a stoppered quartz vessel. The catalyst (10 mg) was dispersed in 50 ml of aqueous solution along with 0.25 (M) Na_2SO_3 and 0.35 (M) Na_2S by ultrasonication. The vessel was purged thoroughly with N_2 to remove all the gases before irradiation. Samples were irradiated under 400 W Xe lamp (Newport 6280) equipped with water filter for IR removal and a 400 nm cutoff filter for blocking the UV light. The amount of H_2 evolved was quantified using gas chromatography (Perkin Elmer, Clarus 580 GC) equipped with TCD detector by manually injecting 1 ml of evolved gases from headspace of the quartz vessel over a constant period of time. The Turn over frequency (TOF) and turn over number (TON) was calculated as mentioned below,

$$\text{TOF } (\text{h}^{-1}) = \frac{\text{moles of } H_2 \text{ evolved per hour}}{\text{moles of active catalysed used}}$$

$$\text{TON } (\text{h}^{-1}) = \frac{\text{moles of hydrogen evolved (fixed time)}}{\text{moles of active catalysed used}}$$

Apparent quantum yield (AQY) is defined by the following equation,

$$\text{A.Q.Y. } (\%) = \frac{\text{The number of evolved } H_2 \text{molecules} \times 2}{\text{The number of incident photons}} \times 100$$

Absorption of light separates the e-h pair in photocatalyst. e is being utilized to reduce the water whereas hole is move towards the sacrificial agent like sulfites and sulfide ions. Photocatalytic reactions are reported to proceed according to the following equations,[11, 15]

$photocatalyst + h\nu \rightarrow e^{-}(CB) + h^{+}(VB)$-------------(1)

$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$-----------(2)

$SO_3^{2-} + H_2O + 2h^{+} \rightarrow SO_4^{2-} + 2H^{+}$-----(3)

$2S^{2-} + 2h^{+} \rightarrow S_2^{2-}$--------(4)

$S_2^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S^{2-}$-----(5)

$SO_3^{2-} + S^{2-} + 2h^{+} \rightarrow S_2O_3^{2-}$----(6)

Table S1: Best-Fit parameters of PL decay profiles of $(ZnS)_{0.4}(AgInS_2)_{0.6}$ NCs capped with different ligands for the corresponding data shown in Figure 1f of the main manuscript. A tri-exponential decay, $I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) + a_3 \exp(-t/\tau_3)$ was used where τ_i correspond to ith lifetime component, and a_i is contribution of ith lifetime.

Capping ligand	τ_1 (ns)	a_1 (%)	τ_2 (ns)	a_2 (%)	τ_3 (ns)	a_3 (%)
Organic Capped	1.7	32	32	32	242	37
S^{2-} Capped	1.8	49	27	34	236	17

Table S2: Activity of H_2 evolution and Turn over frequency (TOF) obtained during three successive cycles for $(ZnS)_{0.4}(AgInS_2)_{0.6}$ NC photocatalyst

Cycles	Activity(mmol/g/h)	TOF (h^{-1})
1	4.99	1.05
2	4.23	0.89
3	3.14	0.66

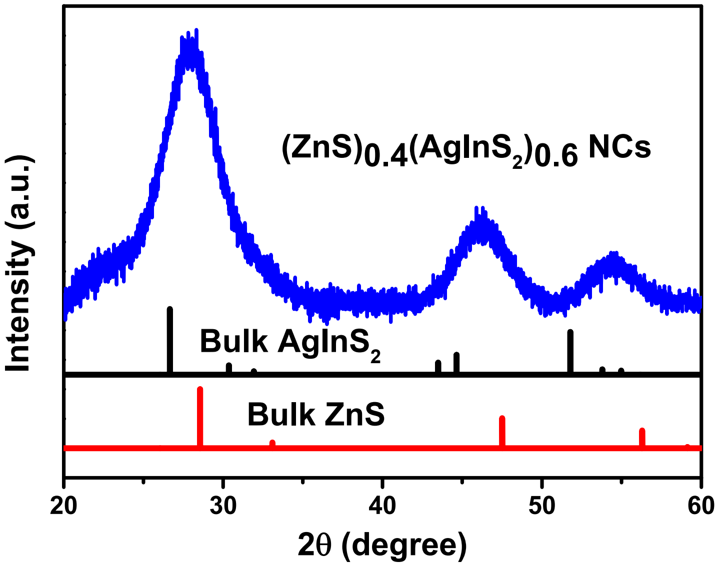

Figure S1: Powder XRD pattern of $(ZnS)_{0.4}(AgInS_2)_{0.6}$ NCs along with standard patterns for bulk $AgInS_2$ and ZnS.

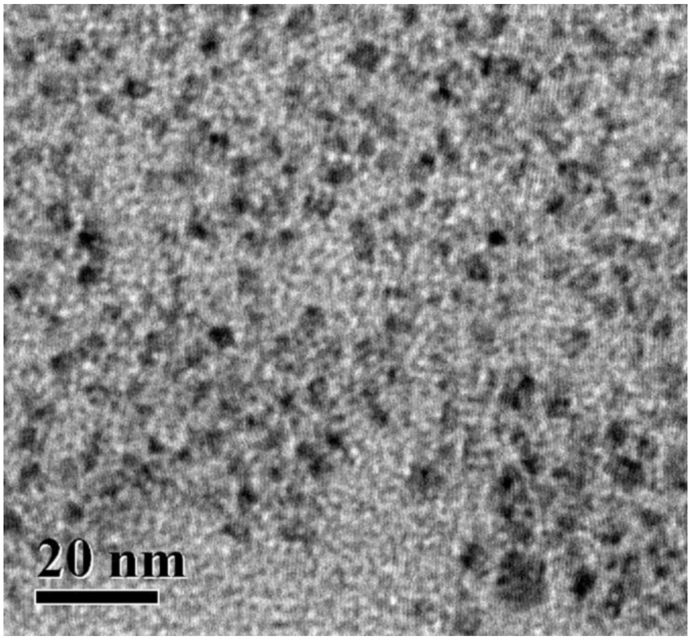

Figure S2: TEM image of colloidal $(ZnS)_{0.4}(AgInS_2)_{0.6}$ NCs.

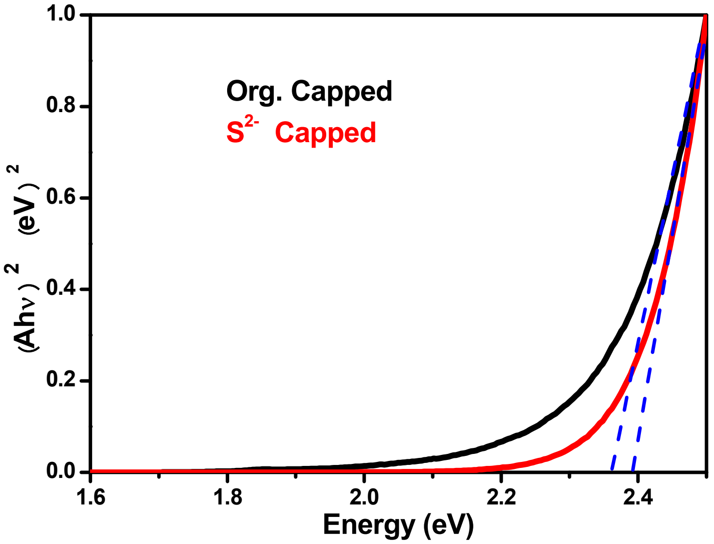

Figure S3: UV-visible absorption spectra plotted as $(Ahv)^2$ versus energy for colloidal organic capped and S^{2-} capped $(ZnS)_{0.4}(AgInS_2)_{0.6}$ NCs respectively. Blue dash lines show the extrapolation of the linear portion of the plot to $(Ahv)^2 = 0$.

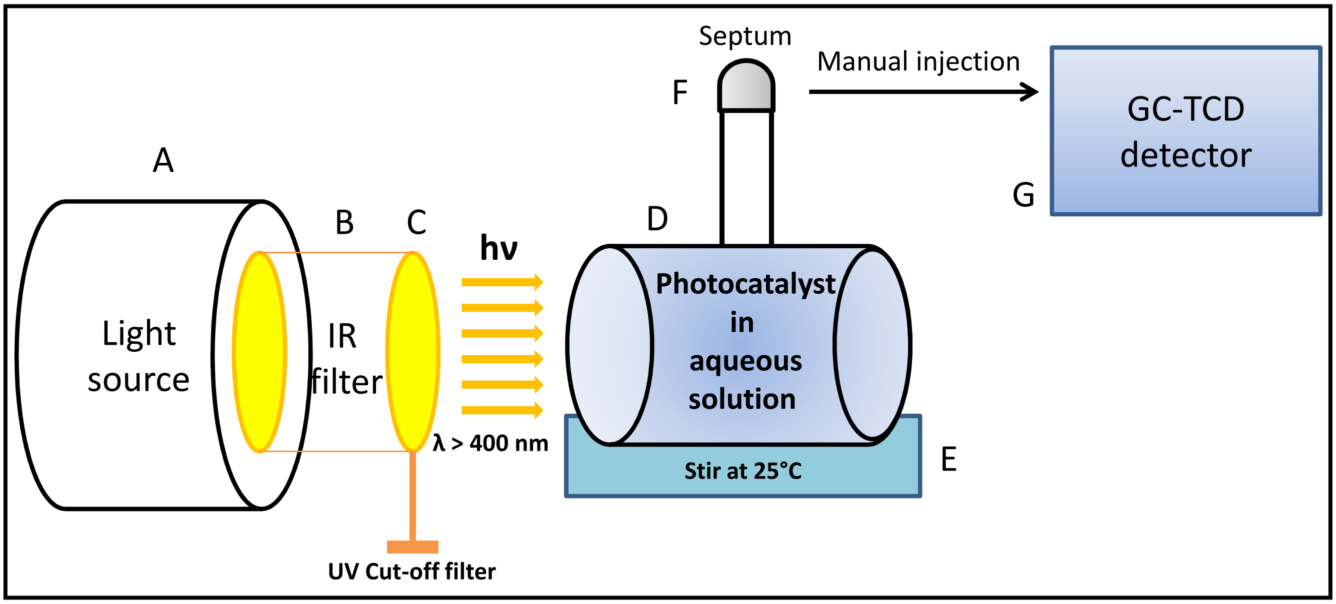

Figure S4: Schematic representation of experimental setup for photocatalytic H_2 evolution from water. A: Xe lamp (working at 400 W); B: IR cut-off filter; C: UV cut-off filter (Newport) to allow λ> 400 nm; D: reaction vessel containing aqueous solution of photocatalyst; E: stirring at room temperature; F: Septum to keep the reaction vessel air-tight; G: GC equipped with TCD. Distance between C and the exposed face of reaction vessel is maintained at 15 cm.

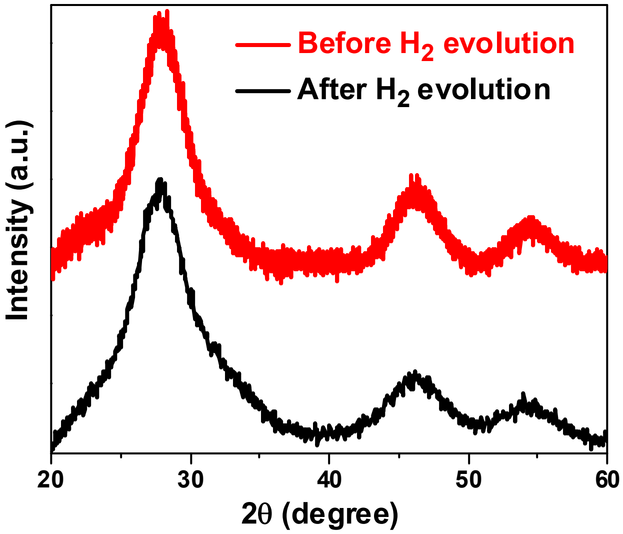

Figure S5: Comparison of powder XRD pattern of as synthesized oleylamine capped $(ZnS)_{0.4}(AgInS_2)_{0.6}$ NCs with that of S^{2-} capped NCs after photocatalytic H_2 evolution reaction. These XRD patterns show that the structure and composition of NCs remain intact after both surface modification and catalysis reaction.

References:

1. T. Torimoto, T. Adachi, K. Okazaki, M. Sakuraoka, T. Shibayama, B. Ohtani, A. Kudo and S. Kuwabata, *J. Am. Chem. Soc.*, 2007, **129**, 12388.