

SUPPORTING INFORMATION

Hydrazine as a hydrogen carrier in the photocatalytic generation of H₂ using CdS quantum dots

Manoj K. Jana^[a], Uttam Gupta^[b] and C. N. R. Rao^{*[a,b]}

[a] New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O, Bangalore-560064 (India)

[b] Chemistry and Physics Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research , Bangalore-560064 (India)

***Email: cnrrao@jncasr.ac.in**

Experimental Section

Synthesis of CdS nanoparticles and QDs: CdS nanoparticles were synthesized by drop wise addition of 50 mM aqueous Na₂S into 50 mM aqueous Cd(CH₃COO)₂ under stirring. Precipitate was washed successively with water and ethanol and dried at 60°C for 12 hr. We have obtained CdS QDs as follows. 1M TOP-S stock solution was prepared by dissolving elemental sulfur in TOP solvent with stirring at room temperature (RT). A mixture containing 128 mg of CdO, 8 ml of octadecene and 0.8 ml of oleic acid was degassed under evacuation in a 50 ml RBF for 60 min at 120°C after which the temperature was increased and maintained at 220°C under N₂ flow. After a clear transparent solution of cadmium oleate was formed, 0.5 ml of 1M TOP-S solution was injected under N₂ flow. Aliquots were taken at different intervals for monitoring the growth of nanocrystals through photoluminescence and UV-Vis absorption spectroscopy. After nanocrystals reached the desired size, the reaction mixture was quenched in water kept at RT. The nanocrystals were purified by washing the contents thrice with 30 ml of hexane-methanol mixture (1:1 by vol.), coagulated with excess ethanol and centrifuged to obtain a pellet. The pellet was dissolved in 6 ml of toluene and stored in dark. CdS QDs of 4.2 nm diameter were chosen for the photocatalytic experiments. The size was inferred from the first exciton peak position ($\lambda = 423$ nm) using a sizing curve for CdS QDs established by Peng and co-workers.¹⁸

Ligand exchange of CdS QDs: Sulfide-capped CdS QDs were prepared by adding 2 ml of 25 mg/ml solution of Na₂S in formamide to 2 ml of QD stock solution in a 15 ml vial and stirred for 30 min under dark condition. After the completion of ligand exchange, the contents of the vial were centrifuged at 1500 rpm for 3 min. After separating both the phases, 4 ml of acetonitrile was added to the formamide phase and centrifuged to precipitate the QDs. The precipitate was

finally dispersed in 5 ml of N₂-degassed millipore water and stored in dark. To obtain CdS QDs capped with mercaptopropionic acid (MPA), the above procedure was repeated with 2 ml of formamide solution of 50 µl of MPA and 80 mg of NaOH.

Characterization: Powder X-ray pattern was recorded on Bruker D8 Advance diffractometer using Cu K α source ($\lambda = 1.541 \text{ \AA}$). Transmission electron microscope (TEM) images were obtained by using a JEOL TEM 3010 instrument fitted with a Gatan CCD camera operating at an accelerating voltage of 300 kV. Absorption spectra were recorded on Agilent-8453 UV-Vis spectrophotometer. Raman spectra were recorded on a Jobin Yvon LabRam HR spectrometer using Ar-laser (514.5 nm) excitation in a back-scattering configuration. The concentrations of CdS QDs used in the photocatalytic experiments were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using Perkin Elmer Optima 7000 DV instrument. Samples were digested in 1:1 HNO₃: HCl mixture and diluted to 10 ml solutions with millipore water before the analysis.

Photocatalytic studies: Photocatalytic activities of CdS nanoparticles and CdS QDs capped with sulfide ligands (CdS/S²⁻) and mercaptopropionic acid (CdS-MPA) were studied using 1 % or 0.2 % (v/v) N₂H₄.H₂O as sacrificial donor. CdS NCs (5 mg) or CdS QDs (0.21 mM or 0.42 mM) were dispersed in 50 ml of aqueous N₂H₄.H₂O (pH of the medium is maintained between 7 and 10) taken in a custom-built quartz flask with flat surfaces being exposed to the light. The solution was degassed with N₂ for 15 min before initiating the photocatalytic reaction. The control experiments were done under similar conditions (see Table. S1, ESI). The solution was illuminated with 400 W Xenon arc lamp (New Port-6280) fitted with infrared and 399 nm cut-off filters. The H₂ gas evolved was detected and quantified using Perkin Elmer-Clarus 580 gas chromatograph equipped with thermal conductivity detector by manually injecting 2 ml of

sample head space at regular intervals of time. Cycling studies were performed by degassing the flask with N₂ for 15 min at regular intervals. Turn over frequency (TOF) was calculated as below:

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

Electrochemical studies: Working electrodes were fabricated by drop casting an aqueous dispersion of CdS/S²⁻ QDs on ITO substrates pre-cleaned by ultrasonication in acetone, isopropanol and deionized water successively and drying overnight in an evacuated desiccator under dark condition. Electrochemical dark scans were performed on ITO: CdS QD films in 1M KCl and 0.1 M Na₂SO₃ aqueous solution at pH 9.7, 12.1 and 12.9 at a scan rate of 10 mVs⁻¹. pH was adjusted by the addition of 1M NaOH.

Table. S1 Summary of control experiments

Conditions	Observations	Reactant solution	Remarks
Aqueous N ₂ H ₄ (Under illumination)	No H ₂ evolution	1% (v/v) N ₂ H ₄ .H ₂ O in water	---
Aqueous N ₂ H ₄ + CdS catalyst (In dark for 12 hr)	No H ₂ evolution	1% (v/v) N ₂ H ₄ .H ₂ O in water	Stable dispersion
Aqueous N ₂ H ₄ + CdS catalyst (In dark at 50°C for 6 hr)	Trace amount of H ₂ in first hour only	1% (v/v) N ₂ H ₄ .H ₂ O in water	Stable dispersion
Aqueous N ₂ H ₄ + CdS catalyst (under illumination for 40 hr)	Continuous H ₂ evolution	1% (v/v) N ₂ H ₄ .H ₂ O in water	Stable dispersion

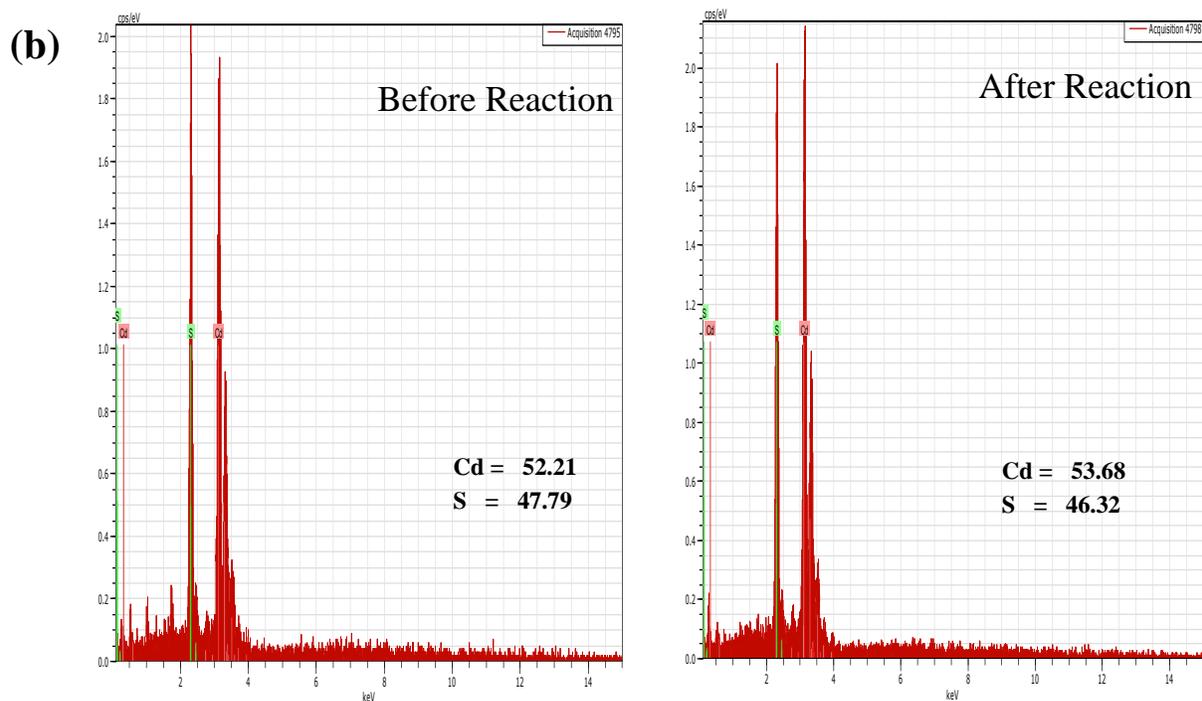
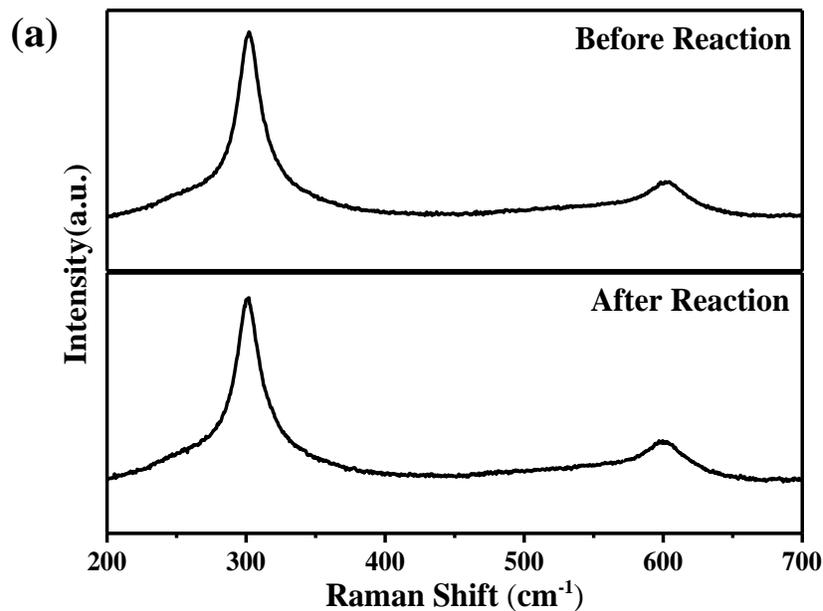


Fig. S1 a) The Raman spectra of CdS nanoparticles before and after HER evolution in presence of hydrazine after 40 hours and b) EDS spectra CdS nanoparticles before and after HER evolution in presence of hydrazine after 40 hours.

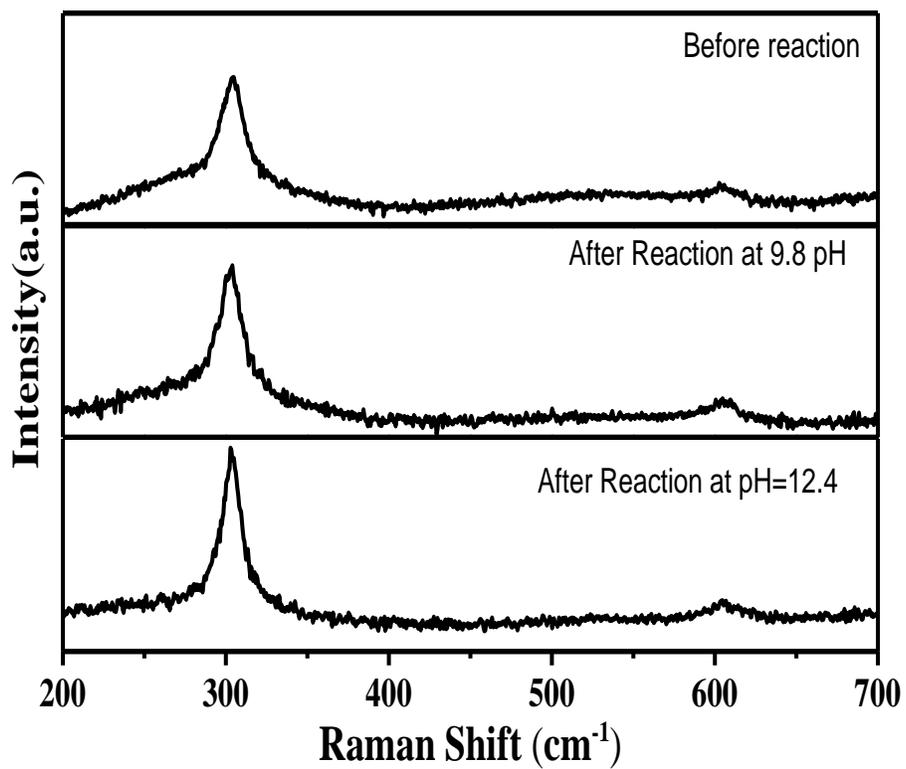


Fig. S2 The Raman spectra of CdS-S²⁻ QDs before and after HER evolution in the presence of hydrazine at pH 9.8 and 12.4

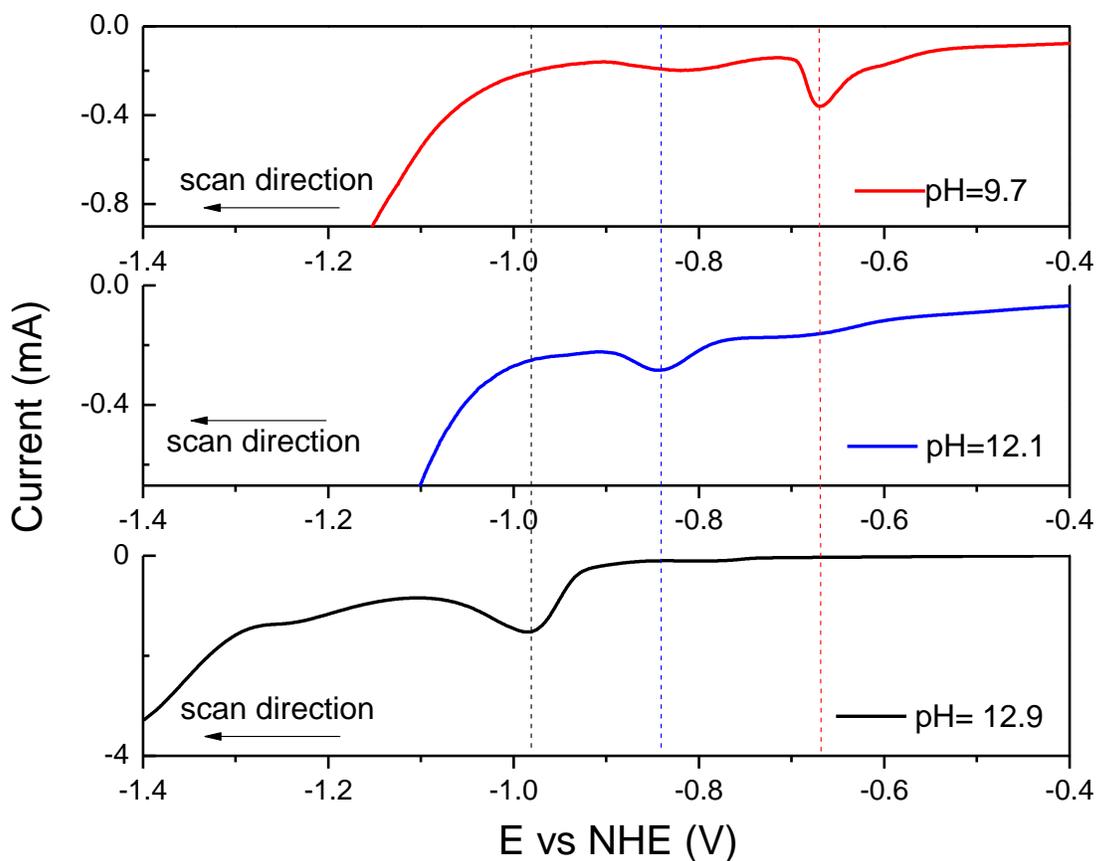


Fig. S3 Dark electrochemical scans of CdS-S²⁻ QDs: ITO in 1M KCl and 0.1 M Na₂SO₃ aqueous electrolyte at pH 9.7, 12.17 and 12.9 recorded at a scan rate of 10mVs⁻¹. Dotted lines intersect the minima of lattice Cd²⁺ reduction peaks at different pH.