Supporting Information for

Dependence of electron recombination time and light to electricity conversion efficiency on shape of nanocrystal light sensitizer

Sayantan Mazumdar[a] and Aninda J. Bhattacharyya*[a]

[a] *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India. Fax: +91 80 23601310; Tel: +91 80 22932616; E-mail: aninda_jb@sscu.iisc.ernet.in*

Materials and Methods

Synthesis of CdS nanocrystals with various shapes: Cadmium acetate, $Cd(CH_3COO)_2.2H_2O$ and thioacetamide, CH_3CSNH_2have been taken in 7:10 ratio in a 50 ml Teflon container. Solvent mixtures (structure directing agents) with various ratios of ethylene glycol (EG) and ethylenediamine (EN) have been added to it while kept in an ice-bath and has been stirred for few minutes. They are then kept in stainless steel autoclaves and the reaction was then carried out at 180^0C, 4 hours. Later the product was collected by centrifugation, washed by water and ethanol for several times and dried at 70^0C in vacuum to get yellow powders which were subjected to further characterization and experiments.

*Preparation of TiO_2layers:*TTIP (Titanium tetra-isopropoxide) has been dissolved in slightly acidic iso-propanol-water mixture and it's been stirred for 24 hours resulting in a clear solution. FTO-glasses has been dipped in it and heated at 120^0 C to get a transparent and compact layer of $TiO_{2.}$ TTIP added in 6 N HCl soln. and stirred for 30 minutes in a ice-bath. Then 15 ml of it has been put in a Teflon container along with the FTO-glasses with compact layer and a hydrothermal reaction has been carried out in autoclave at 150^0 C for 4 hours to grow vertically aligned TiO_2– nanorods on the FTO-glasses. Again, it has been put in a 0.4 N $TiCl_4$ solution at 100^0 C for an hour to get a scattering layer of $TiO_{2.}$ After that the electrodes have been annealed at 450^0 C for an hour resulting a composite TiO_2film with ~15μm thickness.

Sensitization: The electrodes have been put in a solution of Thiolglycolic acid (TGA) in acetonitrile which acts as a bilinker molecule for 12 hours to attach the CdS nanocrystals with $TiO_{2.}$ After that they have been immersed in dispersions of various CdS nanopowders in toluene for 48 hours. The CdS-TiO_2 was additionally co-sensitized by cadmium selenide (CdSe) nanoparticles to shift absorption onset towards longer wavelengths[8] and by zinc sulfide (ZnS)[3] for optimization of the trap states. Both CdSe and ZnS were coated using SILAR method.In brief, the electrodes were dipped in a 0.03 M cadmium nitrate solution (Cd^{2+} source) and a 0.03 M selenium di-oxide solution with 0.06 M sodium borohydride (Se^{2-} source) in cycle, 30s cycles in each cases, total 6 cycles. It's been carried out in Nitrogen-atmosphere. Both solutions were in ethanol and in the second solution, sodium borohydride reduced selenium dioxide to produce selenide-ion. ZnS coating has also been done by SILAR where 0.2 M zinc acetate and 0.2 M sodium sulphide, both in aqueos solution have been served as the Zn^{2+} and S^{2-} sources respectively. 2 cycles of 1miniute each have been carried out.

Solar Cell Fabrication: Scotch-tape (thickness ~ 50 μm) has been put on the sides of the photoanode which acted as the spacer. A drop of sodium polysulphide electrolyte (1 M Na_2S, 1 M S) was used as the electrolyte and Cu_2S electrode obtained from a piece of brass has been served as the dark cathode. A sandwich type cell has been made of typically 5 mm X 5 mm of active area and further characterizations have been carried out.

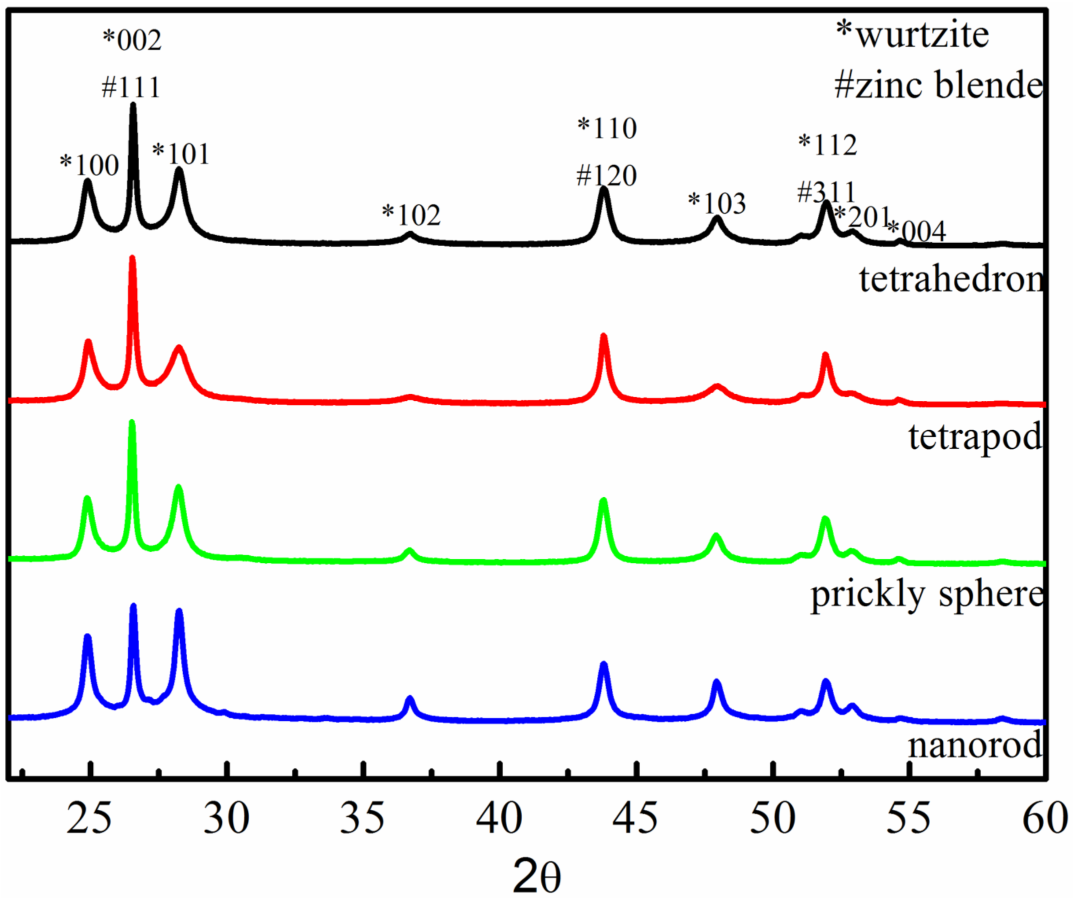

Figure S1: Powder XRD patterns of CdS samples with different morphologies

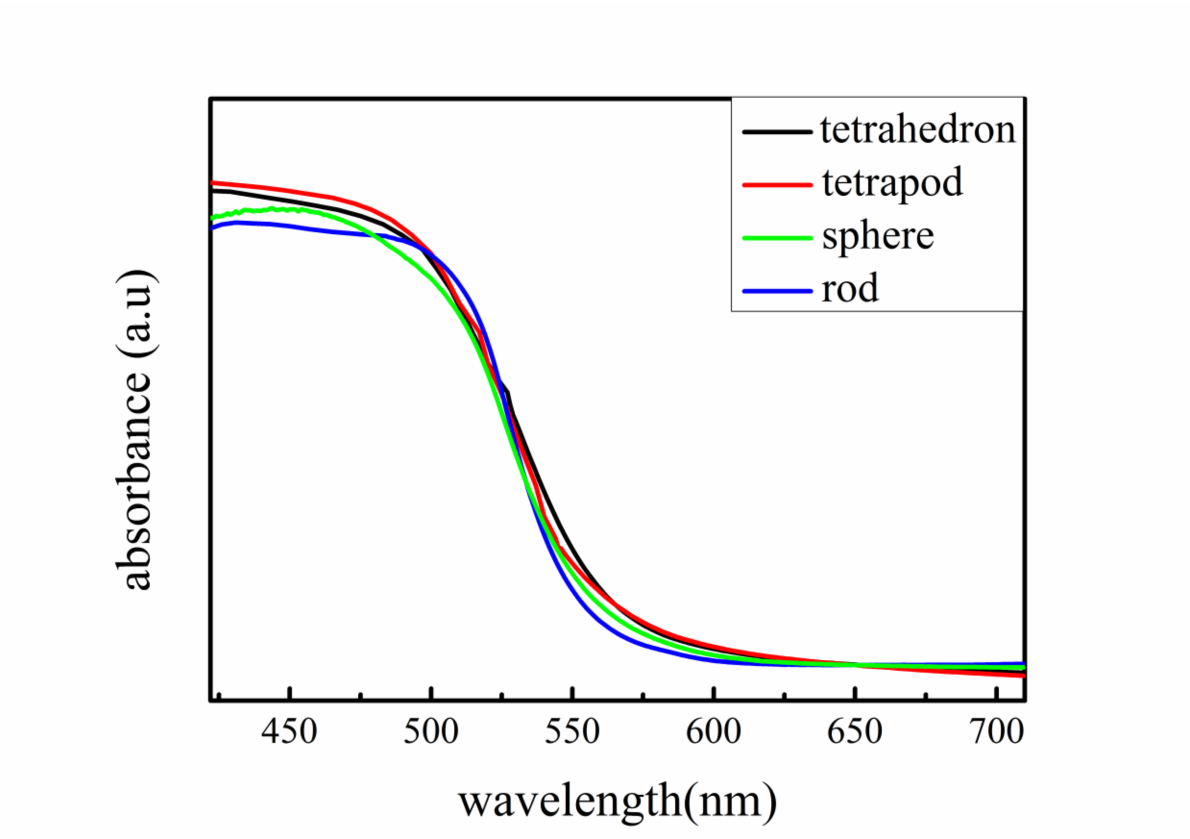

Figure S2: UV-Vis spectra for CdS powder samples of different shapes.

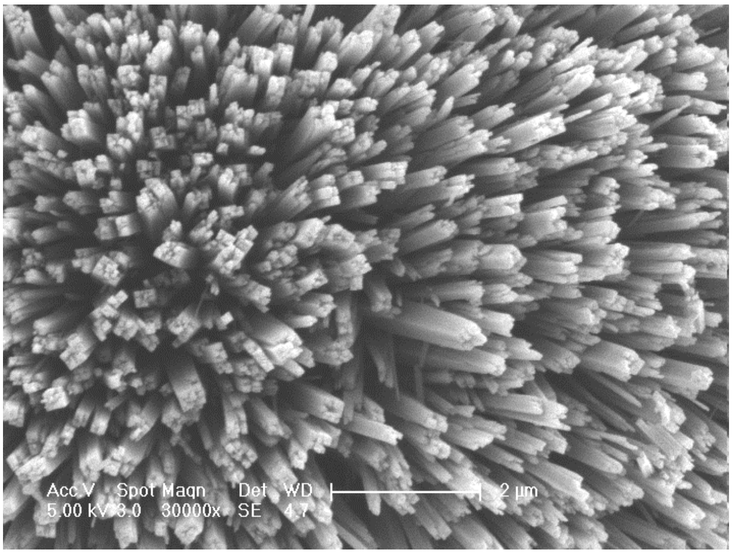

Figure S3: SEM micrograph of as-synthesized TiO_2nanorod (absorption layer) vertically aligned on FTO substrate coated with a compact and transparent layer of TiO_2.

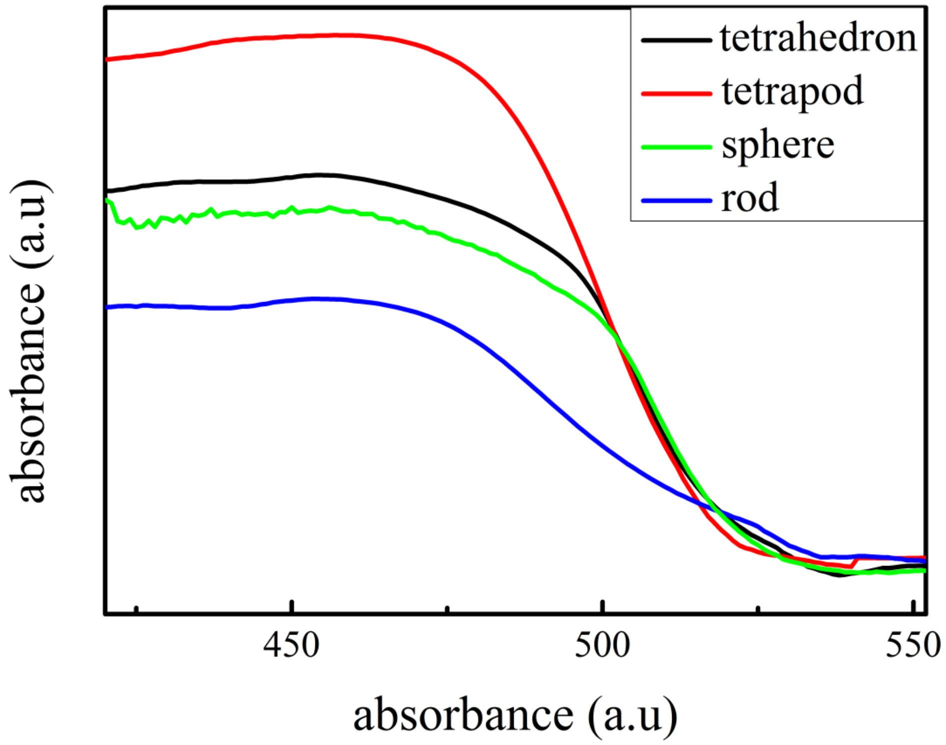

Figure S4: UV-Vis spectra of photoanodes with TiO_2 sensitized by various shapes of CdS

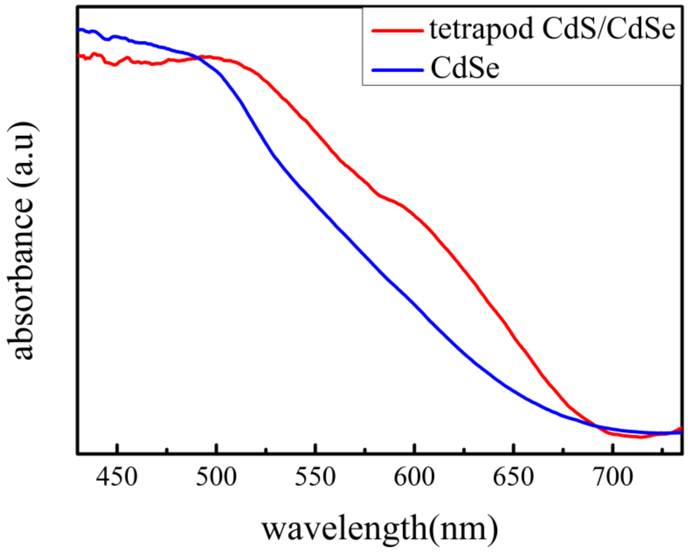

Figure S5: UV-Vis spectra of photoanodes with TiO_2 sensitized by CdSe (SILAR) and tetrapod-CdS(linker assisted)

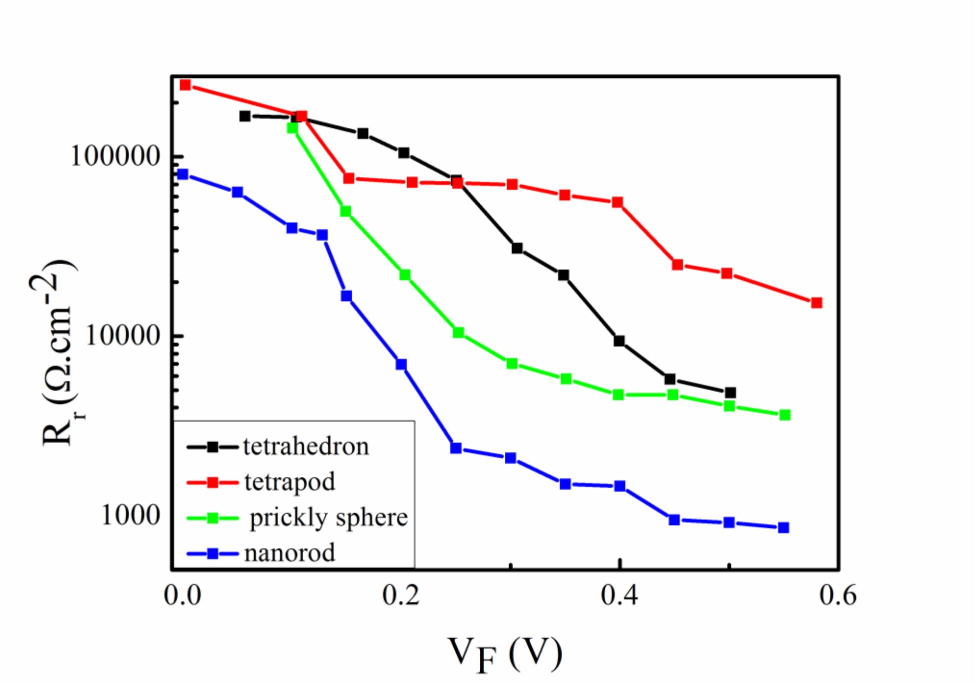

Figure S6: Recombination resistances of solar cells sensitized by various shapes of CdS (only)