Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Ag Plasmonic Nanostructures and a Novel Gel Electrolyte in a High Efficiency TiO_2/CdS Solar Cell

P. Naresh Kumar,[a] Melepurath Deepa,[a,*] Avanish Kumar Srivastava[b]

[a]Department of Chemistry, Indian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram-502205, Telangana (India).

[b]CSIR-National Physical Laboratory, Dr. K.S. Krishnan road, New Delhi-110012 (India).

*Email: mdeepa@iith.ac.in

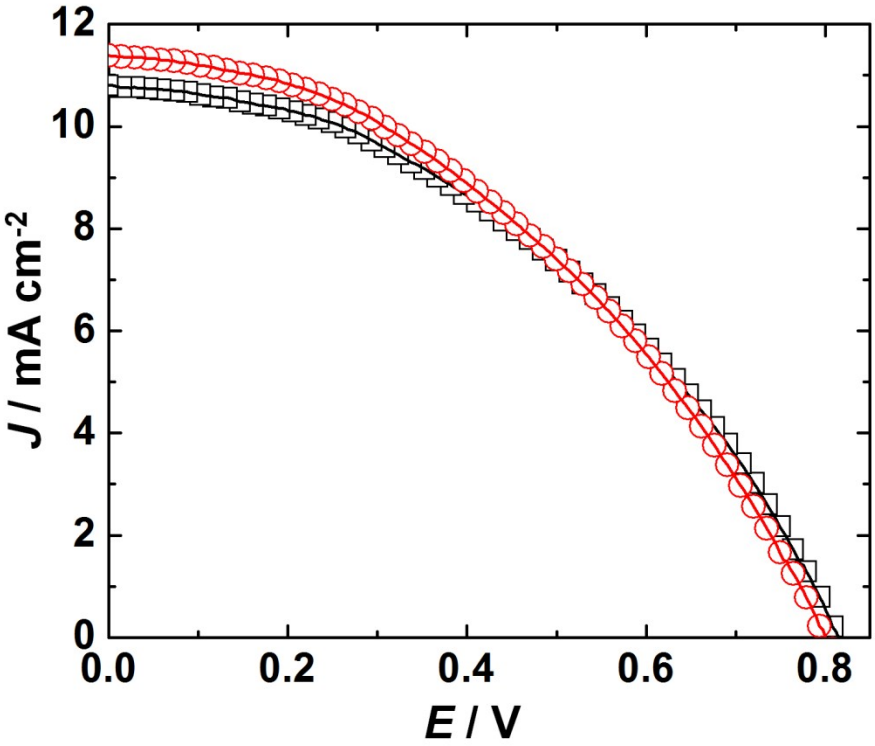

Figure S1 J-V characteristics of photoelectrochemical solar cells (under 1 sun illumination (AM 1.5G)) with the following photoanodes: Ag/TiO_2/CdS (❶) (with Ag product obtained after 20 min. reflux time) and Ag/TiO_2/CdS (①) (with Ag product obtained after 60 min. reflux time). The electrolyte was a 0.1 M Na_2S solution in 3:7 (v/v) water:MeOH and a MWCNT/FTO assembly was used as the counter electrode.

Table S1 Solar cell parameters of cells using 0.1 M Na_2S electrolyte, exposed cell area: 0.10 to 0.15 cm^2, under 1 sun illumination (AM1.5G, 100 mW cm^{-2}) with the listed photoanodes; all cells with MWCNT/FTO as the counter electrode.

Photoanode configuration	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF	η (%)
Ag (nanoparticles)/TiO_2/CdS-Liquid	814	10.79	41.94	3.68
Ag (nanorods)/TiO_2/CdS-Liquid	800	11.35	40.80	3.70

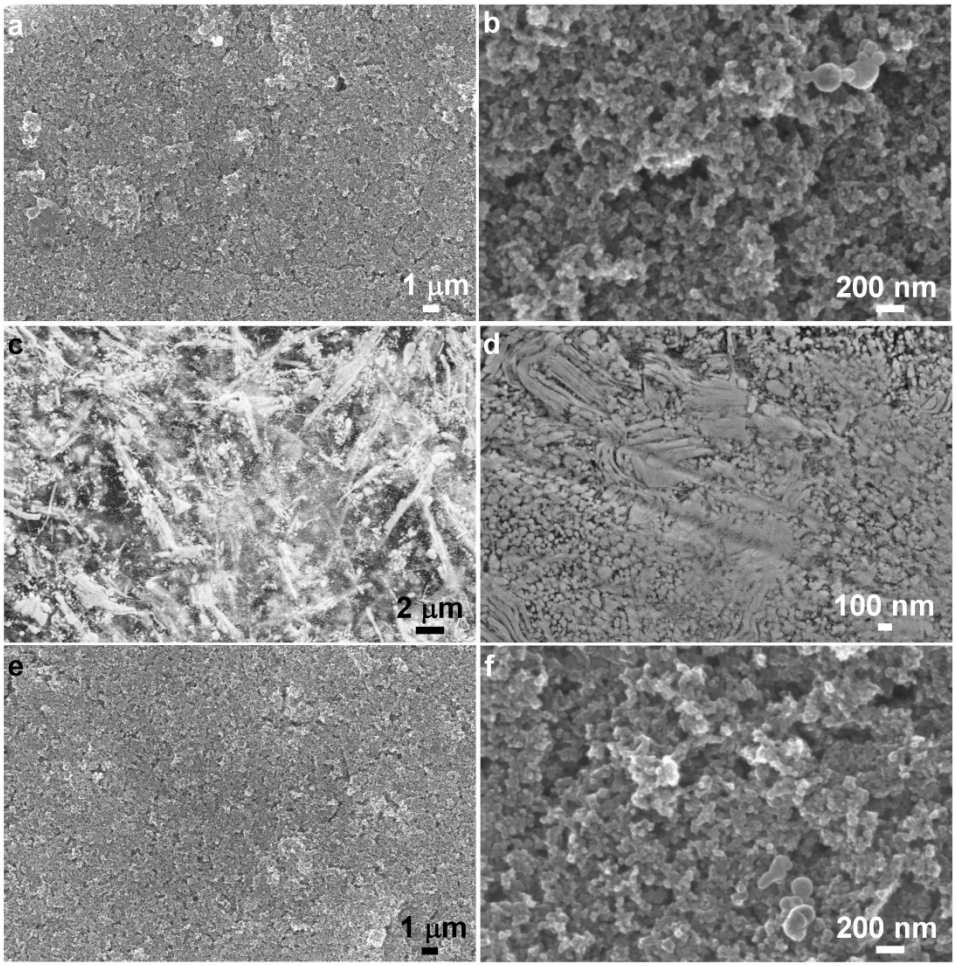

Figure S2 Low and high magnification images of (a and b) TiO_2, (c and d) Ag/TiO_2, and (e and f) Ag/TiO_2/CdS electrodes.

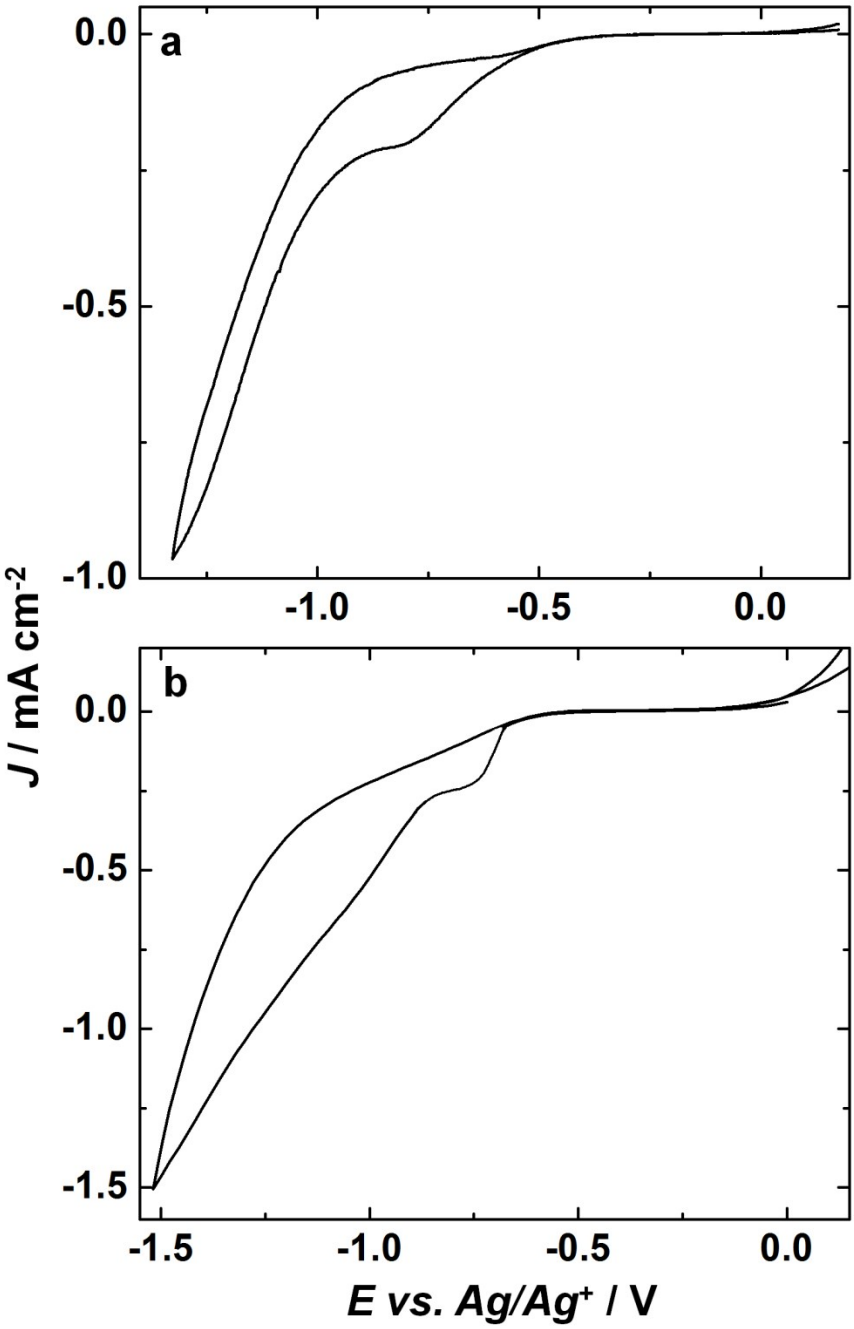

Figure S3 Cyclic voltammograms of (a) a 0.1 M Na_2S solution in 3:7 (v/v) water:MeOH and (b) a 0.1 M Na_2S gel with 4.1 wt.% of SiO_2 in 3:7 (v/v) water:MeOH, recorded at a scan rate of 10 mV s^{-1}, with two Pt electrodes as working and counter electrodes and a Ag/AgCl/KCl as the reference electrode.

The CV plots of the liquid and gel electrolytes show that the reduction potential peaks are observed at –0.71 V for the liquid electrolyte and –0.75 V for the gel electrolyte. These potentials were observed with respect to an Ag/Ag^+ reference electrode, which has a fixed electrode potential of

+0.197 V. Therefore, the reduction potentials of the liquid electrolyte and the gel electrolyte are –0.513 V and –0.553 V *versus* NHE. The S/S^{2-} has a standard redox potential of –0.48 V,[1] which is close to the values observed herein for the liquid and the gel electrolyte. These values are equal to ~ –4.0 eV (E (eV) = –4.5–(–0.513)) for the liquid electrolyte and ~ –3.95 eV (E (eV) = –4.5–(–0.553)) for the gel electrolyte. These values match well with redox potential of sulfide ions in literature.[1]

Table S2 Solar cell parameters of cells by considering standard deviation using 0.1 M Na_2S electrolyte, exposed cell area: 0.10 to 0.15 cm^2, under 1 sun illumination (AM1.5G, 100 mW cm^{-2}) with the listed photoanodes; all cells with MWCNT/FTO as the counter electrode.

Photoanode configuration	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF	η (%)
TiO_2/CdS-Liquid	875.25 ± 2.75	8.2 ± 0.88	40.45 ± 3.74	2.87 ± 0.03
TiO_2/CdS-Gel	921.4 ± 37.4	8.02 ± 0.57	38.9735 ± 3.9365	2.8525 ± 0.0275
Ag/TiO_2/CdS-Liquid	1020.5 ± 0.5	11.465 ± 0.205	35.98 ± 0.14	4.21 ± 0.06
Ag/TiO_2/CdS-Gel	920.55 ± 0.35	9.8575 ± 0.5725	38.235 ± 0.235	3.47 ± 0.18

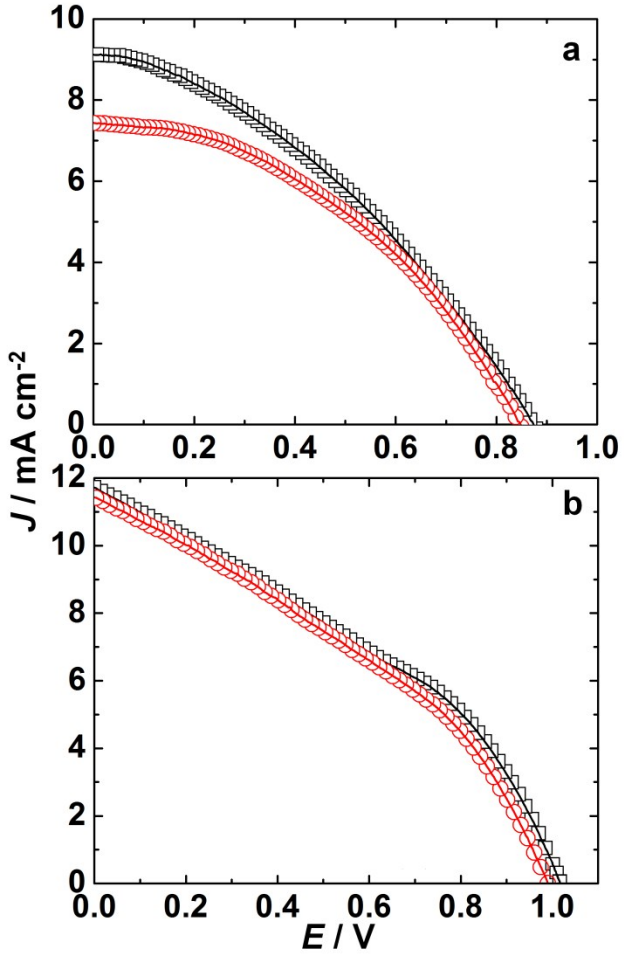

Figure S4 J-V characteristics for (a) TiO_2/CdS, and (b) Ag/TiO_2/CdS based solar cells, before (❍) and after (①) exposure to discontinuous 1 sun illumination for 3 h.

Table S3 Solar cell parameters of cells with 0.1 M Na_2S electrolyte, exposed cell area: 0.10 to 0.15 cm^2, with the listed photoanodes; both cells with MWCNT/FTO as the counter electrode.

Photoanode configuration	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF	η (%)
TiO_2/CdS (after 1 sun discontinuous illumination for 3 h)	850	7.43	35.32	3.62
Ag/TiO_2/CdS (after 1 sun discontinuous illumination for 3 h)	991	11.45	41.55	4.008

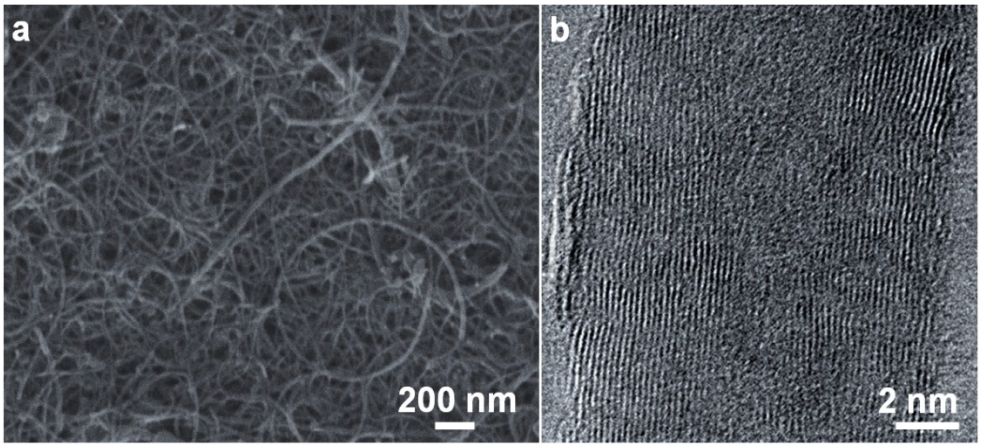

Figure S5 (a) SEM image of a MWCNT counter electrode and (b) the corresponding TEM image.

The EQE data of bare TiO_2 is shown below. The maximum value is about 4% in the UV region. It matches with a value of about 4% (observed in the UV range) reported earlier for a TiO_2 film prepared by a sol-gel route.[2]

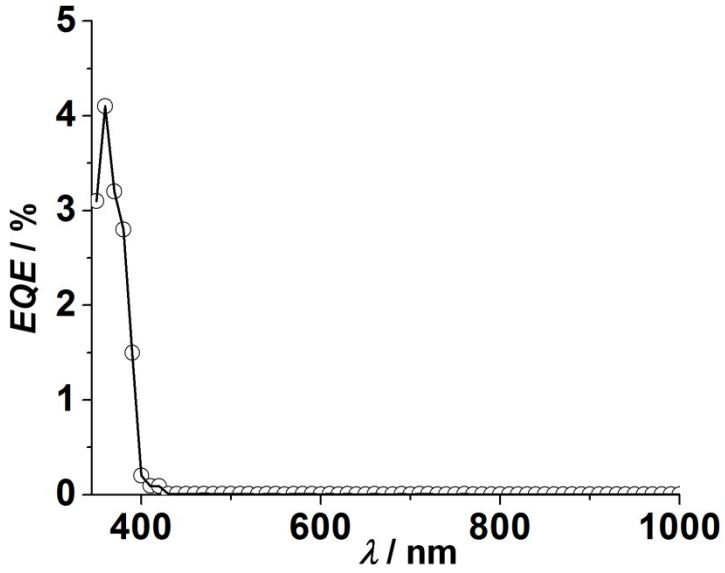

Figure S6 EQE spectrum of a cell with TiO_2 as the photoanode, a 0.1 M Na_2S solution as the electrolyte and a MWCNT/FTO as the counter electrode.

Reference

1. M. Bouroushian, Chapter 2, Electrochemistry of the Chalcogens, Electrochemistry of Metal Chalcogenides, Monographs in Electrochemistry, Springer-Verlag Berlin Heidelberg 2010.

2. J. Hensel, G. Wang, Y. Li and J. Z. Zhang, *Nano Lett.* **2010**, *10*, 478-483.