

Supplimentary Information

**Synergetic effect of ZnS outer layers and electrolyte methanol content on efficiency in
TiO₂/CdS/CdSe sensitized solar cells**

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Preparation of TiO₂ Nanocrystalline electrodes

F-doped tin oxide (FTO, Hartford Glass inc. with 15Ω sq⁻¹ sheet resistance) conducting glass substrates were cleaned, calcined and ozone treated prior to spin casting with 0.2 M di-isopropoxy titanium bis (acetylacetonate) solution in anhydrous ethanol at 3000 rpm for one minute by which a dense underlayer of TiO₂ was formed. The compact TiO₂ layer was subsequently calcined at 450 °C for 30 minutes after which a layer of mesoporous TiO₂ paste (Dyesol®, DSL 18NR-T) diluted in terpineol to optimum viscosity was deposited on top by screen printing using a synthetic 90T mesh screen. For optimized cells used to measure cell efficiency, IPCE and CE/TPV measurements the mesoporous layer thickness was approx. 9 μm and a 4 μm scattering layer of TiO₂ (Dyesol®, DSL 18NR-AO) was also incorporated into the film with cell areas of around 0.16 cm² used. For UV-Vis absorption and TAS measurements the samples consisted of 1cm² films of approx. 4 μm TiO₂. All films were calcined at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min and 500 °C for 15 min and cooled before commencing with SILAR.

SILAR treatment of TiO₂ electrodes

All SILAR solutions were prepared under inert conditions. The CdS SILAR was performed following a slightly modified procedure by Hossain *et al.*,¹ where the TiO₂ electrodes were immersed in a solution containing 0.02 M (0.617 gm in 100 mL) cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O, Fluka, >99.0%) in methanol for 1 minute and then rinsed with methanol for a further minute. The dried electrodes were then dipped into a solution containing 0.02 M sodium sulfide nonahydrate (Na₂S·9H₂O, Sigma Aldrich) in a mixture of methanol and deionized water (1:1, v/v) for 1 minute. The electrodes were then rinsed in methanol for 1 minute and dried again with N₂. This procedure comprises one CdS SILAR cycle and was repeated six times in order to get a suitable CdS loading on the TiO₂ electrode. The CdSe layer was sequentially deposited following the procedure used by Lee *et al.*² 30 mM Cd(NO₃)₂ in ethanol was prepared (0.93 gm Cd(NO₃)₂ in 100 mL). 100 mg of SeO₂ was dissolved in 30mL ethanol (30mM), and purged/stirred for about 2 minutes and 70 mg of NaBH₄ (60mM) added into a round-bottom flask containing SeO₂, and purged/stirred until the colour changed from deep red to clear. The films were then dipped into these two solutions for 30 seconds each. In between each dipping the electrodes were rinsed with pure ethanol and dried. This was repeated for six cycles after which a deep brown colour could be seen on the film surface.

For samples containing ZnS, the TiO₂/(6)CdS/(6)CdSe films were immersed in 0.1 M (1.835 g in 100 mL) aqueous zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, Sigma Aldrich, >99.5%) and 0.1 M aqueous (2.4 gm in 100 mL MilliQ water) Na₂S·9H₂O, dipping for 1 minute in each solution, with 1 minute of rinsing in deionized water between each immersion in the precursor solution. Two ZnS layers were deposited. The sensitized photoanodes were stored in a glove box under nitrogen atmosphere and dark conditions until they were used to make cells.

Device assembly

Device counter electrodes consisted of approx. 25 nm thick Au sputtered onto clean and calcined FTO glass slides at a deposition current of 30mA and a rate of about 9 nm/min. Prior to each measurement, cells were assembled by attaching the working and counter electrodes using a thermoplastic biphenyl frame (surlyn), 60 μm thick, and the electrolyte introduced through a hole and sealed by a cover slide. The contacts at the electrodes were metal-plated by soldering. The electrolyte consisted of fresh polysulfide electrolyte prepared by dissolving 0.60 M Na₂S, 0.20 M S, and 0.20 M KCl in water and methanol solutions.

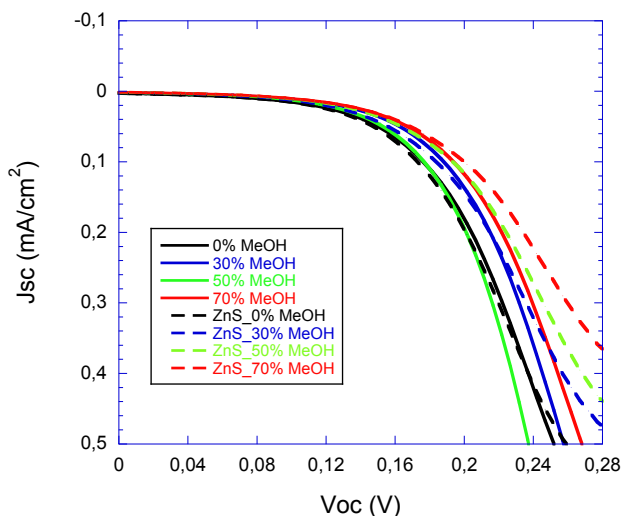


Figure S1. Dark IV curves for all devices analyzed in this work.

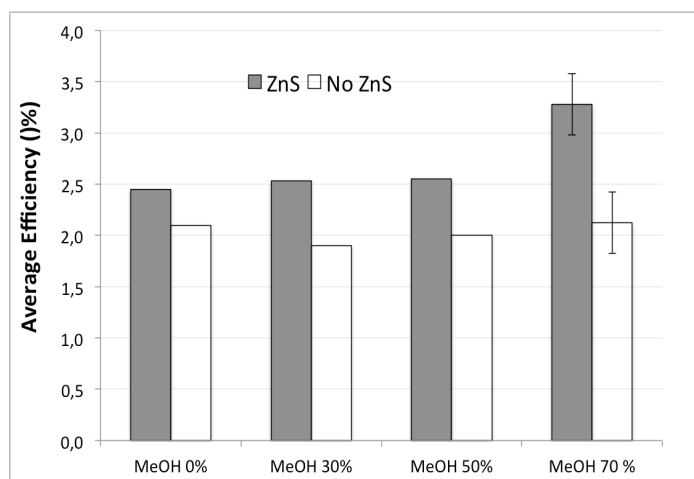


Figure S2. Average cell efficiencies for all device types discussed in this study. Up to 5 sets of samples (3 devices per set) were prepared for each device type. Taking the best cell for each run for each device type the average efficiency is depicted above. As is clear the cell efficiencies in the manuscript are in line with the average overall best efficiencies. Thus cell efficiencies in this study are consistent and repeatable.

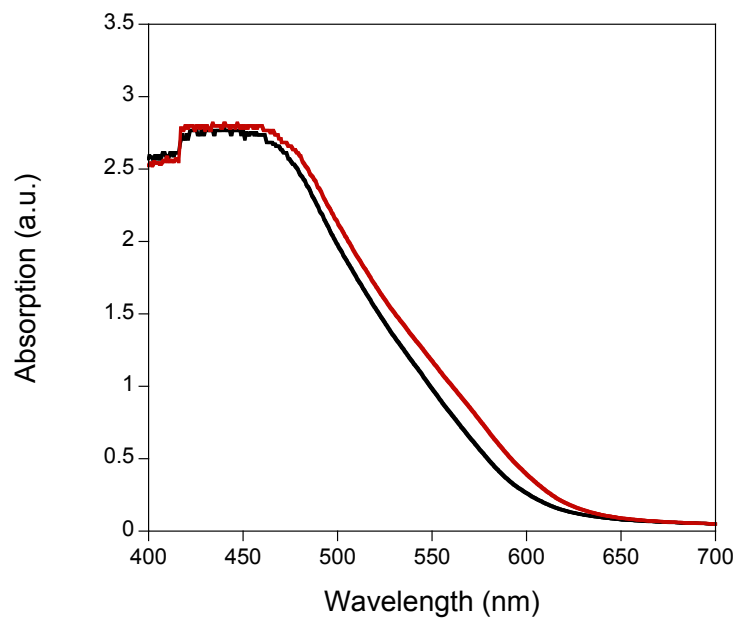


Figure S3. Absorption spectra of $\sim 7\mu\text{m}$ films: $\text{TiO}_2/(6)\text{CdS}/(6)\text{CdSe}$ (black) and $\text{TiO}_2/(6)\text{CdS}/(6)\text{CdSe}/(2)\text{ZnS}$ (red).

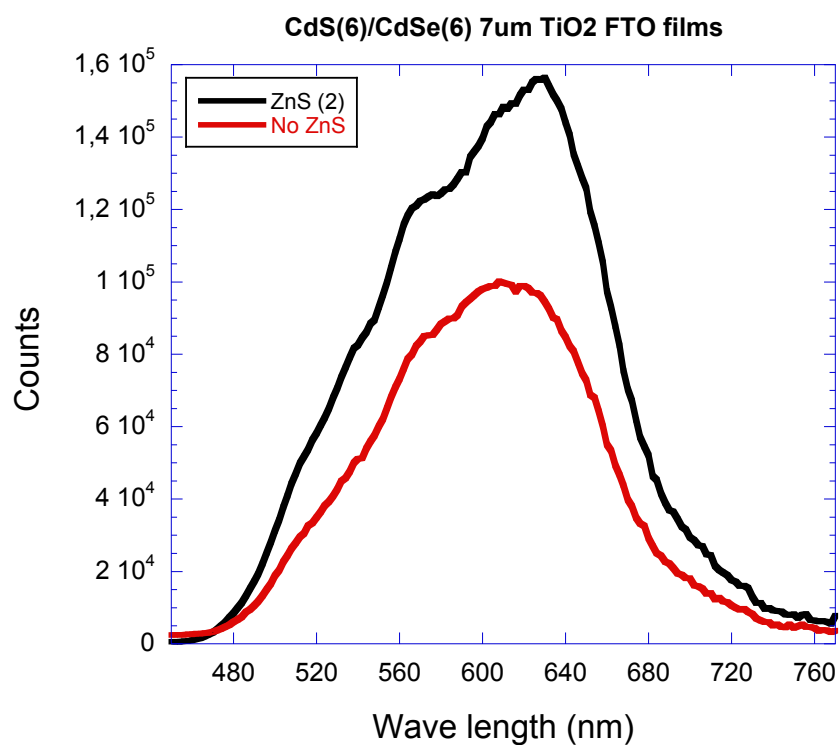


Figure S4. (a) Emission spectra of $\sim 7\mu\text{m}$ films: $\text{TiO}_2/(6)\text{CdS}/(6)\text{CdSe}$ (red) and $\text{TiO}_2/(6)\text{CdS}/(6)\text{CdSe}/(2)\text{ZnS}$ (black). Samples were excited at 405 nm.

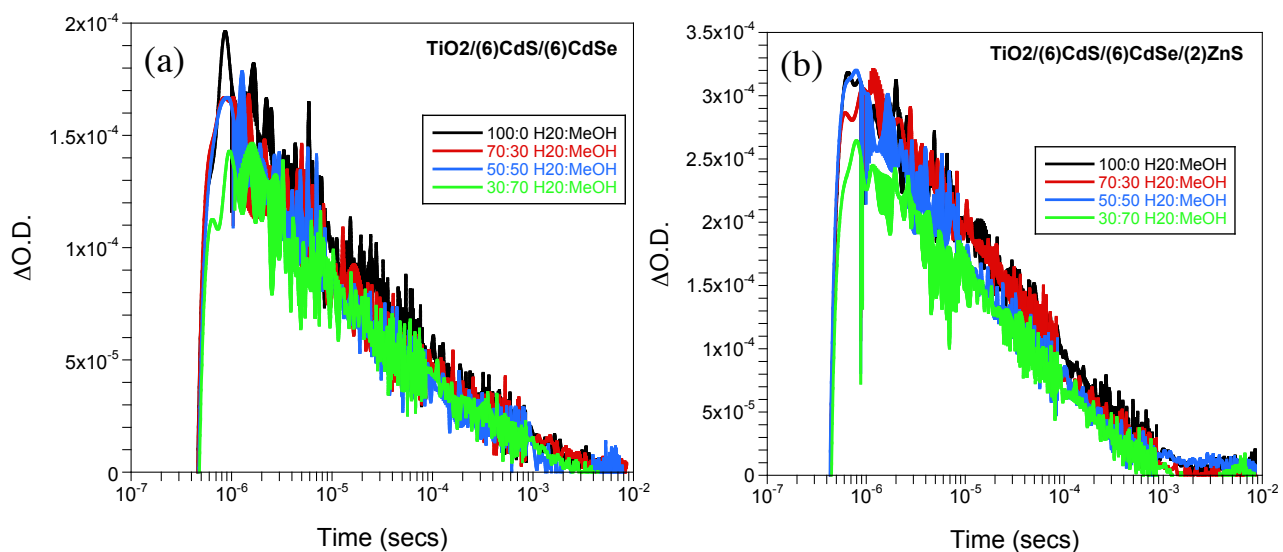


Figure S5. Transient absorption kinetics of $\sim 7\mu\text{m}$ TiO_2 films in different $\text{H}_2\text{O}:\text{MeOH}$ solutions for (a) $\text{TiO}_2/(6)\text{CdS}/(6)\text{CdSe}$ and (b) $\text{TiO}_2/(6)\text{CdS}/(6)\text{CdSe}/(2)\text{ZnS}$. Kinetics were recorded at 700nm following excitation at 450nm under $100\text{mW}/\text{cm}^2$ illumination intensity.

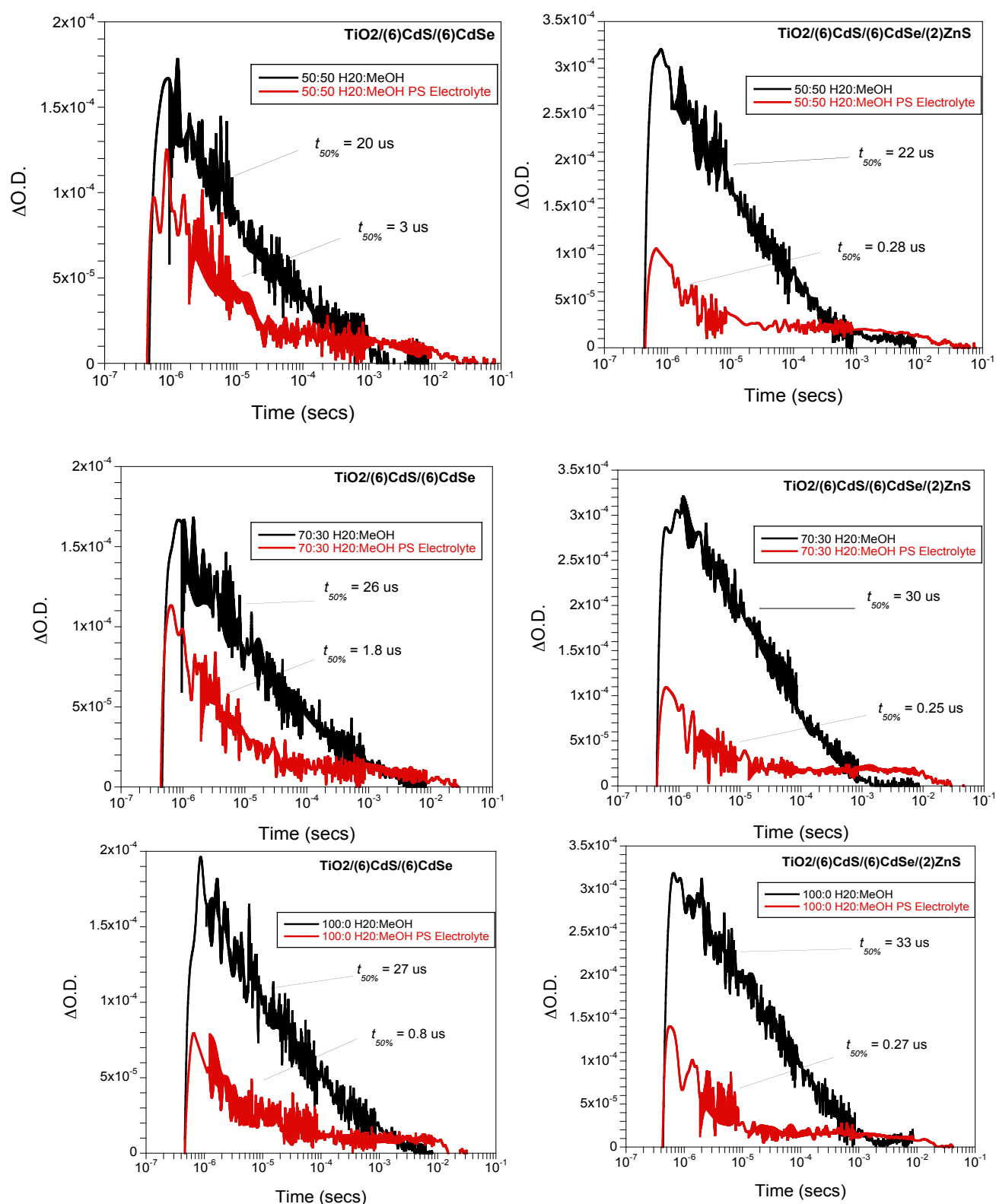


Figure S6. Transient absorption kinetics of $\sim 7\mu\text{m}$ TiO₂ films in the absence (black decays) and presence (red decays) of polysulfide electrolyte in different H₂O:MeOH solutions for TiO₂/(6)CdS/(6)CdSe (left) and TiO₂/(6)CdS/(6)CdSe/(2)ZnS (red) films. Kinetics were recorded at 700nm following excitation at 450nm under 100mW/cm² illumination intensity.

On the Synergism

By definition, one claims for synergy when the combined effect of two or more factors exceeds each factor acting alone. It is an easy and common statistical approach in clinical studies of greater complexity in biology. The synergy factor (SF) is the ratio of the observed *fractional difference* for both factors combined, to the predicted *fractional difference* assuming independent effects of each factor and can be defined as:

$$SF = ZM/(Z \times M) \dots \dots \dots (1)$$

where Z and M represent ZnS and/or 70% MeOH

We hypothesized, and proved the synergism between the use of ZnS coating on CdS/CdSe SILAR TiO₂ DSSC and the use of MeOH in the solution based polysulfide electrolyte, by comparing the overall efficiency of the devices under standard 1 Sun 1.5 AM G conditions.

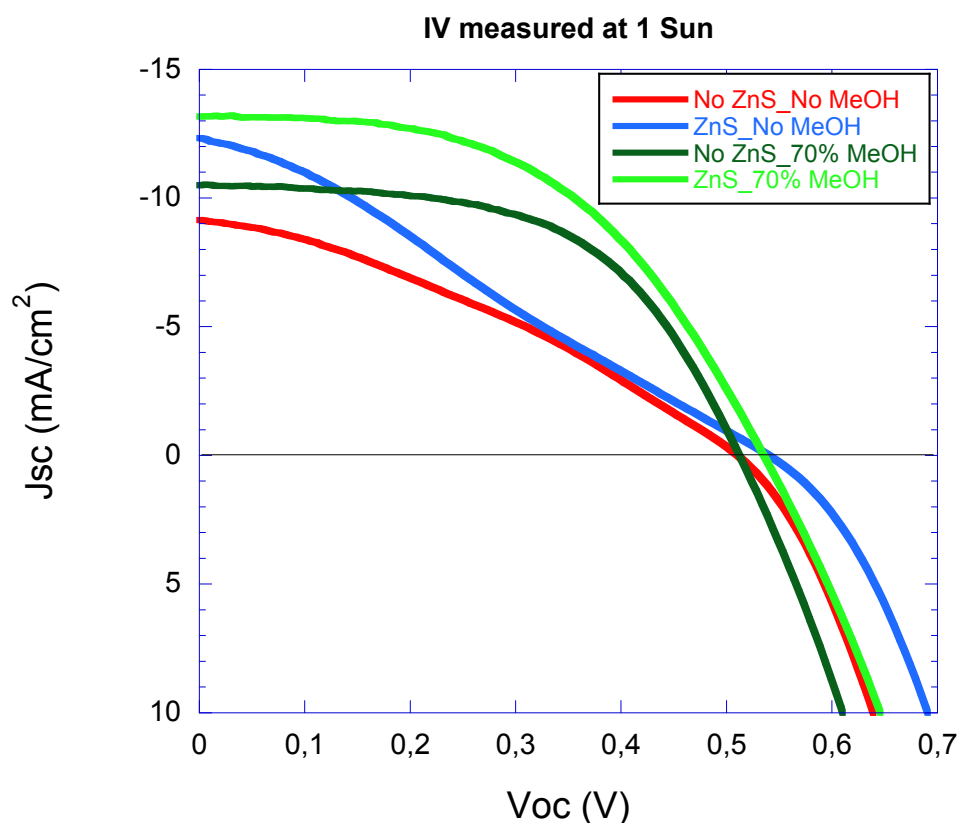


Fig.S7: Photocurrent vs Voltage curves for a set of different DSSC devices.7

Table S1: JV characteristics of TiO₂/CdS/CdSe solar cells at 1 Sun

	Jsc (mA/cm ²)	Voc (V)	FF (%)	EFF (%)
NoZnS_No MeOH	9.14	0.509	33	1.56
No ZnS_70% MeOH	10.49	0.514	56	3.00
ZnS_No MeOH	12.33	0.539	27	1.76
ZnS_70% MeOH	13.17	0.534	51	3.56

Considering the non passivated TiO₂/CdS/CdSe cells in the absence of methanol in the electrolyte as controls, the synergy factor from Table 1 is calculated to be:

$$SF_{1\text{Sun}} = 2 / (1.4 * 0.2) = 6.9 \gg 1 \text{ (There is a synergetic effect)}$$

The same cells were also compared at higher light intensities generating similar photocurrent as the reference combined effect cell (TiO₂/CdS/CdSe/ZnS and MeOH in the electrolyte) as in Fig.S8. The IV characteristics are summarized in Table S2.

Analogous to the above estimation, the effect is even more pronounced although the cells are at different illumination intensities. Calculated synergy factor in this case is **8.7** while one can clearly notice that the effect of methanol alone was more than the combined effect.

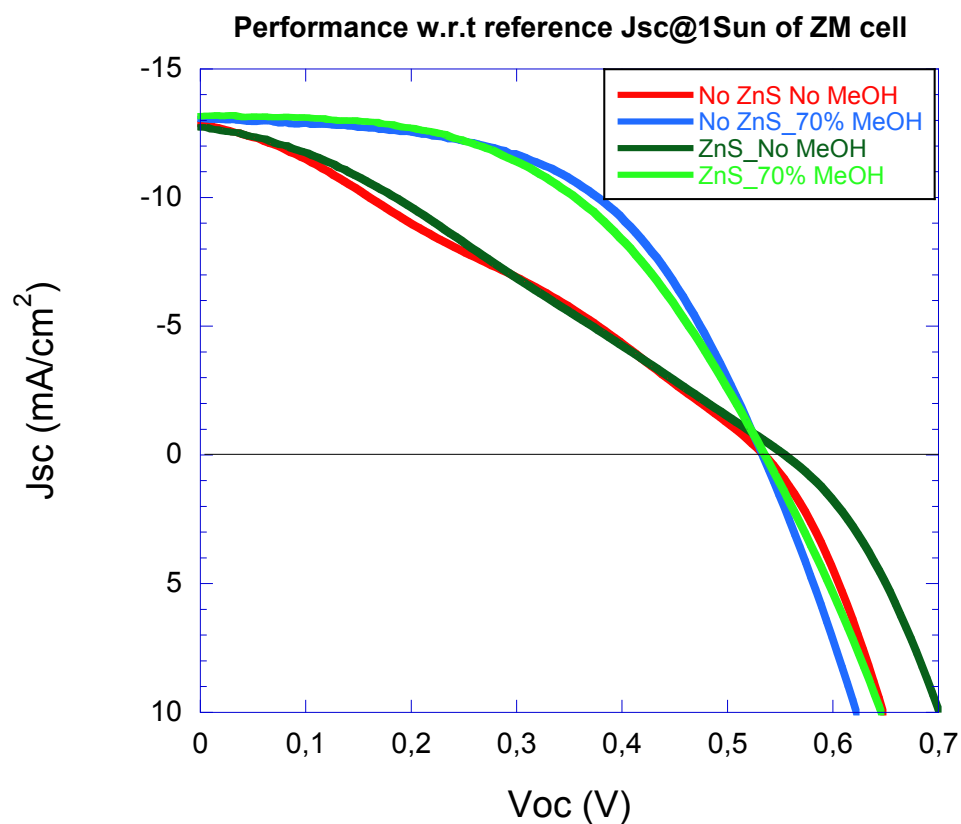


Fig. 2 Measurement of performances at higher light intensities to match the photocurrent between the devices without the ZnS overlayer and the devices with the ZnS overlayer.

Table 2: IV characteristics of C,Z,M and ZM cells as illuminated to photogenerate equivalent J_{sc} to ZM at 1 Sun

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	EFF (%)
NoZnS_No MeOH	12.86	0.534	30	2.07
No ZnS_70% MeOH	13.06	0.534	54	3.78
ZnS_No MeOH	12.75	0.554	29	2.08
ZnS_70% MeOH	13.17	0.534	51	3.56

References

1. M. A. Hossain, J. R. Jennings, Z. Y. Koh and Q. Wang, *ACS Nano*, 2011, **5**, 3172-3181.
2. Lee, M. Wang, P. Chen, D. R. Gamelin, S. M. Zakeeruddin, M. Grätzel and M. K. Nazeeruddin, *Nano Lett.*, 2009, **9**, 4221-4227.