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Industrially scalable and cost-effective Mn^{2+} doped $Zn_xCd_{1-x}S/ZnS$ nanocrystals with 70% photoluminescence quantum yield, as efficient down-shifting material in photovoltaics

Supporting information

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Energy-Dispersive X-ray spectroscopy (EDX). To confirm the growth of the ZnS shell around the $Zn_{0.5}Cd_{0.5}S$:Mn core and the presence of Mn^{2+} doping ions in the crystal lattice, EDX analysis of the elemental composition of the $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS and $Zn_{0.5}Cd_{0.5}S$:Mn d-dots was performed. The results are shown in Figure S1. The growth of the ZnS shell around the $Zn_{0.5}Cd_{0.5}S$:Mn core is reflected by an increased intensity of the Zn peak given in panel (B) compared to the unshelled starting material shown in panel (A). A relatively high intensity of the Mn peaks (panels A and B) confirms the doping concentration of several mol.%.

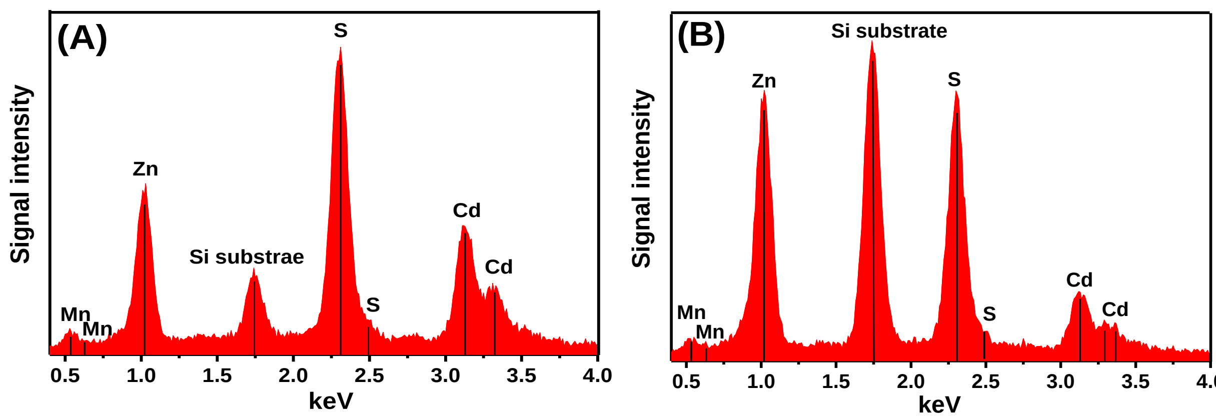

Figure S1. EDX analysis of the elemental composition of the $Zn_{0.5}Cd_{0.5}S$:5% Mn (A) and $Zn_{0.5}Cd_{0.5}S$:5% Mn/ZnS (B) d-dots.

Effect of purification. Unreacted species can influence the photoluminescence (PL) of nanocrystals (NCs). Hence, the $Zn_{0.5}Cd_{0.5}S$:Mn(5%)/ZnS d-dots were purified up to three times by precipation with ethanol followed by redispersion in chloroform and the PL intensity was monitored as a function of the purification steps (Figure S2) to control complete removal of precusors and/or side products. The increase in PL intensity after the first purification step is attributed to the removal of nonreacted starting material and solvent from the surface of nanoparticles. Additional purification steps do not later the PL intensity and can be thus omitted.

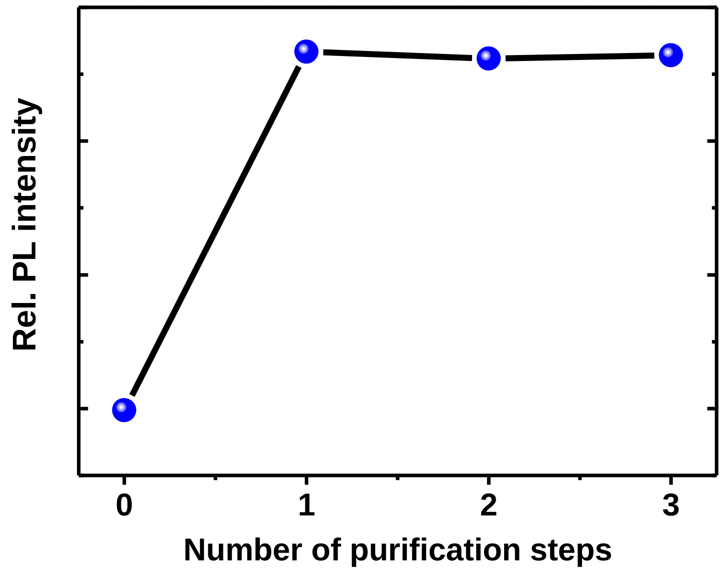

Figure S2. Effect of purification on the PL of $Zn_xCd_{1-x}S$:Mn(5%)/ZnS.

Upscaling. Considering the strong interest in fluorescent quantum dots and d-dots not only for academic research but also for an increasing number of industrial applications like the production of the next generation of solar cells for photovoltaics or as LED converter materials for solid state lightning, we studied the possibility to upscale our simple synthetic procedure to a multigram synthesis of $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS NCs while maintaining the high quality of the NCs. Hence, the volume of all starting components was increased by a factor of 40. This gave 3.5 g of NCs (Figure S3). The resulting powder can be readily dispersed in nonpolar solvents such as chloroform, toluene, hexane, chlorobenzene etc. As a measure for the high quality of the NCs, we determined their photoluminescence quantum yield. The quantum yield of about 70 %) matched the values previously synthesized in a smaller batch, i.e., yielding 0.05 – 0.1 g of NCs.

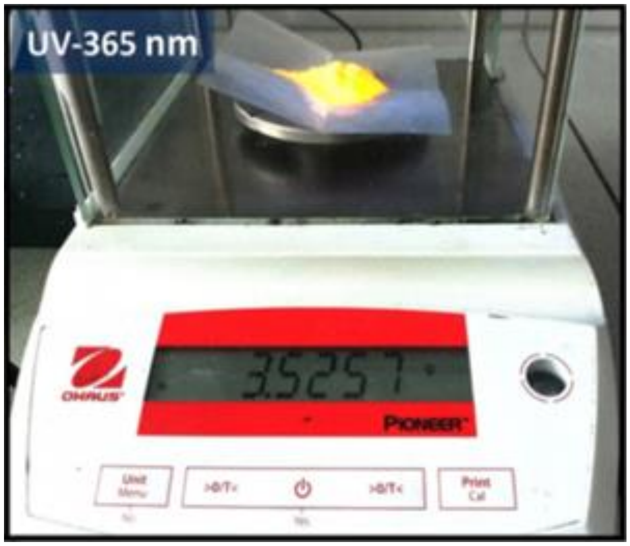

Figure S3. Upscaling of the synthesis of $Zn_{0.5}Cd_{0.5}S$:Mn(5%)/ZnS core shell NCs.

XPS analysis.

NCs $Zn_{0.5}Cd_{0.5}S$ with nominal 10% mol. Mn and without the ZnS shell (Figure S4A) are measured by X-ray photoelectron spectroscopy (XPS) using Mg Kα-radiation (1253.6 eV); note that Al Kα-radiation cannot be used due to an overlap of the Mn 2p levels with the intense Zn LMM Auger lines. In case of $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS (Figure S4B), Mn 2p signal is strongly qunched by ZnS shell, which prevents precise definition of the Mn state. Figure S4A depicts the survey spectrum showing the contributions of all expected elements. The Mn 2p region falls within the spin-orbit split Cd $3p_{1/2}$ and $3p_{3/2}$ levels at 652.4 and 618.4 eV, respectively. While the Mn $2p_{1/2}$ level is hidden under the Cd $3p_{1/2}$ peak, the Mn $2p_{3/2}$ peak is clearly separated in energy and is shown as inset in the figure. The peak has its maximum at 641.8 eV, with a broad shoulder at higher binding energy. This peak shape is due to a complex multiplet structure[13], which cannot be resolved due to the low signal intensity. Within the error bars, the binding energy and peak shape of the Mn $2p_{3/2}$ core level is consistent with an oxidation state of either II, III or IV[13]. From the comparison to the spectra of Biesinger et al.[13], who measured several manganese oxides with different oxidation levels, the large width of the multiplet structure is a hint towards Mn(II) species. Furthermore, we compared ratio between Zn3p/Cd4p and Zn3s/Cd4s signal intensities for $Zn_{0.5}Cd_{0.5}S$:Mn and $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS. In both cases the ratio increases, confirming the ZnS shell growth.

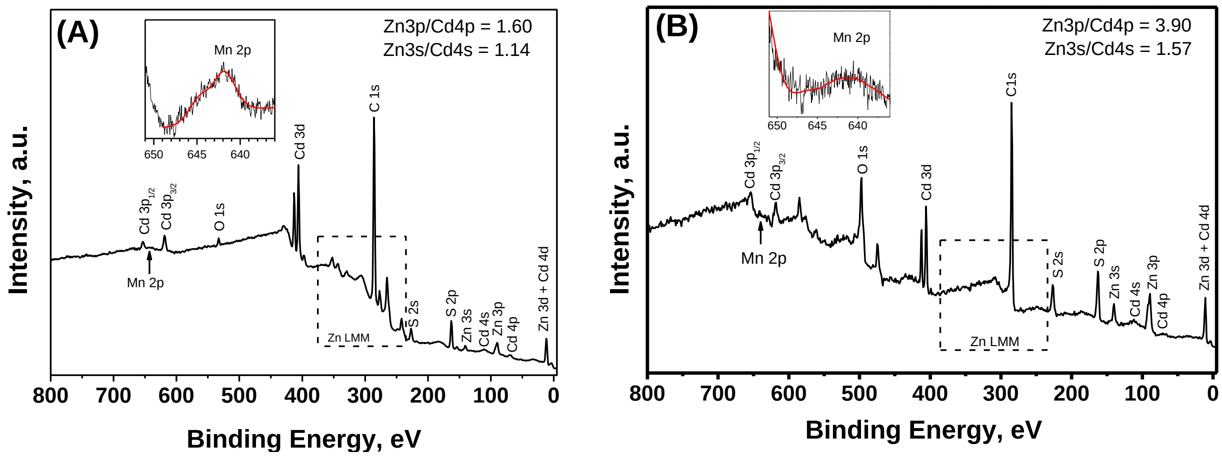

Figure S4. Survey XPS spectrum of $Zn_{0.5}Cd_{0.5}S$:Mn NCs with 10% Mn (A) and $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS (B). In the inset, the detail spectra of the Mn 2p region is shown; the red line is added as guide to the eye.

Mn^{2+}-doped $Zn_{0.5}Cd_{0.5}S$/ZnS NCs as converter material for mono-Si solar cells coating.

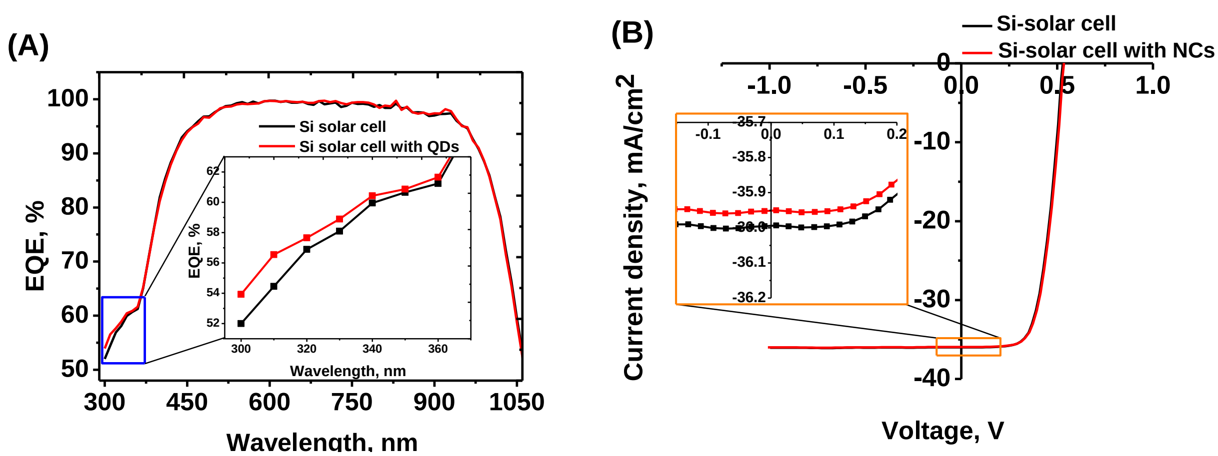

Figure S5. Panel A: Wavelength dependence of the external quantum efficiency (EQE) of a silicon solar cell coated with 0.5 mg/ml of $Zn_{0.5}Cd_{0.5}S$:Mn(5%)/ZnS NCs dispersed in toluene. Panel B J–V curve of the same combination system.

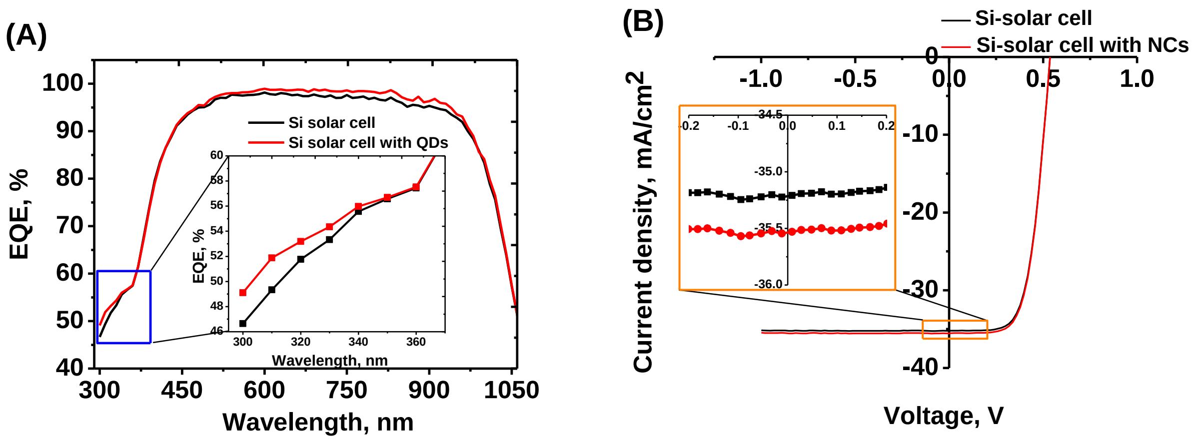

Figure S6. Panel A: Wavelength dependence of the external quantum efficiency (EQE) of a silicon solar cell coated with 1 mg/ml of $Zn_{0.5}Cd_{0.5}S$:Mn(5%)/ZnS NCs dispersed in toluene. Panel B J–V curve of the same combination system.

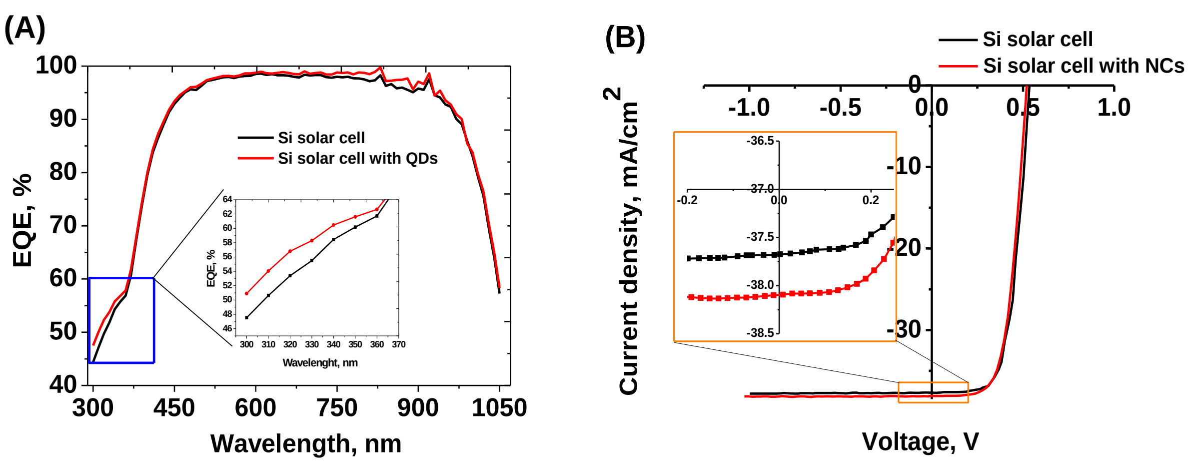

Figure S7. Panel A: Wavelength dependence of the external quantum efficiency (EQE) of a silicon solar cell coated with 2.5 mg/ml of $Zn_{0.5}Cd_{0.5}S$:Mn(5%)/ZnS NCs dispersed in toluene. Panel B J–V curve of the same combination system.

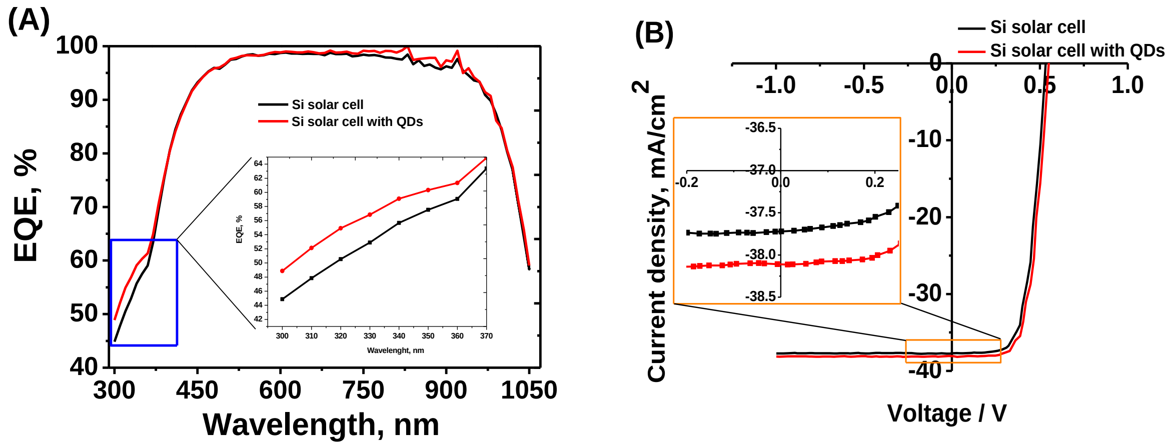

Figure S8. Panel A: Wavelength dependence of the external quantum efficiency (EQE) of a silicon solar cell coated with 5.0 mg/ml of $Zn_{0.5}Cd_{0.5}S$:Mn(5%)/ZnS NCs dispersed in toluene; Panel B: J–V curve of the same system.

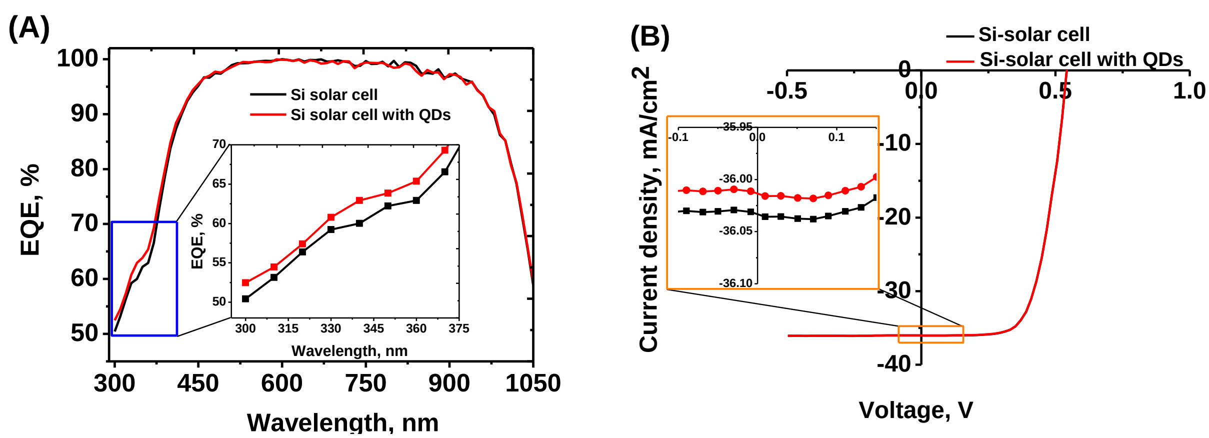

Figure S9. Panel A: Wavelength dependence of the external quantum efficiency (EQE) of a silicon solar cell coated with 15 mg/ml of $Zn_{0.5}Cd_{0.5}S$:Mn(5%)/ZnS NCs dispersed in toluene; Panel B: J–V curve of the same system.

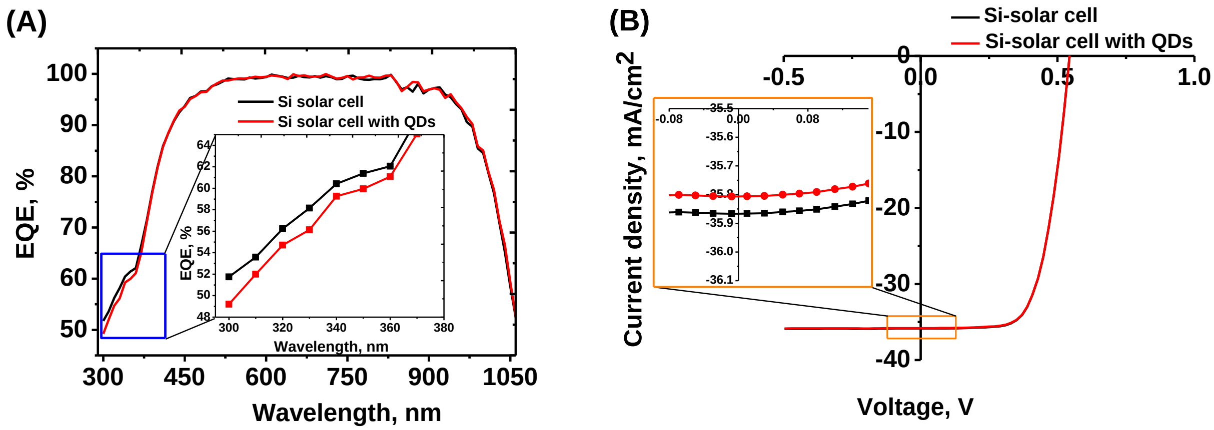

Figure S10. Panel A: Wavelength dependence of the external quantum efficiency (EQE) of a silicon solar cell coated with 20 mg/ml of $Zn_{0.5}Cd_{0.5}S$:Mn(5%)/ZnS NCs dispersed in toluene; Panel B: J–V curve of the same system.

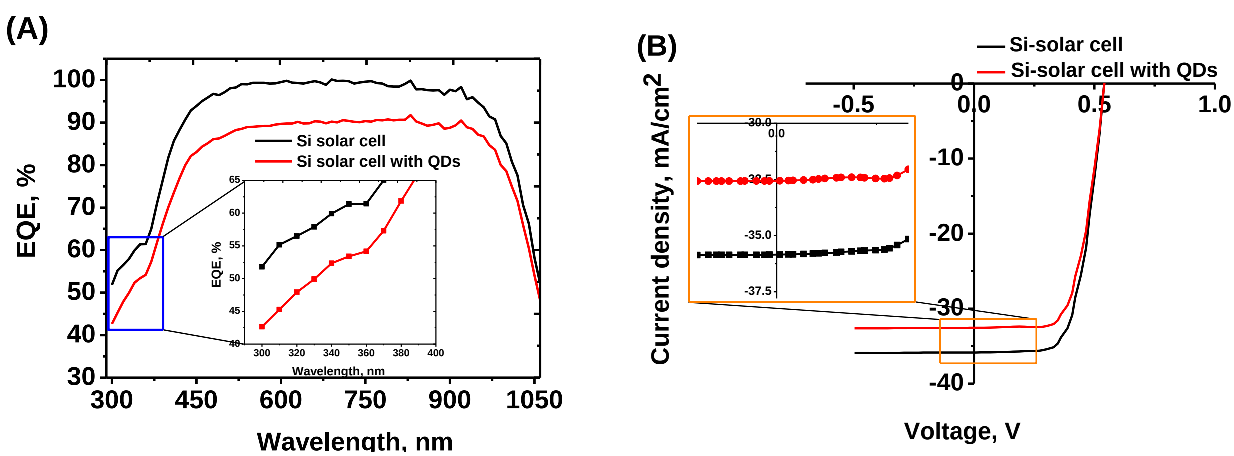

Figure S11. Panel A: Wavelength dependence of the external quantum efficiency (EQE) of a silicon solar cell coated with 25 mg/ml of $Zn_{0.5}Cd_{0.5}S$:Mn(5%)/ZnS NCs dispersed in toluene; Panel B: J–V curve of the same system.

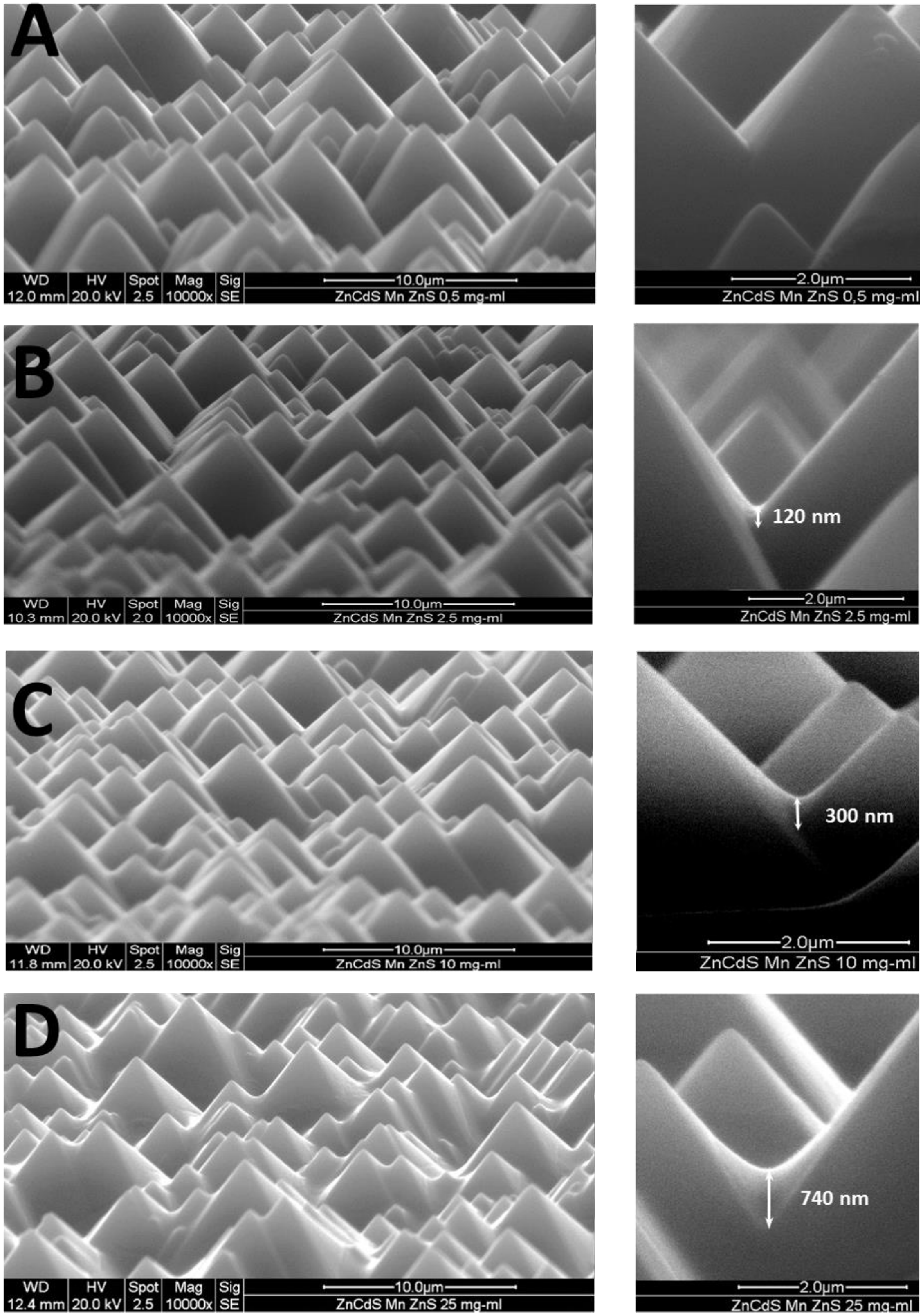

Figure S12. Selected SEM picture of the mono-Si solar cell surface structure cross-section of the same mono-Si solar coated with 0.5 mg/ml (a), 2.5 mg/ml (b), 5 mg/ml (c) and 25 mg/ml (d) NCs solution. The obtained NCs thicknesses varies from <50 to 750 nm.

Table S1. Previously reported Mn^{2+} doped semiconductor nanocrystals and their properties

QDs	**PL QY/(%)**	**Peak/(nm)**	**Lifetime/(ms)**	**Method of synthesis**	**Ref.**
Mn:Zn-In-S	56	600	4.2	Multi-step hot-injection method	1
Mn:ZnS	> 50	585	0.37	One-pot two-steps	2
Mn:CdS	not mentioned	580-620, tunable	not mentioned	Low-temperature injection	3
Mn:ZnSe	35	590	0.38	Hot-injection	4
Mn:ZnSSe	~60	~595	not mentioned	Hot-injection	5
MnS/ZnS/CdS	68	580	**0.68**	Multi-step hot-injection method	6
Mn:ZnCdS	30	580	not mentioned	Reverse micelle	7
Mn:CuInZnS	45	600	2.12	One-pot two-steps	8
Mn:CdInS	17	630	**1.1**	Hydrothernal	9
Mn:CdZnSe	~25	580	**~0.6**	Multi-step hot-injection method	10
Mn:CuInS/ZnS	66	610	3.78	One-pot two-steps	11
Mn:ZnS	> 50	590	1.71	Multi-step hot-injection method	12
ZnCdS:Mn/ZnS	70	598	2.85	One-pot two-steps	This work

Cost-effective calculation

The ultimate goal of our research dedicated to highly luminescent d-dots likee $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS NCs presents the reduction of the manufacturing costs of solar cells by improving their spectral response in the UV spectral region, thereby paving the road for the next generation of highly efficient solar cells. Current price (see Energy Trend, http://pv.energytrend.com/pricequotes.html), of one Watt mono-Si PV modules currently costs 0.61 \$. For this cost estimation, we used the representative PV module Aleo S75L215 with a nominal power of 117 W/m^2 and a PCE of 14.6 %, which is quite similar to the solar cell used in our experiments. Since the PCE increase is not significantly different for mono-Si solar cells coated with 2.5, 5 and 10 mg/ml NCs as best samples for luminescent down-shifting layer (see Table 2, into the body of the paper), we choose for the calculation the device coated the minimum amount of NCs using toluene dispersions containing 2.5 mg/ml NC. For this sample, the PCE could be enhanced from 13.22 % to 13.66 % which equals a relative enhancement of the efficiency (Δ PCE_{rel}) of 3.3 %.

The price for 1 m^2 of Aleo S75L215 is 117×0.61 = 71.37 \$. Due to the increase of the PCE by 3.3 %, the area of the photovoltaic module can be reduced by 3.3 %. The new price for 1W is 0.59\$ (0.61-(0.61×3.3%/100%)), and 69.07 \$ for a module with the same power as Aleo S75L215 respectively. The crucial points of this calculation are the costs for the synthesis of the NCs and the coating.

We calculated the full price of 1g of $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS NCs based on real industrial-scale prices (Table S2, S3) of the materials and created a cost required scenario for the one synthetic group division inside the company, that could synthesize 1000 kg NCs per year.
All calculations are adapted for Germany (fees, salaries, taxes etc.) and summarized in Tables S4.

For the coating of a 8 cm^2 mono-Si solar cell we used 0.2 ml NCs dispersion in toluene containing 2.5 mg/ml NC. For the coating of 1 m^2, 0.5 g of NCs are required. The calculated costs for the fabrication of 1g NCs for our synthesis are ~1.44 $, and 0.77$ for 0.5g respectively.

In this case, we save 71.37 – (69.07 + 0.77) = 1.53 ~ 1.5$ for the fabrication of the module with the same power as Aleo S75L215 (117W). **(Area of module decreases(!))**

Table S2. Industrial prices of the raw material for $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS NCs synthesis

Name of Chemicals	Sigma Aldrich lab scale price	Industrial scale price	Link to the Product
Zinc Acetate, Anhydrous	195 € per 100 g 218.4 $ per 100 g Purity: 99.99%	1200 $ per Ton, Purity: 99-101%	**Sigma Aldrich:** https://www.sigmaaldrich.com/catalog/product/aldrich/383317?lang=de&region=DE **Industrial scale:** http://www.alibaba.com/product-detail/Best-Price-Anhydrous-Zinc Acetate_60272523269.html?spm=a2700.7724857.35.1.lc8BdA
Cadmium Oxide	174 € per 25 g 194.88 $ per 25g Purity: 99.99%	5000 $ per Ton, Purity: 99.99%	**Sigma Aldrich:** http://www.sigmaaldrich.com/catalog/product/aldrich/202894?lang=de&region=DE **Industrial scale:** http://www.alibaba.com/product-detail/High-Purity-Battery-grade-99-Cadmium_2009964487.html?spm=a2700.7724838.35.1.uIUFtc
Manganese Acetate, Anhydrous	277.50 € per 100 g 310.8$ per 100 g Purity: 98%	2000 $ per Ton, Purity: >99%	**Sigma Aldrich:** https://www.sigmaaldrich.com/catalog/product/aldrich/330825?lang=de&region=DE **Industrial scale:** http://www.alibaba.com/product-detail/Supply-99-min-China-Manganese-acetate_60305296071.html?spm=a2700.7724838.35.1.BS9nqS
Sulfur	25.50 € per 1 kg 28.56 $ per 1 kg Purity: 99.99%	250 $ per Ton, Purity: 99.9%	**Sigma Aldrich:** http://www.sigmaaldrich.com/catalog/product/sial/84683?lang=de&region=DE **Industrial scale:** http://www.alibaba.com/product-detail/pharmaceutical-grade-sulfur_763291787.html?spm=a2700.7724838.35.1.yWgjkz
Oleyl Amine	251 € per 1.5kg 281.12 $ per 1.5 kg Purity: 98%	3800 $ per Ton, Purity: 99%, Distilled	**Sigma Aldrich:** https://www.sigmaaldrich.com/catalog/product/aldrich/htoa100?lang=de&region=DE **Industrial scale:** http://www.alibaba.com/product-detail/Oleyl-Amine-Distilled_50014326771.html?spm=a2700.7724838.35.1.IwhjlR
Oleic acid	46,70 € per 0.89 kg 52.30 $ per 0.89 kg Purity: 99%	1330 $ per Ton, Purity: 100%	**Sigma Aldrich:** http://www.sigmaaldrich.com/catalog/product/fluka/75096?lang=de&region=DE **Industrial scale:** http://www.alibaba.com/product-detail/oleic-acid-for-dimer-acid-polyamide_60306220697.html?spm=a2700.7724838.35.1.Ga2wCO
Octadecene	42.80 € per 0.8 kg 48 $ per 0.8 kg Purity: 90%	9000 $ per Ton, Purity: 98%	**Sigma Aldrich:** https://www.sigmaaldrich.com/catalog/product/aldrich/o806?lang=de&region=DE **Industrial scale:** http://www.labseeker.com/goods.php?id=49329
1-Dodecanethiol	41 € per 0.5 kg 46 $ per 0.5 kg Purity: 98%	1000 $ per Ton, Purity: 98%	**Sigma Aldrich:** http://www.sigmaaldrich.com/catalog/product/aldrich/471364?lang=de&region=DE **Industrial scale:** http://www.alibaba.com/product-detail/hot-sale-98-1-Dodecanethiol_60263725155.html?spm=a2700.7724838.35.1.zyqKU1
Chloroform	91.90 € per 1.48 kg 103 $ per 0.8 kg Purity: 90%	400 $ per Ton, Purity: 99.95%	**Sigma Aldrich:** http://www.sigmaaldrich.com/catalog/product/sial/650498?lang=de&region=DE **Industrial scale:** http://www.alibaba.com/product-detail/China-Chloroform-CAS-67-66-3_60246219185.html?spm=a2700.7724838.35.1.C0gy3z&s=p
Ethanol	172 € per 0.8 kg 192.64 $ per 0.8 kg Purity: 99.8%	1000 $ per Ton, Purity: 99.8%	**Sigma Aldrich:** https://www.sigmaaldrich.com/catalog/product/sial/34852?lang=de&region=DE **Industrial scale:** http://www.alibaba.com/product-detail/Ethyl-Alcohol-Ethanol-96-94-99_50012650862.html?spm=a2700.7724838.35.1.pEFEBA

Table S3. Cost calculation for 1g fabrication of the $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS NCs based on the industrial-scale prices of the raw materials. As weight template, we choose amount of the precursors that we used for 1.5g $Zn_{0.5}Cd_{0.5}S$:Mn/ZnS NCs fabrication (up-scaled by factor 10).

Chemicals	Weight	Price (Industrial), $
Zinc Acetate, Anhydrous (Core)	*0.220g = 0.000220 kg*	
Zinc Acetate, Anhydrous (Shell)	*0.878×3g = 0.002634 kg*	
Zinc Acetate, Anhydrous (Total)	2.854g = 0.002854 kg	0,00342
Cadmium Oxide	0.128g = 0.000128 kg	0.00064
Manganese Acetate, Anhydrous	0.017g = 0.000017 kg	0.000034
Sulfur	0.128g = 0.000128 kg	0.000032
Oleyl Amine	8.78g = 0.00878 kg	0,03336
Oleic acid	1.78g = 0.00178 kg	0.0023674
Octadecene	65.62g = 0.06562 kg	0,5906
1-Dodecanethiol	8.5 = 0.0085 kg	0.0085
Chloroform	44.7g = 0.0447 kg	0.01788
Ethanol	205.14g = 0.20514 kg	0.2051
Total		0.862**$**
For one Gramm		**0.862/1.5 = 0.575$**
For one Ton		**575 000$ = 0.575 Mio.$**

Table S4. Cost required scenario for the 1000kg pure NCs per year for one synthetic group division

Object	**Costs**
Cost of all raw materials for synthesis	0.575 Mio. $
Cost of the Equipment (for 5 years) and other consumables	0.3 Mio. $
Overhead costs (electricity, rent, etc.)	0.136 Mio. $ (60% of the salary)
Labor cost (man work). Assume 7 people: 1 academic staff (Control and Management), and 2 employers needed to run the company (CEO, synthesis, marketing etc.). Estimated expenses of 0.108 Mio. $ for academic and 0,060 Mio. $ for employer per person for year (this is the salary plus overhead)	0.228 Mio. $
Other costs (e.g. Patent costs, marketing, lawyers, facility etc.)	0.20 Mio. $
Total costs per year (1000 kg QDs)	**1,439 Mio. $**
Final price of the one gram QDs	**1.439 $**

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