# Supporting information materials for Size dependence of efficiency of PbS quantum dots in NiO-based dye sensitised solar cells and mechanistic charge transfer investigation

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## Preparation of PbS quantum dots

Colloidal quantum dots (PbS OA) were synthesized by a standard method<sup>1</sup>. Typically, in a first Schlenk tube was introduced a mixture of 0.210 ml of bis(trimethylsilyl) sulphide (TMS, synthetic grade) in 1-octadecene (10 ml). The solution was degassed under argon at room temperature for 2h. In second Schlenk tube, PbO (0.45g) was suspended in 15 ml of 1-octadecene and 1.5 ml of oleic acid was added. The mixture was degassed and heated at 120°C under argon during 6h. Then, the temperature of the solution was decreased to the injection temperature of the TMS/octadecene mixture for the growing the PbS QDs. The injection temperatures 90, 100, 110, 120 and 130°C were used and the mixture was heated for 2 min at this temperature to obtain QDs with diameters of 2.8, 2.9, 3, 3.2 and 3.4 nm respectively. After 2 min, the PbS QDs were precipitated with 50 mL of acetone and then centrifuged. The supernatant was removed and the QDs were dispersed in toluene. The QDs were precipitated again in acetone (30 mL) and centrifuged. Finally, the nanocrystals were dispersed in toluene (50 mg/ml).

PbS-OA were treated with tetrabutylammonium iodide (TBAI) by addition of 0.5 mL (50 mg/ml) of PbS-OA solution (5 ml) and stirred at room temperature for 15 min. 10 ml of ethanol were added to precipitate the QDs and the solution was centrifuged. PbS-TBAI were finally dispersed in octane (30 mg/ml).

### Solar cell fabrication

Conductive glass substrates (F-doped SnO<sub>2</sub>) were purchased from Solaronix (TEC15, sheet resistance 15  $\Omega$ /square). Conductive glass substrates were successively cleaned by sonication in soapy water, then ethanol for 10 min before being fired at 450 °C for 30 min. Once cooled down to room temperature, FTO plates were rinsed with ethanol and dried in ambient air.

The NiO compact layer was prepared by spin-coating onto the clean FTO substrates with a 0.5 M nickel acetate solution containing 0.5 M ethanolamine in methoxyethanol at 2000 rpm for 30s followed by thermal treatment at 500°C for 0.5h. The thickness of the NiO dense layer was measured by SEM on sliced substrates ( $30\pm5nm$ ). Then, NiO mesoporous layer was deposited on the dense layer by screen-printing with a semi-automatic screen printer. The NiO screen-printing paste was composed of 3 g of NiO nanopowder (Inframat) suspended in 10 mL of distilled ethanol and ball-milled (500 rpm) for 24 h. The resulting slurry was mixed in a round-bottom flask with 10 ml of 10 wt% ethanoic ethyl cellulose (Sigma Aldrich) solution and 20 ml terpineol, followed by slow ethanol removal by rotary evaporation. Two layers of mesoporous NiO were subsequently screen printed, with intermediate drying of the films. The dried films were then first calcined in air at 400 °C for 0.5 h. The prepared NiO electrodes ( $3 \mu m$  thick) were soaked in a solution nickel acetate in ethanol (20 mM) with 1% tetraethanolamine for 30 min at 60°C followed by ethanol rinsing and drying in air. The cells were then fired at 200°C for 30 min. The thickness of the resulting NiO films was measured by with a DEKTAK Profilometer ( $\sim3 \mu m$ ).

NiO electrodes were treated with 35% MPA (volume/volume) in acetonitrile for 3 min and dried in air. The films were then immersed in PbS QDs solution for 12h. The NiO-PbS films rinsed with octane and dried in air and then treated with a solution of CTAB (cetyltrimethylammonium bromide) in methanol (10 mg/mL) for 5 min and followed by rinsing with methanol to remove excess CTAB. This process was repeated twice.

The cobalt electrolyte was composed of 0.1 M  $[Co^{II}(dtb-bpy)_3](PF_6)_2$ , 0.1 M  $[Co^{II}(dtb-bpy)_3](PF_6)_3$  where dtb-bpy stands for 4,4'-diterbutyl-6,6'-bipyridine (Figure S5), and 0.1 M LiClO<sub>4</sub> in a mixture of propylene carbonate/acetonitrile (5/5 : vol/vol). Counter electrodes were prepared by chemical deposition of platinum from hexachloroplatinic acid in distilled isopropanol (10 mg per mL) on FTO substrates (Solaronix, TEC 7). The two electrodes were assembled on top of each other using a thin transparent film of Surlyn polymer (DuPont, 25  $\mu$ m) as a spacer. The empty cell was tightly held, and the edges were heated to 110 °C to seal the two electrodes together. A drop of electrolyte was introduced through a predrilled hole in the counter electrode by vacuum backfilling, and was sealed afterward with a thin pastille of glass and Surlyn. The cell had an active area of 0.25 cm<sup>2</sup>.

#### **Characterizations**

UV-Visible absorption spectra were recorded on a *UV-2401PC Shimadzu* spectrophotometer. Fluorescence spectra were recorded on a Horiba Jobin-Yvon *SPEX Fluoromax* fluorimeter. Infrared spectra (ATR) were recorded on a *BRUKER Vector 22* spectrometer; frequencies are reported in cm<sup>-1</sup>. Transmission electron microscopy (TEM) was performed with a Hitachi HF2000 (cold FEG, accelerating voltage 100 kV, point resolution 0.23 nm).

Electrochemical measurements were made under an argon atmosphere in acetonitrile with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>. Cyclic voltammetry experiments were performed by using a SP300 Bio-Logic potentiostat/galvanostat. A standard three-electrode electrochemical cell was used. Potentials were referred to a saturated calomel electrode as internal reference. All potentials are quoted relative to SCE. The working electrode was a platinum disk and the auxiliary electrode was a Pt wire. In all the experiments the scan rate was 10 mV·s<sup>-1</sup>.

Electrochemical impedance spectroscopy (EIS) experiments were carried out on the DSSC to access the charge transfer resistance and chemical capacitance of the various interfacial processes with a Potentiostat model VSP from Bio-Logic Science Instruments. The current/voltage characteristics of the solar cells were recorded in the dark and under 1 sun illumination at  $V_{oc}$  in the frequency range of 100 KHz to 50 mHz. The photocathode was connected to the working electrode and the anode to the counter and reference electrodes.

The current-voltage characteristics were determined by applying an external potential bias to the cell and measuring the photocurrent using a Keithley model 2400 digital source meter. An Oriel solar simulator was set to 100 mW/cm<sup>2</sup> using a Si reference solar cell to determine the optical power.

Photoluminescence decays were measured by exciting the samples with 180 femtosecond pulses at 640 nm with 100 kHz and PL was detected at different emission wavelengths using a Hamamatsu infrared streak camera (C11293). The normalised PL decays of 3.4 and 4.0 nm diameter QDs are shown in top panel of Figure S3. The additional decay due to electron or hole transfer was determined by taking the natural logarithm of the ratio of the PL decay of QDs with quencher to the PL decay of QDs without quencher (on Al<sub>2</sub>O<sub>3</sub> substrate) and are shown in middle panel of Figure S3. Then charge transfer (electron or hole transfer) was determined following the procedure given in main manuscript. The time dependent charge transfer is given in the bottom panel of Figure S3. In order to investigate the size dependence of the PL decays,



we plotted the PL decays of 3.0 nm, 3.4 nm and 4.0 nm PbS QDs in Figure S4. This clearly shows that emission lifetime becomes shorter as the size of QDs increases.

**Figure S1.** Absorption (upper panel) and normalized emission (lower panel) spectra of the PbS-TBAI quantum dots recorded in toluene solution. The samples were excited at 700 nm for all emission spectra.



Figure S2. Cyclic voltammogram of PbS quantum dot (straight line) with diameter = 2.9 nm and of the blank Pt electrode (dashed line) recorded in  $CH_3CN + Bu_4PF_6$  (0.1 M).



Figure S3. (top panel) Normalized photoluminescence decays of the PbS (d=3.4 nm, left) and (d=4.0 nm, right) recorded in different environments, (middle panel) ratio of photoluminescence kinetics of PbS QDs with quencher (electron/hole acceptor) to PbS QDs without quencher (on alumina) and (bottom panel) charge transfer rate constants determined by differentiating PL ratios (middle panel); blue line - on Al<sub>2</sub>O<sub>3</sub> with solvent and with Co<sup>II</sup> + Co<sup>III</sup> complexes; red line - on NiO with solvent but

without Co<sup>II</sup> + Co<sup>III</sup> complexes, orange line - on NiO with solvent and with Co<sup>II</sup> + Co<sup>III</sup> complexes.



**Figure S4.** Normalized photoluminescence decays of the PbS with d=3.0 nm (black dots), d=3.4 nm (green dots) and d=4.0 nm (blue dots). The red lines are multiexponential fit.



Figure S5. Structure of the cobalt complexes used as redox mediator in this study.



**Figure S6.** Current/voltage characteristics of the solar cells recorded under simulated AM1.5 (straight line) and under the dark (dashed line).



Figure S7. Absorption spectra of the cobalt complexes redox mediators recorded in acetonitrile along with that of a thin NiO film (400 nm) recorded on glass.

entry	$T^{\circ}C^{\flat}$	$\lambda_{abs}{}^c$	da	d <sup>b</sup>
		(nm)	(nm)	(nm)
1	90	884	2.7	2.8
2	100	905	2.8	2.9
3	110	925	2.9	3.0
4	120	995	3.2	3.2
5	130	1048	3.4	3.4

Table S1. Diameter of the PbS-OA quantum dots

<sup>a</sup>determined from Iwan and Moreels equation 1; <sup>b</sup>determined by HRTEM

Table S2. Absorption and emission data of the prepared PbS-TBAI QDs recorded in toluene.

entry	$d^{a}$	$\lambda_{abs}{}^a$	$\lambda_{em}{}^{b}$	Eg <sup>c</sup>
	(nm)	(nm)	(nm)	(eV)
1	2.8	900	1018	1.38
2	2.9	926	1046	1.34
3	3.0	945	1063	1.31
4	3.2	1014	1096	1.22
5	3.4	1069	1146	1.16

<sup>a</sup>excitonic peak recorded in toluene; <sup>b</sup>emission wavelength recorded in toluene, <sup>c</sup>determined from the equation 2.

#### References

1- D. Aaron, R. Barkhouse, R. Debnath, Illan J. Kramer, D. Zhitomirsky, Andras G. Pattantyus-Abraham, L. Levina, L. Etgar, M. Grätzel, Edward H. Sargent, *Adv. Mater.* 2011, **23**, 3134-3138.