

Electronic Supplementary Information (ESI)

Optimization of TiO₂ Photoanode Film for High Efficiency Quantum Dot Sensitized Solar Cells

Zhonglin Du, Hua Zhang, Huili Bao and Xinhua Zhong*

Synthesis of Oil-Soluble CdSe QDs.

Materials. Cadmium oxide (CdO, 99.99%), selenium powder (99.99%), oleylamine (OAm), 1-octadecene (ODE, 90%), trioctylphosphine (TOP, 90%), 3-Mercaptopropionic acid (MPA, 99%) and oleic acid (OA, 90%).

Oil-soluble OAm capped CdSe QDs with average size of 5.1 nm and corresponding first excitonic absorption peak at $\lambda = 620$ nm were synthesized as follows. Briefly, A Se stock solution (2.1 M) was obtained by dissolving Se powder in TOP. A Cd stock solution (0.4 M) was prepared by dissolving CdO in oleic acid and ODE (v/v, 1:1) at 250 °C. 0.5 mL of Se stock solution and 10.0 mL of OAm were heated to 300 °C under nitrogen atmosphere with stirring. 2.5 mL of Cd stock solution was injected into the reaction flask. The temperature was then set at 280 °C for the growth and annealing of nanocrystals. After, the obtained CdSe QDs were precipitated by adding methanol into the hexane solution and further isolated and purified by centrifugation and decantation.

Preparation of Water-Soluble MPA-Capped CdSe QDs.

Typically, 1.0 ml of MPA-methanol solution (0.4 mM, adjusted to pH 12 with 40% NaOH aqueous solution) was added into 5.0 mL CdSe QDs chloroform solution (containing 0.2 mmol CdSe) and stirred for 30 min to obtain the precipitation of the QDs. Then 10.0 mL water was injected into the mixture and stirred for another 20 min. The aqueous phase containing QDs was collected and purified for the next step use.

Table S1. Photovoltaic parameters derived from J - V measurement for photoanodes undergone different TiCl_4 treatment procedures. (each group has 5 devices in parallel).

cells	$J_{\text{sc}}(\text{mA} \cdot \text{cm}^{-2})$	$V_{\text{oc}} (\text{V})$	FF	PCE (%)
FTO/TiO_2	15.34	562	0.588	5.07
	15.35	562	0.597	5.14
	15.56	550	0.595	5.09
	15.66	554	0.594	5.15
	15.65	560	0.583	5.11
FTO/TiO_2/TiCl_4	15.91	562	0.590	5.29
	15.99	564	0.593	5.35
	15.99	562	0.590	5.30
	16.46	569	0.576	5.39
	16.11	570	0.594	5.45
FTO/TiCl_4/TiO_2	16.19	576	0.592	5.52
	16.22	581	0.582	5.49
	15.97	567	0.608	5.50
	16.10	570	0.605	5.55
	16.16	573	0.605	5.60
FTO/TiCl_4/TiO_2/TiCl_4	16.43	569	0.581	5.44
	15.99	567	0.589	5.34
	16.24	569	0.592	5.47
	16.46	566	0.575	5.36
	17.02	570	0.566	5.49

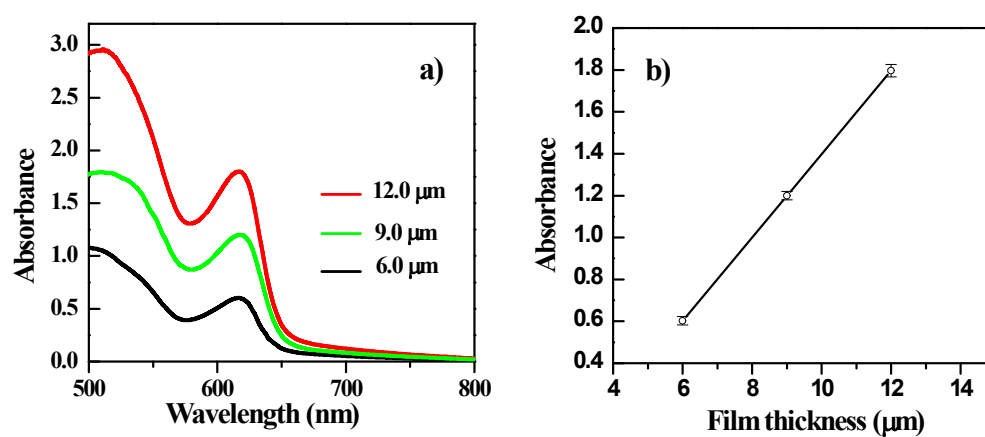


Fig. S1. (a) UV-vis absorption spectra of CdSe QDs sensitized TiO₂ film with different thickness. (b) Dependence of absorbance at the first excitonic absorption peak position on the thickness of TiO₂ film.

Table S2. Photovoltaic parameters based on CdSe solar cells with different TiO₂ transparent layer thickness.

Thickness (μm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
6.0	14.95	0.554	0.619	5.13 \pm 0.02
9.0	16.11	0.570	0.605	5.55 \pm 0.01
12.0	15.46	0.560	0.610	5.28 \pm 0.03

Table S3. Properties of the samples based on different transparent layer pastes with different EC contents.

EC:P25	Porosity	J_{sc} (mA•cm ⁻²)	V_{oc} (V)	FF	PCE (%)
0.25:1	0.53	16.16	0.562	0.587	5.33±0.10
0.5:1	0.59	16.47	0.571	0.589	5.54±0.07
0.75:1	0.65	15.98	0.561	0.599	5.37±0.08

Table S4. J - V characteristics based on various TiO₂ light-scattering-layer pastes.

Sample	Large-size particles (wt %)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
S1	0%	14.11	0.581	0.593	4.86±0.04
S2	30%	16.20	0.572	0.585	5.42±0.09
S3	40%	16.41	0.561	0.604	5.56±0.08
S4	50%	15.54	0.570	0.588	5.21±0.06
S5	100%	15.10	0.563	0.594	5.04±0.04