## Supplementary Information

Spray Deposition of Water-soluble Multiwall Carbon Nanotubes and Cu<sub>2</sub>ZnSnSe<sub>4</sub> Nanoparticles Composites as Highly Efficient Counter Electrodes in Quantum dot-Sensitized Solar Cell System

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Fig. S1 FTIR spectra of (a) the raw-MWCNTs and (b) the modified MWCNTs.

It can be found that in comparison to the raw MWCNTs, there are several newly-presented peaks in the FTIR spectrum of the modified MWCNTs sample. These peaks located at 1725

cm<sup>-1</sup>, 1386 cm<sup>-1</sup>, 1094 cm<sup>-1</sup> could be assigned to v(C=O) stretching vibration,  $\delta(O-H)$  bending vibration and v(C-O) stretching vibration of the carboxylic groups (COOH) respectively. The results demonstrate clearly the surface of MTCNTs has been functionalized by the COOH groups.



**Fig. S2** FTIR spectra of (a) OLA, (b) OLA-capped CZTSe and (c) pyridine modified CZTSe. The peaks located at 2921 cm<sup>-1</sup>, 2865 cm<sup>-1</sup>, 1644 cm<sup>-1</sup>, 1468 cm<sup>-1</sup> are owing to OLA.

From FTIR spectrum of OLA-capped CZTSe nanocrystals, the peaks owing to OLA can be clearly observed, after reflux in pyridine, they disappear. The results also demonstrate the effectiveness of surface modification of CZTSe.



**Fig. S3** Photographs of CdSe sensitized photoanode (the left image), spray deposited MWCNTs-CZTSe composite counter electrode (the middle image) and the completed solar cell (the right image).



Fig. S4 SEM image of TiO<sub>2</sub> nanorods film used as the photoanode in QDSC.



Fig. S5 Raman scattering spectrum of the freshly prepared CZTSe nanoparticles.

The peaks located at 174 cm<sup>-1</sup>, 196 cm<sup>-1</sup>, 233 cm<sup>-1</sup> are corresponding to the signals of pure CZTSe product; no other by-products can be detected.



Fig. S6 EDX spectra of the as-synthesized CZTSe nanoparticles.

The composition of the as-synthesized CZTSe was determined to be  $Cu_{1.98}Zn_{1.21}Sn_{0.92}Se_{3.89}$ , very close to the ideal stoichiometric proportion of Cu: Zn: Sn: Se = 2: 1: 1: 4.



Fig. S7 SEM image and EDX elemental mapping of the MWCNTs-CZTSe composite film.