# **Experimental Section**

## Synthesis of PEG-m-CQDs

2 g of glucose was heated at  $195 \pm 5$  °C using a heating mantle for 6 min until the liquid was changed from colorless to orange. Subsequently, the resultant was dissolved in 50 mL of deionized water for future use. 0.2 g of PEG (M<sub>w</sub> = 4000) was added into 30 mL of above-mentioned solution, and stirred until dissolved completely. Then the solution was transferred into a Teflon lined autoclave and heated at 170 °C for 6 h. After cooling to room temperature, the solution was subjected to filtered, centrifuged (8000 rpm) and dialyzed in a dialysis bag (3500 D) for three days and the pure PEG-*m*-CQDs aqueous solution with the property of down- and up-conversion was obtained.

## Synthesis of transparent CoSe CE

A mixing aqueous solution consisting of 2 mM SeO<sub>2</sub> ultrafine powers, 2 mM CoCl<sub>2</sub> and 100 mM LiCl in deionized water. Subsequently, the CoSe alloy CE on cleaned FTO glass was built on a traditional CHI660E setup comprising a CE of platinum sheet, an Ag/AgCl reference electrode, and a working electrode of FTO substrate. A cyclic voltammetry method was realized by depositing CoSe. The potential range, scan rate and scanning number were controlled at -1.0 to 0.4V, 10 mV s<sup>-1</sup> and 1 cycle, respectively.

#### Synthesis of transparent CQDs-CoSe CE

The above-mentioned CoSe electrode was used as a new work electrode, the pure PEG-*m*-CQDs aqueous solution was a electrolyte. A cyclic voltammetry method was realized by depositing PEG-*m*-CQDs on the surface of CoSe substrate. The fluorescent CE was prepared by scanning from -0.8 to 0.4 V at a scan rate of 10 mV s<sup>-1</sup> for 10 cycle.

#### Assembly of DSSCs and photovoltaic measurements

The N719 dye-sensitized TiO<sub>2</sub> photoanode with an active area of 0.25 cm<sup>2</sup> was prepared according to our previous report.<sup>S1</sup> Each DSSC device was fabricated by sandwiching the redox electrolyte between a dye-sensitized TiO<sub>2</sub> anode and a CoSe or CQDs-CoSe transparent alloy CE. A liquid redox electrolyte consists of 0.1 M tetraethylammonium iodide, 0.1 M tetramethylammonium iodide, 0.1 M tetrabutylammonium iodide, 0.1 M NaI, 0.1 M KI, 0.1 M LiI, 0.05 M I<sub>2</sub> and 0.05 M 4-tertbutyl-pyridine in acetonitrile. The photocurrent density-voltage (*J-V*) curves of various solar cells were recorded on a CHI660E electrochemical work station under irradiation of simulated solar light from an intensity controlled to 100 mW cm<sup>-2</sup> xenon arc lamp.



**Fig. S1.** (a) The photographs of the PEG-*m*-CQDs taken under visible light (left) and 365 nm UV lamp irradiation (right). (b) TEM image of the PEG-*m*-CQDs (insert is the HRTEM image). (c) UV-vis absorption of PEG-*m*-CQDs. PL emission spectra of the PEG-*m*-CQDs under excitation in the range of (d) 350-490 nm and (e) 725-950 nm.

|                  | $J_{ m Red1}$       | Em    | R                       | Rat                     | $J_{ m lim}$        | $J_0$               |
|------------------|---------------------|-------|-------------------------|-------------------------|---------------------|---------------------|
| CEs              | (mA cm <sup>-</sup> | Σpp   |                         |                         | (mA cm <sup>-</sup> | (mA cm <sup>-</sup> |
|                  | <sup>2</sup> )      | (V)   | $(\Omega \text{ cm}^2)$ | $(\Omega \text{ cm}^2)$ | <sup>2</sup> )      | <sup>2</sup> )      |
| CoSe, dark       | -6.304              | 0.510 | 16.13                   | 13.26                   | 1.264               | 0.768               |
| CoSe, light      | -6.421              | 0.502 | 16.21                   | 13.18                   | 1.298               | 0.616               |
| CQDs-CoSe, dark  | -6.592              | 0.502 | 12.69                   | 13.83                   | 1.461               | 0.588               |
| CQDs-CoSe, light | -7.127              | 0.451 | 12.82                   | 9.543                   | 1.624               | 0.590               |

**Table S1.** The electrochemical parameters extracted from CV, EIS and Tafel characterizations.

[1] Y. Duan, Q. Tang, B. He, Z. Zhao, L. Zhu and L. Yu, J. Power Sources, 2015, 284, 349-354.