## The Improved Efficiency of Quantum-Dot-Sensitized Solar Cells with a Wide Spectrum and Pure Inorganic Donor-Acceptor Type Polyoxometalate as a Collaborative Cosensitizer

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## **Supplementary Physical and Chemical Characterizations**



Fig. S1 The normal Raman spectrum for T.

Raman spectrum, which was studied as a kind of scattering spectrum, could provide the structure of POMs by researching their vibration and rotation energy. In the Fig. S1, the bands from 800-900 cm<sup>-1</sup> were associated with the stretching mode of W-O<sub>b</sub>-W or W-O<sub>c</sub>-W and 900-1000 cm<sup>-1</sup> were associated with the stretching mode of W-Ot. Beyond that the lower energy regions were associated with the bending mode of W-Ob-W or W-Oc-W or Si-O. Therefore the normal Raman spectrum can confirm the structure of prepared T.



Fig. S2 TG curve of T. The thermal stability of T was analyzed by its TG curve, which displayed three-step weightlosses occurred in the temperature range of 50-600°C. The three-step weightlosses were all attributed to the loss of water.



Fig. S3 EDS spectrum for a) pure  $TiO_2$ ; b)  $T1@TiO_2$ ; c)  $T2@TiO_2$ ; d)  $T3@TiO_2$ ; f) T4@TiO\_2.



Fig. S4 Element mapping of  $T3@TiO_2$  powder: a) the SEM image of the  $T2@TiO_2$ ; b) the element mapping of Si; c) the element mapping of Ti; d) the element mapping of Co; f) the element mapping of W.



Fig. S5 The X-ray photoelectron spectroscopy of Ti of T3@TiO<sub>2</sub>. The Fig. S5 exhibits two peaks at ca. 458.2 eV in the energy region of  $Ti_{2p3/2}$  and ca. 463.9 eV in the energy region of  $Ti_{2p1/2}$ , which are consistent with the Ti<sup>IV</sup> oxidation state.<sup>S1</sup>



Fig. S6 The elemental mass ratio of W/Ti in T1@TiO<sub>2</sub>, T2@TiO<sub>2</sub>, T3@TiO<sub>2</sub>, T4@TiO<sub>2</sub>. The loading amount of T in the composites was determined by inductively coupled plasma atomic emission spectrometer(ICP-AES), from which the W content in composites was 3.78%, 7.49%, 14.17%, 21.10% respectively.



Fig. S7 The SEM images of the prepared  $T2@TiO_2$  under the low multiples.



Fig. S8 The SEM images of the prepared  $T2@TiO_2$  under the high multiples.



Fig. S9 The SEM images of different photoanode films: a) pure  $TiO_2$  film; b) T3@TiO\_2 film, which showed that pure  $TiO_2$  film consisted of uniform  $TiO_2$  particles, whereas T2@TiO\_2-doped film contained some agminated micropore ball.



Fig. S10 Cyclic voltammetry curve of the T in 0.5M HAc/NaAc buffer solution with pH = 6.00 in the voltage range from 0 V to -1.2 V



Fig. S11 Cyclic voltammetry curve of the T in 0.5M HAc/NaAc buffer solution with pH = 6.00 in the voltage range from 0V to 1.2V.



Fig. S12 the electron lifetime calculated from OCVD of CdSe sensitized T1@TiO<sub>2</sub>, T2@TiO<sub>2</sub>, T3@TiO<sub>2</sub> and T4@TiO<sub>2</sub> cells; the Inset) the electron lifetime calculated from OCVD of CdSe sensitized pure TiO<sub>2</sub> and T0@TiO<sub>2</sub> cells.



Fig. S13 UV-vis absorption spectra of CdSe sensitized pure  $TiO_2$  and  $T@TiO_2$  photoanode films after deposition for 6h.

Absorption spectra of CdSe sensitized pure TiO<sub>2</sub> and T@TiO<sub>2</sub> photoanode films were shown in Fig. S13. As can be see from the Fig. S13, the absorbance of CdSe sensitized TO@TiO<sub>2</sub> photoanode films are slightly larger than the CdSe sensitized pure TiO<sub>2</sub> photoanode films. The possible reason is that the large particles of TiO<sub>2</sub> are conducive to the absorption of the spectrum. Furthermore, the absorbance of CdSe sensitized T@TiO<sub>2</sub> (T1@TiO<sub>2</sub>, T2@TiO<sub>2</sub>, T3@TiO<sub>2</sub>, T4@TiO<sub>2</sub>) photoanode films increased with the increase of the content of T. And the absorbance of CdSe sensitized T@TiO<sub>2</sub> (T1@TiO<sub>2</sub>, T2@TiO<sub>2</sub>, T3@TiO<sub>2</sub>, T4@TiO<sub>2</sub>) photoanode films are obvious wider than the CdSe sensitized pure TiO<sub>2</sub> photoanode films in the range from the 550 to 600nm and after 650nm. Experimental results show that T added to the photoanodes as collaborative cosensitizer can constitute a wider spectrum of absorption.

Table S1 Simulated values of resistance (Rrec) and capacitance (C $\mu$ ) for cell devices based on CdSe sensitized pure TiO<sub>2</sub> and T@TiO<sub>2</sub> photoanodes at the forward bias of -0.60 V.

| Cells                            | TiO <sub>2</sub> | T0@TiO <sub>2</sub> | T1@TiO <sub>2</sub> | T2@TiO <sub>2</sub> | T3@TiO <sub>2</sub> | T4@TiO <sub>2</sub> |
|----------------------------------|------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| $R_{rec}/\Omega\;cm^{\text{-}2}$ | 49               | 65                  | 153                 | 254                 | 310                 | 144                 |
| $C_{\mu}/mF\ cm^{-2}$            | 3.21             | 3.23                | 3.31                | 3.39                | 3.27                | 3.18                |

## References

S1 M. Vasilopoulou, A. M. Douvas, L. C. Palilis, S. Kennou, and P. Argitis, J. Am. Chem. Soc. 2015, 137, 6844–6856.