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ARTICLE TYPE

# Polyoxometalate-CdS quantum dots co-sensitized TiO<sub>2</sub> nanorods array: Enhanced charge separation and light to electricity conversion efficiency

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## 1. Incident photon-to-current conversion efficiency (IPCE) spectra of photoanodes

The IPCE is a useful tool for analyzing light-harvesting efficiency because the spectral response would be changed with the quantity of sensitizer.<sup>[1]</sup> As shown in Figure s1, symmetric increase of IPCE is observed after POM molecules modification. Therefore, efficiency enhancement is not caused by the light-harvesting efficiency of the sensitizer. This result also shows that the amount of CdS sensitizer in the electrode is almost the same, which is in consistent with the absorption result shown in Figure 3a. So the charge-transfer kinetics at the CdS/AMT/TiO<sub>2</sub>-electrolyte interface was mainly investigated by impedance analysis in the manuscript.

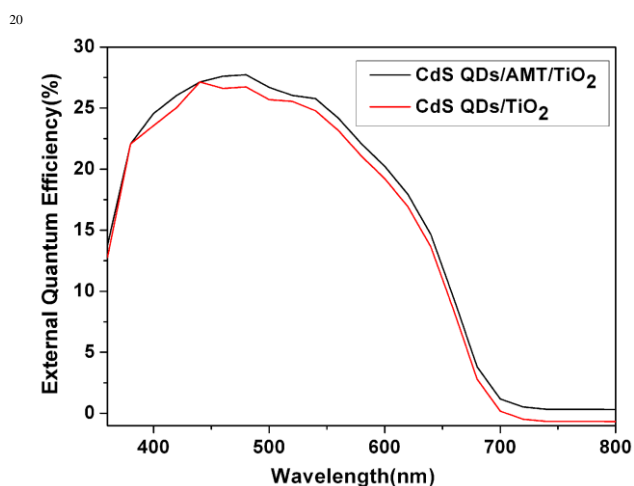


Figure s1 Incident photon-to-current conversion efficiency (IPCE) spectra of CdS QDs/AMT/TiO<sub>2</sub> NRs and CdS QDs/TiO<sub>2</sub> NRs films.

## 2. The influence of deposition cycle on the performance of photoanodes

For the CdS QDs/AMT/TiO<sub>2</sub> NRs system, the photocurrent-voltage (J-V) curves of electrodes with different cycles are shown in Figure s2 and Table s1. It can be seen that both J<sub>sc</sub> and V<sub>oc</sub> increase with the deposition cycles and reach a maximum value, after which they decrease. The highest J<sub>sc</sub> (3.2 mA/cm<sup>2</sup>) and power conversion efficiency (1.12 %) are achieved with 9 cycles. The increase in the photocurrent represents more photon harvesting and possibly lower electron-hole recombination due to larger spatial separation between CdS quantum dots and AMT molecules. The decrease in the photocurrent from 9 to 12 cycles may be related to the

aggregation of CdS, the presence of more recombination sites as the CdS bulk-like properties are reached. On the other hand, the FF of the electrode with 12 cycles is smaller than the others, probably due to the lower driving force for the electron injection.

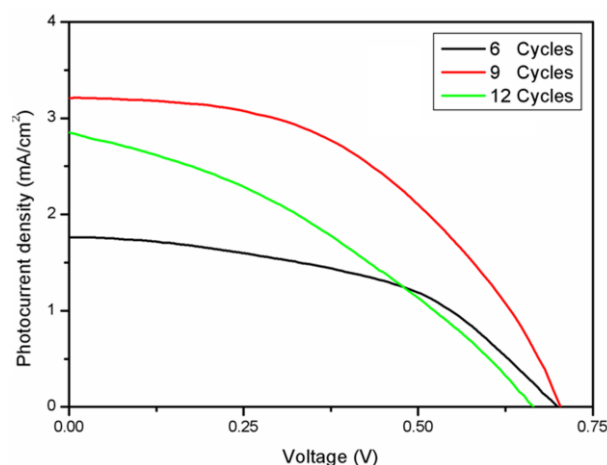


Figure s2 J-V curves of CdS QDs/AMT/TiO<sub>2</sub> NRs structures with different cycles.

Table s1 J-V characteristics of CdS QDs/AMT/TiO<sub>2</sub> NRs structures with different cycles.

Sample	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	η (%)
CdS QDs/AMT/TiO <sub>2</sub> 6 Cycles	0.69	1.75	0.49	0.60±0.10
CdS QDs/AMT/TiO <sub>2</sub> 9 Cycles	0.7	3.2	0.48	1.12±0.06
CdS QDs/AMT/TiO <sub>2</sub> 12 Cycles	0.66	2.8	0.36	0.67±0.08

## 3. PV properties of TiO<sub>2</sub> and TiO<sub>2</sub>/AMT

The PV properties of pure TiO<sub>2</sub> and the TiO<sub>2</sub> nanorods with only the POM adsorbed have been characterized as following and since they can only absorb the UV light which is about 4% of the solar light, both of their conversion efficiency are very low. But we still can observe the significant increase after the AMT molecules modification (0.13% and 0.18%, respectively, for TiO<sub>2</sub> and TiO<sub>2</sub>/AMT films), indicating that AMT molecules play an important role in efficient electron transfer among the components of the nanohybrids as described in the manuscript.

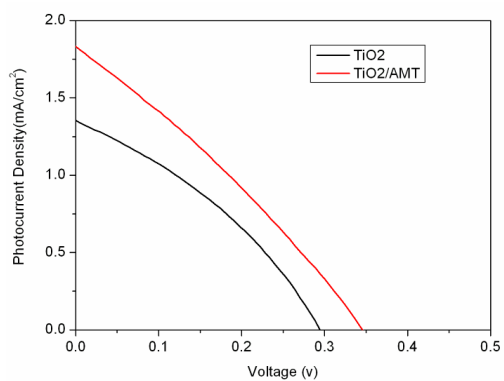


Figure s3 J–V curves of TiO<sub>2</sub> NRs and TiO<sub>2</sub>/AMT NRs films.

### References

- [1] V. González-Pedro, X. Xu, I. Mora-Seró, J. Bisquert, ACS Nano, 2010, 4, 5783.