Electronic Supplementary Information

¹ Fabrication and photoelectrochemical characteristics of CuInS₂ and

PbS quantum dots co-sensitized TiO₂ nanorods photoelectrodes

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Fig. S1 TEM images of (a) $CuInS_2(4)/TiO_2$, (b) $CuInS_2(8)/TiO_2$, (c) $PbS(2)/CuInS_2(6)/TiO_2$, (d) $PbS(6)/CuInS_2(6)/TiO_2$.

Fig. S1a shows the TEM image of $CuInS_2(4)/TiO_2$. It can be seen that there are a small quantity of QDs on the surface of TiO₂ nanorod. After 8 depositing cycles, there are a large number of QDs covered over the surface of TiO₂ nanorod (Fig. S1b). When the PbS QDs are deposited on the TiO₂ nanorod arrays by 2 cycles, the surface of TiO₂ nanorod becomes rougher than that without PbS QDs (Fig. S1c). The QDs aggregate into some large bulk QDs with size out of the quantum size range seriously in the PbS(6)/CuInS₂(6)/TiO₂ photoelectrode (Fig. S1d). The aggregation of excessive QDs weakens or even dissolves the quantum size effect, and increases the series resistance of photovoltaic devices, which decreases the photoelectrochemical performance of QDSSCs eventually.



Fig. S2 XPS spectra of $PbS(4)/CuInS_2(6)/TiO_2$: (a) survey spectrum, (b) Cu 2p, (c) In 3d, (d) Pb 4f, (e) S 2p, (f) Ti 2p and (g) O 1s.

In order to confirm the composition in $PbS(4)/CuInS_2(6)/TiO_2$ and valence states of elements, the XPS analysis of $PbS(4)/CuInS_2(6)/TiO_2$ is conducted as shown in Fig. S2. The survey spectrum shows the presence of Cu, In, Pb, S, Ti and O elements in the sample (Fig. S2a), and confirms the high purity of the PbS QDs, CuInS₂ QDs and TiO₂ nanorods (the carbon content and the C 1s line shape are typical of surface contamination detected in air-exposed oxide surfaces). High-resolution XPS spectrum of the most intense peaks of the six main elements (Cu $2p_{3/2}$, In $3d_{5/2}$, Pb $4f_{7/2}$, S 2p, Ti 2p_{3/2} and O 1s) are shown in Fig. S2b-g. As shown in Fig. S2b, the binding energies of 931.9 eV (Cu 2p_{3/2}) and 951.8 eV (Cu 2p_{1/2}) are consistent with Cu (I). The binding energy of Cu $2p_{3/2}$ for Cu (II) usually centered at 942 eV,¹ does not appear, which can be concluded that only Cu (I) exists in the sample and Cu (II) of the raw material has been reduced during the preparing process. The binding energies of In 3d are 444.5 eV (In $3d_{5/2}$) and 452.08 eV (In $3d_{3/2}$), suggesting the presence of In (III) (Figure S2c). The peaks of the binding energies of 138.6 eV (Pb $4f_{7/2}$) and 143.5 eV (Pb $4f_{5/2}$) are assigned to Pb in PbS (Fig. S2d). The close up survey in S 2p region (161.8 eV) doublet peaks located at 161.38 eV (S $2p_{3/2}$) and 162.5 eV (S $2p_{1/2}$) with an energy difference of 1 eV (Fig. S2e), which are assigned to S coordinated to Cu, In and Pb.² Moreover, the peaks of the binding energies at 458.7 eV and 464.6 eV were assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ (Fig. S2f), which are attributed to that of crystalline rutile TiO₂, and the binding energy of the O 1s peak displayed in Fig. S2g at about 532.1 eV corresponds to that of O in TiO₂.³



Fig. S3 EDS line scan profiles of $PbS(4)/CuInS_2(6)/TiO_2$ for Ti, O (a) and S, Cu, In, Pb (b) elementals. The inset in b is the STEM images.

To elucidate the structures of the $PbS(m)/CuInS_2(n)/TiO_2$ photoelectrodes, the energy dispersive spectroscopy (EDS) line scan in the scanning transmission electron microscope (STEM) is utilized. Fig. S3 shows the EDS line scan profiles of $PbS(4)/CuInS_2(6)/TiO_2$ for Ti, O (a) and S, Cu, In, Pb (b) elementals, which reveals the relative locations of the embedded CuInS₂ QDs and PbS QDs. There is a O-rich area in the middle of the samples (Fig. S3a) and the outer shell is the S-rich QD-layer (Fig. S3b). More importantly, the outermost shell of the QD-layer is Pb-rich and the inner layer is Cu-rich with a very clear line drawn in 30 nm and 170nm, manifesting the cascade structure of $PbS(4)/CuInS_2(6)/TiO_2$ photoelectrode as described in Fig. 1f.



Fig. S4 Plots of $(\alpha hv)^2$ against photon energy (hv) for (a) CuInS₂(6)/TiO₂ and (b) PbS(4)/TiO₂ photoelectrodes.

Fig. S4 presents the plots of $(\alpha hv)^2$ against photon energy (hv) for CuInS₂(6)/TiO₂ and PbS(4)/TiO₂ photoelectrodes. The band gap of CuInS₂(6)/TiO₂ and PbS(4)/TiO₂ electrodes is 1.52 eV and 0.74 eV respectively, which is smaller than that of CuInS₂ and PbS QDs but larger than that of bulk CuInS₂ and PbS. Therefore, it can be determined that the enhanced absorption in the longer wavelength region is



due to the quantum confinement effect of the CuInS₂ and PbS QDs.

Fig. S5 EIS Nynquist plots of various photoelectrodes measured in the dark and under visible light irradiation.

Fig. S5 shows the EIS Nynquist plots of various photoelectrodes measured in the dark and under visible light irradiation with a frequency interval of 10^5 - 10^{-2} Hz. The EIS plot of TiO₂ nanorods is almost a straight line because of its property of non-response within visible light. After the deposition of CuInS₂ QDs, the curve radius reduces, which indicats that CuInS₂/TiO₂ electrode could greatly and effectively improve the separation of photo-generated electron–hole pairs. Meanwhile, the deposition of PbS QDs decrease the curve radius compared with CuInS₂/TiO₂ electrode, confirming the quicker interfacial charge transfer and electron injection process.



Fig. S6 Mott-Schottky plots of various photoelectrodes collected at a frequency of 5 kHz in the dark and under visible light irradiation.

To further elucidate the Fermi level alignment of PbS/CuInS₂/TiO₂ photoelectrodes and evaluate the electron-transfer properties of semiconductor interface, Mott-Schottky plots are measured in the dark and under visible light irradiation. The slope of Mott-Schottky plot represents the charge carrier density N_D as it can be calculated by the equation: N_D = $(2/e_0\epsilon\epsilon_0)[d(1/C^2)/dV]^{-1}$, where e₀ is the elementary electron charge, ϵ is the permittivity of the semiconductor electrode, ϵ_0 is the permittivity of vacuum and $d(1/C^2)/dV$ is the slope of Mott-Schottky plot, which means the smaller the slope of Mott–Schottky plot is, the higher the charge carrier density of photoelectrode increases with the deposition of CuInS₂ and PbS QDs, which could lead to the upwards shift of the Fermi level, and the conduction band of CuInS₂ and

PbS QDs is enhanced relatively. Moreover, according to the literatures,^{5,6} the enlarged band gap of QDs could enhance the conduction band of semiconductor QDs, which lead to the expected higher conduction band of PbS QDs coupled with the upwards shift of the Fermi level as shown in Fig. 9b.



Fig. S7 EDX spectrum of CuInS₂(6)/TiO₂.

To determine the element ratio of Cu: In: S of CuInS₂, the energy dispersive X-Ray (EDX) spectroscopy is conducted on the sample of CuInS₂(6)/TiO₂ and presented in Fig. S7. The atomic ratio of Cu: In: S is around 1: 1: 2, which matches with the stoichiometry of CuInS₂. In addition, the atomic ratio of Ti: O is around 1: 2, corresponding to the stoichiometry of TiO₂. The C element in the spectrum may be due to the carbon layer on the nickel grid. Hence, it can be conclude that the high stoichiometric CuInS₂ QDs are deposited on the surface of TiO₂ nanorods.

Fig. S8 shows the time stability of the unencapsulated QDSSC assembled with $PbS(4)/CuInS_2(6)/TiO_2$ electrode. After two days, there is a slight relative decrease of

7% under ambient air. However, the normalized η decreases by 30% after four days, which is maybe due to the instability and difficult attachment to TiO₂ nanorods of QDs. The stability of QDSSCs is relatively poor and need further investigation.



Fig. S8 Time stability, under ambient air, of the normalized current density (J_{SC}) of QDSSC assembled with PbS(4)/CuInS₂(6)/TiO₂ electrode.

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