Supporting Information

Boosting photoelectrochemical hydrogen generation on Cu-doped AgIn₅S₈/ZnS

colloidal quantum dots sensitized photoanodes via shell-layer homojunction defect

passivation

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Experimental

Materials

Copper iodide (Cul, 99.999%), silver nitrate (AgNO₃, 99.99%), indium acetate (In(Ac)₃, 99.99%), 1-octadecence (ODE, 99.6%), 1-dodecanethiol (DDT, 96%), Sulfur (S, 99%), oleylamine (OLA, 70%), sodium sulfite (Na₂SO₃), zinc acetate dehydrate (Zn(Ac)₂·2H₂O), sodium sulfide nonahydrate (Na₂S·9H₂O), and toluene, ethanol, methanol, acetone were bought from Sigma-Aldrich Inc. Ti-Nanoxide BL/SC was purchased from Solaronix. Titania paste (18 NR-AO) containing a mixture of 20 nm sized anatase nanoparticles and larger (≈450 nm sized) anatase scatter particles paste was obtained from Dyesol (Queanbeyan, Australia). ZrO₂ nanoparticles powder (≈100 nm sized) were purchased from Sigma-Aldrich Inc. The FTO/glass substrates (14 Ω sq⁻¹) were bought from XOP Glass Co., Ltd. All chemicals were used without further purification.

Core CAIS CQDs synthesis

Cu-doped AgIn₅S₈ colloidal quantum dots (core CAIS CQDs) were synthesized by using the modified hot injection method¹. Cul (the content is 0, 5, 10 and 20 % the molar weight of AgNO₃, respectively), 0.1 mmol AgNO₃ and 0.5 mmol In(Ac)₃ were dissolved in 8.0 ml ODE in a flask and degassed with N₂ for 30 min at room temperature, and heated to 80 °C. Then, 1.0 ml DDT was injected into the reaction flask. The reaction solution was heated to 120 °C until became clear. The S precursor with the mixture of 0.80 mmol S and 1.3 mL OLA was quickly injected into the flask under vigorous stirring. The reaction solution continued reacting for 8 min was then quenched with cold water. The product was precipitated with anhydrous ethanol, centrifuged to remove the unreacted precursors. The as-synthesized CAIS CQDs were redispersed in toluene.

ZnS shell growth

In a reaction to synthesize core/shell CAIS/ZnS CQDs, 0.1 mmol S and 0.1 mmol Zn(Ac)₂ dissolved in the mixed solution of OLA and ODE (the ratio of OLA/ODE is 3/2, in all 5 mL) was injected into the above reaction solution containing CAIS core

CQDs. After that, the temperature was retained for 15 min (CAIS/ZnS) and 90 min (CAIS/6ZnS) to promote the growth of the ZnS shell. the resulting CQDs solution was quenched with cold water to room temperature to harvest CQD products. Finally, the as-synthesized core/shell CQDs were dispersed in toluene after washing and purification treatment.

Preparation of c-TiO₂/m-TiO₂ and m-ZrO₂ films

A thin and compact layer of TiO₂ (c-TiO₂ film) was deposited onto a FTO/glass substrate at 6000 r.p.m. for 30 s by using Ti-Nanoxide BL/SC precursor solution, and sintered at 500 °C for 30 min in an oven. Subsequently, mesoporous TiO₂ layer (m-TiO₂ film) blade-coating was tape-casted on c-TiO₂/FTO substrates by using commercial TiO₂ paste (18 NR-AO) according to the previous method.² After coating, the TiO₂ paste layer was kept in air for 12 min and dried at 120 °C for 6 min, and the same procedure was done again. Then, the as-prepared m-TiO₂/c-TiO₂ films were obtained after annealed at 500 °C for 30 min in air. For deposition of m-ZrO₂ film, the mesoporous ZrO₂ layer were deposited on FTO/glass by using the commercial ZrO₂ nanoparticles with the same blade-coating procedure and annealing process.

Fabrication of CQDs-based photoelectrochemical cell

The CQDs were deposited on c-TiO₂/m-TiO₂ film to fabricate CQDs-sensitized photoanodes by electrophoretic deposition (EPD). ³⁻⁵ During the EPD procedure, a pair of m-TiO₂/c-TiO₂/FTO/glass substrates were vertically immersed in CQDs solution and the distance between them was adjusted at 1 cm. A direct current bias of 200 V was applied for 100 min. After that, the CQDs-sensitized photoanodes were rinsed off with toluene several times to wash off the redundant CQDs absorbed on the surface of the m-TiO₂ film, and then dried with N₂ at room temperature. Subsequently, a successive ionic layer adsorption and reaction (SILAR) treatment was used to deposit a ZnS capping layer on the as-prepared CQDs photoanodes with the structure of the CQDs/m-TiO₂/c-TiO₂/FTO/glass substrates

to prevent photodecomposition and/or photocorrosion by the optimized SILAR deposition cycle (two cycles).⁶ For ZnS SILAR passivation treatment, the CQDs-photoanodes was immersed into the Zn^{2+} precursor (0.1 M Zn(Ac)₂ in methanol) for 1 min, and then into the S²⁻ precursor (0.1 M Na₂S in methanol/DI water (1:1 v/v)) for 1 min. After each immersion, the electrode was thoroughly rinsed with corresponding solvents and then dried in N₂ flow. After two SILAR cycles, the epoxy resin was coated on the surface of the CQDs photoanodes to complete photoelectrochemical cell (PEC) fabrication. PEC device was a standard three-electrode electrochemical cell configuration with a working electrode (CQDs photoanodes), Pt counter electrode and an Ag/AgCl (saturated with KCl) reference electrode. The active area of the working electrode ranges is 0.10±0.04 cm².

Theoretical calculation of wave functions

Theoretical wave functions of the 1S states of electron and hole were calculated by using the stationary Schrödinger equation in spherical geometry solved in COMSOL (a commercial software for finite element simulation)^{7,8}. The bulk values were used for the effective masses of electrons (m_e^*) and holes (m_h^*), namely $m_e^* = 0.21 m_0$ and $m_h^* = -2.72 m_0$ for AgIn₅S₈ (AIS), $m_e^* = 0.22 m_0$ and $m_h^* = -2.37 m_0$ for Cu-doped AgIn₅S₈ (CAIS), and $m_e^* = 0.24 m_0$ and $m_h^* = -0.86 m_0$ for ZnS, where m_0 is the electron mass at rest in vacuum. For the bulk materials, the potentials for electrons and holes as a function of position were approximated as the lowest unoccupied molecular orbital and the highest occupied molecular orbital levels, respectively. For AIS, these levels are -3.80 eV and -6.10 eV, respectively; for CAIS, these levels are -3.50 eV and -7.10 eV, respectively. The interaction between electrons and holes was neglected in the calculations.

Characterization

High resolution transmission electron microscopy (HRTEM) images of CQDs images were acquired by using a JEOL ARM200CF TEM/STEM at 200 keV. The tested sample is the

diluent of the colloid solution. ICP-OES was carried out with an Agilent 5100 ICP-OES system. X -ray diffraction (XRD) spectra were carried out on a Philips X'pert diffractometer using Cu K α radiation source (λ = 0.1541 nm) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was performed on using a VG Escalab 220i-XL electron spectrometer applying a Twin Anode X-Ray Source. All binding energies were referenced to the C_{1s} peak at 284.8 eV. Absorption spectra were acquired with using a Cary 5000 UV-Vis-NIR spectrometer (Varian) at a scan rate of 600 nm min⁻¹ in transmission mode. Steady-state photoluminescence (PL) were taken with a Fluorolog-3 system (Horiba Jobin Yvon) and the excitation wavelength was set at 500 nm. Time-resolved PL (TRPL) measurement were performed with fluorescence lifetime spectrometer with a 444 nm laser (Fluo Time 300, Pico-Quant FmbH). The morphology of the device samples was characterized with a JSM-7401F scanning electron microscope (SEM). The performance of the CQDs-photoanodes PEC was evaluated in a typical three-electrode configuration, consisting of 0.35 M Na₂SO₃ and 0.25 M Na₂S (pH = 12.5) as the sacrificial hole scavengers, a Pt counter electrode, and a saturated Ag/AgCl reference electrode. All potentials measured with respect to Ag/AgCl were converted to the RHE scale according to the following equation $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197 + \text{pH} \times 0.059$. Current-potential measurements were carried out with an electrochemical workstation (CHI-760D) by using a solar simulator (SLB-300A Solar Simulator Class AAA) under simulated one-sun (100 mW cm⁻², AM 1.5G), two suns (200 mW cm⁻²), and three suns (200 mW cm⁻²) illumination, respectively. All the current versus potential measurements were carried out at a 20 mV s⁻¹ sweep rate.



Figure S1. Schematic diagram of doping and shell-isolated procedures for synthesis and structure of the CAIS/ZnS core/shell CQDs.



Figure S2. The SAED patterns of a) CAIS and b) CAIS/ZnS CQDs.



Figure S3. X-ray diffraction (XRD) patterns of CuIn₅S₈ PDF#72-0956.



Figure S4. a) Schematic diagram of X-ray photoelectron spectra (XPS) measurement. b) XPS survey spectra of AIS, CAIS, CAIS/ZnS and CAIS/6ZnS CQDs.



Figure S5. a) Cu 2*p* core level spectra in X-ray photoelectron spectra of CAIS/ZnS and CAIS/6ZnS CQDs. b) Ag 3*d*, c) In 3*d* and d) S 2*p* core level spectra in X-ray photoelectron spectra of CAIS/ZnS CQDs.



Figure S6. a) UV-vis absorption spectra and b) photoluminescence spectra of CAIS CQDs (the Cu doping content is 0 %, 5 %, 10 % and 20 %, respectively) with and without ZnS shell (the reaction time is 15 min).



Figure S7. Photoluminescence spectra of a) CAIS/ZnS and b) CAIS/6ZnS CQDs solutions and deposited on TiO_2 and ZrO_2 films.



Figure S8. The as-prepared CQDs were deposited into the mesoporous TiO_2 films via electrophoretic deposition (Left) with CQDs/toluene solutions. The illustrative schematic of the Glass |FTO|c-TiO₂|m-TiO₂-CQDs sensitized photoanode architecture (Right).



Figure S9. Cross-sectional SEM image of the completed the $Glass|FTO|c-TiO_2|m-TiO_2^-$ QDs photoanode architecture and the corresponding EDS 2D mapping of the chemical composition including the essential elements: Ti, Cu, Ag, In, S and Zn, respectively.

Figure S10. Photocurrent density distribution for the $Glass|FTO|c-TiO_2|m-TiO_2-CQDs$ sensitized photoanode photoelectrochemical cell under AM 1.5 G illumination at 100 mW cm⁻² (5 samples).

Figure S11. Photocurrent measurement with linear sweep voltammetry for the $Glass|FTO|c-TiO_2|m-TiO_2-CAIS$ CQDs sensitized photoanode a) with and b) without ZnS SILAR treatment in photoelectrochemical cell under AM 1.5 G illumination at 100 mW cm⁻² with the optimal performance.

Figure S12. Photocurrent measurement with linear sweep voltammetry for the $Glass|FTO|c-TiO_2|m-TiO_2$ photoanode photoelectrochemical cell without the deposition of the CQDs under AM 1.5 G illumination at 100 mW cm⁻².

Figure S13. Photocurrent measurement with linear sweep voltammetry for the $Glass|FTO|c-TiO_2|m-TiO_2-CAIS/ZnS CQDs$ sensitized photoanode photoelectrochemical cell under AM 1.5 G illumination at 100 mW cm⁻² with the optimal performance.

Figure S14. Photocurrent measurement with linear sweep voltammetry for the $Glass|FTO|c-TiO_2|m-TiO_2-CAIS/6ZnS CQDs$ sensitized photoanode photoelectrochemical cell under AM 1.5 G illumination at 100 mW cm⁻² with the optimal performance.

Figure S15. H_2 evolution rate of CAIS/ZnS CQDs-sensitized photoanode as a function of time at 0.5 V vs. RHE under AM 1.5 G illumination (100 mW/cm²). H_2 evolution calculation was based on the obtained photocurrent density. The calculated mole of hydrogen was obtained according to Faraday's laws of electrolysis using the measured current based on the following formula^{9, 10}:

$$n_{H_2} = \frac{1}{z} \frac{q}{F} = \frac{1}{2} \frac{\int_{t_1}^{t_2} I dt}{F} = \frac{1}{2} \frac{I \times t}{F}$$

Where *n* is the number of equivalent and equals to the numbers of H₂ moles. *q* is the quantity of electric charge in coulomb (C) and equals to $I \times t$. *I* is the photocurrent in amperes (A) and *t* is time in seconds (s). When the current is not constant, the quantity of charge passed through the circuit equals to the integration of the measured current over time (t). *F* is the Faraday constant (i.e. 96484.34 C/mole, q = nF) carried by one mole of electrons. *z* is the number of transferred electrons per mole of water (i.e. z = 2). We used the above-mentioned equation to monitor the H₂ evolution as a function of time as CAIS/ZnS CQDs sensitized photoanode for PEC devices, showing very accurate trend between photocurrent density and time. Based on the calibration curve, the evolution rate of H₂ exhibited a nearly linear increase over time. Integrated the photocurrent density in Figure 4e, the calculated hydrogen generation rate was \approx 73.5 µmol cm⁻² h⁻¹.

Table S1 Inductively coupled plasma-atomic emission spectrometry of CAIS, CAIS/ZnS and CAIS/6ZnS CQDs. The wavelength position of the element: Cu (324.754 nm), Ag (324.068 nm), In (230.606 nm), Zn (180.669 nm), and S (180.669 nm), respectively.

Formula ^a	Cu (ppm)	Ag (ppm)	In (ppm)	S (ppm)	Zn (ppm)	Formula ^b
Cu _{0.10} Ag _{0.90} In ₅ S ₈ / ZnS	2.02	16.52	89.43	44.18	33.33	$\begin{array}{c} Cu_{0.18}Ag_{0.90}In_{4.57}Z \\ n_{0.58}S_{8.10} \end{array}$
Cu _{0.10} Ag _{0.90} In ₅ S ₈ / 6ZnS	1.69	15.86	89.74	59.9	31.51	$\begin{array}{c} {\sf Cu}_{0.16}{\sf Ag}_{0.90}{\sf In}_{4.8} \\ {\sf Zn}_{2.95}{\sf S}_{11.4} \end{array}$

^aCalculated by the ratio of [Cu]/[Ag] precursor used. ^bCalculated by ICP-OES analysis results.

Table S2 Fitted parameters of TRPL decay curves in AIS CQDs (The Cu doping content is 0
%) and CAIS CQDs with different Cu doping contents. (The Cu doping content is 5 %, 10 %
and 20 %, respectively)

Cu doping content (%)	B ₁	τ ₁ (ns)	<i>B</i> ₂	τ ₂ (ns)	τ _{av} (ns)
0	0.0114	25.32	0.9886	256.29	256.0
5	0.003	17.54	0.997	344.73	344.7
10	0.0053	27.98	0.9947	371.38	371.2
20	0.0065	20.12	0.9935	310.71	310.6

Table S3 Fitted parameters of TRPL decay curves in CAIS, CAIS/ZnS and CAIS/6ZnS CQDs.The Cu doping content in CAIS CQDs is 10%.

CQDs	Absorptio n edge (nm)	PL peak Positio n (nm)	<i>A</i> ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{av} (ns)
CAIS	640	734	0.0053	27.98	0.9947	371.38	371.2
CAIS/ZnS	610	722	0.0045	17.92	0.9955	400.31	400.2
CAIS/6ZnS	580	720	0.0417	13.66	0.9583	454.12	453.6

Table S4 Electron transfer rate and hole transfer rate calculated from the fitted parameters of TRPL decay curves in CAIS, CAIS/ZnS and CAIS/6ZnS CQDs with different substrates.

CQDs	Substrate s	<i>A</i> ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{av} (ns)	K _{et} (×10 ⁶ s ⁻¹)	<i>K_{ht}</i> (×10 ⁶ s ⁻¹)
	TiO ₂	0.186	11.29	0.814	98.11	95.9	5.71	
CAIS	ZrO ₂	0.0384	28.77	0.9616	212.84	211.9		
	ZrO ₂ /Elec	0.1437	14.99	0.8563	121.97	119.8		3.63
	TiO ₂	0.2084	12.63	0.7916	98.89	96.1	6.34	
CAIS/ZnS	ZrO ₂	0.0291	30.87	0.9709	246.47	245.7		
	ZrO ₂ /Elec	0.1297	13.56	0.8703	124.43	122.7		4.08
CAIS/6ZnS	TiO ₂	0.1422	15.53	0.8578	116.68	114.5	5.29	
	ZrO ₂	0.0079	17.13	0.9921	290.82	290.7		
	ZrO ₂ /Elec	0.0301	14.25	0.9699	189.37	189.0		1.85

CQDs	Electrolyte	Photocurrent density (mA∙cm⁻²) vs RHE (V)	Ref.
TiO₂/Cu-AgIn₅S ₈ /ZnS	NaS ₂ /Na ₂ SO ₃ , pH=12.5	14.6 mA·cm ⁻² at 0.75 V	This work
TiO_2/Zn -CulnSe _x S _{2-x}	NaS ₂ /Na ₂ SO ₃ , pH=12.5	5.3 mA·cm⁻² at 0.80 V	2
TiO ₂ /Cd- CuInSe _x S _{2-x}	NaS ₂ /Na ₂ SO ₃ , pH=12.5	4.62 mA·cm ⁻² at 0.80 V	2
TiO ₂ /CdSe/6CdSeS/6CdS	NaS ₂ /Na ₂ SO ₃ , pH=12.5	11.0 mA·cm ⁻² at 0.90 V	3
TiO ₂ /Zn-AgInS2	NaS ₂ /Na ₂ SO ₃ , pH=12.5	5.70 mA·cm ⁻² at 0.90 V	4
TiO ₂ /g-CdSe/CdS	NaS ₂ /Na ₂ SO ₃ , pH=12.5	10.0 mA·cm ⁻² at 0.92 V	6
TiO ₂ /PdSe _{1-x} S _x	NaS ₂ /Na ₂ SO ₃ , pH=12.5	5.0 mA·cm ⁻² at 0.92 V	10
TiO ₂ /CdSe _x S _{1-x}	NaS ₂ /Na ₂ SO ₃ , pH=12.5	3.8 mA·cm⁻² at 0.92 V	10
TiO ₂ /PbS/CdS	NaS ₂ /Na ₂ SO ₃ , pH=12.5	11.2 mA·cm ⁻² at 0.3 V	11
TiO ₂ /PbS/CdS/CdS	NaS ₂ /Na ₂ SO ₃ , pH=12.5	8.0 mA·cm ⁻² at 0.3 V	11
TiO ₂ /CdS/ZnS	NaS ₂ /Na ₂ SO ₃ , pH=12.5	4.5 mA·cm ⁻² at 0.3 V	11
TiO ₂ /PbS/CdS/ZnS	NaS ₂ /Na ₂ SO ₃ , pH=12.5	7.5 mA·cm ⁻² at 0.6 V	12
TiO ₂ /CdSe/CdS	NaS ₂ /Na ₂ SO ₃ , pH=12.5	5.51 mA·cm ⁻² at 0.92 V	13
TiO ₂ /SnSe	NaS ₂ /Na ₂ SO ₃ , pH=12.5	7.4 mA·cm ⁻² at 0.6 V	14
TiO ₂ /Zn-CuInSe ₂	NaS ₂ /Na ₂ SO ₃ , pH=12.5	4.27 mA·cm ⁻² at 0.92 V	15
$TiO_2/Zn-CuInSe_2/CuInS_2$	NaS ₂ /Na ₂ SO ₃ , pH=12.5	3.1 mA·cm⁻² at 0.92 V	15
NiOOH/FeOOH/(W,Mo)- BiVO ₄ /WO ₃	0.5M K ₂ SO ₄ , pH=7	5.3 mA·cm⁻² at 1.23 V	16
NiOOH/FeOOH/CQD/BiVO ₄	KH ₂ PO ₄ , pH=7	5.9 mA·cm ⁻² at 1.23 V	17
TiO ₂ /CdSe	NaS ₂ /Na ₂ SO ₃ , pH=11.5	14.9 mA·cm ⁻² at 0.6 V	18
TiO ₂ /PbS/Mn-CdS	NaS ₂ /Na ₂ SO ₃ , pH=12.5	22.1 mA·cm ⁻² at 0.6 V	19

Table S5 Summary on photocurrent density versus different CQDs-based photoanodesfor PEC cell.

CQDs	Substrates	ZnS SILAR	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{av} (ns)	K _{e-h} (×10 ⁶ s⁻ ¹)
CAIS	TiO ₂ /Elec	w/o	0.246 9	12.77	0.753 1	92.97	89.5	6.45
CAIS/ ZnS	TiO ₂ /Elec	w/o	0.250 8	9.99	0.749 2	86.33	83.5	7.91
	TiO ₂	w/o	0.208 4	12.63	0.791 6	98.90	96.1	6.34
	TiO ₂	w	0.109 8	14.78	0.890 2	129.3 9	127.8	3.75
	TiO ₂ /Elec	W	0.208 3	13.02	0.791 7	98.89	96.0	6.35
CAIS/ 6ZnS	TiO ₂ /Elec	W	0.083 7	11.00	0.916 3	139.1 1	138.2	3.80

Table S6 Electron transfer rate calculated from the fitted parameters of TRPL decay curves

 in CAIS, CAIS/ZnS and CAIS/6ZnS CQDs with different substrates.

The K_{e-h} is calculated on the basis of Marcus theory with the following equation ^{6, 20}:

$$K_{e-h} = \frac{1}{\tau_{CQDs/(TiO, \text{ or } TiO, / Elec)}} - \frac{1}{\tau_{CQDs/(ZrO, -1)}}$$

Where $\tau_{CQDs/TiO2}$ and $\tau_{CQDs/ZrO2}$ were the average PL lifetime of CQDs on TiO₂ and ZrO₂ substrates, respectively. $\tau_{CQDs/TiO2/$ *Elec* $}$ corresponded to the average PL lifetime of CQDs on TiO₂ substrate with the addition of the electrolyte.

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