Supporting Information

Plasmonic Effect with Tailored Au@TiO_2 Nanorods in Photoanode for Quantum Dot Sensitized Solar Cells

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Chemicals

Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$), Cetyltrimethylammonium bromide (CTAB, 99%), Sodium hydroxide (NaOH), L-ascorbic acid (AA, 99.7%), and Sodium borohydride ($NaBH_4$, 96%) were obtained from Aldrich. Terpineol, ethyl cellulose, Titanium chloride solution ($TiCl_3$, 15.0~20.0% basis in 30% HCl), Poly(sodium 4-styrenesulfonate) (PSS, molecular weight: 70000 g/mol) were obtained from Aldrich. The commercial TiO_2 powder (P25, a mixed phase of 80% anatase and 20% rutile) was purchased from Degussa. Copper iodide (CuI, 99.998%), Indium acetate ($In(OAc)_3$, 99.99%), and 3-mercaptopropionic acid (MPA, 97%) were purchased from Alfa Aesar. Selenium powder (200 mesh, 99.99%), oleylamine (OAm, 95%), and 1-octadecene (ODE, 90%) were obtained from Aldrich. Zinc acetate ($Zn(OAc)_2$, 99.99%) and diphenylphosphine (DPP, 98%) were received from J&K. All chemicals were used as received without further treatment.

Synthesis of Au NRs

The CTAB-stabilized Au NRs was prepared through a seed-mediated growth method in aqueous solutions.[1] Briefly, the freshly seed solution was prepared by the addition of ice-cold $NaBH_4$ solution (0.6 mL, 0.01 M) into a mixture containing $HAuCl_4$ (0.25 mL, 0.01 M) and CTAB (9.75 mL, 0.1 M), and kept at room temperature for 2 h before use. The growth solution was prepared by the sequential addition of $HAuCl_4$ (2 mL, 0.01 M), $AgNO_3$ (0.4 mL, 0.01 M), HCl (0.8 mL, 1.0 M) and ascorbic acid (0.32 mL, 0.1 M) into CTAB (40 mL, 0.1 M). The mixture solution was stirring for 30 s, the seed solution (0.1 mL) was added rapidly for growing the Au NRs with its longitudinal plasmon resonance wavelength at 800 nm. The reaction solution was mixed by gentle inversion for 2 min, then kept at 30 ^oC overnight. After centrifugation, the obtained pellet was redispersed in deionized water.

Synthesis of oil-soluble Zn-Cu-In-Se QDs

The initial oil-soluble Zn-Cu-In-Se (Zn-Cu-In-Se) QDs were prepared according to our reported methods.[2] First, Zn stock solution was prepared by dissolving 110.0 mg $Zn(OAc)_2$ (0.5 mmol) in a mixture of 1.0 mL OAm and 4.0 mL ODE at 130 °C under N_2 atmosphere, while Se precursor was prepared by dissolving 24.0 mg Se powder (0.3 mmol) in a mixture of 0.3 mL DPP and 0.5 mL OAm under ultrasonication at room temperature. Then 19.0 mg CuI (0.1 mmol) and 29.0 mg $In(OAc)_3$ (0.1 mmol) were loaded in a flask containing 2.0 mL OAm, 1.5 mL ODE and 0.4 mL the Zn stock solution prepared. The mixture was heated to 180 °C under N_2 atmosphere followed by the injection of 0.8 mL DPP-Se precursor. After reacting for 5 min, the system was cooled to room temperature. The OAm capped Zn-Cu-In-Se QDs formed were subsequently precipitated by ethanol and sequent centrifuged, and finally dispersed in 10.0 mL dichloromethane.

Preparation of water-soluble Zn-Cu-In-Se QDs

The water-soluble Zn-Cu-In-Se QDs capped by MPA were prepared via ligand exchange following our pervious procedure.[3] Typically, the pH value of 1.0 mL of 2.0 M MPA methanol solution was first adjusted to 10. The MPA solution was then mixed with the purified oil-soluble Zn-Cu-In-Se QD dispersion under stirring. After 2 min, 20 mL deionized water was added into the mixture above, and the QDs were extracted to water phase. The water-soluble QDs were purified through precipitation with acetone and sequent centrifugation. The purified MPA capped Zn-Cu-In-Se QDs were finally redissolved in deionized water for further use.

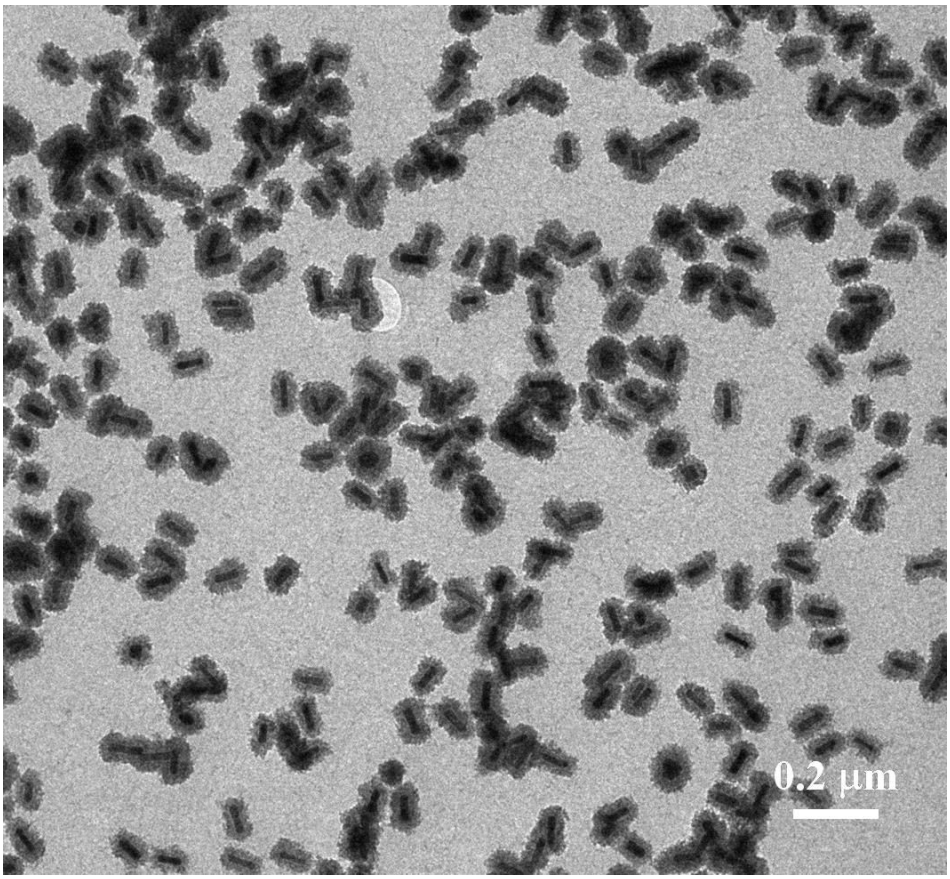

Figure S1. Representative TEM images obtained at low magnification of the Au NRs/TiO_2 samples.

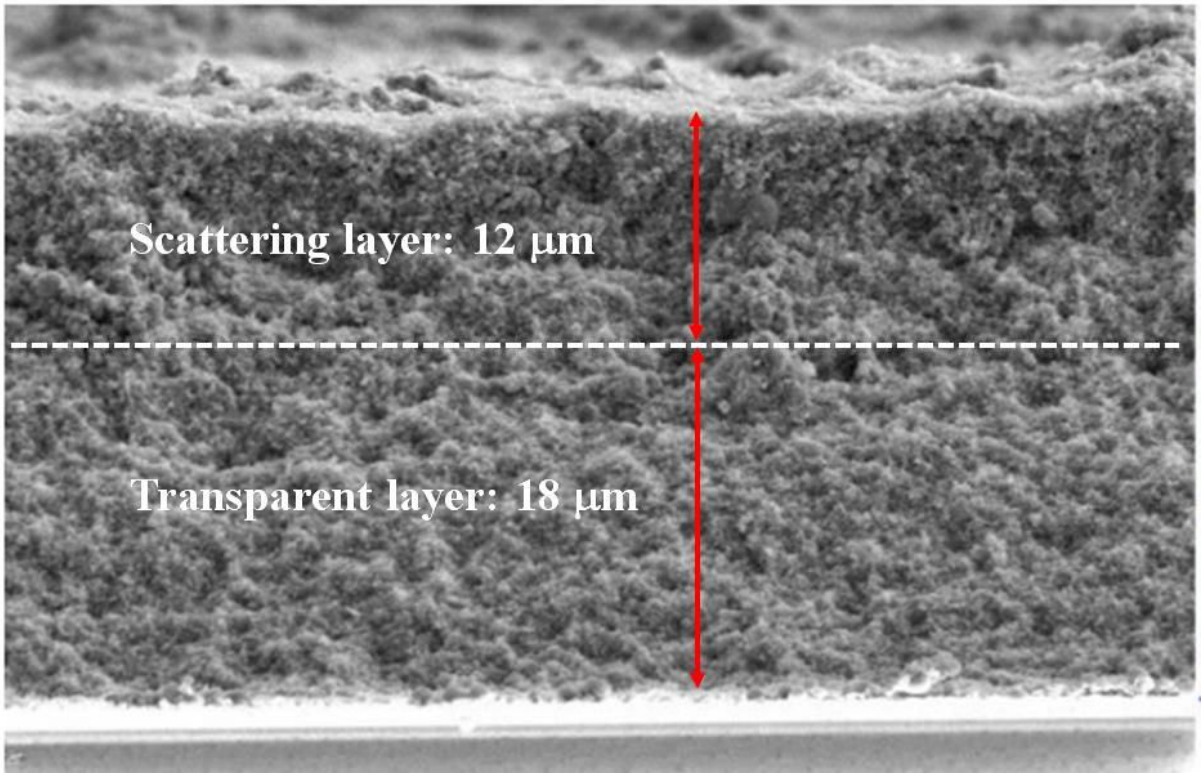

Figure S2. Cross-section SEM images of the traditional double-layer TiO_2 photoanode film.

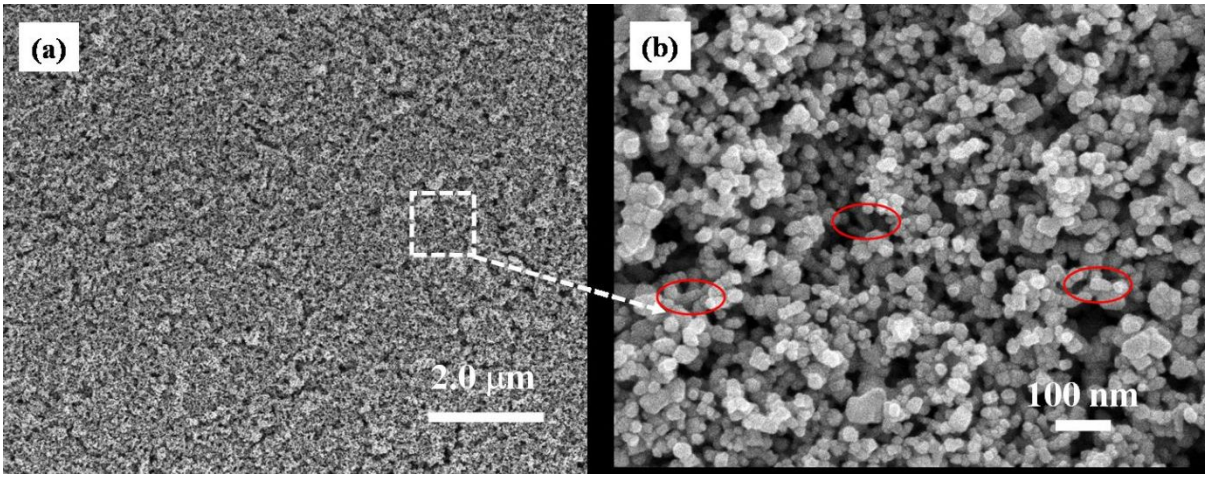

Figure S3. Low-magnification (a) and high-magnification (b) surface SEM images of the photoanode films incorporated with Au NRs/TiO_2, respectively.

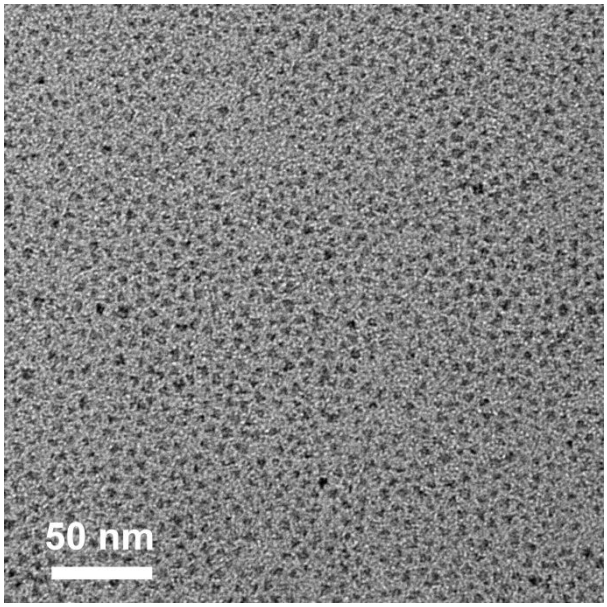

Figure S4. TEM images of the pre-synthesized Zn-Cu-In-Se QDs

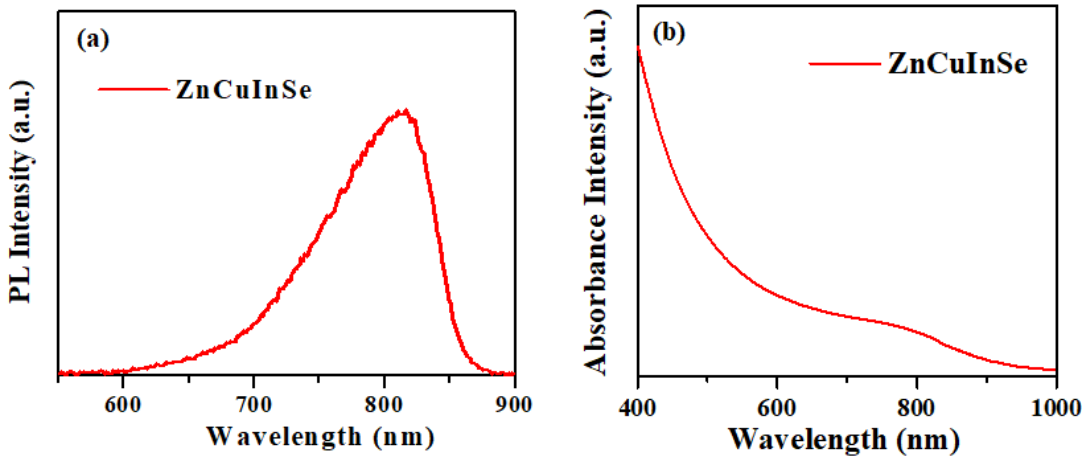

Figure S5. PL and UV-vis absorption spectra of the pre-synthesized Zn-Cu-In-Se QDs.

Table S1. Photovoltaic parameters of individual Zn-Cu-In-Se QDSCs based on three different types of TiO_2 MOMFs under the illumination of 1 full sun intensity.

Photoanode	J_{sc} (mA·cm^{-2})	V_{oc} (V)	FF	PCE (%)
w/o Au NRs in MOMFs	20.76	0.603	0.579	7.25
	20.87	0.605	0.576	7.27
	20.62	0.609	0.573	7.20
Average	20.75 ± 0.10	0.607 ± 0.002	0.576 ± 0.002	7.25 ± 0.03
with Au NRs in MOMFs	24.13	0.610	0.579	8.52
	24.61	0.604	0.577	8.58
	23.95	0.608	0.581	8.46
Average	24.23 ± 0.34	0.608 ± 0.003	0.579 ± 0.002	8.52 ± 0.06
double-layer MOMFs	23.47	0.604	0.583	8.31
	23.85	0.602	0.579	8.31
	23.62	0.608	0.571	8.20
Average	23.64 ± 0.16	0.605 ± 0.002	0.578 ± 0.005	8.26 ± 0.05

Table S2. Fitted impedance values at -0.6 V forward bias for three types of TiO_2 MOMFs in QDSCs.

MOMFs	R_s (Ω)	CPE (mF cm^{-2})	R_{CE} (Ω cm^{-2})	C_μ (mF cm^{-2})	R_{rec} (Ω cm^{-2})	τ_n (ms)
w/o Au NRs	8.44	3.86	3.61	4.32	121.4	524.4
with Au NRs	7.35	3.91	4.04	4.74	200.6	950.8
double-layer MOMFs	9.28	3.70	4.20	4.13	142.1	586.5

Table S3. Photovoltaic parameters of individual Zn-Cu-In-Se QDSC based on Au NRs/TiO_2 nanostructures in MOMFs with different concentration under the illumination of 1 full sun intensity.

Concentration (wt%)	J_{sc} (mA·cm^{-2})	V_{oc} (V)	FF	PCE (%)
0	20.76	0.603	0.579	7.25
	20.87	0.605	0.576	7.27
	20.62	0.609	0.573	7.20
Average	20.75 ± 0.10	0.607 ± 0.002	0.576 ± 0.002	7.25 ± 0.03
0.93 wt%	22.38	0.616	0.589	8.12
	21.93	0.615	0.597	8.05
	21.67	0.613	0.594	7.89
Average	21.99 ± 0.36	0.614 ± 0.002	0.593 ± 0.004	8.02 ± 0.10
1.62 wt%	23.13	0.619	0.581	8.32
	23.09	0.614	0.574	8.14
	22.95	0.616	0.585	8.27
Average	23.06 ± 0.09	0.616 ± 0.003	0.580 ± 0.006	8.24 ± 0.09
2.57 wt%	24.13	0.610	0.579	8.52
	24.61	0.604	0.577	8.58
	23.95	0.608	0.581	8.46
Average	24.23 ± 0.34	0.608 ± 0.003	0.579 ± 0.002	8.52 ± 0.06
3.23 wt%	23.37	0.593	0.564	7.82
	23.21	0.587	0.559	7.62
	23.28	0.585	0.567	7.72
Average	23.28 ± 0.08	0.588 ± 0.004	0.563 ± 0.004	7.72 ± 0.08

Table S4. Fitted impedance values at -0.6 V forward bias for photoanodes undergone different content of Au NRs/TiO_2 in MOMFs.

Concentration	R_s (Ω)	CPE (mF cm^{-2})	R_{CE} (Ω cm^{-2})	C_μ (mF cm^{-2})	R_{rec} (Ω cm^{-2})	τ_n (ms)
0	8.44	3.86	3.61	4.32	121.4	524.4
0.93 wt%	8.96	1.68	7.68	4.25	154.8	657.9
1.62 wt%	7.82	2.63	4.43	4.99	160.2	799.4
2.57 wt%	7.35	3.91	4.04	4.74	200.6	950.8
3.23 wt%	8.97	4.64	7.84	4.28	155.6	665.9

Reference:

1. B. Nikoobakht, M. A. El-Sayed, Preparation and growth mechanism of gold nanorods (NRs) using seed-mediated growth method, Chem. Mater. 15 (2003), 1957-1962
2. J. Du, Z. Du, J.S. Hu, Z. Pan, Q. Shen, J. Sun, D. Long, H. Dong, L. Sun, X. Zhong, L.J. Wan, Zn-Cu-In-Se Quantum Dot Solar Cells with a Certified Power Conversion Efficiency of 11.6%, J. Am. Chem. Soc. 138 (2016) 4201-4209.
3. H. Zhang, K. Cheng, Y. M. Hou, Z. Fang, Z. X. Pan, W. J. Wu, J. L. Hua, X. H. Zhong, Efficient CdSe quantum dot-sensitized solar cells prepared by a postsynthesis assembly approach, Chem. Commun. 48 (2012), 11235-11237.