Electronic Supplementary Information

Colloidal ZnTe quantum dots-based photocathode with metal-insulator-semiconductor structure towards solar-driven CO_2 reduction to tunable syngas

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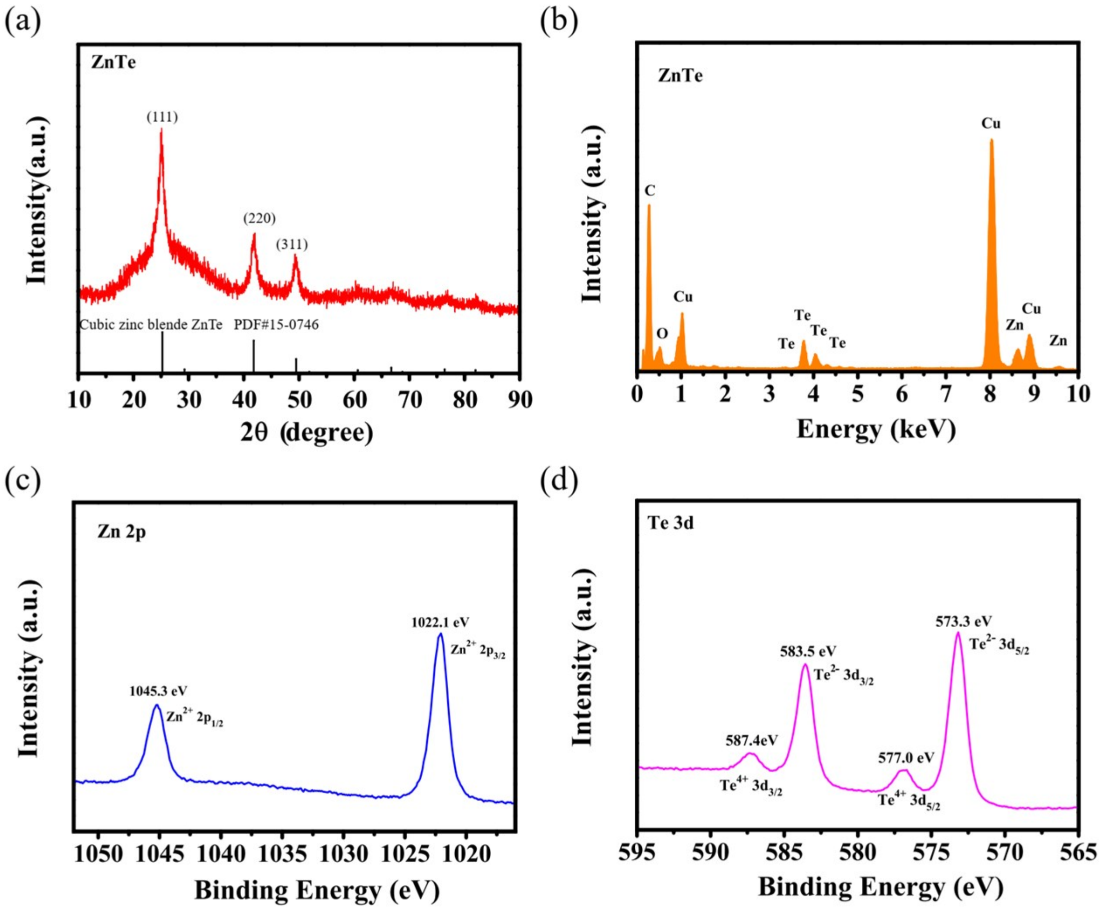

Fig. S1 (a) XRD pattern, (b) EDX spectrum of ZnTe QDs on TEM copper grid, XPS spectra of (c) Zn 2p and (d) Te 3d for the ZnTe QDs.

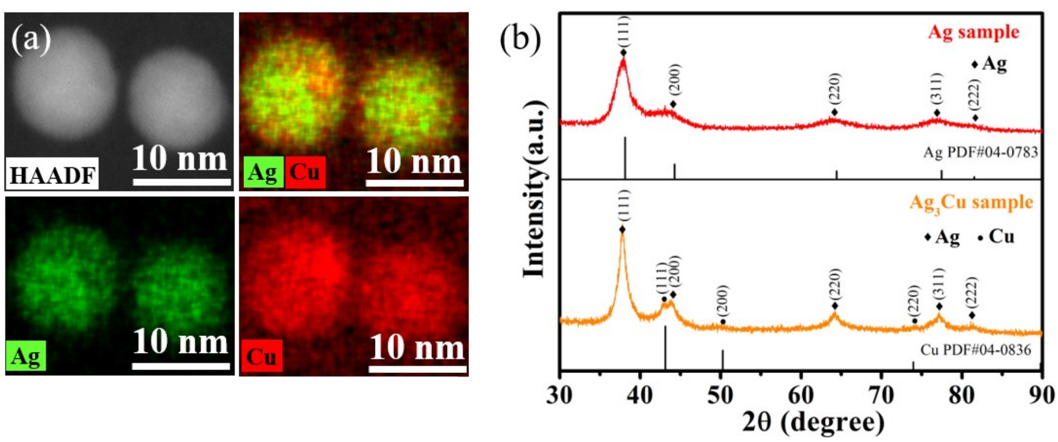

Fig. S2 (a) HAADF-STEM and corresponding EELS mapping of Ag_3Cu NCs, (b) XRD patterns of Ag_3Cu and Ag NCs.

Table S1
Elemental composition of Ag and Cu in colloidal Ag_3Cu NCs.

Sample	Weight% (ICP-MS)		Atomic ratio (ICP-MS)
	Ag	Cu	Ag : Cu
Ag_3Cu	78.8	15.1	3.07

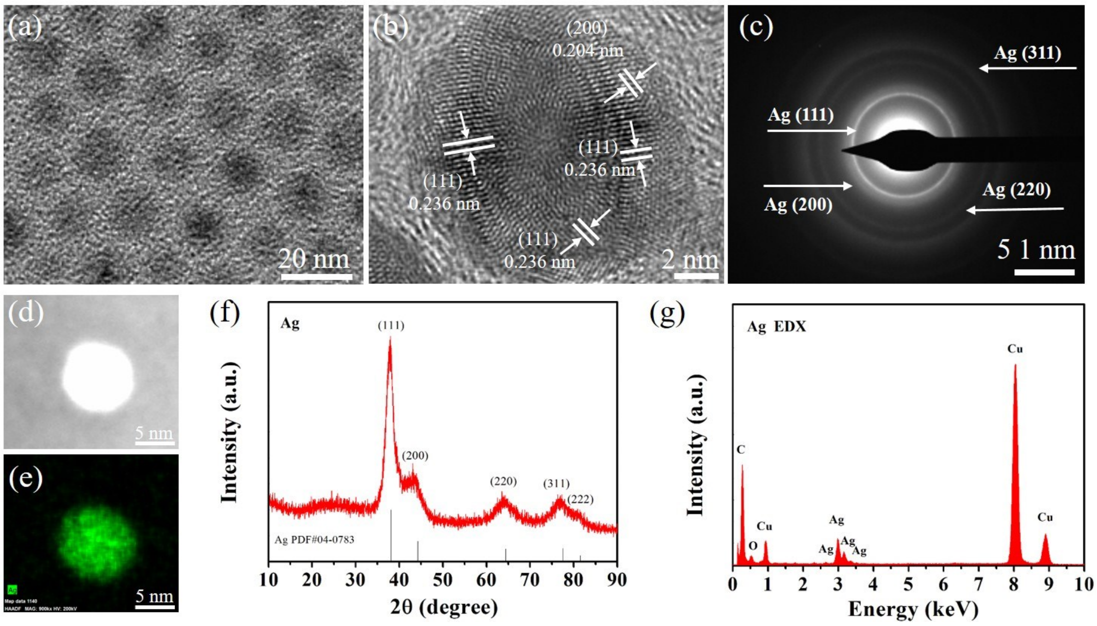

Fig. S3 (a) TEM image, (b) HRTEM image, (c) corresponding SAED pattern, (d) HAADF-STEM, (e) corresponding EELS-elemental mapping image, (f) XRD pattern and (g) EDX spectrum of Ag NCs.

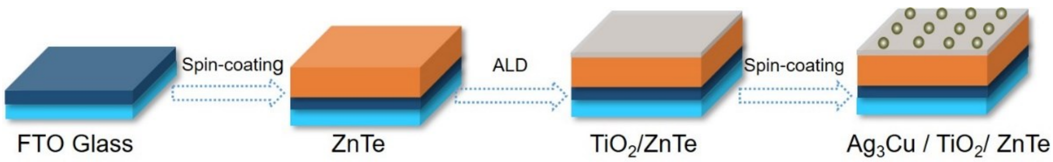

Fig. S4 Schematic of the fabrication procedures of the $Ag_3Cu/TiO_2/ZnTe$ MIS photocathode.

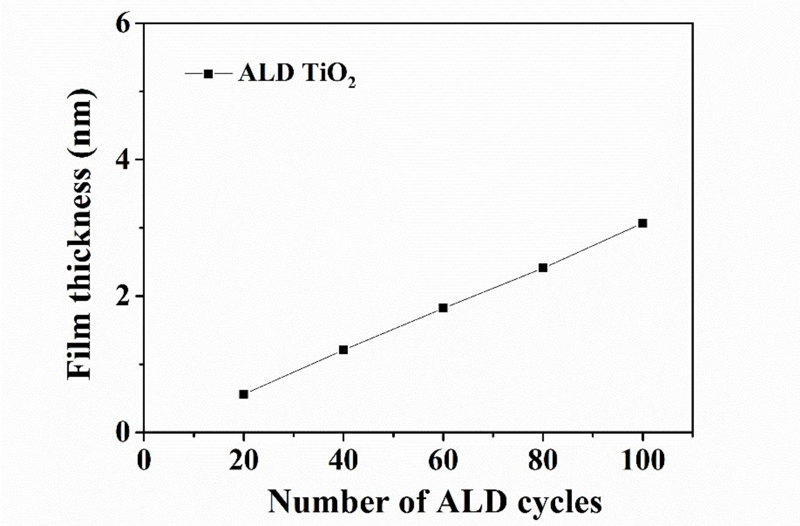

Fig. S5 Thickness of ALD-deposited TiO_2 film determined by ellipsometry results.

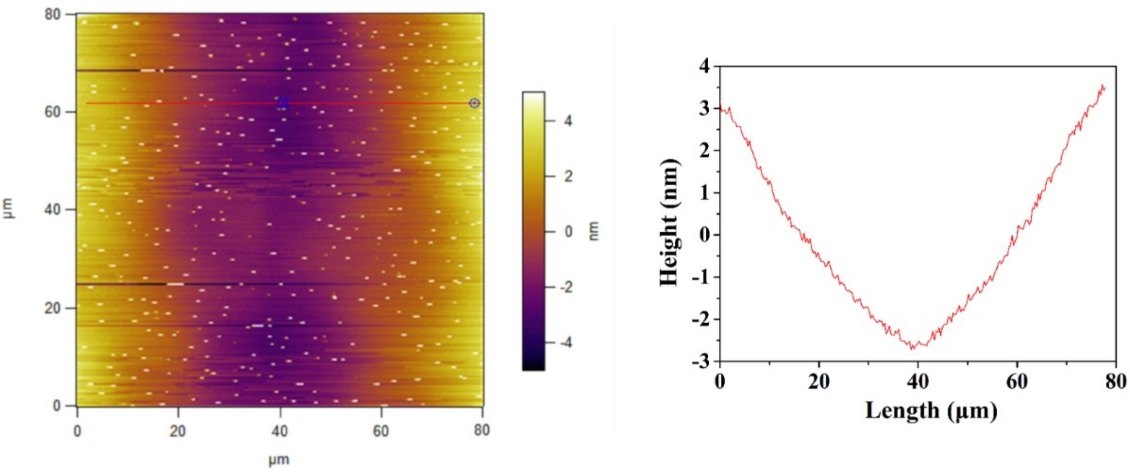

Fig. S6 AFM image of ALD-deposited TiO_2 film on SiO_2/Si substrate.

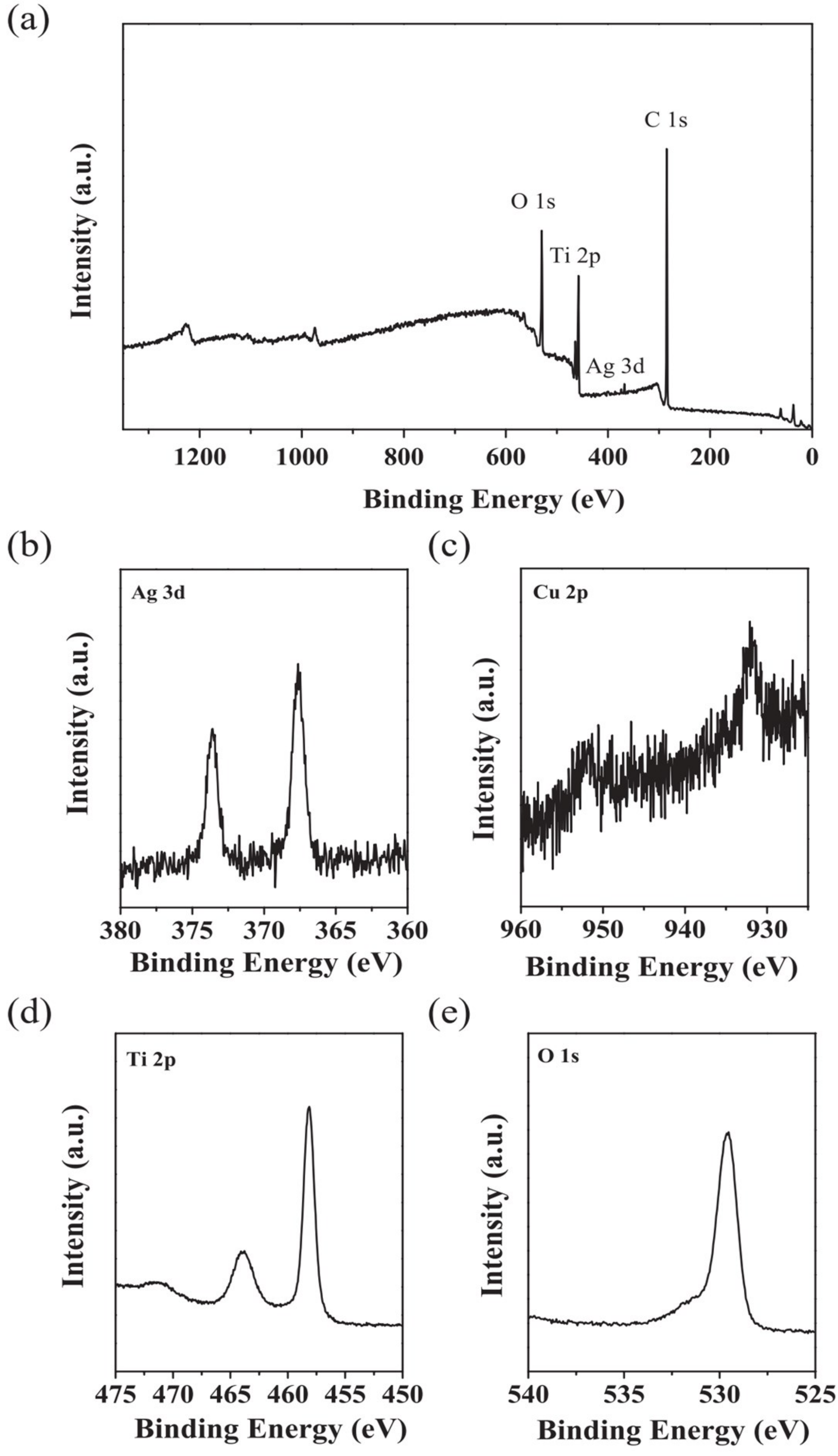

Fig. S7 XPS spectra of $Ag_3Cu/TiO_2/ZnTe$ sample. (a) XPS survey spectrum and high-resolution XPS spectra of (b) Ag 3d, (c) Cu 2p, (d) Ti 2p and (e) O 1s.

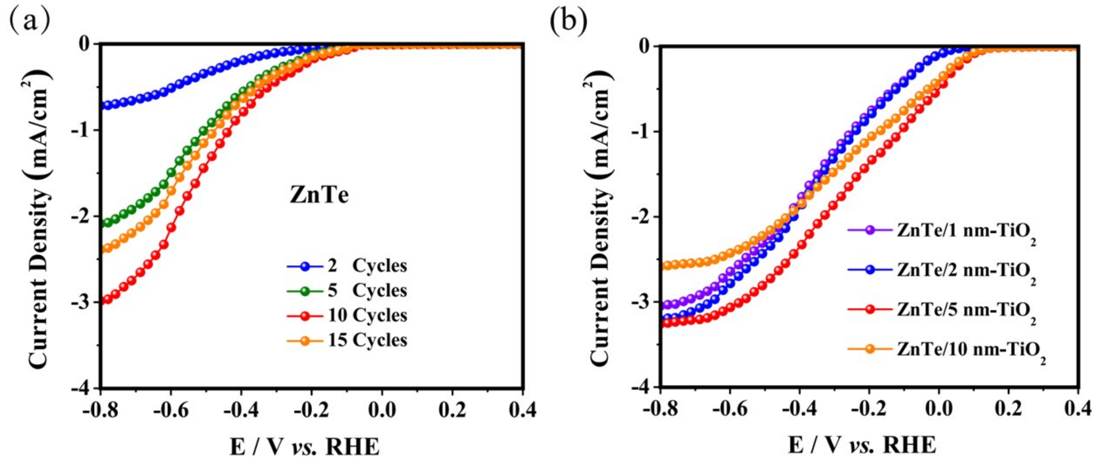

Fig. S8 PEC *J-V* curves of (a) bare ZnTe photocathodes with different spin-coating cycles and (b) TiO_2/ZnTe-based photocathodes with different covered thickness of TiO_2 in CO_2-saturated 0.1 M $KHCO_3$ (pH 6.8) under simulated solar irradiation (AM 1.5G, 100 mW/cm^2).

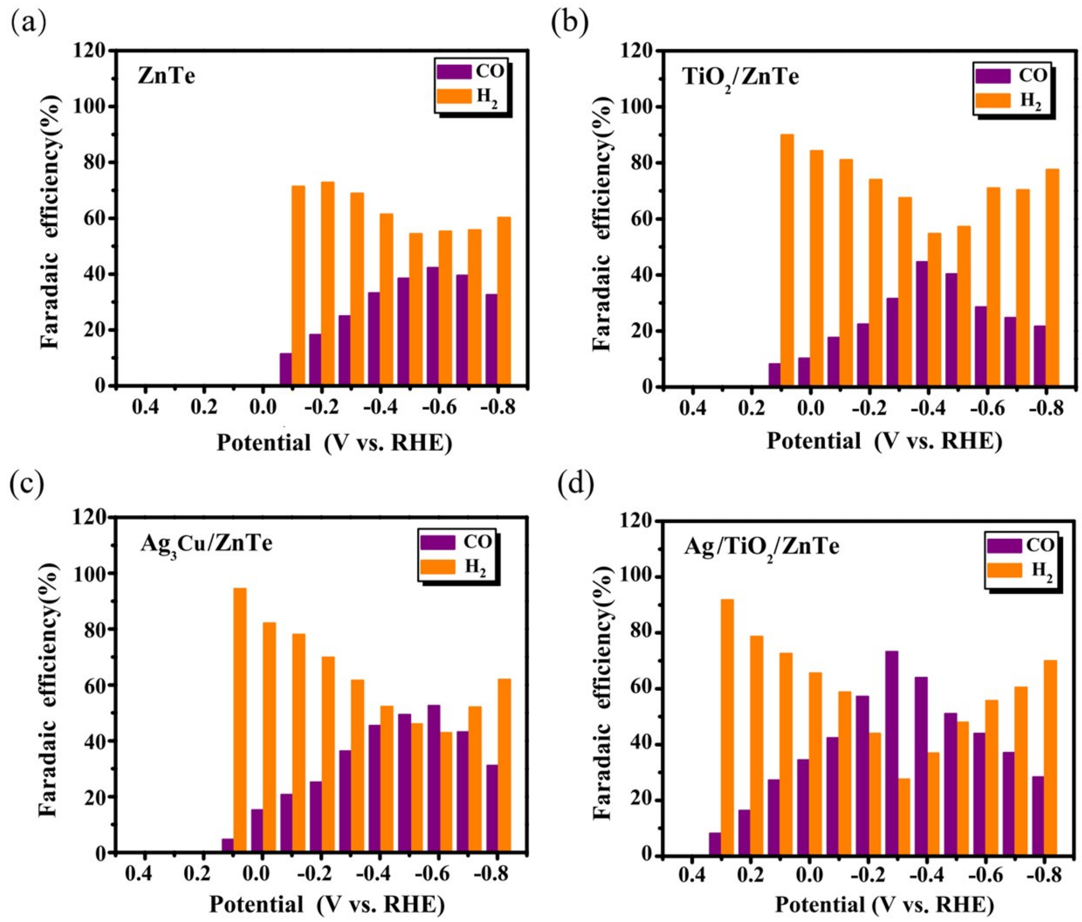

Fig. S9 Faradaic efficiency toward CO and H_2 for (a) ZnTe, (b) TiO_2/ZnTe, (c) Ag_3Cu/ZnTe and (d) Ag/TiO_2/ZnTe photocathodes in CO_2-saturated 0.1 M $KHCO_3$ electrolyte (pH 6.8) under simulated solar illumination (AM 1.5G, 100 mW/cm^2).

Table S2. Comparison of recently reported ZnTe based-photocathodes for PEC CO_2 reduction.

Photocathode	Electrolyte	$E_{onset,}$ (V vs. RHE)	$j_{-0.11\ V}$ (mA cm^{-2})	Maximum FE_{CO}	Ref.
ZnO/ZnTe/CdTe/Au	0.5 M $KHCO_3$	0.60	-3.88	80%	ACS Nano 2016, 10, 6980−6987
Zn/ZnO/ZnTe	0.5 M $KHCO_3$	-0.20	N A	22.9%	*Angew. Chem. Int. Ed. 2014, 53, 5852 –5857*
ZnO/ZnTe/Au	0.5 M $KHCO_3$	-0.10	-3.14	63.0%	*Energy Environ. Sci., 2015, 8, 3597--3604*
N:C/N:ZnTe	0.5 M $KHCO_3$	0.25	-1.21	72.0%	Adv. Energy Mater. 2018, 8, 1702636
PPy/ZnTe	0.1M $KHCO_3$	0	N A	13.8%	J. Mater. Chem. A, 2015, 3, 1089–1095
Ag_3Cu/TiO_2/ZnTe	**0.1 M $KHCO_3$**	**0.40**	**-3.81**	**86.5%**	**This work**

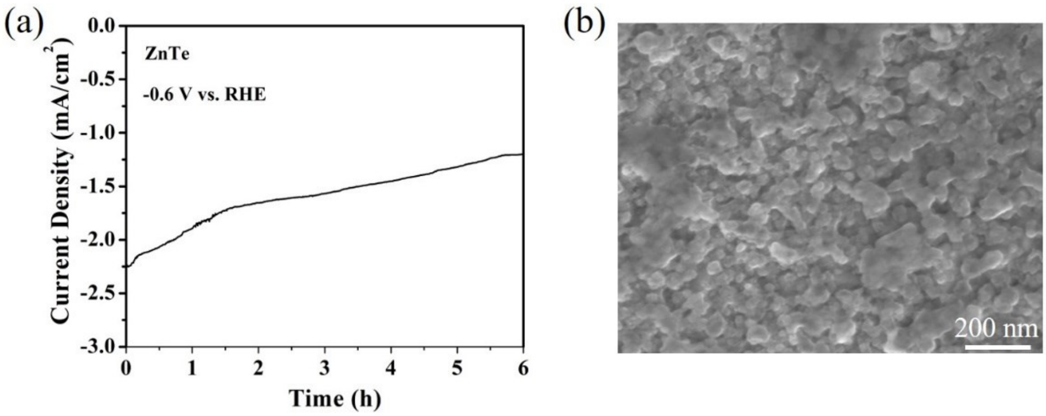

Fig. S10 (a) Time-dependent photocurrents ZnTe photocathode at potential of -0.6 V versus RHE in CO_2-saturated 0.1 M $KHCO_3$ under simulated solar irradiation and (b) SEM image of ZnTe photocathode after stability measurement.

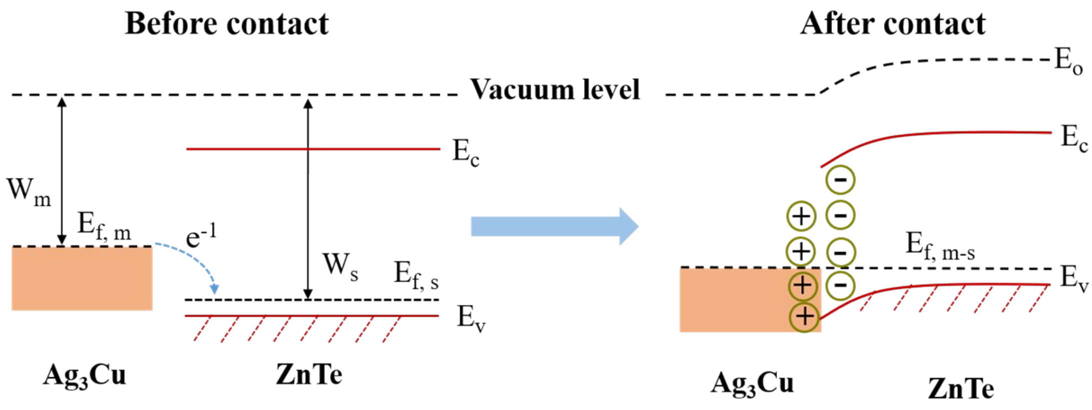

Fig. S11 Schematic diagram of band structure configuration of Ag_3Cu and ZnTe before and after contact.

Table S3

The values of key parameters in Figure 4a, where E_c, E_v, $E_{f,\,s}$, $E_{f,\,metal}$ and $E_{reaction}$ are the conduction band, valance band, Fermi level of ZnTe, Fermi level of metal, and the potential values of the chemical reactions (E_{H^+/H_2} and $E_{CO_2/CO}$) respectively.

Parameters	$E_{f,\,Ag_3Cu}$	$E_{f,\,Ag}$	E_C	E_V	$E_{f,\,s}$	E_{H^+/H_2}	$E_{CO_2/CO}$
E_{vac} (eV)	-4.37	-4.28	-2.94	-5.23	-4.80	-4.5	-4.39
E_{NHE} (V) pH=0	-0.13	-0.22	-1.56	0.73	0.30	0.00	-0.11

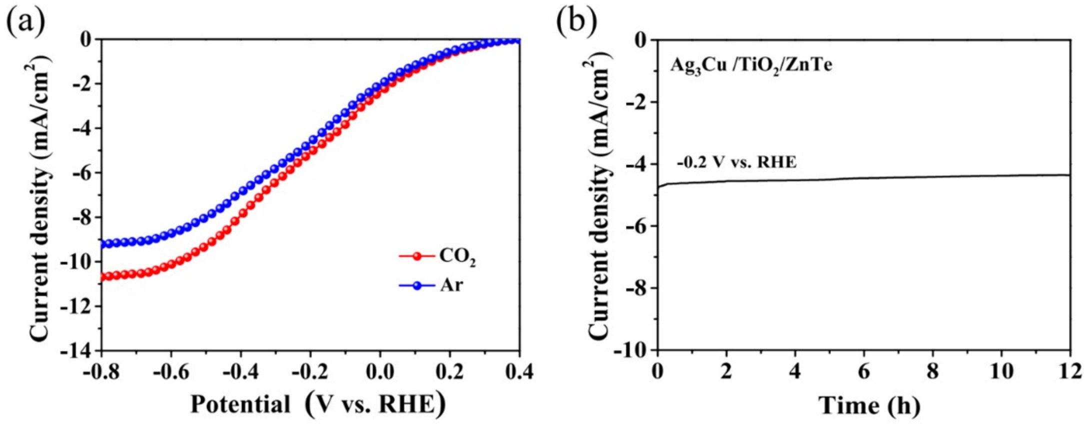

Fig. S12 (a) J-V curves of $Ag_3Cu/TiO_2/ZnTe$ photocathode in CO_2 and Ar-saturated 0.1 M $KHCO_3$ under simulated solar irradiation, (b) Time-dependent photocurrent of $Ag_3Cu/TiO_2/ZnTe$ photocathode at potential of -0.2 V vs. RHE in Ar-saturated 0.1 M $KHCO_3$ under simulated solar irradiation.