Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary material

Design of Three-dimensional Hierarchical $TiO_2/SrTiO_3$ Heterostructures towards Selective CO_2 Photoreduction

Shuaiyu Jiang,[a†] Kun Zhao,[a†] Mohammad Al-Mamun,[a] Yu Lin Zhong,[a] Porun Liu,[a] Huajie Yin,[a] Lixue Jiang,[a] Sean Lowe,[a] Jian Qi,[b] Ranbo Yu,[c] Dan Wang,[a,b]* and Huijun Zhao[a]*

[a]*Centre for Clean Environment and Energy, Gold Coast Campus, Griffith University, QLD 4222, Australia.*

[b]*State Key Laboratory of Biochemical Engineering, CAS Center for Excellence in Nanoscience, Institute of Process Engineering, Chinese Academy of Sciences, Zhongguancun, Beijing, China.*

[c]*Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China.*

**Correspondence and requests for materials should be addressed to D. W. (email: danwang@ipe.ac.cn), H. Z. (email: h.zhao@griffith.edu.au).*

[†]*These authors equally contributed to this work.*

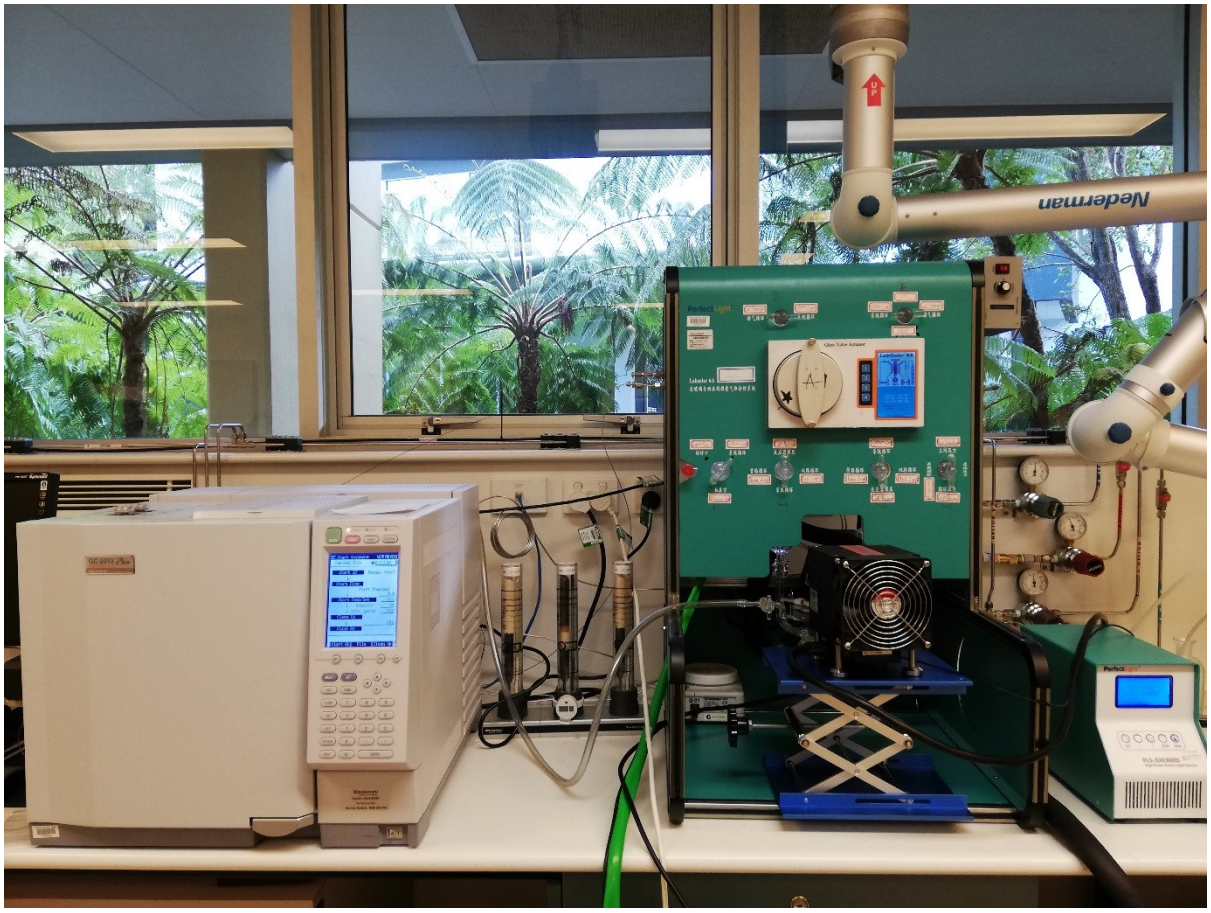

Fig. S1 Digital photograph of CO_2 photocatalytic reduction equipment.

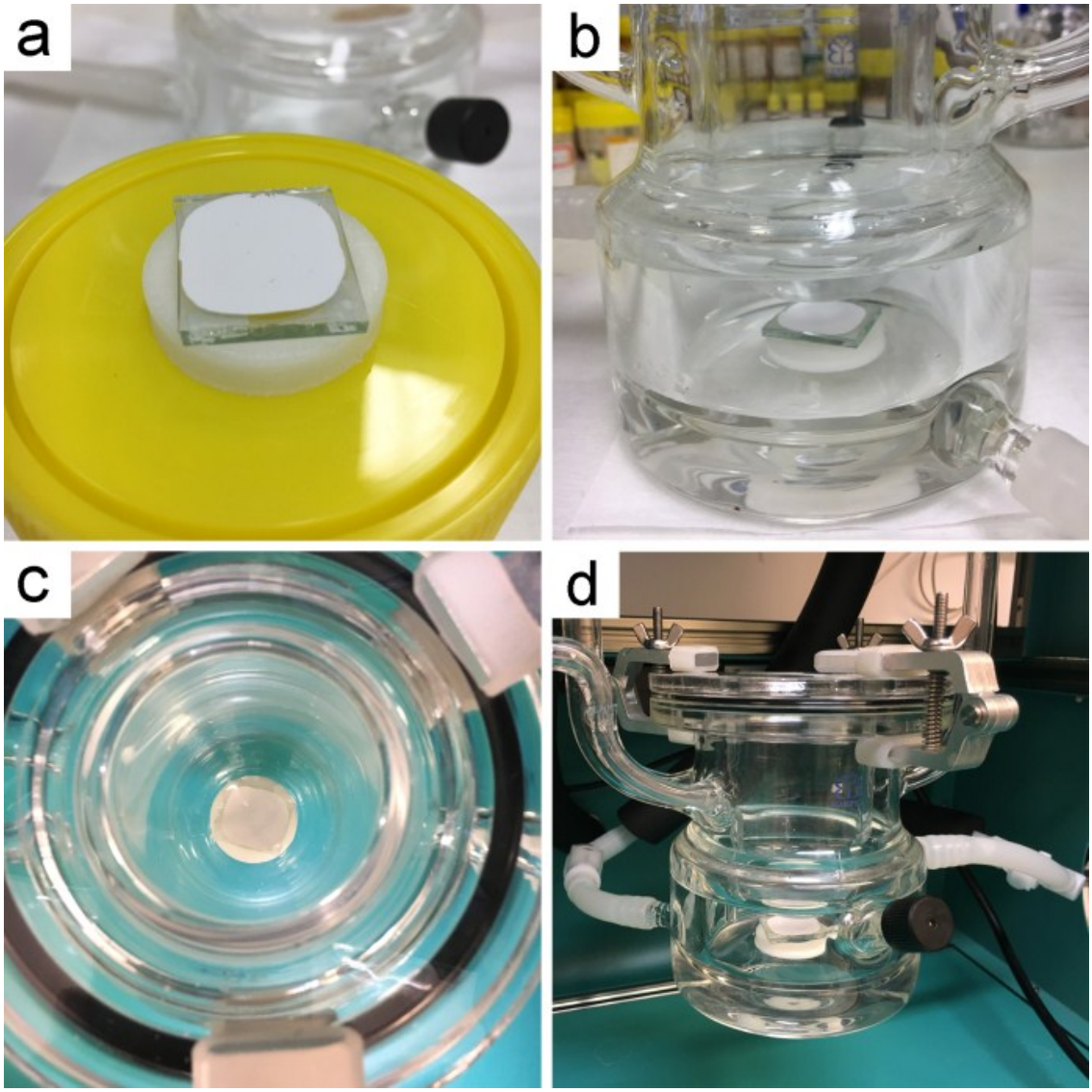

Fig. S2 The experimental setup for the gas-solid interface CO_2 reduction reactor with water.

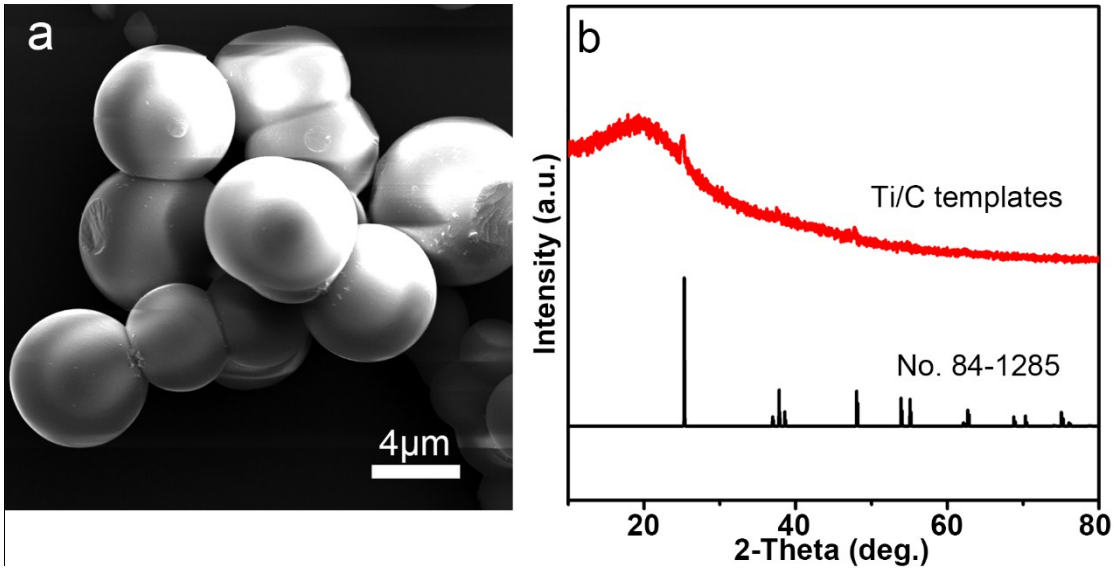

Fig. S3 (a) SEM image and (b) XRD pattern of as-synthesized composite titanium-carbon spherical templates.

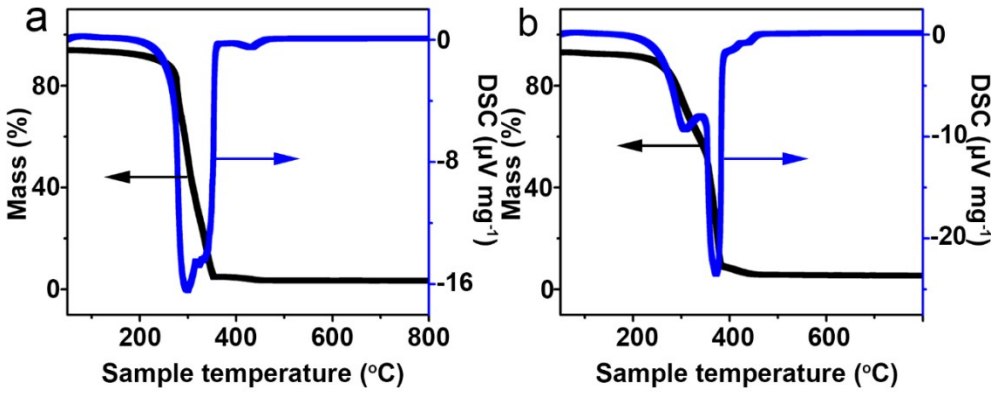

Fig. S4 TGA-DSC curves of (a) virgin Ti/C template and (b) Sr^{2+} adsorbed Ti/C template.

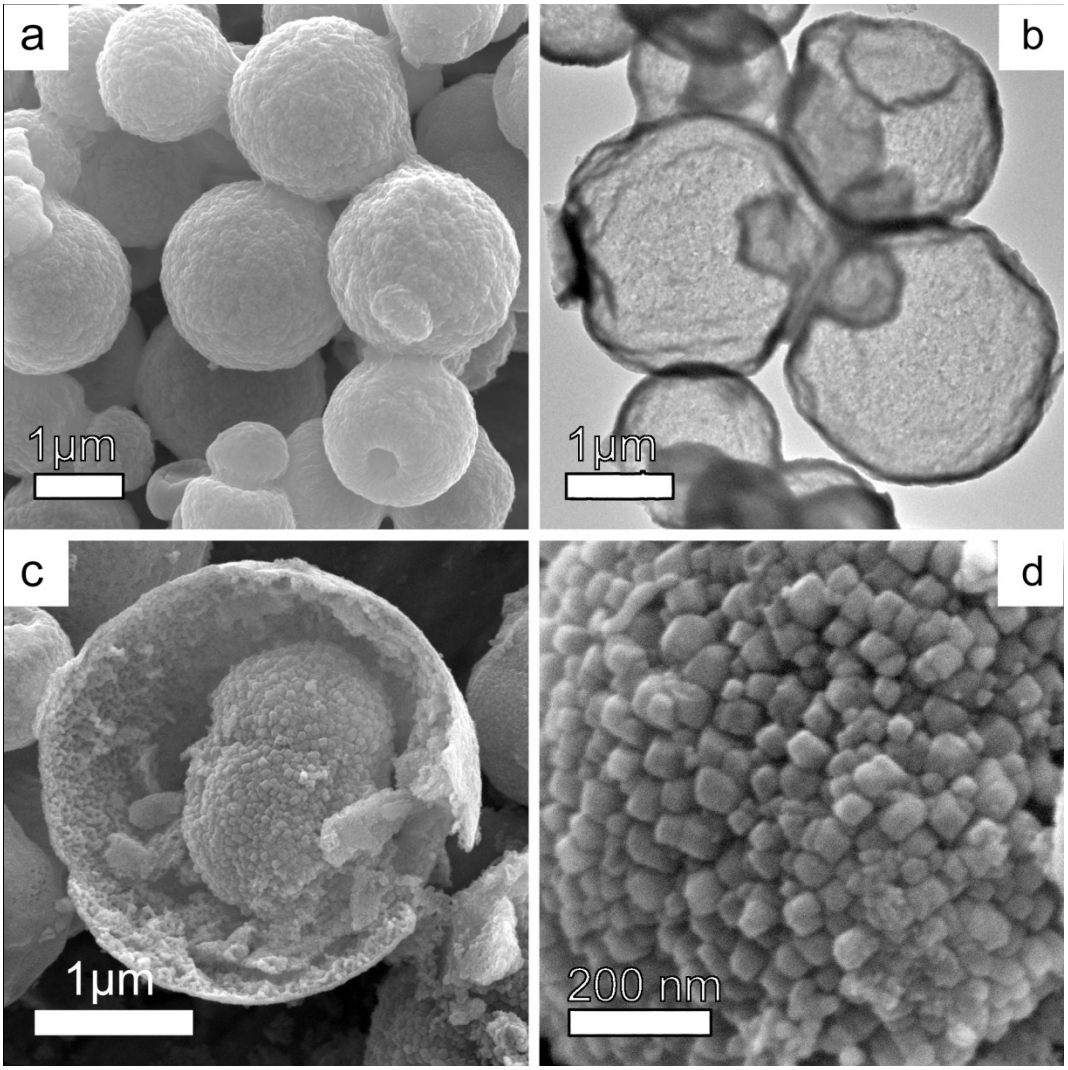

Fig. S5 (a) SEM image and (b) TEM image of as-synthesized HoMSs-T. (c) SEM image and (d) enlarged SEM image of as-synthesized HoMSs-S.

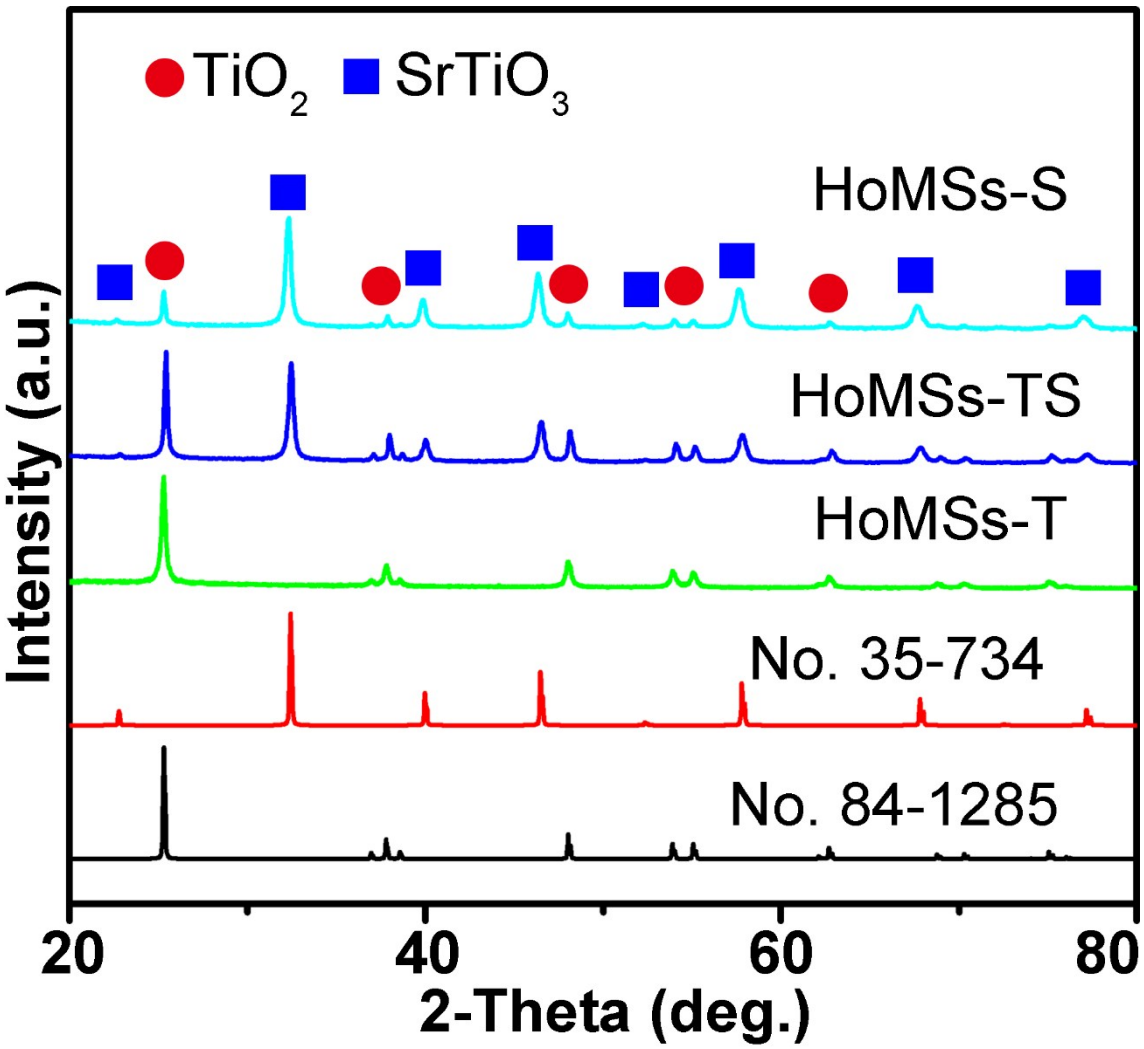

Fig. S6 XRD patterns of the different samples.

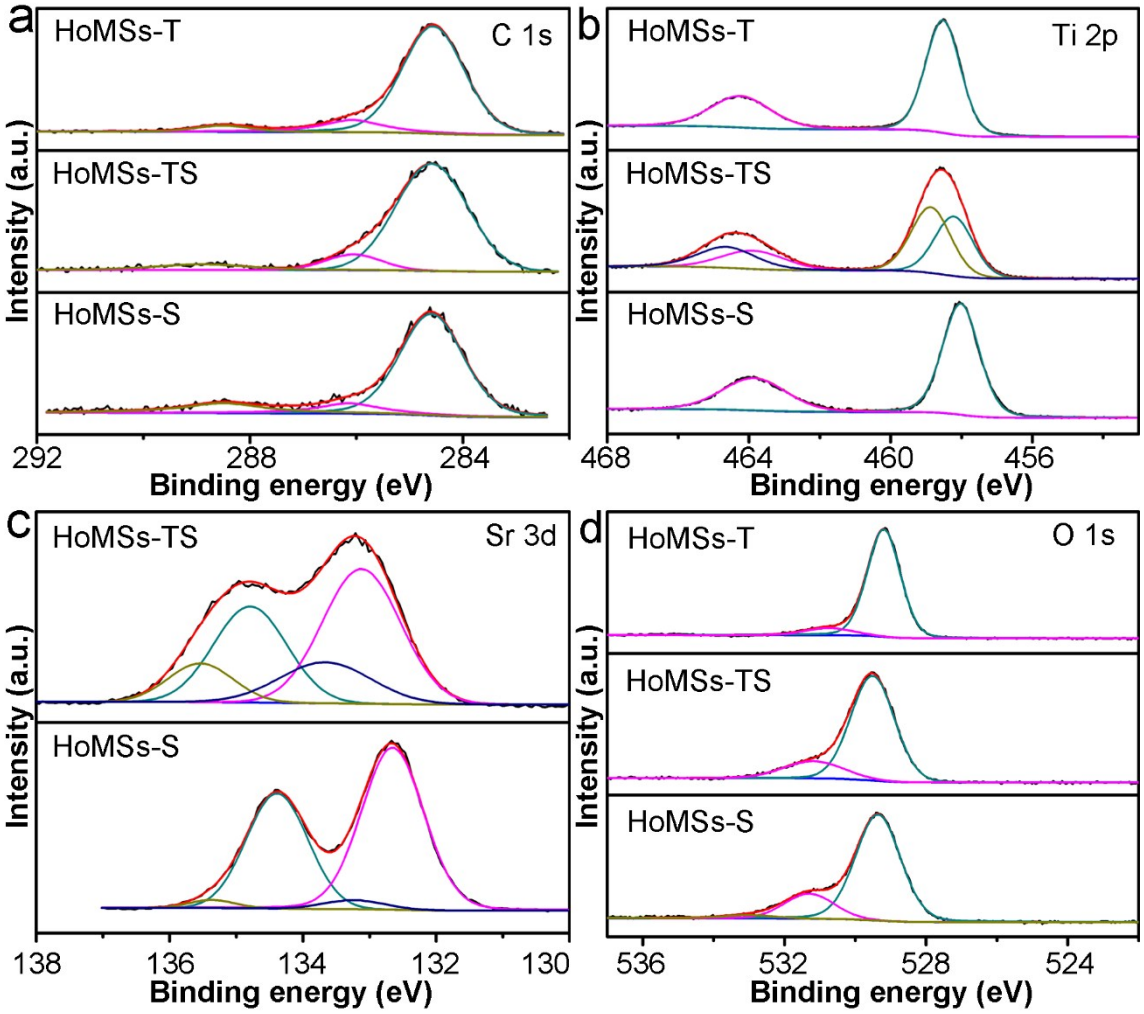

Fig. S7 XPS spectra of (a) C 1s, (b) Ti 2p, (c) Sr 3d, and (d) O 1s for the different samples.

Table S1 Summary of BET surface areas and BJH pore volumes of different samples

Sample name	BET surface areas (m^2 g^{-1})	BJH pore volumes (cm^3 g^{-1})
HoMSs-T	33	0.11
HoMSs-TS	42	0.15
HoMSs-S	23	0.09

Table S2 Summary of photocatalytic CO_2 reduction performances of different TiO_2- and $SrTiO_3$-based composites.

Photocatalyst	Reaction mode	Reactant	Major/minor products	Selectivity for CO_2 reduction (%)	Reference
$TiO_2/SrTiO_3$ spheres	Solid-gas	CO_2 & H_2O vapor	CO/CH_4	~100	Our work
Cr-$SrTiO_3$	Solid-liquid	CO_2 & H_2O	CH_4	100	1
Rh-Au@$SrTiO_3$	Solid-gas	CO_2 & H_2O vapor	CO/H_2	86	2
Pt-$SrTiO_{3-\delta}$	Solid-gas	CO_2 & H_2O vapor	CH_4	100	3
$SrTiO_3$/ZnTe	Solid-gas	CO_2 & H_2O vapor	CH_4/H_2	-	4
$TiO_2/SrTiO_3$ film	Solid-liquid	CO_2 & 0.1 M $KHCO_3$	CH_4/CO	-	5
Pt/$SrTiO_3$:Rh	Solid-liquid	CO/CO_2 & 2mM $FeCl_2$	CH_3OH/H_2	96	6
Cu_xO-$SrTiO_3$	Solid-liquid	CO_2 & 0.5M $KHCO_3$	CO/H_2	-	7
Au-$SrTiO_3$	Solid-liquid	CO_2 & H_2O vapor	CO/CH_4	-	8
Pt-$SrTi_{0.98}Co_{0.02}O_3$	Solid-gas	CO_2 & H_2O vapor	CH_4/H_2	90	9
Au_3Cu@$SrTiO_3/TiO_2$	Solid-liquid	33.3% CO_2 & hydrous hydrazine	CO/CH_4,C_2H_6, C_2H_4, C_3H_6, H_2, N_2	-	10
TiO_2	Solid-liquid	CO_2 & H_2O	H_2/CO,CH_4	19	11
Pt-TiO_2	Solid-liquid	CO_2 & H_2O	H_2/CO,CH_4	11	
TiO_2	Solid-gas	CO_2 & H_2O vapor	H_2/CO, CH_4	56	
Pt-TiO_2	Solid-gas	CO_2 & H_2O vapor	H_2/CO, CH_4	40	
Pd-TiO_2	Solid-gas	CO_2 & H_2O vapor	H_2/CO, CH_4	42	
Rh-TiO_2	Solid-gas	CO_2 & H_2O vapor	H_2/CO, CH_4	45	
Au-TiO_2	Solid-gas	CO_2 & H_2O vapor	H_2/CO, CH_4	41	
Ag-TiO_2	Solid-gas	CO_2 & H_2O vapor	H_2/CO, CH_4	39	
MgO-Pt-TiO_2	Solid-gas	CO_2 & H_2O vapor	CH_4/ H_2, CO	83	
TiO_2	Solid-gas	CO_2 & H_2O vapor	CH_4/H_2	80	12
Au/TiO_2	Solid-gas	CO_2 & H_2O vapor	CH_4/H_2	94	
Cu/TiO_2	Solid-gas	CO_2 & H_2O vapor	CH_4/H_2	97	
(Au, Cu)/TiO_2	Solid-gas	CO_2 & H_2O vapor	CH_4/H_2	97	

TiO_2	Solid-liquid	CO_2 & H_2O	H_2	0
Au/TiO_2	Solid-liquid	CO_2 & H_2O	CH_4/H_2	79
Cu/TiO_2	Solid-liquid	CO_2 & H_2O	CH_4/H_2	91
$(Au, Cu)/TiO_2$	Solid-liquid	CO_2 & H_2O	CH_4/H_2	92

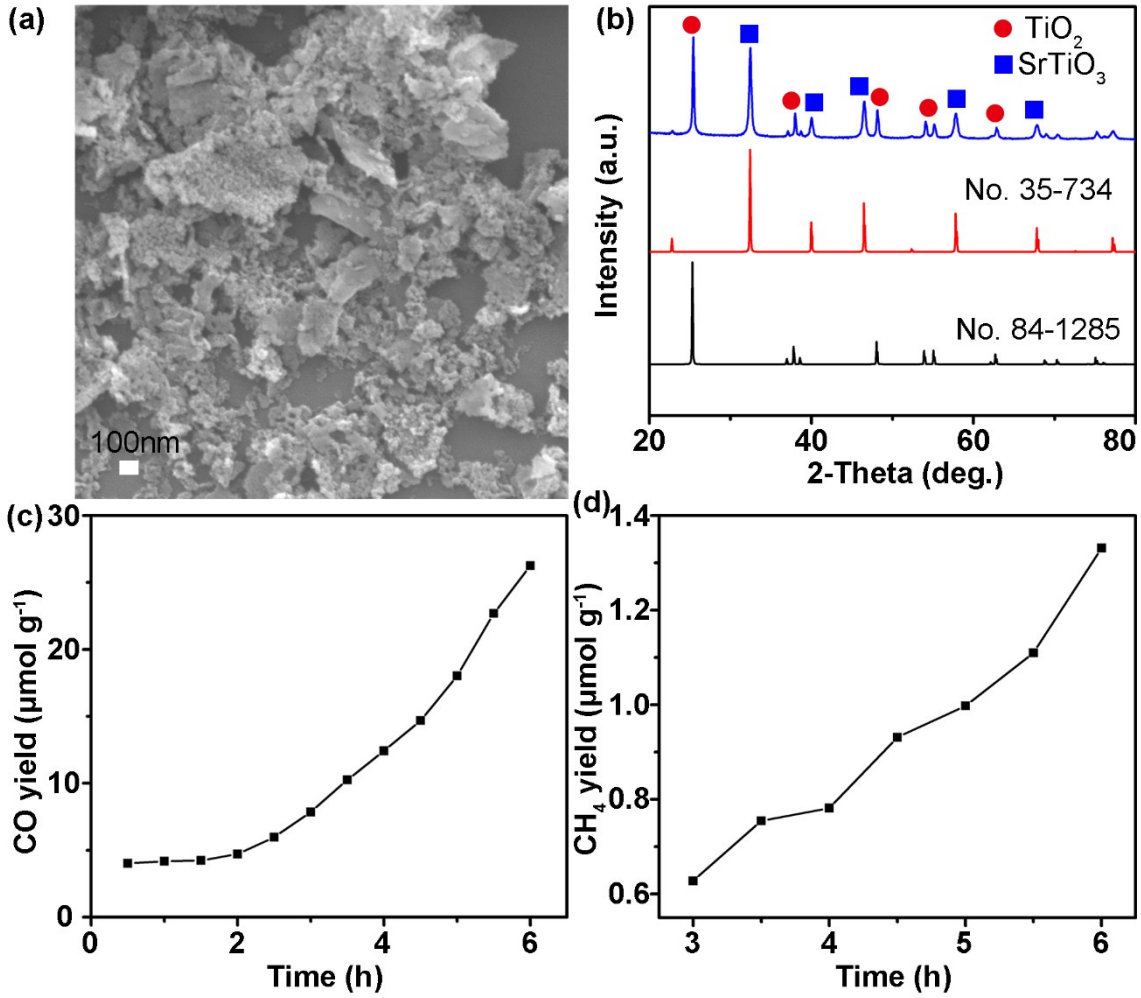

Fig. S8 (a) and (b) SEM image and XRD patterns of fragmentized $TiO_2/SrTiO_3$ sample(frg-TS), (c) and (d) CO and CH_4 yields of frg-TSunder UV-vis irradiation. (Testing condition: 300 W Xe lamp, 320 nm $< \lambda <$ 780 nm; catalyst: 5 mg coated on FTO with a geometric area of 4 cm^2; water 10 mL; mild reaction conditions (30 °C and 1 atm CO_2)).

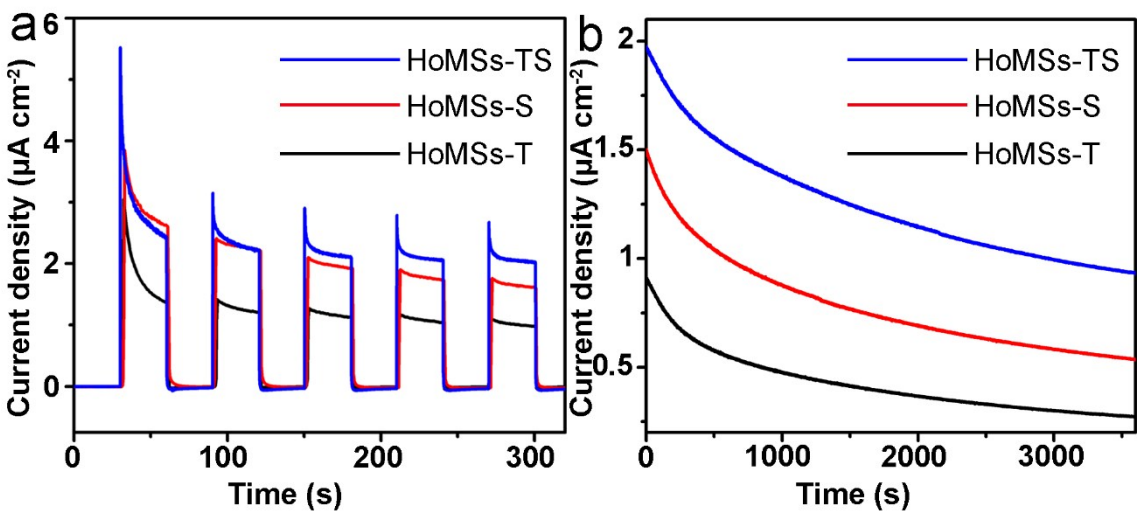

Fig. S9 (a) Transient photocurrent response curves measured under UV-vis irradiation using 0.1 M Na_2SO_4 as the electrolyte solution at a bias of 0.05 V vs. SCE for different samples, (b) Long-term photocurrent curves measured versus SCE as the reference electrode.

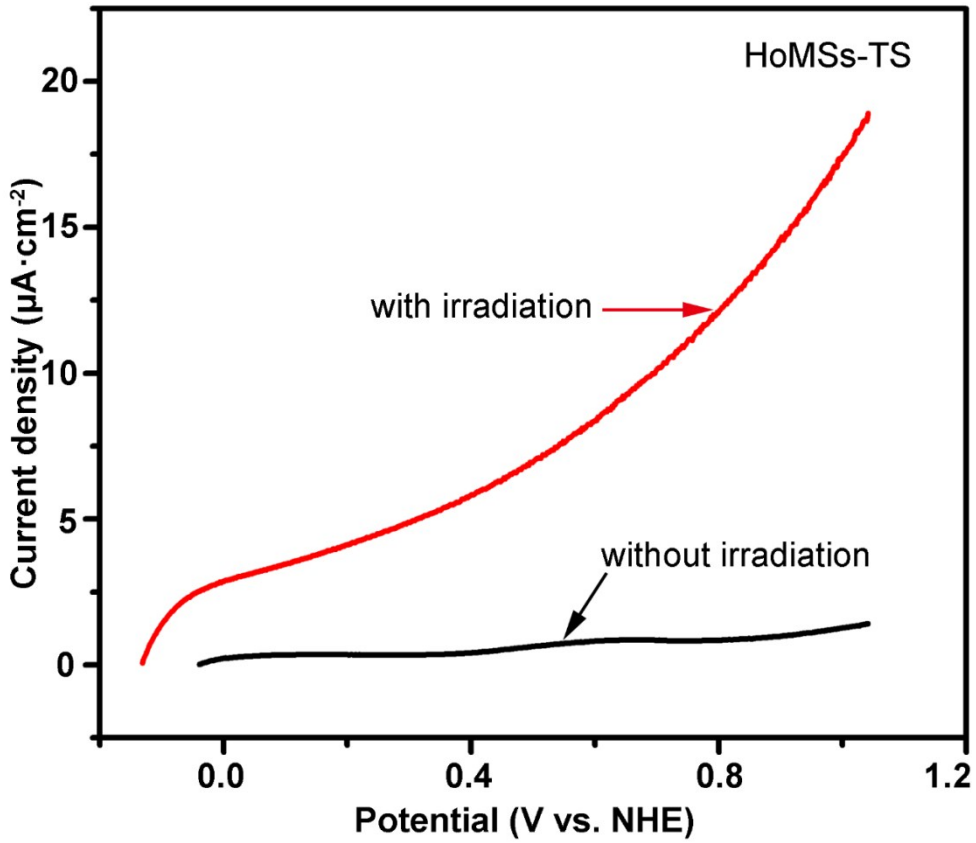

Fig. S10 Line scanning voltage (LSV) curves of HoMSs-TS measured with and without the irradiation of a 300 W Xe lamp, 0.1 M Na_2SO_4 as electrolyte solution, SCE and Pt as reference and counter electrode.

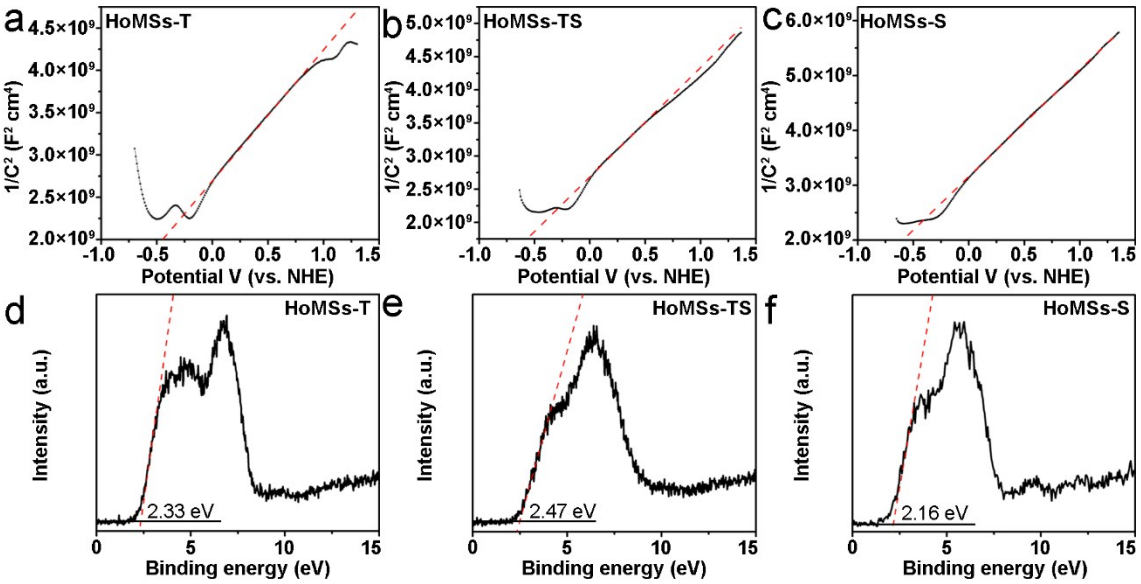

Fig. S11 Mott-Schottky plots and Valence band spectra of (a, d) HoMSs-T, (b, e) HoMSs-TS, and (c, f) HoMSs-S samples.

References

1. Y.Bi, M. F. Ehsan, Y. Huang, J. Jin, and T. He, *J. CO_2 Util.*, 2015, **12**, 43-48.
2. D. Li, S. Ouyang, H. Xu, D. Lu, M. Zhao, X. Zhang, and J. Ye, *Chem. Commun.*, 2016, **52**, 5989-5992.
3. K. Xie, N. Umezawa, N. Zhang, P. Reunchan, Y. Zhang, and J. Ye, *Energy Environ. Sci.*, 2011, **4**, 4211-4219.
4. M. F. Ehsan, M. N. Ashiq, F. Bi, Y. Bi, S. Palanisamy, and T. He, *RSC Adv.*, 2014, **4**, 48411-48418.
5. Y. Bi, L. Zong, C. Li, Q. Li, and J. Yang, *Nanoscale Res. Lett.*, 2015, **10**, 345.
6. Y. H. Cheng, V.H. Nguyen, H. Y. Chan, J. C. S. Wu, and W. H. Wang, *Appl. Energ.*, 2015, **147**, 318-324.
7. S. Shoji, G. Yin, M. Nishikawa, D. Atarashi, E. Sakai, and M. Miyauchi, *Chem. Phys. Lett.*, 2016, **658**, 309-314.
8. H. Zhou, J. Guo, P. Li, T. Fan, D. Zhang, and J. Ye, *Scientific Reports*, 2013, **3**, 1667.
9. J. Kou, J. Gao, Z. Li, H. Yu, Y. Zhou, and Z. Zou, *Catal. Lett.*, 2015, **145**, 640–646.
10. Q. Kang, T. Wang, P. Li, L. Liu, K. Chang, M. Li, and J. Ye, *Angew. Chem. Int. Ed.*, 2015, **54**, 841-845.
11. S. Xie, Y. Wang, Q. Zhang, W. Deng, and Y. Wang, *ACS Catal.*, 2014, **4**, 3644-3653.
12. S. Neaţu, J. A. Maciá-Agulló, P. Concepción, and H. Garcia, *J. Am. Chem. Soc.*, 2014, **136**, 15969-15976.