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SUPPORTING INFORMATION

Hybrid Mesoporous Cu_2ZnSnS_4 (CZTS)-TiO_2 Photocatalyst for Efficient Photocatalytic Conversion of CO_2 into CH_4 under Solar Irradiation

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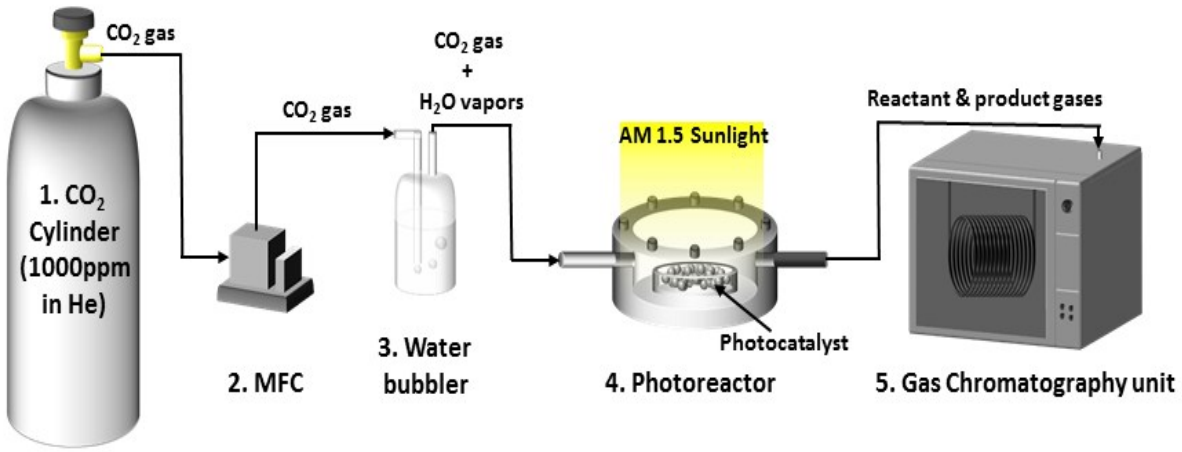


Fig. S1 Schematic representation of experimental setup employed for CO_2 photoreduction involving (1) CO_2 gas cylinder (1000 ppm in He), (2) Mass flow controller, (3) Water bubbler for making CO_2 gas/H_2O vapors mixture, (4) Photoreactor (Stainless Steel, V=15.4 cm^3) loaded with photocatalyst material (50 mg of CZTS-TiO_2 sample), irradiated by simulated solar light and (5) Gas chromatography unit for analysis of product gases from photoreactor (equipped with FID and TCD).

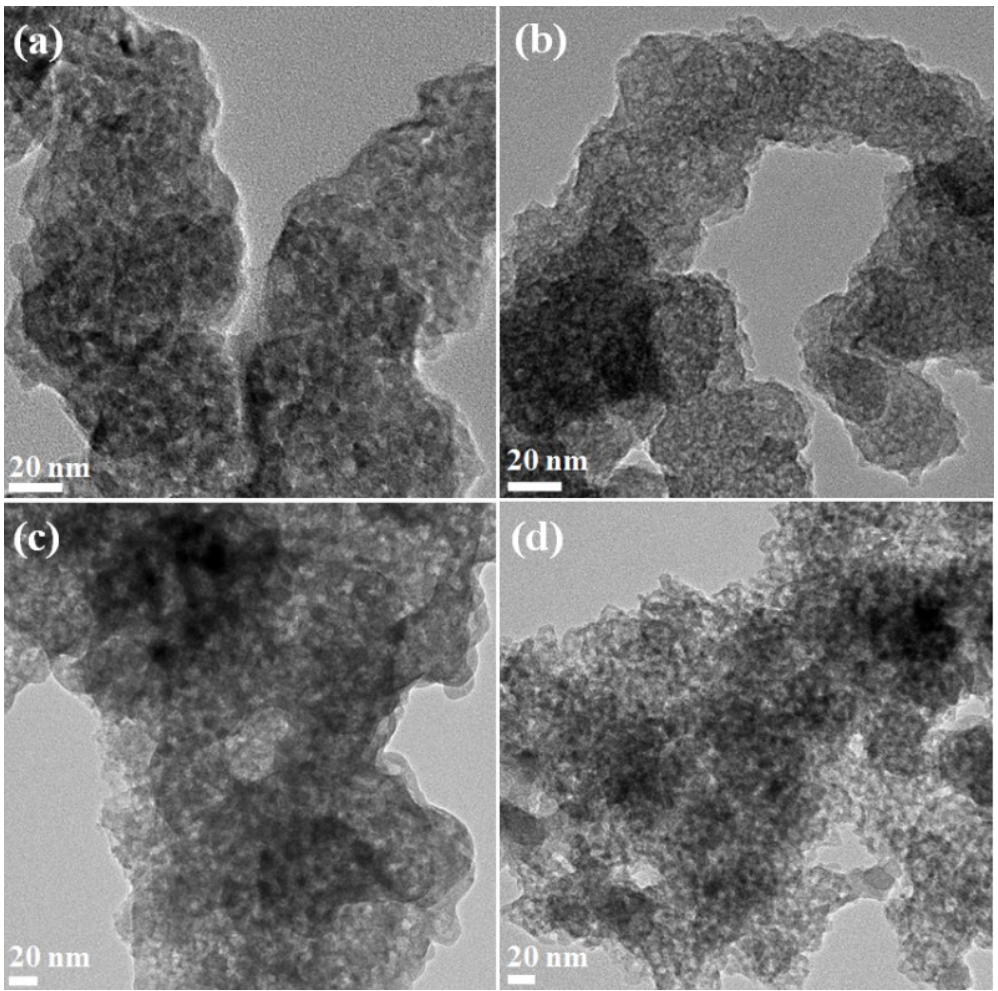
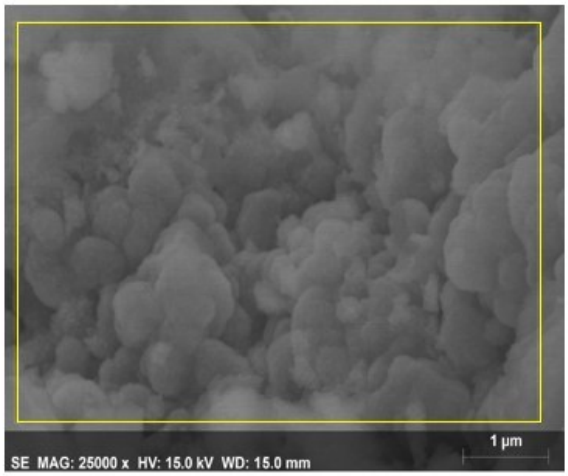
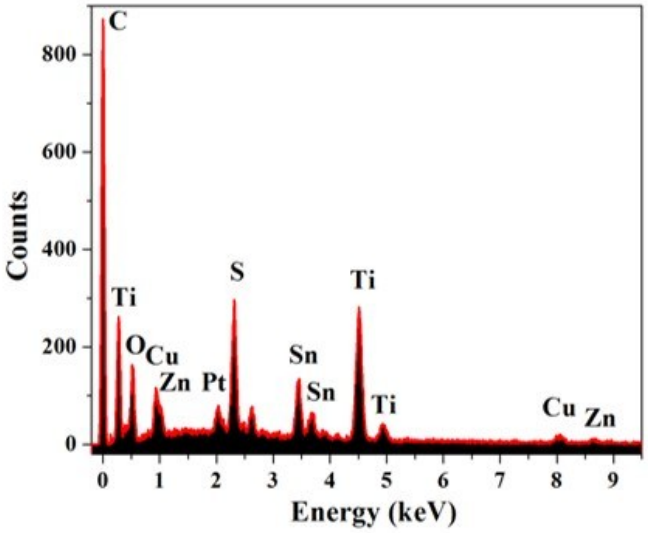


Fig. S2 TEM images of hybrid mesoporous CZTS-TiO_2 samples: (a) CT1, (b) CT2, (c) CT3 and (d) CT4. (CT1, CT2, CT3 and CT4 stands for 1.9 mg, 3.8 mg, 5.7 mg and 7.6 mg of CZTS for 0.1 ml of $TiCl_4$ respectively)





Element	Atomic %
Cu	2.54
Zn	1.51
Sn	1.3
S	4.9
Ti	11.92
O	26.82

Fig. S3 FESEM-EDS of CT4, representative hybrid CZTS-TiO_2 sample. The presence of elemental C peak might be due to the tape used to hold the CT4 sample, whereas the Pt peak appears due to the Pt sputtering for making the sample conductive for FE-SEM imaging.

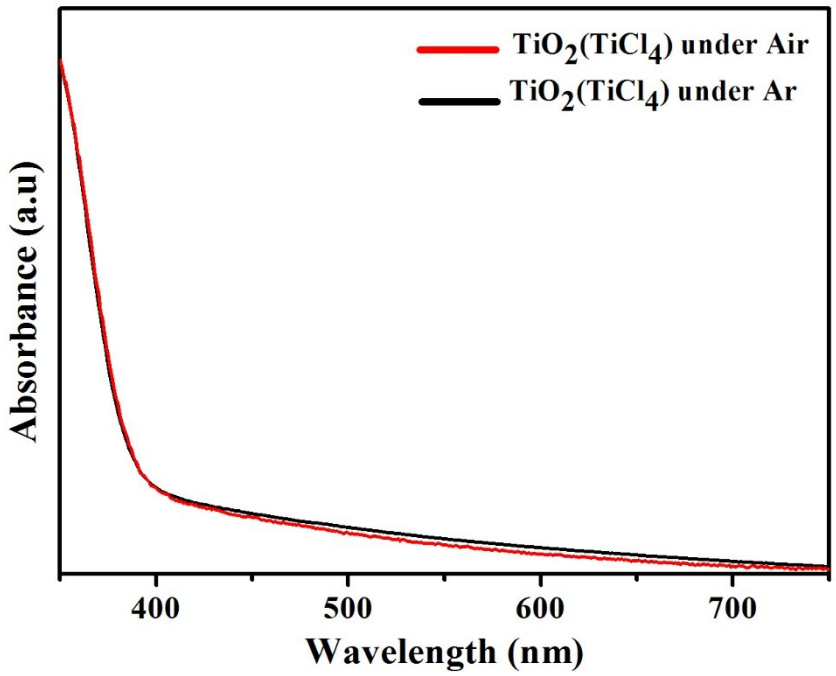


Fig. S4 UV-vis DRS of annealed TiO_2 under Air and Ar atmosphere.

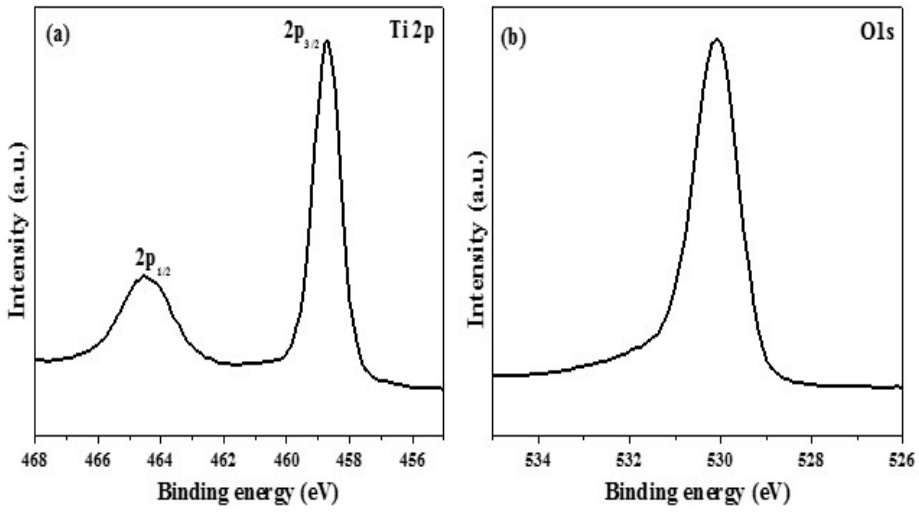


Fig. S5 X-ray photoelectron spectroscopy (XPS) of as synthesized TiO_2 showing the regions of (a) Ti 2p, and (b) O1s.

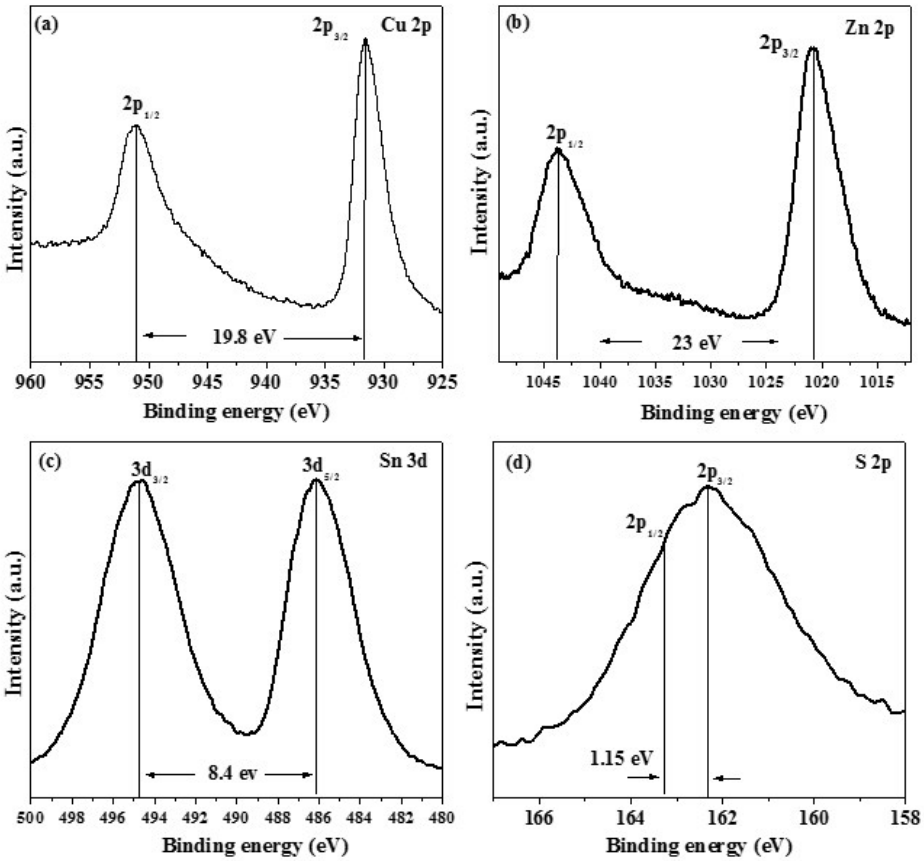


Fig. S6 X-ray photoelectron spectroscopy (XPS) of as-prepared CZTS nanoparticles showing the regions of (a) Cu 2p, (b) Zn 2p, (c) Sn 3d, and (d) S 2p.

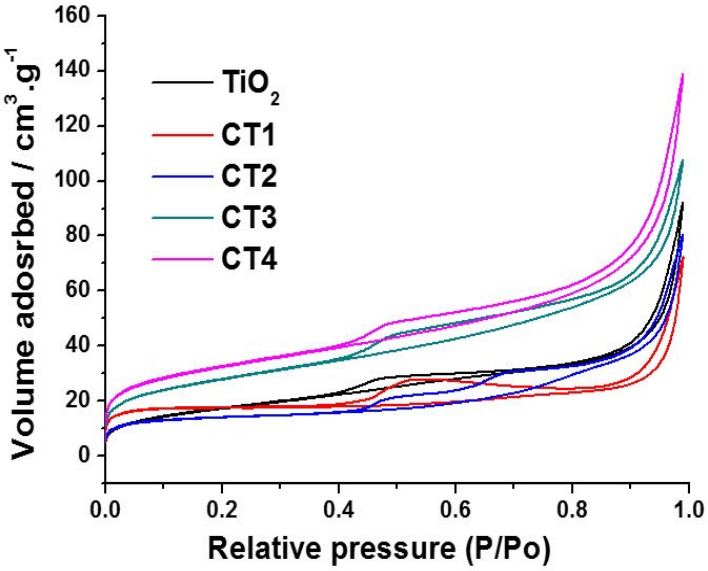


Fig. S7 Nitrogen physiosorption isotherms for BET surface area measurement for pure TiO_2 and hybrid mesoporous CZTS-TiO_2 samples (CT1, CT2, CT3 and CT4 stands for 1.9, 3.8, 5.7 and 7.6 mg of CZTS in $TiCl_4$ respectively).

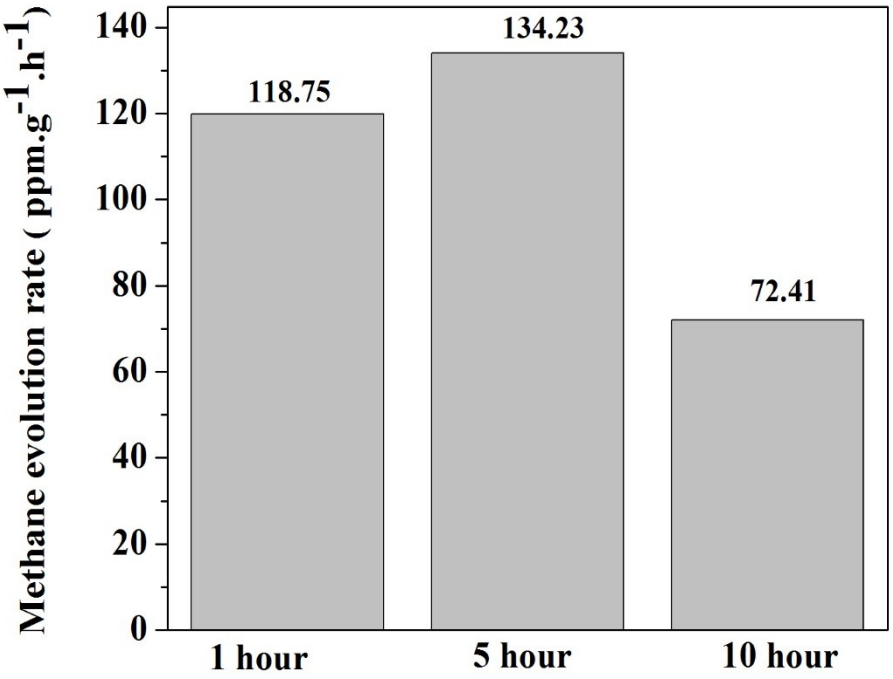


Fig. S8 Stability test employing sample CT4, synthesized from 7.6 mg CZTS in 0.1 ml $TiCl_4$, for CO_2 photoreduction under continous simulated solar light illumination for 5 h and 10 h.

Table S1 BET surface area of pure TiO_2 and hybrid mesoporous CZTS-TiO_2 samples (CT1, CT2, CT3 and CT4 stands for 1.9, 3.8, 5.7 and 7.6 mg of CZTS in $TiCl_4$ respectively).

Sample	Surface area ($m^2 \cdot g^{-1}$)
TiO_2	45.52
CT1	46.83
CT2	52.54
CT3	76.63
CT4	92.71

Table S2 Turnover number (TON) and turnover frequency (TOF) for hybrid CZTS-TiO_2 samples (CT1, CT2, CT3 and CT4 stands for 1.9, 3.8, 5.7 and 7.6 mg of CZTS in 0.1 ml of $TiCl_4$ respectively).

Sample name	**[a]TON**	**[b]TOF (h^{-1})**
CT1	0.31	0.31
CT2	0.37	0.37
CT3	0.76	0.76
CT4	1.48	1.48
CT4 (5 h)	1.7	0.34
CT4 (10 h)	0.9	0.09

The turnover number (TON) and turnover frequency (TOF) were calculated by using the following equations:[1,2]

$$^{a}\,\text{TON} = \frac{\text{moles of } CH_4 \text{ produced}}{\text{moles of } TiO_2 \text{ present on the hybrid photocatalyst}}$$

$$^{b}\,\text{TOF} = \frac{\text{TON}}{\text{Reaction time(hours)}}$$

References:

1. Z. Sun, H. Zheng, J. Li, P. Du. *Energy Environ. Sci.,* 2015, 8, 2668-2676.

2. A. J. Morris, G. J. Meyer, E. Fujita. *Acc. Chem. Res.*, 2009, 12, 1983-1994.