

## Quaternary CZTS nanoparticle decorated CeO<sub>2</sub> as a noble metal free p-n heterojunction photocatalyst for efficient hydrogen evaluation

M. Sridharan<sup>a</sup>, P. Kamaraj<sup>a,\*</sup>, Yun Suk Huh<sup>b</sup>, S. Devikala<sup>a</sup>, M. Arthanareeswai<sup>a</sup>, J. Arockiaselvi<sup>a</sup> and E. Sundaravadivel<sup>a</sup>

<sup>a</sup>Department of Chemistry, SRM Institute of Science and Technology, Kattankulathur-603 203, India.

<sup>b</sup>Department of Biological Engineering, College of Engineering, INHA University, Incheon, Korea.

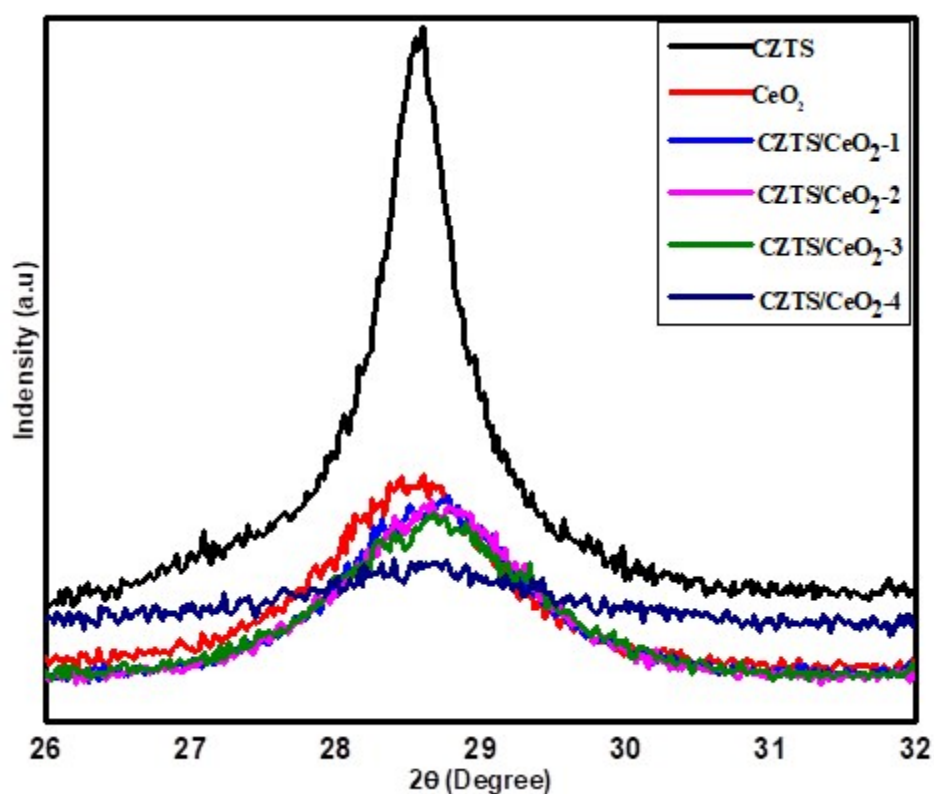


Fig.S1. High resolution XRD patterns of CZTS, CeO<sub>2</sub>, CZTS/CeO<sub>2</sub>-1, CZTS/CeO<sub>2</sub>-2, CZTS/CeO<sub>2</sub>-3 and CZTS/CeO<sub>2</sub>-4.

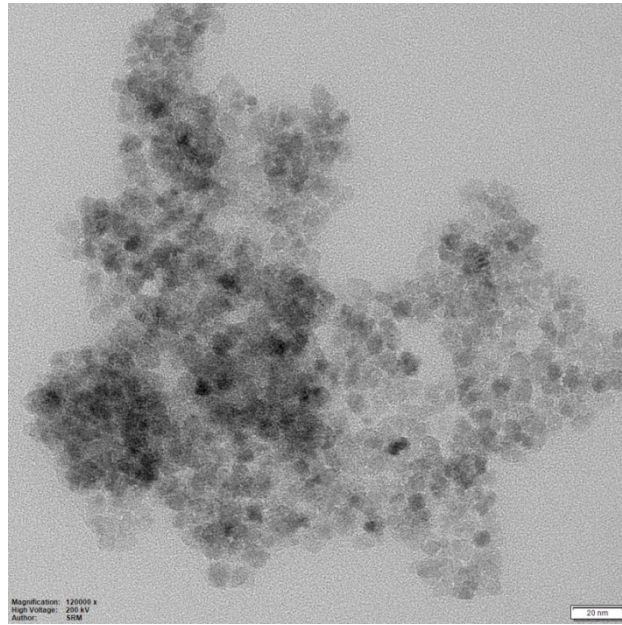


Fig.S2. (a) TEM image of the CZTS nanoparticle

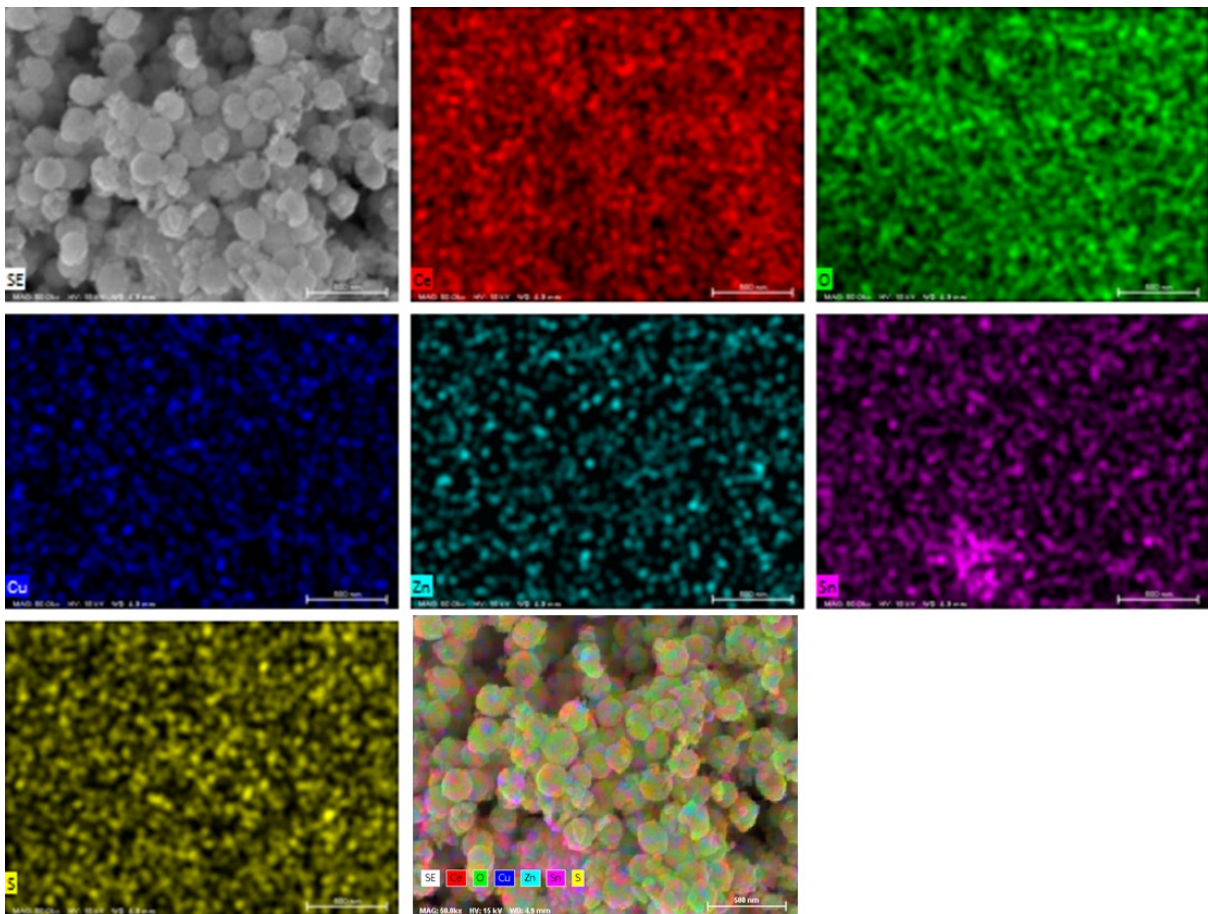


Fig. S3. SEM EDS mapping of Ce, O, Cu, Zn, Sn and S for CZTS/CeO<sub>2</sub>

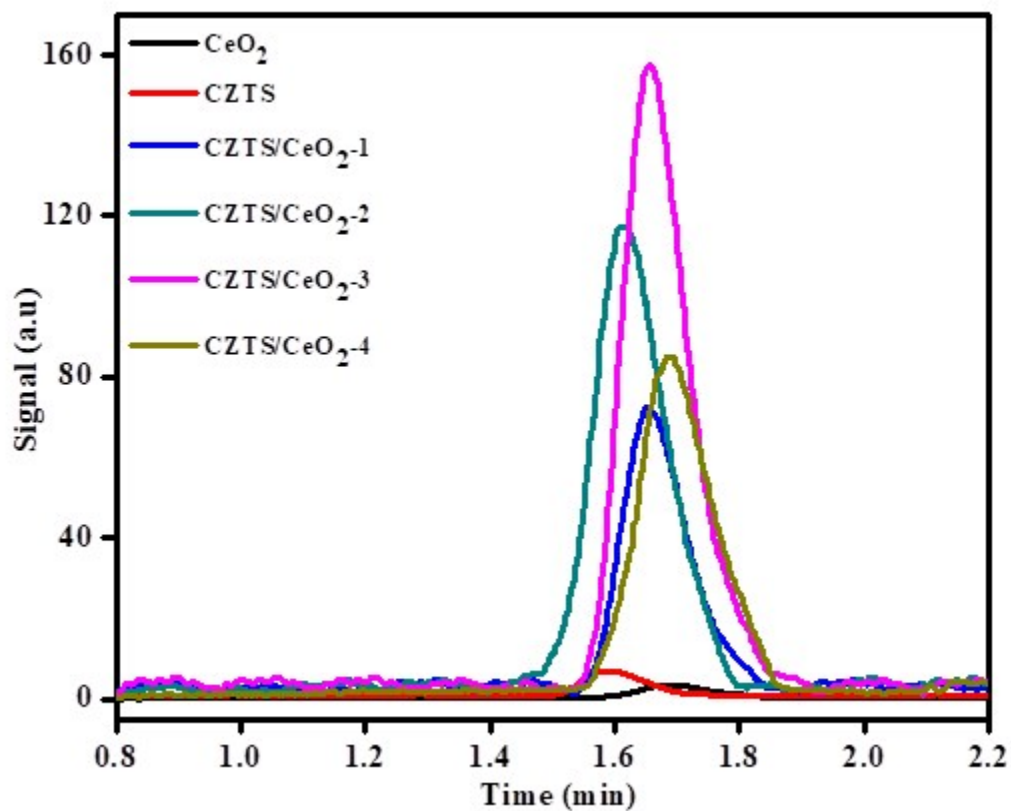


Fig. S4 The H<sub>2</sub> peaks in GC graph for photocatalytic hydrogen production reaction using CeO<sub>2</sub>, CZTS and CZTS/CeO<sub>2</sub> composites

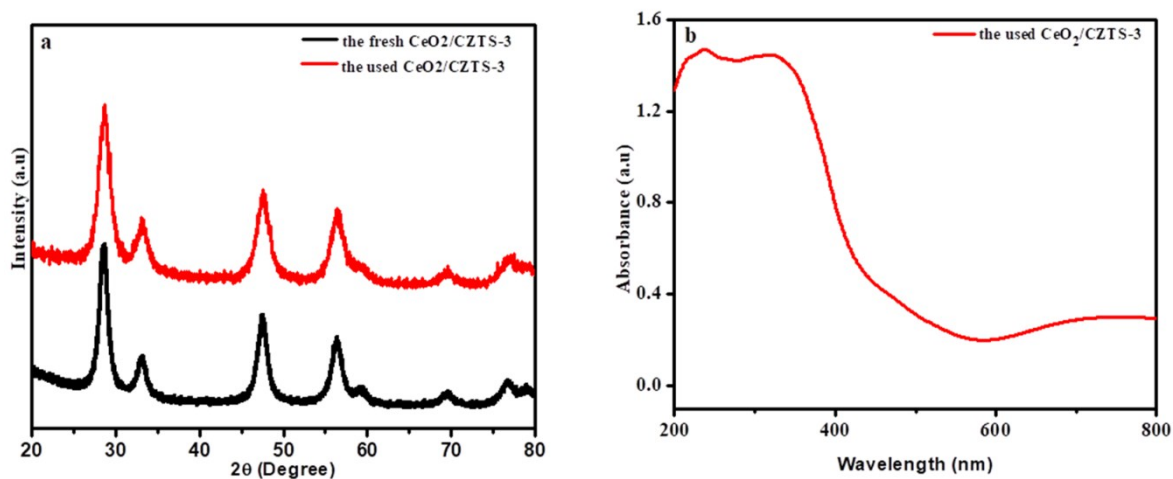


Fig. S5 (a) XRD pattern of the CeO<sub>2</sub>/CZTS-3 before and after photoreaction: (b) UV-Visible spectra of CeO<sub>2</sub>/CZTS-3 after photoreaction

**Table S1.** Comparison Table on Photocatalytic H<sub>2</sub> evaluation rate of CeO<sub>2</sub>/CZTS-3 with Other CeO<sub>2</sub> and CZTS Based Composites

S.No	Photocatalyst	cocatalyst	Reaction condition	H <sub>2</sub> evaluation rate (mmol·g <sup>-1</sup> ·h <sup>-1</sup> )	Ref.
1	CeO <sub>2</sub> /CdS QDs	-	Light source: 300W Xe Lamp -Visible hole scavengers: Na <sub>2</sub> SO <sub>3</sub> and Na <sub>2</sub> S	ca. 0.101	S1
2	CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Pt	Light source : 300W Xe Lamp -Visible hole scavengers: triethanolamine	ca. 1.1	S2
3	CeO <sub>2</sub> /MoS <sub>2</sub>	-	Light source : 150W Xe Lamp -Visible hole scavengers: methanol	ca. 2.542	S3
4	CZTS	Pt	Light source : 300W Xe Lamp -Visible hole scavengers: methanol	ca. 0.645	S4
5	CZTS-Pt	-	Light source : 300W Xe Lamp -Visible hole scavengers: Na <sub>2</sub> SO <sub>3</sub> and Na <sub>2</sub> S	1.02	S5
6	CZTS-PtCo	-	Light source : 300W Xe Lamp -Visible hole scavengers: Na <sub>2</sub> SO <sub>3</sub> and Na <sub>2</sub> S	1.85	S5
7	CZTS-CdS	Pt	Light source :300W Xe Lamp -Visible hole scavengers: Na <sub>2</sub> SO <sub>3</sub> and Na <sub>2</sub> S	11.54	S6
8	CZTS-MoS <sub>2</sub>	-	Light source :500W Tungsten lamp, UV -Visible light hole scavengers: Na <sub>2</sub> SO <sub>3</sub> and Na <sub>2</sub> S	ca. 1.32	S7
9	CZTS-ZnS	-	Light source : UV – Visible light hole scavengers: Na <sub>2</sub> SO <sub>3</sub> and Na <sub>2</sub> S	ca. 0.432	S8
<b>10</b>	<b>CZTS/CeO<sub>2</sub></b>	<b>-</b>	<b>Light source : 300W Xe Lamp - Visible hole scavengers: Na<sub>2</sub>SO<sub>3</sub>and Na<sub>2</sub>S</b>	<b>2.93</b>	<b>This work</b>

## References

- S1. Y.Ma, Y.Bian, Y.Liu, A.Zhu, H.Wu, H.Cui, D.Chu, J.Pan, *ACS Sustainable Chem. Eng.*, 2018, 6, 2552-2562.
- S2. W.Zou, B.Deng, X.Hu, Y.Zhou, Y.Pu, S.Yu, K.Ma, J.Sun, H.Wan, L.Dong, *Appl. Catal., B-Environ.*, 2018, 238, 111-118.
- S3. G.Swain, S.Sultana, B.Naik, K.Parida, *ACS Omega*, 2017, 2, 3745-3753.
- S4. C.Zhi-Xian, C.Rui-Feng, M.Yue-Na, Z.Wen-Hui, K.Dong-Xing, Z.Zheng-Ji, W.Si-Xin, *Int.J.Hydrogen Energy*, 40, 2015, 13456-13462.
- S5. X.Yu, X.An, A.Genc, M.Ibanez, J.Arbiol, Y.Zhang, A.Cabot, *J.Phys.Chem.C*, 2017, 121, 21882-21888.
- S6. M.Yuan, Z.Wen-Hui, K.Dong-Xiang, Z.Zheng-Ji, M.Yue-Na, W.Si-Xin, *Int.J.Hydrogen Energy*, 2018, 45, 20408-20416.
- S7. G.Gogoi, S.Arora, N.Vinoth kumar, M.De, M.Qureshi, *RSC Adv.*, 2015, 5, 40475-40483.
- S8. F.Jiang, B.Pan, D.You, Y.Zhou, X.Wang, W.Su, *Catal. Commun.*, 2016, 85, 39-43.