-Supplementary information-

Construction of organic inorganic hybrid composite derived from C₃N₅ incorporated with CeO₂ nanoparticles for the enhanced photocatalytic hydrogen evolution

Ashil Augustin^a, Manova Santhosh Yesupatham^a, M.D. Dhileepan^a, Sanguk Son^b,

Ezhakudiyan Ravindran^a, Bernaurdshaw Neppolian^a, Hyoungil Kim^{b*}, and Karthikeyan

Sekar^{a*}

^aDepartment of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur, 603203, India

^bDepartment of Civil & Environmental Engineering, Yonsei University, Seoul 03722, Republic of Korea

Corresponding Author E-mail: karthiks13@srmist.edu.in; hi.kim@yonsei.ac.kr



Figure S1. Rietveld analysis of CeO₂ photocatalyst and composition of the CeO₂ photocatalyst



Figure S2. FTIR spectra of C₃N₅, CeO₂ and C₃N₅/CeO₂ Composite.



Figure S3. a) SEM image (b-c) respective energy-dispersive spectroscopy ratio of the CeO_2/C_3N_5 composite (Ce, O, C, and N elements)



Figure S4. Survey XPS spectra of CeO₂, C₃N₅ and C₃N₅/CeO₂ Composite.



Figure S5. high resolution XPS of (a) C1s, (b) N 1s, (c) Ce 3d, (d) O 1s spectra of CeO_2 and C_3N_5 pristine materials.



Figure S6. photoluminescence spectra of the samples.

The conduction band (CB) can be evaluated and converted to reversible hydrogen electrode (RHE) scale according to Nernst equation given as equation S1.

$$E_{RHE} = E_{Ag/AgCl} + E^{0}_{Ag/AgCl} + (0.059*pH)$$
(S1)

where E_{RHE} is the converted potential vs. RHE, $E_{Ag/AgCl}^{0}$ is 0.197 V, $E_{Ag/AgCl}$ is the experimentally measured potential against Ag/AgCl reference and pH of Na₂SO₄ electrolyte is 7 at 25 °C. Further, the valence band (VB) was calculated using Equation S2:

$$E_{\rm VB} = E_{\rm g} + E_{\rm CB} \tag{S2}$$



Figure S7. Mott–Schottky analysis of the samples a) CeO₂ b) C₃N₅



Figure S8. XRD analysis of C_3N_5 /CeO₂ composite after and before the reaction study.

Catalyst	Crystallite size (nm)	Band gap (eV)	VB edge potential (eV)	CB edge potential (eV)
CeO ₂	7.13 nm	2.5	2.03	-0.47
C ₃ N ₅	8.55 nm	1.9	1.09	-0.81

Table S1. Physiochemical properties of the pristine catalyst used for photocatalytic

 application

Table S2. Elemental composition of C_3N_{5} , CeO_2 and C_3N_5/CeO_2 Composites

Catalyst	Elemental Composition (SEM EDAX) (%)			Elemental Composition (XPS) (%)				
CeO ₂	Ce			0	Ce		0	
	69.7			30.3	81.4		19.6	
C ₃ N ₅	С		Ν		С		N	
	29.1		70.9		39.4		60.6	
$\boxed{\text{CeO}_2/\text{C}_3\text{N}_5}$	Ce	0	C	N	Ce	Ο	С	N
	2.6	29.6	27.4	40.4	2.1	20.6	35.6	41.7

 Table S3. Activity comparison of some representative photocatalysts for photocatalytic

 hydrogen production.

SI No	Catalyst	Scavenger	Co- Catalyst	Light Source	Hydrogen evolution	Referenc e
					rate	
1	S-doped C ₃ N ₅	TEOA	-	UV	486	S ^[1]
2	Cr/N-STO	Methanol	Pt	UV	106.7	S ^[2]
3	NiO/C ₃ N ₅	TEOA	-	UV	357	S ^[3]
4	CdS/C ₃ N ₅	TEOA	-	UV	502.11	S ^[4]
5	C ₃ N ₄ /CeCO ₃ OH/CeO ₂	TEOA	-	UV	764	S ^[5]
6	CeO ₂ /MoS ₂	Na ₂ SO ₃ /Na ₂ S	-	UV	112.5	S ^[6]
7	CeO ₂ /MXene	TEOA	-	UV	454.32	S ^[7]
8	Rh-TiO ₂ -CeO ₂	Methanol	-	UV	48.3	S ^[8]
9	NR-CeO ₂ /CdS	Lactic Acid	-	Visible	444	S ^[9]
10	CeO ₂ /C ₃ N ₅	Methanol	-	Visible	1256	This Work

References

1. Guan, X.; Fawaz, M.; Sarkar, R.; Lin, C.-H.; Li, Z.; Lei, Z.; Nithinraj, P. D.; Kumar, P.; Zhang, X.; Yang, J.-H. J. J. o. M. C. A., S-doped C 3 N 5 derived from thiadiazole for efficient photocatalytic hydrogen evolution. *Journal of Materials Chemistry A* **2023**, *11* (24), 12837-12845.

2. Yu, H.; Ouyang, S.; Yan, S.; Li, Z.; Yu, T.; Zou, Z. J. J. o. M. C., Sol–gel hydrothermal synthesis of visible-light-driven Cr-doped SrTiO 3 for efficient hydrogen production. *Journal of Materials Chemistry* **2011**, *21* (30), 11347-11351.

3. LIU, M.-y.; WANG, J.-y.; Lian, D.; Xian, L.; ZHANG, L. J. J. o. F. C.; Technology, Nickel oxide modified C3N5 photocatalyst for enhanced hydrogen evolution performance. *Journal of Fuel Chemistry* **2022**, *50* (2), 243-249.

4. Wang, B.; Qiao, H.; Guan, P.; Yang, B.; Liu, B. J. C. I., Fabrication of CdS/C3N5 photocatalyst for enhanced H2 production. *Composite Interfaces* **2023**, *30* (2), 147-161.

5. Tong, R.; Sun, Z.; Zhong, X.; Wang, X.; Xu, J.; Yang, Y.; Xu, B.; Wang, S.; Pan, H. J. C., Enhancement of visible-light photocatalytic hydrogen production by CeCO3OH in g-C3N4/CeO2 system. *ChemCatChem* **2019**, *11* (3), 1069-1075.

6. Yadav, A. A.; Hunge, Y. M.; Kang, S.-W. J. C., Visible light-responsive CeO2/MoS2 composite for photocatalytic hydrogen production. *Catalysts* **2022**, *12* (10), 1185.

7. Zhu, H.; Fu, X.; Zhou, Z. J. A. o., 3D/2D heterojunction of CeO2/ultrathin MXene nanosheets for photocatalytic hydrogen production. *omega* **2022**, *7* (25), 21684-21693.

8. Hong, J.-W. J. C., Development of visible-light-driven Rh–TiO2–CeO2 hybrid photocatalysts for hydrogen production. *Catalysts* **2021**, *11* (7), 848.

9. Liu, Z.; Zhuang, Y.; Dong, L.; Mu, H.; Li, D.; Zhang, F.; Xu, H.; Xie, H. J. A. A. E. M., Enhancement mechanism of photocatalytic hydrogen production activity of CeO2/CdS by morphology regulation. *Applied Energy Materials* **2023**, *6* (14), 7722-7736.