Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Tuning the N-bonded cerium (III) fraction /g-C_3N_4 interfaces in hollow structures by an in-situ reduction treatment for superior photochemical hydrogen evolution

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Supporting Information

Figure S1 to S4

Table S1-S2

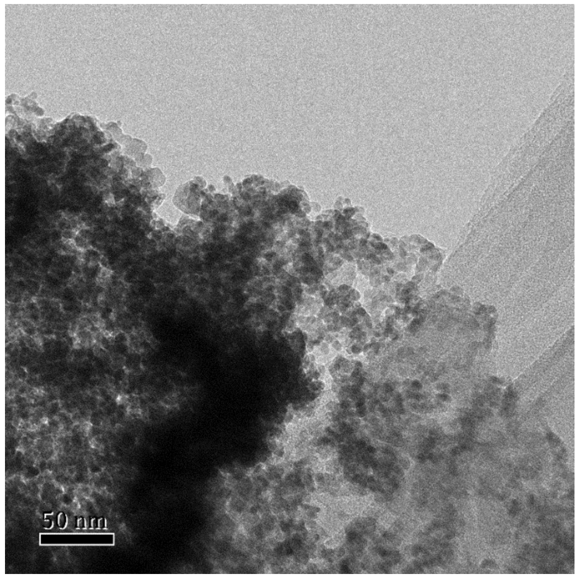

Figure S1. TEM image of the sample NCCN3-S[2] reveals the spherical shape CeO_{2-x} particles having average size 6.01 nm, which is approximately consistent with the calculated particle size by utilizing Scherrer's equation.

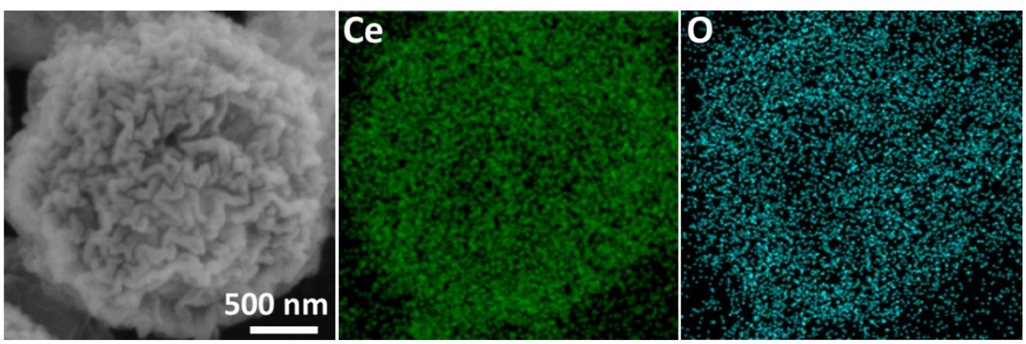

Figure S2. FE-SEM of the sample NCCN1-S[1] hollow structure

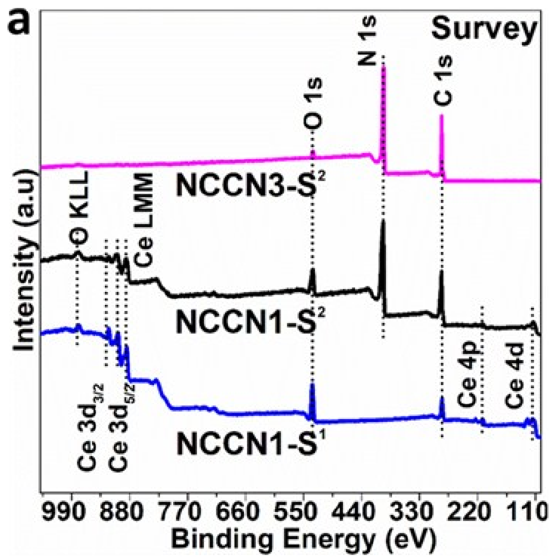

Figure S3. XPS survey spectra's for the as-synthesized NCCNI-S^I, NCCN1-S^2 and NCCN3-S^2 hollow structures.

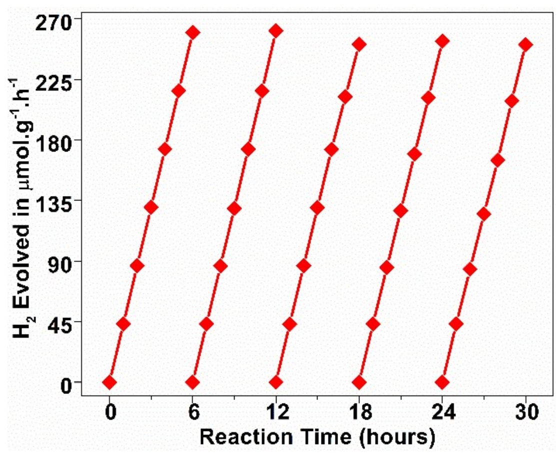

Figure S4. Recycling hydrogen production over NCCN3-S^2 photocatalyst (λ ≥ 420 nm), after each cycle the reactor was flushed with N_2 to evacuate residual H_2 gas.

Table SI. The XPS binding energies position, relative C1s, N1s, O1s surface functionalities, surface Ce (III) / (IV) fraction determined for NCCN1-S[1], NCCN1-S[2], and NCCN3-S[2] photocatalyst.

Catalyst	O 1s (eV) %	N 1s (eV) %	Ce 3d (eV)		C 1s (eV) %	Ce^{3+}/Ce^{4+} At. %
			$3d_{5/2}$ %	$3d_{3/2}$ %		
NCCN1-S[1]	530.38 (Ad-O^{2-}) 48.4%	401.38 (C-N) 100%	885.48 (Ce^{4+})	901.63 (Ce^{4+})	286.68 (C-O) 77.5%	0
	531.95 (C-O) 27.6 %		891.03 (Ce^{4+})	909.23 (Ce^{4+})	288.55 (C=O) 15.1%	
	533.54 (Ad-H_2O) 24 %			918 (Ce^{4+})	290.33 (-CO_3^{2-}) 7.2%	
	O (35.14 %)	N (0.5 %)			C (50.5 %)	
NCCN1-S[2]	531.32 (Ce-O^{2-}) 40.3%	397.91 (Ce-N) 21.4%	883.6 (Ce^{3+})	900.97 (Ce^{3+})	284.8 (C=C) 9.3%	85.43
	533.1 (C-O-C) 33.9%	399 (Ce-N_2) 29.7%	886.89 (Ce^{3+})	904.51 (Ce^{3+})	287.6 (O-C-O) 46%	
	534.79 (Ce-OH) 25%	400.56 (N-C3) 38.6%	890.13 (Ce^{3+})	908.03 (Ce^{4+})	289.4 (O-C=N) 44%	
		402.85 (N-O) 10.3%		918 (Ce^{4+})		
	O (8.57 %)	N (41.54 %)			C (16.5 %)	
NCCN3-S[2]	530.6 (Ce-O) 18.7%	398.57 (C=N-C) 66%	882.1. (Ce^{3+})	900.1 (Ce^{3+})	284.8 (C=C) 10.8%	89
	532.19 (C=O) 49.7%	400.34 (C-N-H) 28.3%	886.08 (Ce^{3+})	906.2 (Ce^{3+})	288.06 (N-C=N) 85%	
	533.52 (-H_2O)31.4%	404.39 (N^+-C) 5.7%	888.82 (Ce^{4+})		293.37 (C-NH_2) 4.1%	
	O (2.86 %)	N (43.82 %)			C (38.6 %)	

Table S2. The comparison of recently published g-C_3N_4 based work for hydrogen evolution reactions.

Catalyst	Hole scavenger	H_2 (μmol h^{-1} g^{-1} cat)	Wavelength (nm)	Reference
CeO_2/g-C_3N_4/Pt	Lactate	73.12	> 420	S1
Rod CeO_2/g-C_3N_4/Pt	TEOA	1100	> 420	S2
TiO_2-B-doped g-C_3N_4	Methanol	150	> 420	S3
$Ni(OH)_2$ g-CN	TEOA	152	> 420	S4
WS_2-*g*-CN	Lactic acid	240	> 420	S5
Ni_2P- g-CN	TEOA	183.6	> 420	S6
N-TCN-700	Methanol	296.4	> 420	S7
NiS- g-CN	TEOA	482	> 440	S8
20 wt % ZnS/g-C_3N_4	Na_2S / Na_2SO_3	713.68	> 420	S9
C-ZrO_2/g-C_3N_4/20%Ni_2P	TEOA	10040	> 420	S10
0.5 wt% Cu_3P/g-C_3N_4	TEOA	808	> 420	S11
N-CeO_{2-x}/g-C_3N_4 Hollow structure	Methanol	43.32	> 420	This work

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