Supplementary Information (SI) for Journal of Materials Chemistry C.

In situ-engineered interfaces in copper oxynitride ($Cu_xO_yN_z$) systems with synergistic properties for photocatalytic H_2 production and N_2 fixation applications

Mithun Prakash Ravikumar,[1] Toan-Anh Quach,[2] Bharagav Urupalli,[3] Mamatha Kumari Murikinati,[3] Shankar Muthukonda Venkatakrishnan,[3] Trong-On Do,[2] and Sakar Mohan[1,*]

[1]*Centre for Nano and Material Sciences, Jain (Deemed-to-be University), Jain Global Campus, Kanakapura, Bangalore 562112, Karnataka, India.*

[2]*Department of Chemical Engineering, Laval University, 1065 Avenue de la Médecine, Québec, QC G1V0A6, Canada.*

[3]*Nanocatalysis and Solar Fuels Research Laboratory, Department of Materials Science & Nanotechnology, Yogi Vemana University, Kadapa 516005, Andhra Pradesh, India.*

*Corresponding author: m.sakar@jainuniversity.ac.in

Table S1. Crystal structure parameters obtained from the Rietveld refinements of XRD patterns of the synthesized bare copper oxide (CuO), O_{rich}-$Cu_xO_yN_z$ (Cu200), N_{rich}-$Cu_xO_yN_z$ (Cu250), and Cu_{rich}-$Cu_xO_yN_z$ (Cu350) systems.

Parameters	**CuO** (Oxide)	**Cu200** (O_{rich}- $Cu_xO_yN_z$)			**Cu250** (N_{rich}- $Cu_xO_yN_z$)			**Cu350** (Cu_{rich}- $Cu_xO_yN_z$)		
Phase (%)	**CuO** 100	**CuO** 74.7	**Cu_3N** 18.2	**Cu** 7.1	**CuO** 33.7	**Cu_3N** 56.9	**Cu** 9.4	**CuO** 61.6	**Cu_3N** 22.2	**Cu** 16.2
Crystal structure	Monoclinic	Monoclinic	Cubic	FCC	Monoclinic	Cubic	FCC	Monoclinic	Cubic	FCC
Space group	C2/c (#15-1)	C2/c (#15-1)	Pm-3m (#221-1)	Fm-3m	C2/c (#15-1)	Pm-3m (#221-1)	Fm-3m	C2/c (#15-1)	Pm-3m (#221-1)	Fm-3m
a (Å)	4.68	4.69	3.81	3.61	4.67	3.81	3.61	4.68	3.81	3.62
b (Å)	3.42	3.43	3.81	3.61	3.43	3.81	3.61	3.43	3.81	3.62

c (Å)	5.13	5.14	3.81	3.61	5.13	3.81	3.61	5.14	3.81	3.62
α (°)	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	99.41	99.07	90.00	90.00	99.32	90.00	90.00	99.09	90.00	90.00
γ (°)	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
Volume ($Å^3$)	81.09	81.71	55.52	47.18	80.98	55.26	47.18	81.50	54.38	47.46
R-factor	3.9	2.9	4.2	3.9	2.3	4.63	3.6	2.8	4.6	3.7
R_P	4.8	4.8	4.7	6.9	4.9	4.6	7.1	4.5	5.3	7.3
R_{WP}	6.0	6.0	5.4	8.7	5.9	5.4	8.4	5.9	5.8	9.3
χ^2	1.3	1.5	1.4	1.3	1.4	1.8	1.6	1.1	1.6	1.2
Cu-Cu bond length (Å)	-	-	-	3.62	-	-	-	-	-	3.62
Cu-Cu bond angle (°)	-	-	-	90.00	-	-	-	-	-	90.00
Cu-O bond length (Å)	1.95	1.98	-	-	1.93	-	-	1.94	-	-
Cu-N bond length (Å)	-	-	1.91	-	-	1.92	-	-	1.90	-
O-Cu-O bond angle (°)	95.59	96.32	-	-	94.67	-	-	95.78	-	-
Cu-N-Cu bond angle (°)	-	-	90.00	-	-	90.00	-	-	90.00	-

Table S2. Parameters obtained from the XPS analysis of the synthesized bare copper oxide (CuO), O_{rich}-$Cu_xO_yN_z$ (Cu200), N_{rich}-$Cu_xO_yN_z$ (Cu250), and Cu_{rich}-$Cu_xO_yN_z$ (Cu350) systems.

Sample	Binding energy of Cu $2p_{3/2}$ (eV)	FWHM (eV)	Area (CPS/eV)	Atomic % (at%)	Formula determined
CuO	CuO: 934.4 Cu_2O: 933.0	3.15 2.08	202062 93335	3.42 1.58	CuO
Cu200	CuO: 934.6 Cu_3N: 933.7 Cu: 932.7	3.75 2.03 1.16	284567 111091 45340	3.93 1.53 0.63	$CuO_{4.57}N_{0.09}$
Cu250	CuO: 934.8 Cu_3N: 933.4 Cu: 932.6	3.16 2.30 1.09	135585 158181 20948	2.09 2.44 0.32	$CuO_{4.07}N_{0.38}$
Cu350	CuO: 935.2 Cu_3N: 934.4 Cu: 932.1	3.46 1.72 2.06	228767 109368 312878	1.82 0.88 2.51	$CuO_{0.55}N_{0.03}$