Electronic Supplementary Information

Bimetallic and Plasmonic Ag and Cu Integrated TiO_2 Thin films for Enhanced Solar Hydrogen Production in Direct Sunlight

Sunesh S. Mani,[a] Sivaraj Rajendran,[a] Pushkaran S. Arun,[a] Thomas Mathew,[*,a] Chinnakonda S Gopinath[*][b,c]

[a] Sunesh S. M, Sivaraj. R, Dr. Thomas Mathew, Department of Chemistry, St. John's College (Affiliated to University of Kerala), Anchal , Kerala – 691308, India, E-Mail: thomasm74@gmail.com

[b]Catalysis and Inorganic Chemistry Division, CSIR - National Chemical Laboratory, Dr.HomiBhabha Road, Pune 411 008, India. E-mail: cs.gopinath@ncl.res.in

[c]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

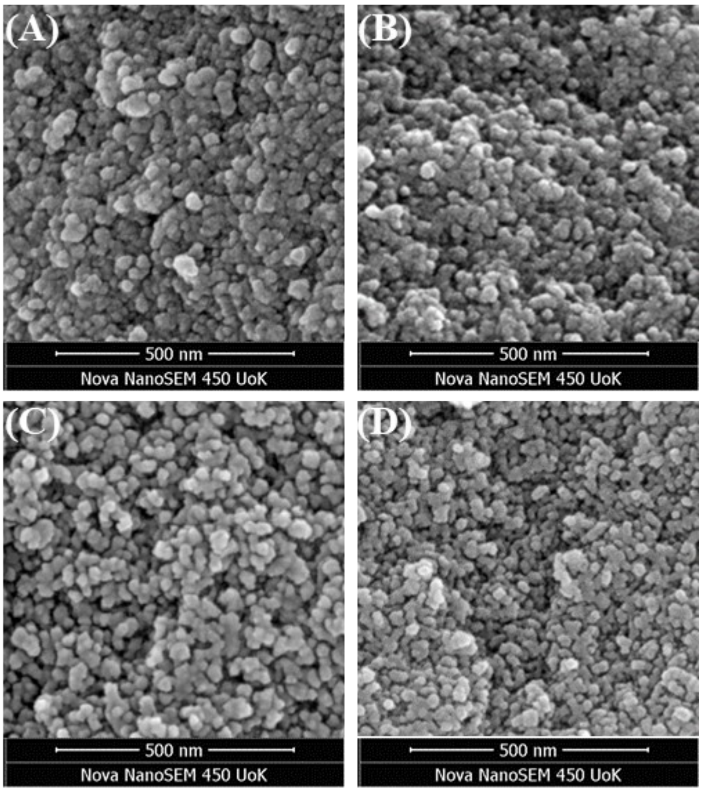

Figure S1. FESEM of mesoporous TiO_2, Ag/TiO_2, Cu/TiO_2, and Ag-Cu/TiO_2nanocomposites: A) TiO_2, B)TiAg-1, C) TiCu-1, and D) TiAgCu-1

It is evident from the FESEM images that both TiO_2 and metal incorporated TiO_2nanocomposites are composed of nearly spherical shaped particles, which are interconnected with each other to form a disordered mesoporous network structure.Although some agglomeration of particles are observed possibly due to the van der Waals forces of interaction between the particles, the segregation of metal nanoparticles as separate entity was not apparent on the metal/TiO_2 surface suggesting that the metal species are in a highly dispersed state and/or partially incorporated in the TiO_2 lattice.[1,]

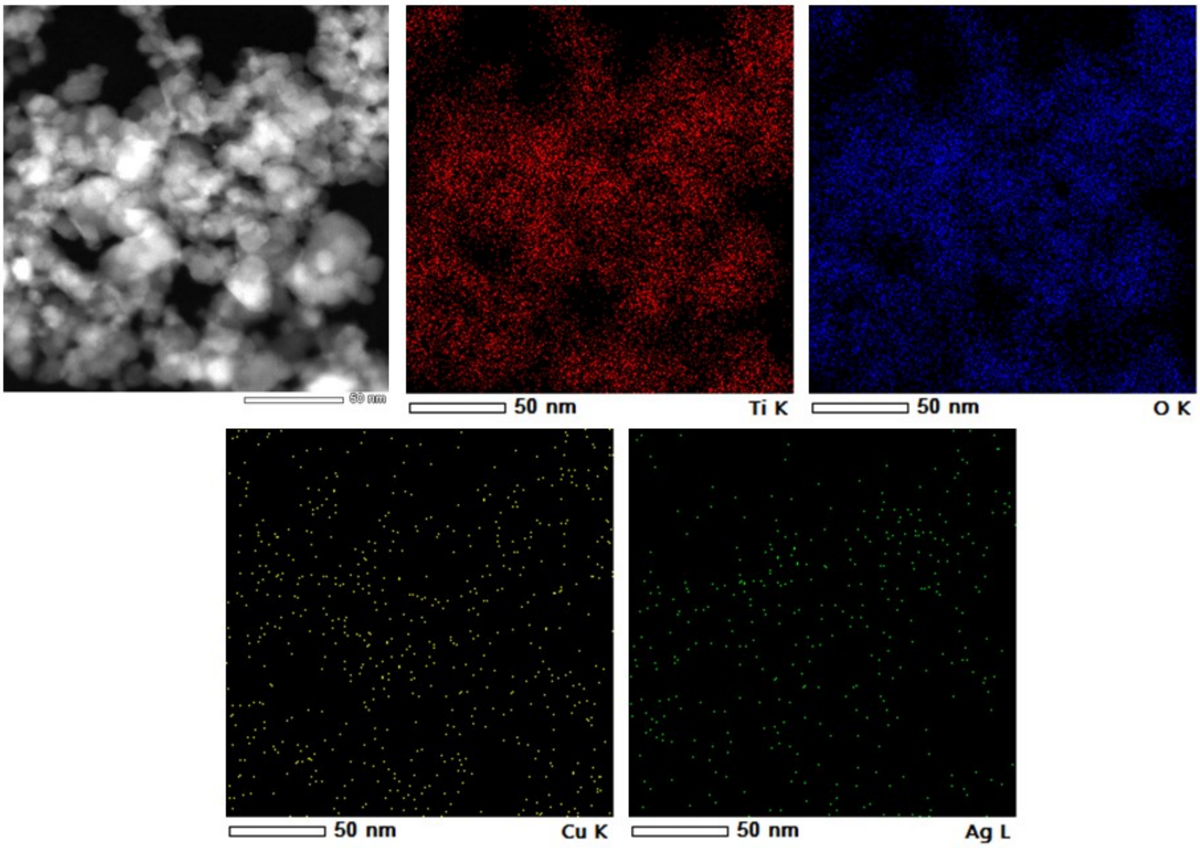

Figure S2. HRTEM-EDS measurements carried out with TiAgCu-1. Very fine distribution of Cu and Ag, and without any clustering underscores the abundance of Schottky junctions.

Table S1: *Impedance parameters of the electrical circuit fitting (model R (CR)*

Catalysts	R_S / Ω	R_{ct}/ Ω	C_{dl} / µF
TiO_2	0.80	329.00	163
TiCu-1	0.59	142.70	300.9
TiAg-1	0.31	99.21	438.6
TiAgCu-1	0.28	27.69	451.4

Table S2*: XPS and XAES Parameters of TiCu and TiAgCuPhotocatalysts and Cu/Ti, Ag/Ti surface atomic ratio*

Photocatalyst	BEof $Ti2p_{3/2}$ [a](SOC) (eV)	BE of Cu $2p_{3/2}$(eV) [a](SOC) (eV)	BE of $Ag3d_{5/2}$ [a](SOC) (eV)	O1s (eV)	KE of CuLMM (eV)	α (Cu) (eV)	Cu/Ti surface ratio(Bulk Ratio)	Ag/Ti Surface Ratio (Bulk Ratio)
TiCu-1	458.8 (5.7)	932.6(19.7)	-	529.6	918.7	1851.37	0.029 (0.012)	-
TiAgCu-1	458.7 (5.7)	932.8 (20)	367.5 (6.0)	529.4	918.9	1851.3	0.040 (0.003)	0.037 (0.006)
TiAgCu-2	458.9 (5.8)	932.8 (20)	367.7 (6.0)	529.6	918.7	1851.3	0.028 (0.006)	0.015 (0.004)
TiAgCu-3	458.8 (5.7)	932.7 (20)	367.5 (6.0)	529.6	918.9	1851.6	0.060 (0.009)	0.018 (0.002)

[a] (SOC) indicates spin orbit coupling constant. [b]Ag/Ti, [b]Cu/Ti bulk atomic ratios calculated are provided in the parenthesis.

The Modified Auger parameter (α) is calculated according to the following equation[2].

$$\alpha = h\nu + (\text{KE } Cu_{LMM} - \text{KE Cu } 2p_{3/2}) \quad [1]$$

where KE Cu_{LMM} and KE Cu $2p_{3/2}$ are the kinetic energies of Auger electron and Cu $2p_{3/2}$ level.

Ag/Cu surface ratio Vs hydrogen evolution

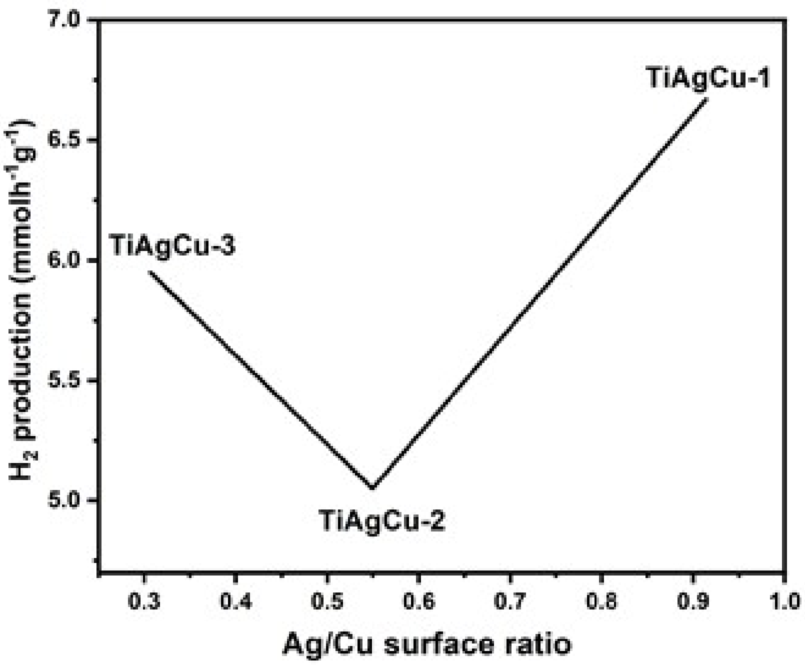

Figure S3. Variation of rate of hydrogen production with Ag/Cu surface ratio

Table S3*: Comparative hydrogen evolution from thin film and powder form of various photocatalyst*

Photocatalyst	**H_2 production (Powder form)$mmolh^{-1}g^{-1}$**	**H_2 production (Thin film form)$mmolh^{-1}g^{-1}$**
TiO_2	0.15	0.16
TiAg-1	1.07	4.59
TiCu-0.5	0.69	2.08
TiCu-1	0.56	1.70
TiCu-5	0.30	1.27
TiAgCu-1	1.34	6.67
TiAgCu-2	1.21	5.05
TiAgCu-3	1.29	5.95

Table S4*: Comparative hydrogen evolution from thin film and powder form of TiAgCu-1 at different catalyst amount*

Amount of TiAgCu-1 (mg)	H_2 ($mmolh^{-1}g^{-1}$) Powder	H_2($mmolh^{-1}g^{-1}$) Thin film
0.5	1.20	6.12
1	1.34	6.67
2	1.42	6.05
5	1.27	3.45
25	0.78	1.56

We optimized the loading of the photocatalyst by performing activity measurements using 0.5, 1, 2, 5, and 25mg of TiAgCu-1 catalyst in both thin film and powder form and the results are provided in **Table S4** in the supporting information. The optimized amount for thin film is 1 mg and with higher or lower amount of catalyst loading the activity declines and our results are in agreement with previous reports. We used 1 mg powder catalyst for comparison purpose though 2 mg loading also show marginally higher activity, but within the 10% error margin. Note that in powder case also the decline of photocatalytic activity with higher amount of catalyst loading is clear.

***Table S5**: Hydrogen production activity of selected catalyst under visible light*

Photocatalyst	H_2 yield under visible light (mmol/h/g)
TiO_2	0
TiAg-1	3.1
TiCu-0.5	1.5
TiCu-1	1.2
TiCu-5	0.6
TiAgCu-1	4.8
TiAgCu-2	3.4
TiAgCu-3	3.9

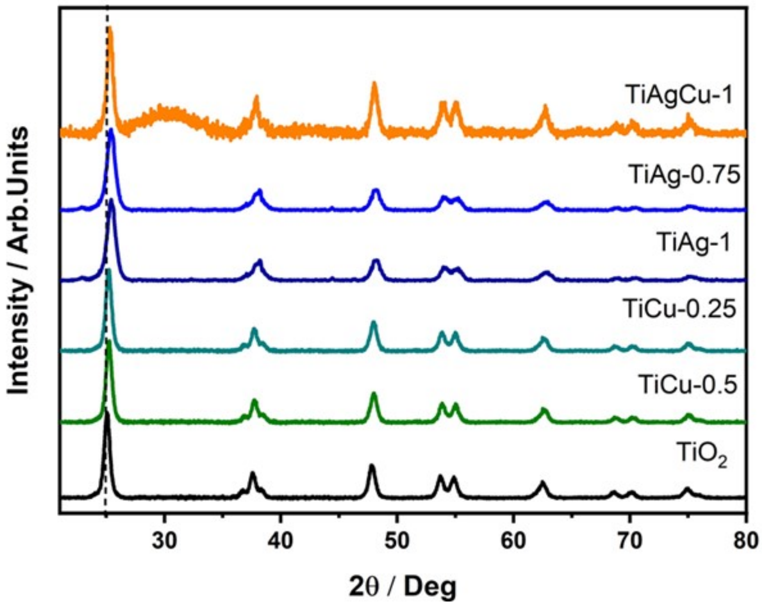

Figure S4. Wide angle XRD patterns of mesoporous TiO_2, TiCu-0.5, TiCu-0.25, TiAg-1,TiAg-0.75 and TiAgCu-1 nanocomposites.

***Table S6**: Atomic mass percentage of elements in TiAgCu-1 catalyst from HRTEM EDS analysis*

Elements	Ti	O	Ag	Cu
Atomic percentage	33.06	66.65	0.19	0.10

References

1 D. Gogoi, A. Namdeo and A. Kumar, *Int. J. Hydrogen Energy*, 2020, **45**, 2729-2744

2 T. Mathew, N. R. Shiju, K. Sreekumar, B. S. Rao and C. S. Gopinath,*J.Catal.,* 2002, **417**, 405–417.