Supporting Information

Prominence of Cu in Plasmonic Cu-Ag alloy Decorated SiO_2@S-doped C_3N_4 Core Shell Nanostructured Photocatalyst towards Enhanced Visible Light Activity

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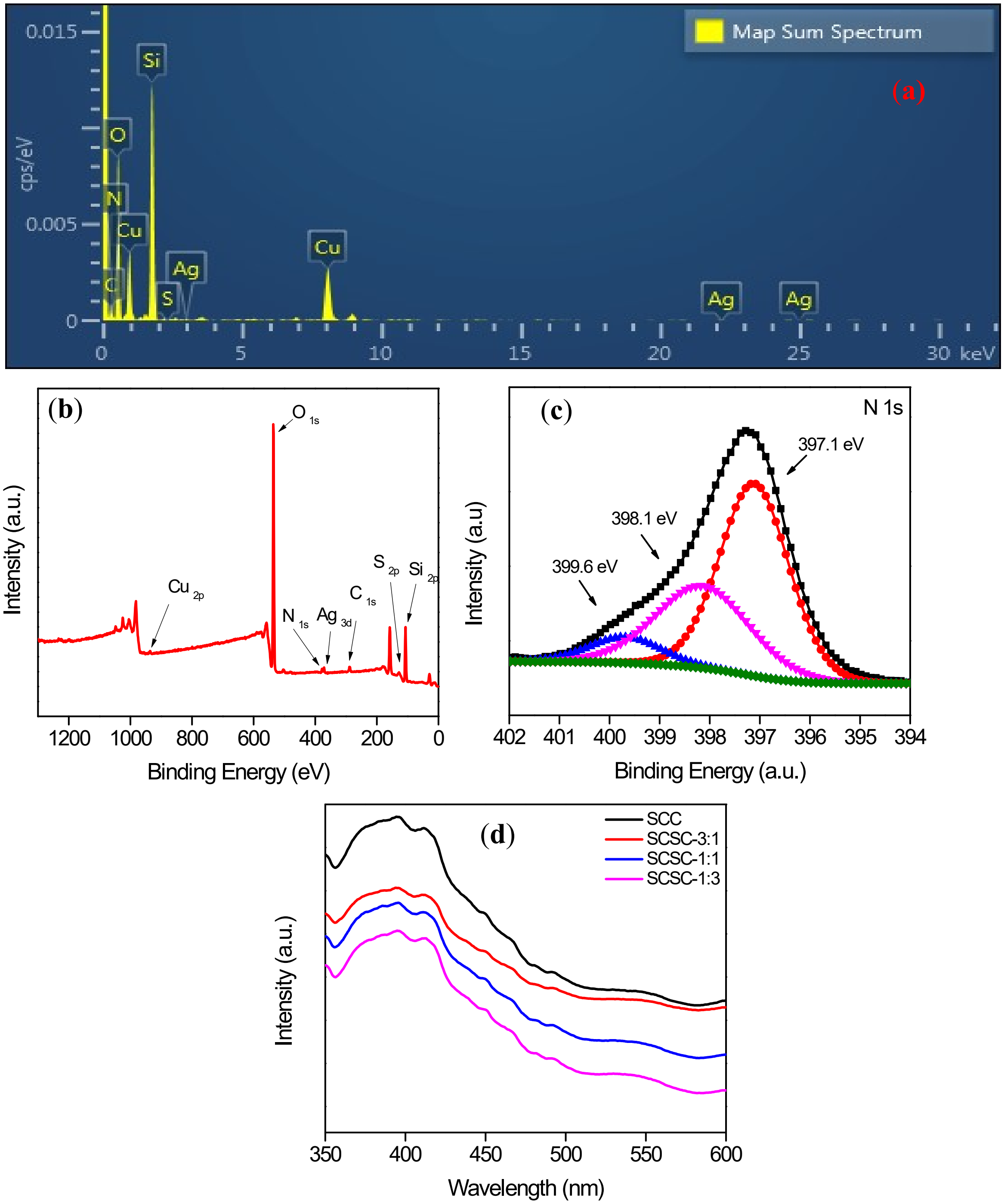
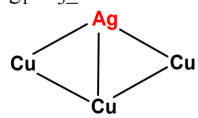
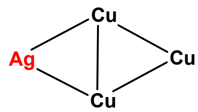


Figure S1. (a) EDX spectra of SCSC-1:3, (b) XPS survey spectrum (c) deconvoluted N 1s spectra (d) Photoluminescence spectra of SCC, SCSC-3:1, SCSC-1:1, SCSC-1:3.

Photocatalyst	**Synthesis method**	**Activity**	**Reference**
Ag-Cu@TiO_2microrod	Surfactant assisted sol-gel method	Water disinfection 8 h	1
Ag-Cu@ZrO_2	Impregnation reduction method	Nitro benzene to azoxy benzene 75%, 16 h	2
Ag-Cu/TiO_2	Wet impregnation method	H_2 generation 16,650 µmol $h^{-1}g^{-1}$	3
Ag-Cu alloy	Impregnation reduction method	4-Nitro phenol reduction 4 min	4
Ag-Cu alloy	Galvanic replacement reaction method	Rhodamine-6g degradation 20 min 88%	5
Montmorillonite decorated MWCNTs/TiO_2	sol-gel and wet impregnation method	1888 ppm h^{-1} of H_2	6
Ni-MMT/TiO_2	sol-gel method	3470 µmole g-cat. $^{-1}$ h^{-1} of H_2	7
SiO_2@Ag-Cu@CS	chemical reduction method	Hydrogen generation 1730µmol $h^{-1}g^{-1}$ Phenol oxidation 81.9%, 90 min	This work

Table S1. Literature survey on various Ag-Cu alloy based photocatalyst

Models	ΔG_f (S=1)
Ag_1Cu_3_Alter 	-92.7 kcal/mol
Ag_1Cu_3 	**-95.1 kcal/mol**

Ag_1Cu_3		
ΔG_f (S=1)	ΔG_f (S=3)	ΔG_f (S=5)
-95.1 kcal/mol	-78.8 kcal/mol	-10.8 kcal/mol

Table S2. (Left) Two probable models of Ag_1Cu_3 with their free energy of formation (ΔG_f) and (Right) Ground state spin multiplicity (S) check for the most stable model (highlighted).

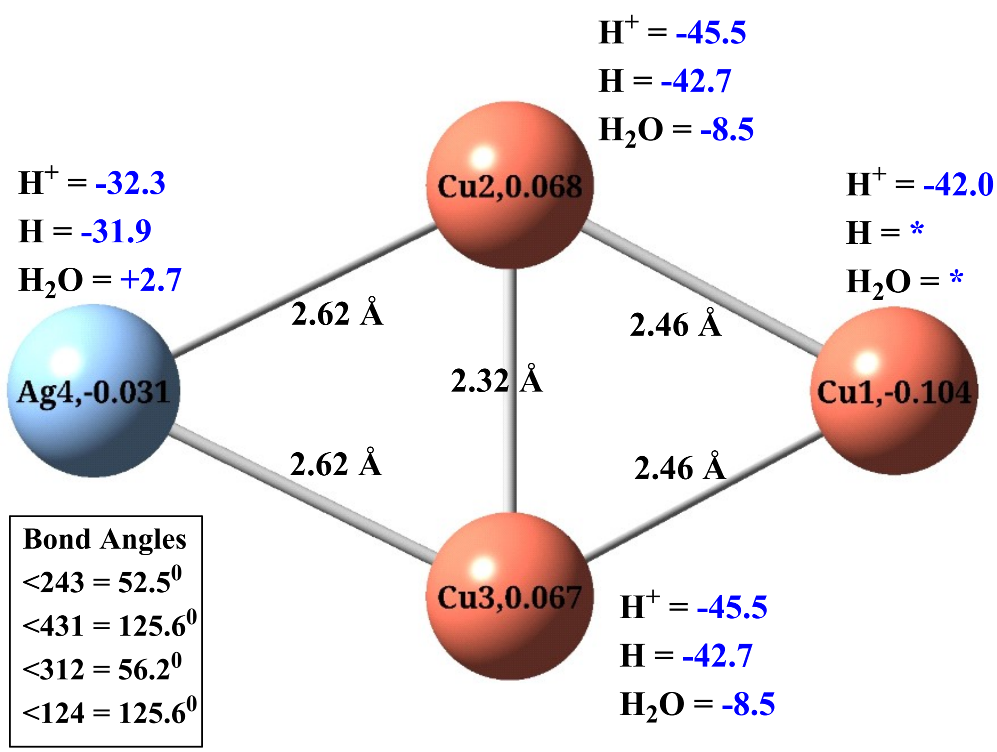


Figure S2. The most stable Ag_1Cu_3 optimized model with label, NBO values, and bond parameters. The binding energy (**ΔG, in kcal/mol**) for water and H^+/H at different sites are shown. *Optimized model for H_2O and H bound to Cu1 could not be obtained.

Optimized Cartesian Coordinates

Models				
Ag_1Cu_3_Alter	Cu	2.21996230	-0.29751054	0.00019307
	Cu	0.00200260	-1.31999956	-0.00022874
	Cu	-2.21845134	-0.30077935	0.00019315
	Ag	-0.00216794	1.18362541	-0.00009717
Ag_1Cu_3	Cu	2.52858158	-0.00022633	-0.00040731
	Cu	0.35542941	1.16078177	0.00039167
	Cu	0.35485973	-1.16062738	0.00039178
	Ag	-1.99845214	0.00004439	-0.00023208
Ag_1Cu_3_H^+ (Cu1)	Cu	1.21245057	1.24370500	-0.01733171
	Cu	0.51078044	-0.93569508	-1.19726966
	Cu	0.52871753	-0.90690360	1.21102745
	Ag	-1.43563358	0.31657660	0.00265116
	H	2.16827060	2.48881670	-0.02096067
Ag_1Cu_3_H^+ (Cu2)	Cu	2.24172711	-1.07335156	-0.18136026
	Cu	0.05369752	-0.17305177	0.44816120
	Cu	1.98655502	1.23703255	-0.07816545
	Ag	-2.61124767	0.01507598	-0.14038396
	H	-1.44876927	-0.43681840	1.12761696
Ag_1Cu_3_H^+ (Cu3)	Cu	-2.24225097	-1.07277692	-0.18142497
	Cu	-1.98551329	1.23702400	-0.07802346
	Cu	-0.05369825	-0.17337591	0.44807835
	Ag	2.61092190	0.01495188	-0.14037084
	H	1.44908354	-0.43800216	1.12716197
Ag_1Cu_3_H^+ (Ag4)	Cu	0.87387761	-0.32218027	1.35497036
	Cu	0.83711928	1.34875310	-0.40911323
	Cu	0.83884787	-1.02077993	-0.96830352
	Ag	-1.50485908	-0.00355975	0.01544855
	H	-3.21712103	-0.00068586	-0.07513656
Ag_1Cu_3_H (Cu2)	Cu	-2.45583028	-0.10981486	0.00003463
	Cu	-0.39232456	1.29461056	-0.00003757
	Cu	-0.34746202	-1.19712836	-0.00003251
	Ag	1.97356055	-0.05297529	0.00001859
	H	-0.08445717	2.84748587	0.00015399

Ag_1Cu_3_H (Cu3)	Cu	2.45583023	-0.10981190	0.00003776
	Cu	0.34746426	-1.19712851	-0.00003594
	Cu	0.39232160	1.29460937	-0.00003985
	Ag	-1.97355944	-0.05297616	0.00002033
	H	0.08442722	2.84747950	0.00014732
Ag_1Cu_3_H (Ag4)	Cu	-2.58188530	-0.00627239	0.00017448
	Cu	-0.39107946	1.17805095	-0.00016125
	Cu	-0.42219706	-1.15621124	-0.00016671
	Ag	2.01521023	-0.00523149	0.00009193
	H	3.74481171	-0.20557225	0.00013024
Ag_1Cu_3_H_2O (Cu2)	Cu	2.48224306	-0.43797130	-0.00391374
	Cu	0.41587804	0.97067946	-0.03361236
	Cu	0.23618434	-1.36356015	0.02336514
	Ag	-2.03974042	-0.14462262	-0.00189448
	O	0.50391326	3.01689194	-0.04295119
	H	1.23962285	3.34728485	0.50071384
	H	-0.29798690	3.40955012	0.34260411
Ag_1Cu_3_H_2O (Cu3)	Cu	2.48200769	-0.43893296	-0.00214574
	Cu	0.23489512	-1.36357902	0.02325259
	Cu	0.41767361	0.97043811	-0.03543715
	Ag	-2.03992503	-0.14371077	-0.00221443
	O	0.48940050	3.01681080	-0.04133851
	H	1.30097687	3.35249669	0.37642162
	H	-0.24242060	3.39756521	0.47394345
Ag_1Cu_3_H_2O (Ag4)	Cu	2.87033351	-0.00515582	0.00178524
	Cu	0.66291997	1.15583803	0.00058301
	Cu	0.67125713	-1.14936818	-0.00121563
	Ag	-1.69479492	0.00558987	-0.00222839
	O	-4.16872693	-0.13345876	-0.00140021
	H	-4.46795956	0.44370156	-0.72464322
	H	-4.45767151	0.32313767	0.80715322
Ag_1Cu_3_H_2O (TS_Cu)	Cu	2.47865031	-0.53937700	0.01018726
	Cu	-0.02269613	-1.40023577	0.00051899
	Cu	0.39050424	0.92140602	-0.03840866
	Ag	-2.08903576	0.10434912	0.00939661
	O	1.48504688	2.58170143	-0.06251963
	H	2.16014998	1.15232463	-0.01405635
	H	1.59686154	2.81765077	0.87594274
Ag_1Cu_3_H_2O (TS_Ag)	Cu	2.57169720	-0.08100949	0.01267018
	Cu	0.53527584	-1.34026472	0.00417181
	Cu	0.38328165	1.00925157	-0.03605578
	Ag	-2.03058033	-0.31494350	0.00373512
	O	-0.48287147	2.78646681	-0.05980607
	H	-0.57805186	3.03085911	0.87809516
	H	-1.33908636	1.42840738	-0.01799735

$Ag_1Cu_3\_H_2O$ (Unfavorable Product)	Cu	-0.02782248	1.17267576	1.19545425
	Cu	-0.02786914	1.17288853	-1.19531741
	Cu	1.41549583	-0.41258752	-0.00007966
	Ag	-1.34222795	-0.85212917	-0.00002930
	O	2.82023800	-1.60577910	-0.00004582
	H	3.64428776	-1.09235647	0.00018828
	H	-2.55580028	-2.06766620	-0.00010267
$Ag_1Cu_3\_H_2O$ (Final Product)	Cu	0.17818690	1.52362615	-0.83970663
	Cu	0.27235314	0.59020926	1.51139345
	Cu	-1.38104414	-0.38948750	-0.00337532
	Ag	1.17832789	-0.95932420	-0.30863423
	O	-3.14182579	-0.77245098	-0.40530724
	H	-3.41383093	-1.51122076	0.16279795
	H	0.15164549	2.77297649	-1.79556449
$Ag_1Cu_3\_2H$ (Int1)	Cu	0.01118499	1.45009595	-0.00005403
	Cu	-2.11642242	0.25164947	0.00004565
	Cu	2.13166815	0.30744331	0.00004966
	Ag	0.06112552	-1.25020941	-0.00002736
	H	-1.67914500	1.87884767	0.00000335
	H	-1.96024556	-1.38547864	0.00008496
$Ag_1Cu_3\_2H$ (TS)	Cu	2.51551430	-0.01527870	0.00001708
	Cu	0.28959920	1.10120901	-0.00003319
	Cu	0.32888630	-1.26088389	-0.00001325
	Ag	-1.99088644	0.01599234	0.00001259
	H	1.80746034	1.71422847	0.00011673
	H	0.87820778	2.60778547	0.00014324
$Ag_1Cu_3\_H_2$ (Int3)	Cu	2.51629965	-0.08261558	-0.00095255
	Cu	0.37335256	1.12815708	-0.00002578
	Cu	0.32979722	-1.19379637	0.00069779
	Ag	-2.00058240	-0.03464094	-0.00003735
	H	0.71795060	2.97451694	0.00499625
	H	-0.05461125	2.95299854	0.00489507

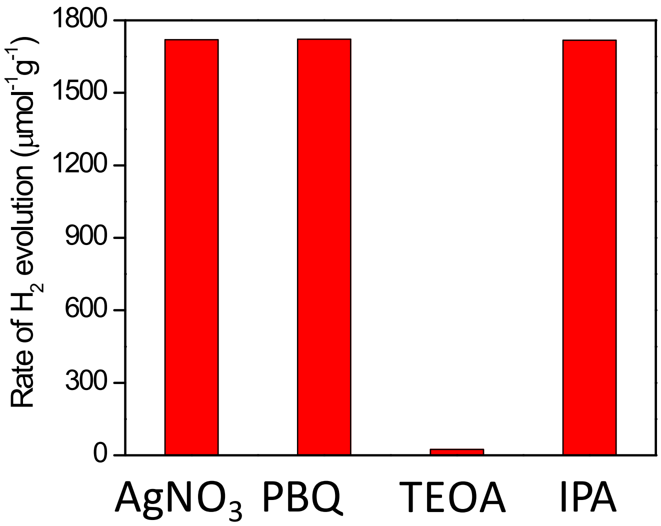


Figure S3. Effect of radical scavenger on hydrogen evolution reaction.

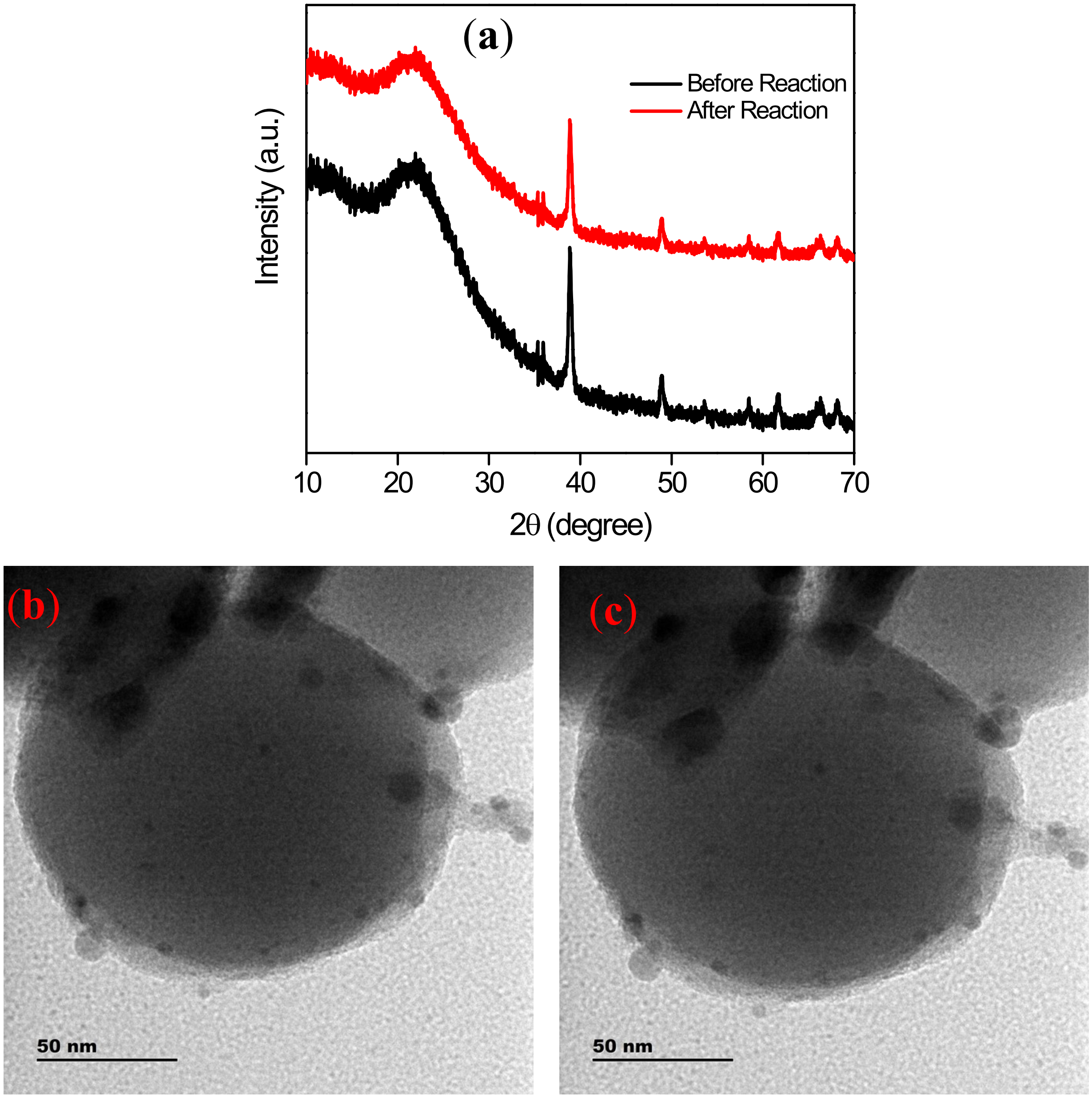


Figure S4. (a) PXRD of SCSC-1:3 before and after photocatalytic reaction, (b,c) HRTEM image of SCSC-1:3 before and after photocatalytic reaction suggesting the crystal phase and morphology remain intact after the reusability test.

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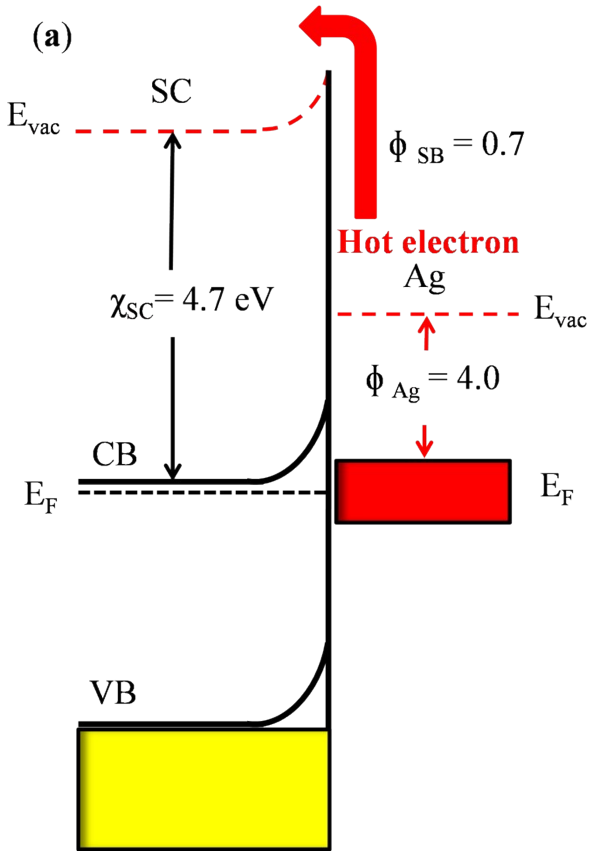

Scheme S1. (a) Energy band diagram of SCS and SCC, where E_F, E_{vac}, χ_{SC}, CB, VB, ϕ_{SB}, ϕ_{Ag}, ϕ_{Cu} represents the Fermi energy level, vaccum energy level, electronegativity of conduction band of SC, conduction band and valance band of SC, Schottky barrier height, and work function of Ag and Cu on monometallic form.

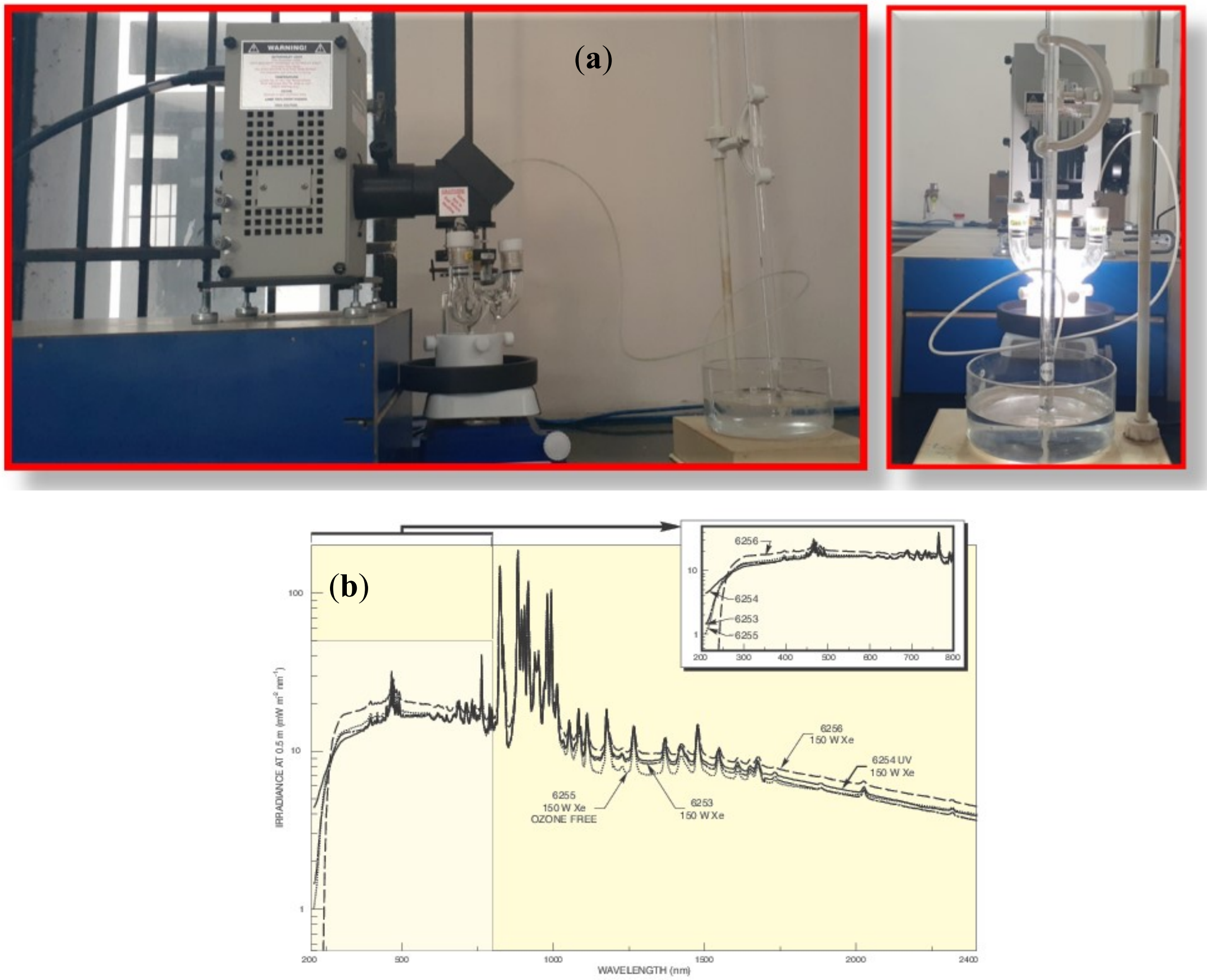

Figure S5. (a) photocatalytic reactor for water splitting reaction, (b) Spectral pattern of 150W Xenon lamp.

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