Supporting Information

In-situ liquid cell transmission electron microscopy guiding the design of large-sized cocatalysts coupled with ultra-small photocatalysts for highly efficient energy harvesting

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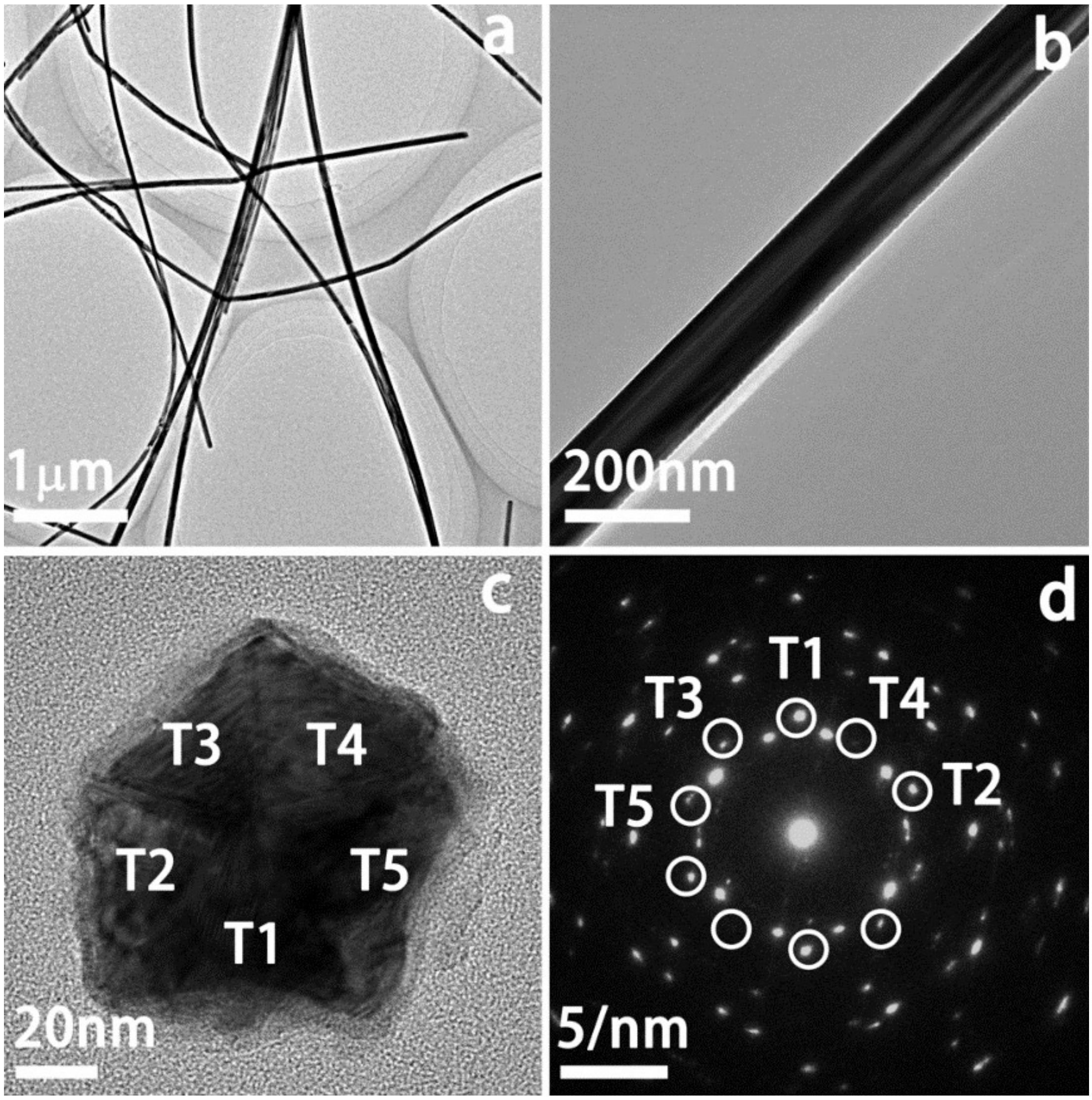

Figure S1. (a) Low magnification TEM image of Cu nanowires. (b) TEM image of a single Cu nanowire. (c) Cross-section TEM image of a Cu nanowire. Twin boundaries can be clearly observed. Five twins are marked by T1-T5. (d) The corresponding selected area electron diffraction (SAED).

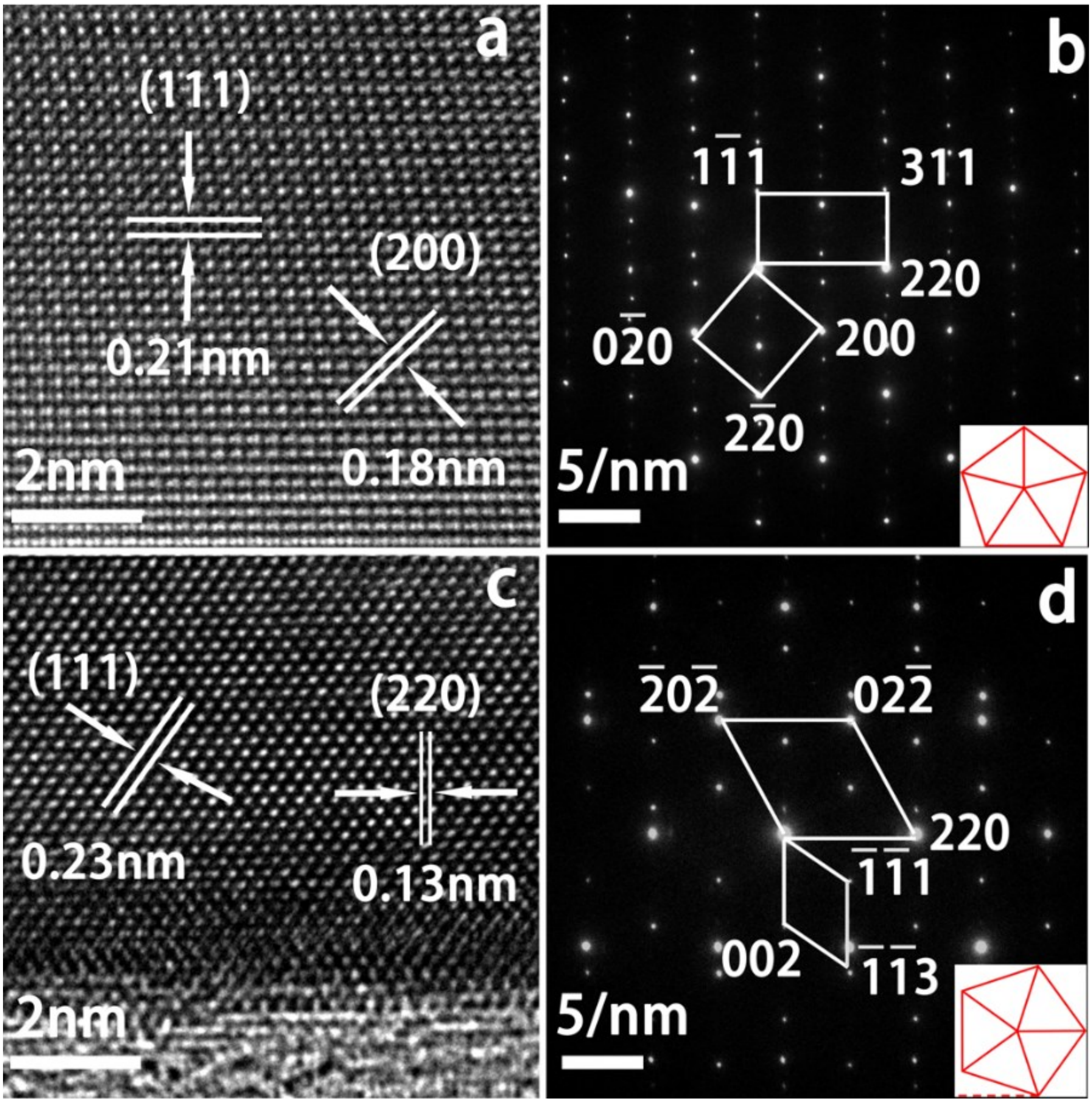

Figure S2. (a) High-resolution atomic image of a Cu nanowire with the [0 1 -1] zone axis. (b) The corresponding SAED of (a). (c) High-resolution atomic image of a Cu nanowire with the [-1 1 0] zone axis. (d) The corresponding SAED of (c). The orientation between electron beam and twin structures is shown in Figure b and d, respectively.

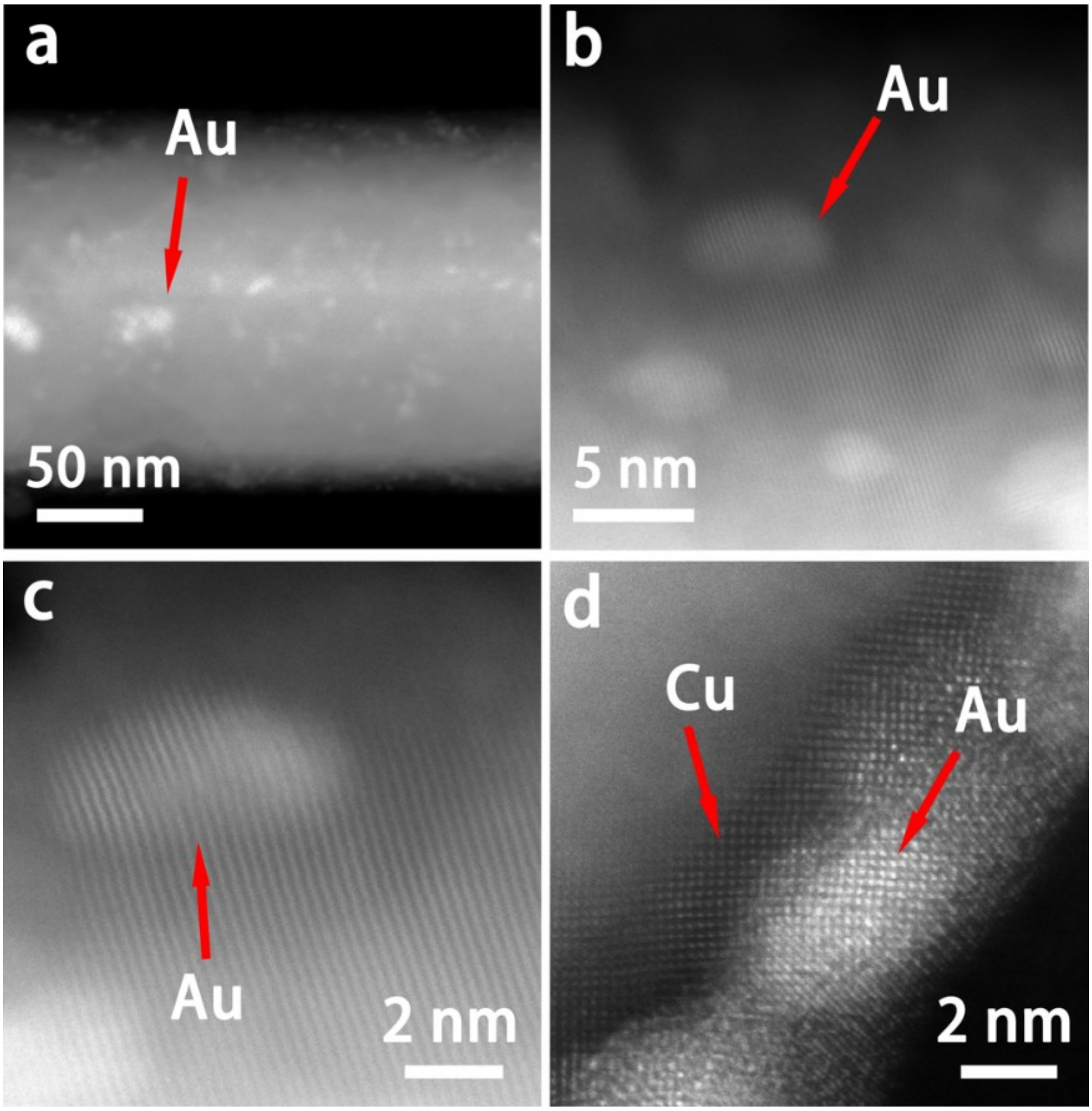

Figure S3. (a) Low magnification STEM-HAADF image of Au nanoparticles on a Cu nanowire. (b) High magnification STEM-HAADF image of Au nanoparticles on a Cu nanowire. (c) Lattice fringes of Au nanoparticles and Cu nanowire characterized by STEM-HAADF. (d) Atomic-scale STEM-HAADF image of Au nanoparticle on Cu nanowire.

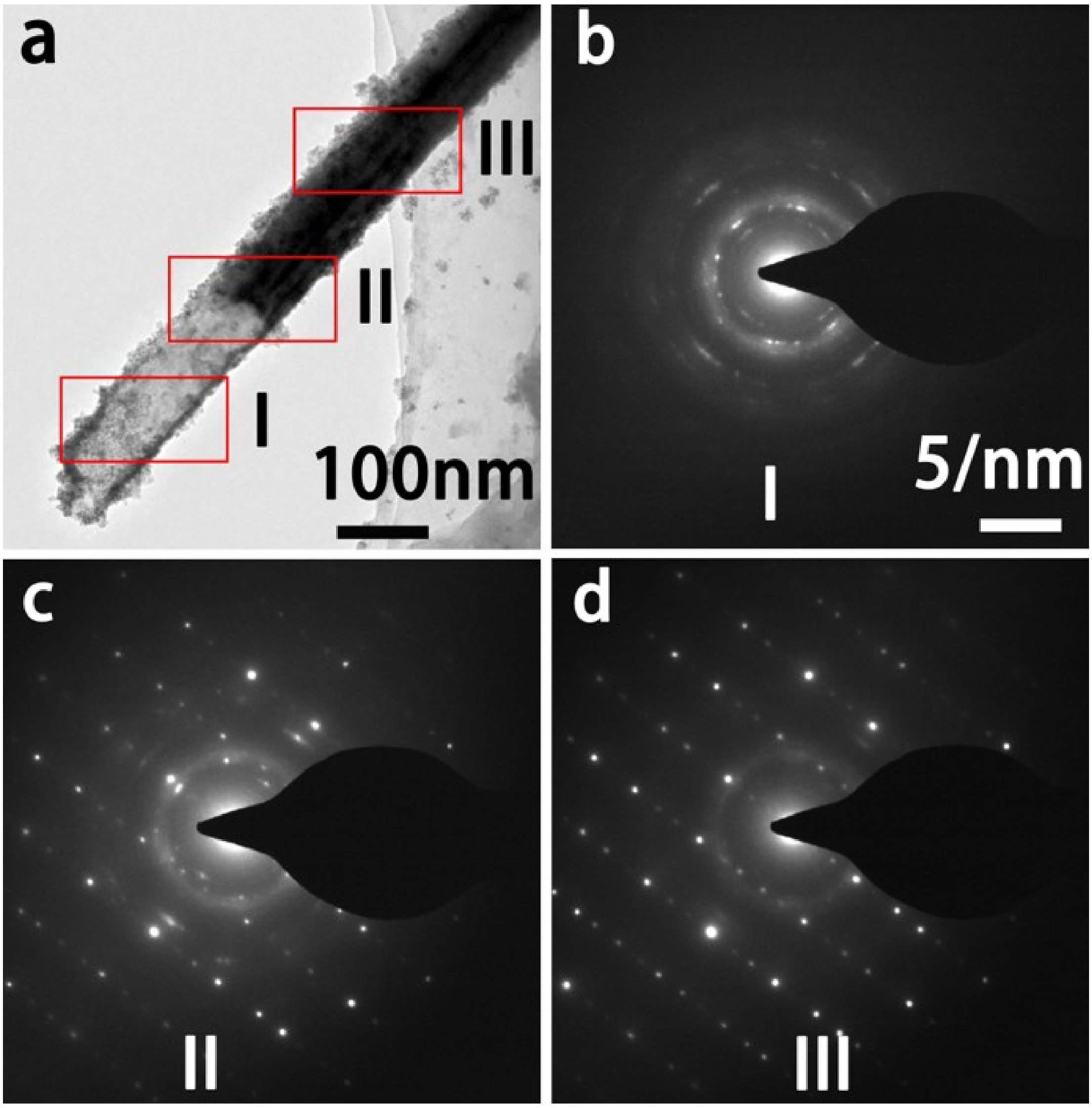

Figure S4. (a) Low magnification TEM image of partially hollowed Cu nanowire with Au nanoparticles. Three locations are marked by red rectangle. (b)-(d) The corresponding SAED to the three locations in (a).

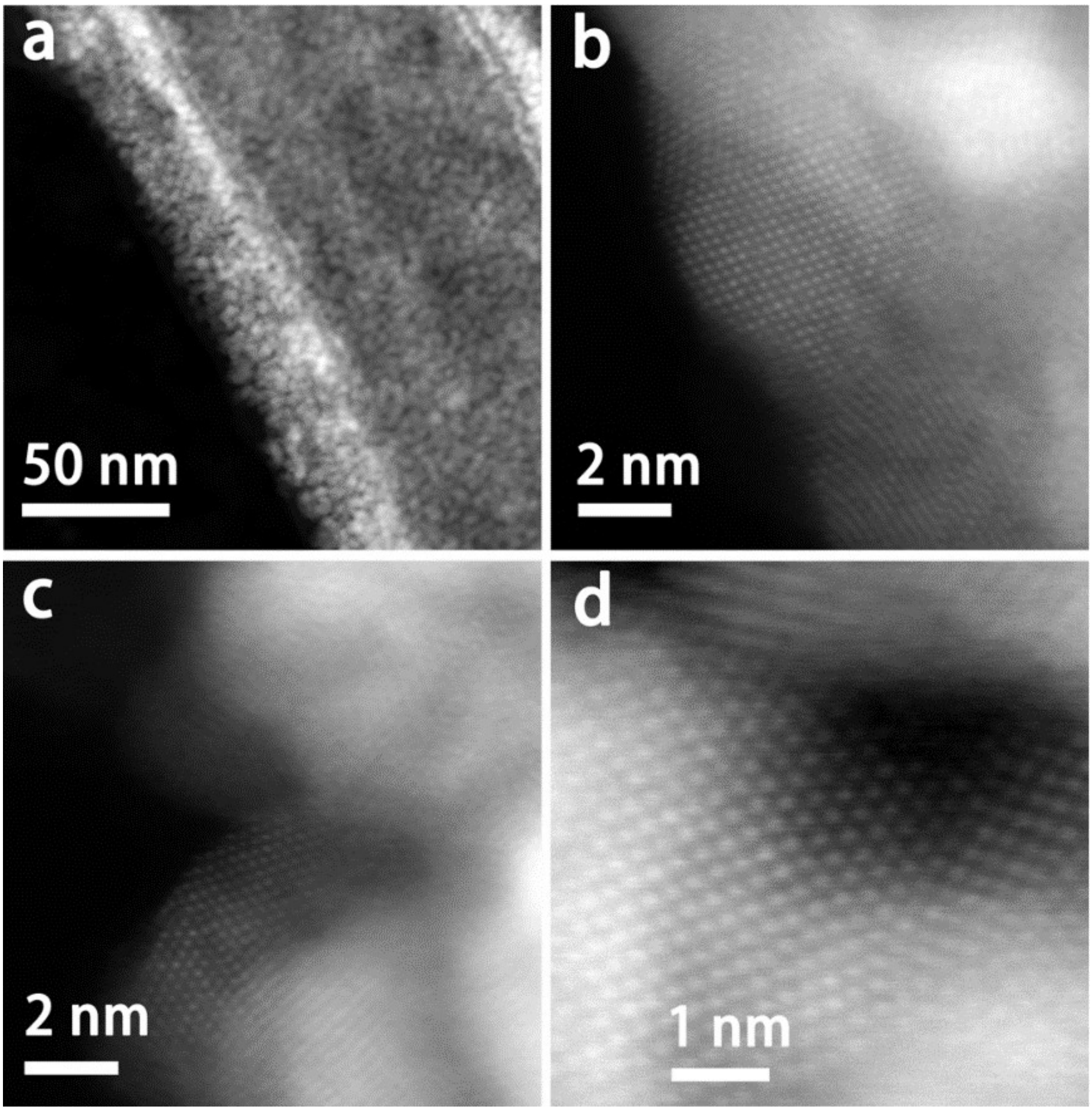

Figure S5. (a) Low magnification STEM-HAADF image of hollowed Cu-Au nanotube. (b)-(d) Atomic-scale STEM-HAADF images of Au nanoparticle on the nanotube.

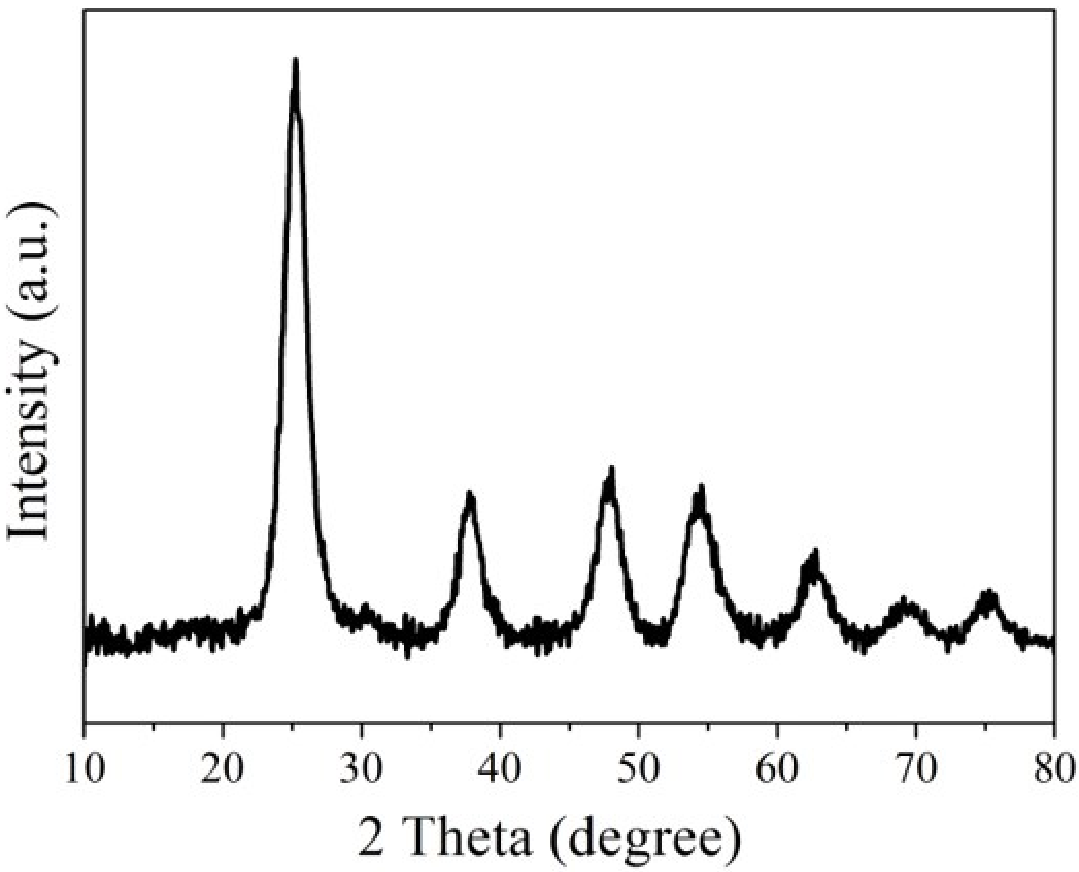

Figure S6. X-ray diffraction of TiO_2 nanoparticles with anatase structure.

Table S1. Comparison of photocatalytic hydrogen production based on Au-Cu cocatalysts coupled with TiO_2 photocatalysts. Other kinds of noble-metal cocatalysts are also shown for comparison.

Co-catalyst	**Photo-catalyst**	**Sacrificial Agent**	**Light source**	**Reaction temperature (ºC)**	**Production (μmol/g/h)**	**Reference**
Au-Cu	TiO_2 quantum dot	10 vol.% Methanol	300 W xenon lamp	5	13100	This work
Au1-Cu1	TiO_2 nanosheet	10 vol.% methanol	PLS-SXE300	–	710	1
Au-Cu	TiO_2 (P25)	–	1000 W Xe lamp	60	286	2
Au-Cu	TiO_2 nanosheet	0.35 M Na_2S 0.25 M Na_2SO_3	PLS-SXE300	–	1310	3
Au_3-Cu	TiO_2 nanotube,	10 vol.% EtOH	UV LED 365 ± 5 nm	–	10560	4
Au-Cu	TiO_2	–	UV LED 365 ± 5 nm	–	4100	5
Au-Pt	TiO_2 nanosheet	30 vol.% Methanol	300 W xenon lamp	20	8010	6
Au-Pt	TiO_2 nanofiber	20 vol.% Methanol	300 W xenon	–	165	7

			lamp			
Ni-Pd	TiO_2 nanoparticle	50 vol.% Methanol	400 W mercury arc	–	4200	8
Cu-Ag	TiO_2 nanoparticle	10 vol.% TEOA	150 W xenon lamp (≥400 nm)	20	1560	9
Au-Ag	TiO_2 (P25)	20 vol.% Methanol	250 W Hg lamp (350–450 nm)	60	12820	10
Au-Pt	TiO_2 (P25)	oxalic acid	150 W UV lamp (λ <365 nm)	–	708.5	11
Au-Pt	TiO_2 (P25)	25 vol.% Methanol	Newport solar simulator 300 W	–	1275	12
Au-Pt	TiO_2	20 vol.% Methanol	Nd-YAG laser 532 nm	–	6200	13
Ag-Ni	TiO_2	0.1 M Methanol	LED, 420 nm	–	2933.9	14
Au-Pt	TiO_2	10 vol.% Methanol	300 W xenon arc lamp	–	23667	15

References

1. Zeng, D.; Yang, L.; Zhou, P.; Hu, D.; Xie, Y.; Li, S.; Jiang, L.; Ling, Y.; Zhao, J., AuCu alloys deposited on titanium dioxide nanosheets for efficient photocatalytic hydrogen evolution. *Int. J. Hydrogen Energy* **2018,** *43* (32), 15155-15163.

2. Stefan, N.; Agullo, M.; Antonio, J.; Patricia, C.; Hermenegildo, G., Gold–Copper Nanoalloys Supported on TiO_2 as Photocatalysts for CO_2 Reduction by Water. *J. Am. Chem. Soc.* **2014,** *136* (45), 15969-15976.

3. Liu, Y.; Xu, C.; Xie, Y.; Yang, L.; Ling, Y.; Chen, L., Au–Cu nanoalloy/TiO_2/MoS_2 ternary hybrid with enhanced photocatalytic hydrogen production. *J. Alloy. Comp.* **2020,** *820*, 153440.

4. Martínez, L.; Soler, L.; Angurell, I.; Llorca, J., Effect of TiO_2 nanoshape on the photoproduction of hydrogen from water-ethanol mixtures over Au_3Cu/TiO_2 prepared with preformed Au-Cu alloy nanoparticles. *Appl. Catal. B: Environ.* **2019,** *248*, 504-514.

5. Bonmati, E.; Casanovas, A.; Angurell, I.; Liorca, J., Hydrogen Photoproduction from Ethanol–Water Mixtures Over Au–Cu Alloy Nanoparticles Supported on TiO_2. *Top Catal.* **2015,** *58*, 77-84.

6. Cheng, L.; Li, Y.; Chen, A.; Zhu, Y.; Li, C., Subnano-Sized Pt–Au Alloyed Clusters as Enhanced Cocatalyst for Photocatalytic Hydrogen Evolution. *Chem. – An Asian J.* **2019,** *14* (12), 2112-2115.

7. Zhang, Z.; Li, A.; Cao, S.-W.; Bosman, M.; Li, S.; Xue, C., Direct evidence of plasmon enhancement on photocatalytic hydrogen generation over Au/Pt-decorated TiO_2 nanofibers. *Nanoscale* **2014,** *6* (10), 5217-5222.

8. Luna, A. L.; Dragoe, D.; Wang, K.; Beaunier, P.; Kowalska, E.; Ohtani, B.; Bahena Uribe, D.; Valenzuela, M. A.; Remita, H.; Colbeau-Justin, C., Photocatalytic Hydrogen Evolution Using Ni–Pd/TiO_2: Correlation of Light Absorption, Charge-Carrier Dynamics, and Quantum Efficiency. *J. Phys. Chem. C* **2017,** *121* (26), 14302-14311.

9. Babu, P.; Naik, B., Cu–Ag Bimetal Alloy Decorated SiO_2@TiO_2 Hybrid Photocatalyst for Enhanced H_2 Evolution and Phenol Oxidation under Visible Light. *Inorg. Chem.* **2020,** *59* (15), 10824-10834.

10. Chiarello, G. L.; Aguirre, M. H.; Selli, E., Hydrogen production by photocatalytic steam reforming of methanol on noble metal-modified TiO_2. *J. Catal.* **2010,** *273* (2), 182-190.

11. Hampel, B.; Kovács, G.; Czekes, Z.; Hernádi, K.; Danciu, V.; Ersen, O.; Girleanu, M.; Focşan, M.; Baia, L.; Pap, Z., Mapping the Photocatalytic Activity and Ecotoxicology of Au, Pt/TiO_2 Composite Photocatalysts. *ACS Sustainable Chem. Eng.* **2018,** *6* (10), 12993-13006.

12. Melvin, A. A.; Illath, K.; Das, T.; Raja, T.; Bhattacharyya, S.; Gopinath, C. S., M–Au/TiO_2 (M = Ag, Pd, and Pt) nanophotocatalyst for overall solar water splitting: role of interfaces. *Nanoscale* **2015,** *7* (32), 13477-13488.

13. Montes-Navajas, P.; Serra, M.; Garcia, H., Influence of the irradiation wavelength on the photocatalytic activity of Au–Pt nanoalloys supported on TiO_2 for hydrogen

generation from water. *Catal. Sci. Technol.* **2013,** *3* (9), 2252-2258.

14. Gao, D.; Liu, W.; Xu, Y.; Wang, P.; Fan, J.; Yu, H., Core-shell Ag@Ni cocatalyst on the TiO_2 photocatalyst: One-step photoinduced deposition and its improved H_2-evolution activity. *Appl.Catal. B: Environ.* **2020,** *260*, 118190.

15. Wang, F.; Jiang, Y.; Lawes, D. J.; Ball, G. E.; Zhou, C.; Liu, Z.; Amal, R., Analysis of the Promoted Activity and Molecular Mechanism of Hydrogen Production over Fine Au–Pt Alloyed TiO_2 Photocatalysts. *ACS Catal.* **2015,** *5* (7), 3924-3931.