Highly enhanced photocatalytic hydrogen activity by constructing large portion of Cu single atoms on the surface of TiO_2

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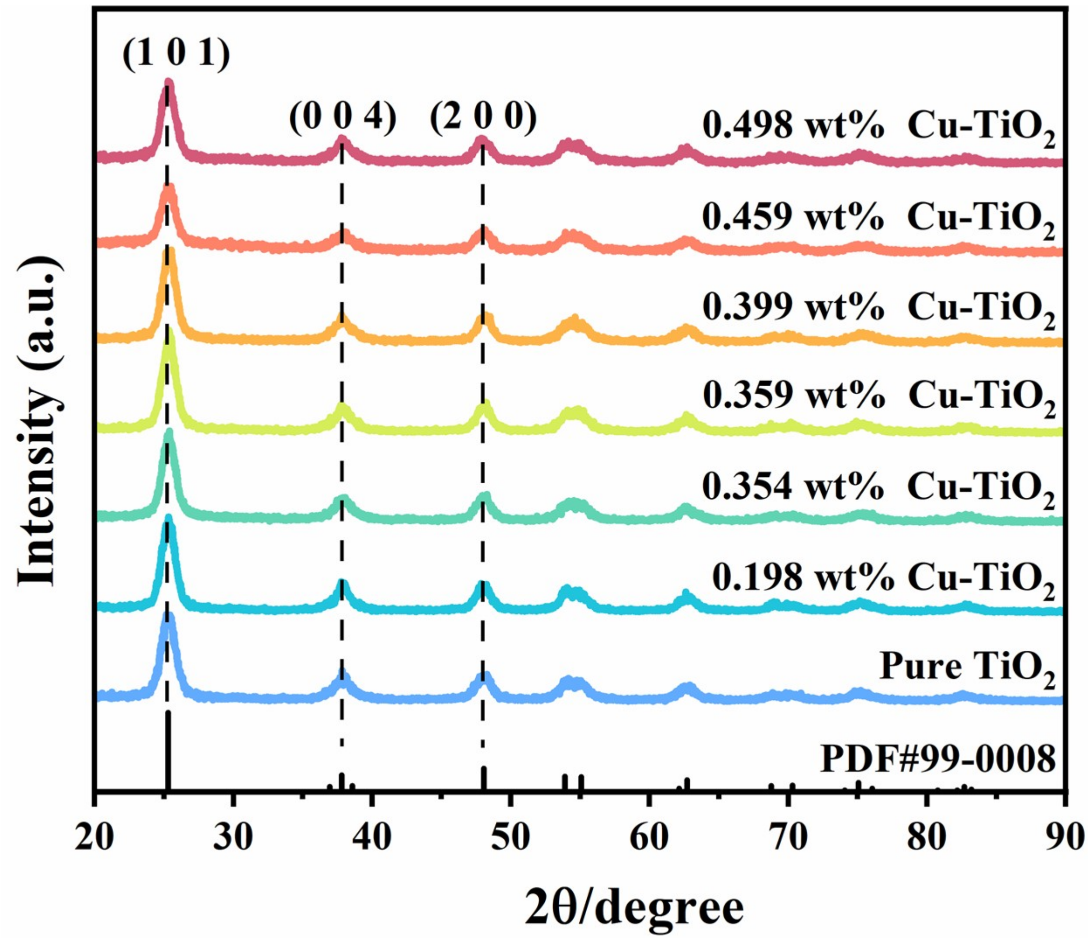


Fig. S1 XRD patterns of TiO_2 samples with different Cu loading.

The crystal structures of Cu-TiO_2 samples and pure TiO_2 were investigated by XRD. As shown in Fig. S1, all TiO_2-based samples are mainly composed of rutile-phase TiO_2 (PDF#99-0008). Well-defined diffraction angles (2θ) at 25.303, 37.792, 48.035º can be indexed as the (1 0 1), (0 0 4), (2 0 0) planes of anatase phase TiO_2.[1]

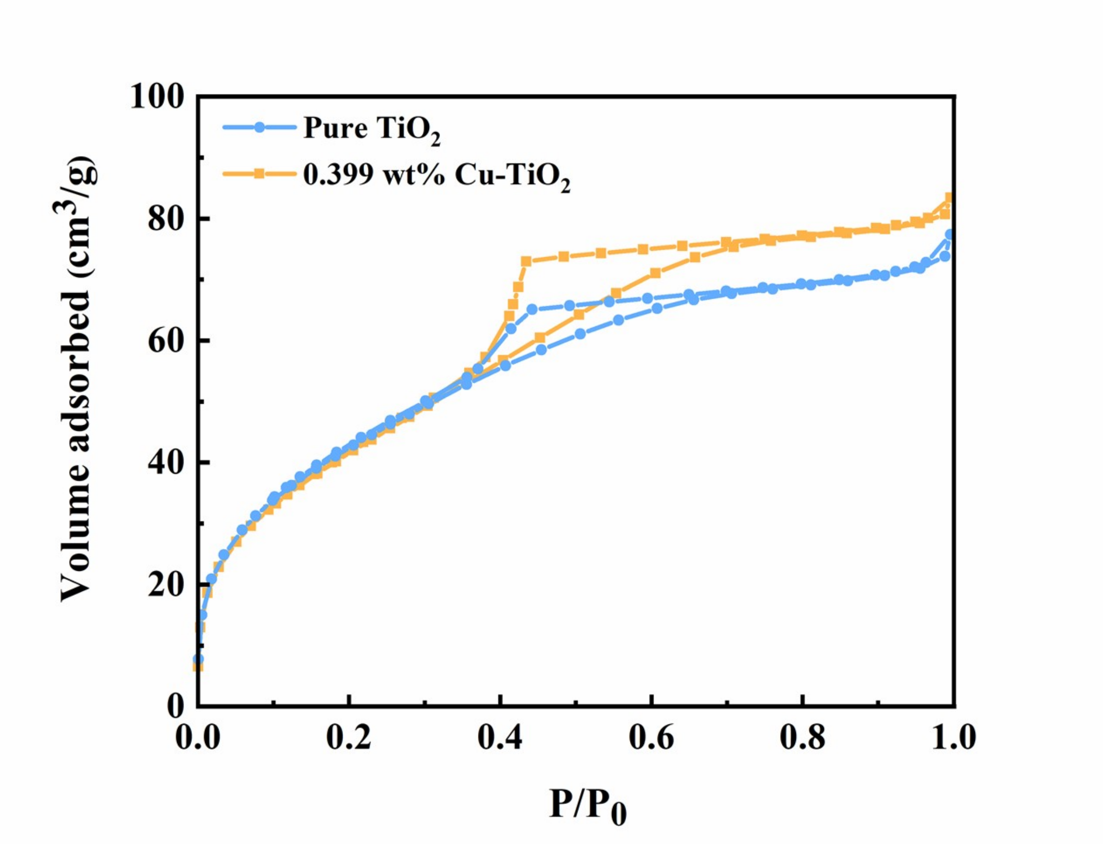


Fig. S2 N_2 sorption isotherms of 0.399 wt% Cu-TiO_2 and pure TiO_2, measured at 77 K.

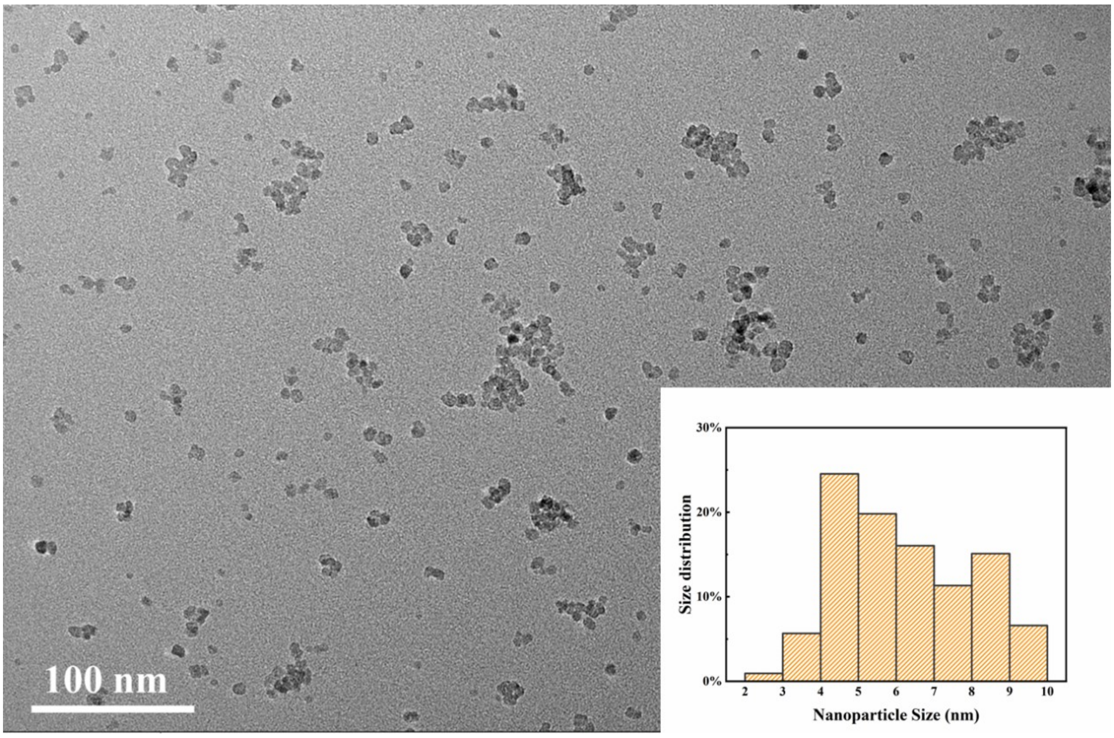
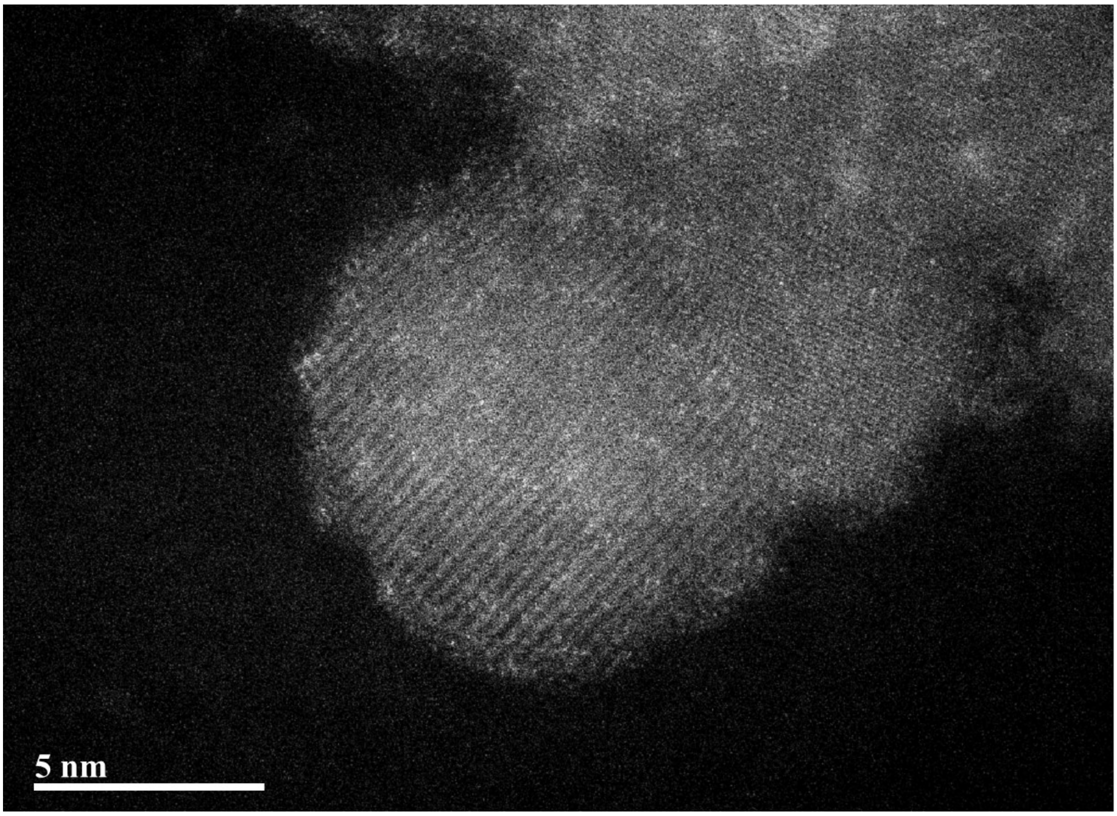


Fig. S3 TEM image of 0.399 wt% $Cu\text{-}TiO_2$.



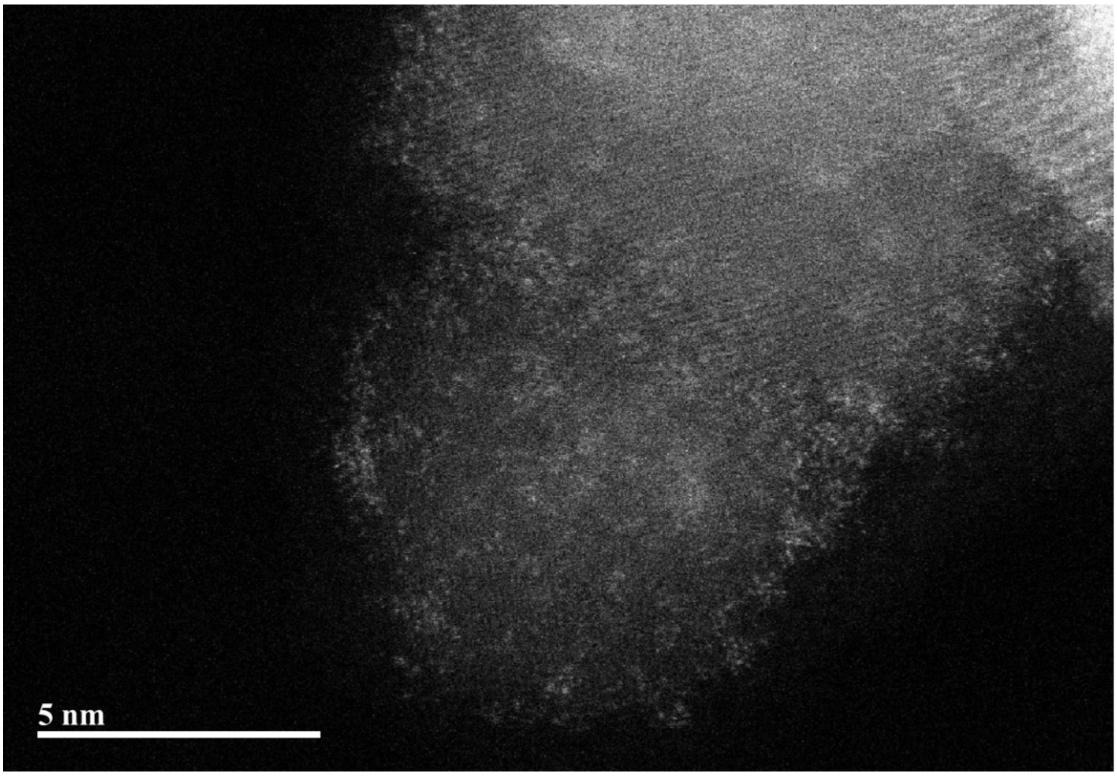


Fig. S4 HAADF-STEM image of Cu-TiO_2

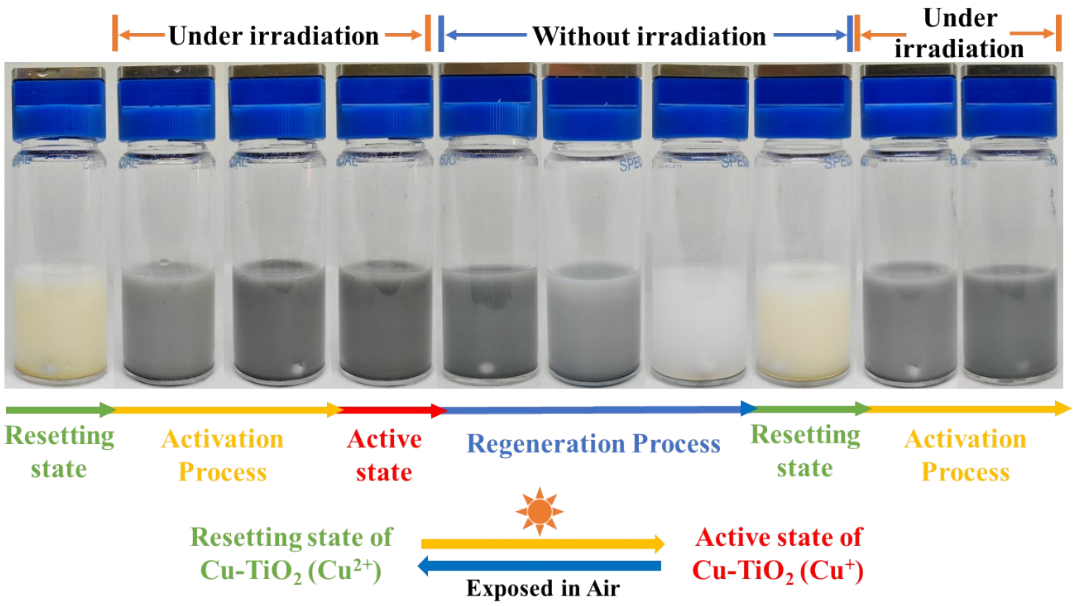


Fig. S5 Cooperative photoactivation process and regeneration process of Cu-TiO_2

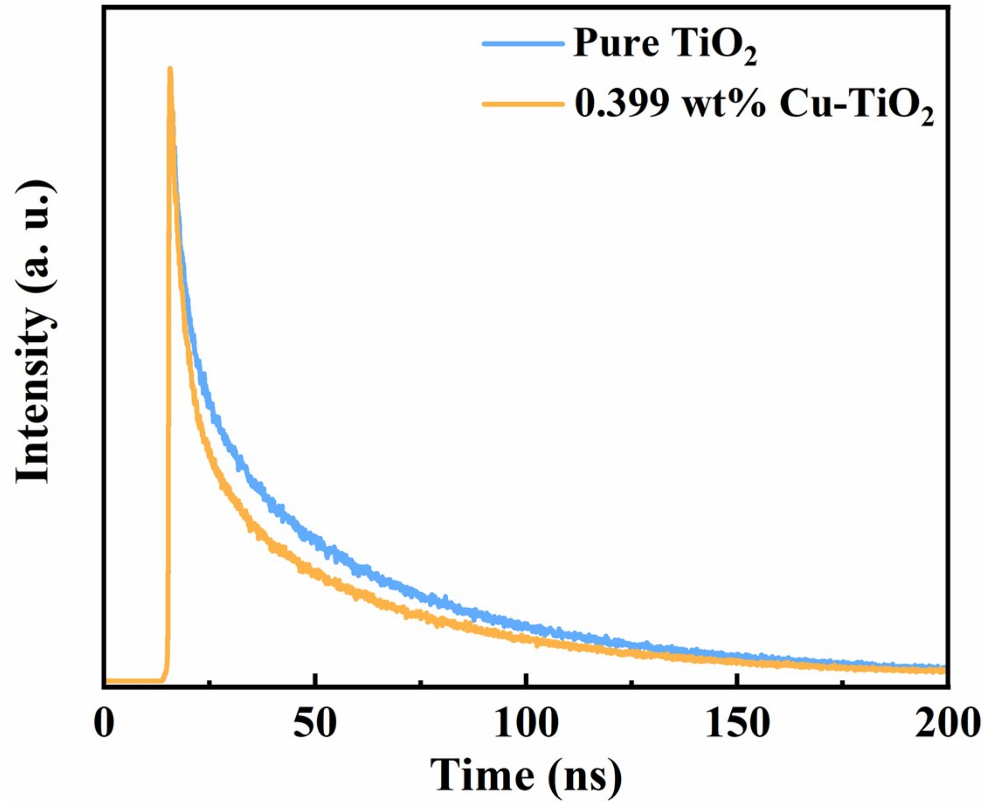


Fig. S6 Fluorescence decay curves of pure TiO_2 and 0.399 wt% Cu-TiO_2.

Table S1. Parameters from inductively couple plasma spectroscopy of Cu-TiO_2

Sample	**Theoretial Cu ratio (wt.%)**	**ICP tested Cu ratio (wt.%)**
pure TiO_2	0.000%	0.000%
Cu-TiO_2-1	0.242%	0.198%
Cu-TiO_2-2	0.362%	0.354%
Cu-TiO_2-3	0.483%	0.359%
Cu-TiO_2-4	0.604%	0.399%
Cu-TiO_2-5	0.725%	0.459%
Cu-TiO_2-6	0.846%	0.498%

Table S2. Table for the specific surface area and efficiency of hydrogen evolution of various materials

Materials	Specific surface area (BET)	The efficiency of hydrogen evolution	Ref.
Co SA-TiO_2	56 $m^2 \cdot g^{-1}$	1.682 $mmol \cdot g^{-1} \cdot h^{-1}$	[2]
Pt SA/Def-s-TiO_2	78.6 $m^2 \cdot g^{-1}$	13.46 $mmol \cdot g^{-1} \cdot h^{-1}$	[3]
SAAg-g-CN	53.2 $m^2 \cdot g^{-1}$	0.498 $mmol \cdot g^{-1} \cdot h^{-1}$	[4]
$Pt_{0.1}$-CN	95.3 $m^2 \cdot g^{-1}$	0.473 $mmol \cdot g^{-1} \cdot h^{-1}$	[5]
Ag@Ni/TiO_2	31.3 $m^2 \cdot g^{-1}$	2.9339 $mmol \cdot g^{-1} \cdot h^{-1}$	[6]
a-MoS_x/TiO_2	31.3 $m^2 \cdot g^{-1}$	1.106 $mmol \cdot g^{-1} \cdot h^{-1}$	[7]
MoS_x-rGO/ TiO_2	50.1 $m^2 \cdot g^{-1}$	0.2066 $mmol \cdot g^{-1} \cdot h^{-1}$	[8]
Co-NG/TiO_2	73.6 $m^2 \cdot g^{-1}$	0.67744 $mmol \cdot g^{-1} \cdot h^{-1}$	[9]
CuO_x/TiO_2	144.6 $m^2 \cdot g^{-1}$	0.1126 $mmol \cdot g^{-1} \cdot h^{-1}$	[10]
Cu-TiO_2	159.02 $m^2 \cdot g^{-1}$	21.053 $mmol \cdot g^{-1} \cdot h^{-1}$	this work

Table S3. The fitted PL decay results of pure TiO_2 and 0.399 wt% Cu-TiO_2

Sample	τ_1(ns)	τ_2(ns)	A_1	A_2	Decay Lifetime(ns)
TiO_2	4.745	47.255	4945.279	4530.26	25.070
Cu-TIO_2	4.259	46.145	5892.575	3550.06	20.007

Reference

[1] Wei X, Zhu G, Fang J and Chen J. Synthesis, characterization, and photocatalysis of well-dispersible phase-pure anatase TiO_2 nanoparticles[J]. International Journal of Photoenergy, 2013, 2013.

[2] Xin W, Shouwei Z, Mei Q, Yang L, Yongfan Z, Pengfei A, Jing Z, Huabin Z, Jian Z. Atomically defined Co on two-dimensional TiO_2 nanosheet for photocatalytic hydrogen evolution[J]. Chemical Engineering Journal, 2021, 420: 127681.

[2] Xiaoling H, Junying S, Jingli L, Hao Z, Zhiming S, Chunquan L, Shuilin Zheng, Qingxia L. Single-atomic Pt sites anchored on defective TiO_2 nanosheets as a superior photocatalyst for hydrogen evolution[J]. Journal of Energy Chemistry, 2021, 62: 1-10.

[4] Xiaojie L, Shiyong Z, Xiaoguang D, Huayang Z, Shi-ze Y, Panpan Z, Sanping J, Shaomin L, Hongqi S, ShaobinW. Coupling hydrothermal and photothermal single-atom catalysis toward excellent water splitting to hydrogen[J]. Applied Catalysis B: Environmental, 2021, 283: 119660.

[5] Yuanqing Z, Tian W, Tao X, Yingxuan L, Chuanyi W. Size effect of Pt co-catalyst on photocatalytic efficiency of g-C_3N_4 for hydrogen evolution[J]. Applied Surface Science, 2019, 464: 36-42.

[6] Gao D, Liu W, Xu Y, Ping W, Jiajie F, Huogen Y. Core-shell Ag@ Ni cocatalyst on the TiO_2 photocatalyst: one-step photoinduced deposition and its improved H_2-evolution activity[J]. Applied Catalysis B: Environmental, 2020, 260: 118190.

[7] Yu H, Yuan R, Gao D, Ying Xu, Jiaguo Yu. Ethyl acetate-induced formation of amorphous MoS_x nanoclusters for improved H_2-evolution activity of TiO_2 photocatalyst[J]. Chemical Engineering Journal, 2019, 375: 121934.

[8] Ying X, Yongan L, Ping W, Xuefei W, Huogen Y. Highly efficient dual cocatalyst-modified TiO_2 photocatalyst: RGO as electron-transfer mediator and MoS_x as H_2-evolution active site[J]. Applied Surface Science, 2018, 430: 176-183.

[9] Lanhua Y, Fujun L, Jing L, Caixian Z. Efficient noble-metal-free Co-NG/TiO_2 photocatalyst for H_2 evolution: Synergistic effect between single-atom Co and N-doped graphene for enhanced photocatalytic activity[J]. ACS Sustainable Chemistry & Engineering, 2018, 6(10): 12766-12775.

[10] Fan Y, Menglei L, Xin C, Zuwei X, Haibo Z. Simultaneous control over lattice doping and nanocluster modification of a hybrid CuO_x/TiO_2 photocatalyst during flame synthesis for enhancing hydrogen evolution[J]. Solar RRL, 2018, 2(12): 1800215.