Electronic Supplementary Information

Self-photoreduced Ag⁰-doped Ag(I)-organic frameworks with efficient visible-light-driven photocatalytic performance

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Experimental

Materials and characterization

All the chemical reagents were obtained commercially and used without further purification. The infrared (IR) spectrum was collected on a Nicolet iS50 FT-IR spectrometer (ThermoFisher, United States). Elemental analysis (C, H, N) was performed on a VarioEL III Elemental Analyzer (Elementar, Germany). The crystalline structures of the materials were analyzed by PXRD (Rigaku, Dmax 2000) with CuKα radiation (λ = 1.5406 Å) at room temperature in the range of 5°-80°. The morphology and size of samples were observed by SEM (Hitachi, Regulus 8100) a. The XPS characterizations were obtained on an ESCALAB250XI electron spectrometer (VG Scientific, America). The UV-vis diffuse reflectance spectra (DRS) were collected by a UV-vis spectrophotometer (UV-2550, Shimidazu). Photocurrents and EIS were recorded using a PGSTAT-302N electrochemical workstation. ESR analyses were performed on the Bruker EPR JES-FA200 spectrometer.

Preparation of [Ag$_3$(psa)(4,4'-bpy)$_3$]·OH·2CH$_3$OH·2H$_2$O (JLNU-91)

A mixture of AgNO$_3$ (0.5 mmol, 0.085 g), H$_2$psa (0.25 mmol, 0.05 g) and 4,4'-bpy (0.5 mmol,0.079 g) was added into a 20 mL deionized water/methanol solution (1:1). Then ammonia water was added dropwise into the mixture with stirring until the solution clear. The solution was placed in dark at room temperature. Light yellow crystals were obtained after slow evaporation in 65 ield (based on AgNO3). C$_{42}$H$_{44}$N$_6$O$_9$Ag$_3$ (Mr = 1083.43): C 44.16, H 3.88, N, 11.03. Found: C 44.12, H, 3.85, N 11.06. IR: (KBr pellet, cm-1): 3398(w), 3382(w), 3034(m), 1593(m), 1589(m), 1394(s), 1380(s), 1369(s), 998(w), 804(s), 790(s), 705(w), 615(s), 494(s).

Preparation of Ag^0-doped JLNU-91/x photocatalysts

The **JLNU-91** crystals (100 mg) were dispersed into 100 mL deionized water, and irradiated using mercury lamp for 0.5-2 h. After filtration and drying, a series of Ag^0-doped crystals were obtained. The obtained samples were denoted as **JLNU-91/x**, in which x represents for irradiation time under mercury lamp.

Photocatalytic experiments

The photocatalytic activity tests were carried out with a typical process: 20 mg of photocatalysts were dispersed into a 50 mL MO aqueous solution (10 mg/L) with the assisting of a 10 W LED

lamp (PCX-50C Discover, $\lambda > 400$ nm, Beijing PerfectLight). Before irradiation, the suspension was constantly stirred for 40 min in dark to establish an adsorption/desorption equilibrium. During the photocatalytic test, 2 mL of MO solution was taken and centrifuged at a 15 min interval. Then, the supernate was analysed by UV-vis spectrophotometer at characteristic 464 nm. The photocatalytic efficiencies were calculated by $(C_0-C)/C_0$, where C and C_0 stand for remaining and initial of concentration of MO solution.

Capture experiments were carried out by a similar procedure except that there were different radical scavengers (1mM) in the catalytic system. Isopropyl alcohol (IPA), ethylene diamine tetraacetic acid (EDTA) and L-ascorbic acid (L-AA) acted as the scavengers for hydroxyl radical species ($\cdot$OH), hole (h^+), and superoxide radical species ($\cdot O^{2-}$).

Photoelectrochemical measurements

Photoelectrochemical performances of the prepared photo-anodes were recorded on an electrochemical work station (CHI760E) with a standard three electrode system. 0.5 M Na_2SO_4 solution was used as the electrolyte. A 300W Xe lamp (Beijing PerfectLight) was used as a light source. Transient photocurrent measurements at a constant bias (0.8 V) with chopped illumination were also conducted to examine the steady-state photocurrent densities of the photoanodes. Electrochemical impedance spectra (EIS) were carried out in the frequency range of $1-10^5$ Hz. The Mott-Schottky measurement was performed at the frequency of 1000 Hz.

X-ray crystallorgraphy

Crystal data was collected Bruker Smart Apex II CCD diffractometer with graphitemonochromatic MoKα radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved by direct methods of SHELXS-2014 and refined on F2 by full-matrix least-squares using the SHELXL-2014 within WINGX [1,2]. All the calculations were performed under WINGX program. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of organic ligands and water molecules were generated geometrically. The crystallographic data for **JLNU-90** is listed in Table S1, selected bond lengths and bond angles are summarized in Table S2.
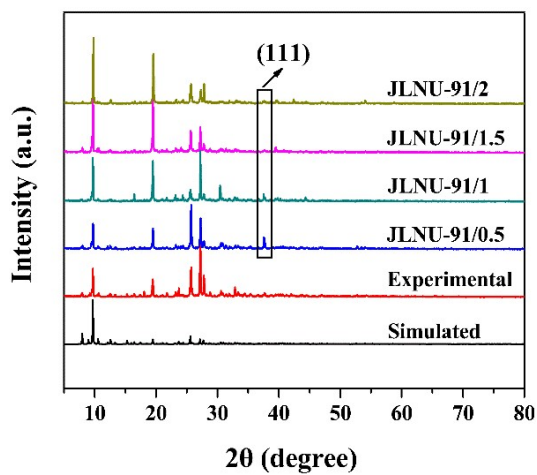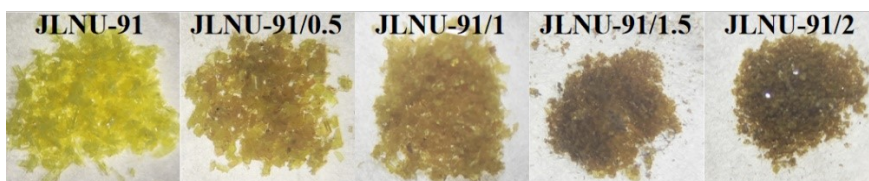
Fig. S1 The PXRD patterns of **JLNU-91** and **JLNU-91/*x***.

Fig. S2 The optical photographs of **JLNU-91** and **JLNU-91/*x***.
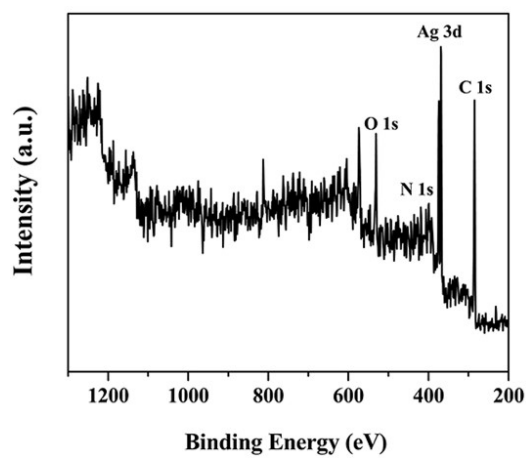

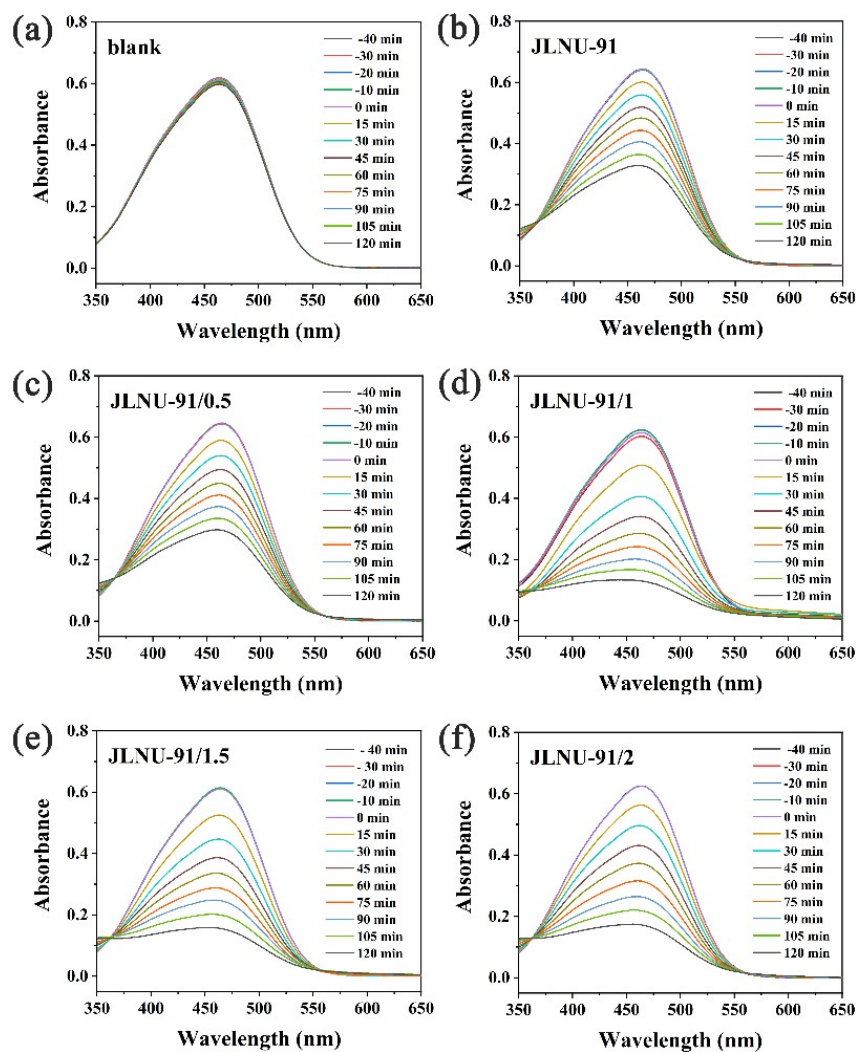**Fig. S3** The survey XPS of **JLNU-91/1**.

Fig. S4 The UV-vis absorption spectra of the MO solution during the photocatalysis without catalyst (a), and with **JLNU-91** (b), **JLNU-91/0.5** (c), **JLNU-91/1** (d), **JLNU-91/1.5** (e), **JLNU-91/2** (f).
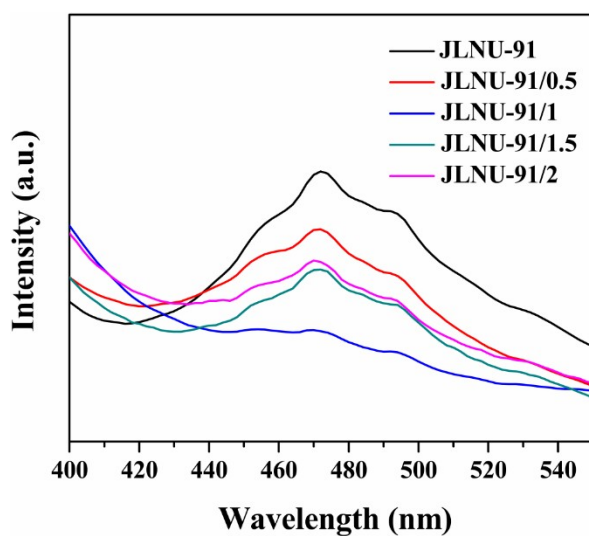

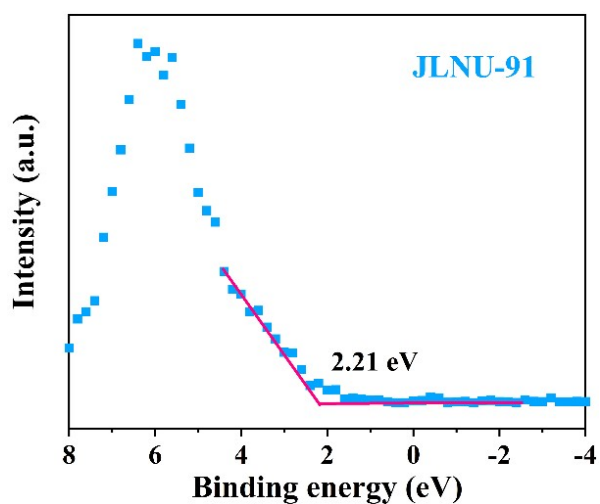**Fig. S5** The photoluminescence (PL) spectra of **JLNU-91** and **JLNU-91/*x*.**

Fig. S6 XPS valence band of **JLNU-91**.

Table S1 Crystal data and structure refinements for **JLNU-91**.

MOF	JLNU-91
Empirical formula	$C_{42}H_{44}N_6O_9Ag_3$
Formula weight	1083.43
Crystal system	Triclinic
Space group	$P\,1$
a (Å)	9.702(5)
b (Å)	10.763(5)
c (Å)	11.435(5)
α (°)	75.894(6)
β (°)	84.943(7)
γ (°)	69.928(8)
V (Å³)	1087.7(9)
Z	1
Goodness-of-fit on F^2	1.067
Reflns collected/unique	7266
θ Range (°)	3.672-54.432
R (I > 2σ(I))	R_1 =0.0421, wR$_2$ =0.1194
R (all data)	R_1 =0.0457, wR$_2$ =0.1225
CCDC	2103757

Table S2 Selected bond distances (Å) and angles (deg) for **JLNU-91**.

Ag(1)-N(1)	2.202(4)	Ag(2)-N(4)[#1]	2.192(4)
Ag(1)-N(2)[#1]	2.216(8)	Ag(2)-O(3)[#2]	2.649(9)
Ag(1)-O(4)[#2]	2.548(9)	Ag(2)-O(1)	2.528(8)
Ag(1)-O(2)	2.542(7)	Ag(3)-N(5)	2.174(3)
Ag(2)-N(3)	2.202(3)	Ag(3)-N(6)[#1]	2.179(3)
N(2)[#1]-Ag(1)-N(1)	161.2(10)	N(3)-Ag(2)-O(3)	90.88
N(2)[#1]-Ag(1)-O(4)[#2]	94.8(8)	N(4)[#1]-Ag(2)-O(3)	90.86
N(1)-Ag(1)-O(4)[#2]	95.7(3)	N(4)[#1]-Ag(2)-O(1)	90.8(8)
N(1)-Ag(1)-O(2)	88.6(2)	N(3)-Ag(2)-O(1)	89.9(2)
N(2)[#1]-Ag(1)-O(2)	89.5(7)	N(4)[#1]-Ag(2)-N(3)	169.6(10)
O(2)-Ag(1)-O(4)[#2]	151.8(3)	O(1)-Ag(2)-Ag(1)	93.28(19)
N(3)-Ag(2)-N(4)[#1]	169.6(10)	N(5)-Ag(3)-N(6)[#1]	170.9(8)

Symmetry codes: [#1]:x, y, 1+z; [#2] -1+x, y, z.

Table S3. Comparison of the MO degradation capacity of the **JLNU-91/1** with other MOFs.

Catalysts	Light source	MO concentration (mg/L)	Dosage of catalysts (mg)	Time (min)	Degradation efficiency (%)	Ref.
JLNU-91/1	10 W LED (vis)	10	20	120	78	This work
{[Zn(L1)]·2DMA·H$_2$O}$_n$	Hg lamp (UV)	6	20	120	54.6	3
{[Zn(L2)]·2DMA·H2O}$_n$	Hg lamp (UV)	6	20	120	48.2	3
{[Mn$_2$(BPDC)$_2$]·DMF}$_n$	Hg lamp (UV)	10	3	75	95.03	4
UIO-66(NA)	UV	20	10	90	10	5
UIO-66(AN)	UV	20	10	90	65	5
MIL-100(Fe)-RT	UV	5	250	420	64	6
HPU-4	Xe lamp (vis)	12.75	30	120	0	7
AgBr@HPU-4	Xe lamp (vis)	12.75	30	120	92%	7

[1]   G. M. Sheldrick *SHELXS-2014*, *Program for the Solution of Crystal Structures* (University of Göttingen, Germany, 2014).

[2]   G. M. Sheldrick *SHELXL-2014*, *Program for the Refinement of Crystal Structure* (University of Göttingen, Germany, 2014).

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