Ag nanoparticles in the cages of MIL-101(Cr) as an efficient and stable photocatalyst for nitrogen reduction reaction

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Equipment and Instruments:

X-ray diffraction (XRD) patterns recorded on an AXS D8 ADVANCE A25 with Cu Kα radiation (40 kV, 40 mA) of wavelength 0.154 nm (Germany). Fourier transform infrared spectroscopy (FTIR) patterns recorded on a TENSOR 27(Germany). Scanning electron microscopy (SEM) images were obtained from the ZEISS EVO18 at an accelerating voltage of 40 kV (Germany). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images and Energy Dispersive Spectrometer (EDS) were collected from a FEI Talos 200S field emission transmission electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) characterization was performed on a Thermo Scientific Escalab 250Xi. 10/12 system. The absorbance data of spectrophotometer was carried out on Persee TU-1901 UV-Vis spectrophotometer. The nitrogen physisorption Brunauer-Emmett-Teller (BET) experiments were collected on a Qutatachrome Autosorb-iQC system. Nitrogen chemisorption Temperature programmed desorption (TPD) was caddied out on Auto Chemll 2920(American). The reaction solution was measured by ion chromatography (IC, Thermo ICS-1100, USA) to determine the ammonia concentration. Metal element content in catalyst was measured by Inductive Coupled Plasma Emission Spectrometer (ICP) on Agilent ICPMS7800. Material performance screening by multichannel

photochemical reaction system (PCX50C Discover Perfect Light)

Photocatalytic tests

Photocatalytic tests were tested in a quartz reactor under UV-vis light irradiation by 300W Xenon lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd.). Typically, the catalyst needs to be vacuum dried at 120 ℃ for 6 h before use to remove small molecules in the pores. the catalyst powder (30 mg) was dispersed in 100 mL of ultrapure water by ultrasound for 10 min. Nitrogen source was offered through air or bubbling N_2. Before irradiation, the solution was stirred in darkness for 30 min with bubbling N_2 to reach equilibration of N_2 adsorption desorption on catalyst surface, and highly pure N_2 was continuously bubbled with a dispersion rate of approximately 80 mL/min through the experiment. The controlling experiments were performed in dark and Ar, respectively for 1 h. The tests in Air air atmosphere (Xe light and dark conditions) are open systems, with nitrogen in the air as the nitrogen source, and the tests in nitrogen and argon atmosphere are closed systems. The concentration of ammonia was measured by the Nessler's reagent method at the indicated time intervals.

NH_4^+ concentration measurement

The NH_4^+ concentration was analyzed by Nessler's reagent method. Firstly, 100 mL of the suspension was filtered through a 0.22 μm membrane filter and transferred to a 50 mL volumetric flask. Then, 1 mL of the potassium sodium tartrate solution was added to the volumetric flask,

after mixing evenly, 1 mL of Nessler's reagent was added to the same volumetric flask and mixed. Then the mixture was left to stand for 15 min for full color processing. Finally, the concentration of NH_3/NH_4^+ was detected using a UV-vis spectrophotometer (Persee TU-1901) at 420 nm wavelength.

The NH_4^+ concentration was analyzed also by ion chromatography method. A little suction-filtered solution was injected into Thermo ICS-1100, the peak area of NH_4^+ was detected, and the yield of NH_4^+ was calculated according to the standard curve.

Electrochemical measurement

The electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai CH Instruments, P. R. China) using a standard three-electrode configuration. A 300W Xe lamp (PLS-SXE300, Beijing Perfect Light Co., Ltd.) was used as light source. For preparing working electrode, catalyst powder was coated on a fluorine-doped tin oxide (FTO) substrate about 2 cm × 2 cm square. Firstly, 5 mg of photocatalyst was dispersed in the mixture of 0.5 mL ethanol solution and 10 μL Nafion solution (5 wt%), and the mixtures were ultrasonically scattered for 60 min. Subsequently, 100 μL of above suspension was coated on the FTO glass, after natural evaporation of ethanol and then dry at room temperature for 12 h under vacuum conditions. The catalyst coated FTO substrate was used as the working electrode, Pt plate was as counter

electrode, and Ag/AgCl was as the reference electrode. The electrolyte was 0.1 M Na_2SO_4 solution with bubbling N_2 or Ar.

Computational Details.

We carried out all the DFT calculations in the Vienna ab initio simulation (VASP5.4.4) code. The exchange-correlation is simulated with PBE functional and the ion-electron interactions were described by the PAW method. The vdWs interaction was included by using empirical DFT-D3 method. The Monkhorst-Pack-grid-mesh-based Brillouin zone k-points are set as 3×3×1 for all periodic structure with the cutoff energy of 450 eV. The convergence criteria are set as 0.01 eV A^{-1} and 105 eV in force and energy, respectively. A 20 Å vacuum layer along the z direction is employed to avoid interlayer interference.

The free energy calculation of specise adsorption (ΔG) is based on Nørskov et al's hydrogen electrode model.

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \quad (1)$$

Herein ΔE, ΔEZPE, and ΔS respectively represent the changes of electronic energy, zeropoint energy, and entropy that caused by adsorption of intermediate. The entropy of $H^{++}e^-$ pair is approximately regarded as half of H_2 entropy in standard condition. The hydrogenation activation barrier is calculated with climbing-image nudged elastic band (CI-NEB) method.

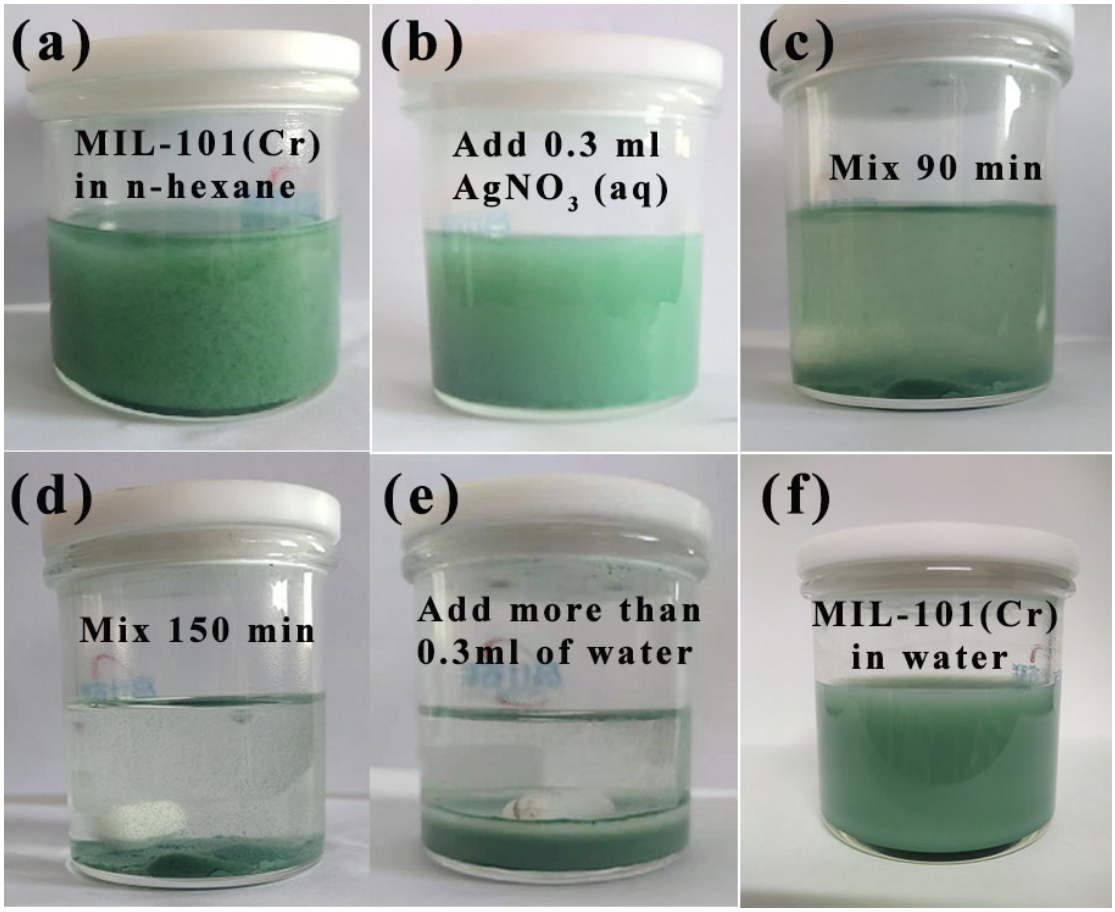

Figure S1. Several states during catalyst synthesis. (a) Adding MIL-101 (Cr) to n-hexane solution and performing ultrasound (b) Dropping silver nitrate aqueous solution under stirring (c) Stirring for 90min (d) Stirring for 150 min (e) Adding too much silver nitrate aqueous solution will cause the solution to stratify (f) Adding MIL-101 (Cr) to water and performing ultrasound.

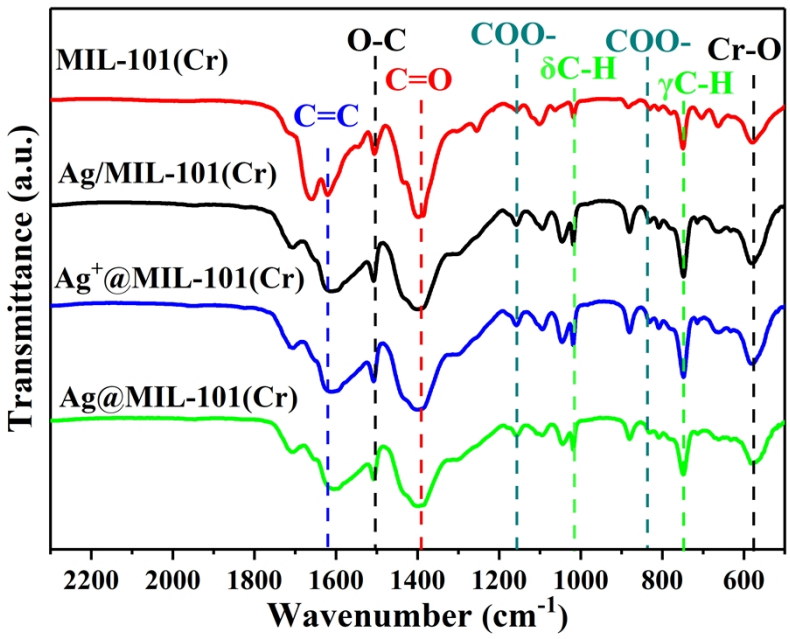

Figure S2. The Fourier Transform Infrared Spectroscopy of MIL-101(Cr), Ag/MIL-101(Cr), Ag^{+}@MIL-101(Cr) and Ag@MIL-101(Cr).

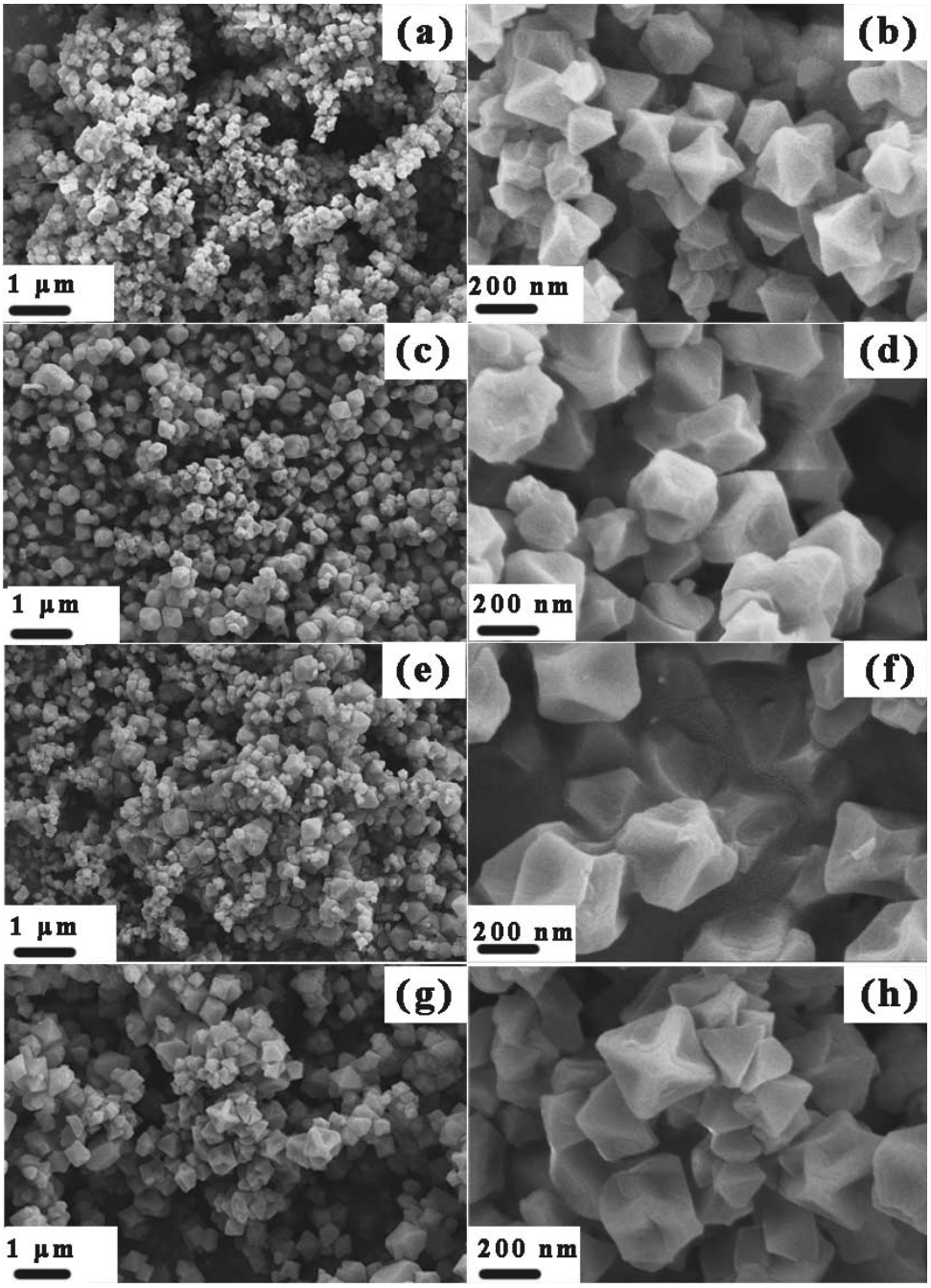

Figure S3. The scanning electron microscopy (SEM) of (a) (b) MIL-101(Cr), (c) (d) Ag/MIL-101(Cr), (e) (f) Ag^{+}@MIL-101(Cr) and (g) (h) Ag@MIL-101(Cr).

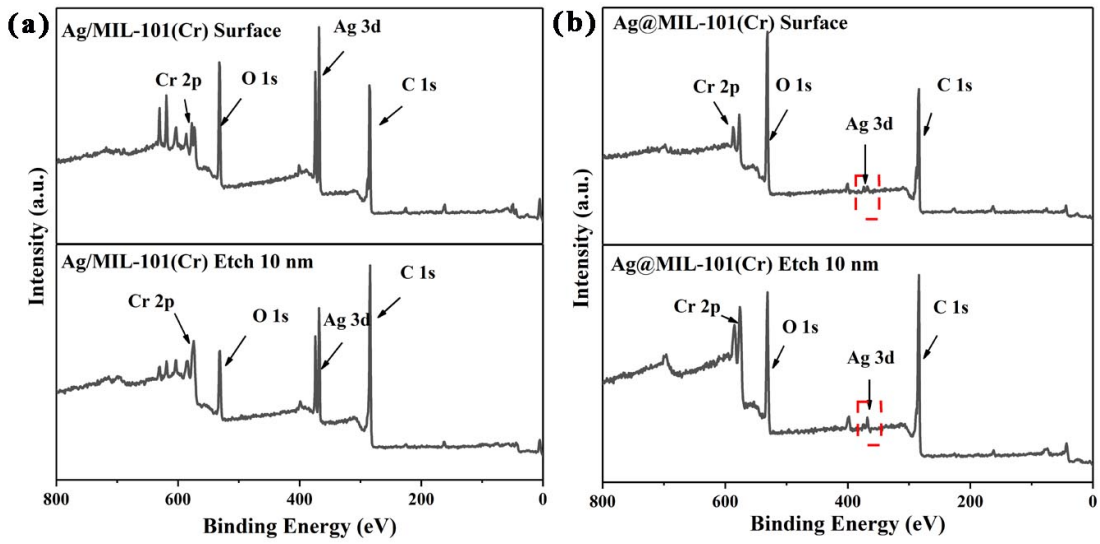

Figure S4. Total XPS spectra of Ag@MIL-101(Cr) and Ag/MIL-101(Cr).

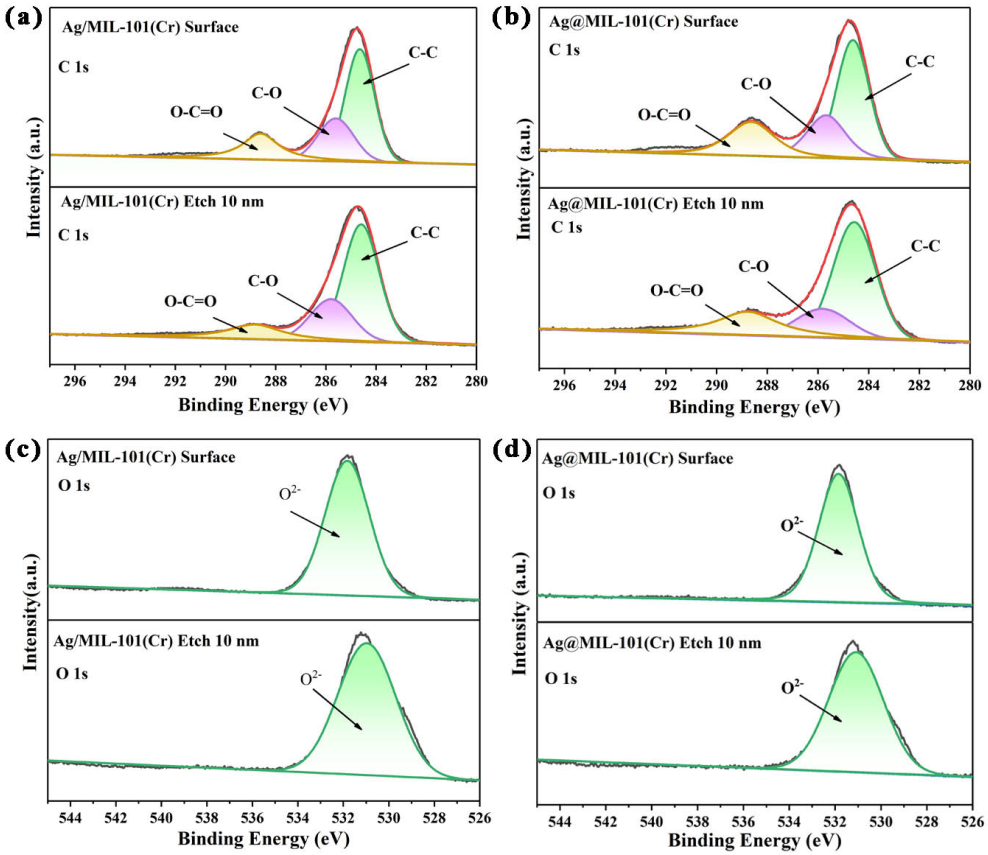

Figure S5. XPS spectra of Ag@MIL-101(Cr) and Ag/MIL-101(Cr) (a)Ag/MIL-101(Cr) C 1s (b) Ag@MIL-101(Cr) C1s (c) Ag/MIL-101(Cr) O 1s (d) Ag@MIL-101(Cr) O 1s

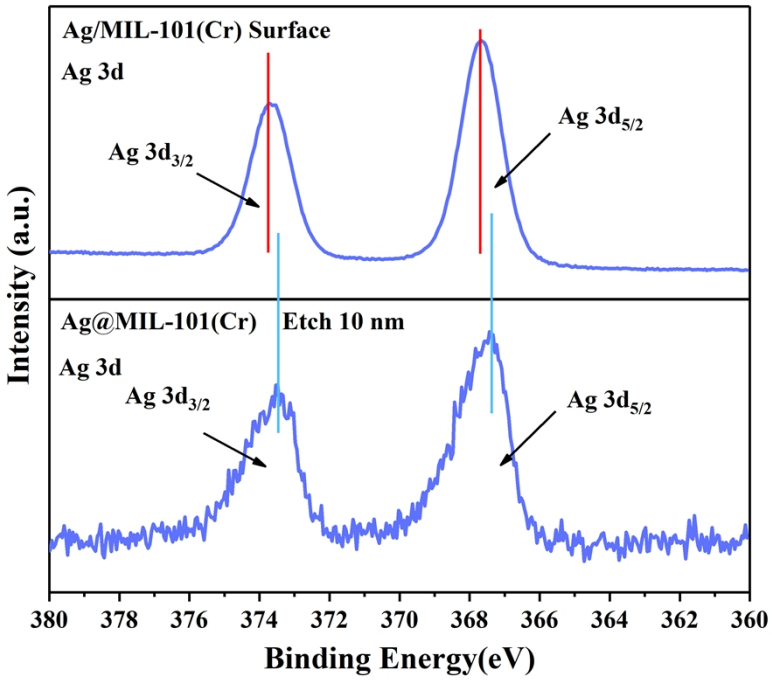

Figure S6. Ag XPS spectra of Ag NPs and Ag@MIL-101(Cr)

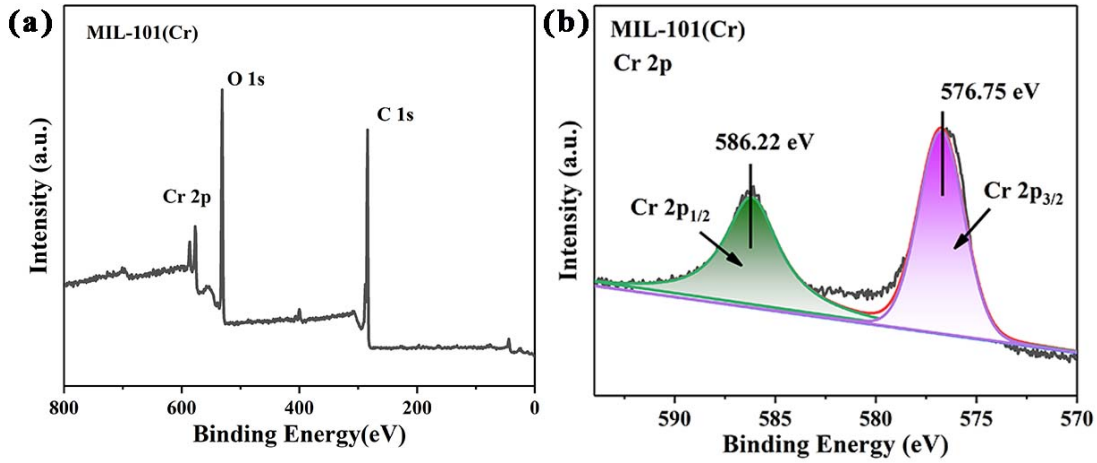

Figure S7. XPS spectra of MIL-101(Cr) (a) Survey (b) Cr 2p

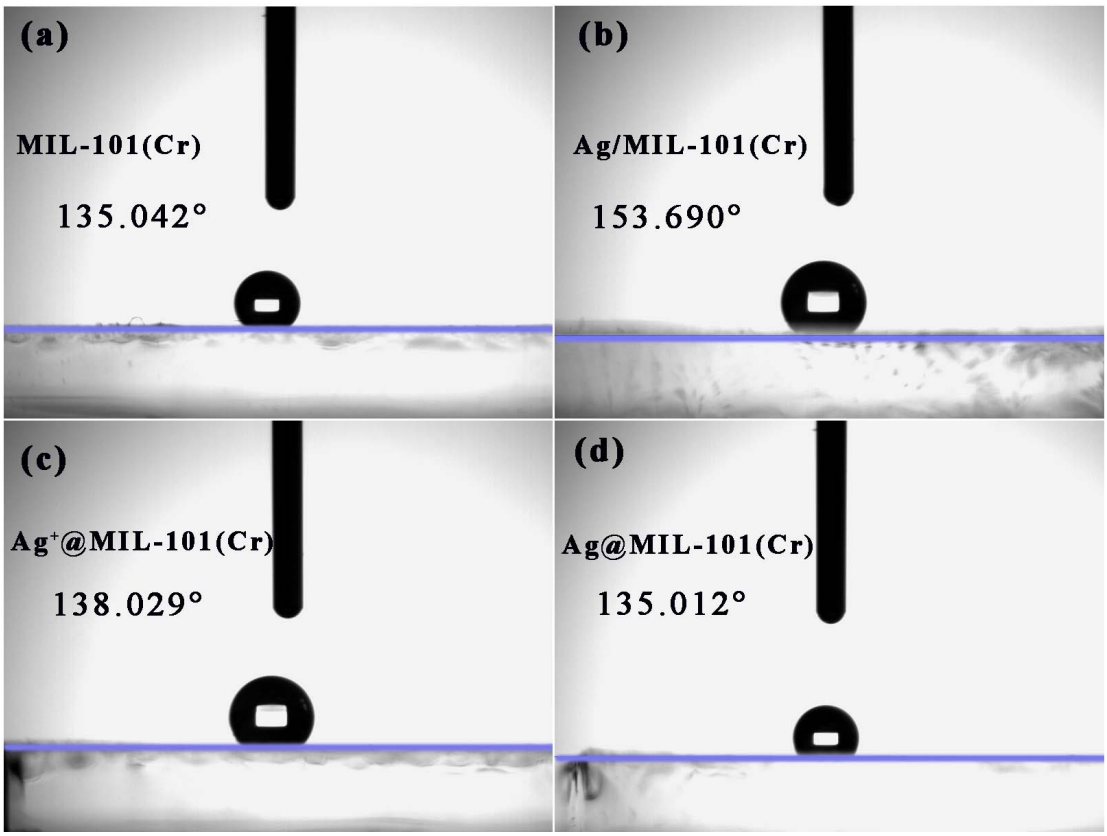

Figure S8. Contact angle testing of four catalysts (a) MIL-101(Cr) (b) Ag/MIL-101(Cr) (c) Ag^{+}@MIL-101(Cr) (d) Ag@MIL-101(Cr)

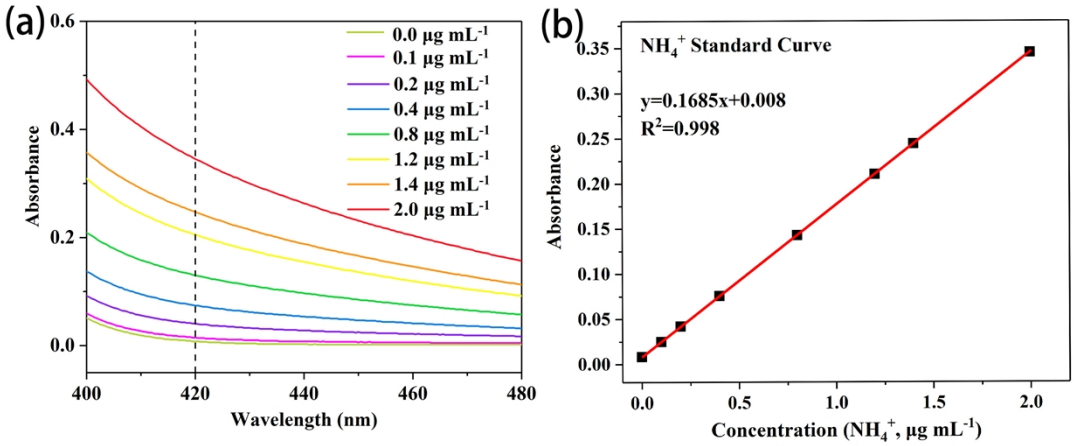

Figure S9. (a) UV-vis absorption curves of different concentrations of NH_4^+ ions were measured by Nessler's reagent method (b) Calibration curve used to calculate NH_4^+ concentration

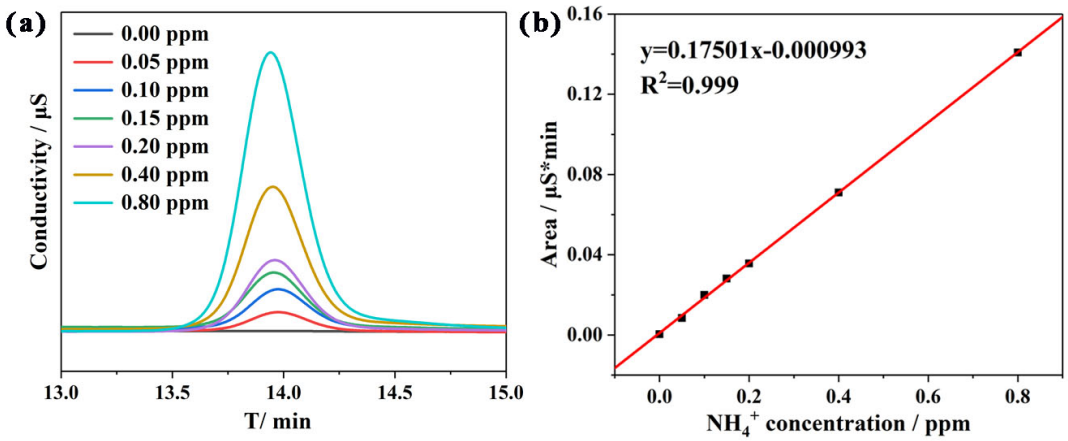

Figure S10. (a) Curves for measuring different concentrations of ammonia by ion chromatography (b) Calibration curve used to calculate NH_4^+ concentration

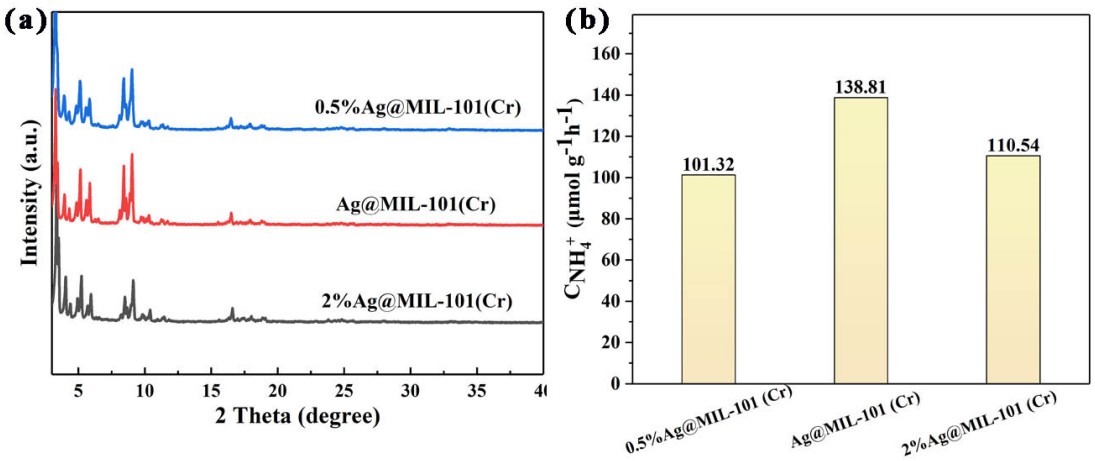

Figure S11. (a) The XRD of 0.5%Ag@MIL-101(Cr), Ag@MIL-101(Cr) and 2%Ag@MIL-101(Cr) (b) Catalytic performance of different catalysts in Air

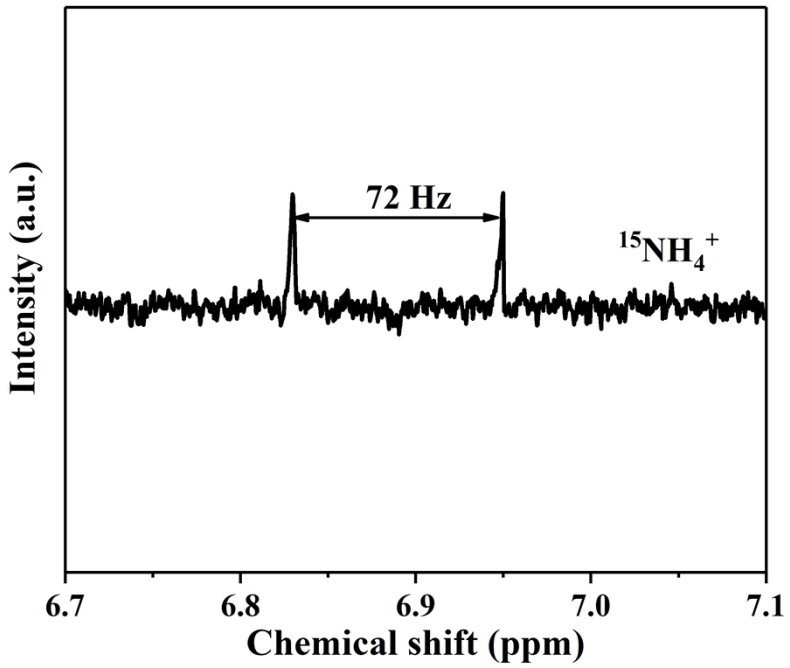

Figure S12. NMR measurements and isotope-labelled experiments**.** 1H NMR (600 MHz) spectra of the extracted supernatant for PNRR reaction with $^{15}NH_4^+$.

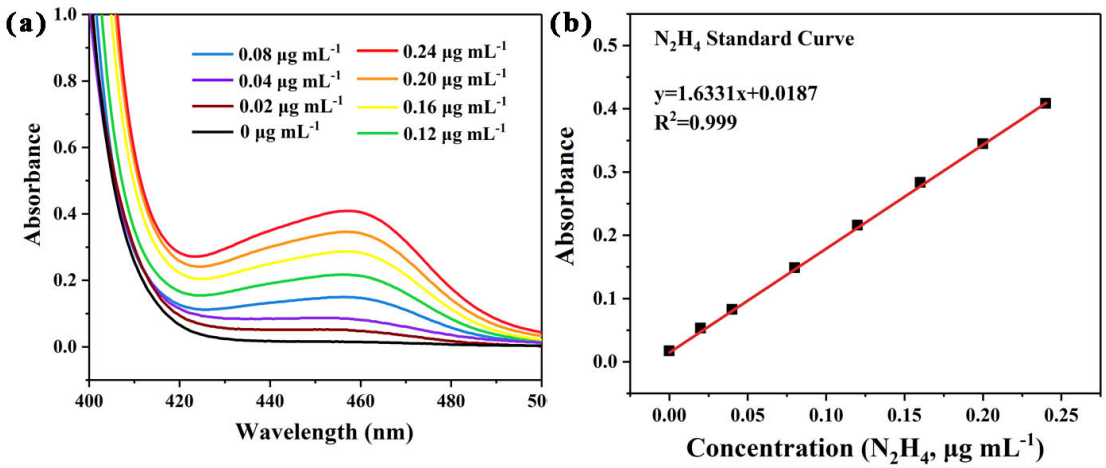

Figure S13. (a) UV-vis absorption curves of N_2H_4 at different concentrations as shown by p-$C_9H_{11}NO$ colorants (b) Calibration curve used to calculate N_2H_4 concentration

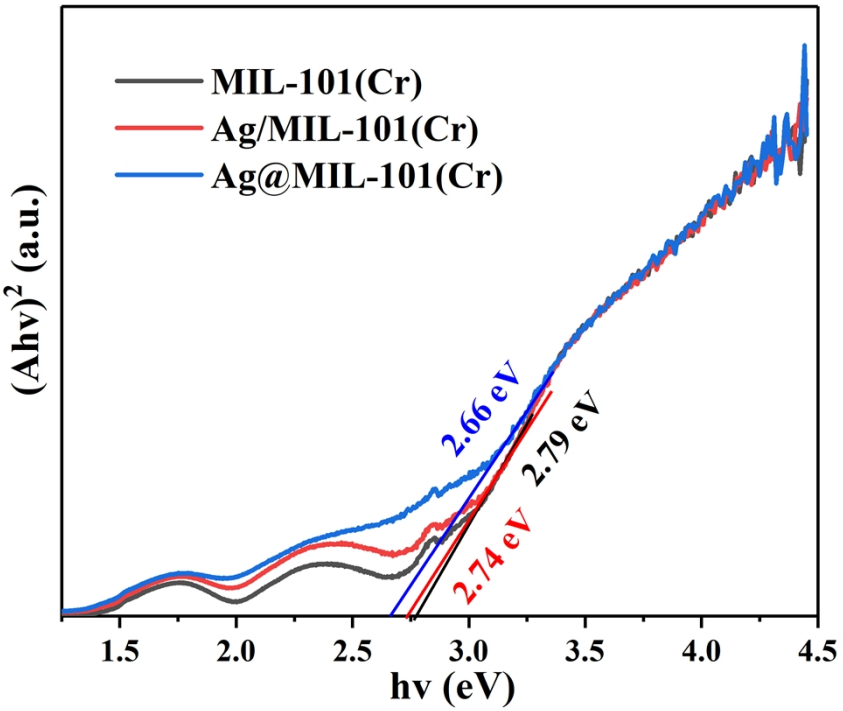

Figure S14. Forbidden bandwidth of the MIL-101(Cr), Ag/MIL-101(Cr) and Ag@MIL-101(Cr).

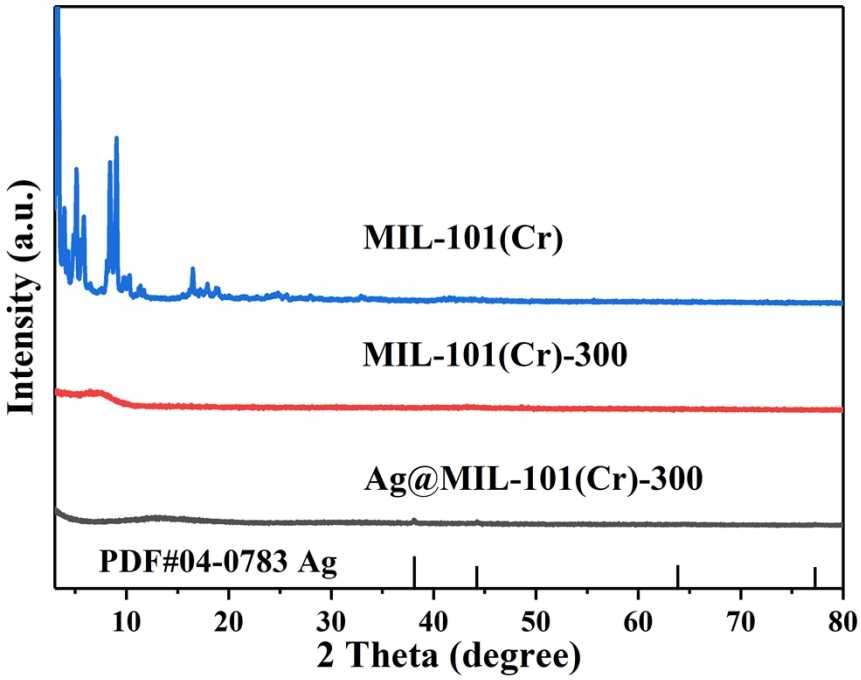

Figure S15. XRD of the MIL-101(Cr), MIL-101(Cr)-300 and Ag@MIL-101(Cr)-300.

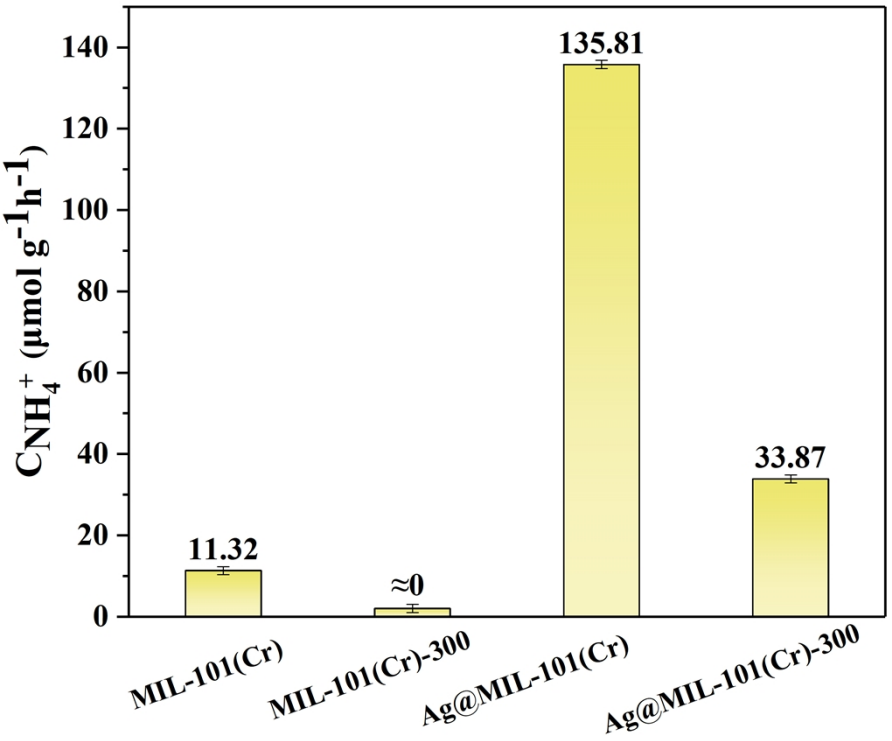

Figure S16. Photocatalytic nitrogen fixation performance testing of several catalysts.

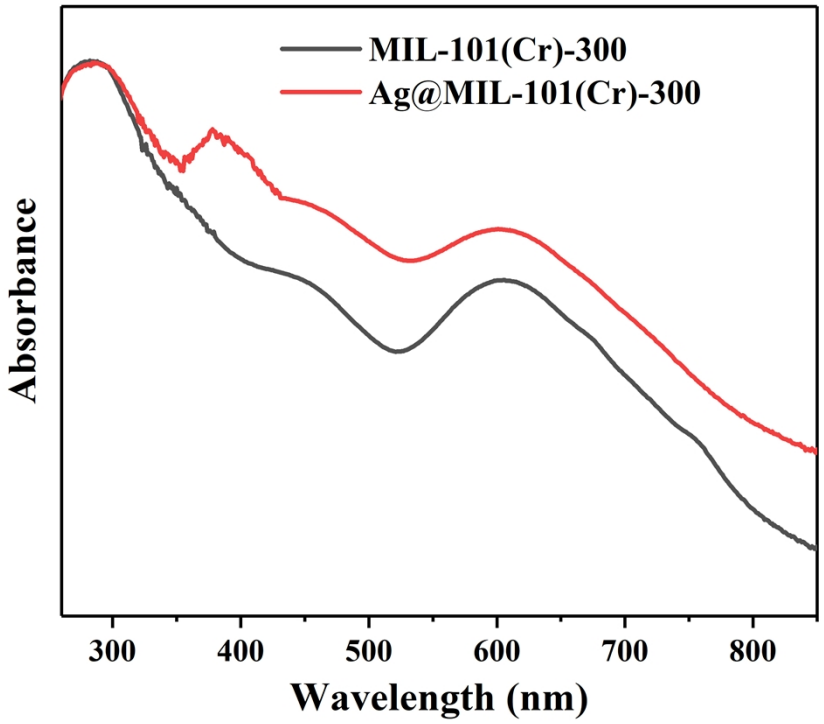

Figure S17. The DRS of Ag@MIL-101(Cr)-300 and MIL-101(Cr)-300.

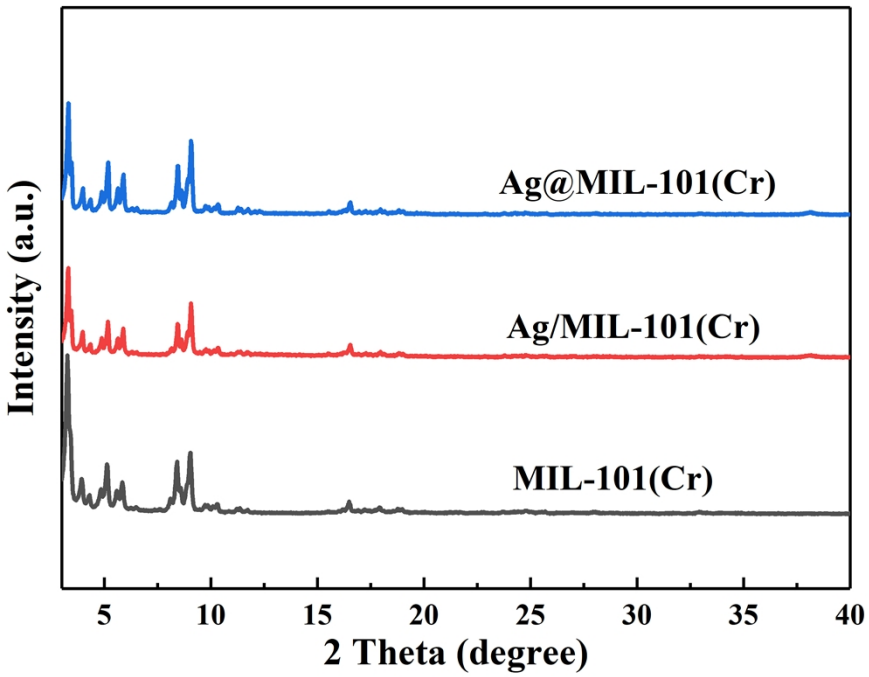

Figure S18. XRD patterns of Ag@MIL-101(Cr) and Ag/MIL-101(Cr) after photocatalysis

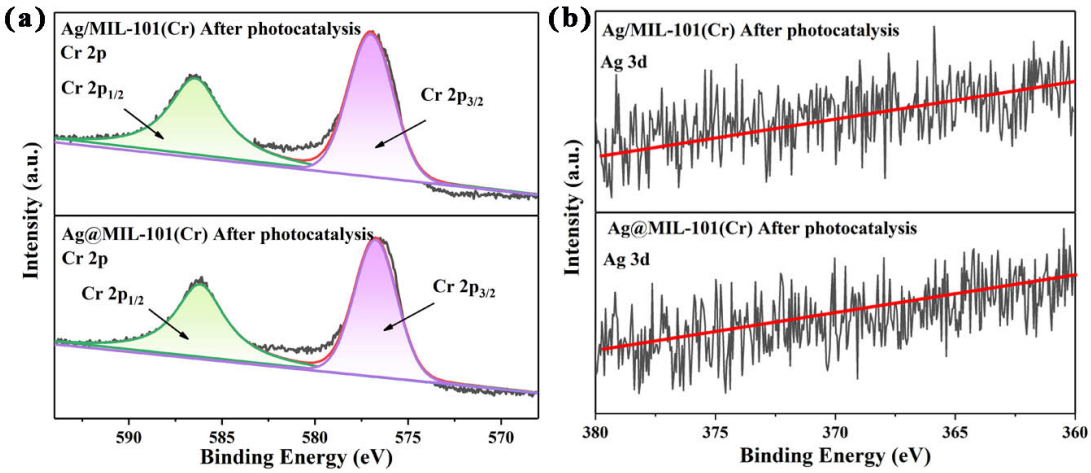

Figure S19. XPS patterns of Ag@MIL-101(Cr) and Ag/MIL-101(Cr) after photocatalysis (a) Cr (b) Ag

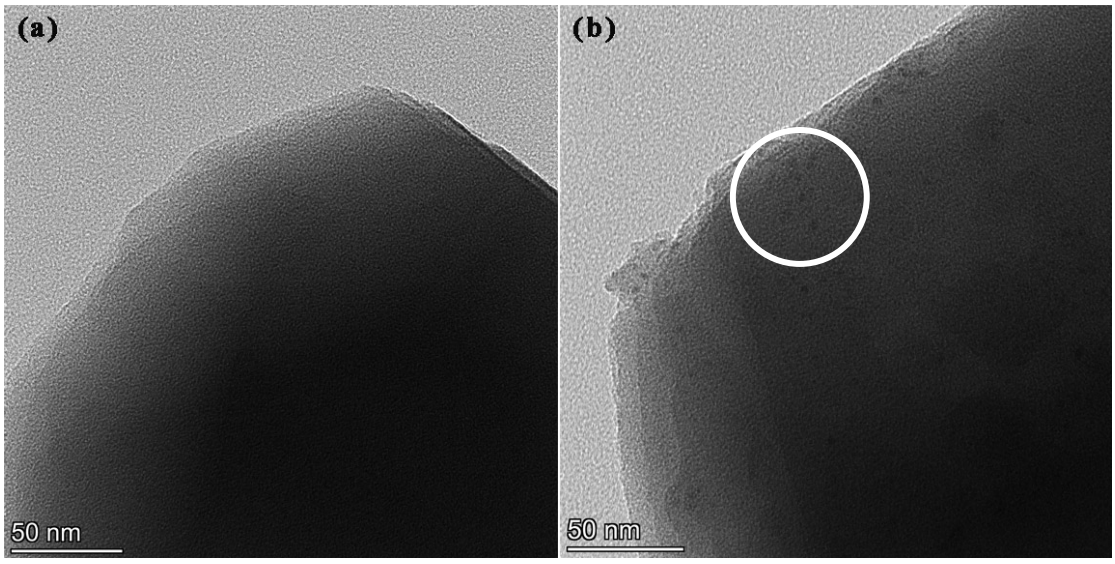

Figure S20. TEM of (a) Ag/MIL-101(Cr) and (b) Ag@MIL-101(Cr) after photocatalysis.

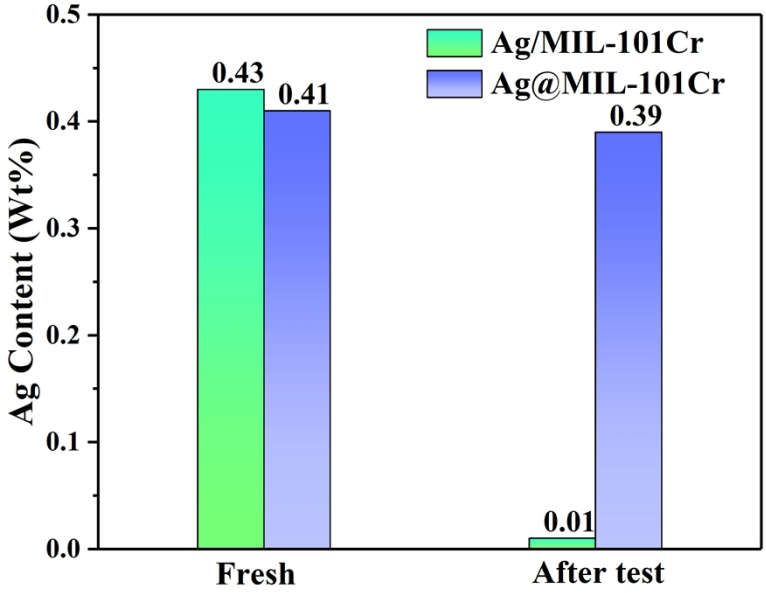

Figure S21. The ICP of Ag/MIL-101(Cr) and Ag@MIL-101(Cr) after photocatalysis

Table S1. Elemental content of XPS analysis

Name	Area	element	Atomic %	Title
Ag/MIL-101 (Cr)	Surface	C	66.01	C 1s
		Cr	4.32	Cr 2p
		O	25.23	O 1s
		Ag	4.44	Ag 3d
Ag/MIL-101 (Cr)	Etch 10 nm	C	77.09	C 1s
		Cr	5.6	Cr 2p
		O	14.63	O 1s
		Ag	2.67	Ag 3d
Ag@MIL-101 (Cr)	Surface	C	64.44	C 1s
		Cr	4.47	Cr 2p
		O	30.89	O 1s
		Ag	0.2	Ag 3d
Ag@MIL-101 (Cr)	Etch 10 nm	C	67.85	C 1s
		Cr	8.37	Cr 2p
		O	23.52	O 1s
		Ag	0.26	Ag 3d

Calculation method of apparent quantum yield (AQY) at different wavelengths

$$\mathrm{AQY}\ (\%) = \frac{3 \times \mathrm{Number\ of\ evolved\ N}H_3\ \mathrm{molecules}}{\mathrm{Number\ of\ indicent\ photons}} \times 100\% = \frac{3 \times C \times N_A}{S \times P \times t \times \frac{\lambda}{h \times c}} \times 100\%$$

Where, C is the rate of NH_3 evolution, N_A is the Avogadro constant (6.02×10^{23} mol^{-1}), S is the irradiation area (S=33.17 cm^2), P is the light intensity and detected by optical power meter (W/cm^2, Perfect Co., Ltd.), t is the irradiation time (3600 s), λ is the wavelength of the monochromatic light (nm), h is the Plank constant (6.626×10^{-34} J·s), c is the speed of light (3.0×10^{8} $m\cdot s^{-1}$).

Table S2 The AQY of Ag@MIL-101(Cr) at different wavelengths

Wavelength (nm)	**Light Intensity (mW/cm^2)**	**Rate of NH_3 evolution (μmol//h)**	**AQY (%)**
350	15.79	0.9144	0.04989
500	166.2	1.3715	0.005
650	173.9	1.5239	0.0042