Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Bimetallic $CeZr_5$-UiO-66 as highly efficient photocatalytic 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 an 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_3/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.

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 × 2.5 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.

The pre-processing method of TPD

First, the catalyst was vacuum dried at 120 °C for 6 hours, next, the

catalyst was pretreated with He gas flow at 150 °C for 2 hours and then cooled to 50 °C. The adsorption of nitrogen is performed in a 99.999% N_2 gas flow at 50 °C for 2h. It was heated from 50 °C to 490 °C at a heating rate of 10 °C/min, and the TPD signal was recorded with a thermal conductivity detector. All gas flow rates are set to 25 ml/min.

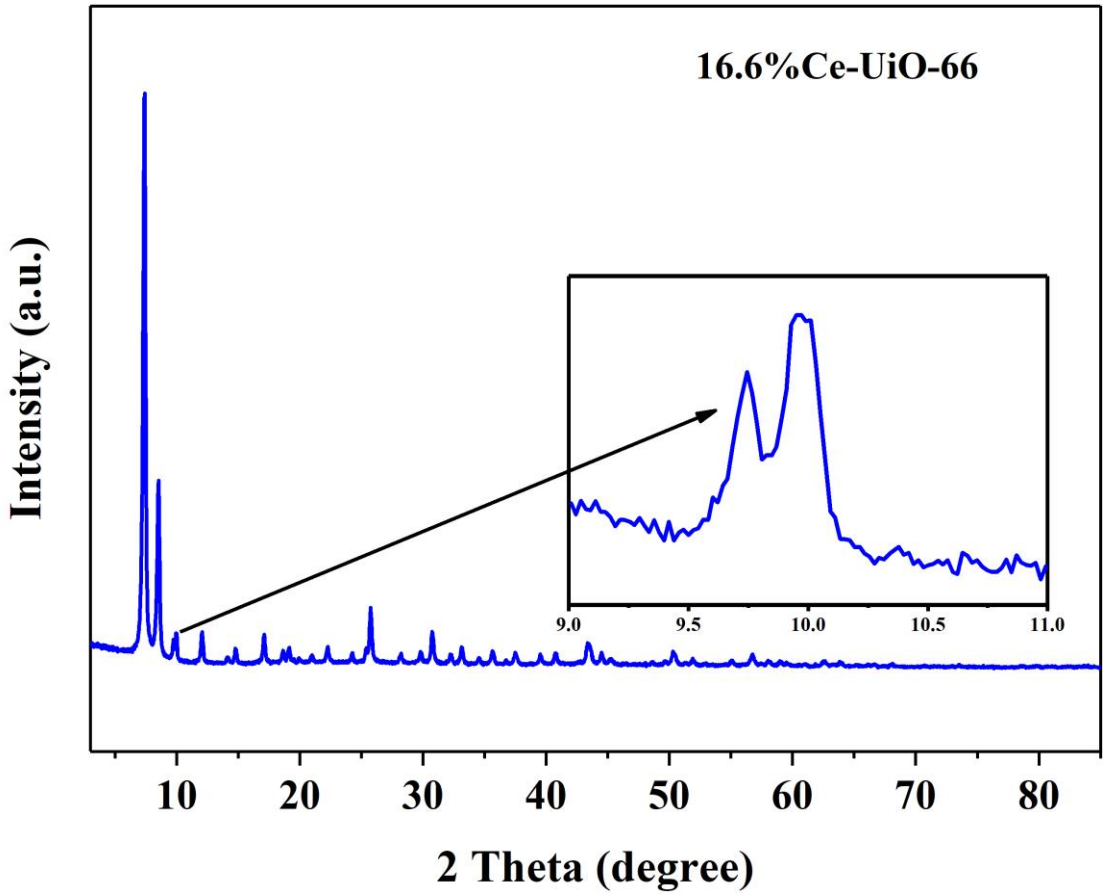

Figure S1. The XRD of 16.6%Ce-UiO-66

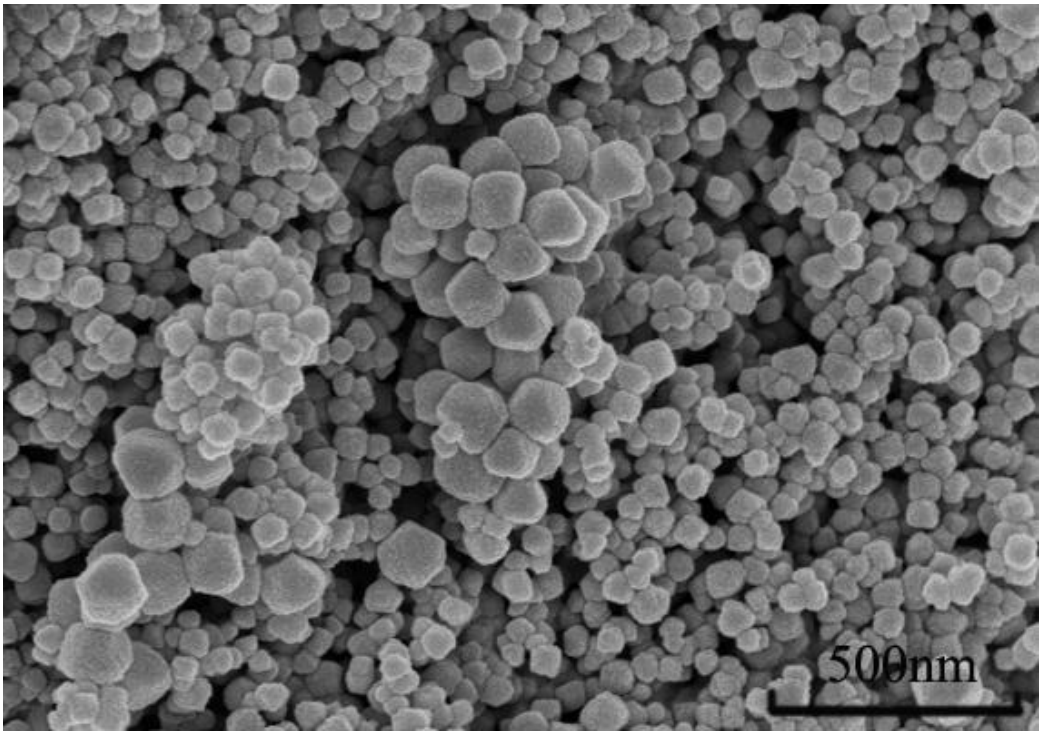

Figure S2. The SEM of 7%Ce-UiO-66

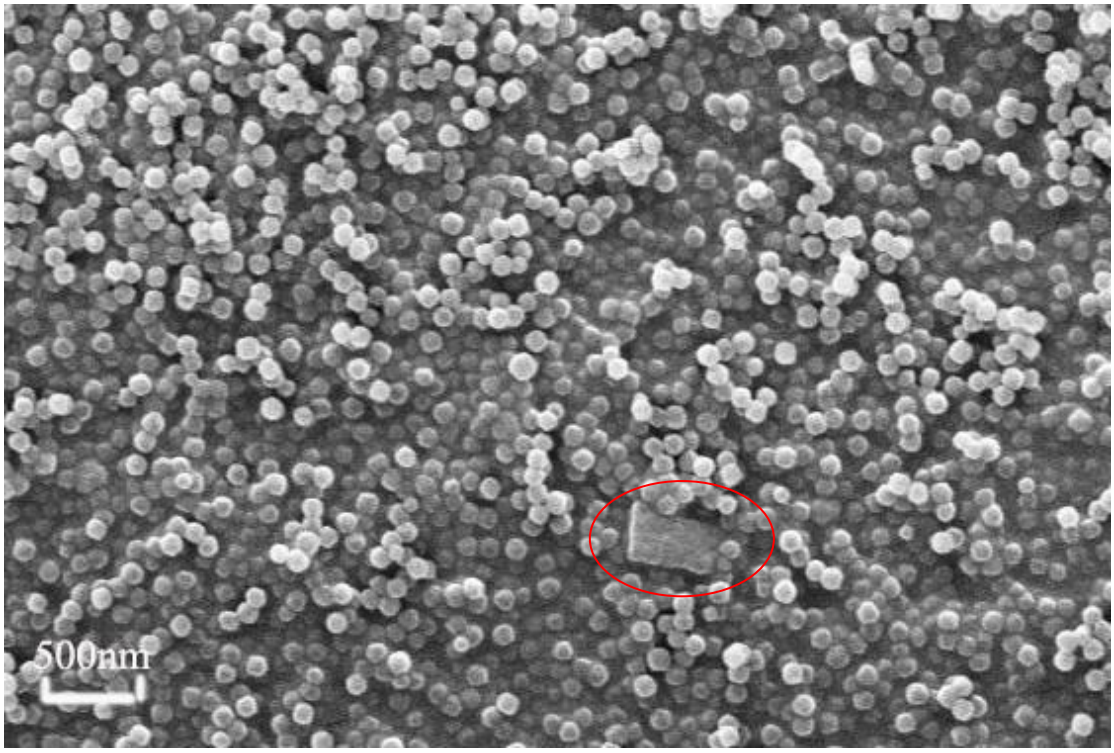

Figure S3. The SEM of 16.6%Ce-UiO-66

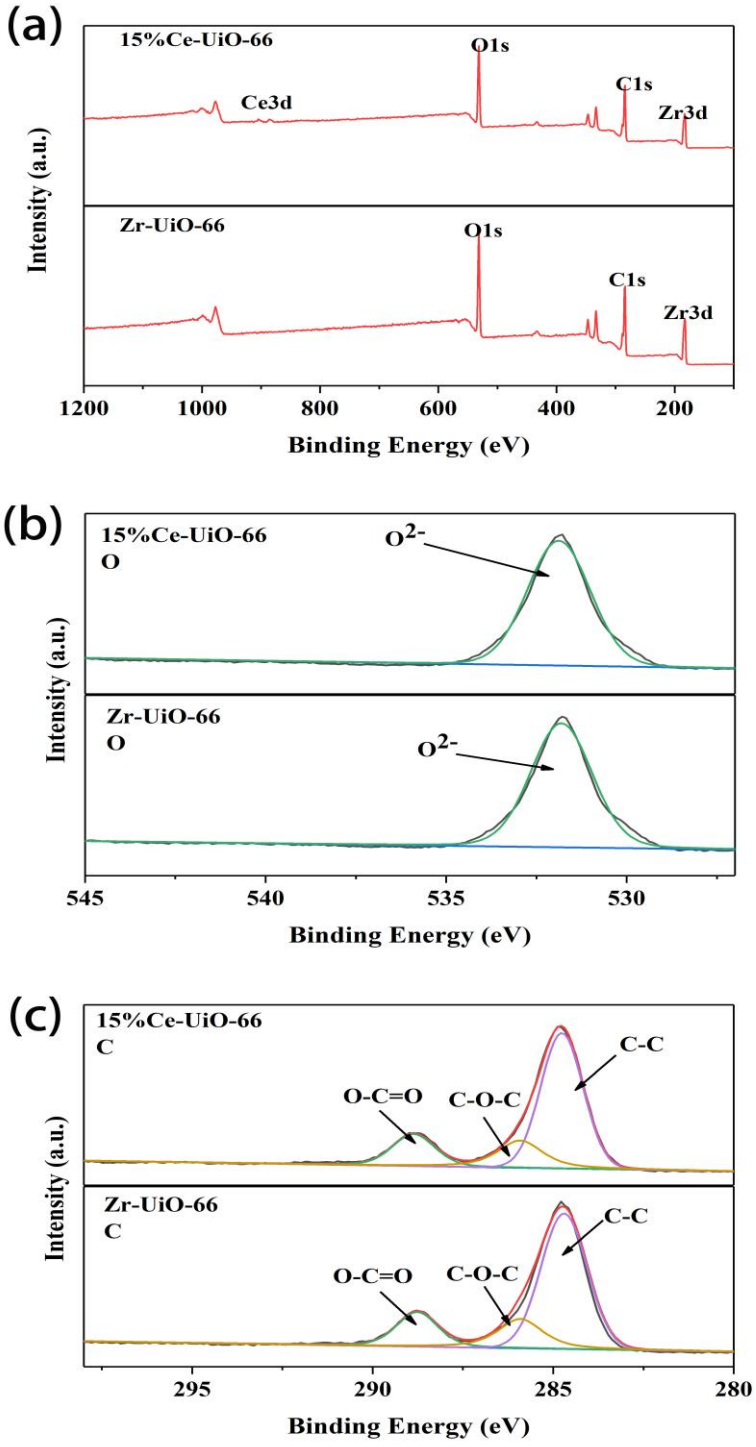

Figure S4. The XPS of 15%Ce-UiO-66 and Zr-UiO-66 (a) O (b) C (c)

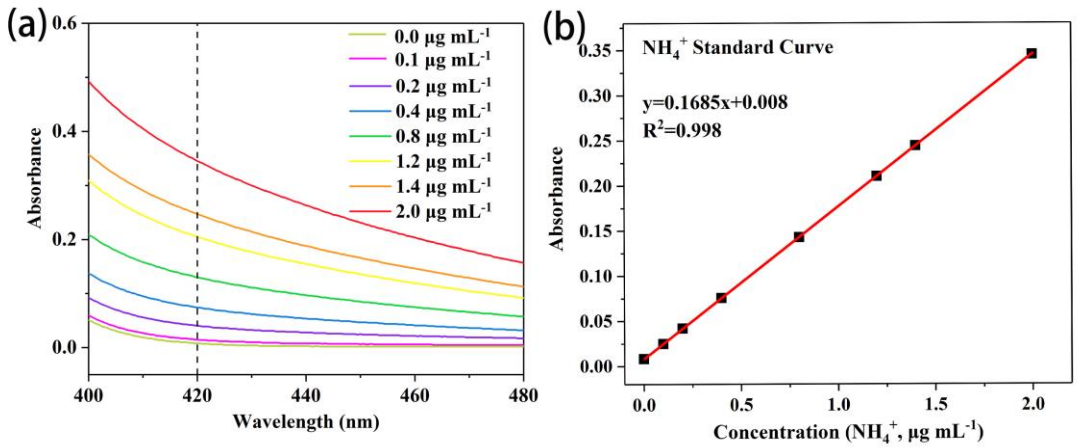

Figure S5. UV-Vis absorption curves of different concentrations of NH_4^+ ions were measured by Nessler's reagent method (a) Calibration curve used to calculate NH_4^+ concentration (b)

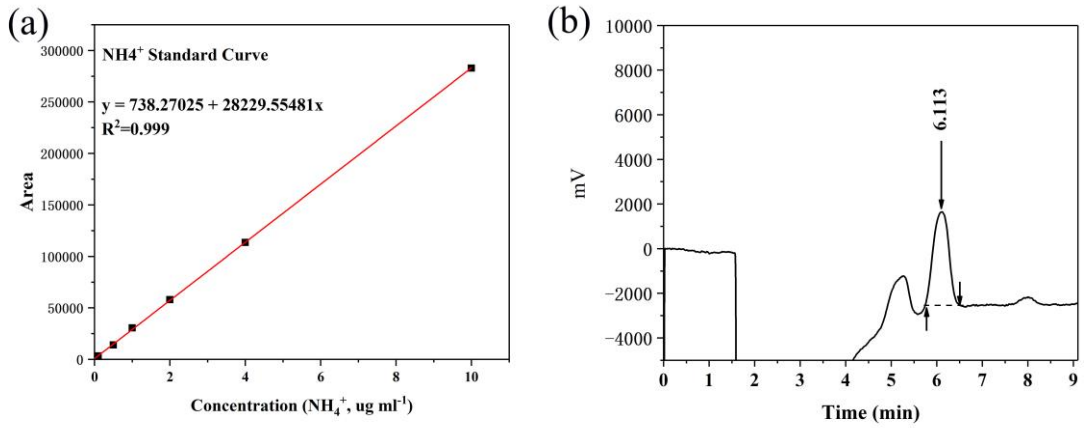

Figure S6. Standard curve of measurement of ammonia by ion chromatography (a), concentration of NH_4^+ after catalysis for 4 hours by 15%Ce-UiO-66 (b)

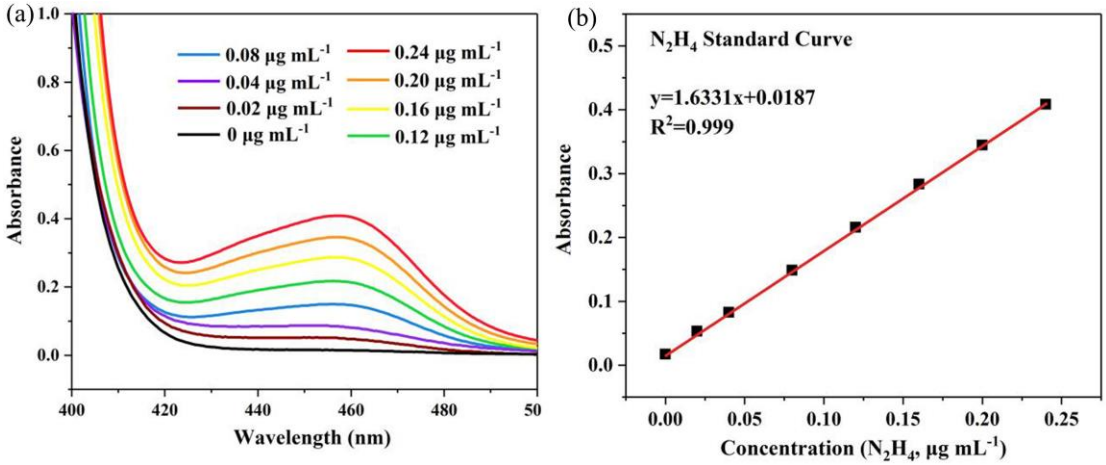

Figure S7. UV-vis absorption curves of N_2H_4 at different concentrations as shown by p-$C_9H_{11}NO$ colorants(a) Calibration curve used to calculate N_2H_4 concentration (b)

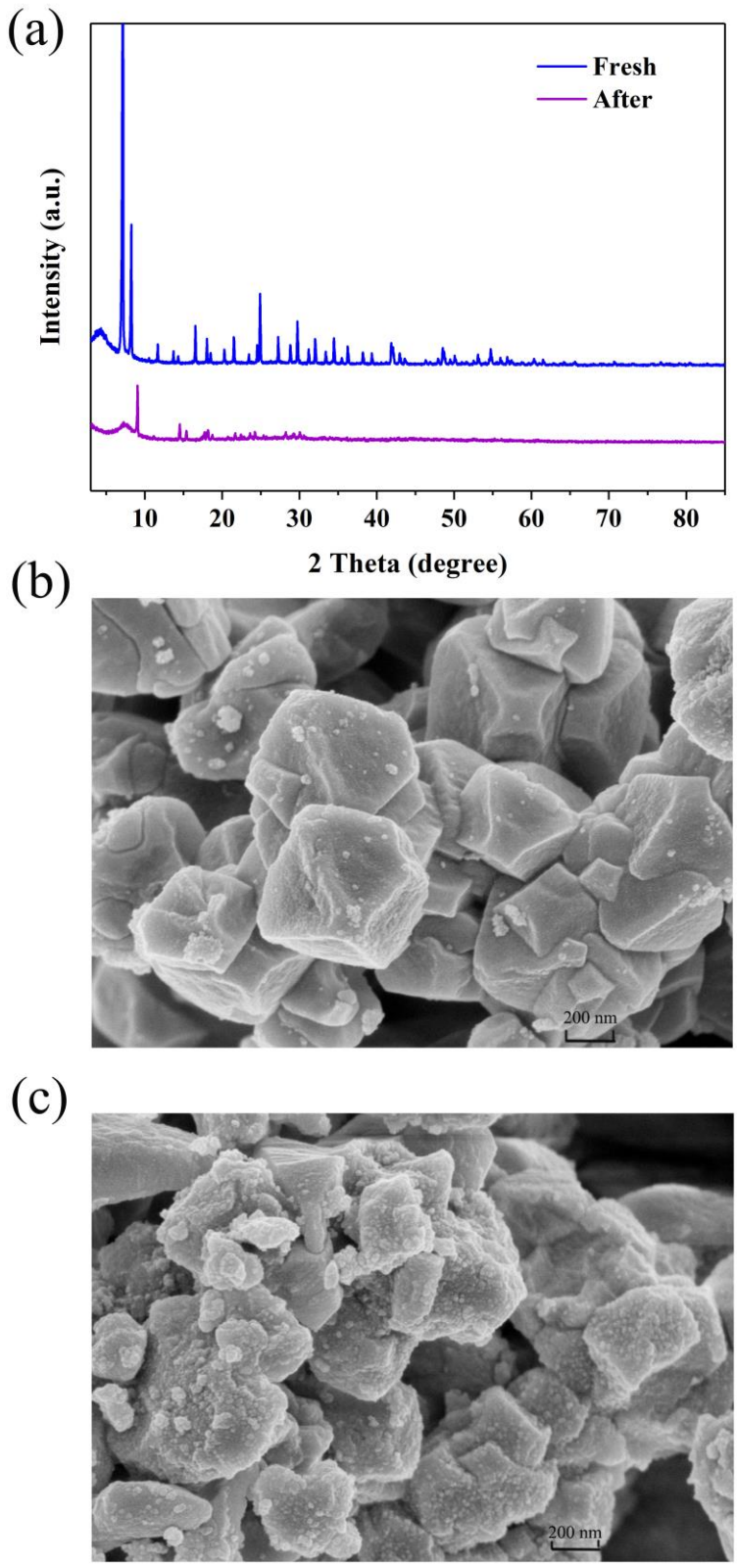

Figure S8. The XRD of Ce-UiO-66 (a) The SEM about Ce-UiO-66 before the photocatalytic reaction (b) after the reaction (c)

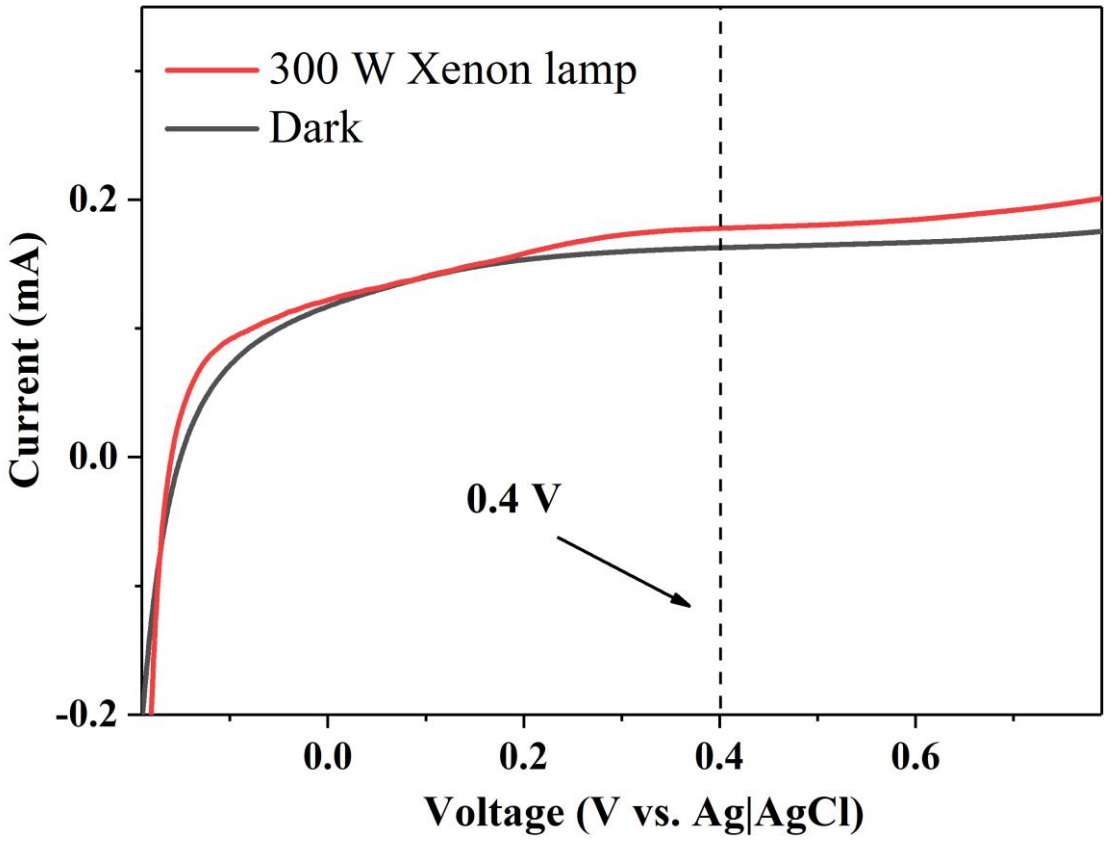

Figure S9. Linear sweep voltammetry (LSV) spectra of 15%Ce-UiO-66

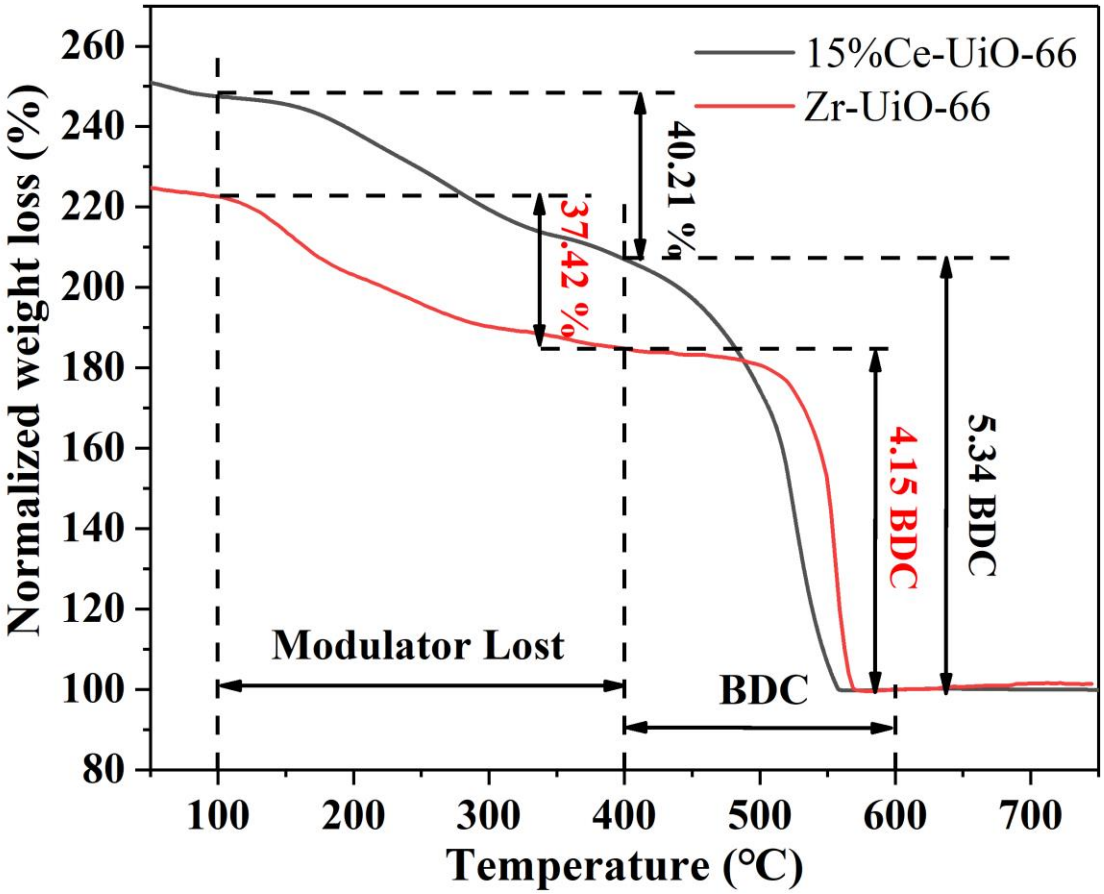

Figure S10. Thermogravimetric analysis of Zr-UiO-66 and 15%Ce-UiO-66

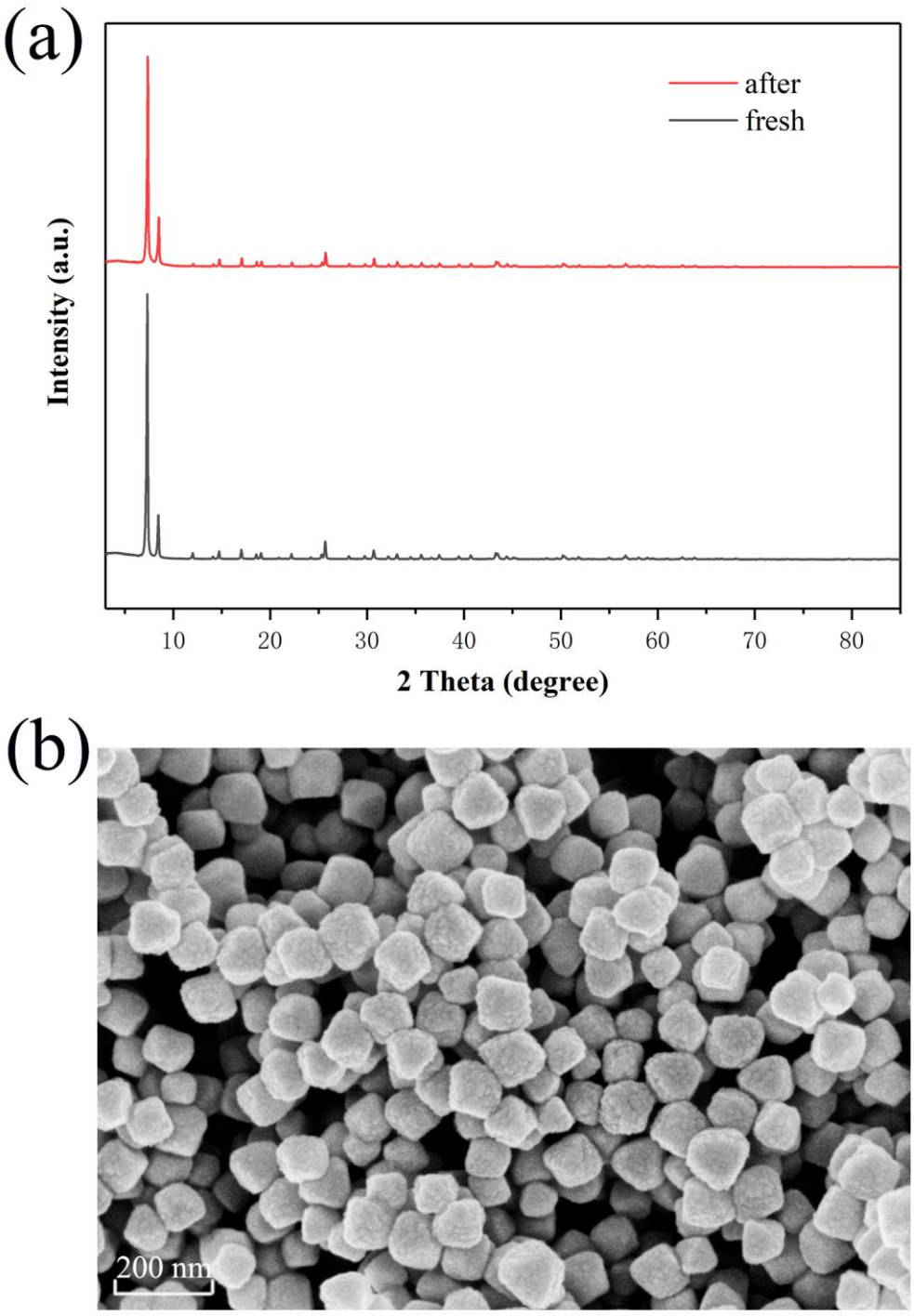

Figure S11. After the photocatalytic reaction of 15%Ce-UiO-66 XRD (a) and SEM (b)

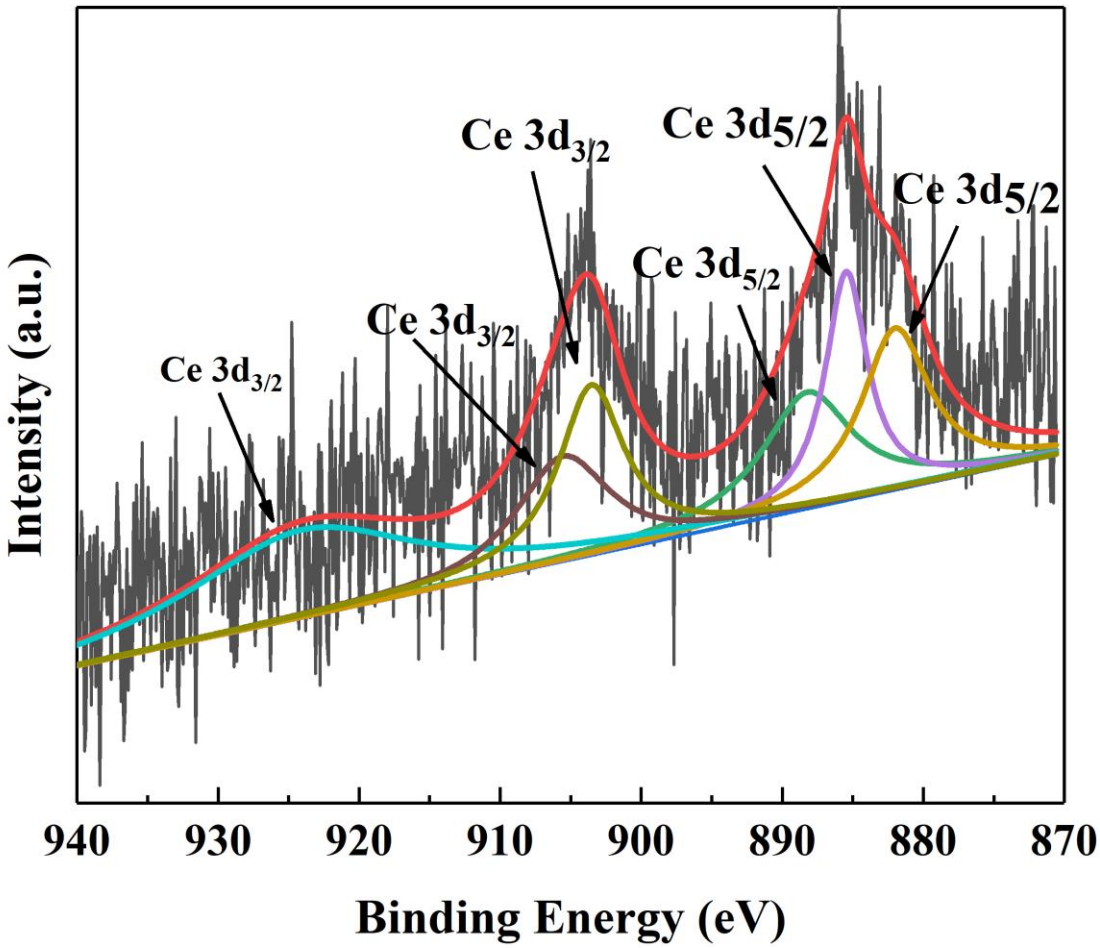

Figure S12. After the photocatalytic reaction of 15%Ce-UiO-66 (XPS)

Figure S13. Synthesis of the 15%Ce-UiO-66

Table S1. The ICP of Zr-UiO-66 and Ce-UiO-66

Catalyst	metallic element	Logging (mg/L)	Wt%	Actual Zr,Ce/ metallic Molar ratio
Zr-UiO-66	Zr	6.4350	26.9022	100%
	Ce	0	0	0%
15%Ce-UiO-66	Zr	4.1348	23.0552	85.73%
	Ce	1.0457	5.8886	14.27%

Table S2. Concentration of metal ions in solution after photocatalytic reaction

Element	Concentration (ng/ml)
Zr	none
Ce	none

Table S3. The result of catalyst desorption in acid after photocatalytic reaction

Reaction conditions	$C_{NH_4^+}$ (μmol/g)
Desorption after photocatalytic reaction in air	3.59
Desorption after photocatalytic reaction in Ar	None

Table S4. Photocatalytic nitrogen fixation performance of different MOF-based materials.

Catalyst	Light source	Detection method	organic scavengers	NH_3 evolution rate/μmol h^{-1} g^{-1}	Reference
MOF-76(Ce)	Full spectrum	IB [b]	None	34.0	[1]
MIL-101(Fe)	Full spectrum	NR [a]	None	50.4	[2]
$Bi_4O_5Br_2$/ZIF-8	Full spectrum	IB [b]	None	327.3	[3]
ZIF-67@PMo_4V_8	Full spectrum	NR [a]	None	149.0	[4]
NH_2-MIL-125 (Ti)	≥400 nm	IC [a]	ethanol	12.3	[5]
MIL-53(Fe^{II}/Fe^{III})	≥420 nm	IC [c]	K_2SO_3	306.0	[6]
15%Ce-UiO-66	Full spectrum	NR[a]	None	200.14	This work

[a] The detection method of Nessler's reagent.

[b] The detection method of indophenol blue.

[c] The detection method of ion chromatography.

[1] C. Zhang, Y. Xu, C. Lv, X. Zhou, Y. Wang, Weinan Xing, Qingqiang Meng, Y. Kong, G. Chen, Mimicking π backdonation in Ce-MOFs for solar-driven ammonia synthesis, ACS Appl. Mater. Interfaces. 11 (2019) 29917-29923. https://doi.org/10.1021/acsami.9b08682.

[2] G. Li, F. Li, J. Liu, C. Fan, Fe-based MOFs for photocatalytic N_2 reduction: key role of transition metal iron in nitrogen activation, J. Solid State Chem. 285 (2020) 121245. https://doi.org/10.1016/j.jssc.2020.121245.

[3] Jianxin Liu, R. Li, X. Zu, X. Zhang, Y. Wang, Y. Wang, C. Fan, Photocatalytic conversion of nitrogen to ammonia with water on triphase interfaces of hydrophilic-hydrophobic composite $Bi_4O_5Br_2$/ZIF-8, Chem. Eng. J. 371 (2019) 796-803. https://doi.org/10.1016/j.cej.2019.03.283.

[4] X. Li, P. He, T. Wang, X. Zhang, W. Chen, Y. Li, Keggin-type polyoxometalate-based ZIF-67 for enhanced photocatalytic nitrogen fixation, ChemSusChem. 13 (2020) 2769-2778. https://doi.org/10.1002/cssc.202000328.

[5] H. Huang, X. Wang, D. Philo, F. Ichihara, H. Song, Y. Li, D. Li, T. Qiu, S. Wang, J. Ye, Toward visible-light-assisted photocatalytic nitrogen fixation: a titanium metal organic framework with functionalized ligands, Appl. Catal. B-Environ. 267 (2020) 118686. https://doi.org/10.1016/j.apcatb.2020.118686.

[6] Z. Zhao, D. Yang, H. Ren, K. An, Y. Chen, Z. Zhou, W. Wang, Z. Jiang, Nitrogenase-inspired mixed-valence MIL-53(Fe^{II}/Fe^{III}) for photocatalytic nitrogen fixation, Chem. Eng. J. 400 (2020) 125929. https://doi.org/10.1016/j.cej.2020.125929.