

Supplementary Data

The role of 13X molecular sieve in photocatalytic nitrogen fixation

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Preparation of 13X

Molecular sieve 13X was synthesized by using sodium silicate nine-hydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), sodium meta-aluminate (NaAlO_2) and sodium hydroxide (NaOH). The molar ratio of raw materials was $\text{SiO}_2:\text{Al}_2\text{O}_3=2.8$, $\text{Na}_2\text{O}:\text{SiO}_2=2.1$, $\text{H}_2\text{O}:\text{SiO}_2=100$.

The details are as follows: 7.958 g of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was fully dissolved in 23 mL of deionized water containing 1.964 g of NaOH , which was recorded as solution A; 1.639 g of NaAlO_2 was dissolved in 23 mL of deionized water containing 0.5 g of NaOH , which was noted as solution B. Then solution B was added dropwise into solution A and stirred magnetically for 40 min. Afterwards, the mixed solution was transferred into a stainless-steel Teflon-lined autoclave and crystallized at 105°C for 12 hours. The product was obtained after cooling, centrifugation, washing and drying.

Preparation of BOB

BiOBr was prepared using a reported method with slight modification.¹ 0.97 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 50 mL aqueous solution. Subsequently, 50 mL of aqueous solution containing 0.238 g of KBr was slowly dropped in the above solution under magnetic stirring. After stirring at room temperature for 2 hours, the faint-yellow precipitate was collected by centrifugation and washed with deionized water and ethanol for several times. Finally, the product was dried in oven at 60°C , which was denoted as BOB.

Preparation of BOB-13X-m

A series of BOB-13X-m samples were synthesized via a liquid-phase self-assembly strategy.

A certain mass ($m = 13, 17, 20, 25, 30, 40, 50$ mg) of 13X was added to 10 mL of deionized water containing 200 mg of BOB. The above mixture was ultrasonically dispersed for 2 hours and then heated at 60°C overnight. The final powder obtained after grinding was named BOB-13X-m.

Characterization

Morphological features of the samples were obtained by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images on a JEOL JSM-6380 and a Tecnai G2 F30 S-TWIN microscope, respectively. Zeta potentials were carried on a Zetasizer Nano-ZS90 instrument. X-ray powder diffraction (XRD) patterns were recorded with a Purkinje XD-3 X-ray diffractometer using Cu K α irradiation ($\lambda = 1.5418$ nm). Fourier transform infrared (FT-IR) spectroscopy was recorded on a Nicolet-iS10 spectrometer. The Brunauer–Emmett–Teller (BET) surface areas were measured by a Quantachrome instrument. N₂-temperature programmed desorption (N₂-TPD) measurements were performed on a ChemiSorb 2040 instrument using a TCD as detector. UV-vis diffuse reflectance spectra (DRS) of the samples over a range of 220–800 nm were recorded on a Shimadzu UV-2600 spectrophotometer.

Electrochemical Measurements

Electrochemical impedance spectroscopy (EIS) and transient photocurrents were measured on a three-electrode quartz cell using an electrochemical workstation (CHI 760E). Na₂SO₄ (0.5 M) is employed as the electrolyte. The working electrode was made by depositing the sample of interest onto a transparent fluorine-doped tin oxide (FTO) conducting glass slide (1 cm \times 2 cm). Platinum foil (1.0 cm \times 1.0 cm) and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively.

Photocatalytic N₂ Fixation

The nitrogen fixation tests were carried out in the reactor, which was cooled with water circulation to ensure the experiments were conducted at a constant temperature of 35°C. Briefly, 5 mg of the photocatalyst was uniformly dispersed in the solution of 40 mL of deionized water and 10 mL of methanol. N₂ was first bubbled into the solution at a flow rate of 30 mL/min for 30 min in the dark to obtain N₂-saturated mixture. The ammonia synthesis process was conducted with continuous stirring and N₂ bubbling for 240 min under Xe lamp (300 W, without cutoff filter) illumination. After given time, 20 mL of the reaction solution was taken out and separated by centrifugation at 6500 rpm/min for 10 min. The NH₃ yield was measured by Nessler's reagent method (JB7478-87) and electrochemical method (DWS-296 ammonia nitrogen analyzer).

The ¹⁵N₂ isotope labeling experiment

The isotopic labeling experiment was conducted in the 100 mL quartz photoreactor. In a typical experiment, 50 mg of the wet photocatalyst was distributed on the bottom of the photoreactor. After the air was completely evacuated by a mechanical pump, 100 mL of ¹⁵N₂ or ¹⁴N₂ gas was injected into the photoreactor. Then the photocatalyst was irradiated by a 300 W Xe lamp. After 12 h of light irradiation, 5 mL of deionized water was added into the photoreactor to form a mixture solution, which was centrifuged at 5000 rpm for 5 min. The solution was mixed with 0.2 mL of a phenol solution (0.3 g of phenol in 2.5 mL of ethanol), 0.2 mL of a 0.5 g/L sodium nitroprusside aqueous solution, and 0.7 mL of a NaClO solution (0.1 g of NaOH, 2.3 g of sodium citrate, 0.11 g of NaClO in 10 mL of deionized water) and stirred for 1 h. The indophenol in the mixture solution was analyzed by AB 5500 HPLC/MS (Agilent 1290 UPLC-QTOF6550) system with a waters BEH C 18 column.

Supplementary Figures

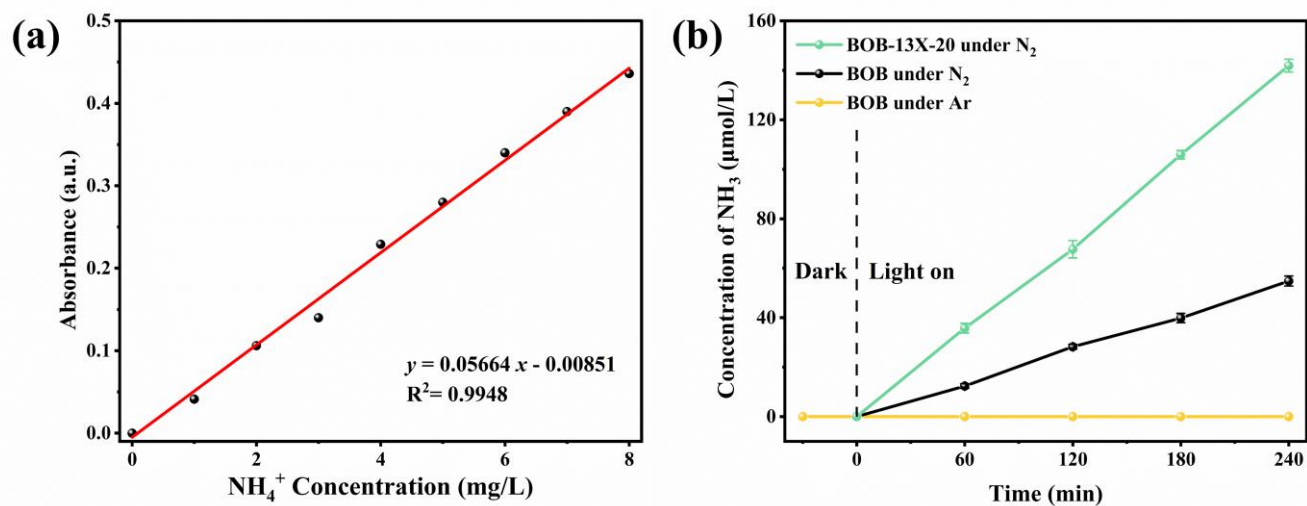


Fig. S1. (a) Standard curve of NH_4^+ with Nessler's reagent. (b) Time dependent NH_3 production over BOB and BOB-13X-20 under N_2 or Ar.

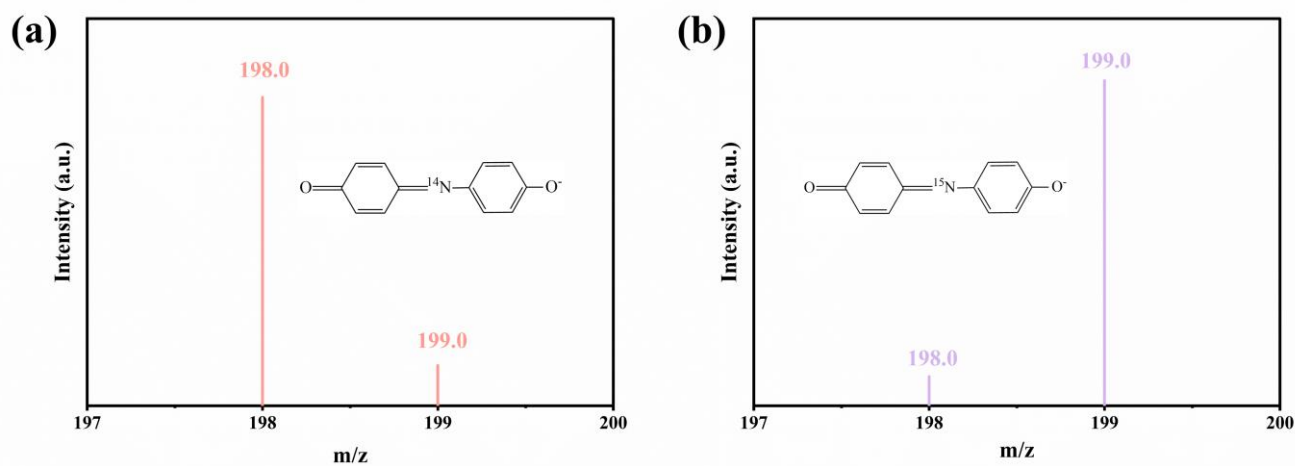


Fig. S2. (a, b) Mass spectra of the indophenol products formed using $^{14}\text{N}_2$ and $^{15}\text{N}_2$ in the photocatalytic N_2 fixation tests. The inset is the chemical structure of the indophenol product, with $m/z = 199.0$ (indophenol containing ^{15}N) and $m/z = 198.0$ (indophenol containing ^{14}N).

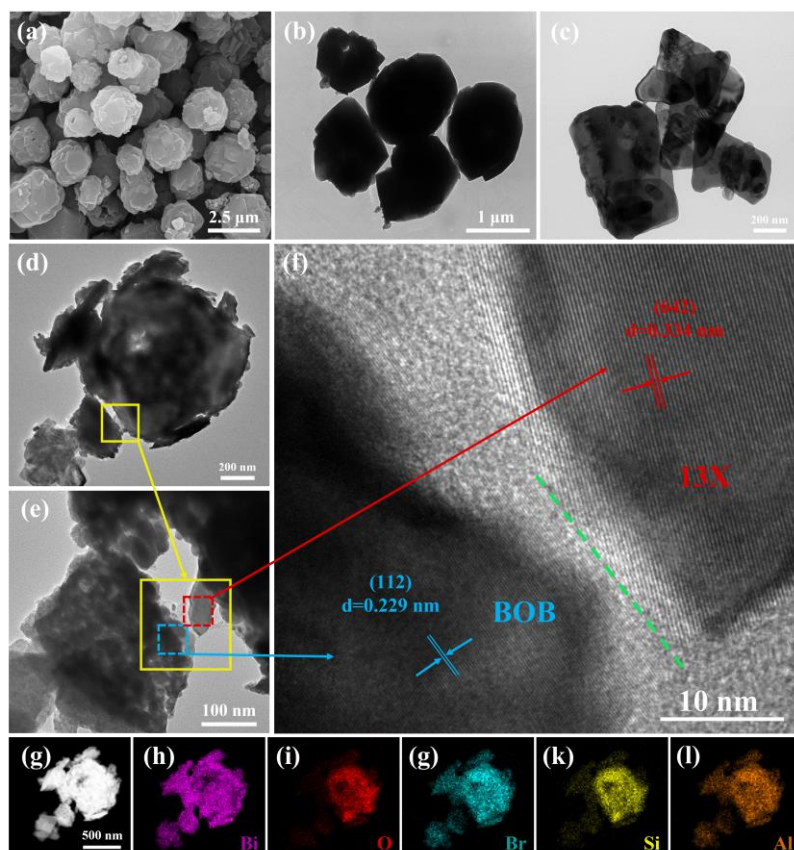


Fig. S3. (a, b) SEM image and TEM image of 13X; (c) TEM image of BOB; (d, e) TEM image of BOB-13X-20 and corresponding partial enlarged view; (f) HRTEM image of BOB-13X-20; (g-l) EDX elemental mapping images of BOB-13X-20.

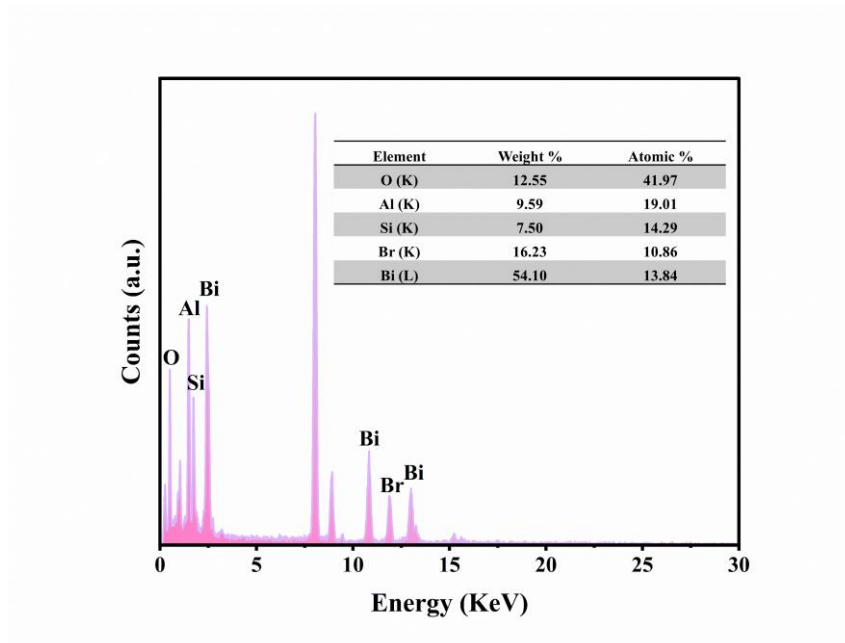


Fig. S4. EDS spectrum with elements ratio of BOB-13X-20.

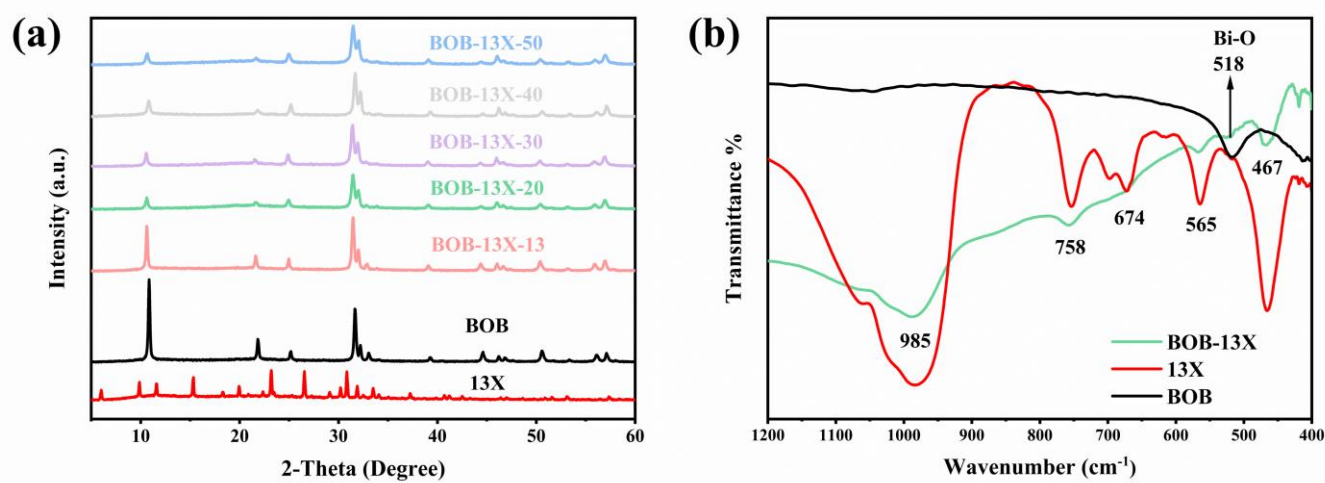


Fig. S5. (a) XRD patterns and (b) FT-IR of different samples.

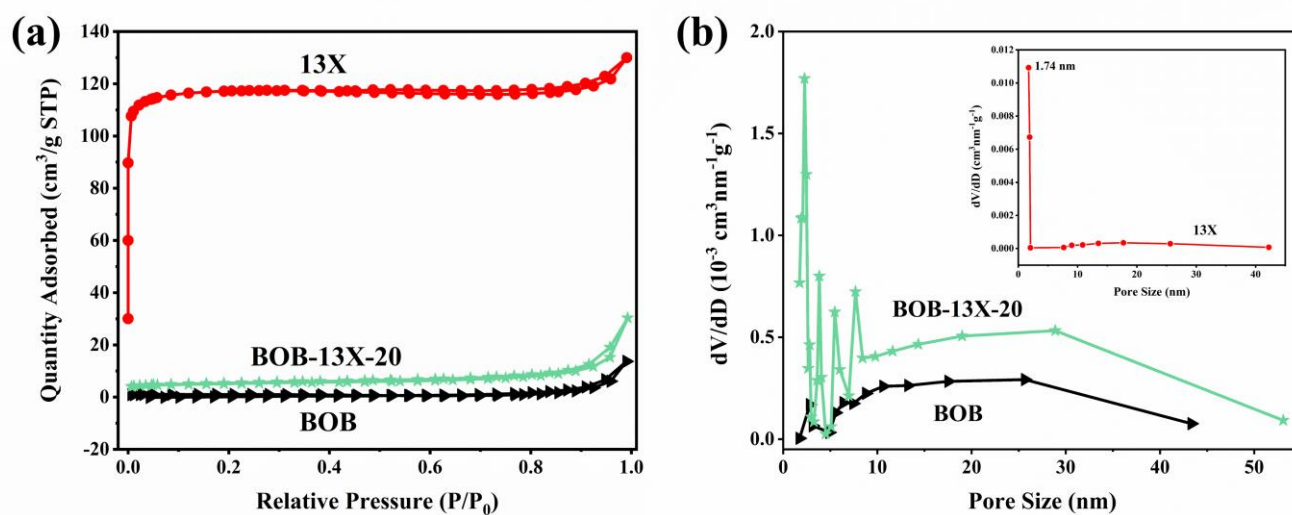


Fig. S6. (a) N₂ adsorption–desorption isotherm and (b) pore size distribution of 13X, BOB and BOB-13X-20.

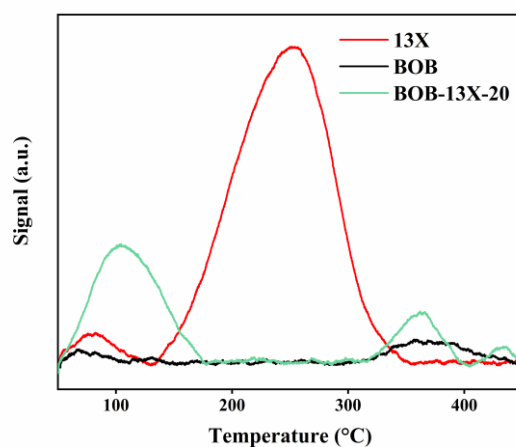


Fig. S7. N₂-TPD of 13X, BOB and BOB-13X-20.

NOTE: In brief, 50 mg catalyst was first pre-treated with pure He (99.999%) at 300°C for 30 min, then cooled down to 50°C in the same atmosphere and then dosed with pure N₂. The catalyst was then purged with pure He gas to remove the residual N₂. The N₂-TPD measurement was performed up to 450°C in the pure He atmosphere.

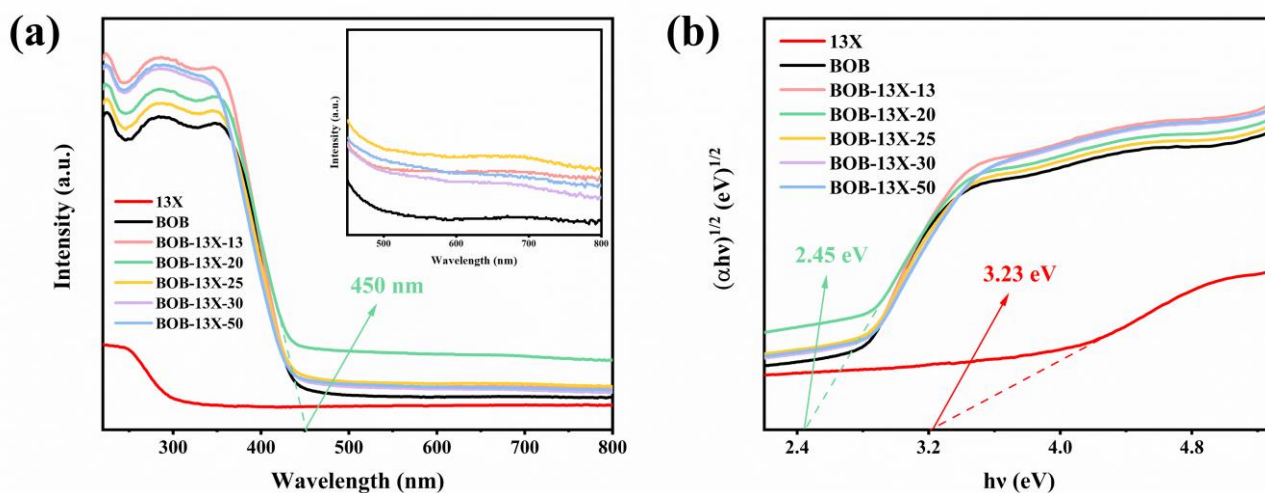


Fig. S8. (a) UV-vis DRS spectrum and (b) the band gap of different samples.

Supplementary Tables

Table S1. Calculated ammonia production rates based on different methods.

Catalyst	Sacrificial agent	Light source	NH ₃ production rate ($\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$)	
			Nessler's reagent method	Electrochemical method
BOB-13X-20	Methanol	300 W Xe lamp (Full spectrum)	360.5	375.0

Reaction conditions: catalyst (BOB-13X-20, 5 mg), Solution (40 mL of deionized water and 10 mL of methanol), temperature (35°C), reaction time (4 h).

The NH₃ formation rates determined using these two methods were consistent with one another, confirming the reliability of the results obtained.

Table S2. The zeta potential measurements of 13X, BOB and BOB-13X-20.

Samples	Zeta potential (mV)
13X	-35.4
BOB	8.4
BOB-13X-20	-25.6

Table S3. The surface area, average pore size and pore volume of 13X, BOB and BOB-13X-20 calculated via the BET method.

Samples	Surface area (m^2/g)	Average pore size (nm)	Pore volume ($\text{cm}^3/\text{g STP}$)
13X	352.05	9.47	0.024
BOB	2.98	24.52	0.021
BOB-13X-20	16.58	19.70	0.042

Table S4. The band gaps (E_g) of different samples.

Samples	E_g (eV)
13X	3.23
BOB	2.63
BOB-13X-13	2.61
BOB-13X-20	2.45
BOB-13X-25	2.54
BOB-13X-30	2.55
BOB-13X-50	2.58

Table S5. A summary of the main photocatalysts used for photocatalytic N_2 fixation in the recent literature.

Photocatalyst	Light source power (Wavelength)	Scavenger agent	Ammonia production rate	Ref. (Year)
BOB-13X-20	300 W Xe lamp (Full spectrum)	Methanol	$360.5 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	This work
BOB-P	300 W Xe lamp (Full spectrum)	None	$246 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ²] (2022)
BOB-001-OV	300W Xe lamp ($\lambda > 420$ nm)	None	$223.3 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ³] (2015)
BiOBr-Fe-S-1	300W Xe arc lamp ($\lambda > 400$ nm)	None	$46.1 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ⁴] (2021)
0.20 wt% Pd-EG-BOB	300 W Xe lamp (UV-vis)	Methanol	$124.63 \mu\text{mol h}^{-1}$	[S ⁵] (2021)
10 wt% BiOBr/Ti ₃ C ₂	Xe lamp (320-780 nm)	Methanol	$234.6 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ⁶] (2021)
BiOBr/BiOI/Bi	300W Xe lamp (Full spectrum)	None	$221.9 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ⁷] (2022)
BiOBr/g-C ₃ N ₄	300W Xe lamp (Vis)	None	$255.04 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ⁸] (2023)
10GQD/Bi ₂ WO ₆	300W Xe lamp (Vis)	Ethanol	$241.07 \mu\text{mol g}_{\text{cat}}^{-1}$	[S ⁹] (2019)
Zn _{0.8} Cd _{0.2} S	300W Xe lamp ($\lambda > 420$ nm)	Na ₂ SO ₃	$66.9 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ¹⁰] (2020)
N-Black In ₂ O _{3-x} /InVO ₄	300W Xe lamp ($\lambda > 400$ nm)	None	$2.07 \text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ¹¹] (2021)
Mn-MoS _{2-x} -4	300W Xe lamp (Full spectrum)	None	$213.2 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ¹²] (2022)
TR-1.0	300W Xe lamp (280-400 nm)	Ethanol	$56.3 \mu\text{g h}^{-1} \text{g}_{\text{cat}}^{-1}$	[S ¹³] (2019)

References

1. Y. Guo, H. Wen, T. Zhong, H. Huang and Z. Lin, *Chemical Engineering Journal*, 2022, 445.
2. L. Zhang, F. Xie, J. Liu, Z. Sun, X. Zhang, Y. Wang, Y. Wang, R. Li and C. Fan, *Chemical Engineering Journal*, 2022, 450.
3. H. Li, J. Shang, Z. Ai and L. Zhang, *J Am Chem Soc*, 2015, 137, 6393-6399.
4. X. Chen, X. Zhang, Y.-H. Li, M.-Y. Qi, J.-Y. Li, Z.-R. Tang, Z. Zhou and Y.-J. Xu, *Applied Catalysis B: Environmental*, 2021, 281.
5. J. Liu, F. Li, J. Lu, R. Li, Y. Wang, Y. Wang, X. Zhang, C. Fan and R. Zhang, *J Colloid Interface Sci*, 2021, 603, 17-24.
6. Y. Fang, Y. Cao, B. Tan and Q. Chen, *ACS Appl Mater Interfaces*, 2021, 13, 42624-42634.
7. K. Gao, H. Zhu, C. Zhang, X. Song, L. Lao, L. Ni, J. Chen, C. Cheng and X. Wang, *Solar RRL*, 2022, 6, 2200869.
8. K. Gao, C. Zhang, H. Zhu, J. Xia, J. Chen, F. Xie, X. Zhao, Z. Tang and X. Wang, *Chemistry*, 2023, 29, e202300616.
9. T. Fei, L. Yu, Z. Liu, Y. Song, F. Xu, Z. Mo, C. Liu, J. Deng, H. Ji, M. Cheng, Y. Lei, H. Xu and H. Li, *J Colloid Interface Sci*, 2019, 557, 498-505.
10. W. Dong, Y. Liu, G. Zeng, T. Cai, L. Shao, H. Chen, W. Zeng and X. Xia, *Journal of Photochemistry and Photobiology A: Chemistry*, 2020, 401.
11. J. Ye, J. Xu, C. Li, D. Tian, X. Zhao, Q. Wang, W. Lv, J. Wang, H. Xie, Y. Li, Z. Liu and Y. Fu, *Journal of Materials Chemistry A*, 2021, 9, 24600-24612.
12. B. Hu, B.-H. Wang, Z.-j. Bai, L. Chen, J.-K. Guo, S. Shen, T.-L. Xie, C.-T. Au, L.-L. Jiang and S.-F. Yin, *Chemical Engineering Journal*, 2022, 442.
13. S. Liu, Y. Wang, S. Wang, M. You, S. Hong, T.-S. Wu, Y.-L. Soo, Z. Zhao, G. Jiang, Q. Jieshan, B. Wang and Z. Sun, *ACS Sustainable Chemistry & Engineering*, 2019, 7, 6813-6820.