Supporting information

Efficient photocatalytic selective oxidation of 5-hydroxymethylfurfural on $Bi_{24}O_{29}Br_{10}(WO_4)_2$solid solution via enhanced charge separation

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Material synthesis method

Preparation of $Bi_{24}O_{31}Br_{10}$

Add 4.850g of bismuth nitrate pentahydrate to a 150mL beaker containing 40ml of ethylene glycol, and sonicate until completely dissolved. Then add 1.190g of potassium bromide, stir, and slowly add 20mL of ultrapure water dropwise, followed by stirring for 4 h. After the reaction is complete, filter the resulting solid to obtain BiOBr.

After thoroughly mixing and grinding 1.524g of BiOBr and 1.638g of bismuth oxide (with a molar ratio of BiOBr to bismuth oxide of 5:7), the mixture was placed in a 50mL crucible and heated from room temperature to 650°C at a rate of 5°C/min and maintained at that temperature for 12 h. After the reaction was completed, the mixture was cooled to room temperature, resulting in the solid catalyst $Bi_{24}O_{31}Br_{10}$.

Preparation of Bi_2WO_6

10.10 g of dihydrated sodium tungstate and 0.24 g of pentahydrated bismuth nitrate were weighed and added to 20 mL of water, followed by stirring for 45 min. The resulting milky suspension was transferred to a 40 mL stainless steel hydrothermal autoclave with a polytetrafluoroethylene lining and placed in a high-temperature oven at 160 °C for 24 h. After cooling to room temperature, the obtained milky suspension was centrifuged, washed three times with water, and then dried in an oven at 60 °C for 24 h. The resulting white powder was ground and designated as Bi_2WO_6.

Preparation of Bi_2WO_6/ $Bi_{24}O_{31}Br_{10}$ heterogenous junction

Add 400mg of $Bi_{24}O_{31}Br_{10}$, 21.5mg of sodium tungstate dihydrate (containing 12mg of tungsten), and 63.3mg of bismuth nitrate pentahydrate to 80mL of water, and stir for 30 min. Then transfer the mixture to a 100mL stainless steel autoclave lined with polytetrafluoroethylene substrate, and heat at 160°C for 24 h. After the reaction is complete, centrifuge and wash the resulting yellow solid with deionized water and anhydrous ethanol three times. Dry at 60°C for 24 h to obtain the Bi_2WO_6/$Bi_{24}O_{31}Br_{10}$.

Supplementary Chart

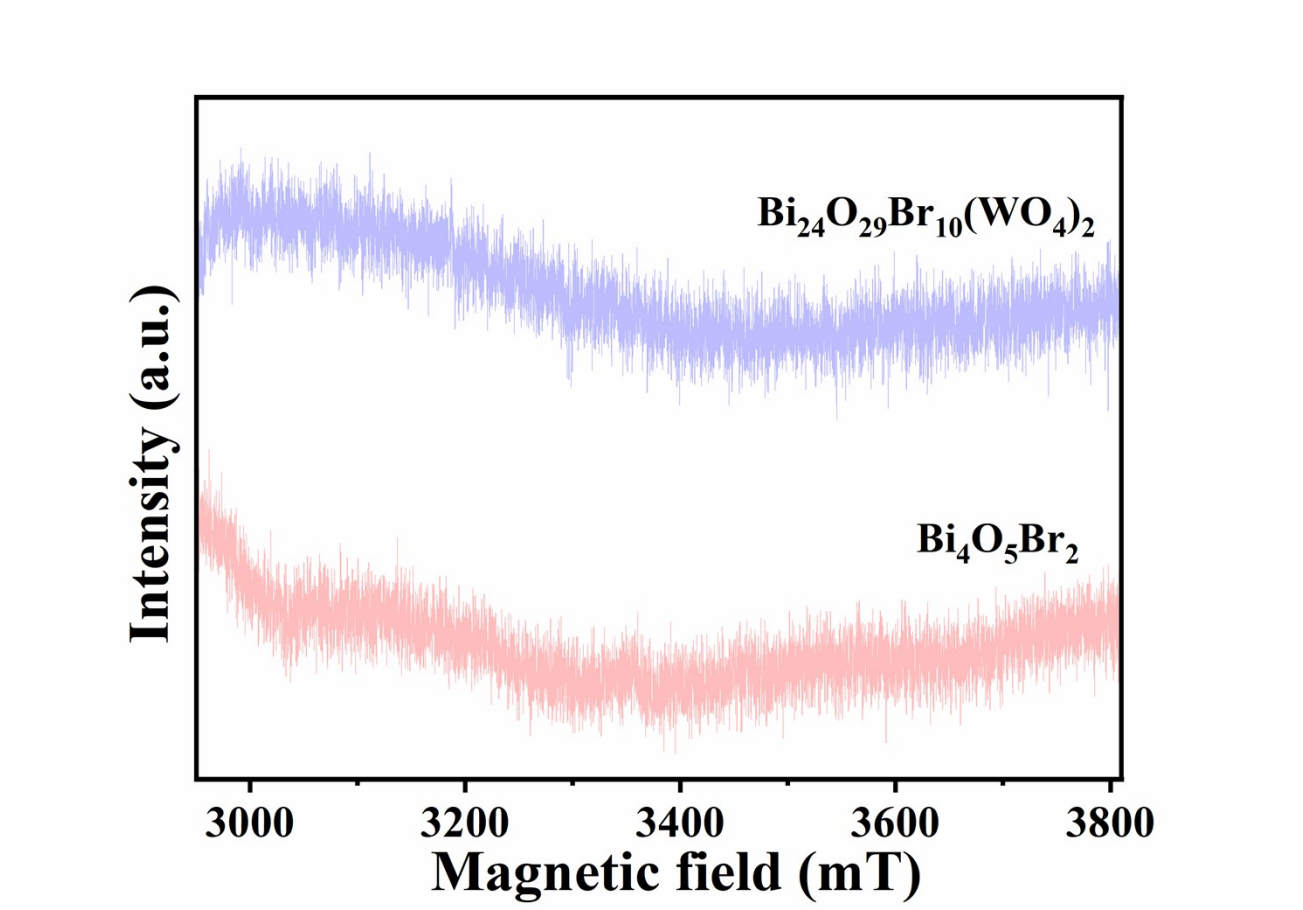

Fig. S1 ESR spectrum of $Bi_{24}O_{29}Br_{10}(WO_4)_2$ and $Bi_4O_5Br_2$

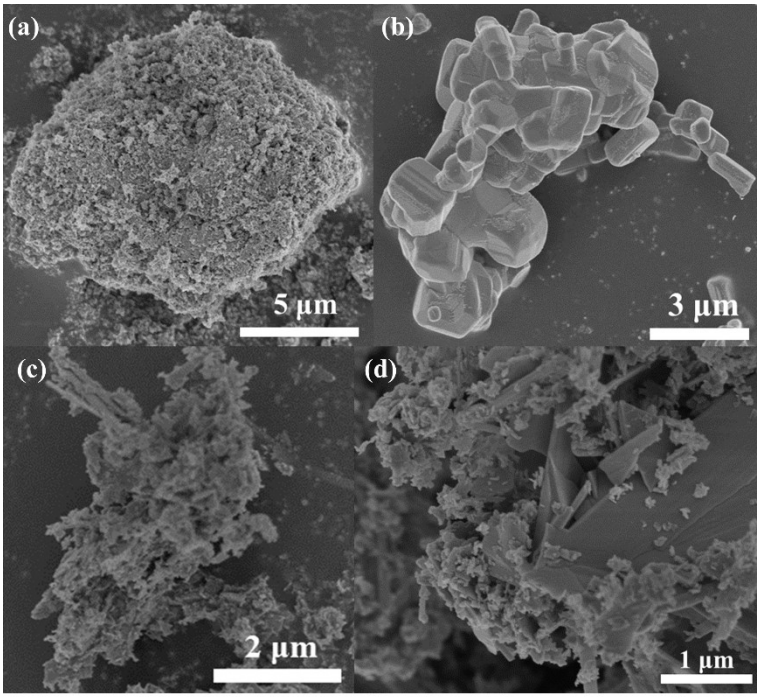

Fig. S2 SEM images of (a) $Bi_4O_5Br_2$, (b) $Bi_{24}O_{31}Br_{10}$ and (c-d) $Bi_{24}O_{29}Br_{10}(WO_4)_2$

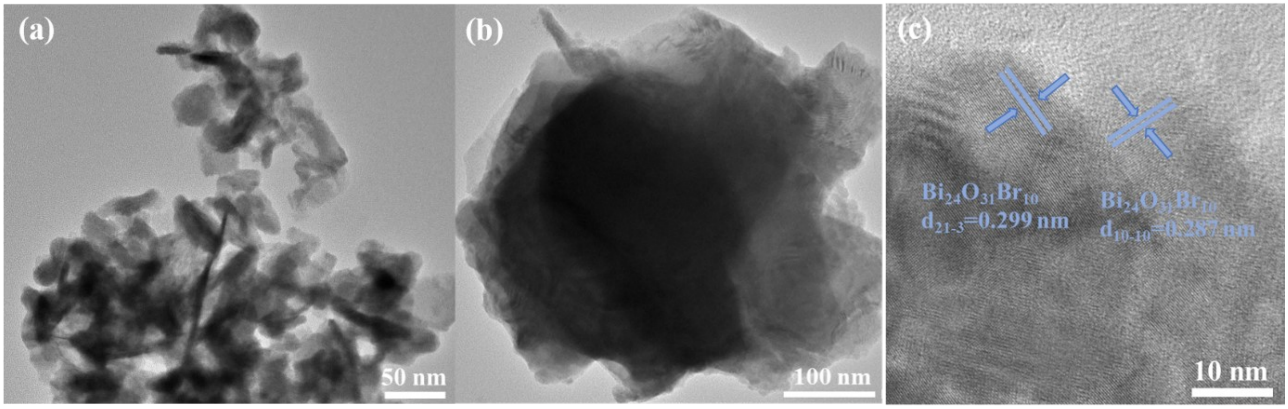

Fig. S3 TEM images of (a) $Bi_4O_5Br_2$ and (b-c) $Bi_{24}O_{31}Br_{10}$

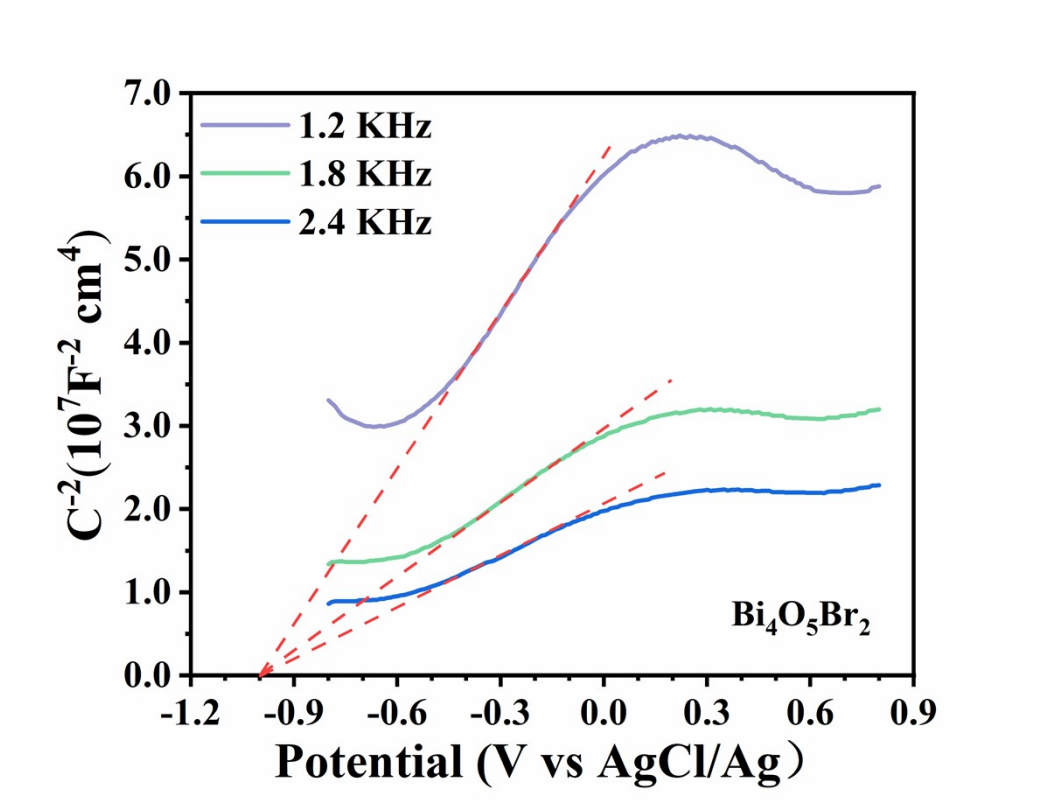

Fig. S4 Motschottky curves of $Bi_4O_5Br_2$

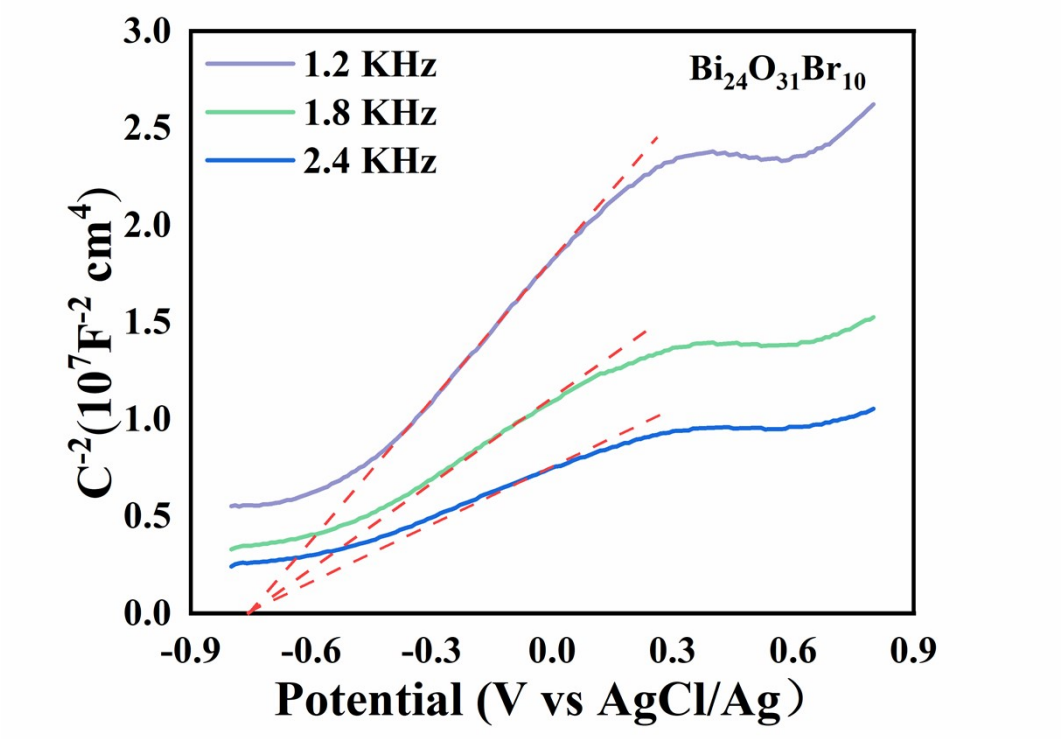

Fig. S5 Motschottky curves of $Bi_{24}O_{31}Br_{10}$

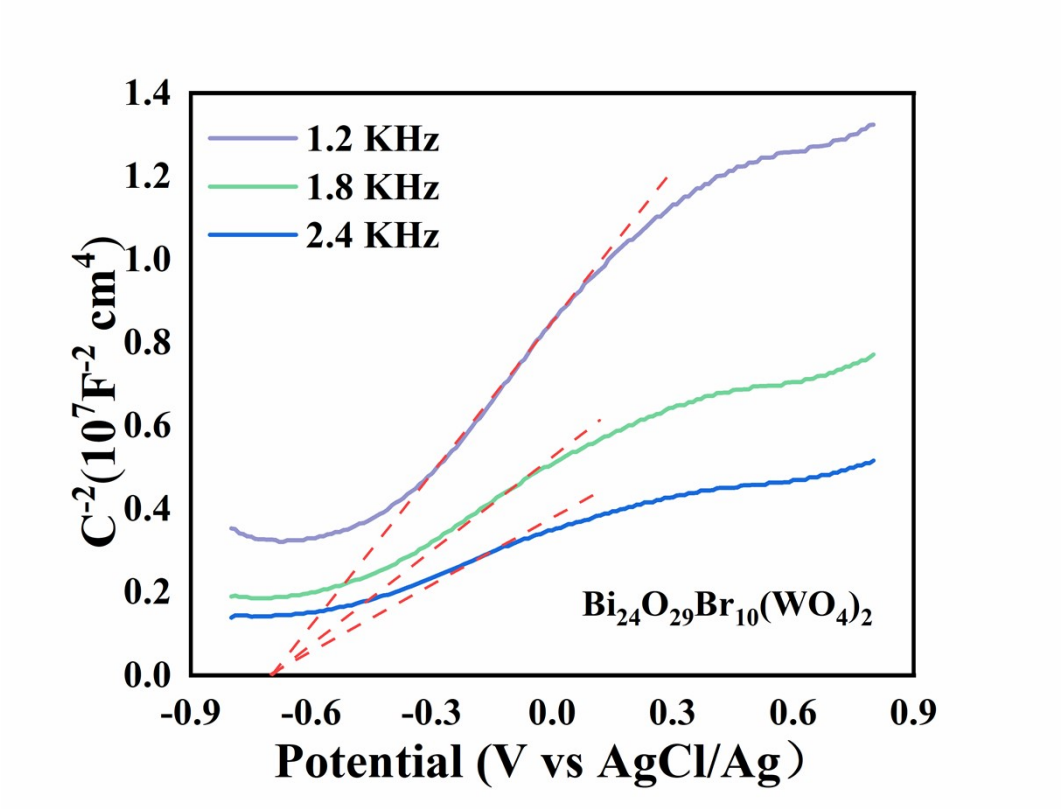

Fig. S6 Motschottky curves of $Bi_{24}O_{29}Br_{10}(WO_4)_2$

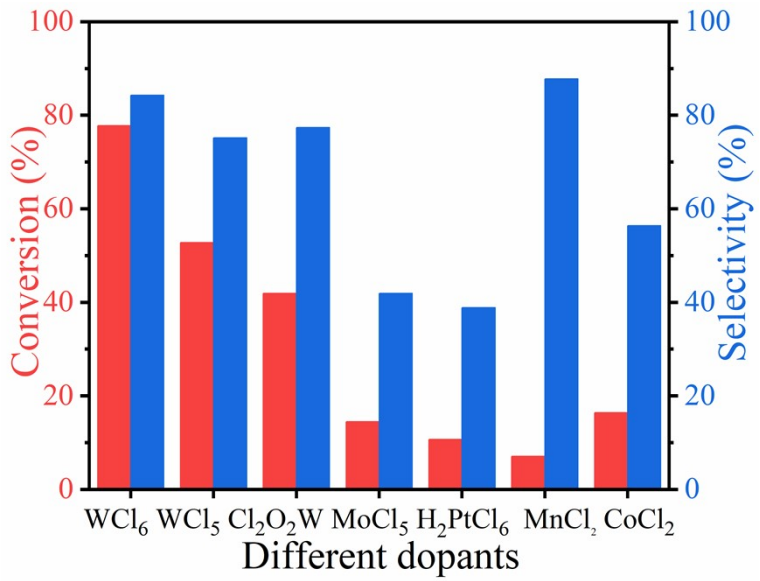

Fig. S7 HMF selective oxidation performance of catalysts with different precursors [Reaction condition : 20 mg photocatalyst, 10 mL 2 mM HMF acetonitrile solution, AM 1.5 filter, O_2, reaction for 3 h]

As shown in Figure S7, we evaluated the photocatalytic activity of a series of solid solutions doped with different tungsten sources. The conversion rate and selectivity of W(V) were 52.7% and 72.1%, respectively, while the conversion rate and selectivity of W(VI) were 41.8% and 77.3%, respectively. Among them, W(VI) might be the most suitable tungsten source, as its valence state is consistent with that of WO_4^{2-}. In addition, the non-metal element chlorine is prone to volatilization at high temperatures, which further facilitates the coordination of tungsten oxides. The above results further confirm that the introduction of tungsten can effectively change the photocatalytic properties of solid solutions.

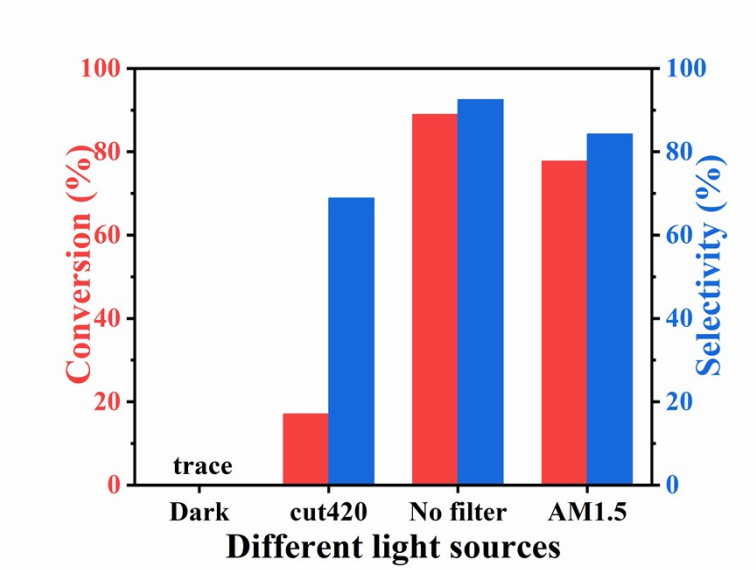

Fig. S8 HMF selective oxidation performance of catalysts with different precursors [Reaction condition : 20 mg photocatalyst, 10 mL 2 mM HMF acetonitrile solution, O_2, reaction for 3 h]

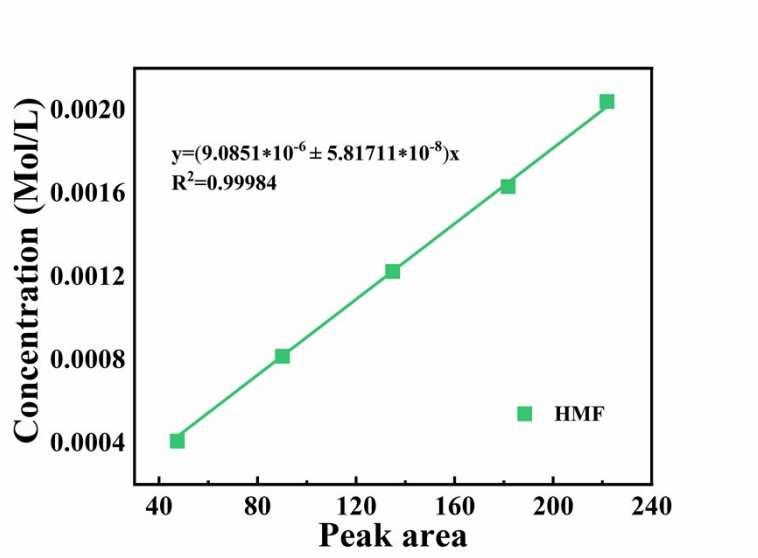

Figure S9. Standard curve of HMF.

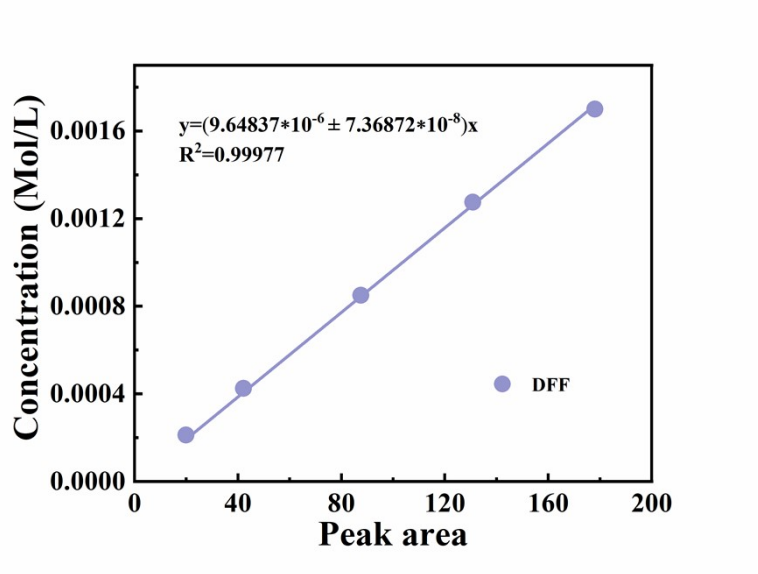

Figure S10. Standard curve of DFF.

TableS1 Photocatalyst Activity Comparison

Photocatalyst	Solvent	Light	Atmosphere	Time	Cov. (%)	Sel. (%)	Ref.
$Bi_{24}O_{29}Br_{10}(WO_4)_2$	ACN	All light	O_2	6 h	**98.8**	**92.5**	**This work**
SGH-TiO_2	ACN	AM1.5	O_2	4 h	59	87	1
Fe-Bi_2MoO_6	Water	AM1.5	O_2	8 h	32.62	95.30	2
Bi_2WO_6/mpg-C_3N_4	ACN	>400 nm	O_2	6 h	59.3	84.3	3
Bi_2WO_6	ACN	AM1.5	O_2	10 h	58	99.5	4
Cu_2O-TiO_2	Water	AM1.5	O_2	90 min	50	40	5
MnO_2-NPs	ACN	365 nm	O_2	6 h	99	100	6
Nb_2O_5	ACN	>400 nm	O_2	6 h	19.2	90.6	7
Cu SAs/p-CNS	ACN	455 nm	O_2	24 h	77.1	85.6	8
$Cd_{1.5}In_2S_{4.5}$	Water	>420 nm	O_2	6 h	68.8	62.7	9
C_3N_4	Water	365 nm	O_2		40	45	10
MIL-53(Fe)/g-C_3N_4	ACN/$PhCF_3$	$\lambda > 360$	O_2		77	49	11
Pt-Ov-BiOBr	ACN	AM1.5	O_2		91	77	12
CN-WO_3@MnO_2	ACN	λ=420 nm,	O_2		78	80	13

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