Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

BiOBr Photocatalyzed Decarboxylation of Glutamic Acid: Intermediates and Mechanism Study

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Experimental details

Materials and methods. BiOBr photocatalyst were synthesized using our patented method [1] and was characterized by XRD and SEM (Fig. S9(ESI†)). Other chemicals were commercially obtained and used as received without further purification. Deionized and doubly distilled water was used throughout this study.

Visible light irradiation was conducted with a 300 W Xe lamp (purchased from Xujiang Electromechanical Plant, Nanjing, China) cutoff below 420 nm as visible light source. UV light irradiation was set with a 100 W high-pressure Hg lamp (Toshiba, SHL-100UVQ-2) through a cutoff filter (λ > 270 nm). The ^{1}H NMR spectra were measured with a Bruker 400 MHz NMR spectrometer equipped with a NanoBay spectrometer (model AVANCE). GC-MS analysis was carried out with a Finnigan Trace GC ultragas chromatograph equipped by a Trace DSQ MS spectrometer and a 25 mm DB-5 capillary column. A Brucker ESR spectrometer (moder E500) equipped with Quanta-Ray Nd:YAG laser (355 and 532 nm) was used to record the electron spin resonance (ESR) signals of the radicals trapped by dimethylpyrrolidine 1-oxide (DMPO). To minimize experimental errors, the same quartz capillary tube was used for all ESR measurements.

Photocatalytic degradation. The degradation experiments were performed in a Pyrex vessel (25 mL) with the D_2O suspension (10 mL) containing BiOBr (10 mg) and Glu (10 mmol L^{-1}). Prior to irradiation, the suspension was stirred in the dark for 2 h to ensure the establishment of an adsorption/desorption equilibrium. After irradiation for a given time, ca. 1.0 mL aliquot was collected, centrifuged, and then filtered to remove the photocatalyst. The filtrate was subject to ^{1}H NMR analysis after the addition of 0.5 mg TSP as internal standard.

Isotope labelling experiments. These experiments were carried out with the same photocatalyst and substrate concentrations as above experiments. $H_2{}^{18}O$ isotope labeling experiments was performed in $H_2{}^{18}O$ suspension using $^{16}O_2$ in the air as oxidant. $^{18}O_2$ isotope labeling experiment was performed in a 50 mL seal hard glass bottle. The bottle containing the reaction suspension underwent ten cycles of pumping to vacuum and then purging with argon to remove the air, and then was filled with $^{18}O_2$. After irradiation, the reacted solution was extractedwith ethyl ether (5 mL). The organic phase was dried with anhydrous Na_2SO_4, and evaporated to about 0.1 mL by Ar purging. The concentrated sample was treated with HMDS (100 mL) and TMSCl (50 mL), centrifuged, and then subject to GC-MS analysis. Each measurement was repeated three times to ensure the accuracy. The measured isotope abundance of the product was corrected with the oxygen isotope abundance of the used ^{18}O enriched reagent and the natural isotope abundance of the product by the previously used method.

Table S1 Average isotope abundances of the oxygen atoms in the formed carbonyl group of SA in $^{18}O_2$ isotope labeling experiments [a]

System	Time (min)	Substrate conv. (%)	SA yiel. (%)	Abundance [b] (%)	
				$^{18}O_2$-derived	$H_2{}^{16}O$-derived
BiOBr/Vis	480	24.7	10.9	22.85	77.15
BiOBr/UV	90	24.2	17.2	22.7	77.3
TiO_2/UV	20	20.6	9.9	4.9	95.1

[a] 1 g L^{-1} photocatalyst, $c_{Glu}{}^0$ = 10 mmol L^{-1}, 2 mL H_2O; [b] Average value of the two O atoms of the formed carboxyl group, corrected with the oxygen isotope abundance of $^{18}O_2$ and the natural isotope abundance of solvent H_2O.

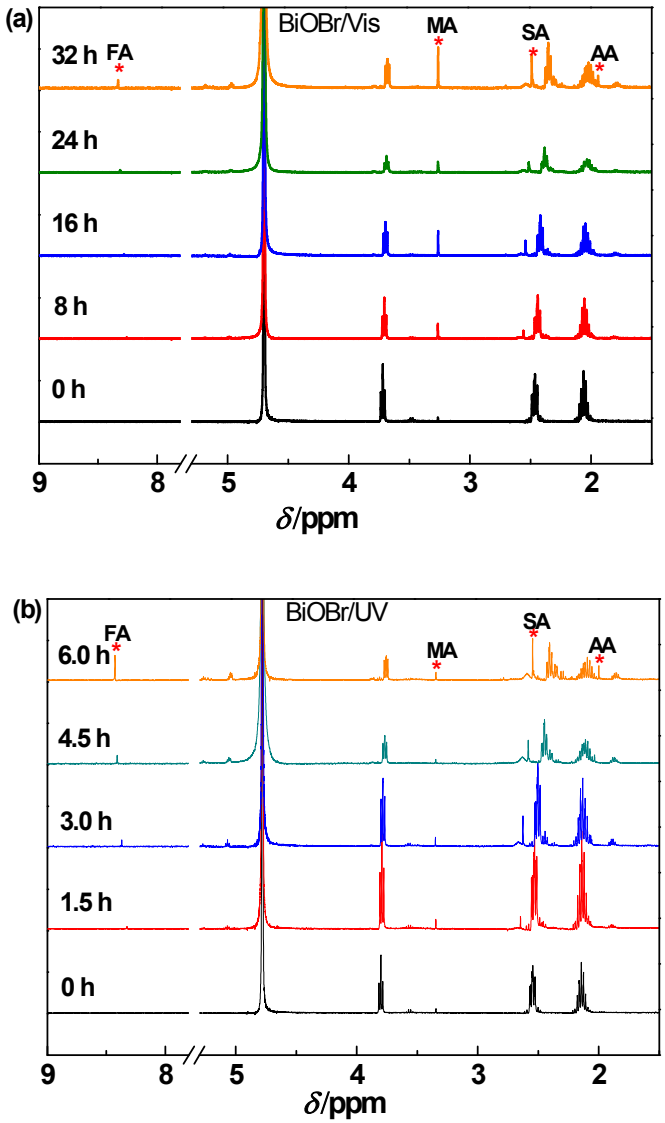

Fig. S1 The change of ^{1}H NMR spectrum with reaction time in (a) BiOBr/Vis and (b) BiOBr/UV systems, 1 g L^{-1} BiOBr, c_{Glu}^{0} = 10 mmol L^{-1}, 10 mL D_2O.

Fig. S2 GC-MS spectra of succinic acid formed in the photocatalytic oxidation of glutamic acid in BiOBr/Vis system with $H_2{}^{18}O$ as solvent, 1 g L^{-1} BiOBr, $c_{Glu}{}^0$ = 10 mmol L^{-1}, 2 mL $H_2{}^{18}O$.

Fig. S3 GC-MS spectra of succinic acid formed in the photocatalytic oxidation of glutamic acid in BiOBr/UV system with $H_2{}^{18}O$ as solvent, 1 g L^{-1} BiOBr, $c_{Glu}{}^0$ = 10 mmol L^{-1}, 2 mL $H_2{}^{18}O$.

Fig. S4 GC-MS spectra of succinic acid formed in the photocatalytic oxidation of glutamic acid in TiO_2/UV system with $H_2{}^{18}O$ as solvent, 1 g L^{-1} TiO_2, $c_{Glu}{}^0$ = 10 mmol L^{-1}, 2 mL $H_2{}^{18}O$.

Fig. S5 GC-MS spectra of succinic acid formed in the photocatalytic oxidation of glutamic acid in BiOBr/Vis system with $^{18}O_2$ as oxidant, 1 g L^{-1} BiOBr, $c_{Glu}{}^0$ = 10 mmol L^{-1}, 2 mL H_2O.

Fig. S6 GC-MS spectra of succinic acid formed in the photocatalytic oxidation of glutamic acid in BiOBr/UV system with $^{18}O_2$ as oxidant, 1 g L^{-1} BiOBr, c_{Glu}^0 = 10 mmol L^{-1}, 2 mL H_2O.

Fig. S7 GC-MS spectra of succinic acid formed in the photocatalytic oxidation of glutamic acid in TiO_2/UV system with $^{18}O_2$ as oxidant, 1 g L^{-1} TiO_2, c_{Glu}^0 = 10 mmol L^{-1}, 2 mL H_2O.

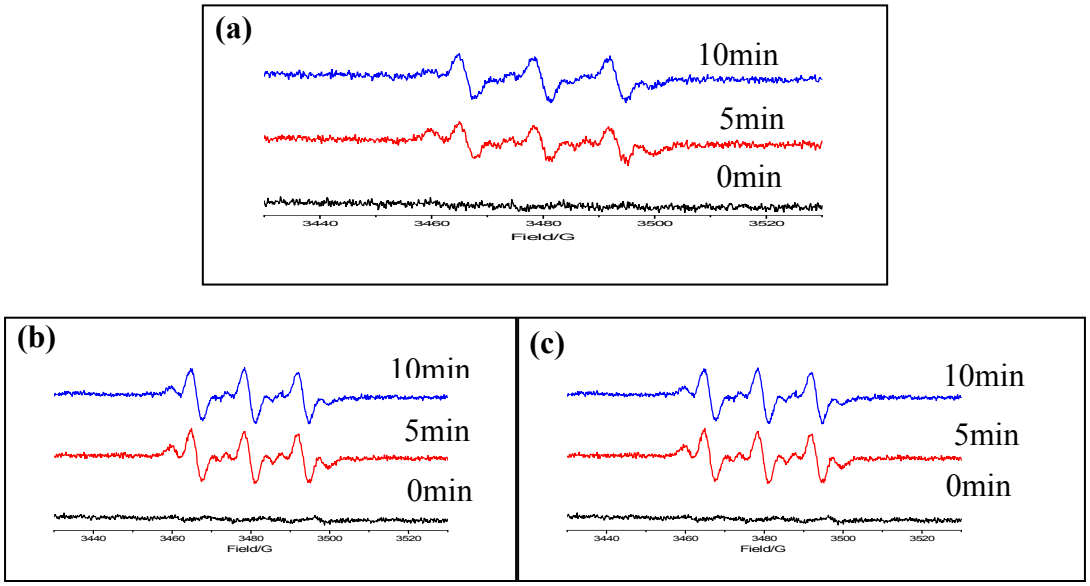

Fig. S8 ESR signals of DMPO-$O_2^{\cdot-}$ adducts formed in (a) BiOBr/Vis, (b) BiOBr/UV and (c) TiO_2/UV systems. 1 g L^{-1} photocatalyst, c_{Glu}^0 = 10 mmol L^{-1}, c_{DMPO}^0 = 0.4 mol L^{-1}, methanol was used as solvent.

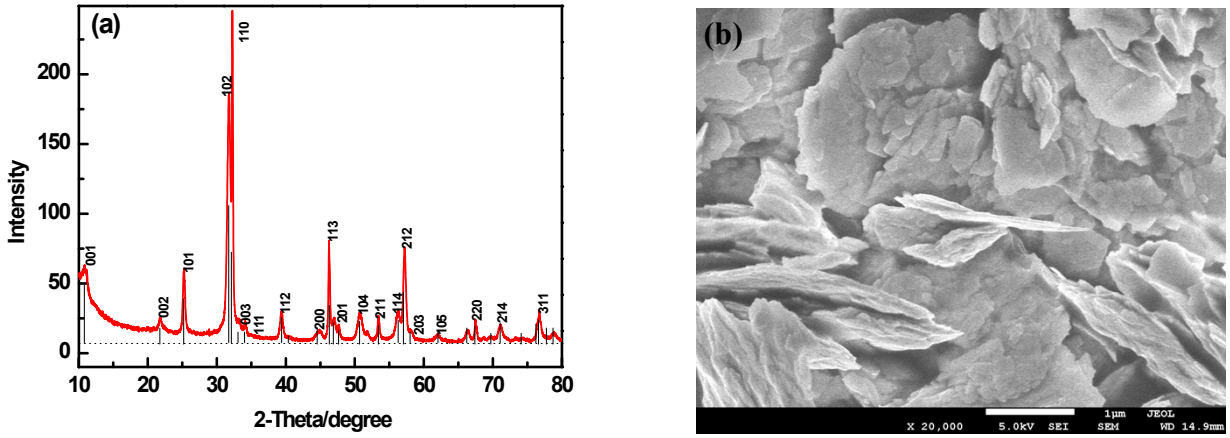

Fig. S9 XRD pattern (a) and SEM graph (b) of the synthesized BiOBr sample.

References

1 Y. F. Fang, G. W. Cheng and X. Y. Lu, China Pat., 101786006., 2010.