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Supporting Information

Identification of Bi_2WO_6 as a highly selective visible light photocatalyst toward oxidation of glycerol to dihydroxyacetone in water

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Fig. S16. The HPLC spectra to identify reactant glycerol and main product DHA for selective oxidation of glycerol in water over Bi_2WO_6 (B) photocatalyst under the irradiation of visible light for 4 h in the reaction system.

Experimental Details

Preparation of flower-like Bi_2WO_6 samples:

The procedures for synthesis of flower-like Bi_2WO_6 spherical superstructures in the present work are based on a modified hydrothermal approach.[S1] Typically, 0.98 g of $Bi(NO_3)_3{\cdot}5H_2O$ was ultrasonicated in 40 mL of 0.3 M HNO_3 aqueous solution to dissolve it evenly. Then, 20 mL of 0.05 M Na_2WO_4 solution was added with vigorous stirring and a white precipitate was formed. Subsequently, 20 mL of 0.2 M NaOH solution was added and the mixing solution was kept stirring for 24 h. After that, it was transferred to 100 mL Teflon-sealed autoclave and maintained at 433 K for 4, 8 and 16 h, respectively. The resulting sample was recovered by filtration, washed by water, and fully dried at 333 K in oven to get the final flower-like Bi_2WO_6 samples.

Ref. S1: L. Zhang, W. Wang, Z. Chen, L. Zhou, H. Xu and W. Zhu, *J. Mater. Chem.*, 2007, **17**, 2526.

Characterization:

The morphology information was determined by a field-emission scanning electron microscope (FESEM, FEI Nova NANOSEM 230). The crystalline structure of the catalysts was determined by powder X-ray diffraction (XRD), using Ni-filtered Cu Kα radiation in the 2θ range from 5° to 80° with a scan rate of 0.08° per second. The optical properties of the catalysts were analyzed by UV-vis diffuse reflectance spectroscopy (DRS) using a Cary-500 spectrophotometer over a wavelength range of 200-800 nm, during which $BaSO_4$ was employed as the internal reflectance standard. Nitrogen adsorption-desorption isotherms and the Brunauer-Emmett-Teller (BET) surface area were collected at 77K using Micromeritics ASAP 2010 equipment.

The photoluminescence (PL) spectra was measured on an Edinburgh FL/FS900 spectrophotometer. For the PL analysis of solid samples of Bi_2WO_6, the excitation wavelength is 340 nm. The PL spectra are often employed to study surface processes involving the electron-hole fate of semiconductor. With the electron-hole pairs recombination after a semiconductor photocatalyst is irradiated, photons are emitted, thus resulting in PL. Thus, the PL analysis of solid Bi_2WO_6 sample reflects the fate of electron-hole pairs photogenerated from semiconductor Bi_2WO_6.

For the PL analysis of hydroxyl radicals photogenerated in solution, the terephthalic acid (TA) was used as a probe molecule which can capture hydroxyl radicals photogenerated in Bi_2WO_6 aqueous suspension to produce 2-hydroxyl terephthalic acid (TAOH) and the as-formed TAOH exhibits the characteristic PL peak. Such a well-established PL-TA method is widely used to detect the hydroxyl radicals photogenerated in an aqueous suspension of semiconductors.[S2]

In particular, for the PL analysis of hydroxyl radicals photogenerated in solution, the terephthalic acid (TA) was used as a probe molecule which can react with hydroxyl radicals and the as-formed complex

exhibits characteristic PL spectra. Typically, the as-prepared catalyst powder was dispersed in TA/NaOH aqueous solution (1:2, mol/mol). The mixture was stirred for 1 h in the dark to blend well and allow the adsorption-desorption equilibrium before the irradiation of visible light (λ>420 nm). The suspension was magnetically stirred before and during the irradiation. A 3 mL sample solution was drawn form the system at a certain time interval during the experiment, which was subject to the PL analysis with an excitation wavelength of 312 nm.

The analysis of H_2O_2 generated in the photocatalytic reaction system was performed by a photometric method. Typically, the measurement of H_2O_2 was carried out in a 10 mL Pyrex glass bottle under the irradiation of visible light. In a typical process for measurement the concentration of H_2O_2 under visible light irradiation, a mixture of 8 mg catalyst and 1.5 mL of water, which was saturated with pure molecular oxygen. The above mixture was transferred into a 10 mL Pyrex glass bottle and stirred for 10 min to make the catalyst blend evenly in the solution. The suspensions were irradiated by a 300 W Xe arc lamp with a UV cutoff filter (λ>420 nm). After the reaction, the mixture was centrifuged at 12,000 rmp for 20 min to completely remove the catalyst particles, and then 10 μL of *N*, *N*-diethyl-*p*-phenylenediamine (DPD) and 10 μL of peroxidase (POD) was added. The solution was analyzed on a Varian UV-vis spectrophotometer (Cary-50, Varian Co.).

Electron spin resonance (ESR) signal of the radicals spin-trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was measured using Bruker EPR A300 spectrometer. The settings for the ESR spectrometer were as follows: center field=3507 G, microwave frequency=9.84 GHz and power=6.36 mW; the visible light irradiation source was a 300 W Xe arc lamp system equipped with a UV cutoff filter (λ > 420 nm).

The electrochemical measurements were carried out in a three-electrode quartz cell. A Pt plate was used as the counter electrode, and a Ag/AgCl electrode used as the reference electrode. The working electrode was prepared in indium–tin oxide (ITO) conductor glass. A 5 mg sample was ultrosonicated in 0.5 mL of anhydrous ethanol to disperse it evenly to get slurry. The slurry was spreading onto ITO glass whose side part was previously protected using scotch tape. The working electrode was dried overnight under ambient conditions. A copper wire was connected to the side part of the working electrode using a conductive tape. Uncoated parts of the electrode were isolated with epoxy resin. The electrolyte was 0.2 M aqueous Na_2SO_4 solution (pH=6.8) without additive. The photocurrent measurements were conducted on a BAS Epsilon workstation without bias. The visible light irradiation source was a 300 W Xe arc lamp system equipped with a UV cutoff filter (λ > 420 nm).

Ref. S2: N. Zhang, S. Liu, X. Fu and Y. J. Xu, *J. Phys. Chem. C*, 2011, **115**, 9136.

Photocatalytic activity

As previously done for photocatalytic oxidation of alcohols in the organic solvent of benzotrifluoride (BTF),[S3-S6] selective oxidation of glycerol in the solvent of water was carried out in a 10 mL Pyrex glass bottle under the irradiation of visible light. In a typical process, a mixture of 8 mg catalyst and 0.1 mmol of glycerol were dissolved in the solvent 1.5 mL of water, which was saturated with pure molecular oxygen from a gas cyclinder. The above mixture was transferred into a 10 mL Pyrex glass bottle and stirred for 10 min to make the catalyst blend evenly in the aqueous phase with a pH value ca. 6.7 (Notably, without the catalyst, the pH value of glycerol solution in water is ca. 6.8). The suspensions were irradiated by a 300 W Xe arc lamp with a UV cutoff filter (λ>420 nm). After the reaction, the mixture was centrifuged at 12,000 rmp for 20 min to completely remove the catalyst particles. The remaining solution was analyzed with a Shimadzu Liquid Chromatograph (DGU-20A3, equipped with a 512 Diode Array Detector and a C18 analysis column). In order to confirm if the as-prepared Bi_2WO_6 photocatalyst is very active and, in particular, highly selective toward oxidation of glycerol to DHA, we have also performed the scale-up experiments by using five times the amount glycerol, i.e., 0.5mmol, while other reaction conditions are the same as that described above.

Controlled photoactivity experiments using different radicals scavengers (ammonium oxalate as scavenger for photogenerated holes,[S7] tert-butyl alcohol as scavenger for hydroxyl radicals,[S7] $AgNO_3$ as scavenger for electrons,[S8,S9] and benzoquinone as scavenger for superoxide radical species[S10,S11]) were performed similar to the above photocatalytic oxidation of glycerol except that radicals scavengers (0.1 mmol) was added to the reaction system.

Conversion of glycerol (GC), yield of dihydroxyacetone (DHA) and selectivity for dihydroxyacetone (DHA) based on a GC analysis were defined as the follows:

$$Conversion\ (\%) = [(C_0 - C_{GC})/C_0] \times 100$$

$$Yield(\%) = C_{DHA}/C_0 \times 100$$

$$Selectivity(\%) = [C_{DHA}/(C_0 - C_{GC})] \times 100$$

Where C_0 is the initial concentration of glycerol, C_{GC} and C_{DHA} are the concentration of glycerol and dihydroxyacetone (DHA), respectively, at a certain time after the photocatalytic reaction. In order to confirm the nature of product DHA by ^{13}C NMR nucluear magnetic resonance (NMR) analysis, a post-separation and purification process of DHA using the column chromotograph on silica get with acetone as eluent[S12] is performed, which is described in the Appendix in Supporting Information. The ^{13}C NMR nucluear magnetic resonance (NMR) spectra were performed using a Bruker Avance III 400 spectrometer. Details for the separation of residual reactant glycerol and product DHA for ^{13}C NMR analysis are provided in the Appendix in Supporting Information.

Ref. S3: Y. Zhang, Z. R. Tang, X. Fu and Y. J. Xu, *ACS Nano*, 2011, **5**, 7426.

Ref. S4: M. Zhang, C. Chen, W. Ma and J. Zhao, *Angew. Chem. Int. Ed.*, 2008, **47**, 9730.

Ref. S5: N. Zhang, X. Fu and Y. J. Xu, *J. Mater. Chem.*, 2011, **21**, 8152.

Ref. S6: N. Zhang, S. Liu, X. Fu and Y. J. Xu, *J. Phys. Chem. C*, 2011, **115**, 22901.

Ref. S7: W. Li, D. Li, Y. Lin, P. Wang, W. Chen, X. Fu and Y. Shao, *J. Phys. Chem. C*, 2012, **116**, 3552.

Ref. S8: O. Carp, C. L. Huisman and A. Reller, *Prog. Solid State Chem.*, 2004, **32**, 33.

Ref. S9: A. Primo, T. Marino, A. Corma, R. Molinari and H. García, *J. Am. Chem. Soc.*, 2011, **133**, 6930.

Ref. S10: M. Stylidi, D. I. Kondarides and X. E. Verykios, *Appl. Catal., B*, 2004, **47**, 189.

Ref. S11: P. Raja, A. Bozzi, H. Mansilla and J. Kiwi, *J. Photochem. Photobio., A*, 2005, **169**, 271.

Ref. S12: R. M. Painter, D. M. Pearson and R. M. Waymouth, *Angew. Chem. Int. Ed.*, 2010, **49**, 9456.

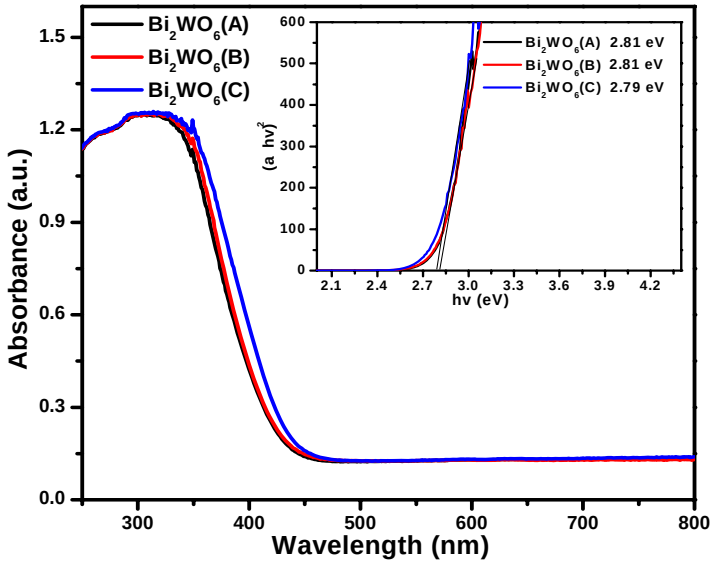


Fig. S1. The UV–visible diffuse reflectance spectra (DRS) of Bi_2WO_6(A), Bi_2WO_6(B), and Bi_2WO_6(C); inset is the estimated energy band gap by the plot based on the Kubelka-Munk function versus the energy of light.

Table S1. Photocatalytic selective oxidation of glycerol over Bi_2WO_6 (B) under the irradiation of visible light for 4 h in different solvents.

Solvent	Conversion (%) glycerol	Selectivity (%)	
		DHA	glyceraldehyde
H_2O	91	93	7
CH_3CN	84	91	9
BTF	73	89	11
DMF	77	90	10

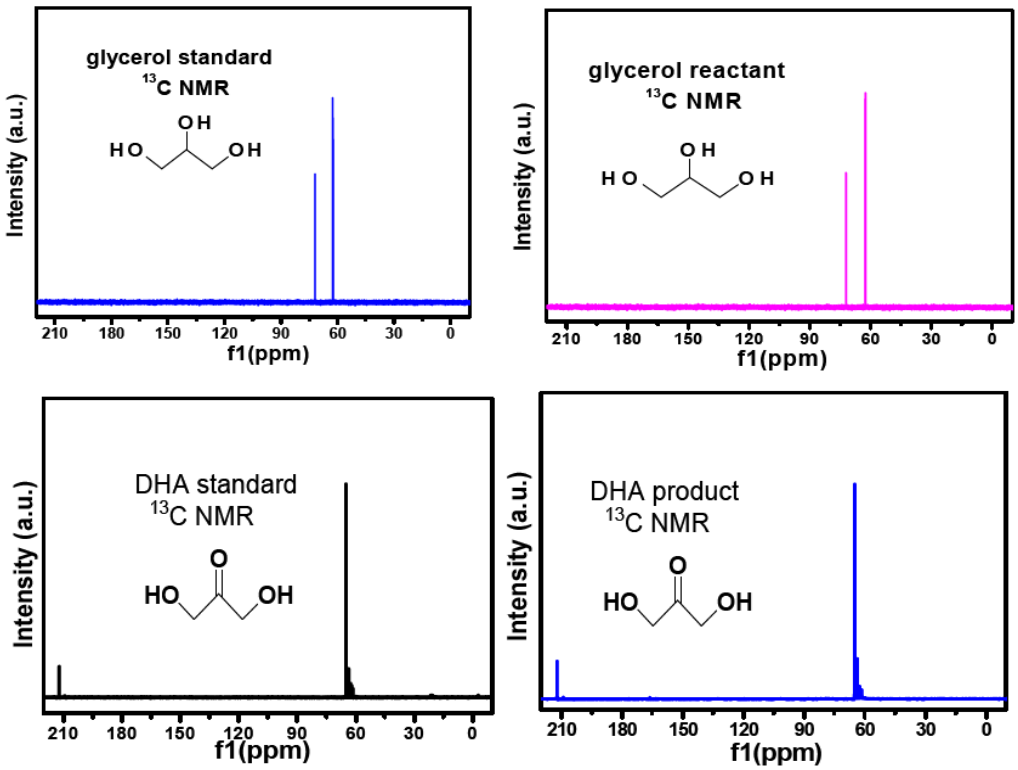


Fig. S2. ^{13}C nuclear magnetic resonance (NMR) spectra of glycerol and dihydroxyacetone (DHA).

Note: left column is the ^{13}C NMR of standard samples of glycerol and DHA; right column is the ^{13}C NMR of sample glycerol and DHA after the photocatalytic reaction and separation process of reactant and product.

The details for the separation of product DHA and purification of DHA by chromotograph column on silica gel using acetone as eluent after photocatalytic reaction and ^{13}C NMR analysis are provided in the Appendix below.

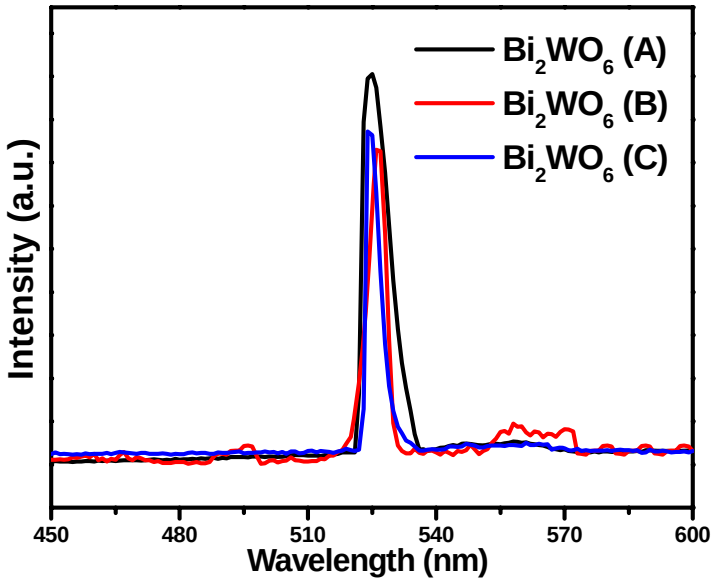


Fig. S3. The photoluminescence (PL) spectra of samples of flower-like Bi_2WO_6(A), Bi_2WO_6(B), and Bi_2WO_6(C) with an excitation wavelength of 340 nm.

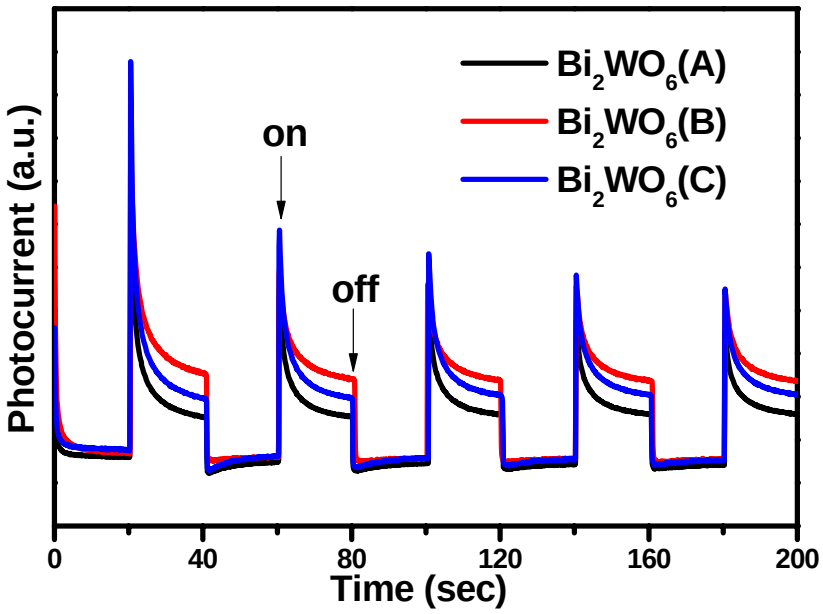
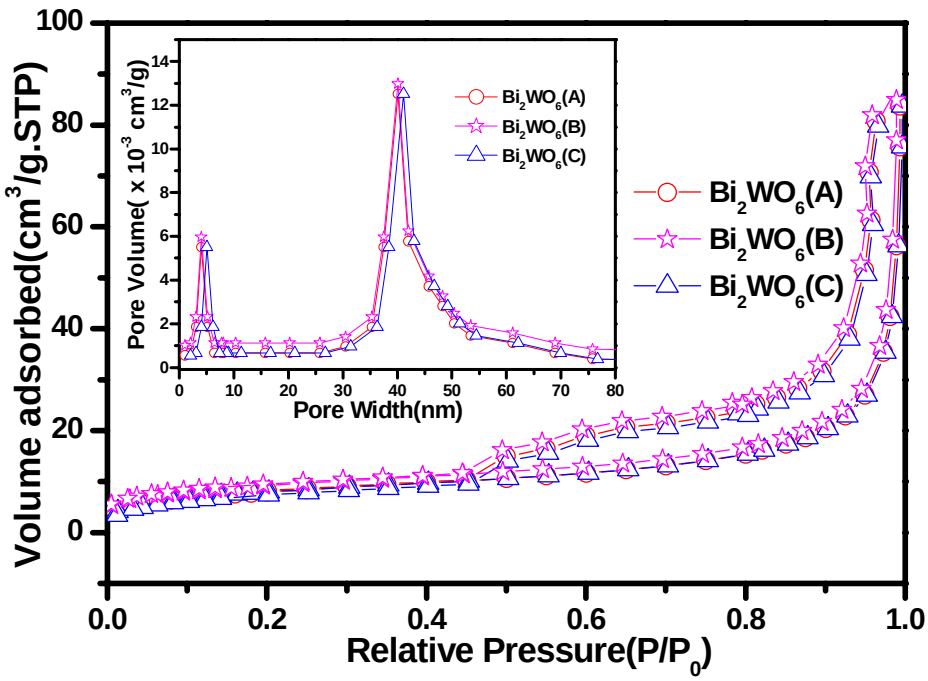


Fig. S4. Photocurrent transient responses of the samples of Bi_2WO_6(A), Bi_2WO_6(B), and Bi_2WO_6(C) under the irradiation of visible light at a 0 V bias condition.



Sample	Bi_2WO_6 (A)	Bi_2WO_6 (B)	Bi_2WO_6 (C)
surface area (m^2/g)	30	31	31
pore volume (cm^3/g)	0.16	0.16	0.16

Fig. S5. N_2 adsorption–desorption isotherms of the samples of Bi_2WO_6(A), Bi_2WO_6(B), and Bi_2WO_6(C); and the summary of surface area and pore volume. Inset is the pore size distribution curve.

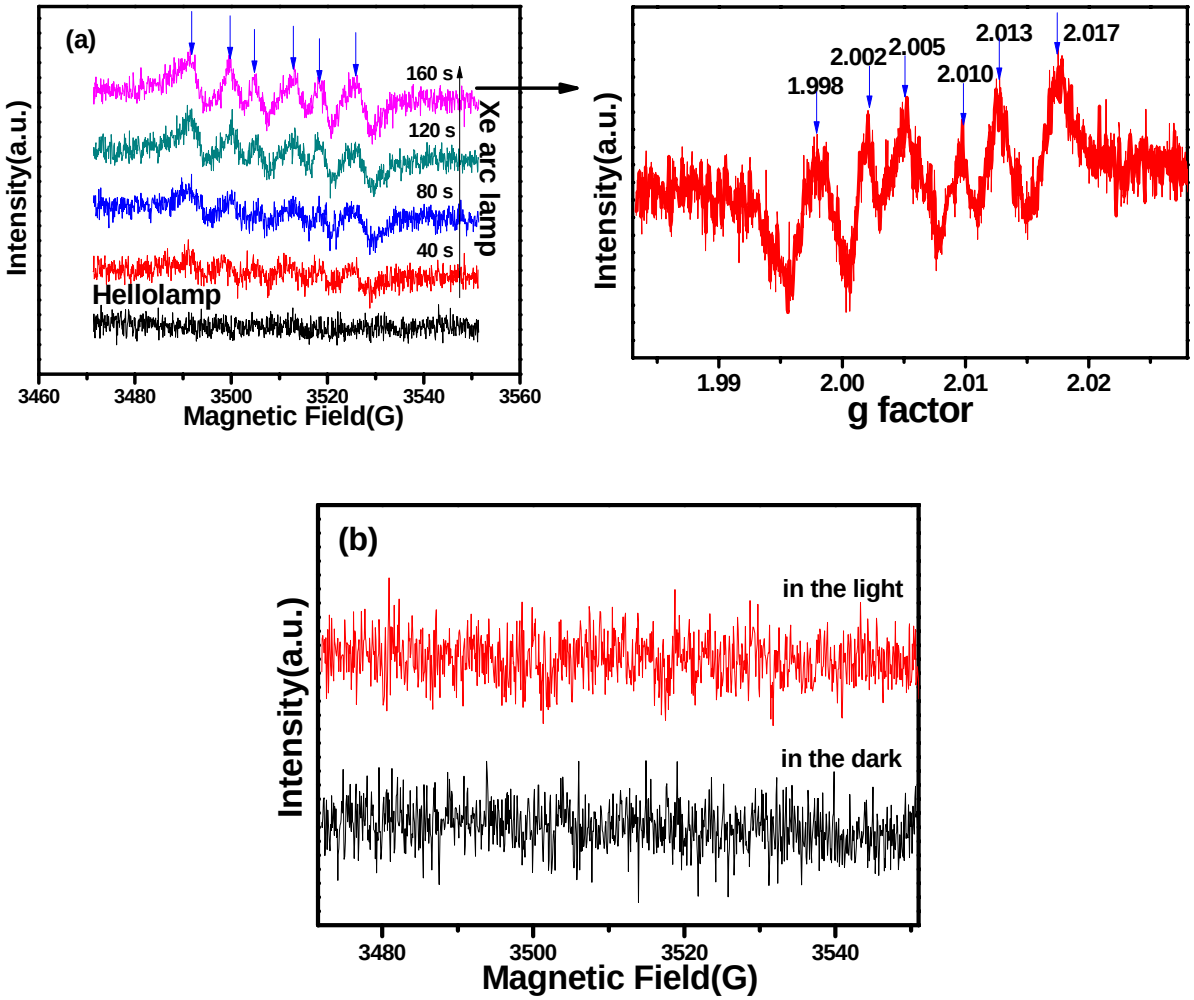


Fig. S6. Electron spin resonance (ESR) spectra of superoxide radicals trapped by DMPO and corresponding g factor over Bi_2WO_6 suspension in methanol solution (a); no hydroxyl radicals trapped by DMPO are detected by ESR over Bi_2WO_6 suspension in aqueous solution (b).

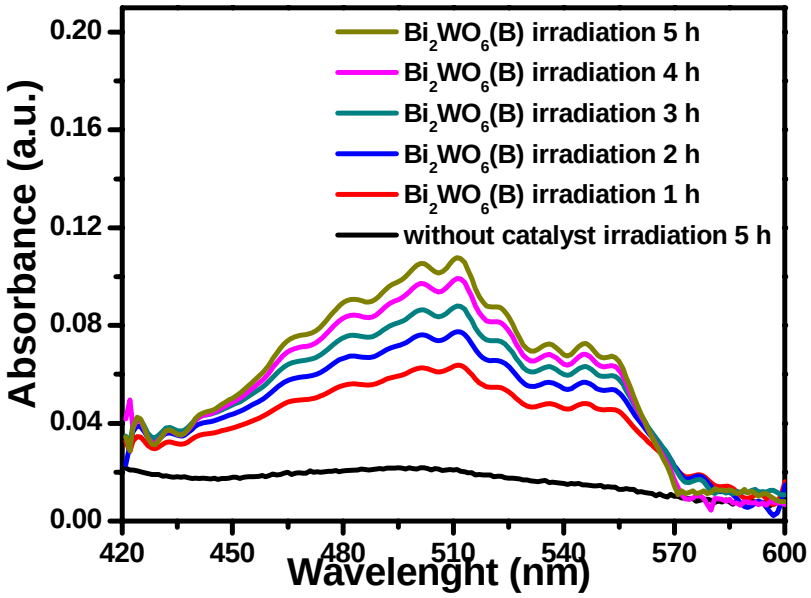


Fig. S7. The absorption spectra of the flower-like Bi_2WO_6(B) aqueous solution in the presence of peroxidase (POD) and N, N-diethyl-*p*-phenylenediamine (DPD) after visible light irradiation for 2 h.[S13] Note: the appearance of absorption peaks located at ca. 510 nm and 551 nm indicates the presence of H_2O_2 formation in our photocatalytic reaction system.

Ref. S13: H. Bader, V. Sturzenegge and J. Hoigné, *Wat. Res.*, 1988, **22**, 1109.

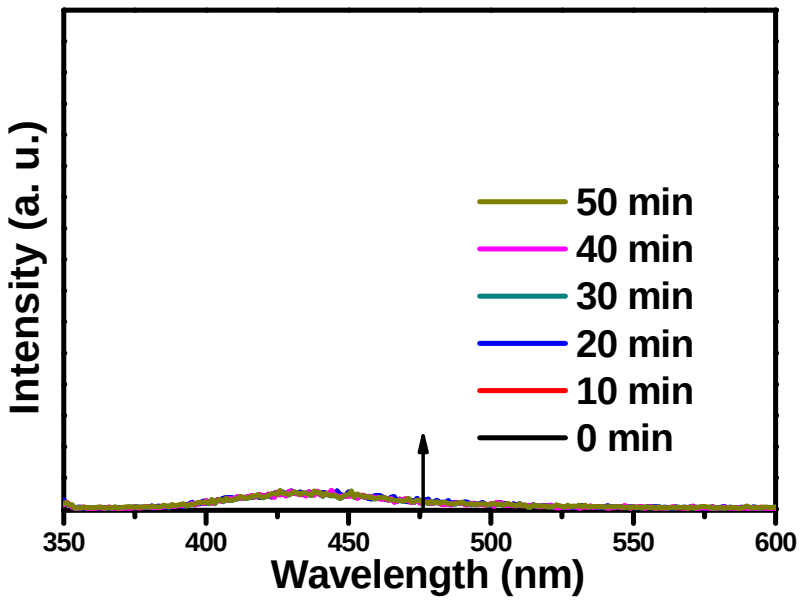
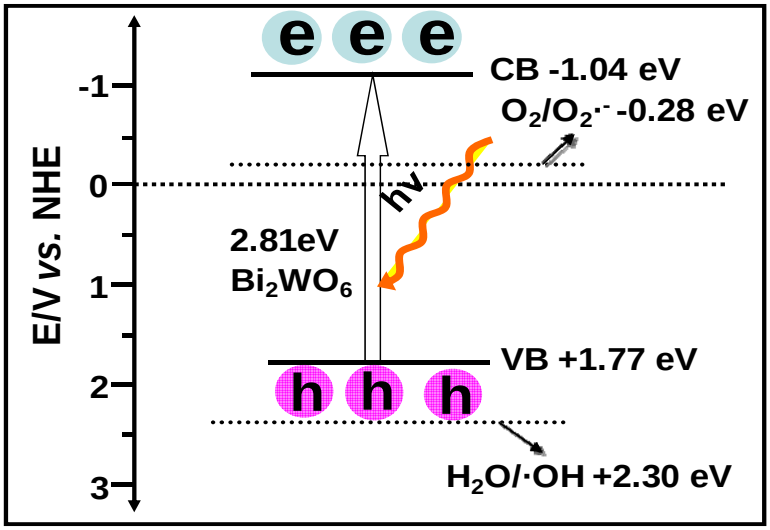


Fig. S8. The $^{\bullet}$OH-trapping photoluminescence (PL) spectra (excitation wavelength, 312 nm) of the sample of flower-like Bi_2WO_6(B) aqueous solution.



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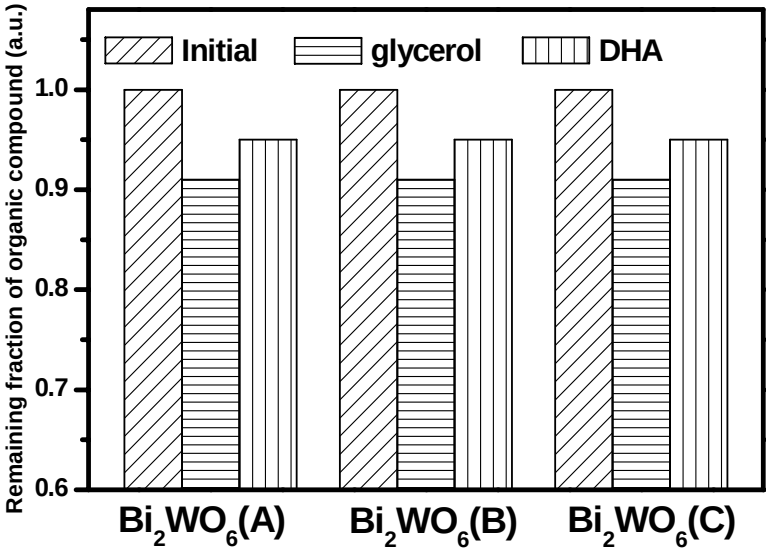

Fig. S10. Remaining fraction of glycerol and dihydroxyacetone (DHA) after the adsorption-desorption equilibrium in the dark is achieved over the samples of Bi_2WO_6 (A), Bi_2WO_6 (B), and Bi_2WO_6 (C).

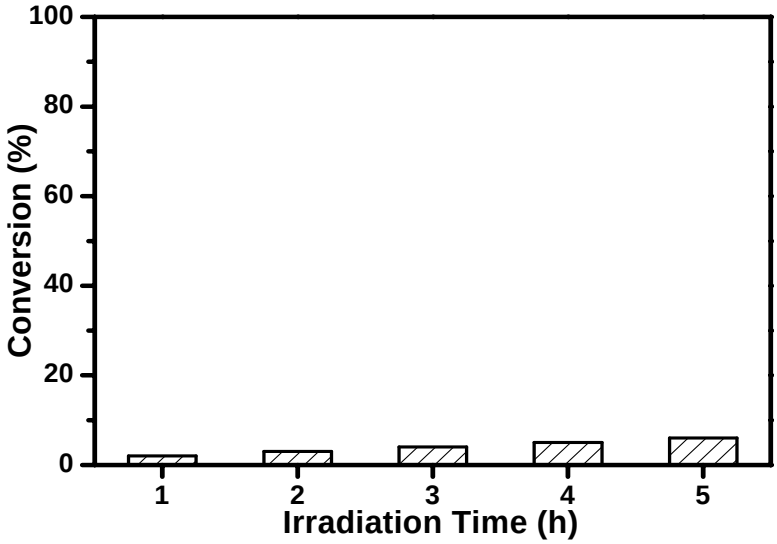

Fig. S11. Stability photoactivity test of only DHA in water over Bi_2WO_6(B) photocatalyst under visible light irradiation.

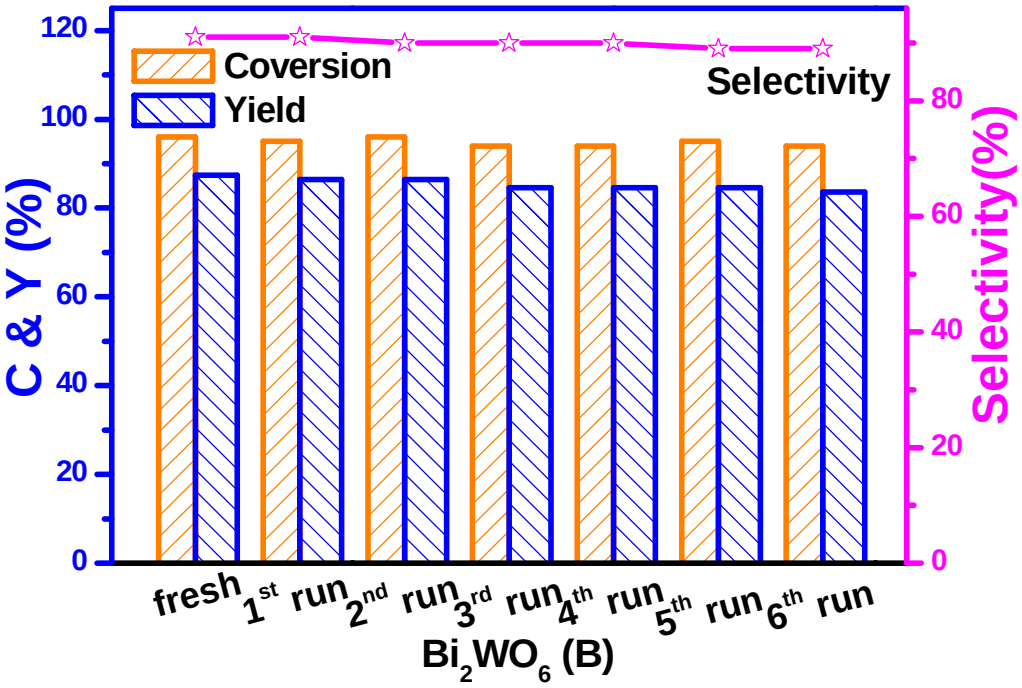

Fig. S12. Recycled photoactivity test for six times operational runs of the optimum sample Bi_2WO_6(B) toward selective oxidation of glycerol to DHA in water under visible light irradiation for 5 h.

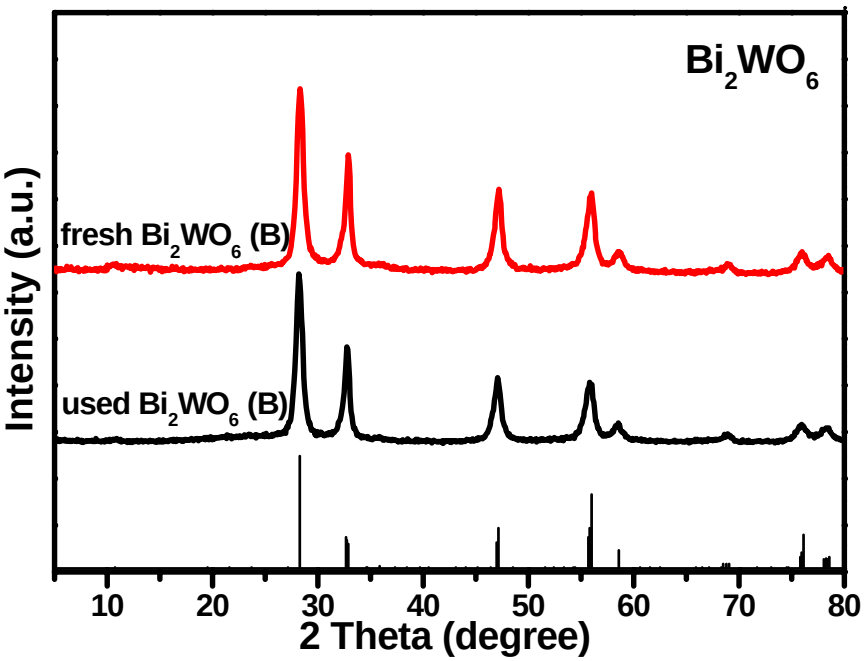

Fig. S13. XRD patterns of fresh Bi_2WO_6(B), and used Bi_2WO_6(B) after selective oxidation of glycerol to DHA in water under visible light irradiation for 5 h.

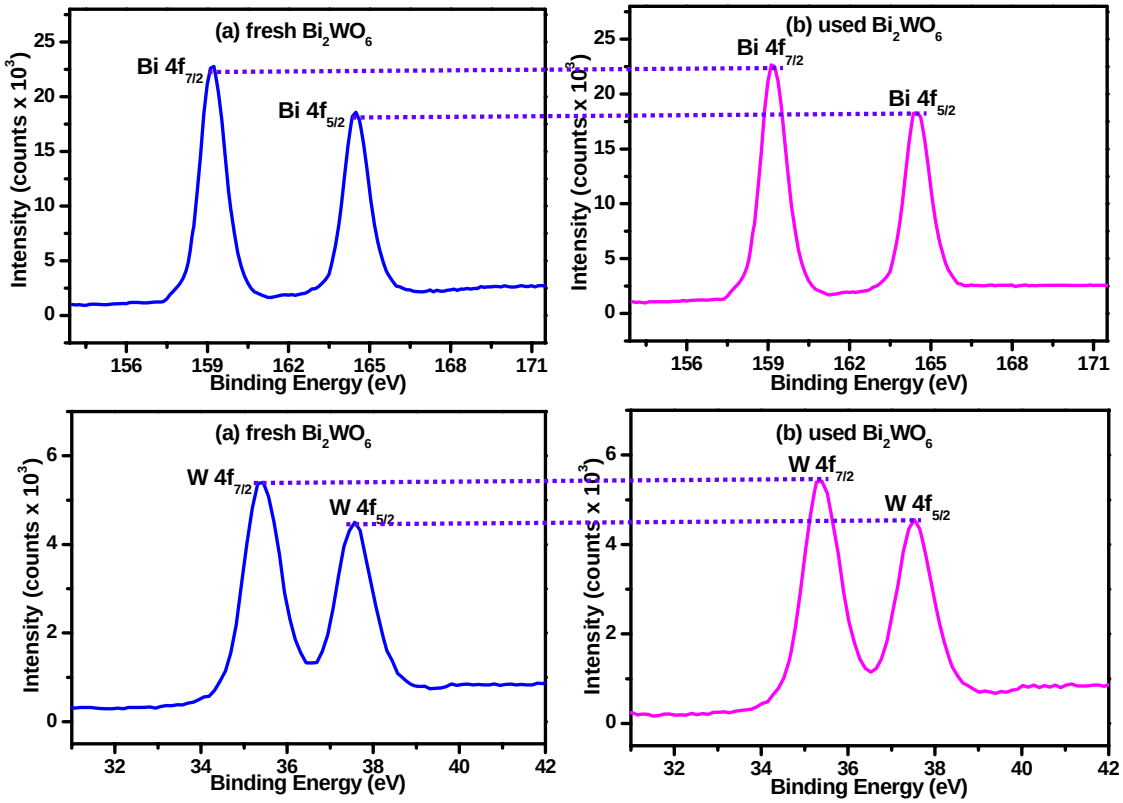

Fig. S14. XPS spectra of fresh Bi_2WO_6(B), and used Bi_2WO_6(B) after selective oxidation of glycerol to DHA in water under visible light irradiation for 5 h.

Appendix.

It is well known that the melting point and boiling point of DHA are about 75-80 ℃ and 213.7 ℃, whereas the melting point and boiling point of glycerol are about 17.8 ℃ and 210 ℃. However, the boiling point of water is 100 ℃. Therefore, the suspension of glycerol and DHA after photocatalytic reaction can be easily separated from the solvent of water by a simple rotary evaporation process.

Typically, after the reaction by visible light irradiation by a 300 W Xe arc lamp with a UV-cutoff filter (λ>420 nm) for 2 h, the mixture suspension (**panel a**, **Fig. S15**) was centrifuged to completely remove the catalyst particles. And then, the as-obtained solution was transferred into a Round-bottom glass flask (**panel b**, **Fig. S15**). The solution was then evaporated in a rotary evaporator with water-bath at 328 K in vacuum, by which the solvent of water was separated and removed. Consequently, the products and reactants were left in the round bottom flask (**panel c**, **Fig. S15**). This mixture solution was then transferred into a 1.5 mL centrifugal tube; followed by a centrifugation process, a two-layer separated solution was obtained (**panel d**, **Fig. S15**). The upper layer solution is primarily the remaining reactant glycerol while the lower layer solution with a slight yellow color is primary product DHA. The upper layer solution was then extracted from the centrifugal tube, which was subject to the ^{13}C nuclear magnetic resonance (^{13}C NMR) analysis. On the other hand, the lower solution was quickly transferred to a filter paper, which turns into a solid sample at room temperature because the melting point of DHA are about 75-80 ℃.

To further purify the product dihydroxyacetone (DHA), we further apply the column chromatography on silica gel using acetone as the eluent.[S12] The as-obtained product DHA after this purification process was subject to the ^{13}C nuclear magnetic resonance (^{13}C NMR) analysis. Typically, the sample (1 mmol) was dispersed in the solvent deuterated oxide (D_2O, 0.6 mL). ^{13}C NMR was recorded using a Bruker Avance III 400 spectrometer. The corresponding ^{13}C NMR spectra of samples are displayed in the right column in Fig. S2.

Ref. S12: R. M. Painter, D. M. Pearson and R. M. Waymouth, *Angew. Chem. Int. Ed.*, 2010, **49**, 9456.

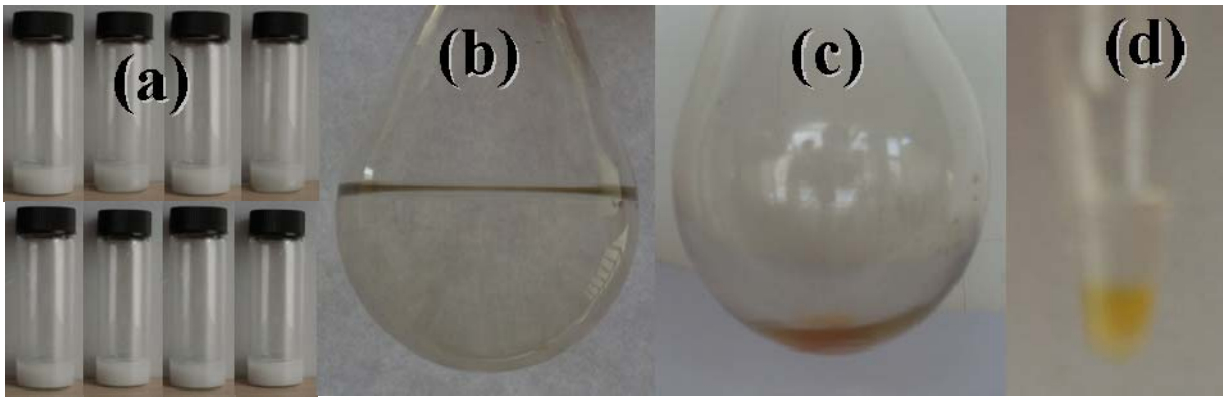

Fig. S15. The sample pictures of the suspension after the photocatalytic reaction under visible light irradiation for 2h (a); the suspension after removing the catalyst particles *via* a centrifugation process (b); the remaining solution after removing the solvent of water *via* a rotary evaporation process in a water-bath at 328 K in vacuum (c); the two-layered solution in a 1.5 mL centrifugal tube after a centrifugation process (d).

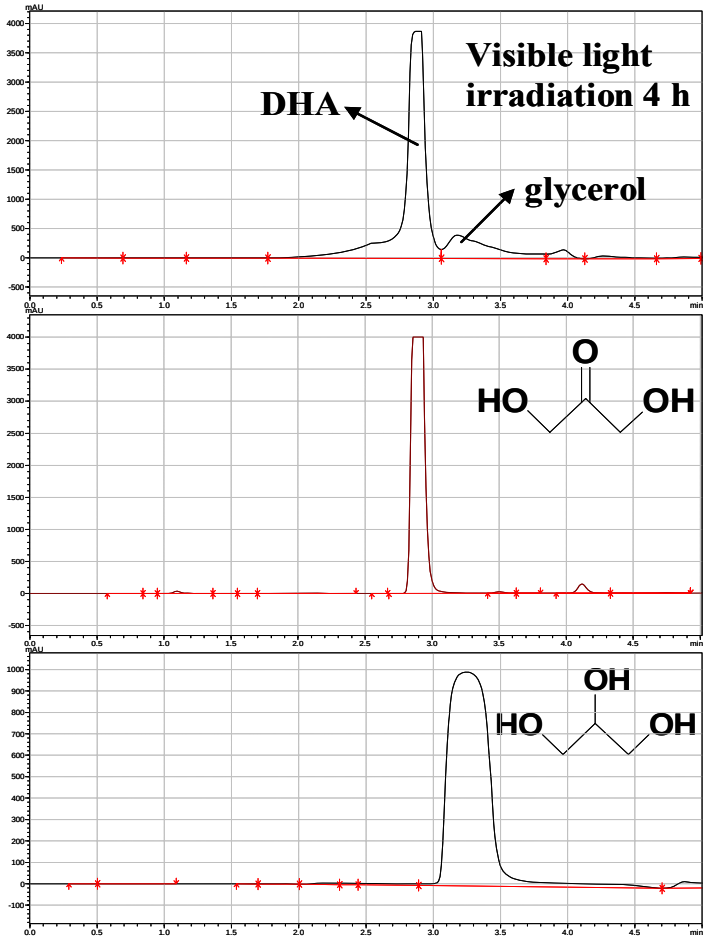

Fig. S16. The HPLC spectra to identify reactant glycerol and main product DHA for selective oxidation of glycerol in water over Bi_2WO_6 (B) photocatalyst under the irradiation of visible light for 4 h in the reaction system.