Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

$CuWO_4$ as a Photocatalyst for Room Temperature Aerobic Benzylamine Oxidation

Aaron D. Proctor, Shobhana Panuganti, Bart M. Bartlett*

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan, 48109-1055, United States

Table of Contents

Materials and Methods

Benzylamine (99%), *N*-benzylidenebenzylamine (99%), chlorobenzene (99+%, for spectroscopy), copper (II) oxide, tungsten oxide, and bismuth nitrate pentahydrate were purchased from Sigma-Aldrich. Acetonitrile (Certified ACS), dichloromethane (Certified ACS), ethanol (200 proof), and ammonium metavanadate were purchased from Fisher. Acetonitrile-d_3 was purchased from Cambridge Isotope Laboratories. Benzylamine was vacuumed distilled over NaOH and stored on sieves under N_2. All other reagents were used as received. Nylon syringe filters (25 mm, 0.2 μm membrane) were purchased from VWR or Macherey-Nagel.

Catalyst Preparation

Copper tungstate was synthesized by grinding a 1:1 mole ratio of copper (II) oxide (0.51 g) and tungsten oxide (1.49 g) in a mortar and pestle for 15 minutes followed by heating in a muffle furnace at 800 °C for 6 hours. The oven temperature ramped up to and down from 800 °C at a rate of 10 $°C \bullet min^{-1}$. Bismuth vanadate was synthesized by grinding a 1:1 mole ratio of ammonium metavanadate (0.500 g) and bismuth (III) nitrate pentahydrate (2.07 g) for 15 minutes. This was heated in a muffle furnace at 500 °C for 6 hours. The oven temperature ramped up to and down from 500 °C at a rate of 10 $°C \bullet min^{-1}$. Both $CuWO_4$ and $BiVO_4$ were placed in a 12 mL polypropylene centrifuge with 7 mL of Milli-Q (18.2 $M\Omega \bullet cm^{-1}$) water and vortexed for about 30 seconds before centrifuging at 3500 rpm for 5 minutes. The water was then decanted and the process was repeated twice more. The powder was then washed three times with ethanol before drying overnight in a vacuum oven at 60 °C.

Photocatalytic Reactions

All photocatalytic reactions were carried out in a custom-built aluminum LED assembly (Figure S1). Royal blue LEDs (λ_{max} = 460 nm) with a power rating of 1.03 W were purchased from Mouser Electronics (Mouser Part#: 997-LXML-PR02-A900). Reactions contained 20 mg of catalyst, 2 mL of substrate solution, and were run in 4 mL dram vials that had their flat bottoms visible to the LEDs while receiving a power density of 200 $mW \bullet cm^{-2}$. Reactions were capped with rubber septa, kept under O_2 using a balloon, and stirred for an hour in the dark before having an aliquot taken out to determine the initial concentration of benzylamine in each solution (procedure for making GC samples is described below). The reactions were then illuminated. For reactions run under N_2, the solutions had N_2 bubbled through them during the one hour of stirring in the dark. They were then run under an N_2 atmosphere for the rest of the experiment. A concentration of 250 mM benzylamine was used as the starting concentration of benzylamine for kinetics and selectivity experiments. Aliquots of 10 μL were taken out for each time point (every 12 hours for 60 hours) of the kinetics experiments. These were added to a GC vial that contained 990 μL of a 1.01 mM solution of chlorobenzene in acetonitrile. Conversion data for three reactions were collected and averaged for each catalyst. Reactions were analyzed by gas chromatography with a flame ionization detector. These were then converted to first order rate plots. GC-FID analysis was conducted on a Trace 1310 GC-FID system with a TG-5MS Amine column. Argon was used as the carrier gas. The heating method used for analysis was to ramp from 40 °C to 300 °C at a rate of 10 $°C \bullet min^{-1}$ and hold at 300 °C for 10 minutes before cooling. Before NMR analysis each reaction was filtered through a nylon syringe filter to remove the catalyst. A volume of 500 μL of the filtered reaction solution was added to an NMR tube that contained 100 μL of a 0.6 M dichloromethane internal standard solution in acetonitrile-d_3. Selectivity data for four reactions was collected and averaged for each catalyst. The concentration of *N*-BB was calculated using both the imine and benzylic protons and averaged. ^1H NMR data was collected on a Varian MR400

NMR spectrometer equipped with a Varian 5 mm PFG AutoX Dual Broadband probe. All NMR data was processed in MestReNova software.

Materials Characterization

The post-photolysis powders were washed with acetonitrile by adding the powder and 7 mL of acetonitrile to a 12 mL polypropylene centrifuge tube and vortexing for about 30 seconds before centrifuging at 3500 rpm for 5 minutes. This was decanted and repeated twice more. The powders were then dried in a vacuum oven at 60 °C overnight. Powder x-ray diffraction data were collected on a Panalytical Empyrean diffractometer at a power of 1.8 kW (45 kV, 40 ma) with Cu Kα (λ = 1.5418 nm) radiation. The detector was a X'Celerator Scientific, a position sensitive 1D detector equipped with Bragg-Brentano^{HD} x-ray optic delivering only Kα radiation. Patterns were collected with a sampling step of 0.020 and a scan rate of 0.080°• s^{-1} while spinning at a rate of 0.25 Hz. A Zeiss LEO 1455VP scanning electron microscope at an accelerating voltage of 10 kV and working distance of 5 mm was used for imaging the catalysts. SEM samples were sputter-coated with gold with a Cressington 108auto sputter coater for eight seconds prior to imaging. BET surface areas of the catalysts were obtained using nitrogen adsorption measurements on a Quantachrome NOVA4200e. A Varian Cary 5000 spectrophotometer equipped with an external diffuse reflectance accessory was used for UV-vis measurements. Spectra were collected in reflectance mode and transformed into absorbance using the Kubelka-Monk function. Barium sulfate was used as a 100% reflectance standard. Infrared spectroscopy was conducted using a Thermo Scientific Nicolet iS50 FT-IR with an ATR attachment.

Catalyst Recyclability and Metal Leaching

Multiple photochemical oxidations of benzylamine were done with the same batch of catalyst to determine recyclability of both $CuWO_4$ and $BiVO_4$. Dissolved metal content in each successive reaction solution was also determined. The method used for carrying out these photocatalytic reactions is identical to that described above. Each reaction was illuminated for 24 hours. After this illumination time, the reactions were centrifuged for 10 minutes at 2500 rpm and 500 µL was removed. This was filtered through a nylon syringe filter and diluted with aqueous HNO_3 / 0.01% TritonX-100 to give a solution 0.5% in reaction solution by volume. This was used for ICP-MS analysis of the dissolved metal content in the post-photolysis solution. All ICP-MS measurements were conducted on a PerkinElmer NexION 2000 ICP-MS instrument. The conversion of benzylamine in each reaction was determined with GC as it was with the kinetics experiments described above. The reaction then had the majority of the remaining solution removed with a pipet, being careful to not remove any catalyst. A volume of 2 mL of acetonitrile was added to the dram vial. This was stirred for 5 minutes in the dark before being centrifuged. The solution was again removed, and a new volume of acetonitrile was added. This washing procedure was repeated four times. The catalyst was then put in a vacuum oven at 50 °C to dry overnight. This catalyst was then used in further photochemical oxidation reactions of benzylamine. Four trials of five successive reactions were conducted for each catalyst.

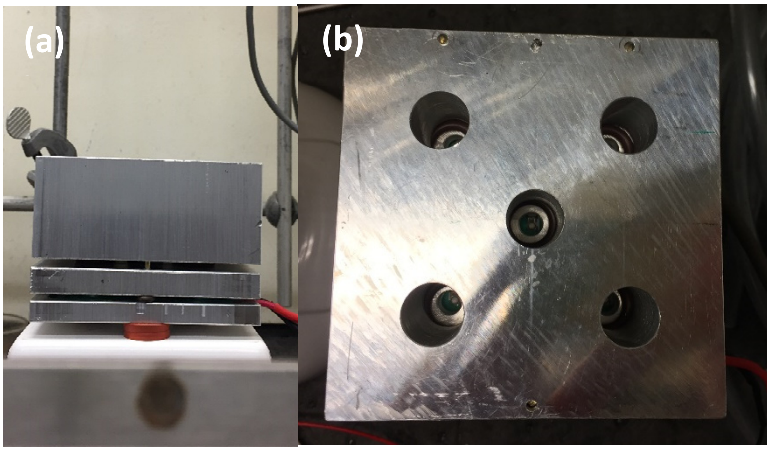


Figure S1: Custom-built blue LED setup. View from (a) side-on and (b) top-down.

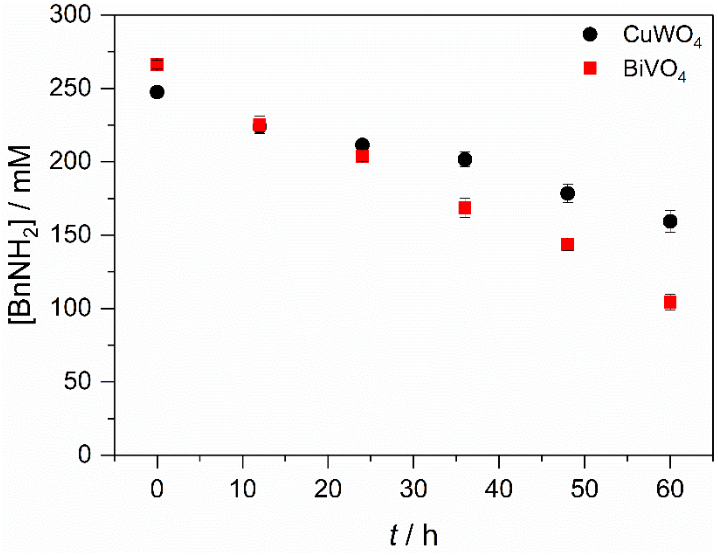


Figure S2: Decrease in benzylamine concentration over the course of the photochemical oxidation on $CuWO_4$ (black circles) and $BiVO_4$ (red squares).

Table S1: Values calculated for the decrease in benzylamine concentration over time during the photocatalytic oxidation on $CuWO_4$.

Time (h)	Trial 1 [$BnNH_2$] (mM)	Trial 2 [$BnNH_2$] (mM)	Trial 3 [$BnNH_2$] (mM)
0	248	245	249
12	225	218	229
24	209	211	213
36	207	195	203
48	173	174	187
60	166	149	164

Table S2: Values calculated for the decrease in benzylamine concentration over time during the photocatalytic oxidation on $BiVO_4$.

Time (h)	Trial 1 [$BnNH_2$] (mM)	Trial 2 [$BnNH_2$] (mM)	Trial 3 [$BnNH_2$] (mM)
0	263	265	270
12	230	217	229
24	207	206	198
36	164	178	163
48	146	147	138
60	104	111	98

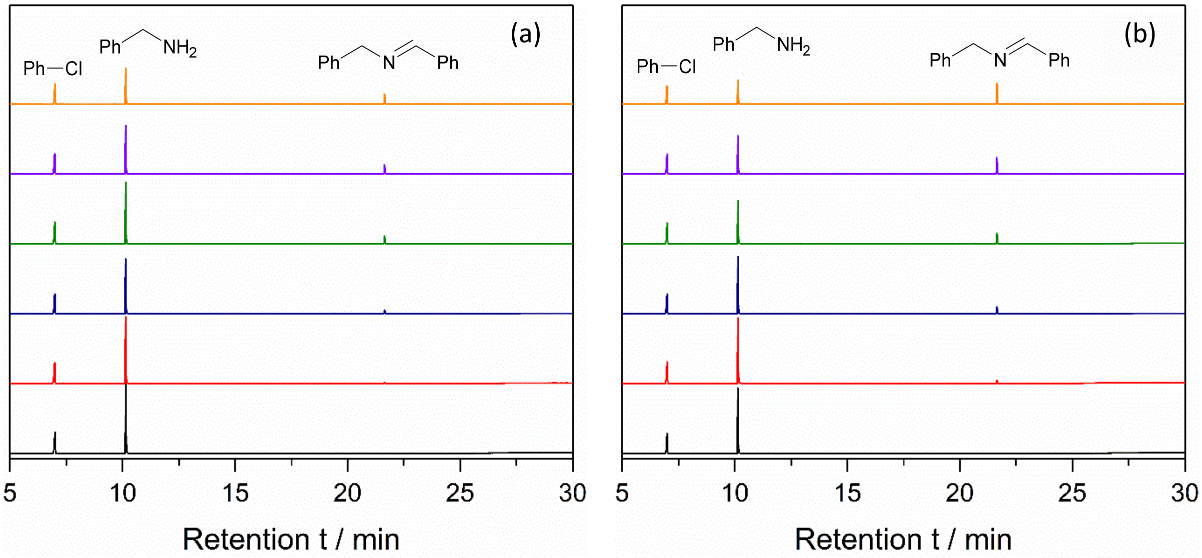
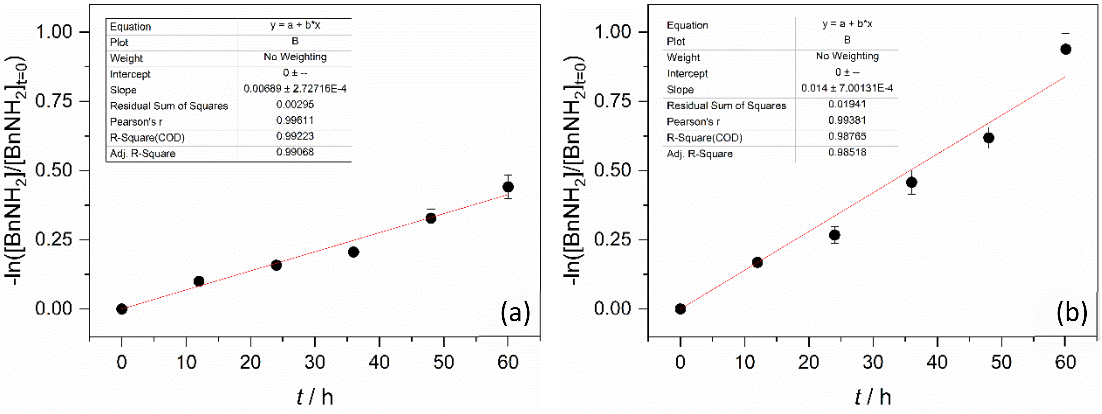


Figure S3: GC-FID traces of the photochemical oxidation of benzylamine on (a) $CuWO_4$ and (b) $BiVO_4$ at times 0 h (black), 12 h (red), 24 h (navy), 36 h (green), 48 h (violet), and 60 h (orange).



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	0 ± --
Slope	0.00689 ± 2.72716E-4
Residual Sum of Squares	0.00295
Pearson's r	0.99611
R-Square(COD)	0.99223
Adj. R-Square	0.99068

Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	0 ± --
Slope	0.014 ± 7.00131E-4
Residual Sum of Squares	0.01941
Pearson's r	0.99381
R-Square(COD)	0.98765
Adj. R-Square	0.98518

Figure S4: Linear fits for the rate constants obtained from the photochemical oxidation of benzylamine on (a) $CuWO_4$ and (b) $BiVO_4$.

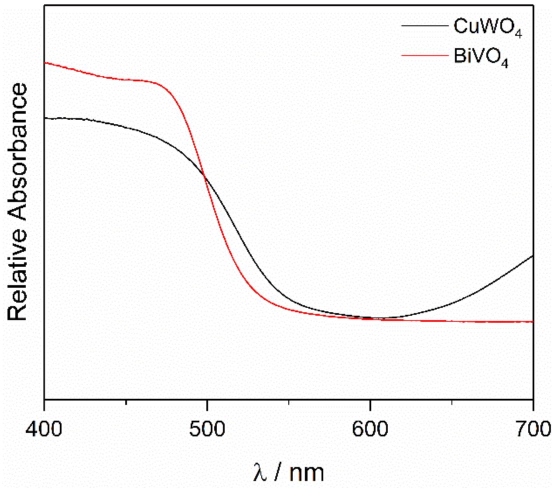


Figure S5: Diffuse reflectance spectra of as synthesized $CuWO_4$ (black) and $BiVO_4$ (red).

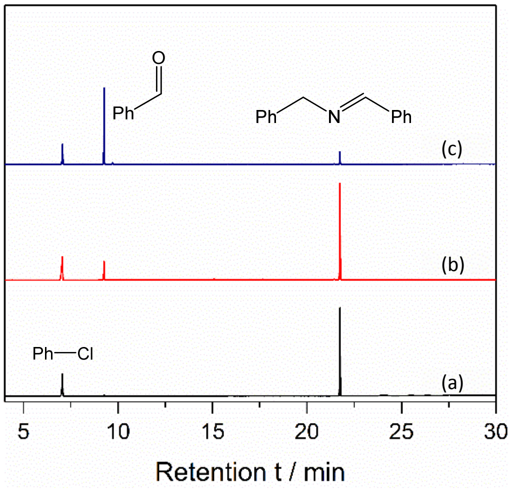


Figure S6: Oxidation of *N*-BB to BnAld. GC-FID trace of (a) 5 mM *N*-BB in acetonitrile (b) post-photolysis solution of reaction containing $CuWO_4$ and (c) post-photolysis solution of reaction containing $BiVO_4$. Reaction conditions: 20 mg of catalyst, 2 mL of 5 mM *N*-BB in acetonitrile, blue LED, O_2 atmosphere, 24 h.

Table S3: Determined concentrations of $BnNH_2$ and *N*-BB by ^1H NMR after photochemical oxidation on $BiVO_4$. The *N*-BB concentration was calculated using both the benzylic protons and imine proton. An internal standard of 1 M dichloromethane was used.

Concentration	Trial 1	Trial 2	Trial 3	Trial 4
$BnNH_2$ (mM)	28	26	22	33
N-$BB_{benzylic}$ (mM)	114	116	123	120
N-BB_{imine} (mM)	115	118	123	121

Table S4: Determined concentrations of $BnNH_2$ and *N*-BB by ^1H NMR after photochemical oxidation on $CuWO_4$. The *N*-BB concentration was calculated using both the benzylic protons and imine proton. An internal standard of 1 M dichloromethane was used.

Concentration	Trial 1	Trial 2	Trial 3	Trial 4
$BnNH_2$ (mM)	35	18	16	30
N-$BB_{benzylic}$ (mM)	97	106	105	102
N-BB_{imine} (mM)	96	106	108	104

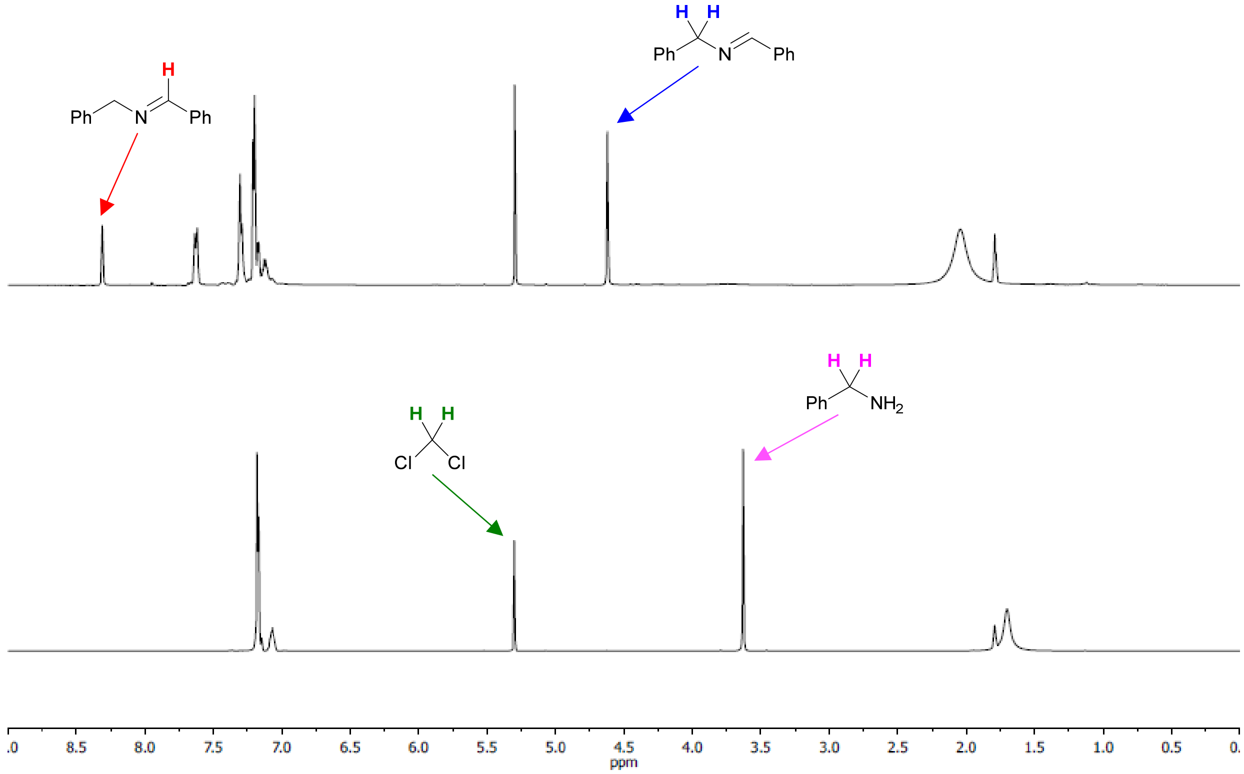


Figure S7: ^{1}H NMR spectra of 250 mM benzylamine solution pre-photolysis (bottom) and the reaction solution after 93% conversion of the benzylamine has been achieved after photochemical oxidation by $CuWO_4$ (top).

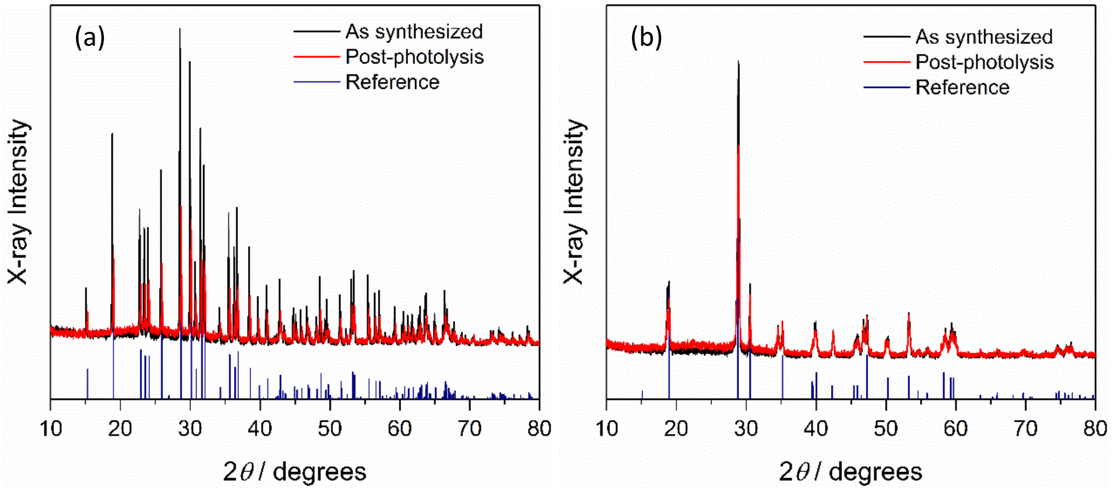


Figure S8: XRD diffractograms of (a) $CuWO_4$ and (b) $BiVO_4$. Patterns were obtained for the as synthesized powders (black) and for the catalyst collected after benzylamine oxidation (red). Reference patterns (navy) included are ICSD#24339 for $CuWO_4$ and ICSD#31550 for $BiVO_4$.

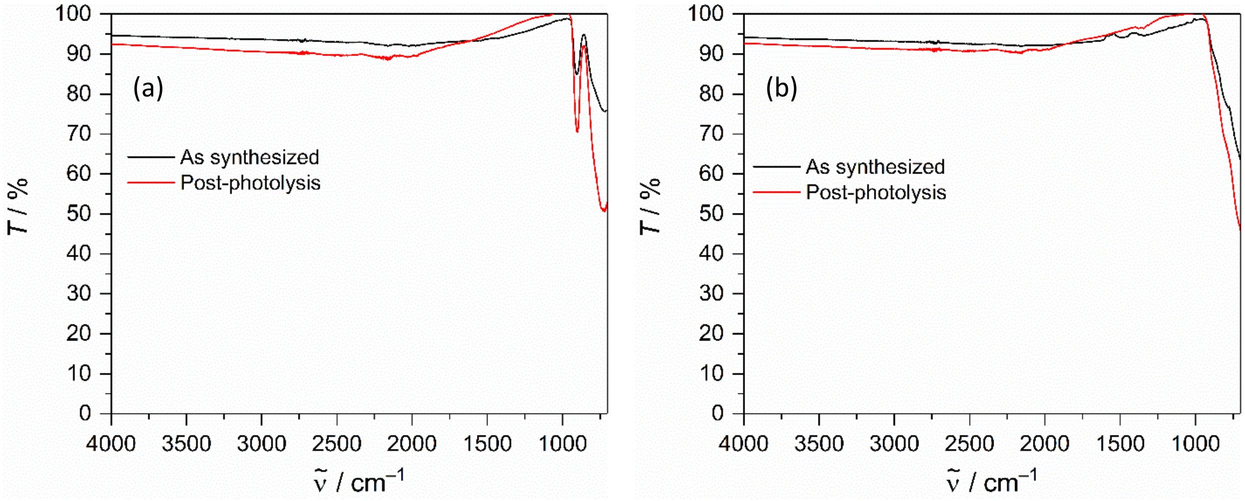


Figure S9: IR spectra of (a) $CuWO_4$ and (b) $BiVO_4$. Spectra were collected for the as synthesized powders (black) and for the catalyst collected after benzylamine oxidation (red).

Table S5: The percent of the total quantity of catalyst detected as dissolved metal detected by ICP-MS measurements of post-photolysis solutions of successive photochemical oxidations of $BnNH_2$ to *N*-BB with the same batch of catalyst.

Catalyst	Metal	Reaction Number (% of Total Catalyst Detected as Dissolved Metal)				
		1	2	3	4	5
$CuWO_4$	Cu	0.02	0.02	0.02	0.01	0.02
	W	0	0	0	0	0
$BiVO_4$	Bi	0	0	0	0	0
	V	0.01	0.01	0.01	0.01	0.01