Electronic Supplementary Information

Visible-light Photocatalytic Aerobic oxidation of amine to imine by $BiVO_4$

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: yanliu503@dicp.ac.cn, canli@dicp.ac.cn

Materials and Instruments:

All reagents and solvents used were obtained commercially and used without further purification. GC measurements were made with GC7890 equipped with a FID detector and HP-5 or β-DEX 225 column using Argon as the carrier gas. The ultraviolet–visible diffuse reflectance (Uv-Vis) spectra were collected on a JASCO V-550 spectrometer. The X-ray diffraction (XRD) of these samples were carried at room temperature on an X-ray diffractometer (Rigaku) using Cu Kα as X-ray radiation under 40kV and 30mA. The scanning electron microscopy (SEM) images were taken on a Quanta 200 FEG scanning electron microscope. N_2 adsorption–desorption isotherms (BET) were measured at 77 K, using a Micromeritics ASAP 2000 analyzer.

Catalyst preparation:

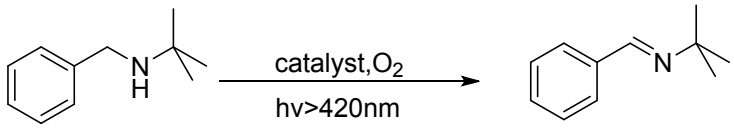
The procedures for synthesis of $BiVO_4$ samples in the present work are based on a hydrothermal approach. Typically, 1.4575g (3mmol) of $Bi(NO_3)_3{\cdot}5H_2O$ was ultrasonicated in 300mL water to dissolved it evenly. Then 1.2020g (3mmol) of $Na_3VO_4{\cdot}12H_2O$ was added with vigorous stirring and a yellow precipitate was formed. Subsequently, the yellow solution was stirred for 30 minutes and tuned the pH from 7-2 with 2M HNO_3 solution. After that, the solution was stirred for another 1 hour and transferred to 100mL Telfon-sealed autoclave and maintained at 433K for 12 hours. The resulting sample was recovered by filtration, washed by water and dried at 333K in oven.

Typical Procedure for the Oxidation of Amines:

The photocatalytic reactions were carried out under irradiation by a 300W Xe lamp with continuous stirring in a 15mL Pyrex glass bottle (cut-off light below 420nm). The Pyrex glass bottle was sealed with a glass stopper, connected to a O_2 balloon and surrounded with water to cool between 18°C and 22°C. A typical reaction system contained 0.1mmol substrate and 20mg $BiVO_4$ in 8mL CH_3CN. The products were analyzed by GC using 1,4-diisopropylbenzene as the internal standard. After the photocatalytic oxidation, the mixture was filtrated and the solvent in filtrate was removed by evaporation. Then the imine was characterized by ^1H NMR.

The procedure for the amine oxidation using $AgNO_3$ as electron acceptor

The photocatalytic reactions were carried out under irradiation by a 300W Xe lamp with continuous stirring in a 15mL Pyrex glass bottle (cut-off light below 420nm). The Pyrex glass bottle was sealed with rubber stopper. After 0.1mmol of substrate, 0.1mmol of $AgNO_3$ and 8mL of CH_3CN was added, the bottle was flushed with Argon for 1h. After the reaction, the products were analyzed by GC.



substrate	O_2	$BiVO_4$	light	time	Conversion
√	√	X	√	2h	1%
√	√	√	X	2h	0
√	X	√	√	2h	3%
√	√	√	√	2h	47%

Figure S1 Condition control experiment of N-t-butylbenzylamine oxidation

Reaction conditions: λ>420nm, catalyst (100mg), N-t-butylbenzylamine (0.1mmol), CH_3CN as a solvent (8mL), irradiation time : 2h, oxygen balloon (1 atm)

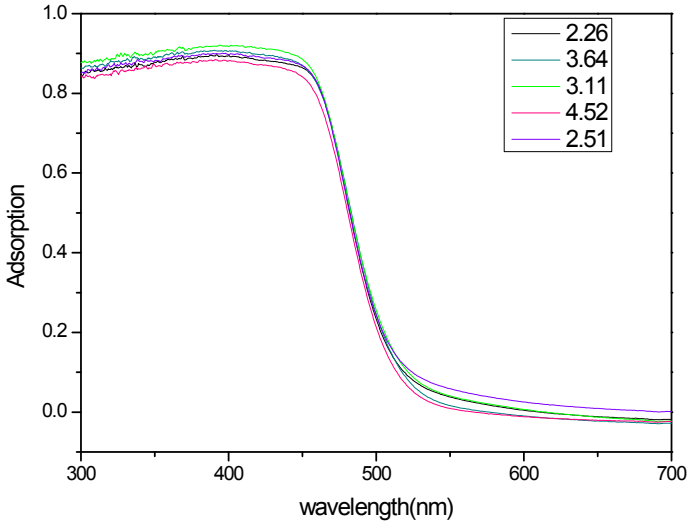


Figure S2 Uv-Vis of various $BiVO_4$ photocatalyst prepared under different PH

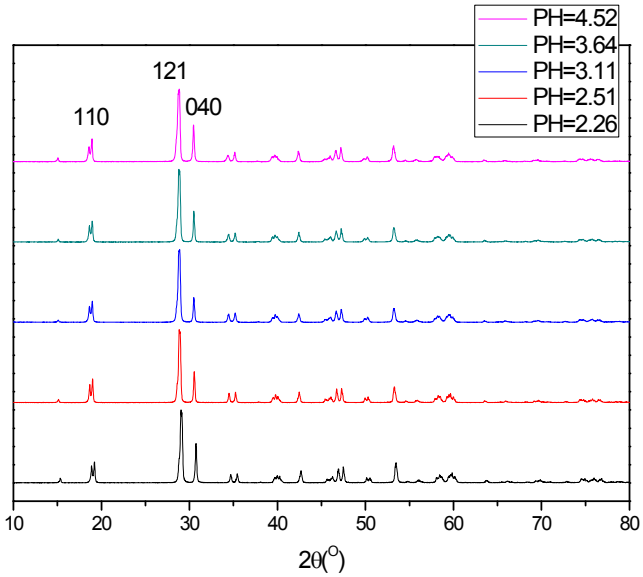
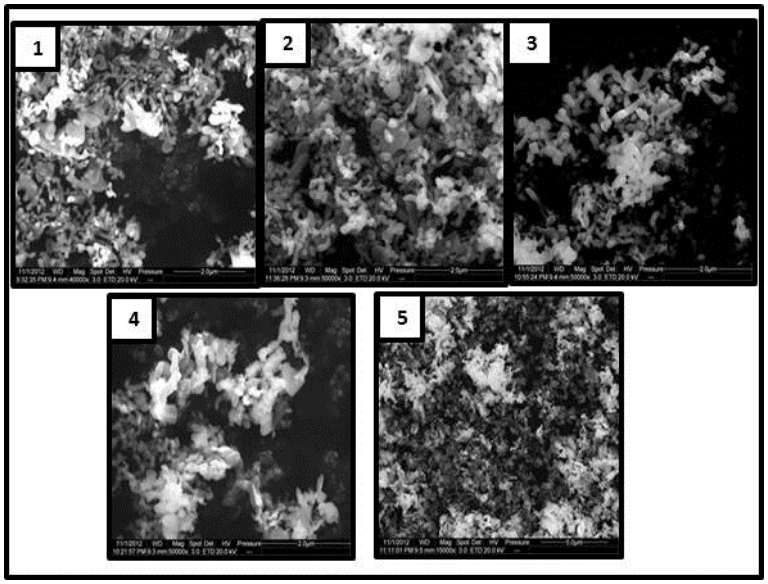


Figure S3 XRD of various $BiVO_4$ photocatalyst prepared under different PH

PH	2.26	2.51	3.11	3.64	4.52
BET (m^2g^{-1})	7	7	8	7	7
Particle size (nm)	36.2	34.7	34.2	33.8	30.8

Figure S4 BET value and particle size (calculated by Scherrer equation on the 2θ of

30.548°) of various $BiVO_4$ photocatalyst prepared under different PH



(1. PH=2.26; 2. PH=2.51; 3. PH=3.11; 4. PH=3.64; 5. PH=4.52)

Figure S5 SEM of various $BiVO_4$ photocatalyst prepared under different PH

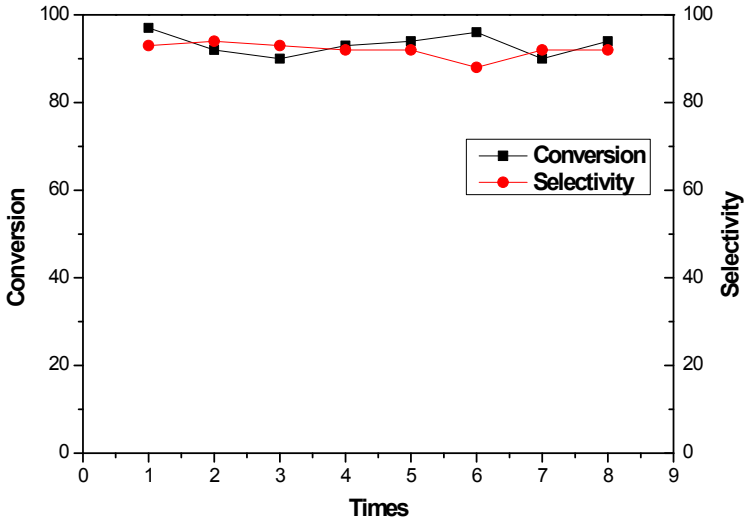


Figure S6 The recycle test on the photocatalytic oxidation of N-t-butylbenzylamine Reaction conditions: λ>420nm, catalyst (100mg), N-t-butylbenzylamine (0.1mmol), CH_3CN as a solvent (8mL), irradiation time : 7h, oxygen balloon (1 atm)

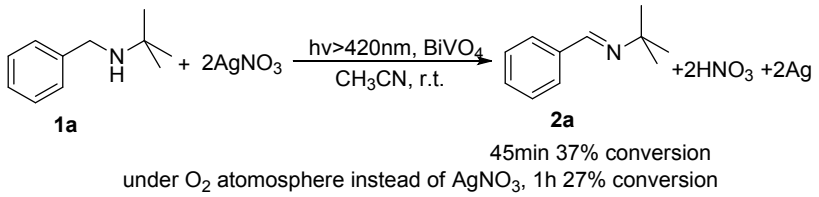


Figure S7 The photocatalytic oxidation of amine 1a using $AgNO_3$ as the electron acceptor.