Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

$ZnNb_2O_6$ fibre surface as an efficiently product-selective controller for near-UV-light-induced nitrobenzene reduction reaction†

Jie Wang,[ab] Zhenyu Ge,[c] Linjuan Pei,[ab] Peng Kong,[a] Ruiyi wang,[a] Pengqi Zhu,[ab] Meixian Liu,[ab] Xianmo Gu*[a] and Zhanfeng Zheng*[ab]

[a]*State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China.*

[b]*Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.*

[c]*School of Material Science and Engineering, Shandong University, Jinan 250100, China.*

*Corresponding authors:

E-mail addresses: zfzheng@sxicc.ac.cn (Z. F. Zheng); guxm@sxicc.ac.cn (X. M. Gu)

Table of contents

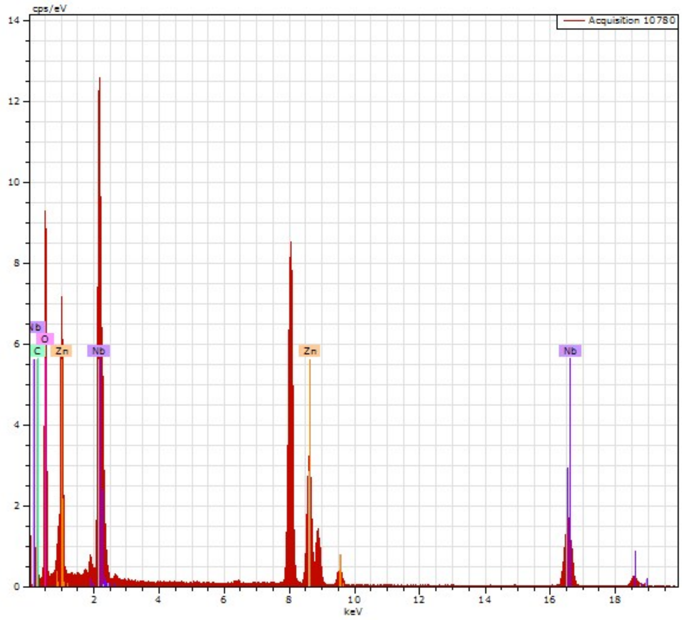

Fig. S1 The EDX spectrum of $ZnNb_2O_6$ attached to TEM. The Zn and Nb atomic ratio is 1:1.96.

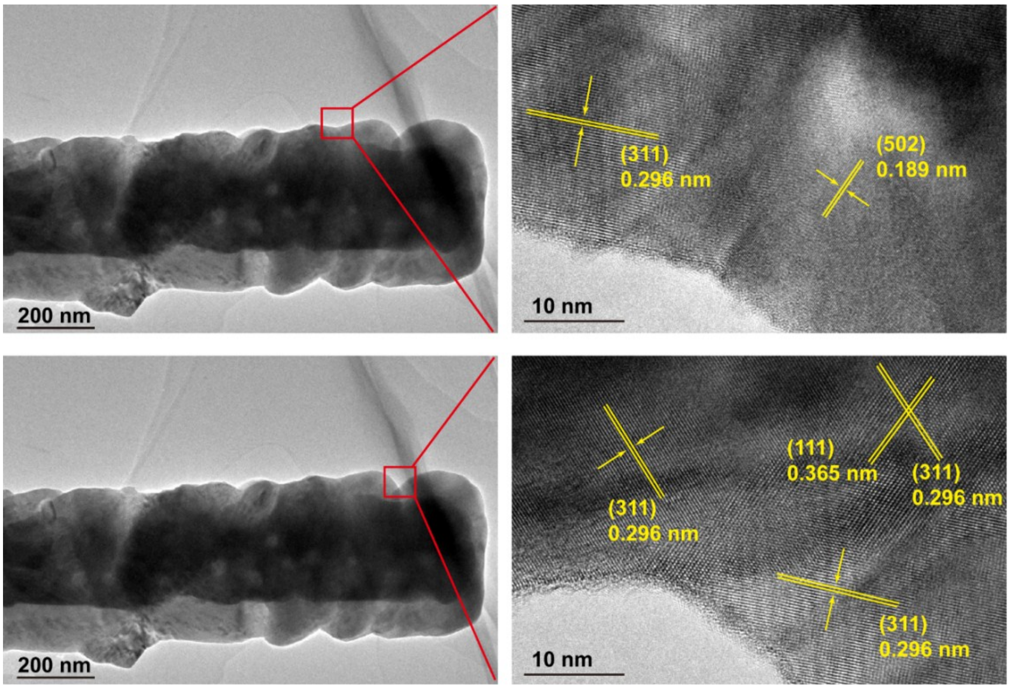

Fig. S2 The TEM and HRTEM images of different position of $ZnNb_2O_6$ fibre.

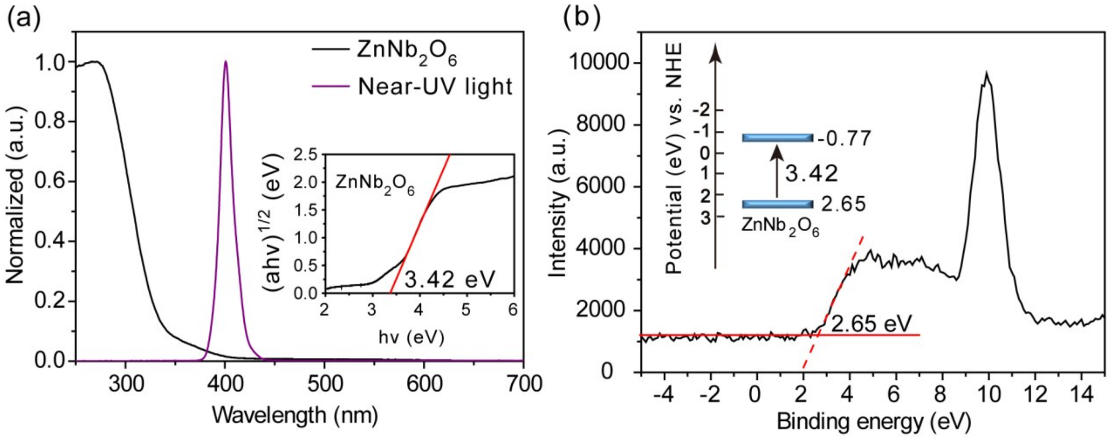

Fig. S3 (a) UV-Vis absorption spectrum of ZnNb$_2$O$_6$ (The inset is the function of photon energy) and optical spectrum of near-UV light and (b) Valence-band XPS spectrum and proposed band structure of ZnNb$_2$O$_6$.

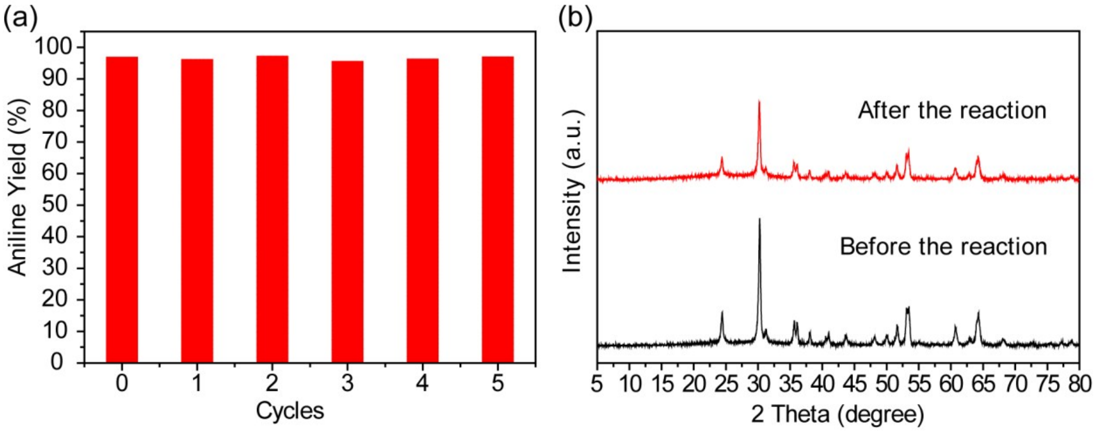

Fig. S4 The stability of ZnNb$_2$O$_6$ in five cycles and (b) the XRD patterns of the ZnNb$_2$O$_6$ catalyst before and after the reaction.

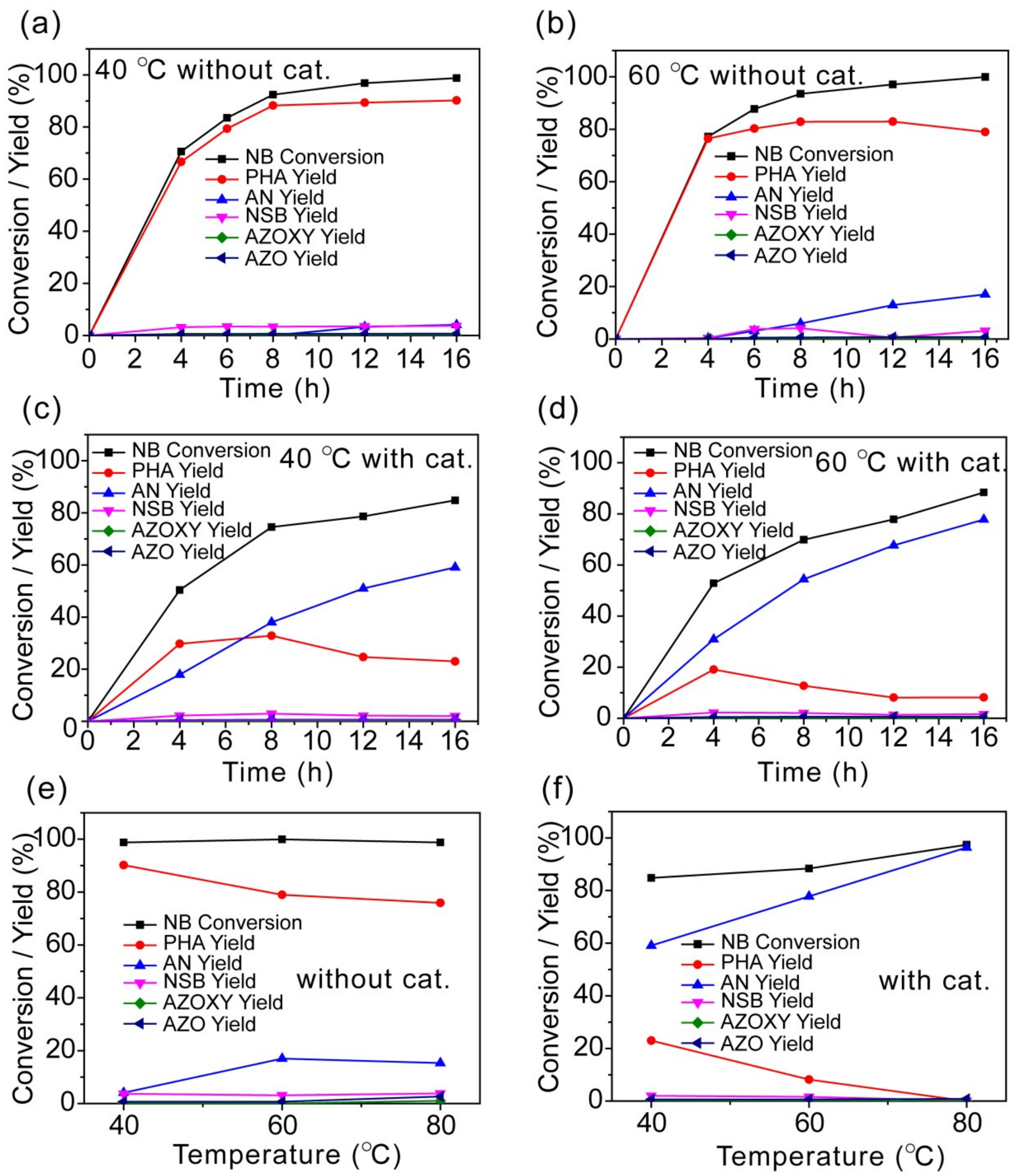

Fig. S5 Kinetic plots for nitrobenzene reduction under near-UV light irradiation without $ZnNb_2O_6$ as catalyst at 40 °C (a) and 60 °C (b). Kinetic plots for nitrobenzene reduction under near-UV light irradiation with $ZnNb_2O_6$ as catalyst at 40 °C (c) and 60 °C (d). Reaction conditions: 30 mg of catalyst (if applicable), near-UV light (380 - 420 nm, peak at 399 nm, 100 mW cm^{-2}), 2 ml of 0.05 M nitrobenzene in isopropyl alcohol solution. The effect of temperature on the nitrobenzene reduction reaction without (e) or with $ZnNb_2O_6$ (f). The experiments are proceeded for 16 h at 40 °C, 60 °C and 80 °C, respectively.

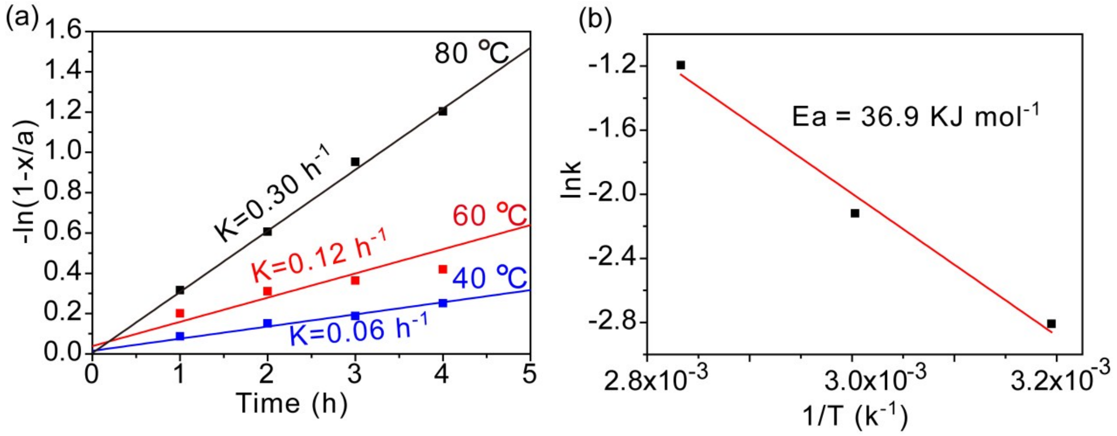

Fig. S6 (a) Kinetic plots of -ln(1-x/a) versus reaction time t with $ZnNb_2O_6$ catalyst at different temperature: 40, 60 and 80 °C. (b) Plot of the lnk versus 1/T according to the Arrhenius equation.

Calculation details of activation energy:

At first, the conversions for phenylhydroxylamine to aniline were counted at different periods of reaction time in 5 h. According to the first-order rate law equation,[1] the kinetic plots of -ln(1-x/a) versus reaction time t make several straight lines at different temperature: 40, 60 and 80 °C (x is the productive amounts of aniline, a is the amounts of phenylhydroxylamine by direct irradiation for 6 h with near-UV light). The values of the slopes calculated from the kinetic plots, as shown in Fig. S6a, are equal to the value of the rate constant k. According to the Arrhenius equation, one straight line of lnk versus (1/T) was obtained (Fig. S6b), from which the activation energy of hydrogenation of phenylhydroxylamine with $ZnNb_2O_6$ could be calculated from the value of the slope value (-Ea/R), being 36.9 KJ mol^{-1}.

Table S1 Product distribution over modulation of PHA selectivity.

Entry	NB Con. (%)	PHA	AN	NSB	AZOXY	AZO
		Yield (%)				
Solution-A	99	76	15	4	2	3
1[a]	99	24	31	3	41	1
2[b]	99	28	38	3	10	21
3[c]	99	70	17	5	1	7

The reaction was conducted under argon atmosphere at 80 °C using 2 ml of isopropyl alcohol solution with 0.1 mmol of nitrobenzene under near-UV light irradiation (Light intensity: 100 mW cm^{-2}) for 16 h in the first reaction stage (designated as Solution-A). In the second reaction stage, 30 mg of $ZnNb_2O_6$ was added to Solution-A in glove box. After that, the reaction was conducted continually for 16 h under [a]dark and [b]light situation; [c]the Solution-A was conducted continually for 16 h under near-UV light irradiation.

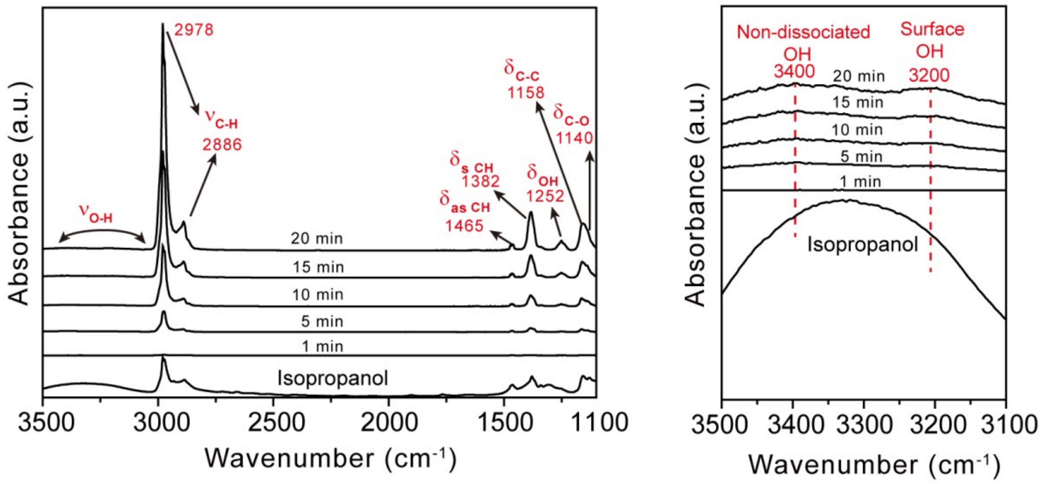

Fig. S7 *In situ* FT-IR spectra recorded during isopropyl alcohol adsorption on $ZnNb_2O_6$ at 80 °C.

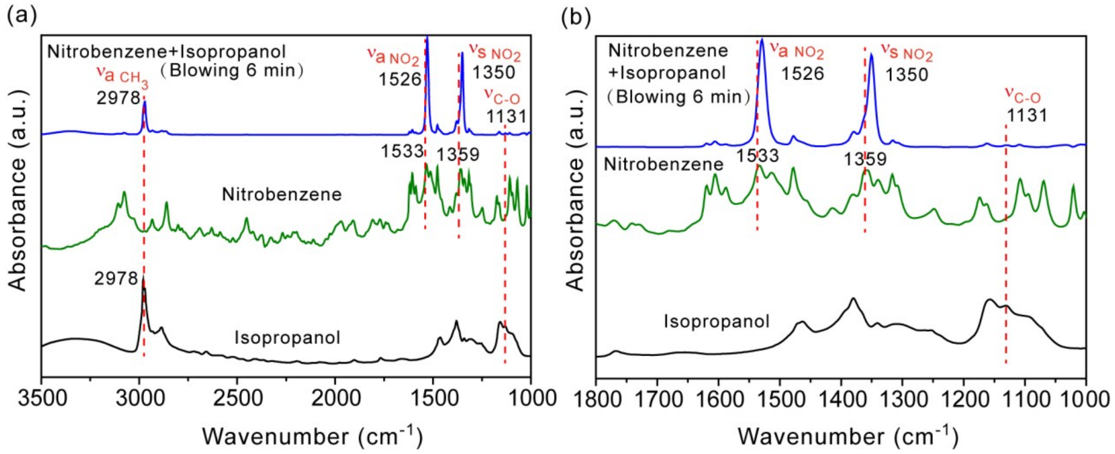

Fig. S8 (a) FT-IR absorbance spectra recorded during isopropyl alcohol and nitrobenzene adsorption on $ZnNb_2O_6$. (b) The amplified spectra for (a) at 1800-1000 cm^{-1}. The standardized spectra of isopropyl alcohol or nitrobenzene were obtained based on KBr background at roommate. The spectra of isopropyl alcohol and nitrobenzene were obtained by blowing the closed cell for 6 min after 10 μL of 0.05 M nitrobenzene in isopropyl alcohol was added to the centre of the situ cell at 80 °C.

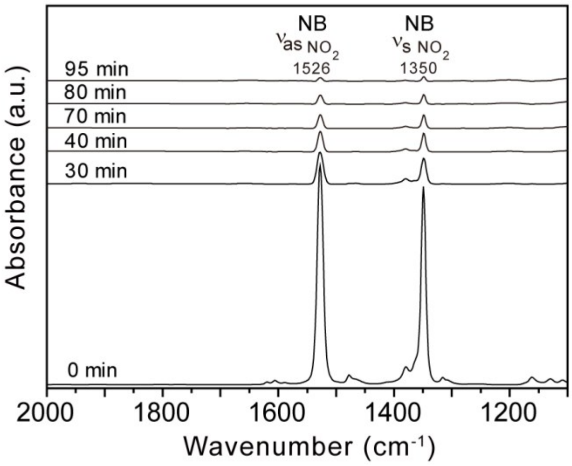

Fig. S9 *In situ* FT-IR spectra about the time profiles of the substrates under the near-UV light irradiation.

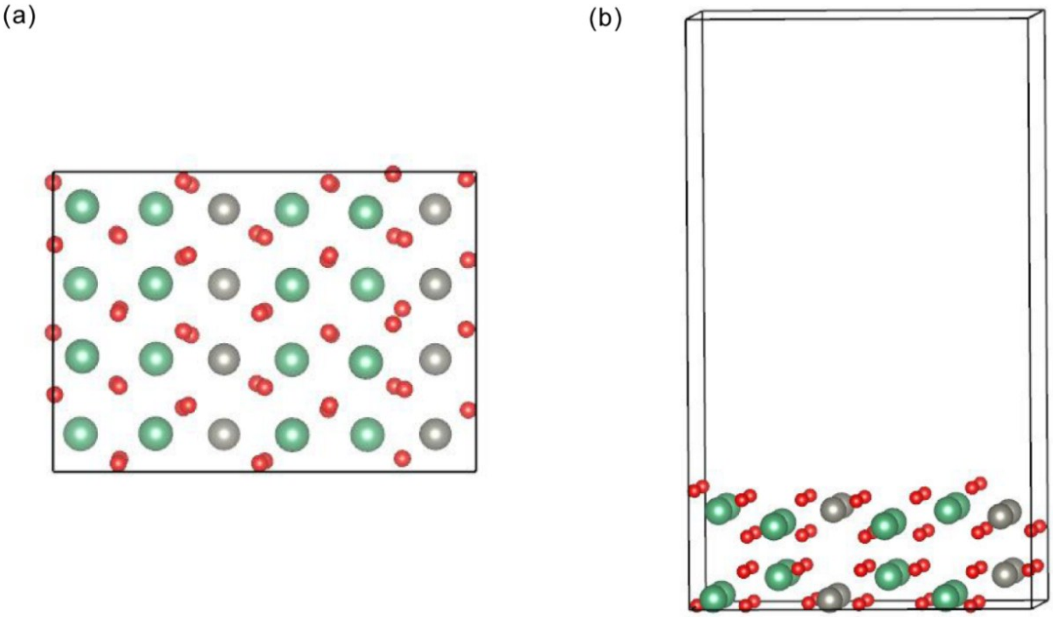

Fig. S10 The top (a) and side (b) views of the optimized the (040) surface of $ZnNb_2O_6$. Red ball is O; green ball is Nb; gray ball is Zn.

Table S2. Surface density of acidic and basic sites and comparison of nitrobenzene conversion and aniline yield of different catalysts.

Entry	Catalysts	Acidic sites (μmol/m^2)	Basic sites (μmol/ m^2)	Ratio of acidic to basic sites	NB con. (%)	AN Yield (%)
1[a]	$ZnNb_2O_6$	0.30	0.02	15.00	97	96
2[a]	Nb_2O_5	0.60	0.34	1.76	80	78
3[a]	ZnO	1.01	0.84	1.20	99	10
4[a]	Acid-Al_2O_3	6.05	1.25	4.84	96	91
5[a]	Base-Al_2O_3	5.25	1.56	3.37	97	66
6[b]	—	—	—	—	99	15

[a]Conditions: 30 mg catalyst, 399 nm near-UV light (380-420 nm, 100 mW/cm^2), 80 °C, 2 ml of 0.05 mol/L nitrobenzene in isopropyl alcohol solution, 16 h. The Nb_2O_5 was obtained by the calcined H-niobate at 700 °C for 3 h. [b]There is no catalyst in the reaction system.

1. S. Challagulla, S. Payra, C. Chakraborty and S. Roy, *Phys. Chem. Chem. Phys.*, 2019, **21**, 3174-3183.