Supplementary Information

Visible light-initiated selective aerobic oxidation of alcohols over niobium oxide nanowires: An oxygen isotope labeling study

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1. Typical procedure for the photocatalytic selective oxidation of benzyl alcohol

In the 10 mL Pyrex reactor with 0.3 mmol of benzyl alcohol, 50 mg of Nb_2O_5 nanowires, and 1 mL of CH_3CN were added in turn. The prepared mixture was then maintained, under ultrasonication for 10 min and stirred for 20 min in the dark, to achieve adsorption equilibrium. Then, connected to air by punching a hole in the rubber septum. Next, the Pyrex reactor was stirred at 1500 rpm under violet LEDs (light-emitting diodes, 3 W × 4) irradiation. Finally, Nb_2O_5 was stripped away from the reaction mixture by centrifugation. The liquid product was tested by GC–FID. The liquid products were certified by comparing the retention time of the standard sample and further certified by GC–MS.

2 Instrumentations

Transmission electron microscopy (TEM) and high-resolution TEM images were collected on a JEOL JEM2012–FEF operated at 200 kV. Powder X-ray diffraction (PXRD) measurement was carried out using a Rigaku/Miniflex 600 diffractometer with filtered Cu Kα radiation, and the data were collected from 10° to 80°. X-ray photoelectron spectroscopy (XPS) measurements were taken on a Thermo Scientific K–Alpha using monochromatic Al Ka radiation (hν = 1486.6eV). The UV-vis absorbance of Nb_2O_5 and BA–Nb_2O_5 samples were measured on UV–3600 UV-vis spectrophotometer (Shimadzu, Japan) equipped with a diffuse reflectance measurement accessory, $BaSO_4$ was used as a reflectance standard. The specific surface areas were determined by N_2 physisorption using an ASAP automated system and the Brunauer–

Emmet–Teller (BET) method. Each sample was degassed under vacuum ($<1\times10^{-5}$ bar) in the Micromertics system at 300 °C for 6 h prior to N_2 physisorption. The electron paramagnetic resonance (EPR) tests were executed on an EPR spectrometer (JEOL, JES–FA300). Gas chromatography (GC) quantitative measurements of the conversions of substrates and the selectivity of products were carried out on a gas chromatograph equipped with a flame ionization detector (GC–FID, Agilent 7890B) using high purity N_2 as the carrier gas. Gas chromatography-mass spectrometry (GC–MS) analysis was performed on an Agilent GC 8890 gas chromatograph equipped with an Agilent 5977B GC/MSD mass spectrometer. Conversion and selectivity for selective oxidation of substrates to target products were defined as follows:

$$\text{Conv. (\%)} = [(C_0 - C_S)/C_0] \times 100$$

$$\text{Sel. (\%)} = [C_P/(C_0 - C_S)] \times 100$$

where C_0 is the initial concentration of reactant, C_s and C_p are the concentrations of substrate and target product, respectively, at a certain time during the photocatalytic reaction.

3. Results

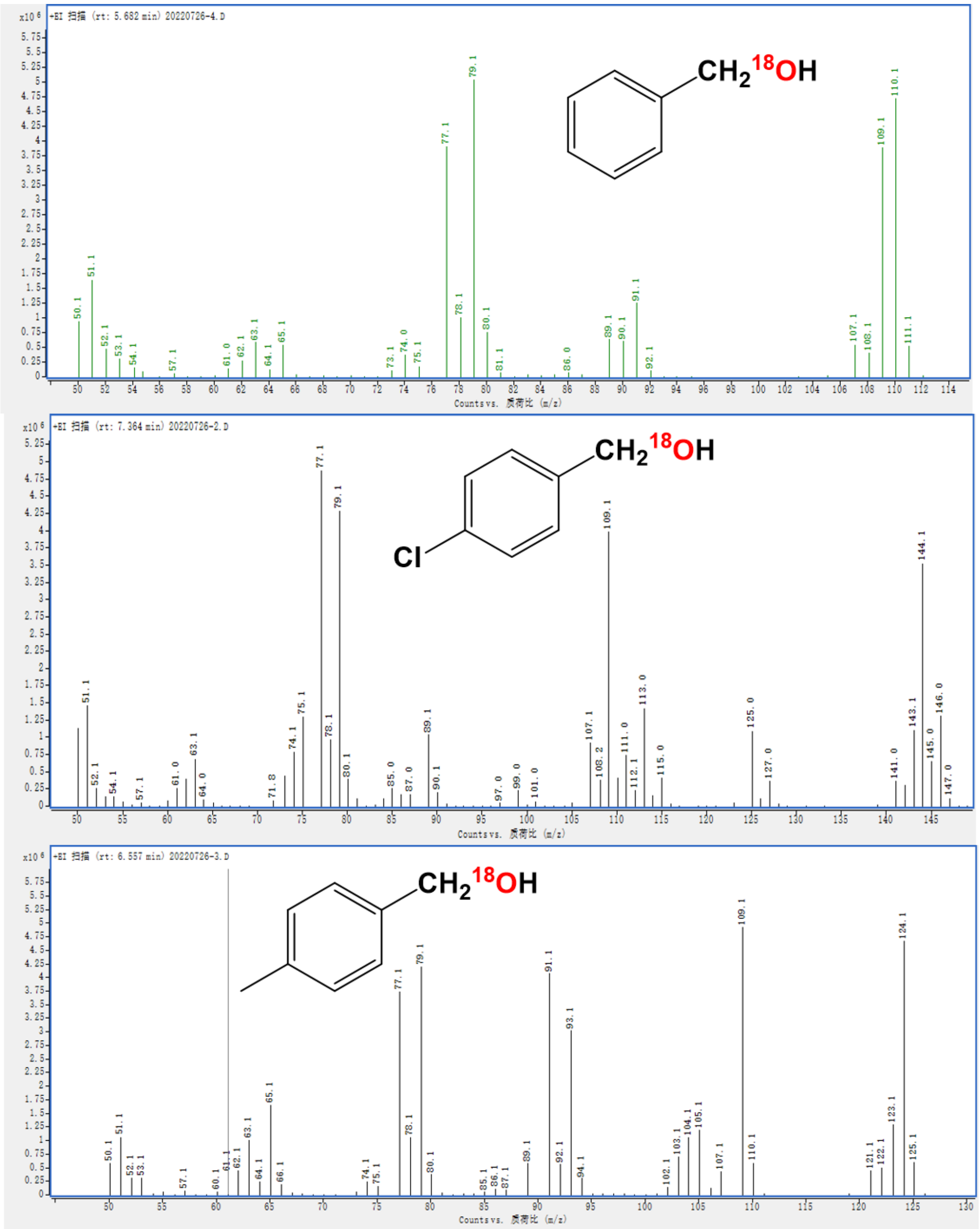


Fig. S1. The raw mass spectra of ^{18}O-labeled benzaldehyde, ^{18}O-labeled *p*-tolualdehyde, and ^{18}O-labeled *p*-tolualdehyde.

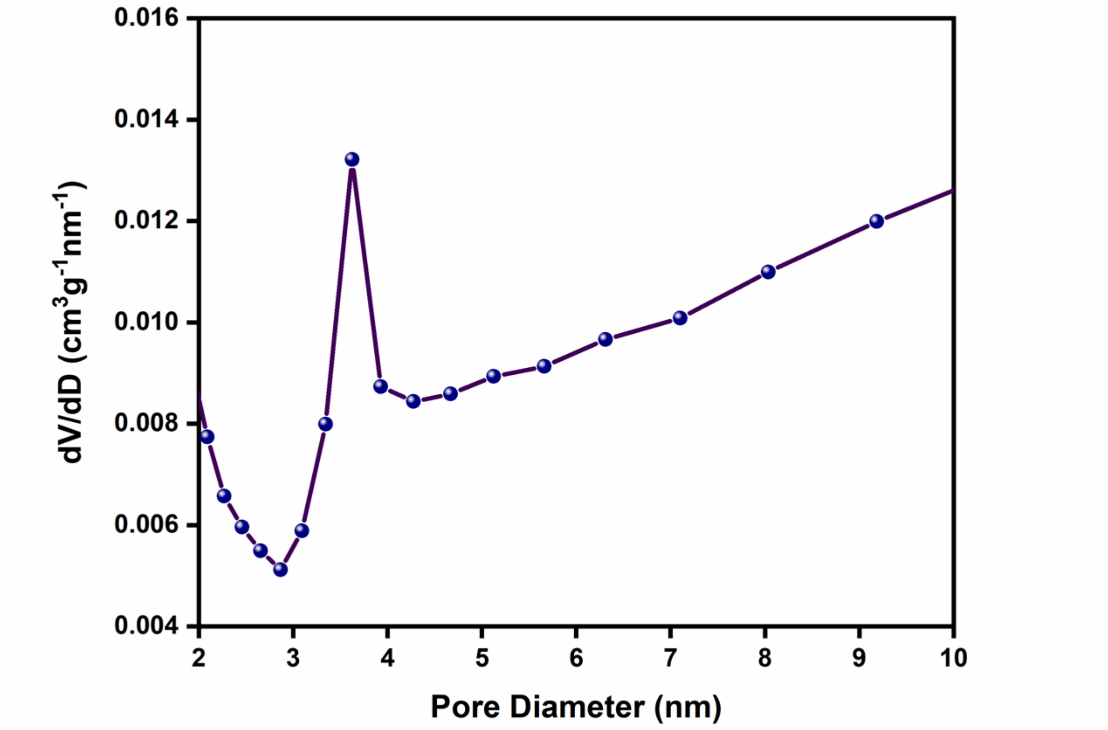


Fig. S2. BJH pore size distribution of the Nb_2O_5 nanowires.

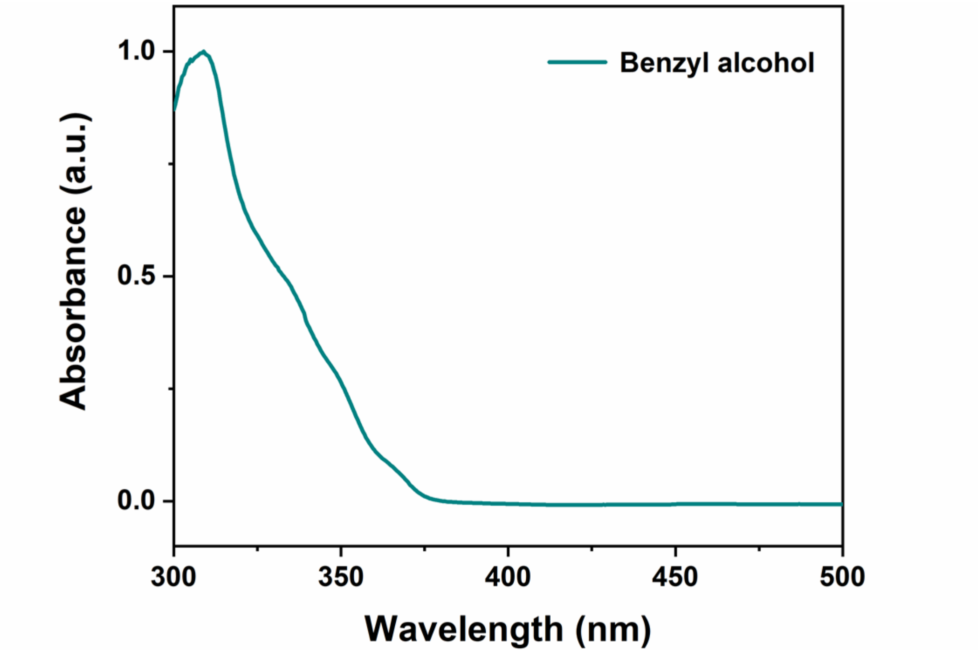


Fig. S3. UV–vis DRS of of benzyl alcohol (BA).

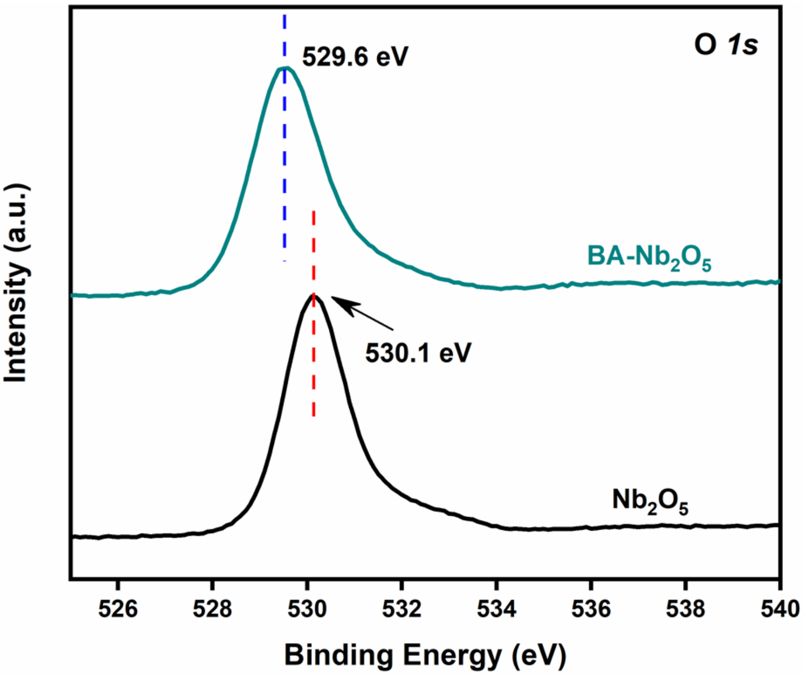


Fig. S4. O 1*s* XPS spectra of Nb_2O_5 and BA–Nb_2O_5.

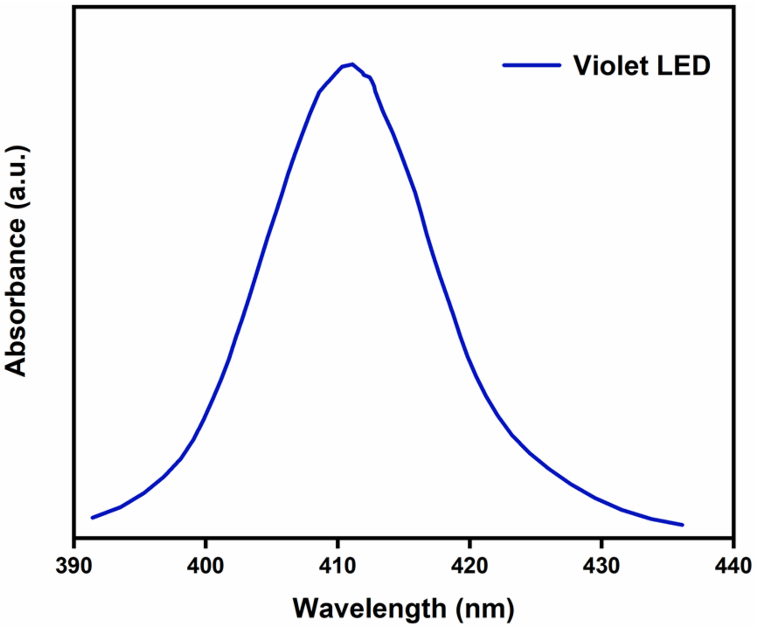
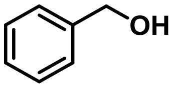
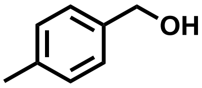
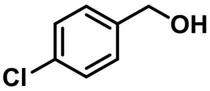


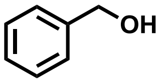
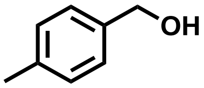
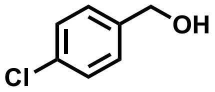
Fig. S5. The emission spectrum of the violet LED.

Table S1 Abundance of ^{18}O in the substrates and products.[a]

Entry	Substrate (^{18}O:^{16}O)	t (min)	Conv. (%)	Sel. (%)	Product (^{18}O:^{16}O)
1	 (95:5)	30	48	99	23:77
2		45	64	99	18:82
3	 (92:8)	30	52	99	22:78
4		45	73	99	22:78
5	 (91:9)	30	41	99	20:80
6		45	53	99	18:82

[a]Standard reaction conditions: ^{18}O-labeled alcohol (0.2 mmol), Nb_2O_5 (50 mg), violet LEDs (410 ± 6 nm, 3 W × 4), O_2 (0.1 MPa), anhydrous CH_3CN (1 mL).

Table S2 Abundance of ^{18}O in the substrates and products with the introduction of dry 3A molecular sieve.[a]

Entry	Substrate (^{18}O:^{16}O)	*t* (min)	Conv. (%)[a]	Sel. (%)[b]	Product (^{18}O:^{16}O)
1		30	32	99	84:16
2	(95:5)	45	57	99	81:19
3		30	48	99	82:18
4	(92:8)	45	66	99	80:20
5		30	24	99	74:26
6	(91:9)	45	44	99	72:28

[a] Standard reaction conditions: ^{18}O-labeled alcohol (0.2 mmol), Nb_2O_5 (50 mg), violet LEDs (410 ± 6 nm, 3 W × 4), O_2 (0.1 MPa), anhydrous CH_3CN (1 mL), dry molecular sieve 3A.

Table S3. Control experiments for the selective photocatalytic aerobic oxidation of benzyl alcohol.[a]

Entry	Deviation from standard conditions	Conv. (%)[b]	Sel. (%)[b]
1	Blank	0	--
2	Dark	0	--
3	N_2	1	--
4	None	61	99

[a] Standard reaction conditions: benzyl alcohol (0.3 mmol), Nb_2O_5 (50 mg), violet LEDs (410 ± 6 nm, 3 W × 4), aerial O_2, CH_3CN (1 mL), 2 h.

[b] Determined by GC–FID using chlorobenzene as the internal standard.