Electronic Supplementary Information (ESI)

Surface-Mediated Selective Photocatalytic Aerobic Oxidation Reactions on TiO₂ Nanofibers

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Parameter	Value	
Method	Mixed Gaussian and Plane-wave (GPW)	
Functional	revPBE	
Dispersive interaction correction	DFT-D3	
Pseudo-potential	Goedecker-Teter-Hutter(GTH)	
Gaussian-type basis set sets	Molecular optimized double zetha-valence	
	Shorter Range	
	basis sets with a polarization function	
	(DZVP-MOLOPT-SR)	
Plane-wave cut-off	280Ry	
k-point sampling	Gamma-point only	
SCF optimizer	Orbital transformation with the direct inverse	
	in the iterative subspace optimizer (OT/DIIS)	
Electron density convergence	$1.0 imes 10^{-7}$	
criteria		
Convergence criteria for geometry	maximum force 4.5×10^{-5} Hartree/Bohr	
optimization	RMS force 3.0×10^{-5} Hartree/Bohr	
	maximum coordinate change 3.0×10^{-4} Bohr	
	RMS coordinate change 1.5×10^{-4} Bohr	

Table S1 The parameters for CP2K simulations.

Entry	Substrate	Product	Conv.(mol %)	Select. (mol %)
1	NH ₂		91	>99
2	NH ₂	N	88	98
3	NH ₂		- 98	>99
4	CI NH2		70	91
5	NH ₂	N N	17	27

Table S2 Oxidation of amines photocatalyzed by TiO₂.^{*a*}

^{*a*}Reaction conditions: 0.2 mmol reactant, 50 mg catalyst, 5 ml acetonitrile, 1 atm O₂, 40 °C, reaction time at 5 h and light intensity at 0.45 Wcm⁻² (LED white light)

Table S3 The apparent activation energy of the aerobic oxidation of benzylamine and

Reaction	Catalyst	light ^a	E _a (KJ/mol) ^b
Oxidation of benzylamine	BF	UV	12
$NH_2 \xrightarrow{BF/N-BF} N$		Visible	23
	N-BF	UV	17
· · · ·		Visible	15
Oxidation of 4-methoxybenzyl alcohol	BF	UV	2
		Visible	22
$\frac{\text{On } BF/N-BF}{hv,O_2, CH_3CN, 40^{\circ}C} \rightarrow 0$	N-BF	UV	14
H3C0 V		Visible	14

4-methoxybenzyl alcohol on BF and N-BF NFs

^a UV range: 320 – 415 nm

Visible range: >420 nm ^b calculated by using the Arrhenius equation in which the kinetic data obtained at the temperatures from 25°C to 60°C



Fig. S1 The output spectrum of white color LED light source used in this work.



Fig. S2 The output spectrum of Xe light used in this work.



Fig. S3 The supercell of TiO_2 (100) surface.



Fig. S4 XRD patterns of pristine (BF), N-doped $TiO_2(B)$ (N-BF) and calcined N-doped $TiO_2(B)$ (in air, N-BF-A180) nanofibres.



Fig. S5 UV-Vis spectra (A) of BF, N-BF and N-BF-A and their IR spectra (B). As can been seen clearly, after N doping, the light absorption extends to the visible range. The stronger absorption in the UV-Vis spectra of the doped samples is related to a high N-doped content.



Fig. S6 UV-Vis spectra of bare BF and N-BF NFs, and benzylamine (A) and 4-methoxybenzyl alcohol (B) adsorbed BF and N-BF NFs.



Fig. S7 Effect of temperature on the activities of aerobic oxidation of benzylamine (A) and 4-methoxybenzyl alcohol (B) on BF NFs under light irradiation with different wavelength.



Fig. S8 The DMPO spin-trapped EPR spectrum. Sample was taken during the selective photocatalytic aerobic oxidation of benzylamine on BF.