Amine coupled Ordered Mesoporous (Co-N) co-doped TiO_2: Green Photocatalyst for Selective Aerobic Oxidation of Thioether

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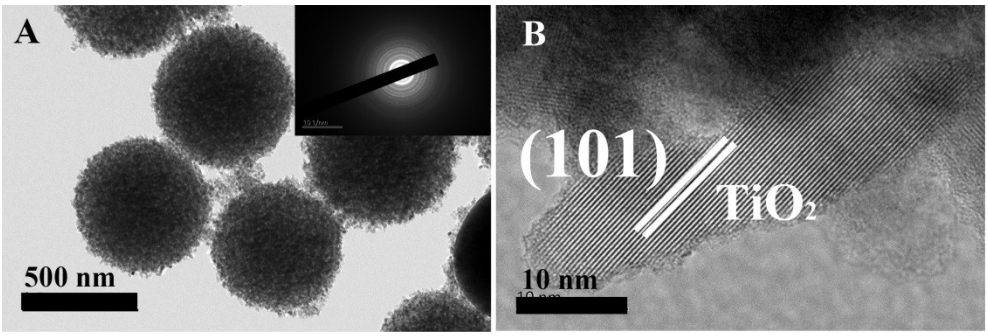


Fig. S1 TEM image (A) (inset SAED patterns) and Lattice resolution HRTEM image (b) of Co-N-TiO_2.

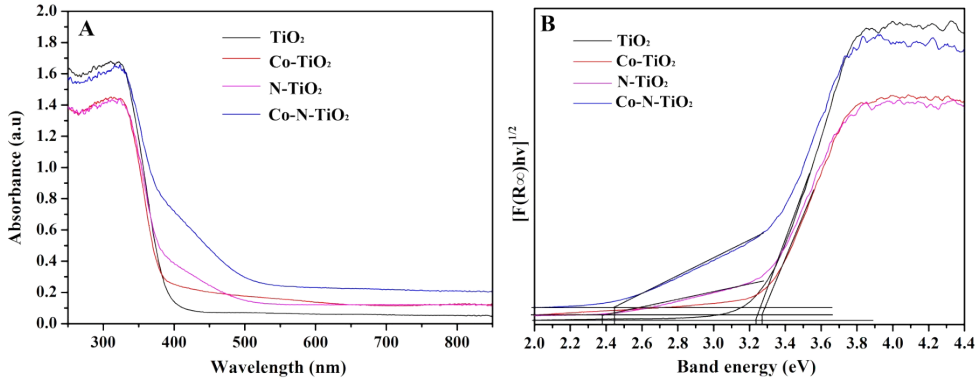


Fig. S2 UV-Vis DRS of TiO_2, Co-TiO_2, N-TiO_2 and Co-N-TiO_2 (A). Tauc plots showing indirect band gap (B).

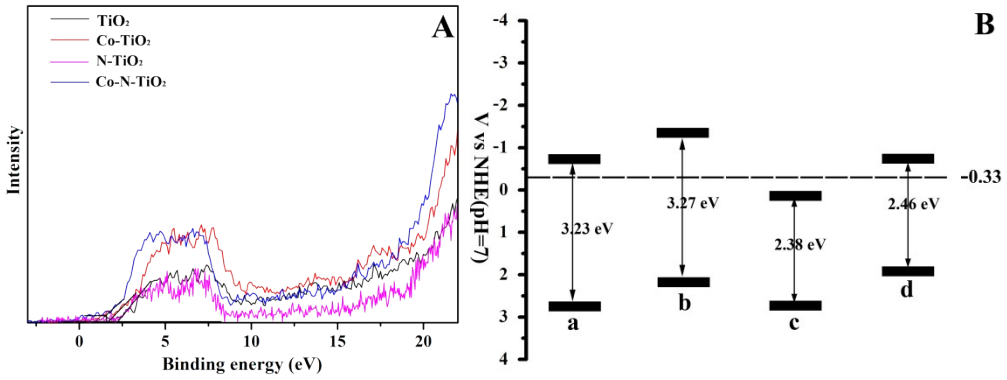


Fig. S3 (A) XPS valence band spectra of TiO_2, Co-TiO_2 and Co-N-TiO_2; (B) Band alignments of (a) TiO_2, (b) Co-TiO_2, (c) N-TiO_2, (d) Co-N-TiO_2.

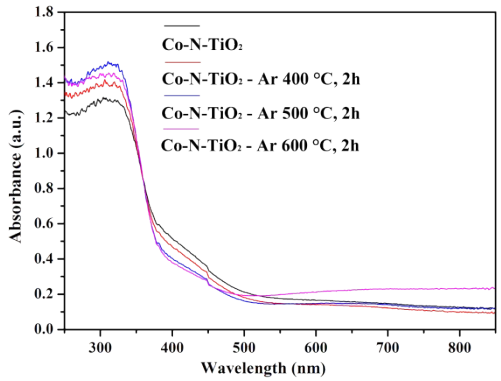


Fig. S4 UV-Vis DRS of Co-N-TiO_2 and Co-N-TiO_2 treated in different temperature under argon gas.

Table S1 Control experiment.

Entry	Conditions	Conv. (mol%)	Select.(mol%)
1	>420 nm	16.97	98.96
2	>420 nm, N_2 without O_2	0	--
3	>420 nm, without catalytic	0	--
4	Without visible light	0	--

[a] Reaction conditions: 0.3 mmol of thioanisole, 0.06mmol of Triethylamine, 5 mL of methanol, 40 mg of [Co-N-TiO_2], 300 W Xe lamp λ>420 nm, 1 bubble / 2s of O_2, 5 h. [b] Determined by GC using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of sulfoxide.

Table S2 The influence of amine on the selective aerobic oxidation of thioanisole under visible-light irradiation.

Entry		Conv. (mol%)	Select.(mol%)
1	None	12.88	95.12
2	Isopropylamine	13.58	94.3
3	Tert-Butylamine	14.43	100

4	Triethylamine	16.97	98.96
5	Triethanolamine	25.69	86.9

[a] Reaction conditions: 0.3 mmol of thioanisole,0.06 mmol of amines, 5 mL of methanol, 40 mg of [Co-N-TiO_2], 300 W Xe lamp λ>420 nm, 1 bubble / 2s of O_2, 5 h. [b] Determined by GC using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of sulfoxide.

Table S3 The effect of the amount of TEA on the photocatalytic oxidation of thioanisole under visible-light irradiation.

	Amount of TEA (mmol)	Nsubstrat/nTEA	Conv. (mol%)	Select.(mol%)
1	0.03	10	10.1	100
2	0.06	5	16.97	98.96
3	0.12	2.5	17.52	96.53
3	0.18	1.67	17.95	95.28

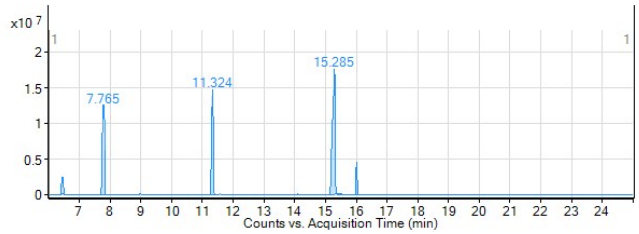
[a] Reaction conditions: 0.3 mmol of thioanisole, 5 mL of methanol, 40 mg of [Co-N-TiO_2], 300 W Xe lamp λ>420 nm, 1 bubble / 2s of O_2, 5 h. [b] Determined by GC using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of sulfoxide.

Table S4 The influence of the solvents on the visible-light-induced selective oxidation of thioanisole.

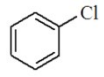
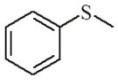
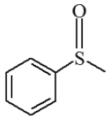
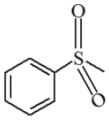
Solvent	Amine	Conv. (mol%)
CH_3CN	Triethylamine	32.99
C_2H_5OH	Triethylamine	19.53
CH_3OH	Triethylamine	76.4

[a] Reaction conditions: 0.3 mmol of thioanisole,0.06mmol of Triethylamine, 5 mL of solvent, 40 mg of [Co-N-TiO_2], 300 W Xe lamp λ>420 nm, 1 bubble / 2s of O_2, 12 h. [b] Determined by GC using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of sulfoxide.

Entry 1



The GC-FID of Table 6 entry 1:

6.375	7.765	11.324	15.285	15.938
$N(C_2H_5)_3$				

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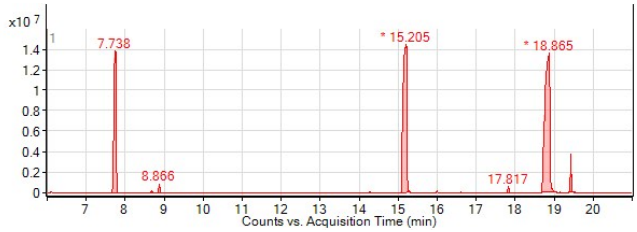

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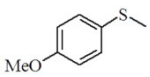
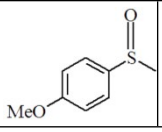
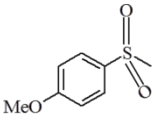
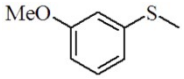
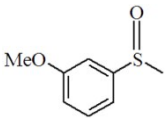
7.738	15.205	18.865	19.36
			

Entry 3

The GC-FID of Table 6 entry 3:

7.736	15.242	18.865
		

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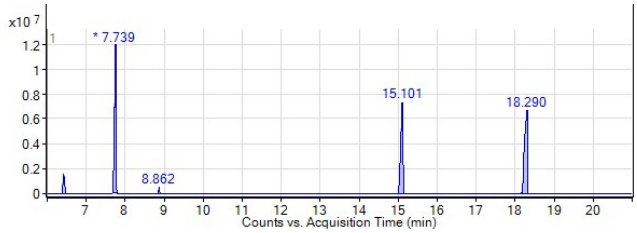

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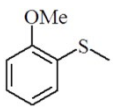
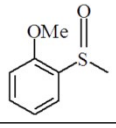
6.361	7.739	15.101	18.290
$N(C_2H_5)_3$			

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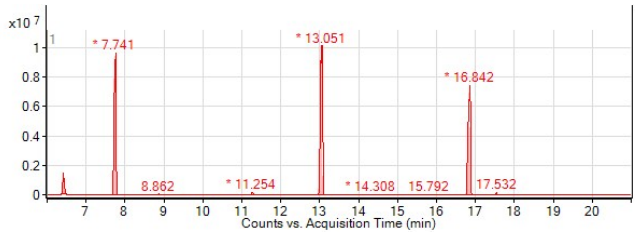

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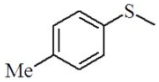
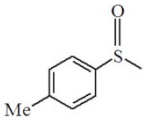
6.354	7.741	13.051	16.842
$N(C_2H_5)_3$			

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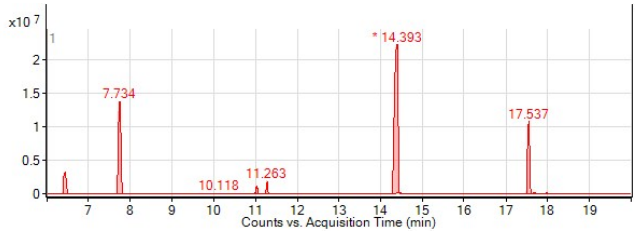

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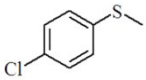
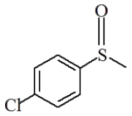
6.349	7.734	11.263	14.393	17.537
$N(C_2H_5)_3$				

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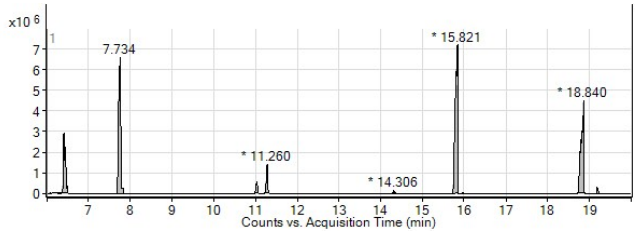

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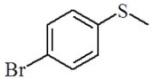
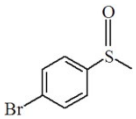
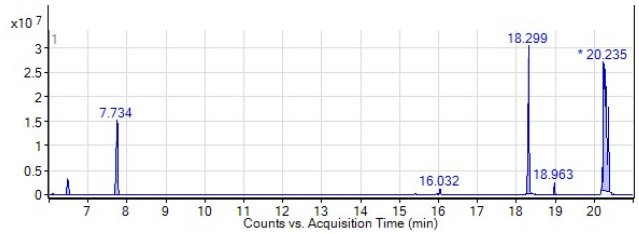
6.329	7.734	11.260	15.821	18.840
$N(C_2H_5)_3$				

Entry 8



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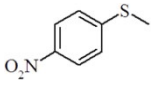
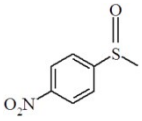
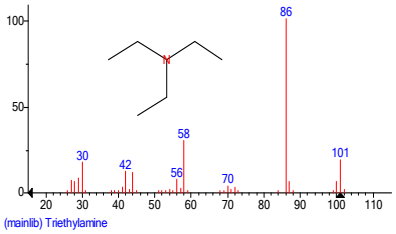
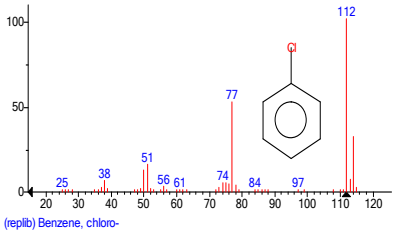
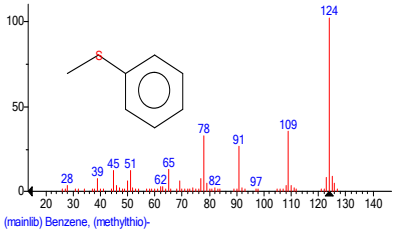
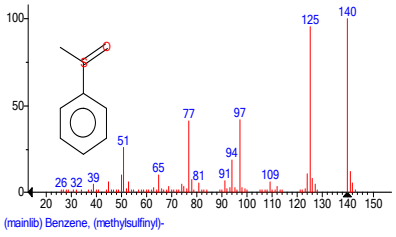
6.325	7.734	18.299	20.235
$N(C_2H_5)_3$			

Fig. S5 GC-FID results for Table 6.









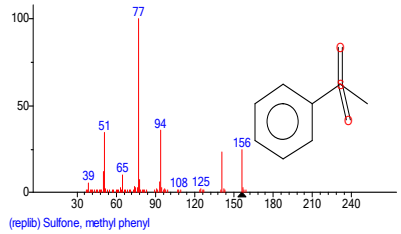


Fig. S6 Mass Spectrometry.

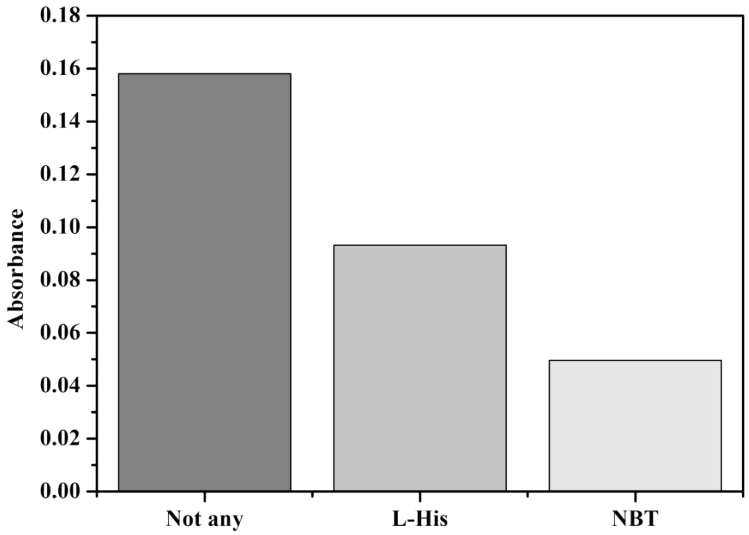


Fig. S7 Absorbance of DPCO in DPCI solution in the presence of Co-N-TiO_2 with Triethylamine under visible-light irradiation with various quenching reagents. ([DPCI] = 1.00×10^{-3} mol/L, [Co-N-TiO_2 with Triethylamine] = 1.00 g/L, [L-His] = [NBT] = 5.00×10^{-3} mol/L, T = 298 K and t = 60 min.).