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

Supporting information

Oxygen vacancy-rich MoO_{3-x} nanobelts for photocatalytic N_2 reduction to NH_3 in pure water

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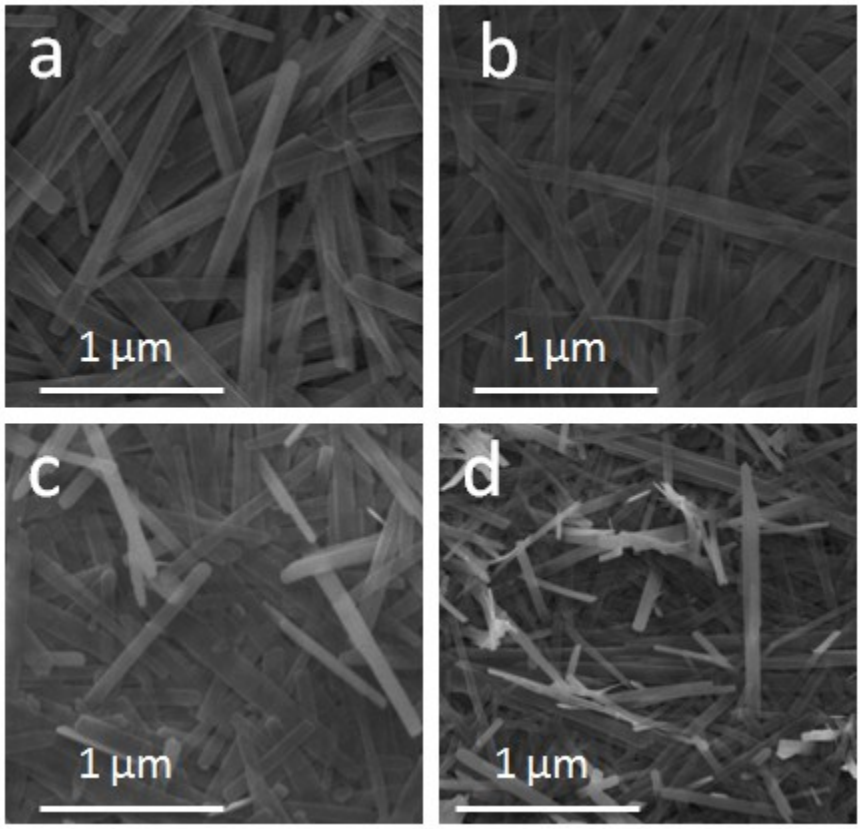

Fig. S1 SEM images of the as-synthesized and annealed MoO_{3-x} nanobelts for different time: (a) MoO_{3-x}, (b) MoO_{3-x}-1 min, (c) MoO_{3-x}-5 min, and (d) MoO_{3-x}-30 min.

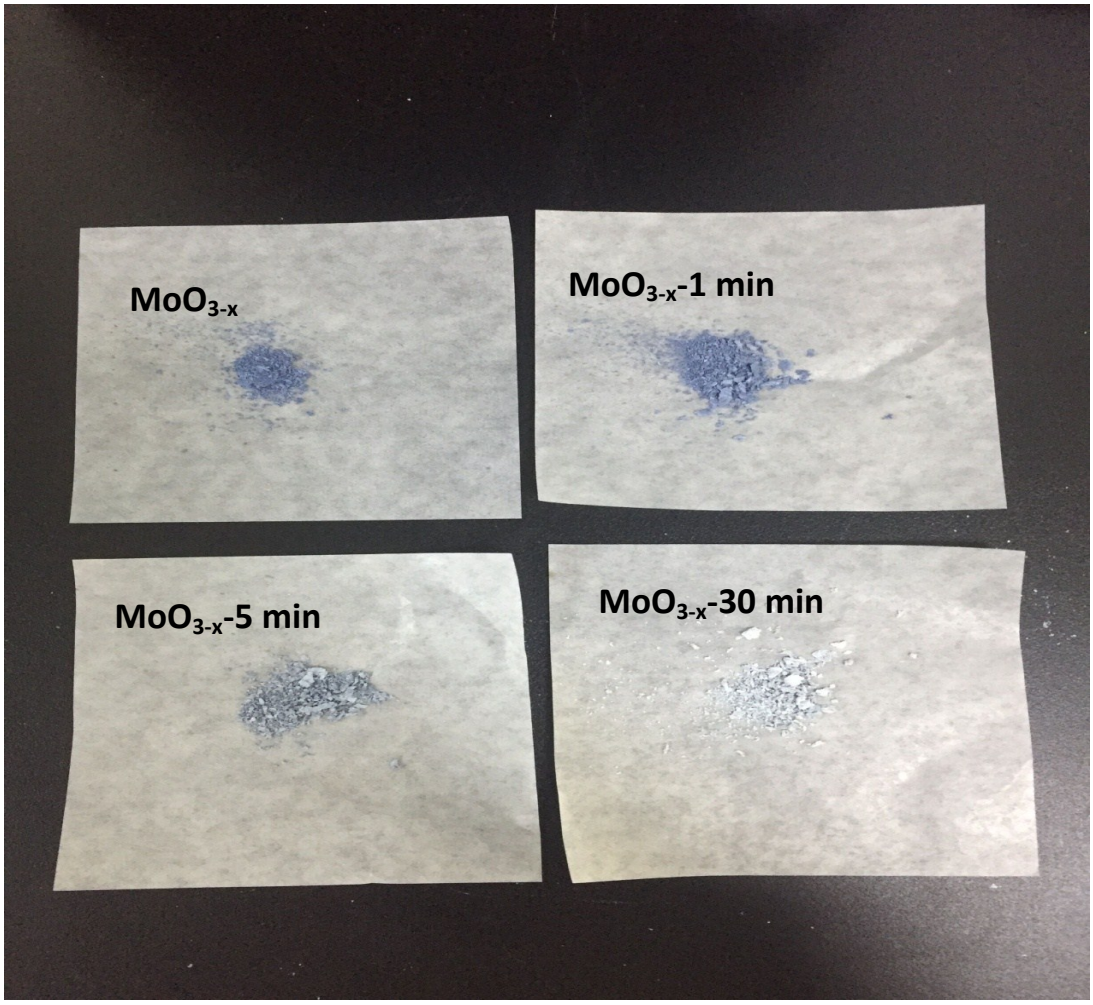

Fig. S2 Color change of the as-synthesized and annealed MoO_{3-x} for different time.

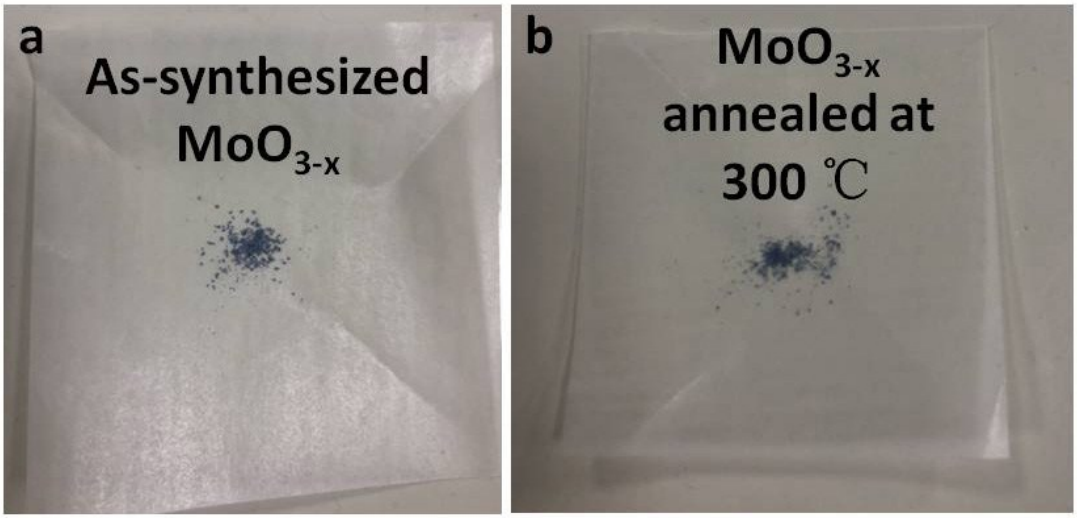

Fig. S3 (a) The as-synthesized MoO_{3-x}, and (b) the sample annealed at 300 ˚C for 1 h.

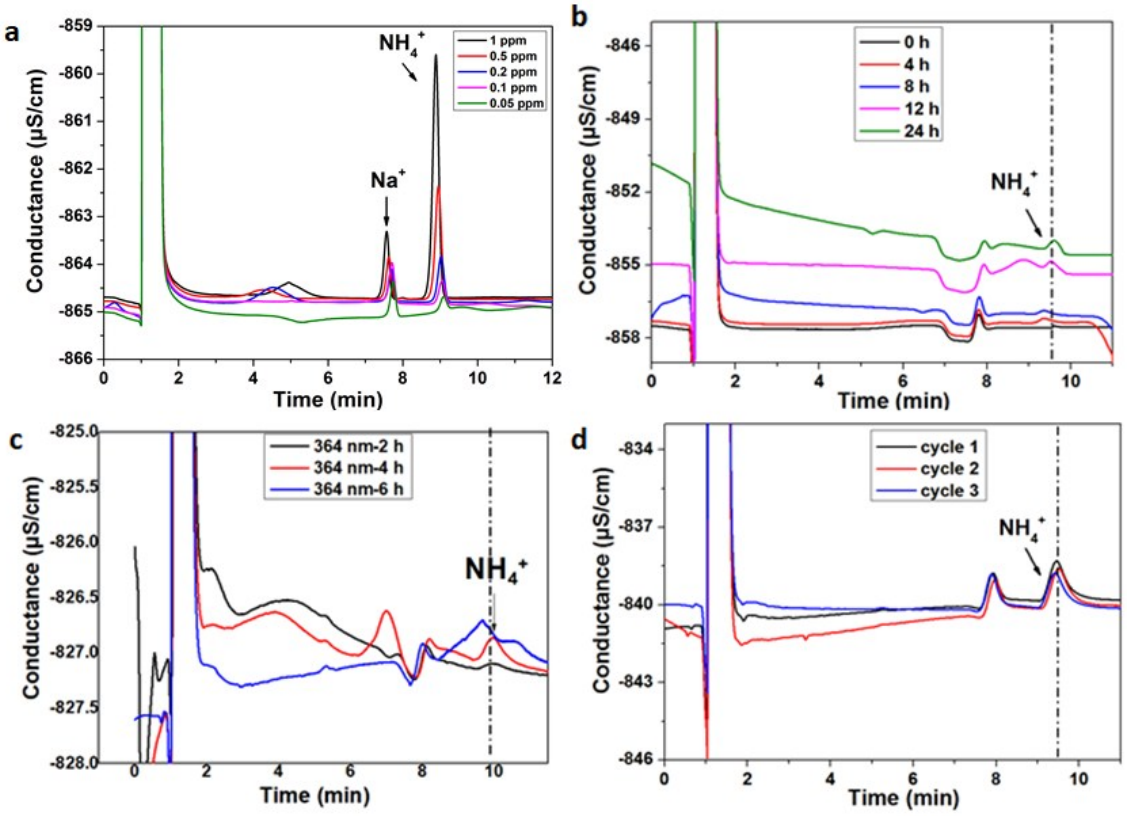

Fig. S4 (a) Standard curves of NH_4^+ from 0.05 ppm to 1 ppm tested by the ion chromatography, (b) Conductance curves of NH_4^+ for the as-synthesized MoO_{3-x} under the irradiation of a 300 W of Xeon lamp, (c) Conductance curves of NH_4^+ of the as-synthesized MoO_{3-x} under the irradiation of LED (365 nm), and (d) Conductance curves of recycled photocatalytic reaction for the as-synthesized MoO_{3-x} nanobelts (each cycle lasts for 8 h).

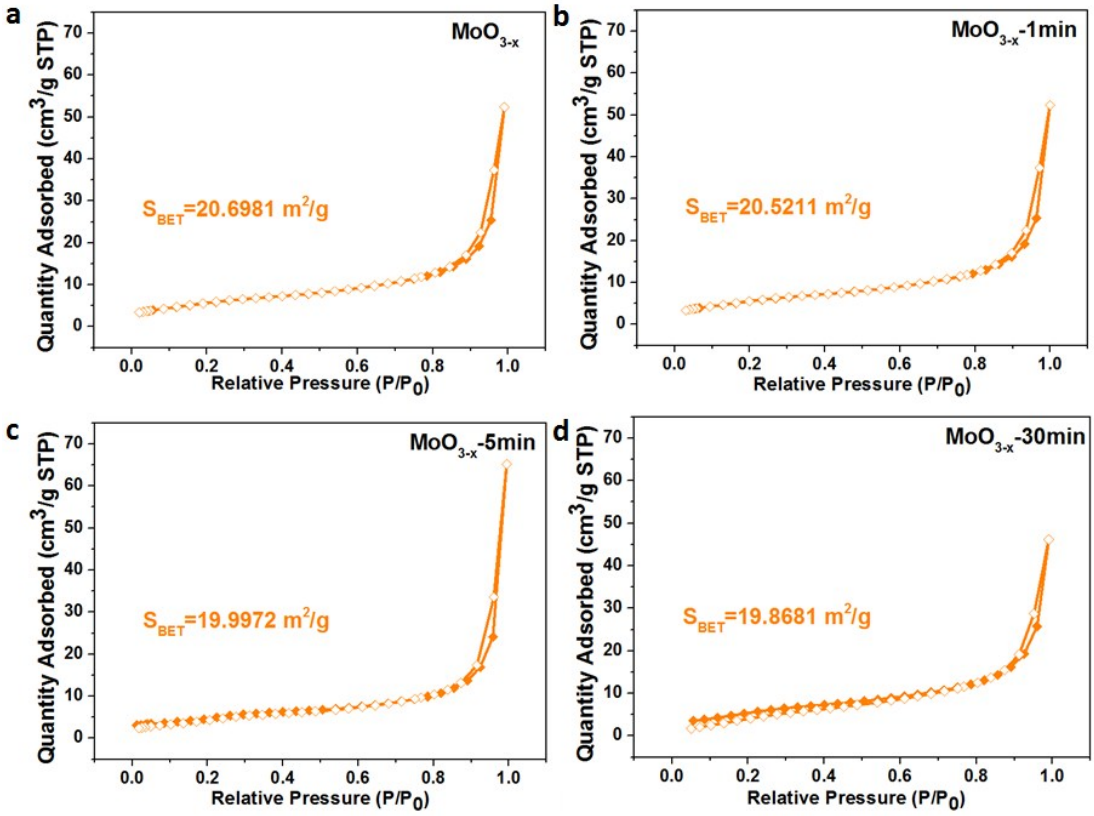

Fig. S5 N_2 adsorption/desorption isotherms of (a) the as-synthesized MoO_{3-x} nanobelts; (b) MoO_{3-x}-1 min; (c) MoO_{3-x}-5 min; and (d) MoO_{3-x}-30 min.

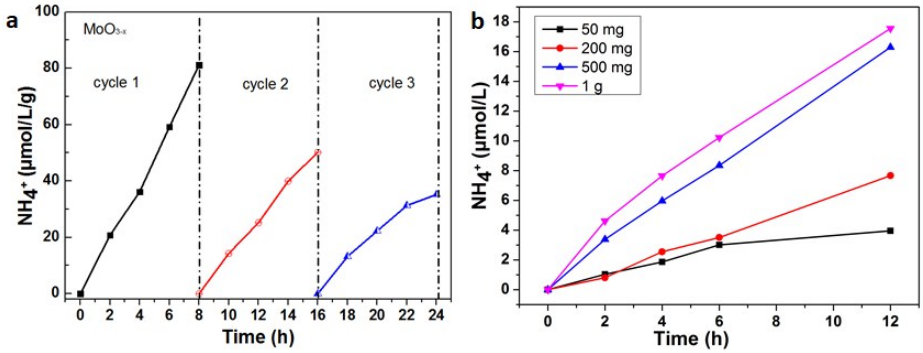

Fig. S6 (a) Recycle photocatalytic experiments for the as-synthesized MoO_{3-x} nanobelts (photocatalyst: 0.05 g; solution: 100 ml of pure water). (b) Photocatalytic activities for nitrogen fixation of the as-synthesized MoO_{3-x} nanobelts with various dosages of catalyst.

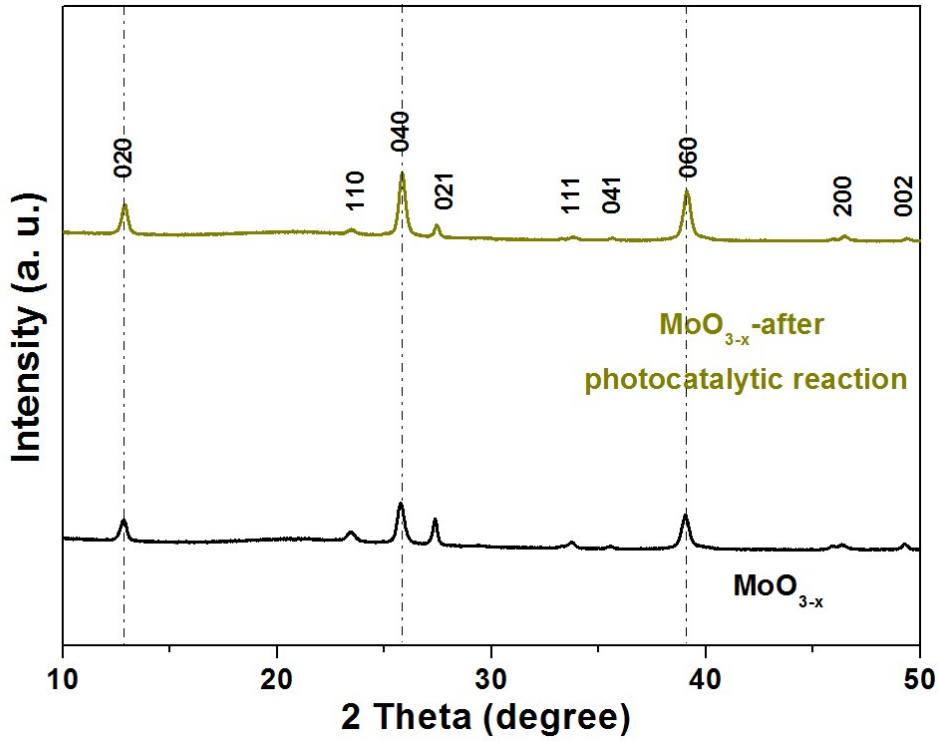

Fig. S7 XRD patterns of the sample before and after photocatalytic reaction.

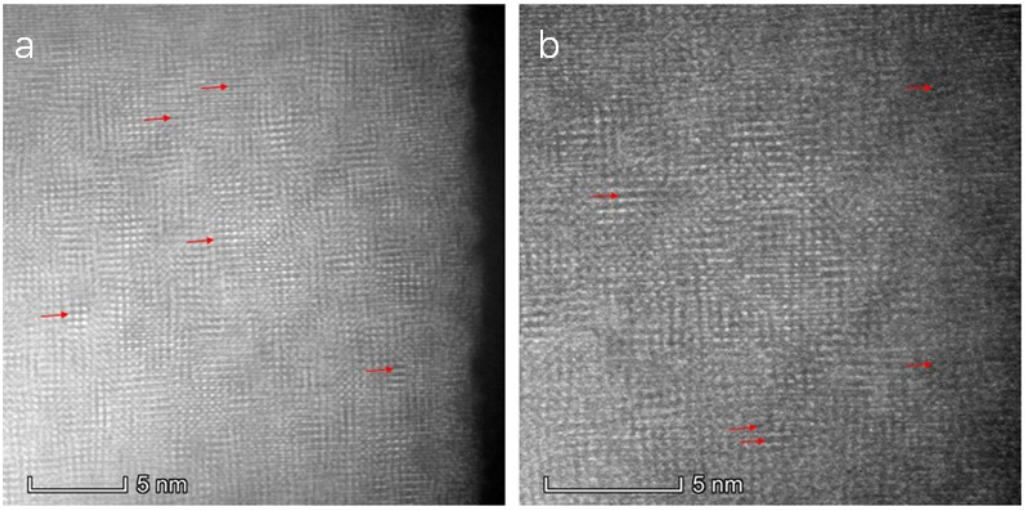

Fig. S8 The atomic scale HAADF images of the sample (a) before and (b) after the photocatalytic reaction, respectively. The red arrows show the areas with ordered oxygen-vacancies.

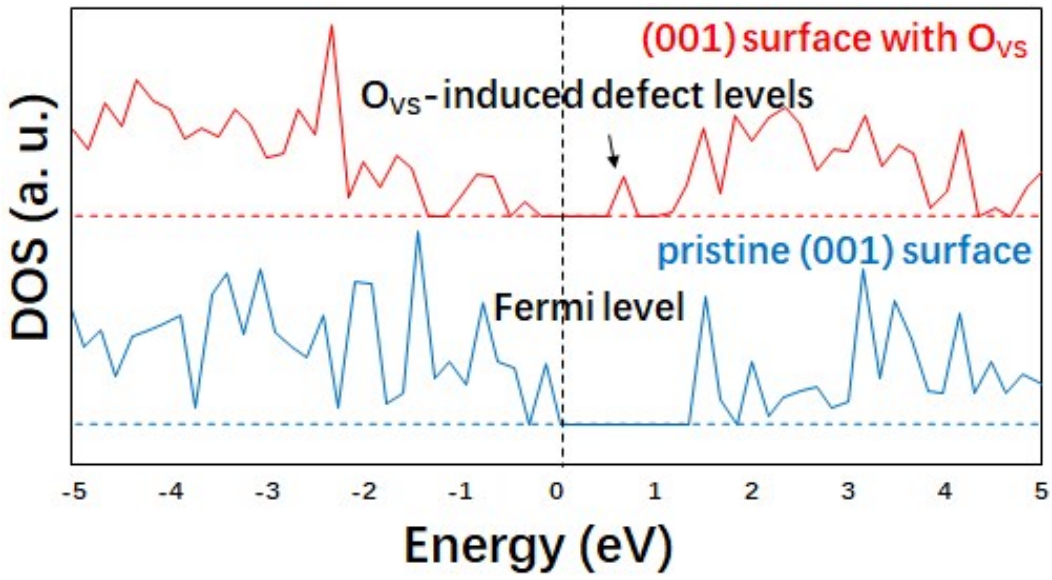

Fig. S9 The density of states (DOS) of (001) plane with and without O_{VS}.

Table S1. Atomic Populations (Mulliken) of Mo_4O_{12} unit cell and Mo_4O_{11} unit cell.

Unit cell	Species	Ion	Charge(e)	Average Charge(e)
Mo_4O_{12}	O	1	-0.59	-0.451
	O	2	-0.45	
	O	3	-0.40	
	O	4	-0.59	
	O	5	-0.45	
	O	6	-0.40	
	O	7	-0.59	
	O	8	-0.45	
	O	9	-0.40	
	O	10	-0.59	
	O	11	-0.45	
	O	12	-0.40	
	Mo	1	1.44	1.44
	Mo	2	1.44	
	Mo	3	1.44	
	Mo	4	1.44	
Mo_4O_{11}	O	1	-0.71	-0.499
	O	2	-0.45	
	O	3	-0.39	
	O	4	-0.59	
	O	5	-0.46	
	O	6	-0.40	
	O	7	-0.59	
	O	8	-0.43	
	O	9	-0.64	
	O	10	-0.45	
	O	11	-0.38	
	Mo	1	1.45	1.37
	Mo	2	1.44	
	Mo	3	1.16	
	Mo	4	1.43	

Table S2. Summary of metal oxides for photocatalytic reduction of N_2 to NH_3 at room temperature in pure water.

Catalysts	Light source	NH_3 production rate	Reference
MoO_{3-x}	UV-Vis	1.11 $\mu mol.g^{-1}.h^{-1}$	This work
Fe-doped TiO_2	UV-Vis	10 $\mu mol.g^{-1}.h^{-1}$	1
Ru-doped TiO_2	UV-Vis	22.7 $\mu mol.g^{-1}.h^{-1}$	2
Fe^{3+}-doped TiO_2	UV-Vis	6 $\mu mol.g^{-1}.h^{-1}$	3
$BaTiO_3$	UV-Vis	0.87 $\mu mol.g^{-1}.h^{-1}$	4
$SrTiO_3$	UV-Vis	0.41 $\mu mol.g^{-1}.h^{-1}$	4
Fe_2O_3+Fe_3O_4	UV-Vis	10 $\mu mol.g^{-1}.h^{-1}$	5
Mo-doped $W_{18}O_{49}$	UV-Vis	61.9 $\mu mol.g^{-1}.h^{-1}$	6
P25	UV-Vis	28.4 $\mu mol.g^{-1}.h^{-1}$	7
Ti^{3+}-TiO_2	UV-Vis	35.0 $\mu mol.g^{-1}.h^{-1}$	7

Table S3. The formation energy of O_{VS} for different planes.

Vacancy site	001		100
O1(O2)	1.05 eV	O2(O1)	-1.97 eV
O3	1.29 eV	O3(O4)	2.24 eV

Notes and references

1 S. Sun, X. Li, W. Wang, L. Zhang and X. Sun, *Appl. Catal. B Environ.*, 2017, **200**, 323–329.

2 K. T. Ranjit and B. Viswanathan, *Indian J. Chem. - Sect. A Inorganic, Phys. Theor. Anal. Chem.*, 1996, **35**, 443–453.

3 J. Soria, J. C. Conesa, V. Augugliaro, L. Palmisano, M. Schiavello and A. Sclafani, *J. Phys. Chem.*, 1991, **95**, 274–282.

4 *Synthesis (Stuttg).*, 1983, **2**, 321–324.

5 M. M. Khader, N. N. Lichtin, G. H. Vurens, M. Salmeron and G. A. Somorjai, *Langmuir*, 1987, **3**, 303–304.

6 N. Zhang, A. Jalil, D. Wu, S. Chen, Y. Liu, C. Gao, W. Ye, N. Zhang, A. Jalil, D. Wu, S. Chen, Y. Liu, C. Gao and W. Ye, *J. Am. Chem. Soc.*, 2018, **140**, 9434–9443.

7 H. Hirakawa, M. Hashimoto, Y. Shiraishi and T. Hirai, *J. Am. Chem. Soc.*, 2017, **139**, 10929–10936.