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

Electronic Supplementary Information

Charge separation and molecule activation promoted by Pd/MIL-125-NH_2 hybrid structures for selective oxidation reactions

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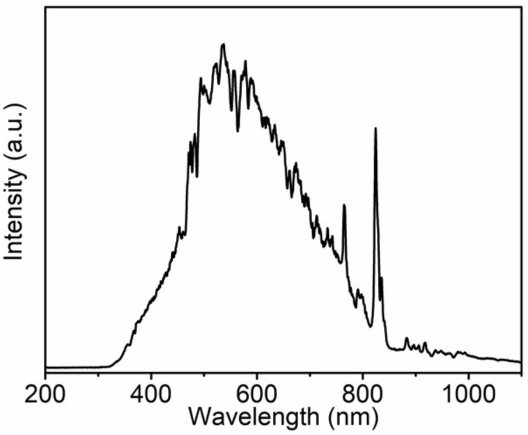


Fig. S1. The simulated sunlight spectrum from the Xe lamp used in our photocatalytic experiments.

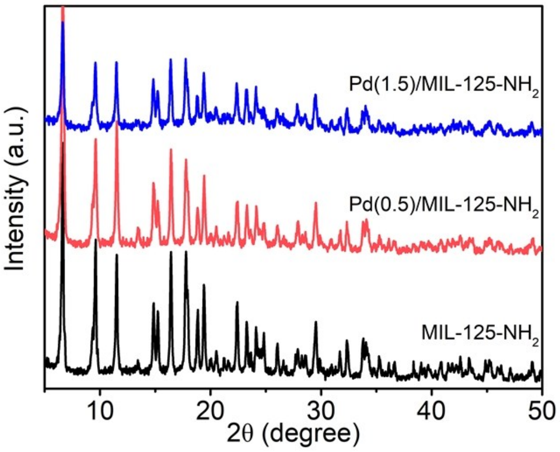


Fig. S2. XRD patterns of Pd(x)/MIL-125-NH_2 samples with different Pd loading contents.

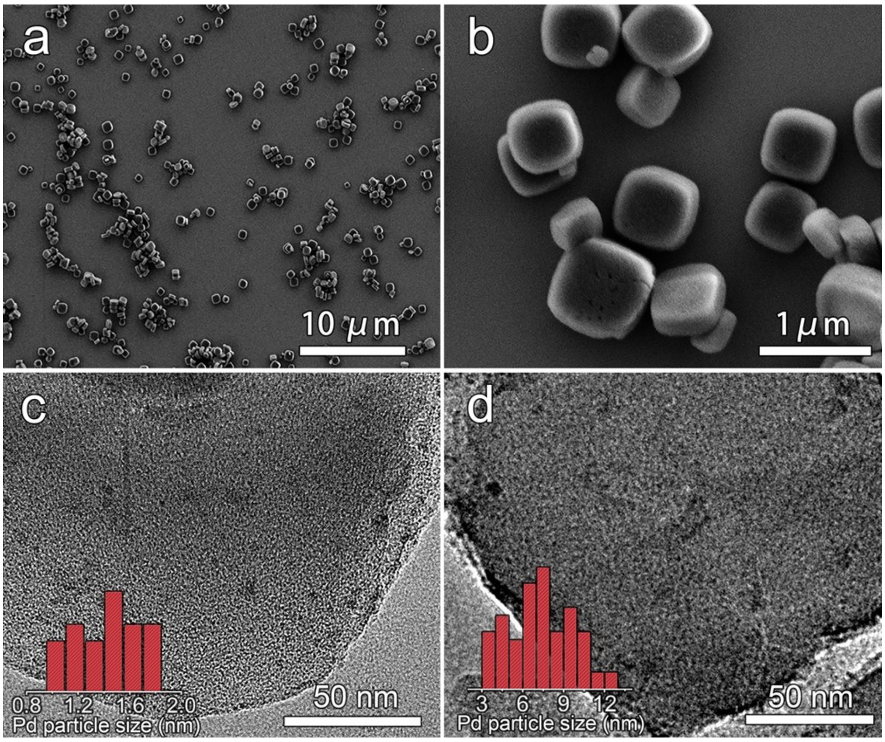


Fig. S3. (a, b) SEM images of the pristine MIL-125-NH_2. (c, d) TEM images of (c) Pd(0.5)/MIL-125-NH_2 and (d) Pd(1.5)/MIL-125-NH_2 (insets: the corresponding size distributions of Pd nanocrystals).

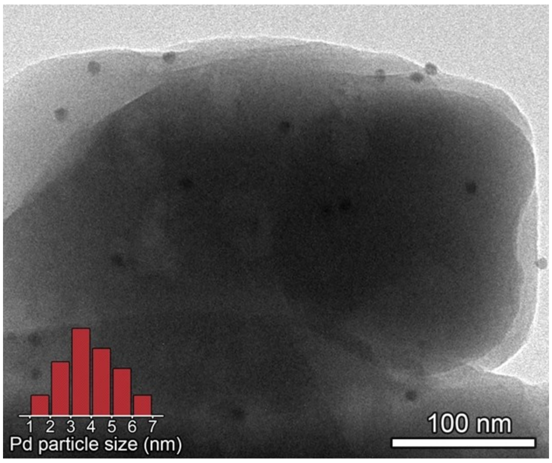


Fig. S4. TEM image of the contrast Pd/MIL-125-NH_2 sample prepared by the direct reduction-deposition of Pd nanocrystals on MIL-125-NH_2 in the suspension of $(NH_4)_2PdCl_4$ precursor and MIL-125-NH_2 particles according to the raw material ratio of Pd(1.0)/MIL-125-NH_2, without the long-time adsorption before ascorbic-acid reduction. Inset is the corresponding size distributions of Pd nanocrystals.

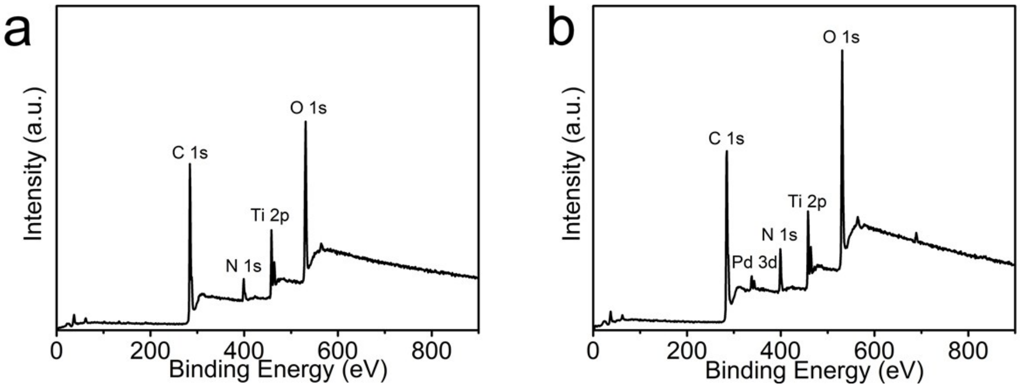


Fig. S5. Survey XPS spectra of (a) MIL-125-NH_2 and (b) Pd(1.0)/MIL-125-NH_2.

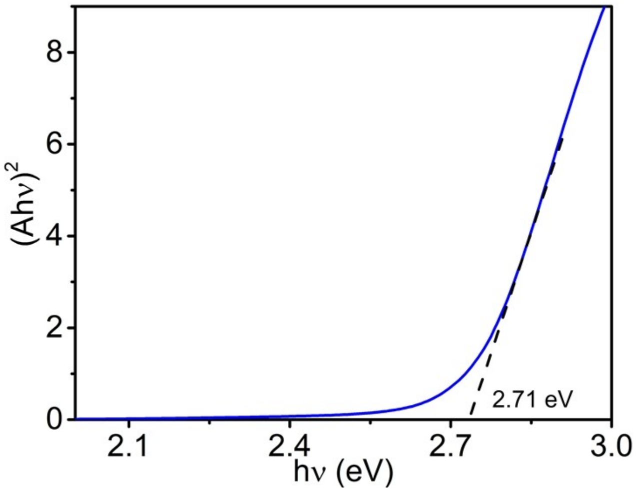


Fig. S6. Tauc plot of the pristine MIL-125-NH_2 for calculating its bandgap (2.71 eV).

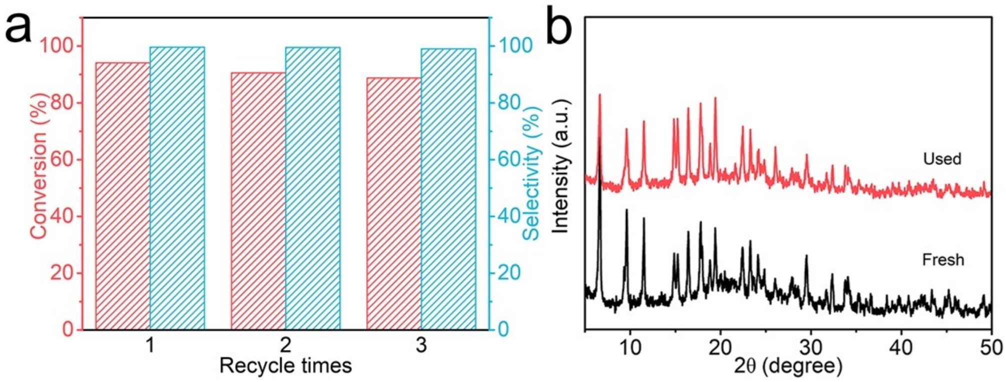


Fig. S7. (a) Recycling tests on Pd(1.0)/MIL-125-NH_2 for photocatalytic oxidation of benzylamine, (b) XRD patterns of Pd(1.0)/MIL-125-NH_2 catalyst before and after the three cycles.

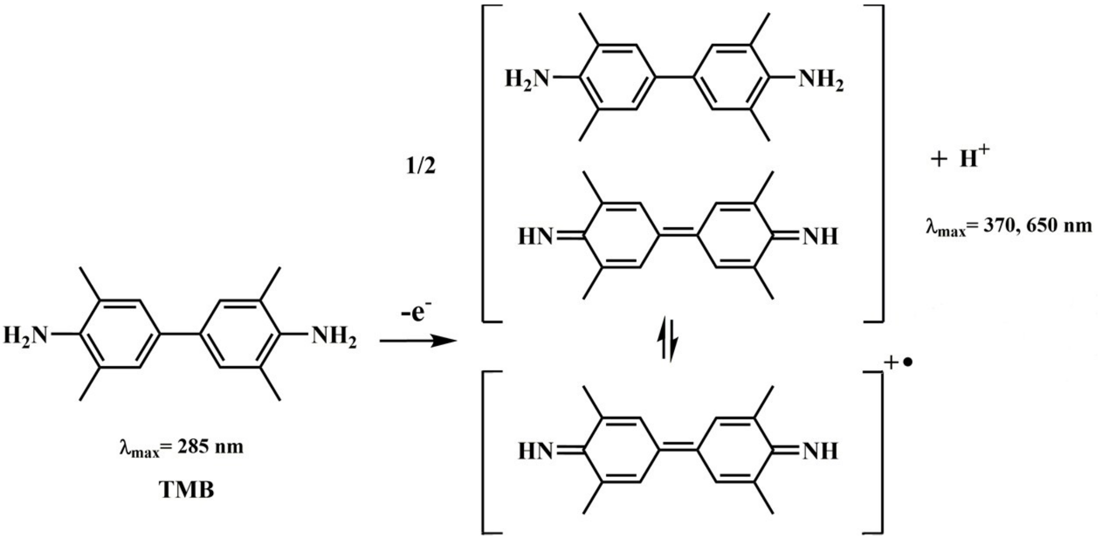


Fig. S8. TMB oxidation mechanism in the presence of Pd(1.0)/MIL-125-NH_2 photocatalyst.[1,2]

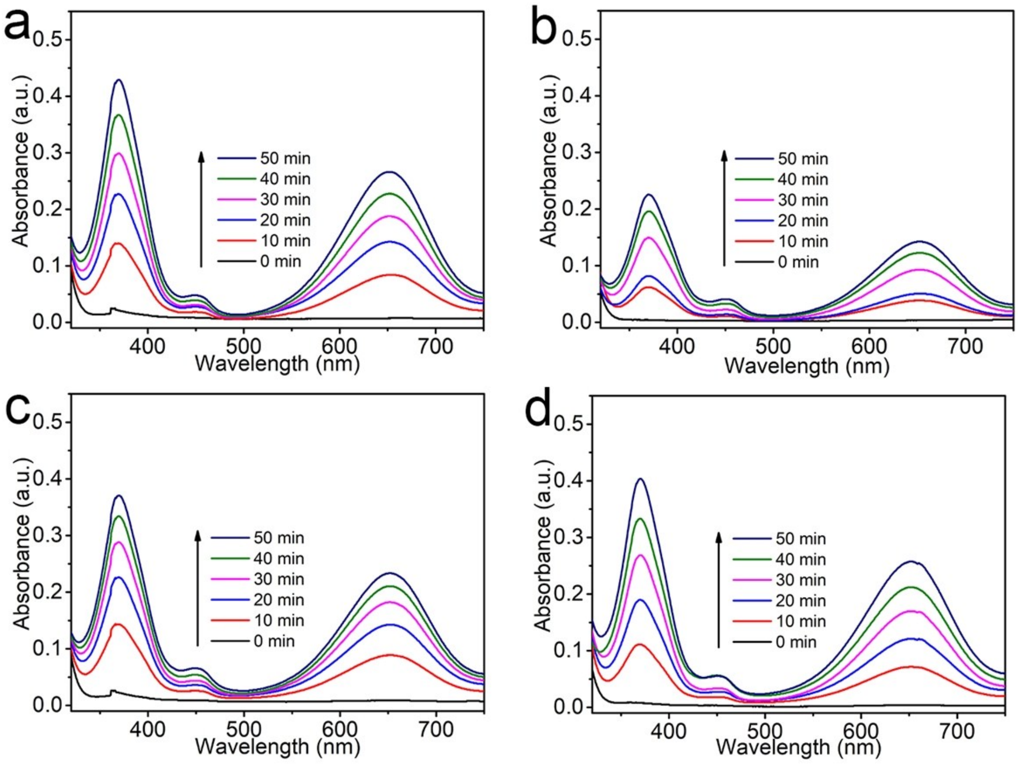


Fig. S9. UV-Vis spectra of TMB solution under the simulated sunlight and in the presence of MIL-125-NH_2 and various scavengers: (a) catalase (3500 unit/mL, 200 μL), (b) superoxide dismutase (2000 unit/mL, 2 mL), (c) mannite (10 mg), and (d) carotene (5 mg).

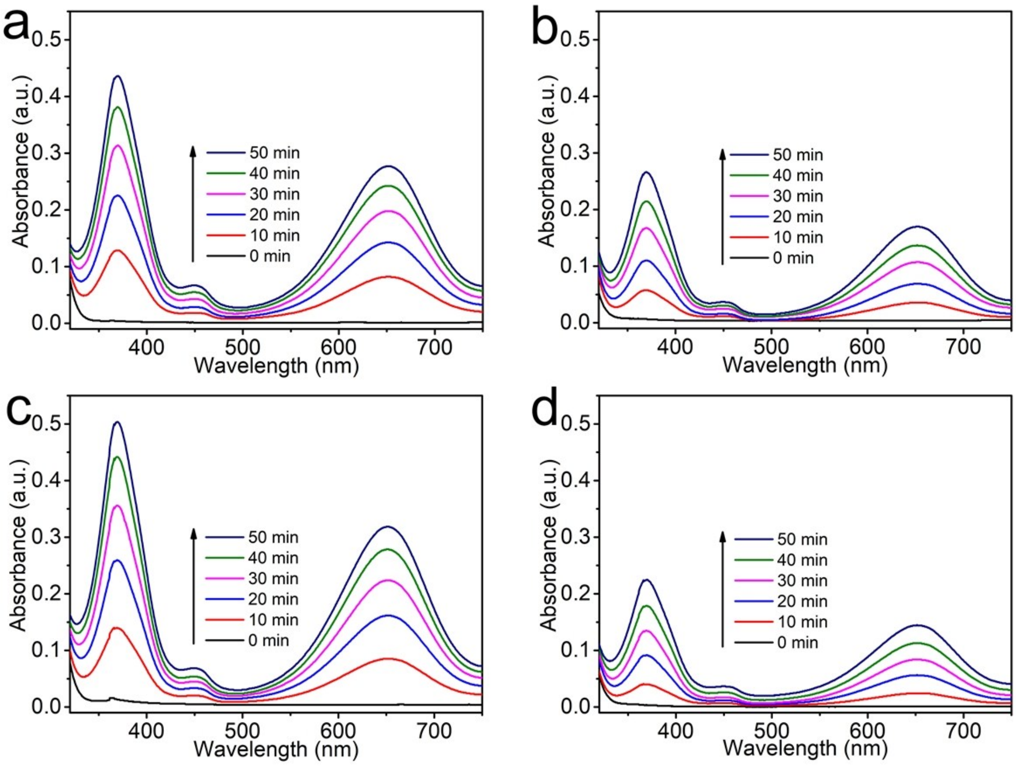


Fig. S10. UV-Vis spectra of TMB solution under the simulated sunlight and in the presence of Pd(1.0)/MIL-125-NH_2 and various scavengers: (a) catalase (3500 unit/mL, 200 μL), (b) superoxide dismutase (2000 unit/mL, 2 mL), (c) mannite (10 mg), and (d) carotene (5 mg).

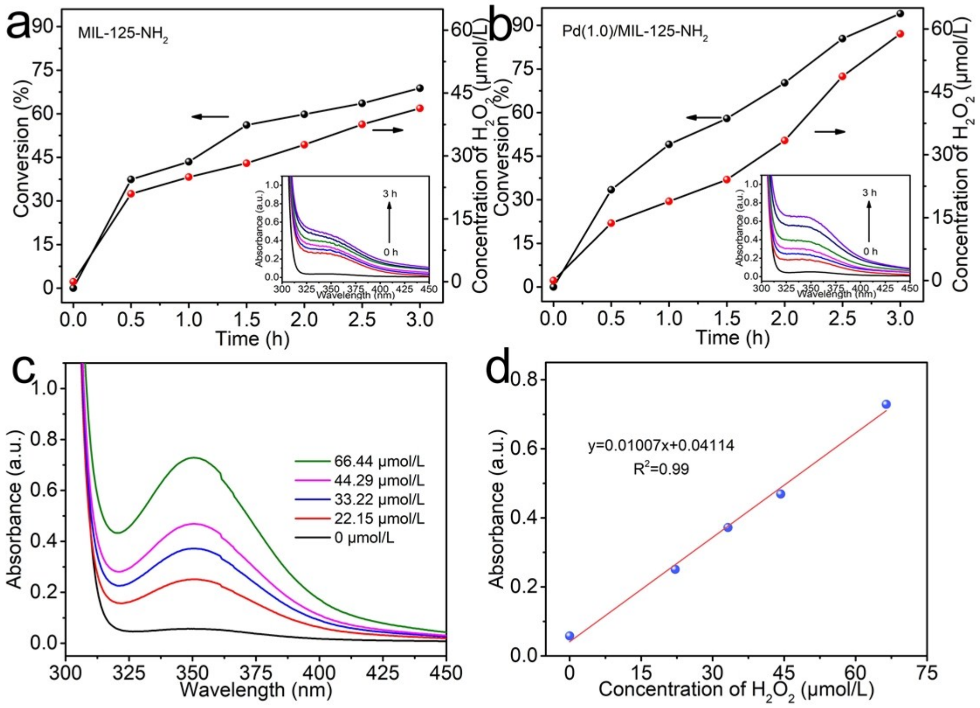


Fig. S11. Time-dependent benzylamine conversions and H_2O_2 concentration in the photocatalytic reaction suspensions of (a) MIL-125-NH_2, (b) Pd(1.0)/MIL-125-NH_2 (insets: the corresponding UV-vis absorption spectra for detecting H_2O_2 produced in the reaction suspensions). (c) UV-vis absorption spectra for detecting different concentrations of H_2O_2, (d) the standard curve of H_2O_2 concentration vs. spectral absorbance at 350 nm.

The hydrogen peroxide (H_2O_2) produced during the photocatalytic oxidation of benzylamine was detected according to the iodimetry method described as follows. After finishing the photocatalytic reaction, the reaction solution was filtered through a syringe filter to remove the catalyst particles. 1 mL of the filtrate was mixed with 1 mL of 0.1 M potassium hydrogen phthalate ($C_8H_5KO_4$) aqueous solution and 1 mL of 0.4 M potassium iodide (KI) aqueous solution, and then kept for 5 min. H_2O_2 could quantificationally react with I^- ions to produce the I_3^- ions which showed the strong absorption at 350 nm. The absorption spectra were recorded on UV-Vis spectrophotometer (UV-2700, Shimadzu) in the wavelength range of 200-800 nm. Therefore, the H_2O_2 amount generated in the reaction system can be evaluated by the absorbance of the resultant I_3^- ions.

Table S1. Specific surface areas and pore volumes of pristine MIL-125-NH_2 and Pd(1.0)/MIL-125-NH_2 hybrid material.

Sample	**BET Surface area (m^2/g)**	**Average pore width (nm)**
MIL-125-NH_2	857.1	2.3
Pd(1.0)/MIL-125-NH_2	789.7	2.8

Table S2. The parameters from fitting the time-resolved PL decay profiles.

Sample	**τ_1 (ns)**	**τ_2 (ns)**	**A_1**	**A_2**	**τ_m (ns)**
MIL-125-NH_2	0.017	7.6	96.3	3.7	7.2
Pd(1.0)/MIL-125-NH_2	0.021	6.2	94.1	5.9	5.9

Table S3. Photocatalytic oxidation of benzylamine in the presence of various photocatalysts. Reaction conditions: 5 mg catalyst, 0.05 mmol benzylamine, 2 mL acetonitrile, 300 W Xe lamp (360~780 nm), 3 h, in air and room temperature.

Photocatalyst	**Conversion (%)**	**Selectivity (%)**
MIL-125-NH_2	68.82	86.01
Pd(0.2)/MIL-125-NH_2	79.97	99.34
Pd(0.5)/MIL-125-NH_2	86.07	99.22
Pd(1.0)/MIL-125-NH_2	94.08	99.96
Pd(1.5)/MIL-125-NH_2	62.46	99.82

Table S4. Photocatalytic oxidation of benzylamine under different conditions. Reaction conditions: 5 mg catalyst, 0.05 mmol benzylamine, 2 mL acetonitrile, 3 h, room temperature.

Entry	**Photocatalyst**	**Conditions**	**Conversion (%)**	**Selectivity (%)**
1	Blank	Visible light, air	/	/
2	Pd(1.0)/MIL-125-NH_2	Dark, air	/	/
3	MIL-125-NH_2	Visible light, air	52.61	82.61
4	Pd(1.0)/MIL-125-NH_2	Visible light, air	77.41	99.70
5	Pd(1.0)/MIL-125-NH_2	UV-vis light, O_2	94.06	99.83
6	Pd(1.0)/MIL-125-NH_2	UV-vis light, N_2	42.74	99.43

Table S5. Photocatalytic oxidation of benzylamine over Pd(1.0)/MIL-125-NH_2 under different monochromatic irradiations. Reaction conditions: 5 mg catalyst, 0.05 mmol benzylamine, 2 mL acetonitrile, 300 W Xe lamp with the corresponding optical filters, 3 h, in air and room temperature.

Wavelength (nm)	**Conversion (%)**	**Selectivity (%)**
365	60.88	99.85
420	60.47	99.75
450	47.05	99.36
500	27.23	99.44
550	26.11	99.46
600	24.41	99.76

700	23.57	99.88

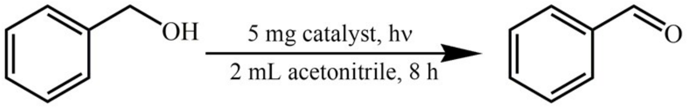
Table S6. Photocatalytic oxidation of para-substituted derivatives of benzylamine in the presence of Pd(1.0)/MIL-125-NH_2. Reaction conditions: 5 mg catalyst, 0.05 mmol substrate, 2 mL acetonitrile, 300 W Xe lamp (360~780 nm), 3 h, in air and room temperature.

Sample	**Conversion (%)**	**Selectivity (%)**
4-H	94.08	99.96
4-F	84.82	99.43
4-Cl	80.22	99.23
4-CH_3	77.22	99.76
4-OCH_3	91.76	99.62

Table S7. Recycling tests on Pd(1.0)/MIL-125-NH_2 for photocatalytic oxidation of benzylamine. Reaction conditions: 5 mg catalyst, 0.05 mmol benzylamine, 2 mL acetonitrile, 300 W Xe lamp (360~780 nm), in air and room temperature, 3 h for each cycle.

Recycle times	**Conversion (%)**	**Selectivity (%)**
1	94.08	99.96
2	90.55	99.81
3	88.56	99.22

Table S8. Photocatalytic selective oxidation of benzyl alcohol in the presence of various photocatalysts. Reaction conditions: 5 mg catalyst, 0.05 mmol benzyl alcohol, 2 mL acetonitrile, 300 W Xe lamp (360~780 nm), 8 h, in air and room temperature.



Photocatalyst	Conversion (%)	Selectivity (%)
MIL-125-NH_2	15.18	100
Pd(0.5)/MIL-125-NH_2	20.45	100
Pd(1.0)/MIL-125-NH_2	35.89	100
Pd(1.5)/MIL-125-NH_2	16.50	100

References:

1 Y.-Z. Chen, Z. U. Wang, H. Wang, J. Lu, S.-H. Yu and H.-L. Jiang, *J. Am. Chem. Soc.*, 2017, **139**, 2035-2044.

2 P. Josephy, T. Eling, and R. Mason, *J. Biol. Chem.*, 1982, **257**, 3669-3675