Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Thermo-enhanced photocatalytic oxidation of amines to imines over MIL-125-NH_2@Ag@COF hybrid under visible light

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Figure S1. PCX50C photo catalytic instrument.

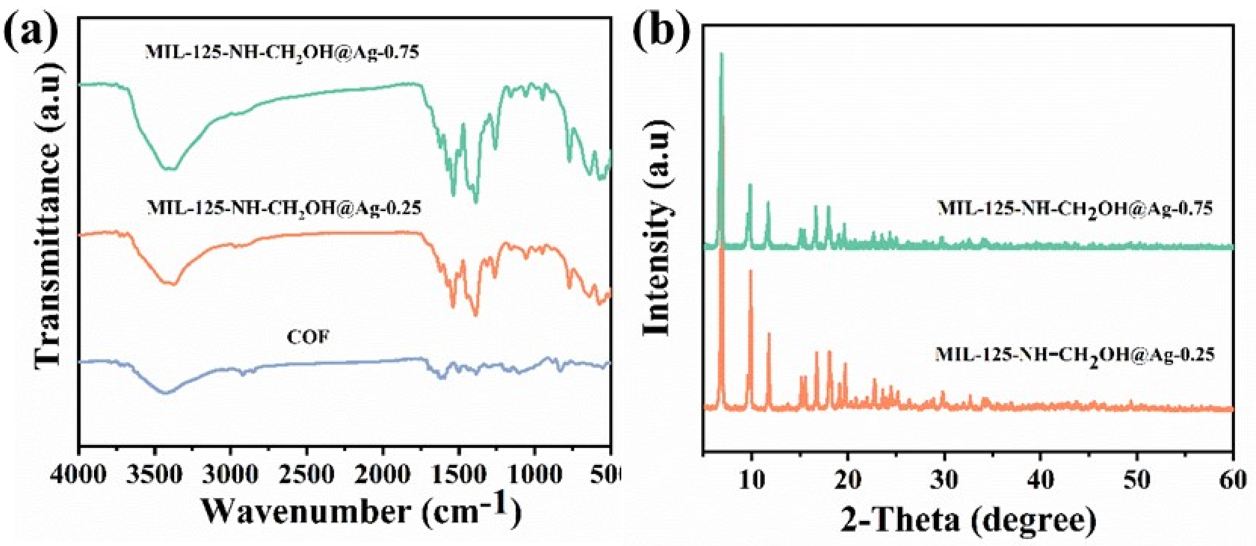

Figure S2. (a) FTIR image of MIL-125-NH-CH_2H@Ag-0.25, MIL-125-NH-CH_2OH@Ag-0.75 and pure COF; (b) XRD pattern of MIL-125-NH-CH_2OH@Ag-0.25 and MIL-125-NH-CH_2OH@Ag-0.75.

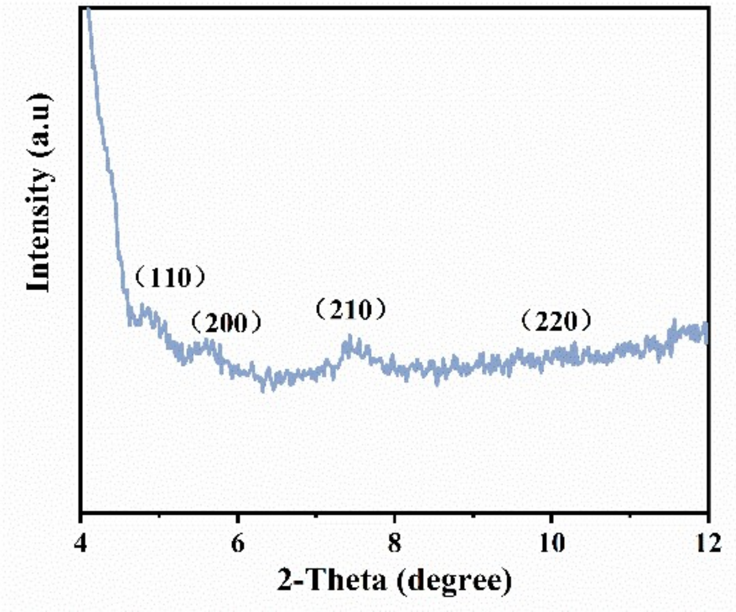

Figure S3. XRD pattern of pure COF.

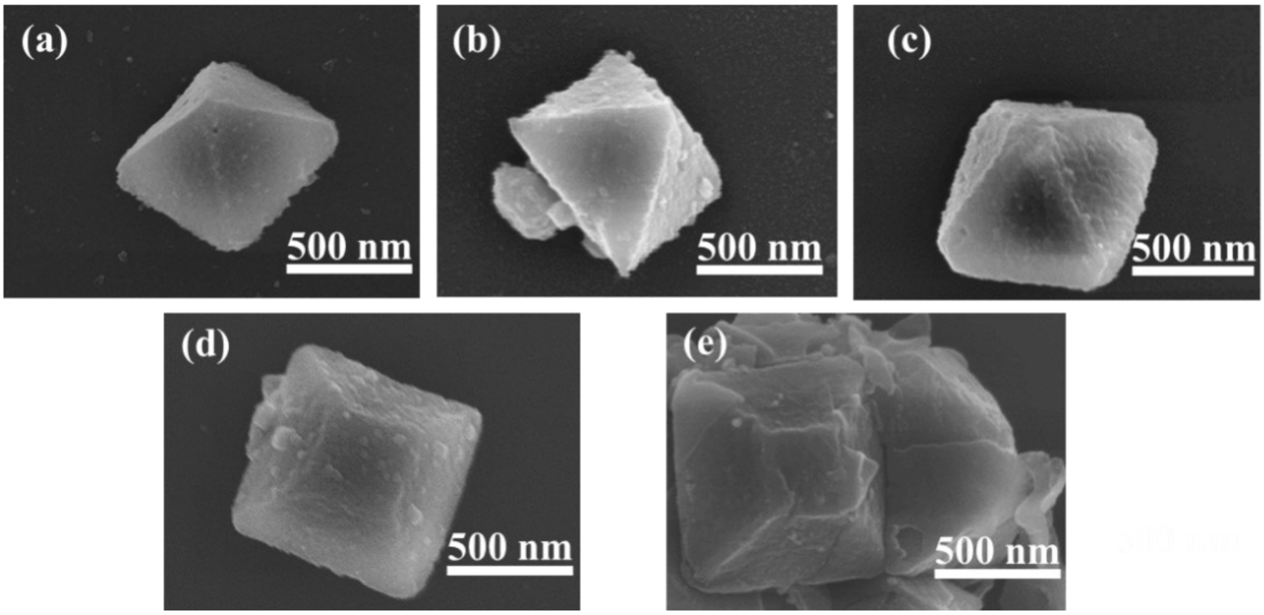

Figure S4. SEM images of (a) MIL-125-NH-CH_2OH, (b) MIL-125-NH-CH_2OH@Ag-0.25, (c) MIL-125-NH-CH_2OH@Ag-0.75, (d) MIL-125-NH-CH_2OH@Ag-0.5@COF-1, (e) MIL-125-NH-CH_2OH@Ag-0.5@COF-3.

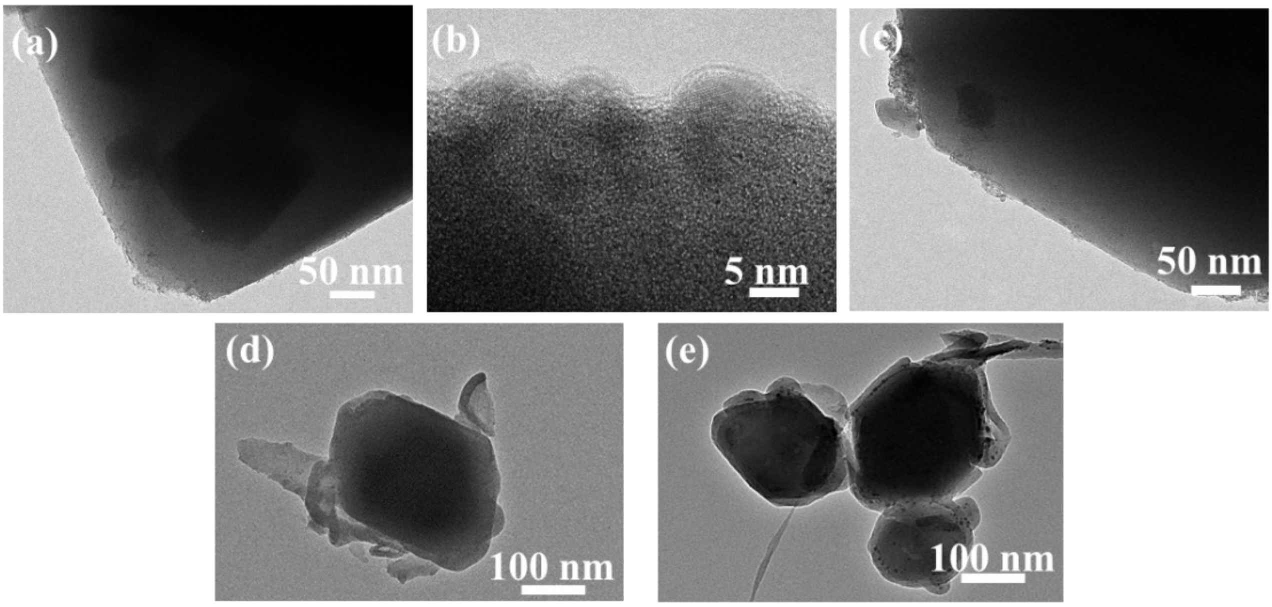

Figure S5. TEM images of (a, b) MIL-125-NH-CH_2OH@Ag-0.25, (c) MIL-125-NH-CH_2OH@Ag-0.75, (d) MIL-125-NH-CH_2OH@Ag-0.5@COF-1, (e) MIL-125-NH-CH_2OH@Ag-0.5@COF-3.

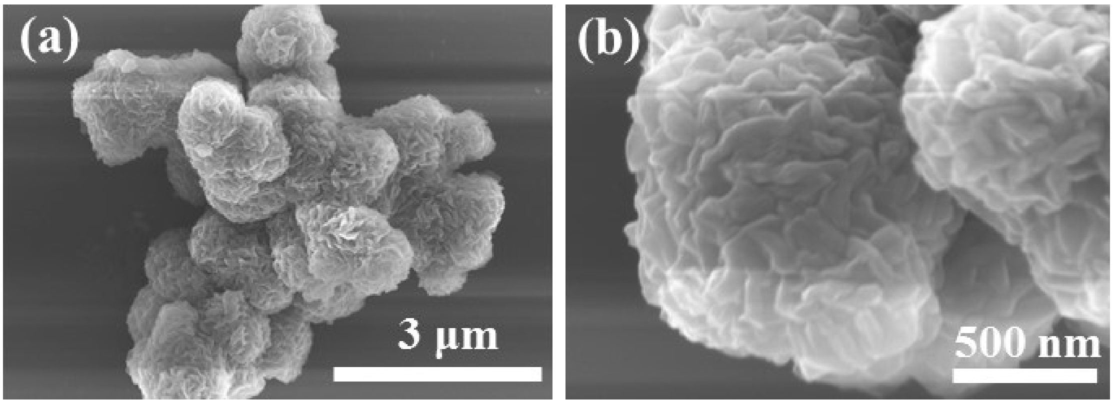

Figure S6. SEM of pure COF with different magnification (a) 20 K and (b) 60 K

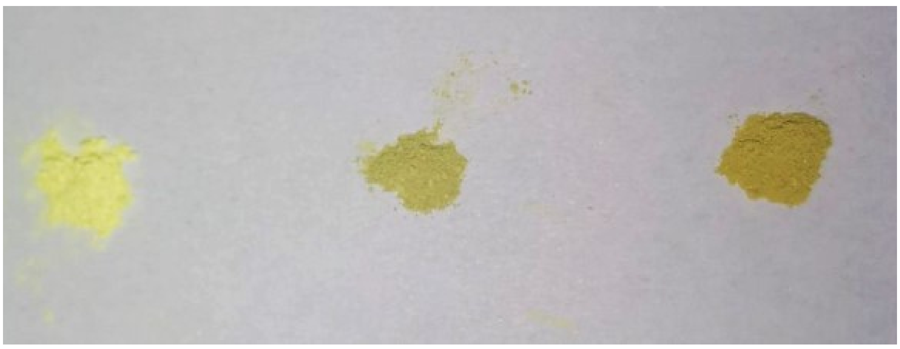

Figure S7. From left to right is MIL-125-NH_2, MIL-125-NH-CH_2OH@Ag-0.5 and MIL-125-NH-CH_2OH@Ag-0.5@COF-2.

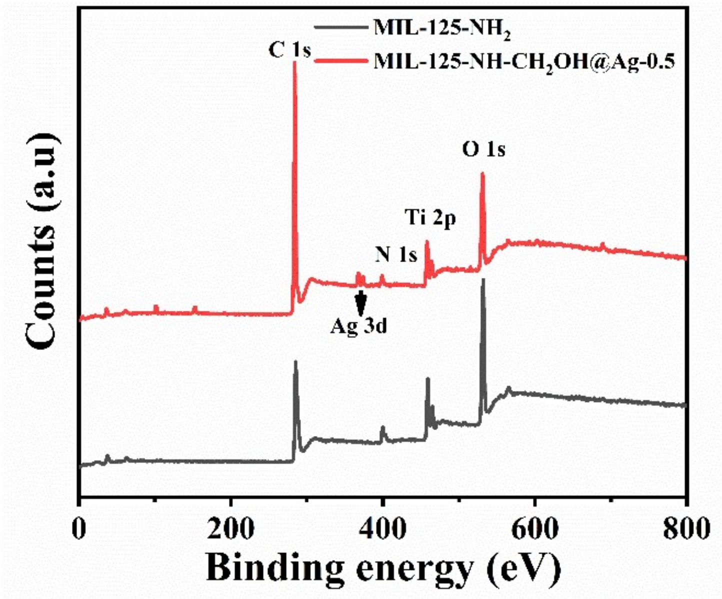

Figure S8. XPS survey spectra of MIL-125-NH_2 and MIL-125-NH-CH_2OH@Ag-0.5.

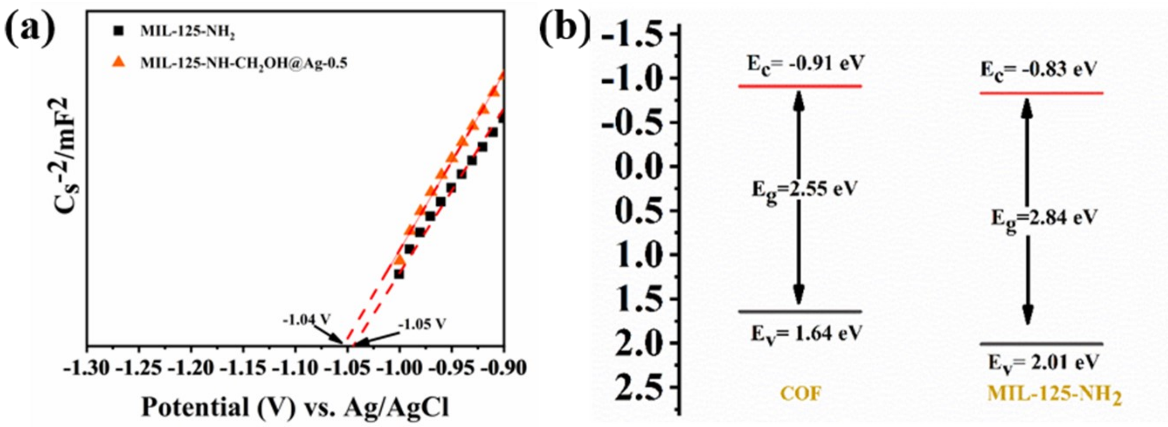

Figure S9. Mott–Schottky plots of (a) MIL-125-NH_2 and MIL-125-NH-CH_2OH@Ag-0.5, (b) Schematic diagram of conduction band and price band of COF and MIL-125-NH_2.

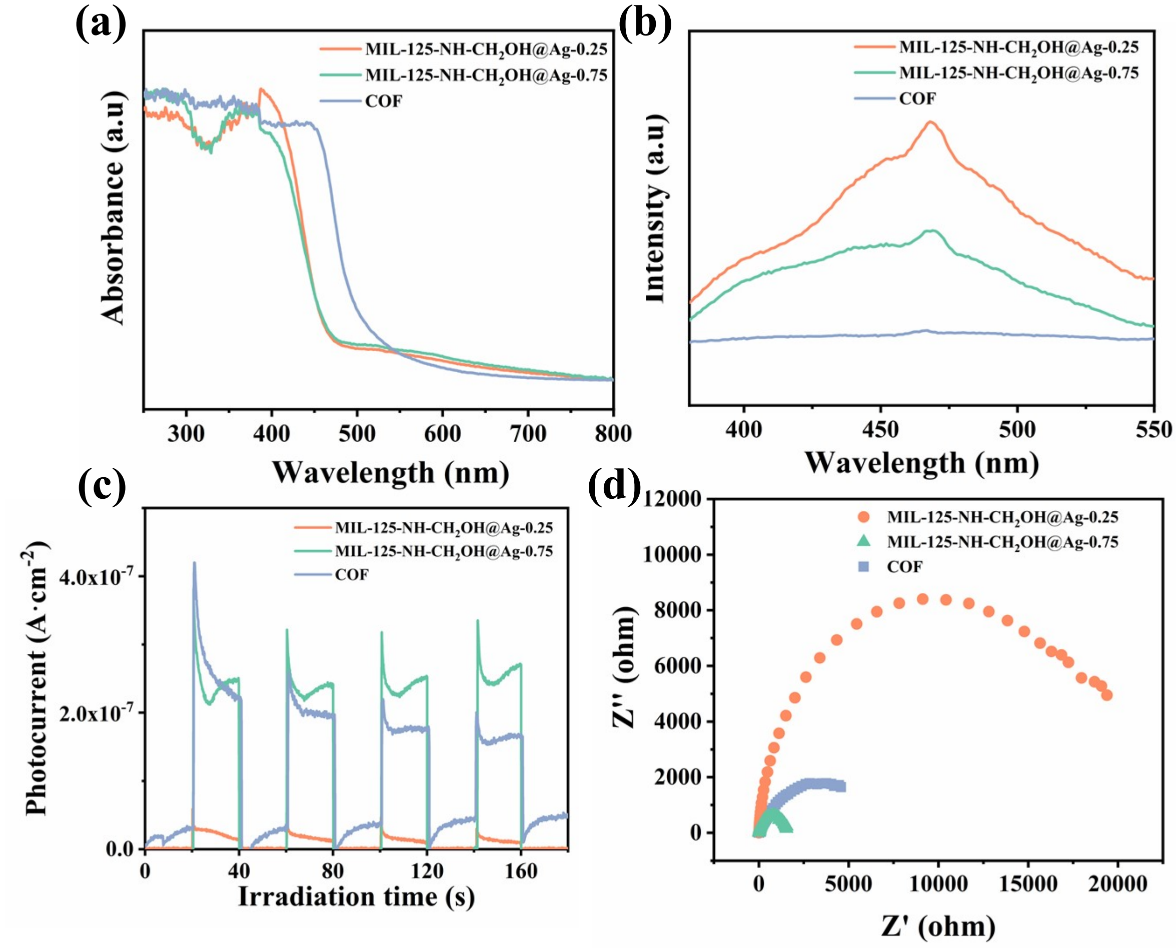

Figure S10. (a) UV-vis DSR, (b) PL spectra plots, (c) Transient photocurrent response and (d) EIS Nyquist plots of MIL-125-NH-CH$_2$OH@Ag-0.25, MIL-125-NH-CH$_2$OH@Ag-0.75 and COF.

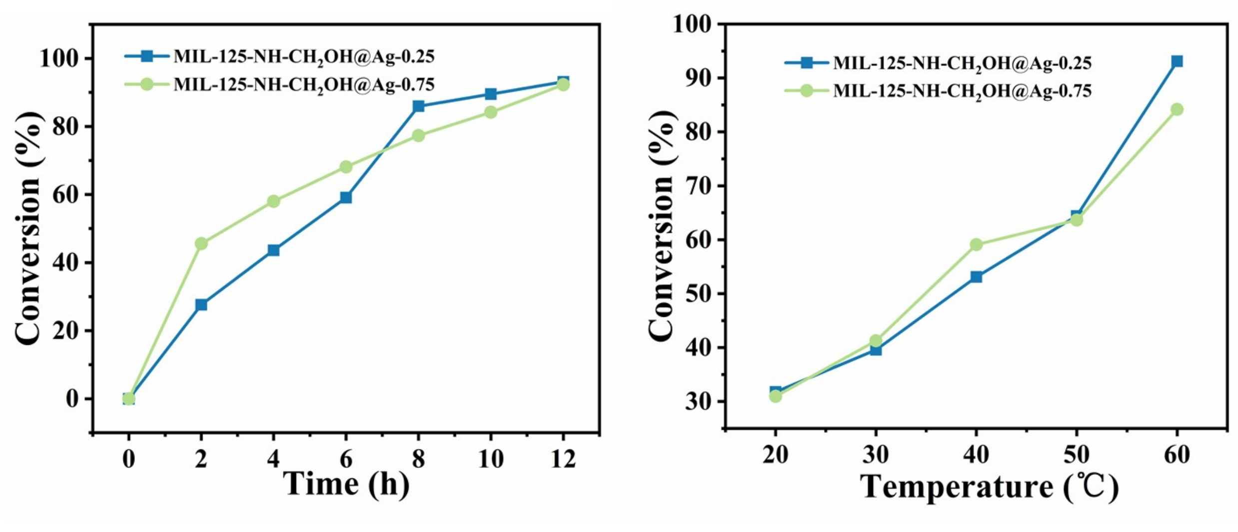

Figure S11. Kinetic curve (a) and effect of reaction temperature (b) over MIL-125-NH-CH$_2$OH@Ag-0.25 and MIL-125-NH-CH$_2$OH@Ag-0.75.

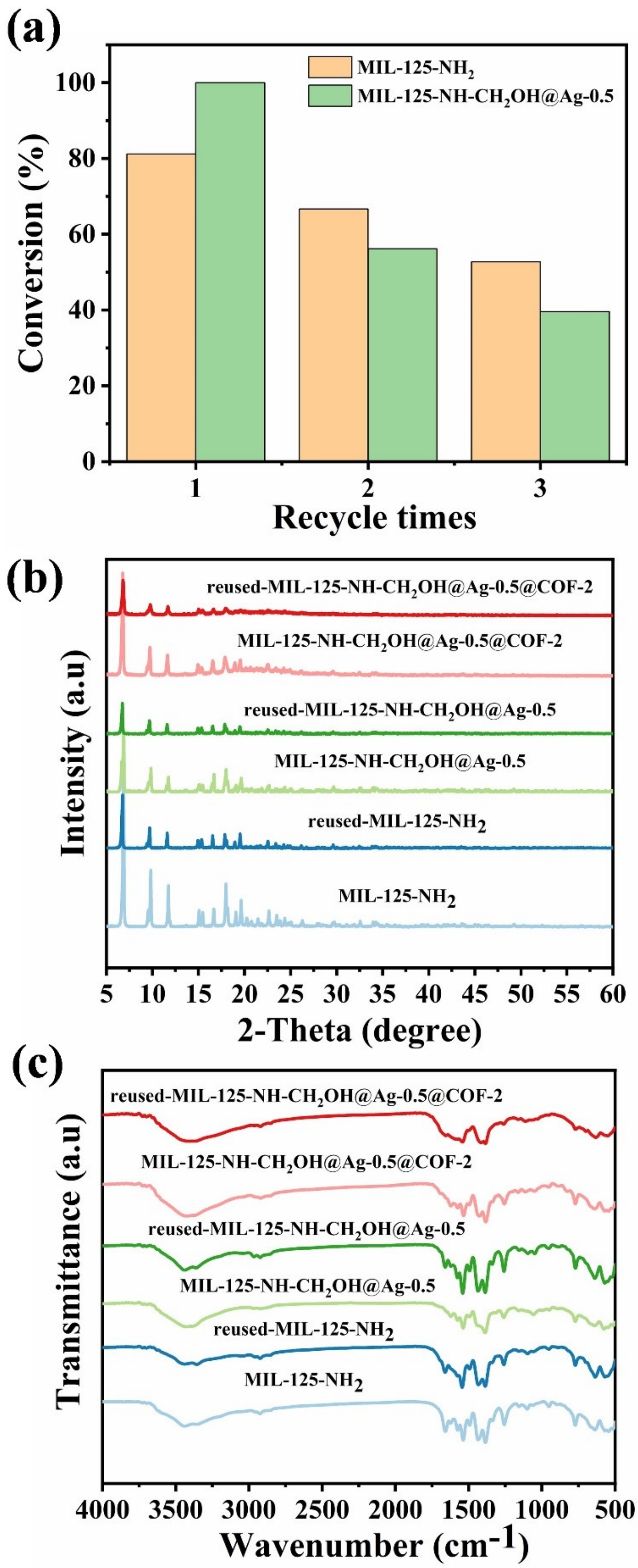

Figure S12. (a) Recyclability of MIL-125-NH_2 and MIL-125-NH-CH_2OH@Ag-0.5, (b) XRD patterns and (c) FT-IR spectra of fresh and reused MIL-125-NH_2, MIL-125-NH-CH_2OH@Ag-0.5, MIL-125-NH-CH_2OH@Ag-0.5@COF-2.

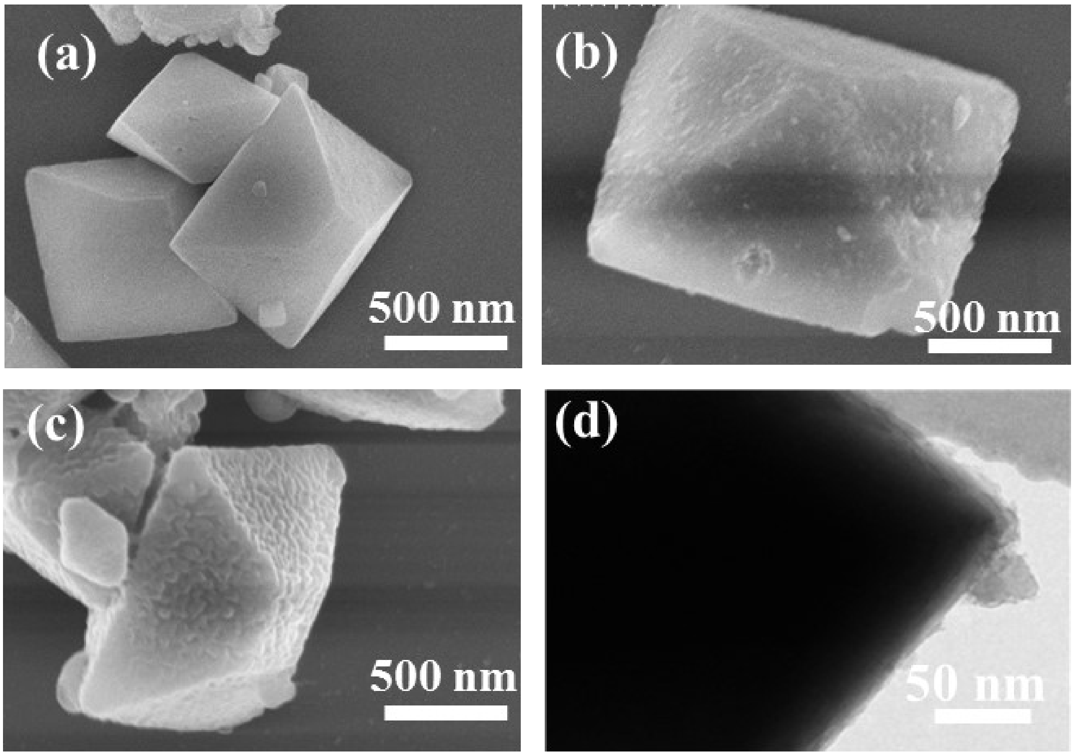

Figure S13. SEM images of (a) reused MIL-125-NH_2, (b) reused MIL-125-NH-CH_2OH@Ag-0.5 and (c) reused MIL-125-NH-CH_2OH@Ag-0.5@COF-2; (d) TEM image of reused MIL-125-NH-CH_2OH@Ag-0.5.

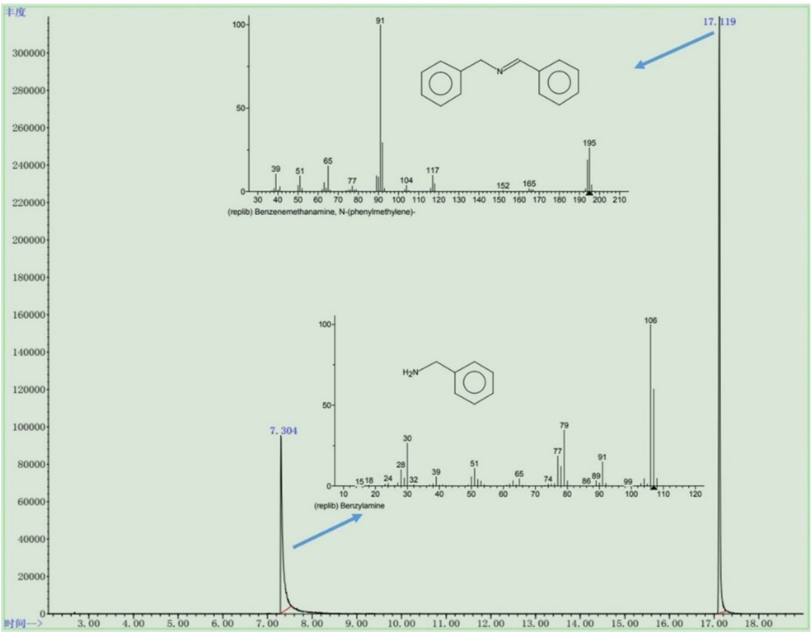

Figure S14. GC-MS results of using MIL-125-NH-CH_2OH@Ag-0.5@COF-2 as photocatalyst for oxidation of benzylamine.

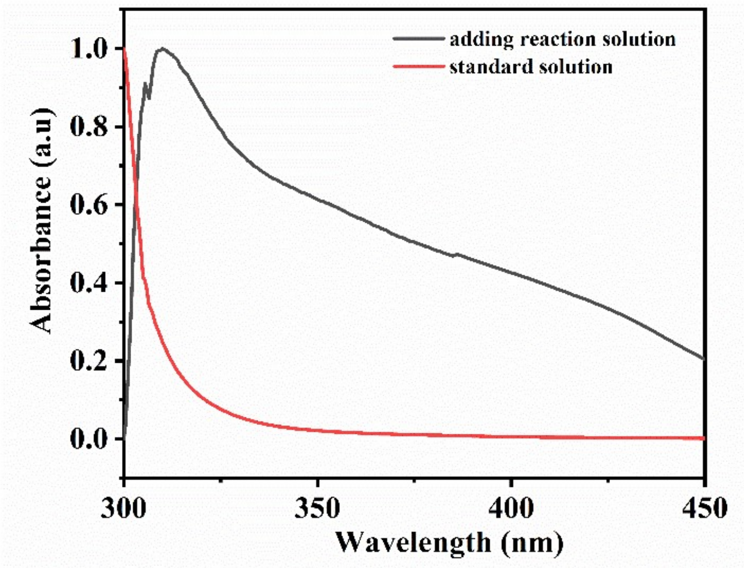

Figure S15. UV-vis absorption spectra for detecting different concentrations of H_2O_2. The detection method of hydrogen peroxide is iodization.

Table S1. Photocatalytic oxidation of benzylamine using various amounts of MIL-125-NH-CH_2OH@Ag-0.5@COF-2.

Entry	Quality (mg)	Conversion (%)	Selectivity (%)
1	5	88.5	> 99.9
2	10	100	> 99.9
3	15	90.8	> 99.9
4	20	85.8	> 99.9
5	30	61.8	> 99.9
6	40	55.7	> 99.9

Reaction conditions: 0.25 mmol benzylamine, 5 mL CH_3CN, air, 60 °C, visible light irradiation, 12 h.

Table S2. Photocatalytic oxidation of benzylamine with different photocatalysts at different reaction time.

Catalyst	Conversion (%)					
	2 h	4 h	6 h	6 h	10 h	12 h
MIL-125-NH_2	10.4	30.3	44.0	57.9	68.5	81.2
MIL-125-NH-CH_2OH	20.8	44.0	58.5	77.4	88.7	92.9
MIL-125-NH-CH_2OH@Ag-0.25	27.6	43.6	59.1	86.0	89.5	93.1
MIL-125-NH-CH_2OH@Ag-0.5	30.8	42.3	73.3	85.6	91.8	100
MIL-125-NH-CH_2OH@Ag-0.75	45.6	58.0	68.2	76.3	77.3	84.2
MIL-125-NH-CH_2OH@Ag-0.5@COF-1	14.8	30.2	40.8	56.5	63.2	71.4
MIL-125-NH-CH_2OH@Ag-0.5@COF-2	28.2	54.3	73.8	81.5	88.9	100
MIL-125-NH-CH_2OH@Ag-0.5@COF-3	14.3	30.8	37.4	40.4	49.2	70.3

Reaction conditions: 0.25 mmol substrates, 10 mg photocatalyst, 5 mL CH_3CN, air, visible light irradiation, 60 °C.

Table S3. Recycle experiment.

Entry	Conversion (%)		
	MIL-125-NH_2	MIL-125-NH-CH_2OH@Ag-0.5	MIL-125-NH-CH_2OH@Ag-0.5@COF-2
1	81.2	100	100
2	66.7	56.2	92.9
3	52.8	39.6	93.9

Reaction conditions: 0.25 mmol benzylamine, 10 mg photocatalyst, 5 mL CH_3CN, air, visible light irradiation, 12 h.

Table S4. Photocatalytic oxidation of benzylamine over different photocatalysts at different temperature.

Catalyst	Conversion (%)				
	20 °C	30 °C	40 °C	50 °C	60 °C
MIL-125-NH_2	26.2	30.2	33.2	51.8	81.2
MIL-125-NH-CH_2OH	26.0	31.6	43.7	57.4	92.9
MIL-125-NH-CH_2OH@Ag-0.25	31.8	39.6	47.3	64.4	93.1
MIL-125-NH-CH_2OH@Ag-0.5	34.0	34.5	39.8	74.3	100
MIL-125-NH-CH_2OH@Ag-0.75	31.0	41.3	55.0	63.7	84.2
MIL-125-NH-CH_2OH@Ag-0.5@COF-1	41.8	49.0	52.4	67.8	71.4
MIL-125-NH-CH_2OH@Ag-0.5@COF-2	53.6	64.0	73.3	92.9	100
MIL-125-NH-CH_2OH@Ag-0.5@COF-3	47.3	49.5	44.0	66.4	70.3

Reaction conditions: 0.25 mmol benzylamine, 10 mg photocatalyst, 5 mL CH_3CN, air, visible light irradiation, 12 h.