

# **Boosting photocatalytic degradation of ethyl acetate by Z-scheme Au-TiO<sub>2</sub>@NH<sub>2</sub>-UiO-66 heterojunction with ultrafine Au as electron mediator**

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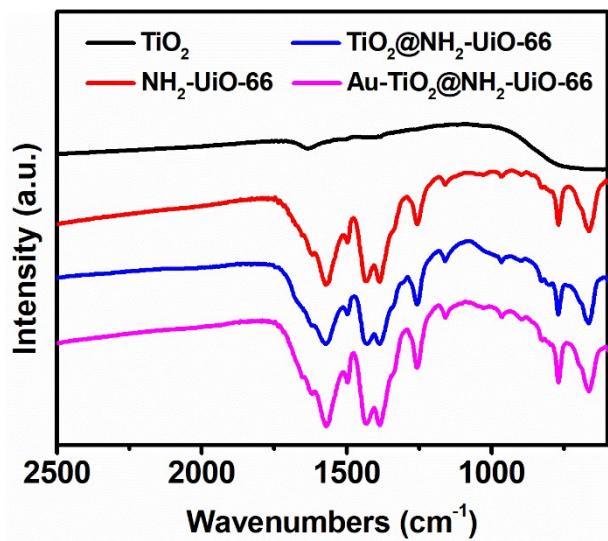
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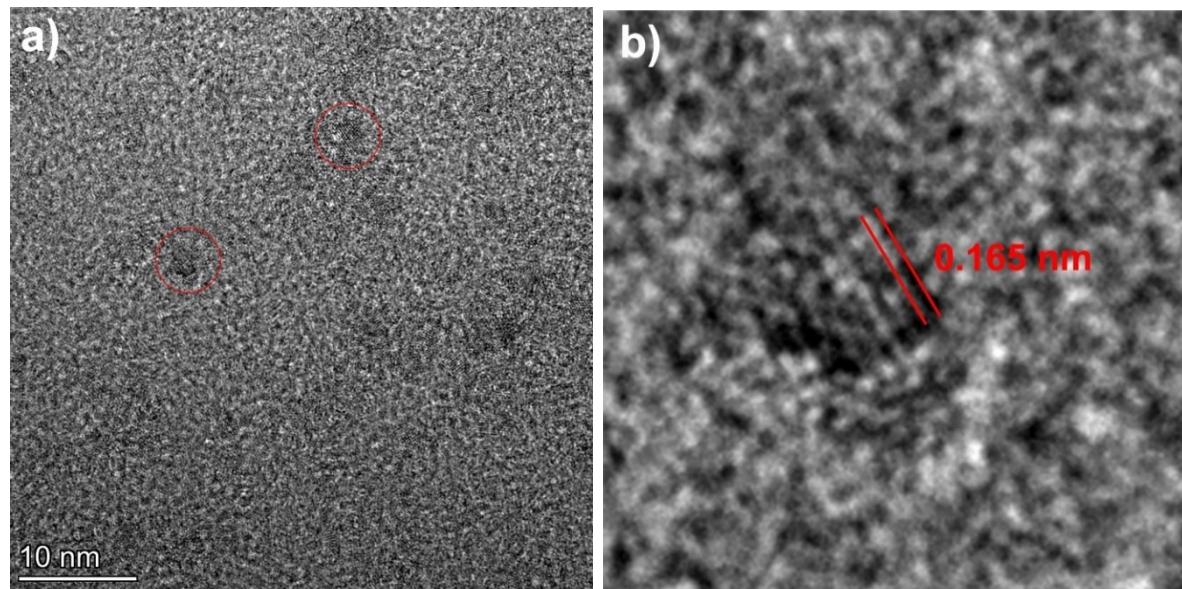
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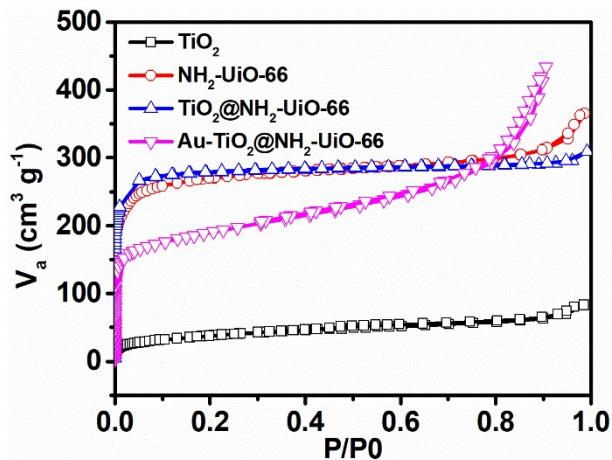
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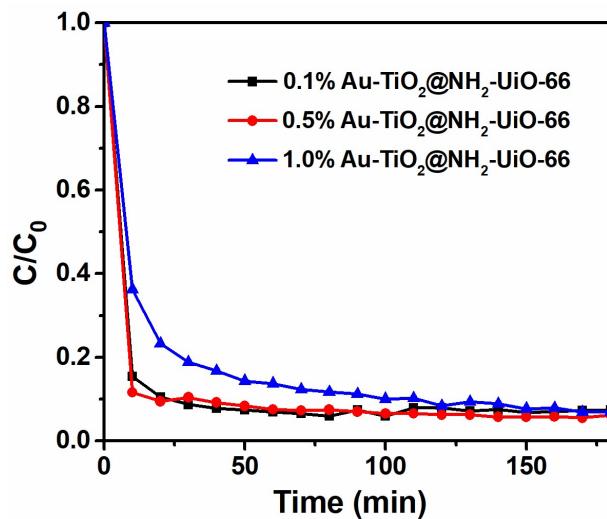
**Fig. S1** FT-IR spectra of  $\text{TiO}_2$ , pure  $\text{NH}_2\text{-UiO-66}$ ,  $\text{TiO}_2@\text{NH}_2\text{-UiO-66}$  and  $\text{Au-TiO}_2@\text{NH}_2\text{-UiO-66}$  in the range of 400-2500  $\text{cm}^{-1}$ .



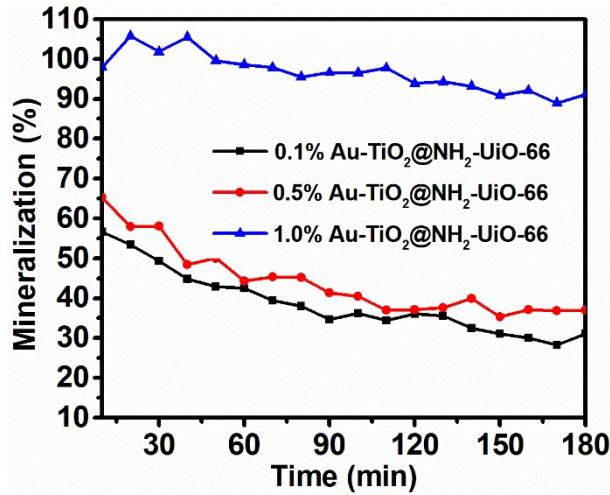
**Fig. S2** TEM images of  $\text{TiO}_2$ .



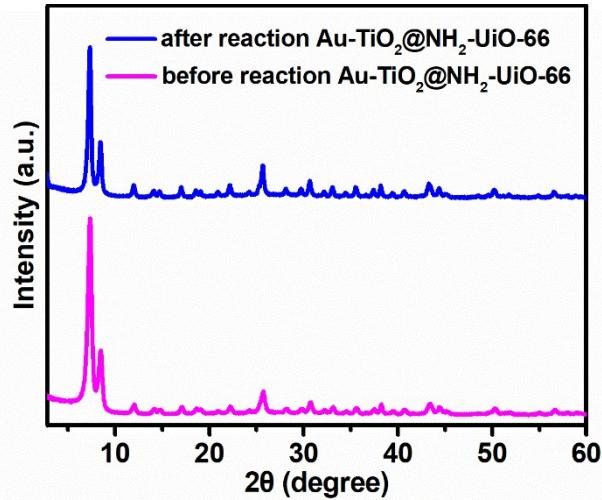
**Fig. S3**  $\text{N}_2$  adsorption-desorption isotherms of  $\text{TiO}_2$ , pure  $\text{NH}_2\text{-UiO-66}$ ,  $\text{TiO}_2@\text{NH}_2\text{-UiO-66}$  and  $\text{Au-TiO}_2@\text{NH}_2\text{-UiO-66}$ .



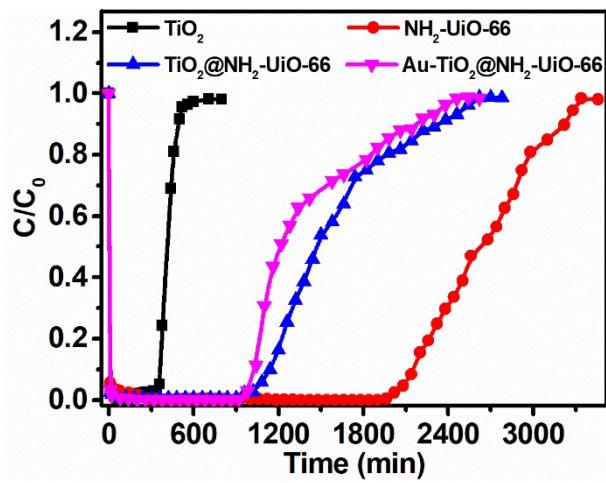
**Fig. S4** Removal efficiencies of ethyl acetate during the photocatalytic oxidation by  $\text{Au-TiO}_2@\text{NH}_2\text{-UiO-66}$  with different Au content.



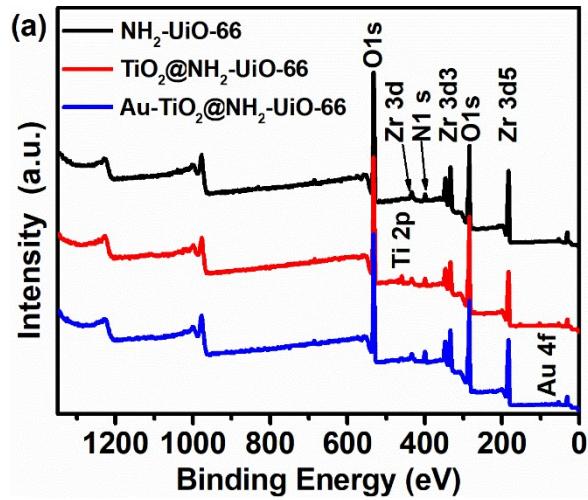
**Fig. S5** Mineralization efficiencies of ethyl acetate during the photocatalytic oxidation by Au-TiO<sub>2</sub>@NH<sub>2</sub>-UiO-66 with different Au content.



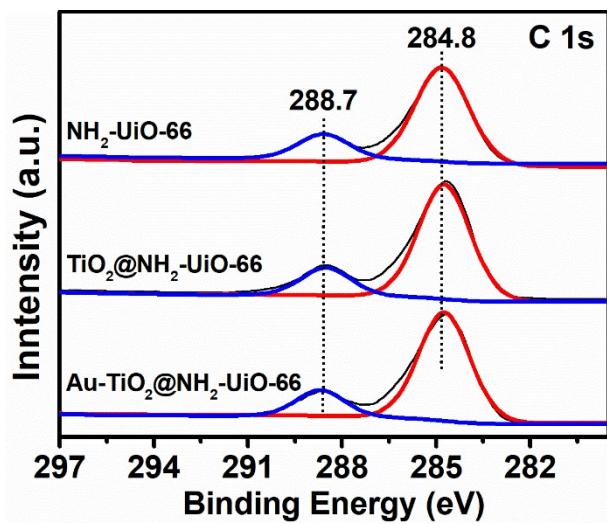
**Fig. S6** Powder XRD patterns of before reaction (a)and after reaction Au-TiO<sub>2</sub>@NH<sub>2</sub>-UiO-66 samples.



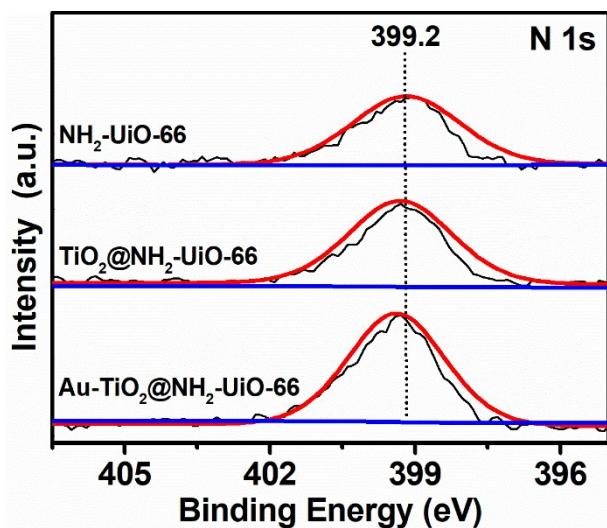
**Fig. S7** Adsorption kinetic curves of ethyl acetate on  $\text{TiO}_2$ , pure  $\text{NH}_2\text{-UiO-66}$ ,  $\text{TiO}_2@\text{NH}_2\text{-UiO-66}$  and  $\text{Au-TiO}_2@\text{NH}_2\text{-UiO-66}$ .



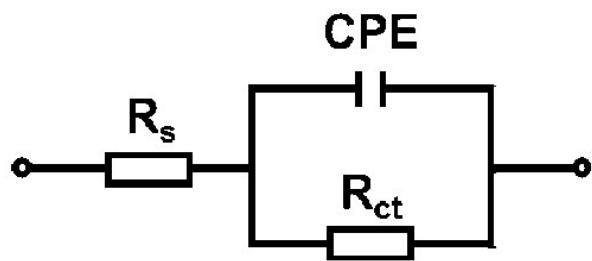
**Fig. S8** XPS survey spectra of pure  $\text{NH}_2\text{-UiO-66}$ ,  $\text{TiO}_2@\text{NH}_2\text{-UiO-66}$  and  $\text{Au-TiO}_2@\text{NH}_2\text{-UiO-66}$  samples, respectively.



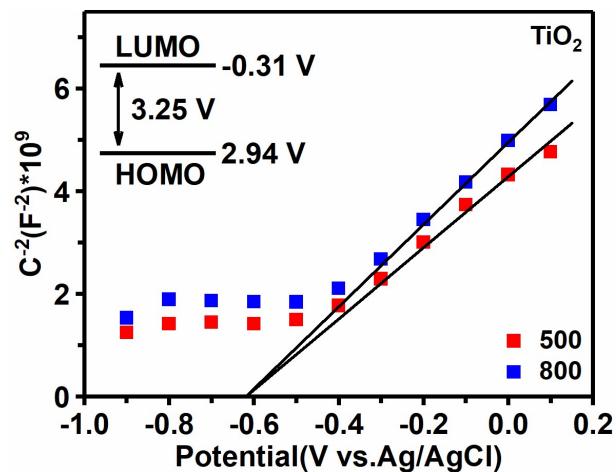
**Fig. S9** XPS spectra of C 1s for pure  $\text{NH}_2\text{-UiO-66}$ ,  $\text{TiO}_2@\text{NH}_2\text{-UiO-66}$  and  $\text{Au-TiO}_2@\text{NH}_2\text{-UiO-66}$  samples, respectively



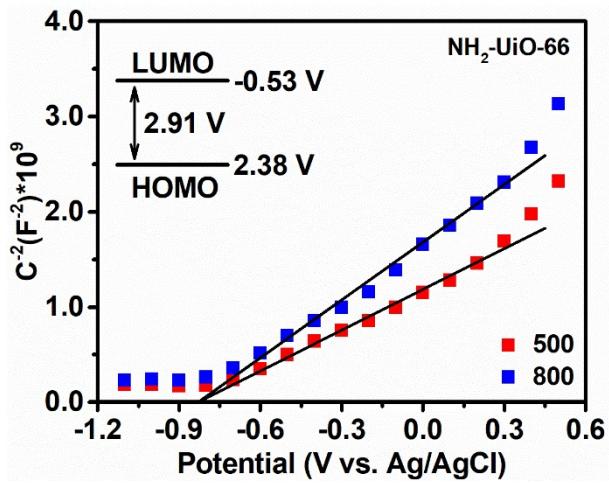
**Fig. S10** XPS spectra of N 1s for pure  $\text{NH}_2\text{-UiO-66}$ ,  $\text{TiO}_2@\text{NH}_2\text{-UiO-66}$  and  $\text{Au-TiO}_2@\text{NH}_2\text{-UiO-66}$  samples, respectively



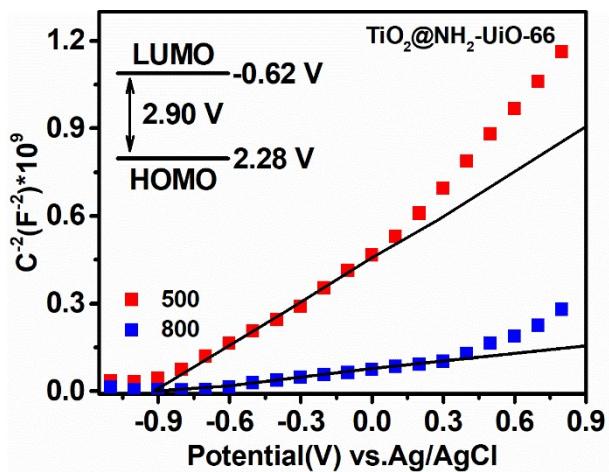
**Fig. S11** the equivalent electrical circuit for EIS.



**Fig. S12** Mott-Schottky plots for  $\text{TiO}_2$  at frequencies of 500 and 800 Hz.



**Fig. S13** Mott-Schottky plots for pure  $\text{NH}_2\text{-UiO-66}$  at frequencies of 500 and 800 Hz.



**Fig. S14** Mott-Schottky plots for  $\text{TiO}_2@\text{NH}_2\text{-UiO-66}$  at frequencies of 500 and 800 Hz.

**Table S1** Characterization results of the samples by N<sub>2</sub> adsorption-desorption.

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>Langmuir</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>pore</sub> (cm <sup>3</sup> g <sup>-1</sup> )
TiO <sub>2</sub>	126.9	134.0	0.07
NH <sub>2</sub> -UiO-66	910.3	1275.6	0.41
TiO <sub>2</sub> @NH <sub>2</sub> -UiO-66	725.4	807.1	0.36
Au-TiO <sub>2</sub> @NH <sub>2</sub> -UiO-66	609.1	627.4	0.33

**Table S2** Fitted TRPL parameters of TiO<sub>2</sub>, TiO<sub>2</sub>@NH<sub>2</sub>-UiO-66 and Au-TiO<sub>2</sub>@NH<sub>2</sub>-UiO-66.

Sample	$\tau$ (ps)	$\tau_1$ (ns)	A <sub>1</sub> (%)	$\tau_2$ (ns)	A <sub>2</sub> (%)	$\tau_3$ (ps)	A <sub>3</sub> (%)
NH <sub>2</sub> -UiO-66	358.00	3.06	14.04	22.39	10.90	273.89	75.06
TiO <sub>2</sub> @NH <sub>2</sub> -UiO-66	100.47	2.92	13.01	23.71	12.17	75.55	74.82
Au-TiO <sub>2</sub> @NH <sub>2</sub> -UiO-66	88.75	2.92	14.03	24.01	11.24	70.59	74.73

**Table S3** Fitting results for equivalent electrical circuits of different samples

Sample	Rs ( $\Omega$ )	Rct ( $k\Omega$ )	CPE ( $\mu F$ )
TiO <sub>2</sub>	43.93	11.47	10.42
Pure MOF	44.32	15.21	9.73
TiO <sub>2</sub> @MOF	50.12	3.67	10.94
Au-TiO <sub>2</sub> @MOF	46.99	2.89	12.19

**Table S4** Activity comparison between Au-TiO<sub>2</sub>@NH<sub>2</sub>-UiO-66 and the other typical MOF based photocatalysts for the photocatalytic degradation of VOCs

Catalyst	Dose (g)	VOCs Concentration	Flow rate (mL/min)	Light source	Con. (%)	Mineralization rate (%)	Time (min)	Stability	Ref.
GC-N-TiO <sub>2</sub> 46 wt%	0.1	toluene, 25 ppmv	100	300W, Xe lamp	70	76	1440	Stable, 24 h	1
TiO <sub>2</sub> @NH <sub>2</sub> -MIL-125	0.1	methanal, 10 ppmv	600	125W, Mercury lamp	90	>99	2880	Stable, 122 h	2
Mesoporous TiO <sub>2</sub>	1.0	benzene, 25 ppmv	1000	4W, 254 nm, UV lamp	90	15	130	90.0 % to 60.4% (18 h)	3
Pd-TiO <sub>2</sub>	-	toluene, 105 ppmv	800	10 W, Mercury lamp	58	23	2280	Stable, 40 h	4
MIL-100(Fe)/ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> -15 5 wt%	0.095	o-xylene, 50 ppmv	10	250 W, Xe lamp	100	-	300	Stable, 20 h	5
TiO <sub>2</sub> @NH <sub>2</sub> -UiO-66	0.1	styrene, 30 ppmv	35	300W, Xe lamp	99	35	600	Stable, 10 h	6
Ni-MOF/NF	2×3 cm	ethyl acetate, 70 ppmv	35	300W, Xe lamp	90	41	360	Stable, 6 h	7
1 wt% Au-TiO <sub>2</sub> @NH <sub>2</sub> -UiO-66	0.1	n-butanol, ethyl acetate	70	300W, Xe lamp	94.6	85	360	Stable, 6 h	This work

## References

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