Ferrocenylselenoether and its Cuprous Cluster Modified TiO_2 as Visible-light Photocatalyst for Synergistic Transformation of N-Cyclic Organics and Cr (VI)

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Preparation of L0 and fcSe

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All starting materials were analytical grade reagents and purchased from Aladdin or Source Leaf, and used without further purification unless otherwise specified. TiO_2 was commercial P25 (75% anatase, 25% rutile). 1,2,3-Triselena[3]ferrocenophane $fcSe_3$ (fc = $[Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4)]$) was prepared according to literature method[1].

L0: $fcSe_3$ (0.426 g, 1 mmol) and $NaBH_4$ (0.378 g, 10 mmol) were added into anhydrous ethanol (150 mL) under nitrogen atmosphere. The reaction was performed at 0 °C for 30 min, then at 25 °C for 2 h. A THF solution of methyl 4-(bromomethyl)benzoate (0.458 g, 2 mmol) was added, and the reaction was carried out at 25 °C for 24 h. The solid precipitation was obtained by evaporation under reduced pressure, and was treated with water (50 mL) and extracted with dichloromethane (3×50 mL). The extract was dried over magnesium sulfate, evaporated to dryness. The yellowish solid 1,1'-bis[1-(methyl-4-benzoic acid methyl ester)-seleno]ferrocene (**L0**) was obtained by elution with petroleum ether/ethyl acetate (15:1 v/v). Yield 0.457 g (68%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.89, 7.87, 7.11, 7.09 (m, 8H, -ArH), 4.16, 4.09 (dd, 8H, -fcH), 3.91(s, 4H, -Se-CH_2-) 3.79 (s, 6H, -CH_3). ESIMS: 642.8 ($[M+H]^+$).

KOH (0.310 g, 5.5 mmol) was added to ethanol (150 mL) solution of **L0** (0.450 g, 0.7 mmol), then the mixture was left to react at 80 °C for 2 h. Part of the solvent was removed by evaporation under reduced pressure, then treated with dichloromethane (50 mL) and extracted with water (3×50 mL). Concentrated hydrochloric acid was added dropwise to the aqueous phase to adjust the acidity to pH=1.0. The yellow precipitation was collected to obtain the target product 1,1'-bis((4-carboxybenzyl)seleno)ferrocene (**fcSe**). Yield 0.381g (86%). ^{1}H NMR (400 MHz, DMSO-d^6, δ): 12.84 (s, -COOH), 7.78, 7.76 (m, 8H, -ArH), 4.20, 4.09 (dd, 8H, -fcH), 3.87 (s, 4H, -Se-CH_2-). ESIMS: 614.9 ($[M+H]^+$).

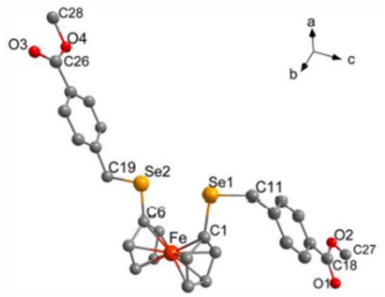


Figure S1. Crystallographic structure of **L0**.

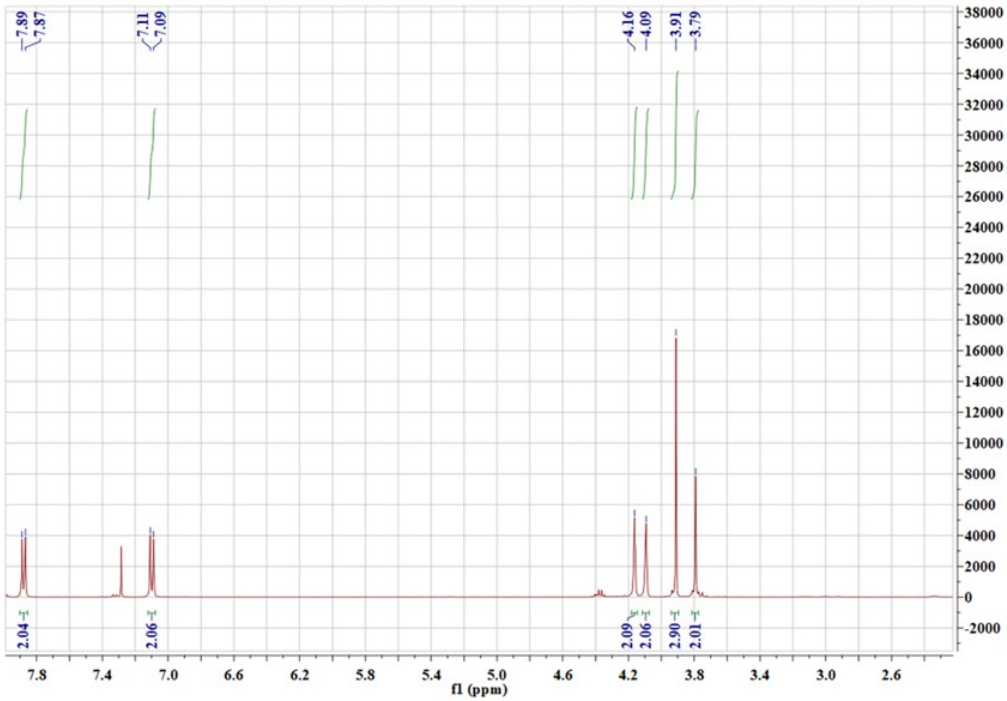
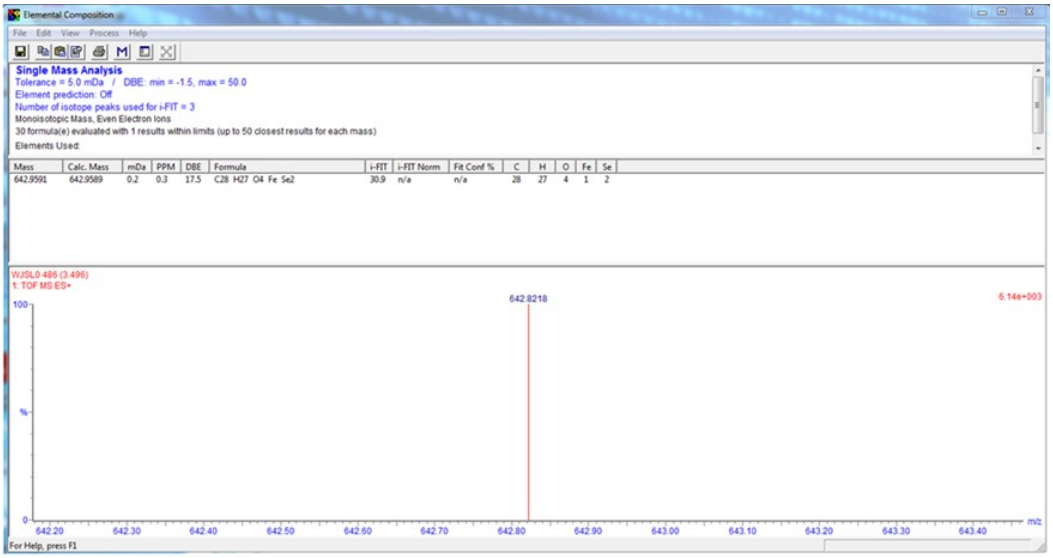


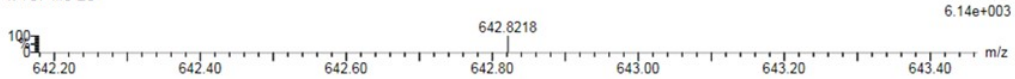
Figure S2. ^{1}H NMR spectrum of **L0**.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 24-30 H: 22-28 O: 2-6 Fe: 0-2 Se: 0-2
WJSL0 486 (3.496)
1: TOF MS ES+



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
642.9591	642.9589	0.2	0.3	17.5	30.9	n/a	n/a	C28 H27 O4 Fe Se2

Figure S3. HRMS spectrum of **L0**.

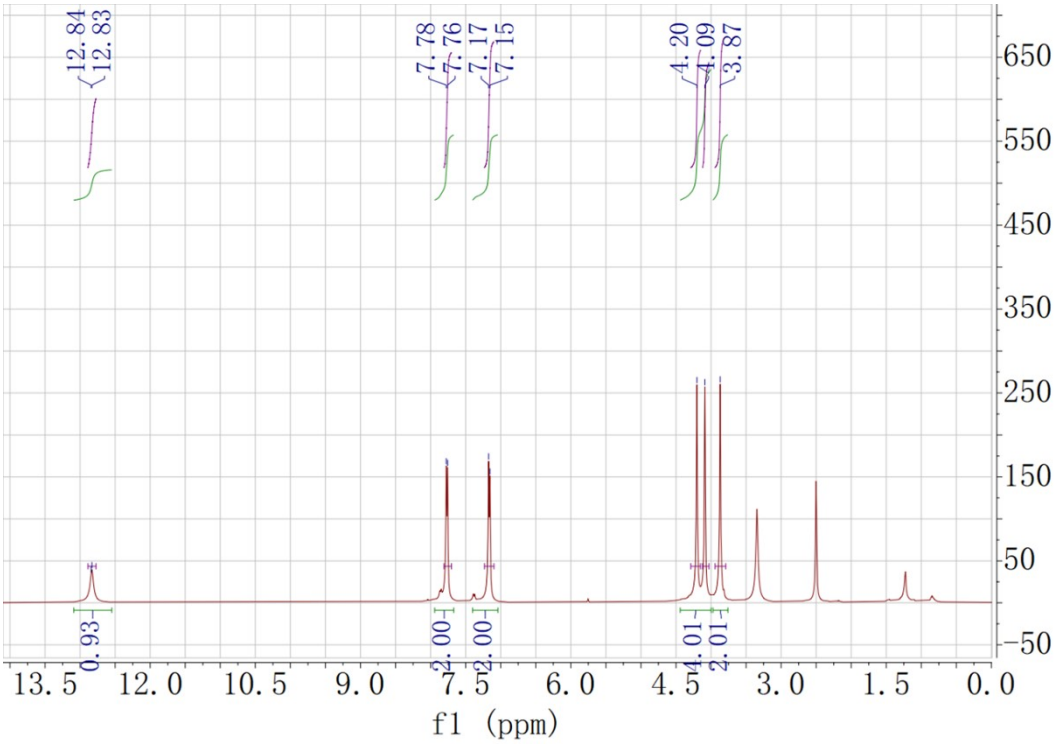
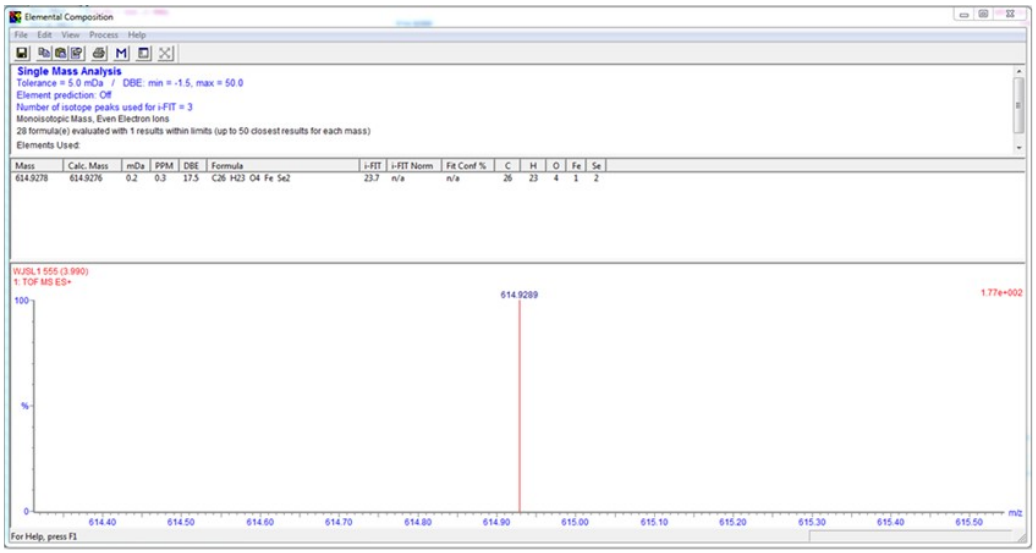


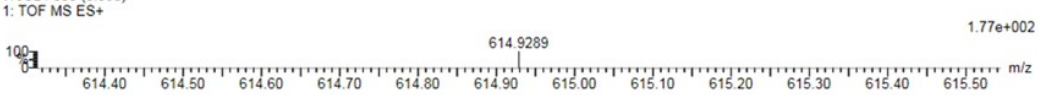
Figure S4. ^{1}H NMR spectrum of **fcSe**.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
28 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 24-30 H: 22-28 O: 2-6 Fe: 0-2 Se: 0-2
WJSL1 555 (3.990)
1: TOF MS ES+



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
614.9278	614.9276	0.2	0.3	17.5	23.7	n/a	n/a	C26 H23 O4 Fe Se2

Figure S5. HRMS spectrum of **fcSe**.

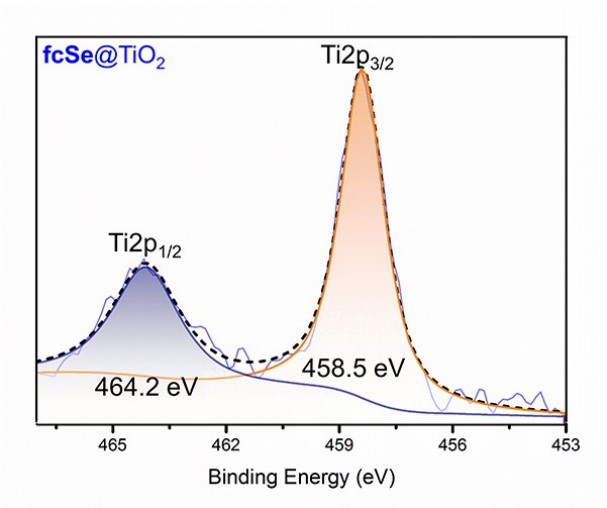


Figure S6. High-resolution XPS spectrum of Ti 2p in **fcSe**@TiO_2.

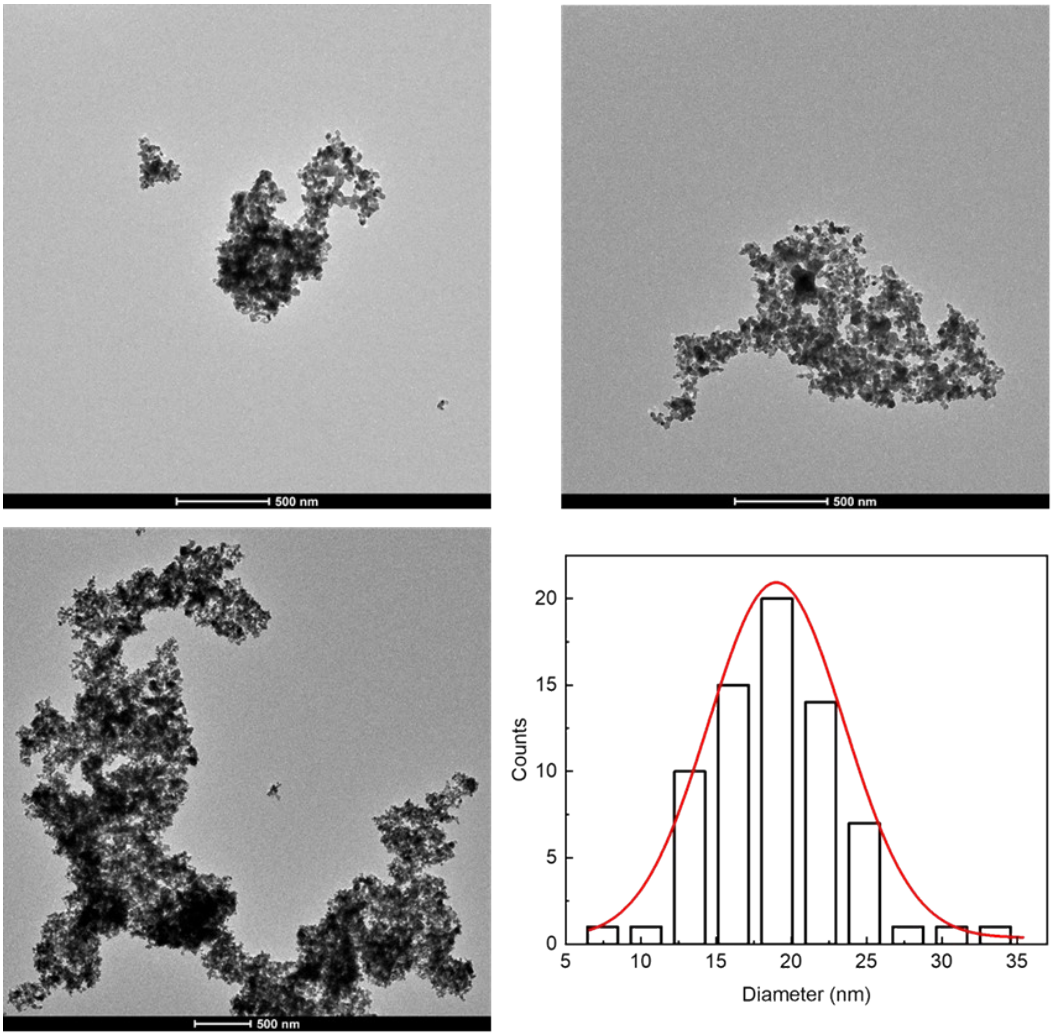


Figure S7. TEM images of **fcSe**@TiO_2 nanoparticles and size distribution.

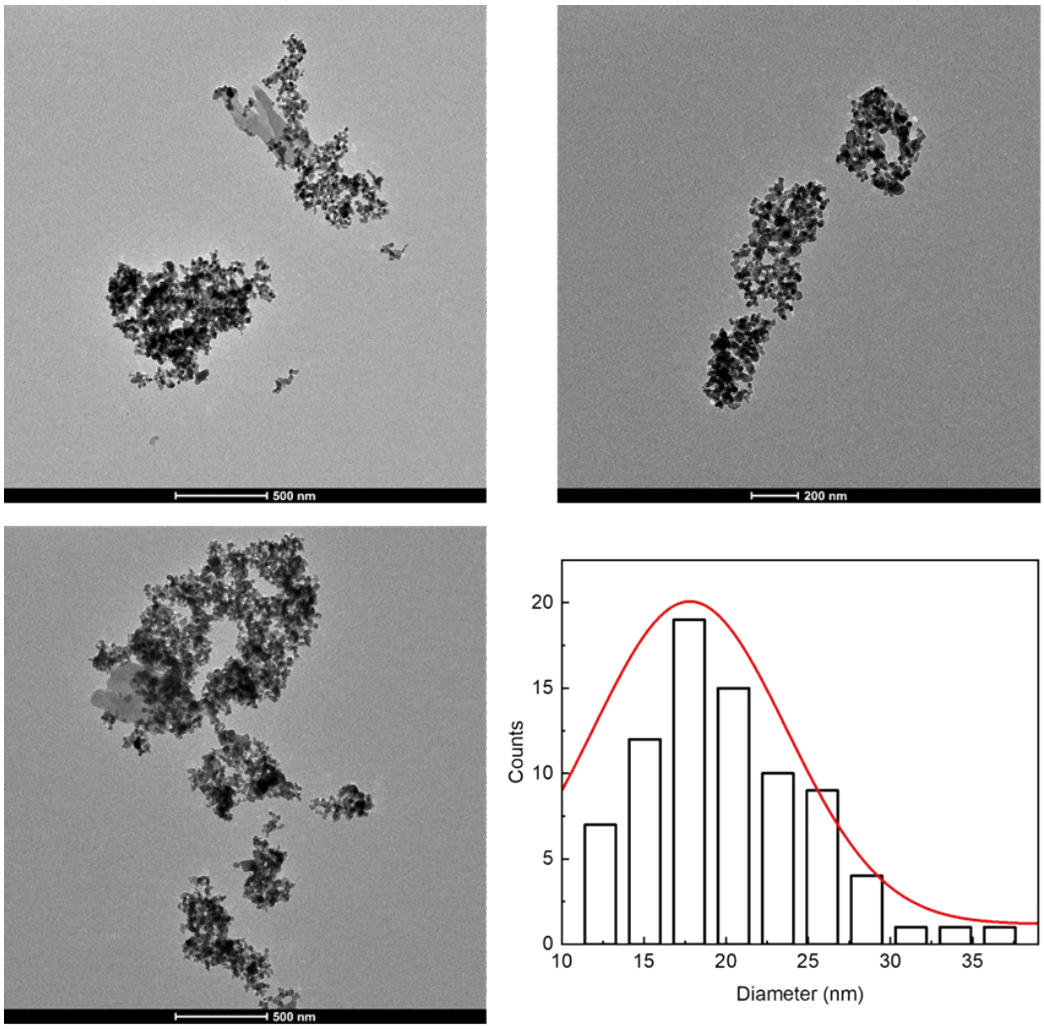


Figure S8. TEM images of $[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$ nanoparticles and size distribution.

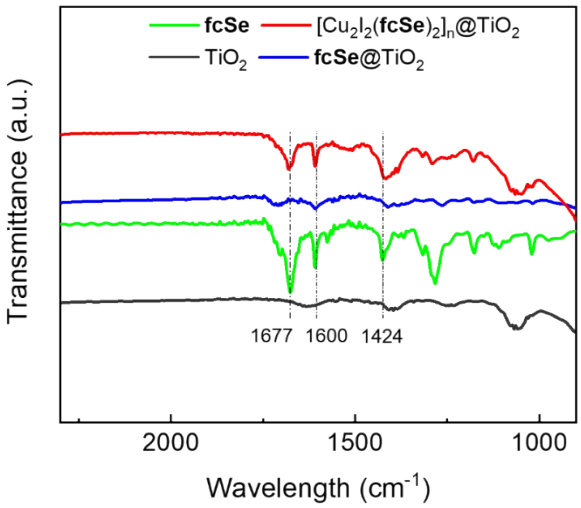


Figure S9. FTIR spectra of TiO_2, **fcSe**, **fcSe**@TiO_2 and $[Cu_2I_2(\mathbf{fcSe})_2]_n$@ TiO_2

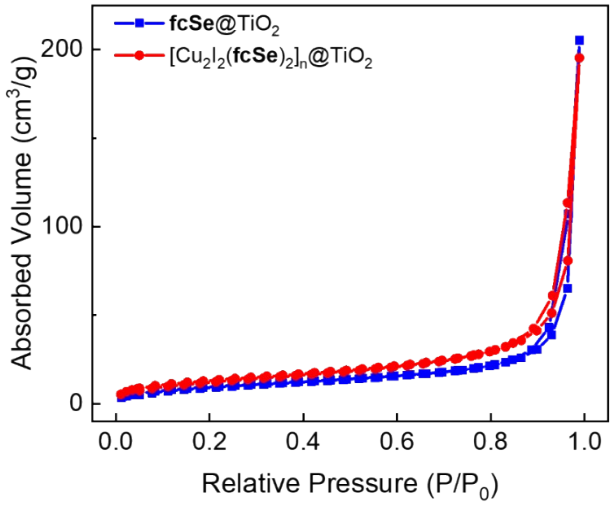


Figure S10. Nitrogen adsorption-desorption isotherms of **fcSe**@TiO_2 (blue) and $[Cu_2I_2(\mathbf{fcSe})_2]_n$@ TiO_2 (red).

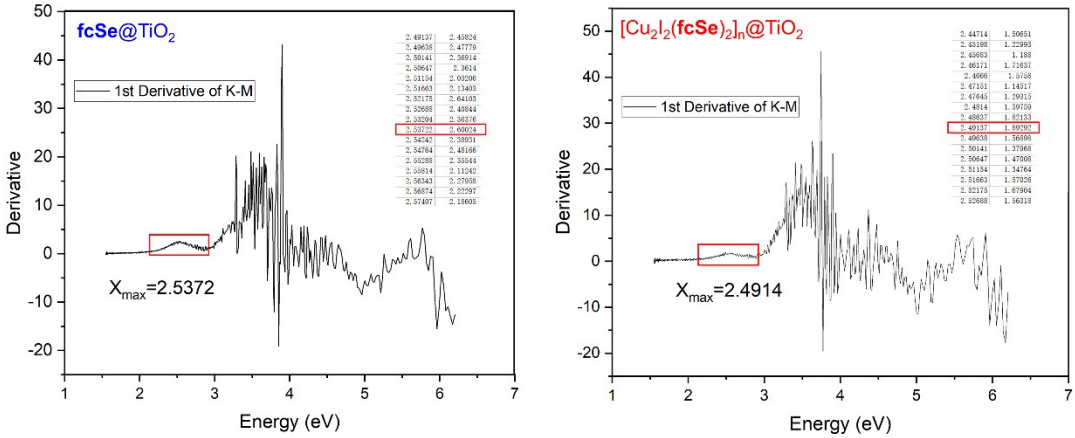


Figure S11. The first derivative of the Tauc Plot curve for **fcSe**@TiO_2 and $[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$.

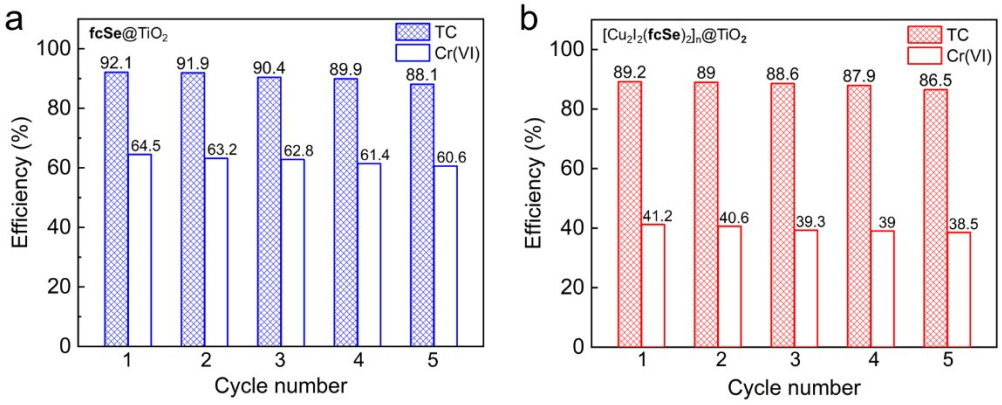


Figure S12. Transformation efficiency of (a) **fcSe**@TiO_2, (b) $[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$ for TC and Cr(VI) in multiple catalytic cycles.

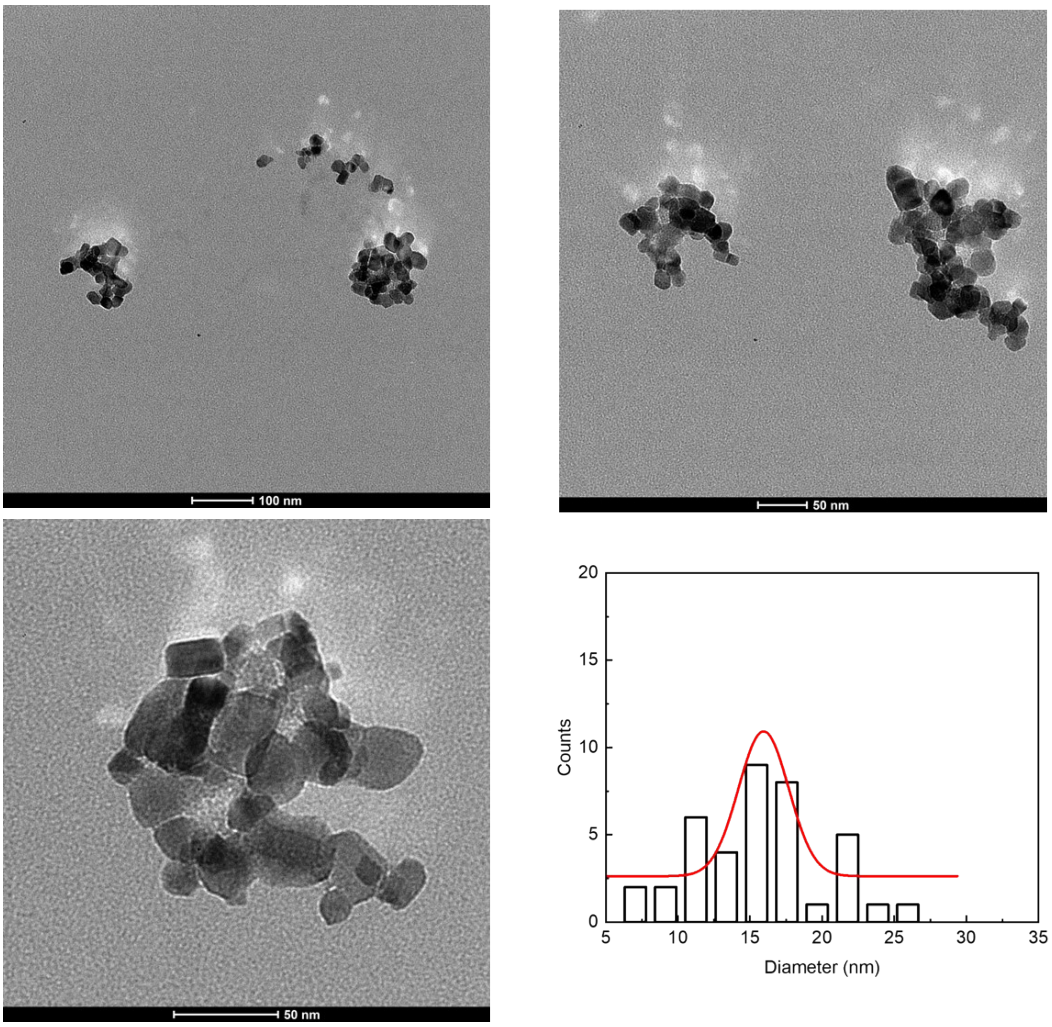


Figure S13. TEM images of **fcSe**@TiO_2 nanoparticles and size distribution after five catalytic cycles.

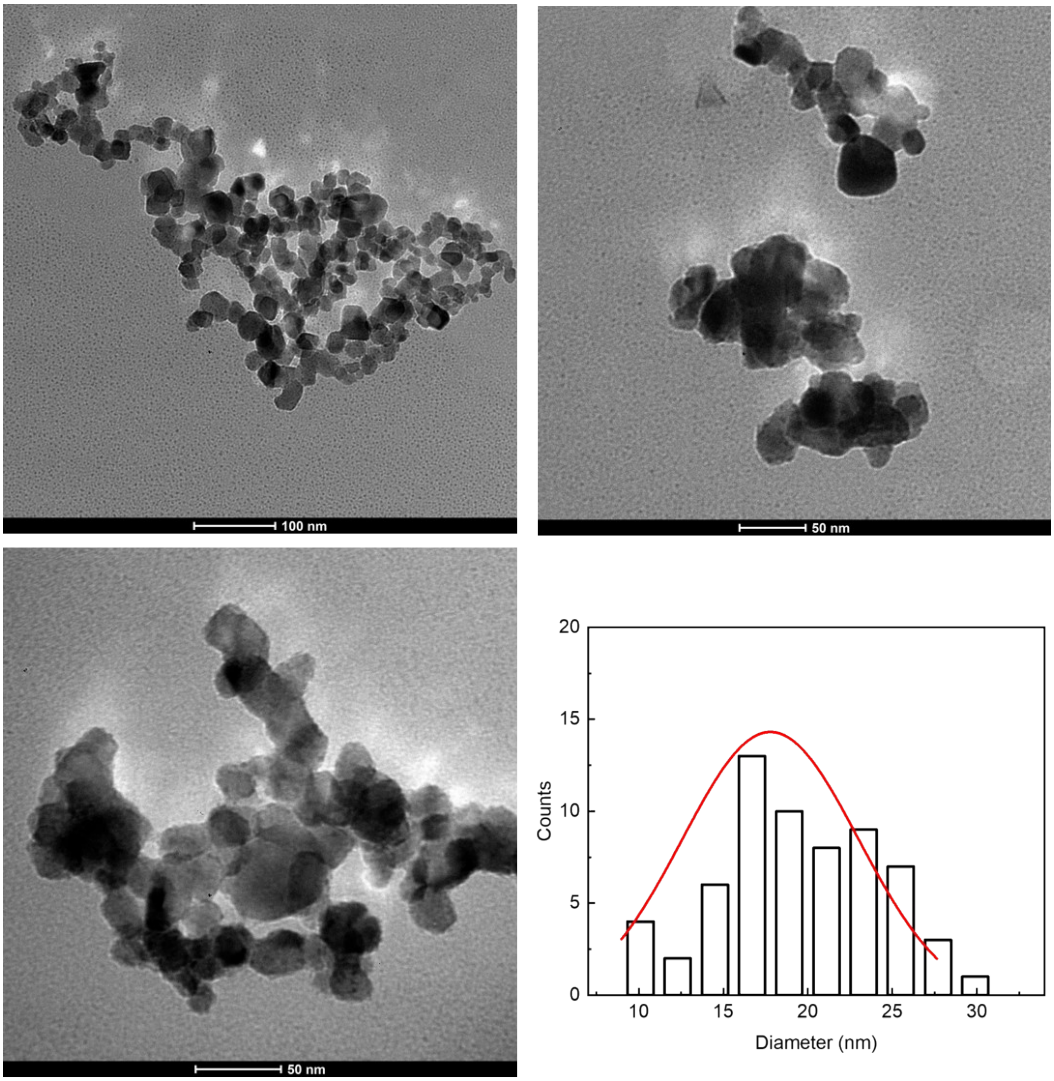


Figure S14. TEM images of $[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$ nanoparticles and size distribution after five catalytic cycles.

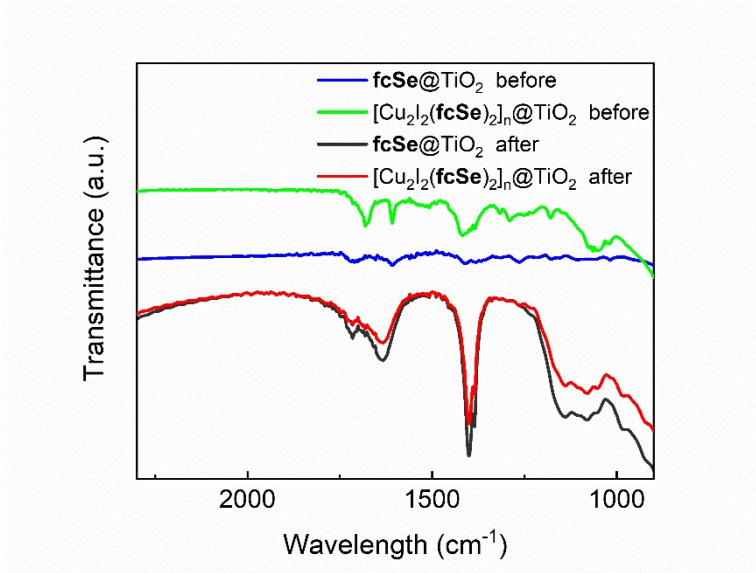


Figure S15. FTIR spectra of TiO_2, **fcSe**, **fcSe**@TiO_2 and $[Cu_2I_2(\mathbf{fcSe})_2]_n$@ TiO_2 after five cycles.

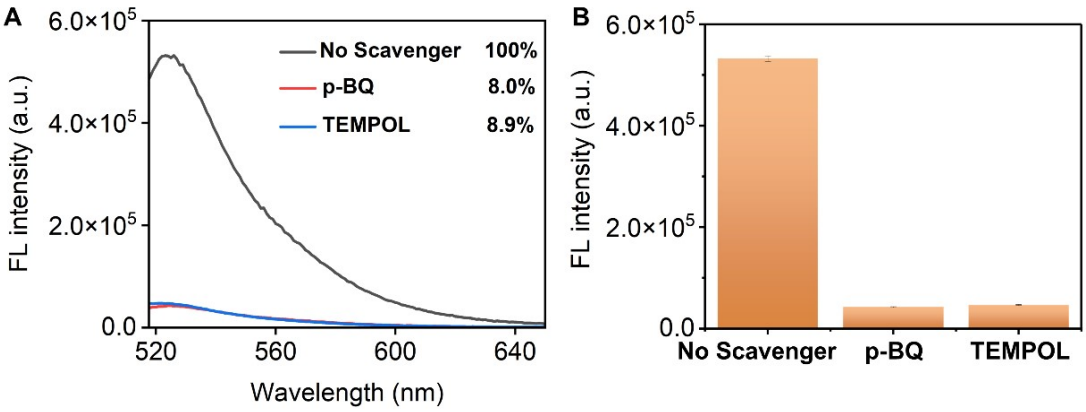


Figure S16. The fluorescence change of SOSG in response to $^1O_2$ generated in the $[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$ system with $\cdot O_2^-$ scavenger p-BQ (red line) or TEMPOL (blue line). Experimental conditions are 25-30 °C, pH = 7, $[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$ dosage = 0.2 g/L, H_2O_2 concentration = 20 mM, p-BQ or TEMPOL concentration = 2.5 mM, SOSG concentration = 0.25 μM, 5 min of visible light irradiation.

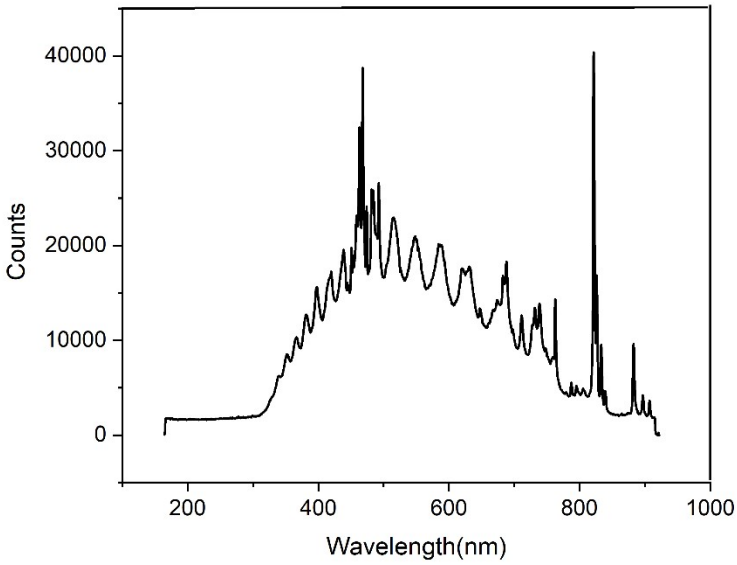


Figure S17. The spectrum of the Xenon Lamp MC-PF300C.

Table S1. Crystallographic data for **L0**

Complexes	**L0**
Empirical formula	$C_{28}H_{26}FeO_4Se_2$
Formula weight	640.26
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	12.387(3)
b (Å)	6.2596(17)
c (Å)	33.747(9)
α (°)	90
β (°)	91.613(3)
γ (°)	90
V (Å^3)	2615.6(12)
Z	4
D_c (g·cm^{-3})	1.626
μ (mm^{-1})	3.392
F (000)	1280
Crystal size (mm^3)	0.18 × 0.06 × 0.05
θ Range	1.645-25.000
Reflections collected	17262
Independent reflections	4578 [R_{int} = 0.0610]
Reflections observed [$I > 2\sigma(I)$]	3384
Data/restraints/parameters	4578/316/0
Goodness-of-fit on F^2	1.101
R_1/wR_2 [$I > 2\sigma(I)$]	0.1038/0.1999
R_1/wR_2 (all data)	0.0785/0.1908
Max., Min. $\Delta\rho$ (e·Å^{-3})	1.663, -1.490

Table S2. Selected bond lengths (Å) and bond angles (°) for **L0**

Bond lengths		Bond lengths		Bond angles	
Se1-C1	1.921(8)	Se1-C11	1.972(8)	C1-Se1-C11	98.6(3)
Se2-C6	1.892(9)	Se2-C19	1.943(9)	C6-Se2-C19	95.4(4)
O1-C18	1.199(15)	O2-C18	1.343(17)	C18-O2-C27	117.0(11)
O3-C26	1.212(14)	O4-C26	1.327(15)	C26-O4-C28	117.2(11)

Table S3. Zeta potentials and Z-average hydrodynamic diameters of **fcSe**@TiO_2 and $[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$ at different pH.

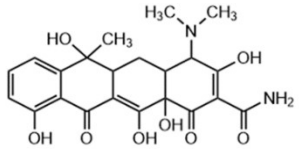
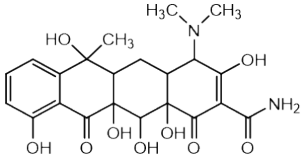
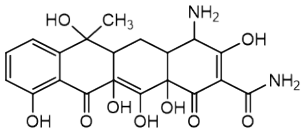
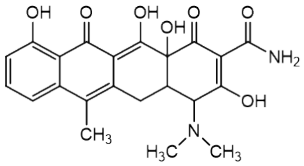
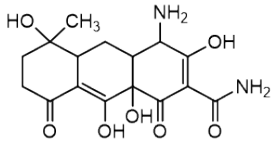
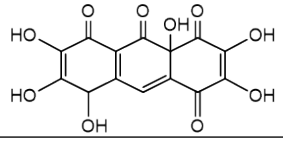
	fcSe@TiO_2		$[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$	
pH	ζ (mv) ± SD	Z-average size (nm) ± SD	ζ (mv) ± SD	Z-average size (nm) ± SD
3	9.07 ± 1.0	6716 ± 57.0	3.70 ± 0.8	4933 ± 32.0
5	5.06 ± 3.6	1530 ± 22.0	9.77 ± 2.2	4338 ± 63.0
7	25.3 ± 2.0	673.3 ± 43.0	-7.46 ± 1.2	3141 ± 24.0
9	-40.8 ± 6.5	366.2 ± 48.0	-23.1 ± 4.3	345.4 ± 30.0

Table S4. TC photocatalytic degradation efficiency comparison of **fcSe**@TiO_2 and $[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$ with other representative systems.

Catalyst	Catalyst dosage g/L	H_2O_2 mM	Initial pH	TC initial concentration mg/L	Degradation effect	Reference
fcSe@TiO_2	0.2	19.8	7	20	30 min 93.1%	**This work**
$[Cu_2I_2(\mathbf{fcSe})_2]$@$TiO_2$	0.2	19.8	7	20	30 min 91.3%	**This work**
Fe^{2+}	0.005	0.59	7.5	100	60 min 97.1%	2

Fe-MOFs	0.15	10 mL/L	4.1	50	20 min 82.5%	3
C@FONC	0.5	5	3	150	180 min 97.9%	4
Fe-POM/CNNS-N_{vac}	1	10	4.5	20	18 min 96.5%	5
15-yCeO_2/Fh	0.4	50	4	20	60 min 93.6%	6
Fe-R-2	0.4	10	3.81	100	120 min 98.1%	7
APRM-110	0.5	20	4.3	40	60 min 87.8%	8
MFO-Au_3	0.1	50	6	20	90 min 88.3%	9
0.8MLD/CN/Fe_3O_4	0.5	80	7	20	80 min 95.8%	10
Cu-HNCN/PF	0.2	20	6.5	10	50 min 96%	11
Fe-g-C_3N_4/Bi_2WO_6	0.4	1	6.5	10	120 min 93.9%	12
FMCNEP	1.3	20	5	25	60 min 97.5%	13

Table S5. LC-MS information and proposed structure of photocatalytic products in the catalytic degradation of TC by **fcSe**@TiO_2 and $[Cu_2I_2(\mathbf{fcSe})_2]n$@$TiO_2$

Intermediate Products	Retention Time (min)	MS (m/z)	Molecular Formula	Supposed Structure	**fcSe**@TiO_2	$[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$
TC	6.49-6.59	445	$C_{22}H_{24}N_2O_8$		√	√
I1	6.62-6.72	461	$C_{22}H_{26}N_2O_9$		√	√
I2	6.77-6.86	433	$C_{20}H_{22}N_2O_9$		√	√
I3	6.87-6.94	427	$C_{22}H_{22}N_2O_7$		√	√
I4	6.48-6.45	353	$C_{16}H_{20}N_2O_7$		√	√
I5	6.21-6.3	337	$C_{14}H_8O_{10}$		√	√

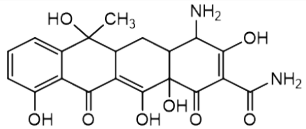
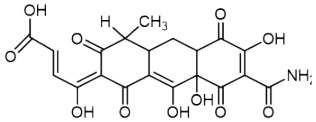
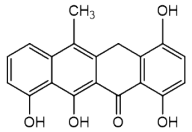
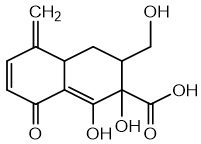
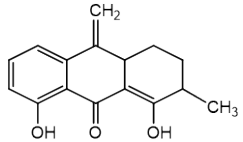
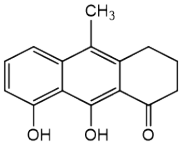
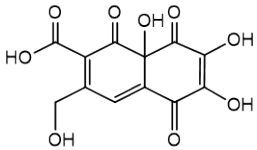
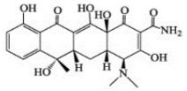
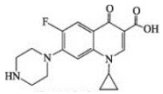
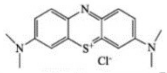
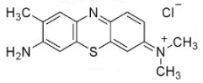
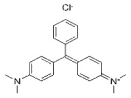
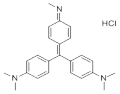
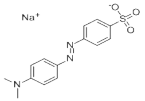
I6	7.19-7.27	417	$C_{20}H_{22}N_2O_8$		√	√
I7	7.04-7.11	447	$C_{20}H_{17}NO_{11}$		√	√
I8	7.13-7.19	325	$C_{19}H_{14}O_5$		√	-
I9	6.8-6.91	266	$C_{13}H_{14}O_6$		√	-
I10	6.2-6.39	256	$C_{16}H_{16}O_3$		√	√
I11	5.85-6.04	242	$C_{15}H_{14}O_3$		√	√
I12	6.73-6.82	297	$C_{12}H_8O_9$		-	√

Table S6. Evaluation of **fcSe**@TiO_2 and $[Cu_2I_2(\mathbf{fcSe})_2]_n$@$TiO_2$ in the visible light photo-degradation of representative N-cyclic organics[a].

N-cyclic organics	Structural formula	**fcSe**@TiO_2		$[Cu_2I_2(\mathbf{fcSe})_2]_n$ @TiO_2	
		Removal efficiency	$\eta_{CO+HCOOH}$[b]	Removal efficiency	$\eta_{CO+HCOOH}$[b]
Tetracycline		93.1%	7.2%	91.3%	6.1%
Ciprofloxacin		86.2%	11.8%	64.9%	20.8%
Methylene blue		93.9%	8.1%	41.4%	6.6%
Toluidine blue		94.2%	6.9%	88.9%	10.8%
Pigment Green		92.0%	3.0%	93.7%	4.3%
Basic violet		92.3%	4.4%	86.2%	3.7%
Methyl Orange		17.1%	7.9%	16.0%	7.3%
Imidazole		16.6%	4.7%	25.9%	5.9%

[a] Experimental conditions are 25-30 °C, pH = 7, catalyst dosage = 0.2 g/L, H_2O_2 concentration = 20 mM.
[b] The conversion rate CO and HCOOH $\eta_{CO+HCOOH}$ was calculated by Eq. (4).

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