Supporting Information

Selective photocatalytic oxidation of cyclohexene coupled with hydrogen evolution from water splitting over Ni/NiO/CdS and mechanism insight

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Content

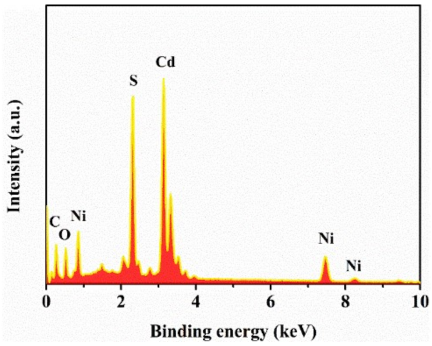


Figure S1. EDX spectrum of the synthesized Ni/NiO/CdS compostite.

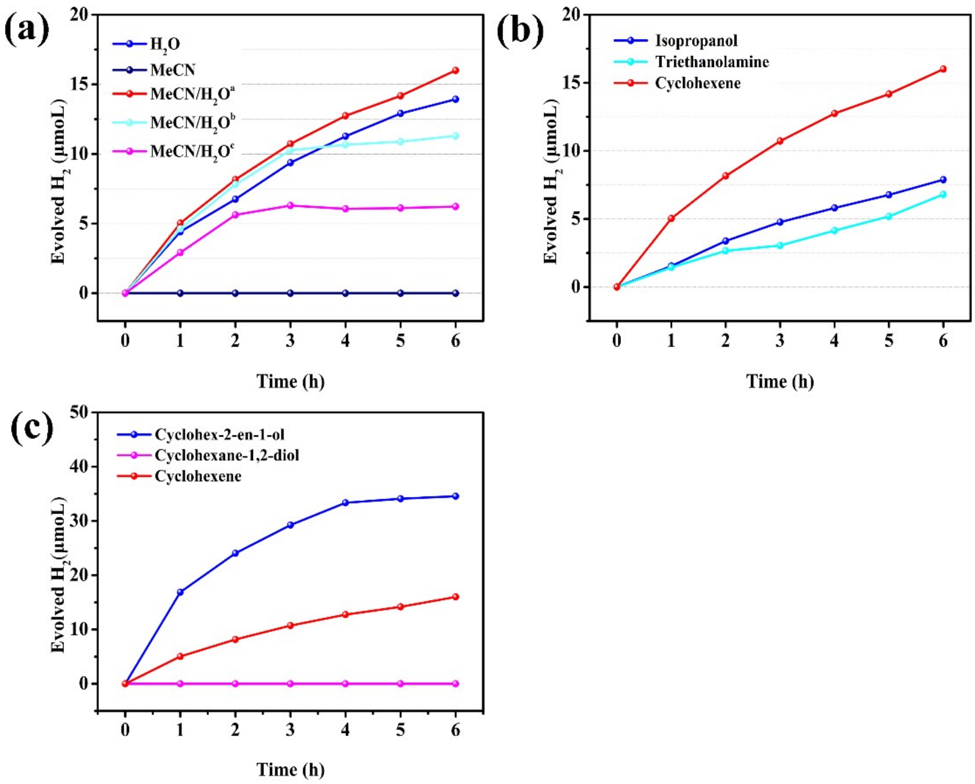


Figure S2. Time-dependent H_2 evolution (a) in different ratios (v/v) of water and MeCN as reaction solvent (MeCN/H_2O^a: 1/9, MeCN/H_2O^b: 3/7, MeCN/H_2O^c: 5/5); (b) Radical capture experiment for photocatalytic oxidation of cyclohexene; (c) photocatalytic oxidation cyclohexene, cyclohex-2-en-1-ol and cyclohexane-1,2-diol.

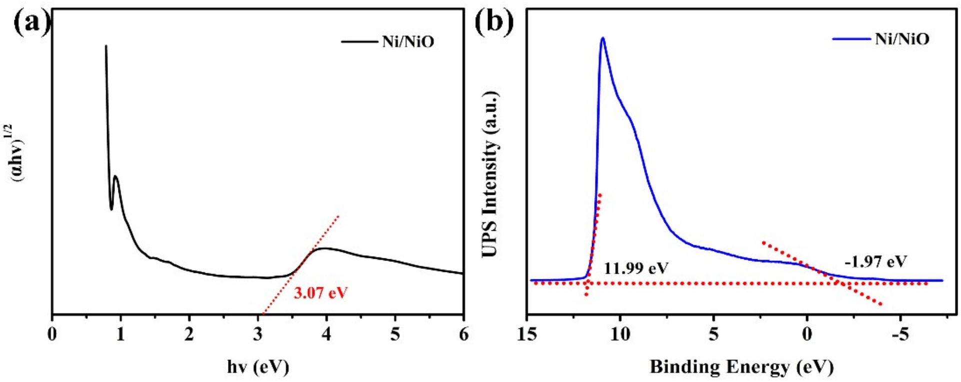


Figure S3. (a) Band gap energies of Ni/NiO; (b) UPS spectrum of Ni/NiO.

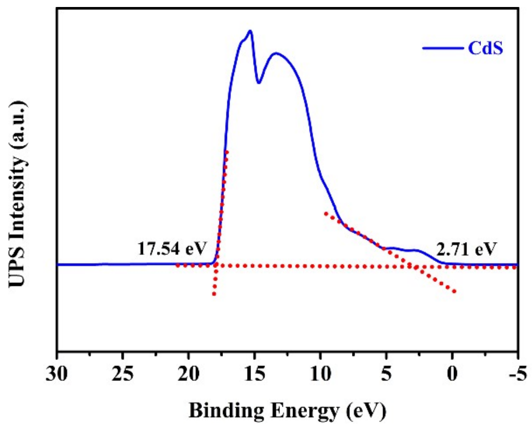


Figure S4. UPS spectrum of CdS.

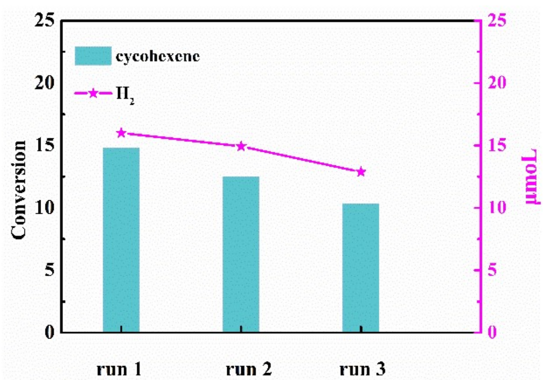
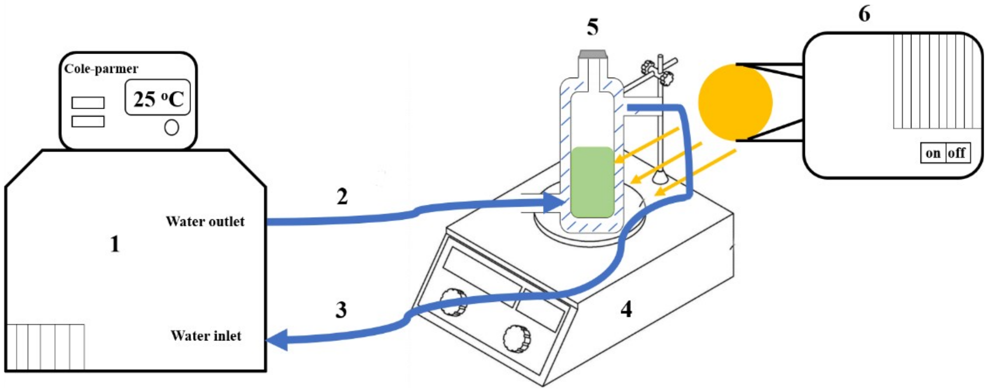


Figure S5. Photocatalytic recycling performance.



The reactor system and setup

Legend: 1. Cold recirculating cooler (Cole-parmer, 12101-36, USA); 2. Condensate pipe (water outlet); 3. Condensate pipe (water inlet); 4. Magnetic stirrer (ChangZhou yuexin, 78-1); 5. Photoreaction flask; 6. Xenon lamp (Perfectlight, PLS-SXE 300)

Figure S6. The reactor system and setup.

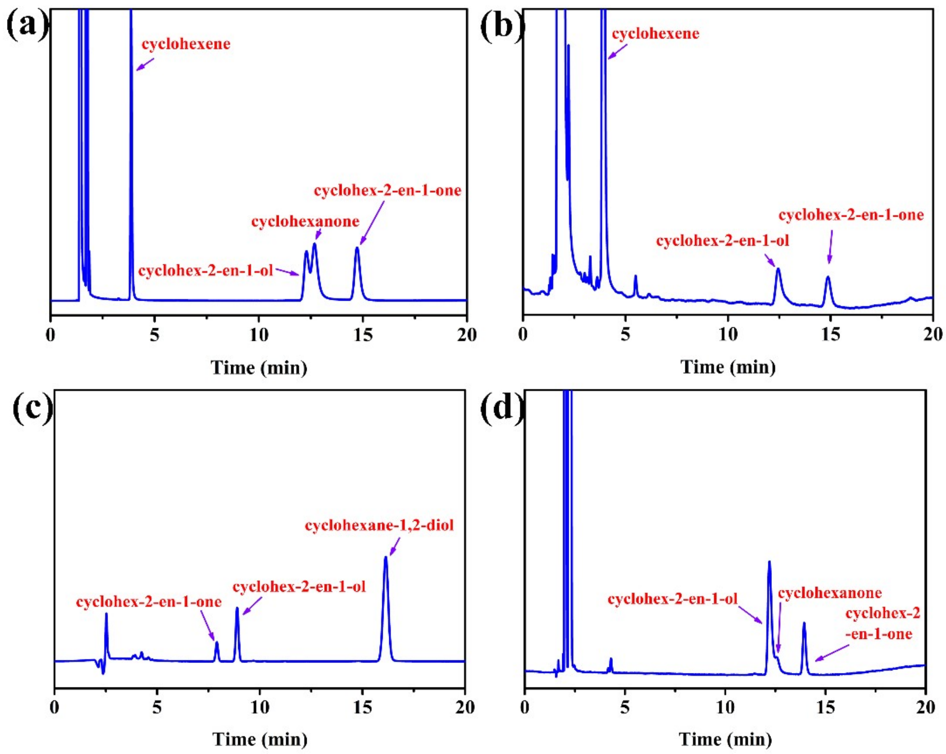


Figure S7. (a) Gas chromatogram of photocatalytic oxidation of cyclohexene products distribution under Ar; (b) gas chromatogram of photocatalytic oxidation of cyclohexene products distribution under O_2; (c) liquid chromatogram of photocatalytic oxidation of cyclohexene products distribution under Ar; (d) gas chromatogram of photocatalytic oxidation of cyclohex-2-en-1-ol products distribution under Ar.

Table S1. The content of each element in the composite catalyst by EDS results.

Elem	Mass%	M	Atom%
C	32.37	12.011	0.60
O	17.14	15.999	0.24
S	9.66	32.059	0.07
Ni	7.97	58.693	0.03
Cd	32.86	112.41	0.06

Table S2. Under different solvent conditions, the cyclohexene conversion rate.

Solvent	Solvent ratio ($MeCN/H_2O$, v/v)	Conv. (%)	H_2 rate (μmol)
H_2O	10	3.4	13.9
MeCN	10	0	0
$MeCN/H_2O^{a*}$	1/9	14.8	16.0
$MeCN/H_2O^{b}$	3/7	10.9	11.3
$MeCN/H_2O^{c}$	5/5	5.3	6.2

*Different ratios (v/v) of water and MeCN as reaction solvent: $MeCN/H_2O^{a}$: 1/9, $MeCN/H_2O^{b}$: 3/7, $MeCN/H_2O^{c}$: 5/5.

Table S3. Radical capture reaction cyclohexene conversion rate and product yield under argon conditions.

Compound	Conv. (%)	Selectivity (%)				H_2 rate (μmol)
		cyclohex-2-en-1-ol	cyclohex-2-en-1-one	cyclohexanone	cyclohexane-1,2-diol	
Blank	14.8	2.6	8.2	1.7	2.1	16.0
Triethanolamine	1.7	0.5	0.7	0.3	0.1	6.8
Isopropanol	2.1	0.6	0.9	0.2	0.3	7.9

Table S4 Comparison with the reported results for oxidation of cyclohexene coupled.

Catalysts	Light source	Solvent	Oxidation conditions	Tem. (°C)	Time (h)	Conv. (%)	Products*	Ref.
UiO-66	none	MeCN	H_2O_2	50	1	31	C, D	1
Fe-Co-g-C_3N_4	none	H_2O	O_2 (4 MP)	90	5	27.6	A, B, C, D	2
CoMo	420-500 nm	4-ethyltoluene	O_2 (1 atm)	50	12	69.8	A, B, C, D	3
Fe-TiO_2	400 W/D	H_2O	Air (1 bar)	37	3	/	A, B, C	4
TiO_2	λ>280 nm	MeCN	O_2 (1 atm)	40	3	27	A, B, C	5
Degussa P25 TO_2	λ>340 nm	MeCN	O_2	RT.	8	/	C	6
Ni/NiO/CdS	λ>420 nm	MeCN/H_2O=1/9	none	25	6	14.8	A, B, D, E	This work
UiO-66	none	MeCN	H_2O_2	50	1	31	C, D	

Products*: in scheme 1 and scheme 2

Table S5 Cyclohexene conversion rate and product yield under argon atmosphere and oxygen atmosphere.

Oxidation conditions	Solvent (v/v)	Conv. (%)	Yield (%) A	B	E	D	H_2 (μmol)
Argon	MeCN/H_2O=1/9	14.8	2.6	8.2	1.7	2.1	16.0
Argon*	MeCN/H_2O=1/9	0	0	0	0	0	trace
Oxygen	MeCN/H_2O=1/9	11.9	0.4	11.3	trace	0.2	trace

Reaction conditions: cyclohexene (10 mM), Photocatalyst (10 mg), Solvent (10 mL), visible light irradiation (λ>420 nm, 6 h). Argon*: no reactants (cyclohexene).

Table S6. The content of Ni and Cd in the catalysts.

Type of catalyst	Ni constant (%)[a]	Cd constant (%)[b]
Ni/NiO/CdS_0.5	1.26	5.33
Ni/NiO/CdS_1	2.34	4.75
Ni/NiO/CdS_2	3.94	4.25
Ni/NiO/CdS_4	5.33	3.31
Ni/NiO/CdS_8	5.61	2.40

a: Percentage of Ni element content, b: Percentage of Cd element content

Table S7. Cyclohexene conversion rate and product yield in different time.

Time (h)	Conv. (%)	Selectivity (%)				H_2 rate (μmol)
		cyclohex-2-en-1-ol	cyclohex-2-en-1-one	cyclohexanone	cyclohexane-1,2-diol	
0	0	0	0	0	0	0
1	4.7	1.6	1.7	0	1.2	5.0
2	8.3	2.8	3.9	0	1.5	8.2
3	10.5	3.1	5.4	0	1.8	10.7
4	12.4	3.5	6.9	0	1.9	12.8
5	13.2	2.7	7.6	0.8	2.0	14.2
6	14.8	2.6	8.2	1.7	2.1	16.0

Table S8. Photocatalytic reaction products and yield.

Compound	Conv. (%)	Yield (%)				H_2 rate (μmol)
		cyclohex-2-en-1-ol	cyclohex-2-en-1-one	cyclohexanone	cyclohexane-1,2-diol	
cyclohexene	14.8	2.6	8.2	1.7	2.1	16.0
cyclohex-2-en-1-ol	41.2	/	24.5	16.3	trace	34.5
cyclohexane-1,2-diol	0	trace	trace	trace	/	trace

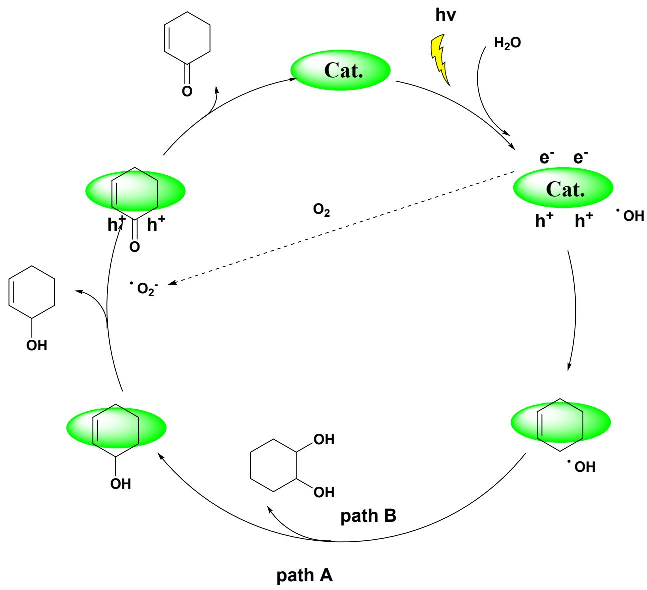
Table S9. GC Method validation of linearity in five sample matrices.

Analytes	Linear range (μg·mL^{-1})	Regression equation	Correlation coefficient (r^2)
cyclohexene	10 -1000	Y = 1158.35X + 3989.38	0.9992
cyclohex-2-en-1-ol	10 -200	Y = 899.66X - 2661.63	0.9926

cyclohex-2-en-1-one	10 -200	Y = 842.22X + 5615.86	0.9905
cyclohexanone	10 -200	Y = 658.21X + 3241.70	0.9954

Table S10. Radical capture reaction cyclohexene conversion rate and product yield under oxygen conditions.

Entry	Compound	Conv. (%)	Selectivity (%)				H_2 rate (μmol)
			cyclohex-2-en-1-ol	cyclohex-2-en-1-one	cyclohexanone	cyclohexane-1,2-diol	
(a)	Blank	11.9	0.4	11.3	trace	0.2	trace
(b)	Benzoquinone	0.5	trace	0.5	trace	trace	trace
(c)	Isopropanol	0.2	trace	0.2	trace	trace	trace



Scheme S1. Under oxygen atmosphere, proposed potential mechanism of the photocatalytic oxidation cyclohexene by Ni/NiO/CdS.

References

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