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## **Supporting information**

## Core-Shell Co@CoO Catalysts for the Hydroformylation of Olefins

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Fig. S1. XPS spectra of Co 2p for Co@CoO-PEG after Argon ion sputtering.



Fig. S2. (a) FT-IR spectra of the filtrate after reaction on  $CoO_x$ -W catalyst; (b) XRD patterns of the residual solid after the solvent in the filtrate was evaporated.



Fig. S3. Time profile of the 1-octene hydroformylation catalyzed by Co@CoO-PEG. The solid squares denoted the original time profile of hydroformylation. The solid circles represent the catalytic activities without catalyst after hot filtration. Reaction condition: 50 mg catalyst, 2 mmol 1-octene, 4 MPa (CO/H<sub>2</sub>, V/V=1), 10 ml toluene, 130 °C.



Fig. S4. The catalytic performance of Co@CoO-PEG in different solvents. Reaction condition: 50 mg catalyst, 2 mmol 1-octene, 4 MPa (CO/H<sub>2</sub>, V/V=1), 10 ml solvent, 130 °C, 8 h. L:linear and B: branch



Fig. S5. The selectivity and conversion of 1-octene with different reaction time on (a)  $CoO_x$ -W and (b) Co@CoO-GLY catalysts. Reaction condition: 50 mg catalyst, 2 mmol 1-octene, 4 MPa (CO/H<sub>2</sub>, V/V=1), 10 ml toluene, 130 °C. L:linear and B: branch



Fig. S6. XRD patterns of the spent Co@CoO-PEG catalyst after nine rounds.



Fig. S7. Co 2p XPS spectra of for the used Co@CoO-PEG catalyst after nine rounds.

Entry	Catalyst	Substrate	P <sub>H2/CO</sub> (MPa)	T/°C	t/h	Con.(%)	Aldehyde Sel.(%)	Ref.
1	Fibrous	1-octene	5.5	150	12	92ª	-	1
	Co <sub>3</sub> O <sub>4</sub>							
2	Octahedral	1-heptene	4	170	12	88	75	2
	Co <sub>3</sub> O <sub>4</sub>							
3	Co/β-Mo <sub>2</sub> C	propene	4	160	10	28 <sup>b</sup>	-	3
4	CoZrP-2.0	1-octene	4	160	6	99	91	4
5	Co/Q-6	1-hexene	5	130	2	37	88	5
6	Co-B	1-octene	5	120	2.5	71	99	6
7	Ultrafine	1-hexene	2.4	100	1	95	38	7
	cobalt							
8	Co/SiO <sub>2</sub>	1-hexene	5	100	5	61	90	8
9	Co/phen@C	1-octene	4	100	18	94	73	9
10	Co@CoO-	1-octene	4	130	8	99	97	This
	PEG							work

Table S1. Comparison of the catalytic performance of Co@CoO-PEG with those reported cobalt-based catalysts in the hydroformylation of olefin.

<sup>a</sup>The products includes alcohols, isomerized and hydrogenated substrates. <sup>b</sup>The butyraldehydes and butanols were detected as products.

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