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Design of Highly Active Cobalt Catalysts for CO_2 Hydrogenation via the Tailoring of Surface Orientation of Nanostructures

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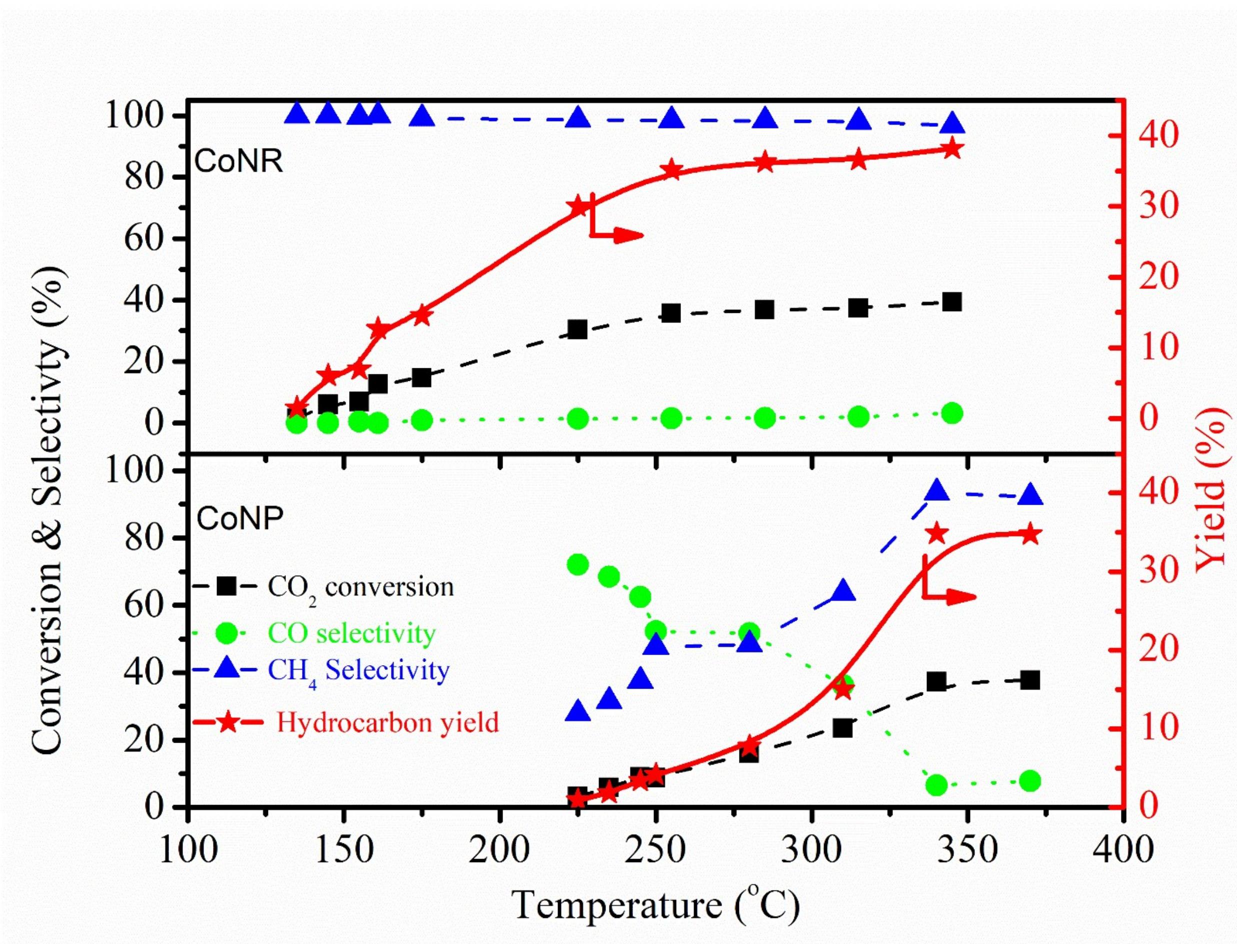
Supplemental Information



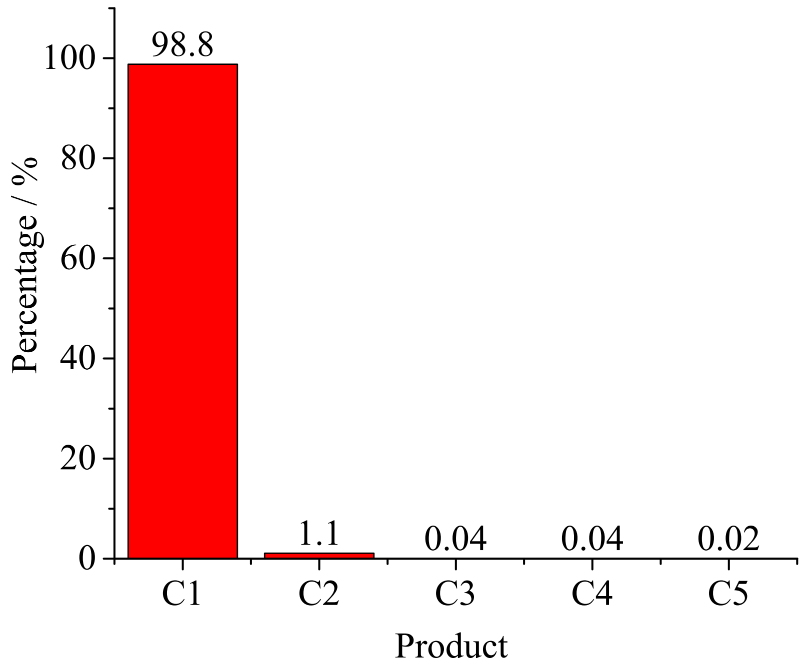


Figure S1. (top) CO_2 conversion and methane selectivity on nanorods and nanoparticles for CO_2 hydrogenation with H_2 to CO_2 ratio of 2 (bottom) product distribution for CO_2 hydrogenation using a 4:1 ratio of CO_2:H_2

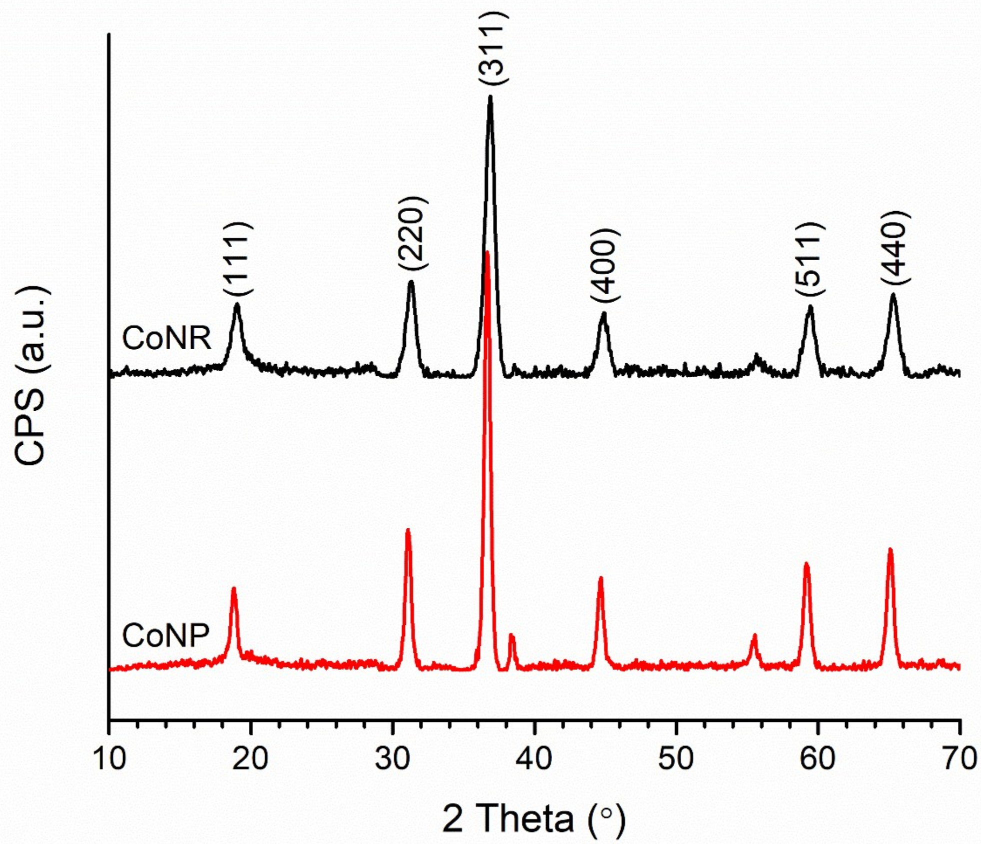


Figure S2. XRD patterns of cobalt nanorods (black) and nanoparticles (red)

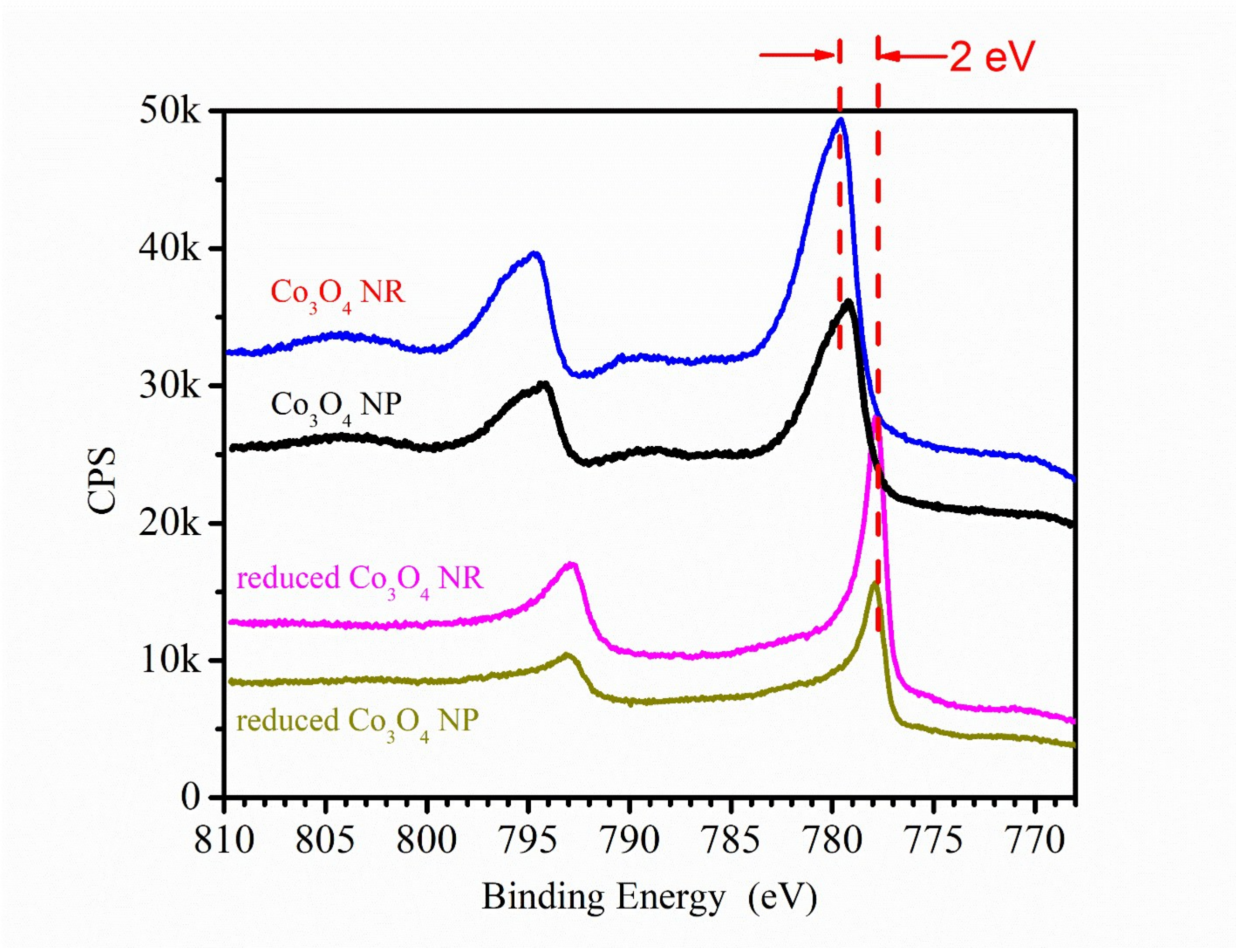


Figure S3: XPS of the reduced cobalt catalyst at 450^{o}C under pure hydrogen for 3 hours.

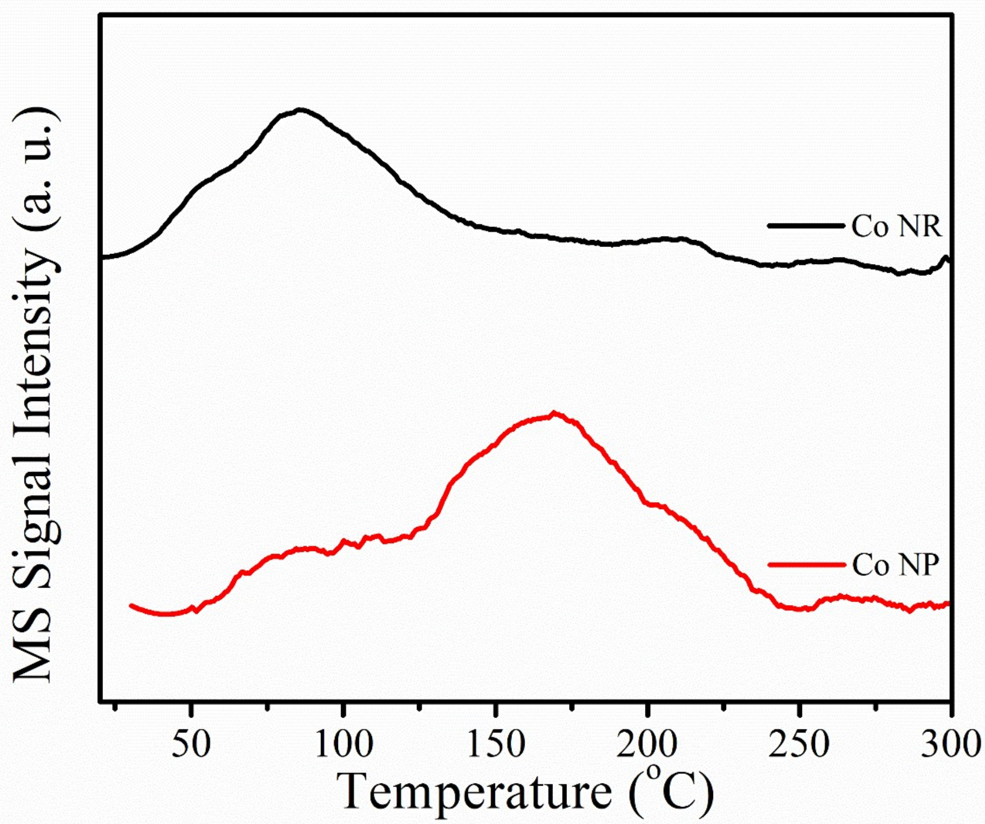
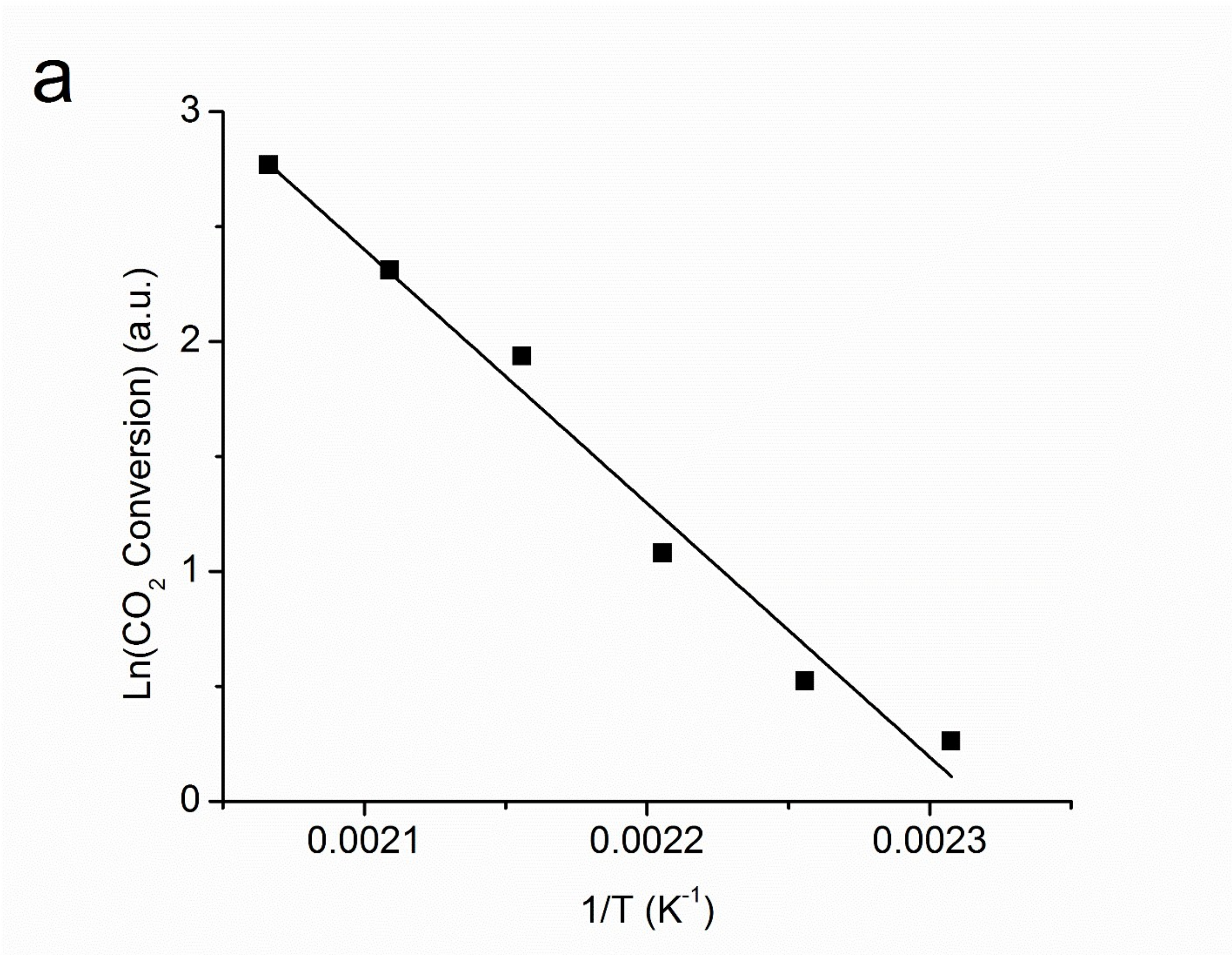


Figure S4. CO_2 TPD profiles on nanorods and nanoparticles, mass 44 is tracked in the mass spectrometer for CO_2.


a
Ln(CO2 Conversion) (a.u.)
1/T (K-1)
0
1
2
3
0.0021
0.0022
0.0023

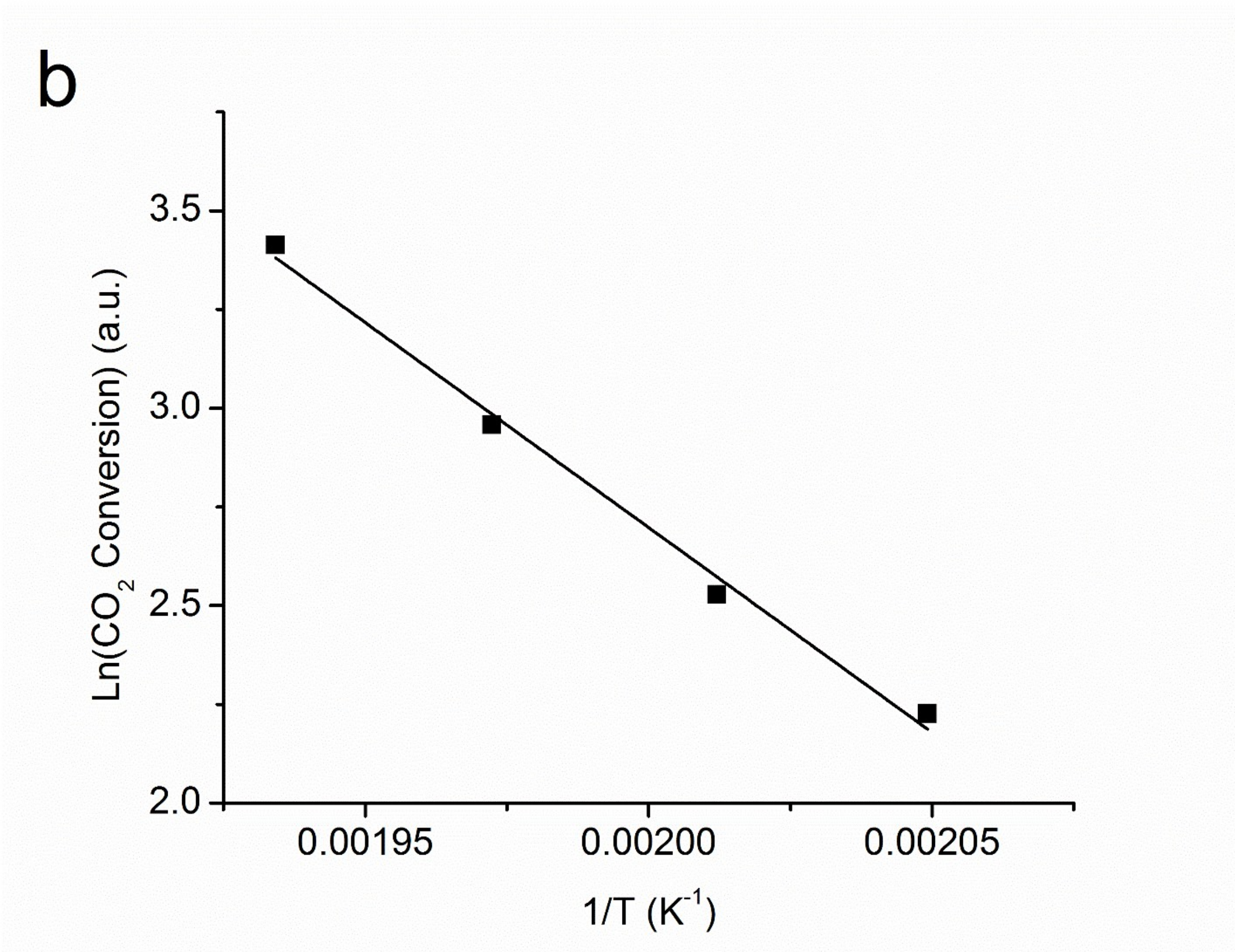


Figure S5. Arrhenius plot of CO_2 hydrogenation on a) nanorods and b) nanoparticles.

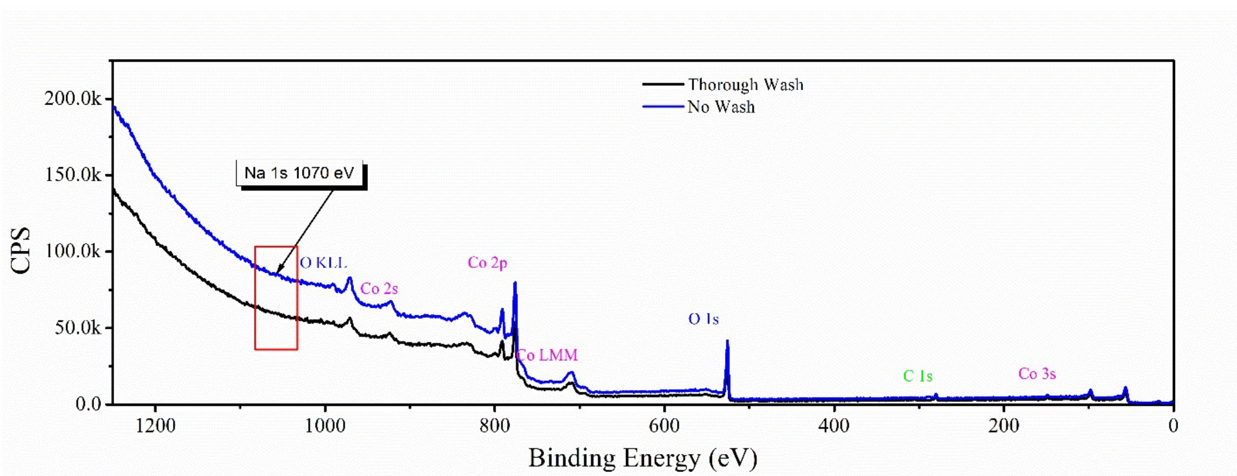


Figure S6. XPS survey scan of Co nanorods and nanoparticles

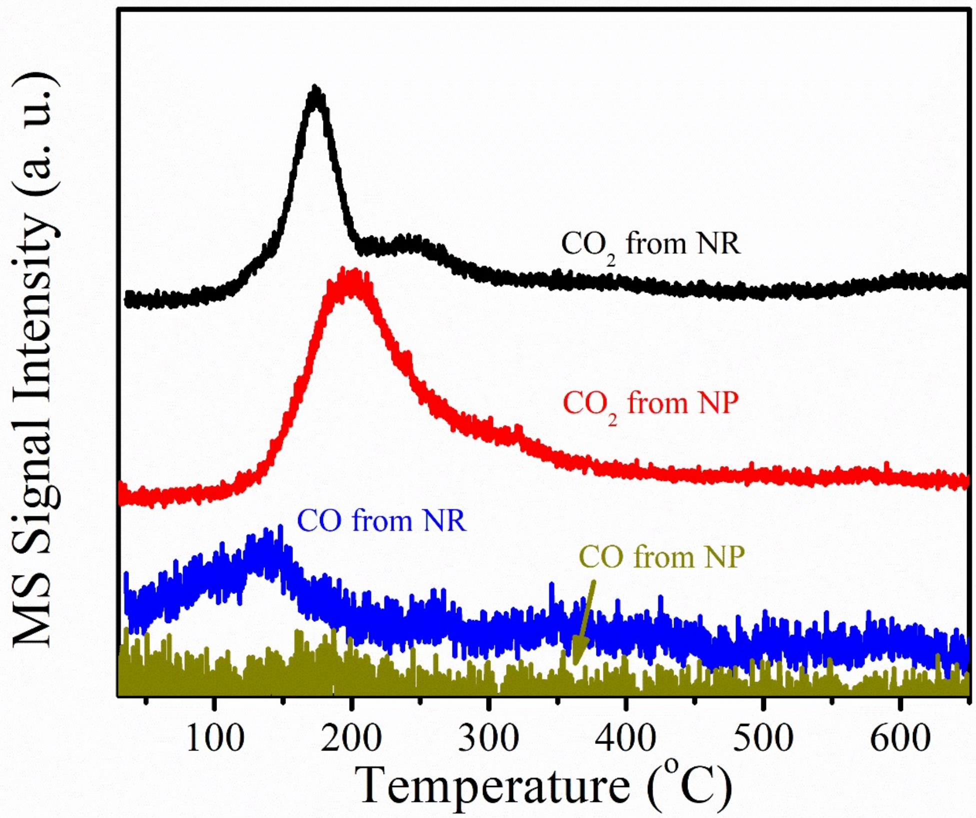


Figure S7. CO TPD profiles on nanorods and nanoparticles, mass 28 and 44 are tracked in the mass spectrometer for CO and CO_2.

Table S1: Comparison of selected outstanding catalyst for CO_2 hydrogenation

Catalyst	***H_2:CO_2*** *Ratio*	***Temp.*** *°C*	***Pressure*** *MPa*	***CO_2 Conv.*** *(%)*	***CH_4 Sel.*** *(%)*	***TOF of CH_4**** ***(s^{-1})***	***Ref.***
Co/SiO_2	3:1	300	6.0	N/A	~40	0.030	[1]
Ru/TiO_2	4:1	160	0.1	100	100	0.015	[2]
0.1%Ru/Al_2O_3	3:1	350	0.1	~2	~0	0.83	[3]
NGQDs/Al_2O_3	4:1	359	1.0	41	26	1.57	[4]
Ni/$Ce_xZr_{1-x}O_2$	4:1	350	0.1	79	99	0.426	[5]
PtCo/TiO_2	2:1	300	0.1	8.2	85	0.51	[6]
CoNR	4:1	220	1.0	57	98	2.83	This
CoNP	4:1	220	1.0	7.3	15	0.05	Work

*Turnover frequency (TOF) was calculated based on the turnover number of CO_2 ($mol_{CO2}\cdot g_{cat}^{-1}\cdot s^{-1}$) normalized by the number of active sites measured via CO chemisorption ($mol_{CO}\cdot g_{cat}^{-1}$). The TOF of CH_4 is equivalent to the TOF of CO_2 multiplied by its selectivity towards methane. TOF values taken from literature were used as originally reported.

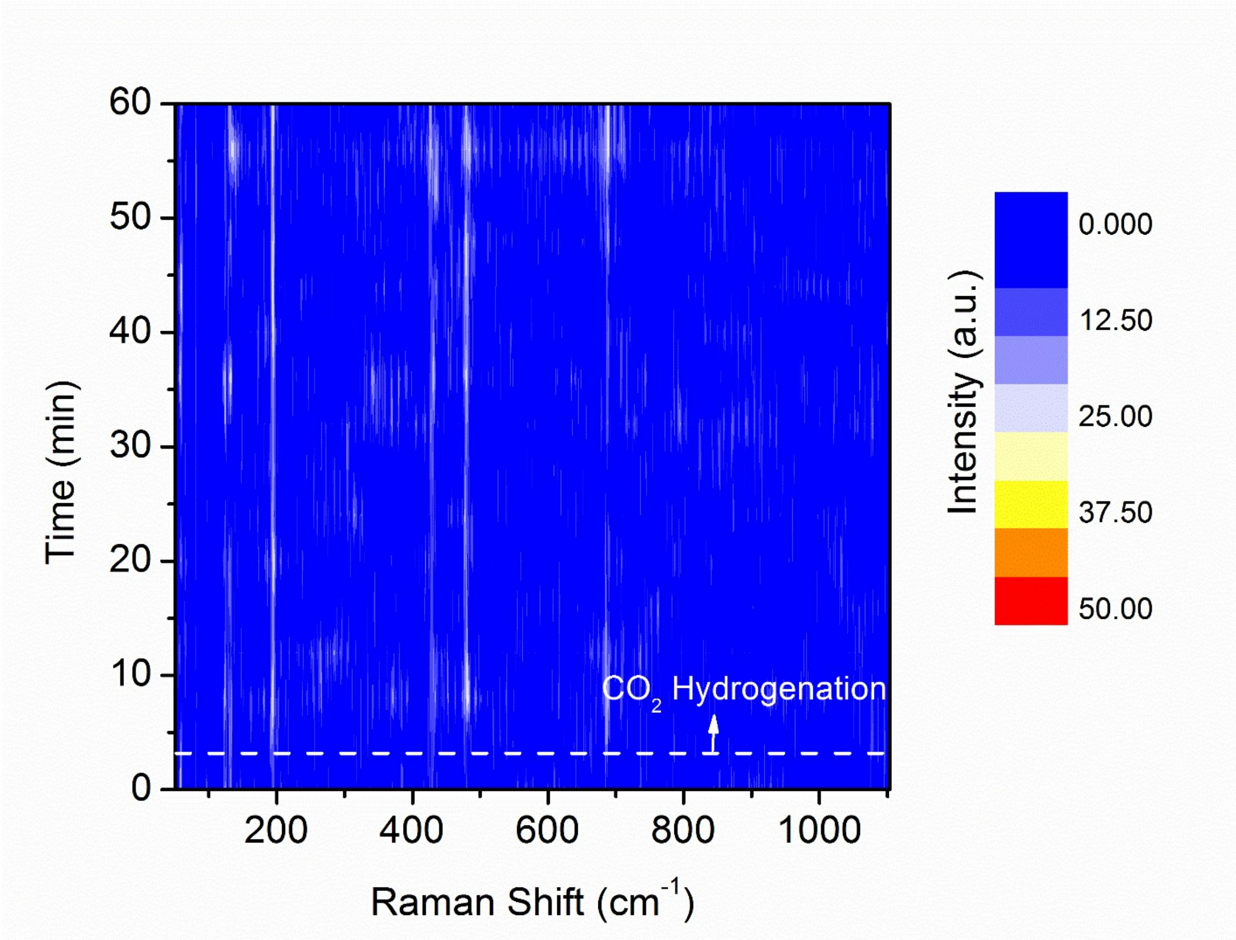


Figure S8: *in situ* Raman spectra of the Co nanoparticles. 450°C H_2 for 3hr pretreatment, 4:1 H_2 to CO_2 inlet gas composition, operating temperature of 230°C.

References

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