Surpporting Information

Nitrogen-Coordinated Cobalt Nanocrystals for Oxidative Dehydrogenation and Hydrogenation of N-Heterocycles

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EXPERIMENTAL DETAILS

Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), 2-methylimidazole, methanol and acetone were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 1,2,3,4-tetrahydroquinoline, 8-methyl-1,2,3,4-tetrahydroquinoline, 1,2,3,4-tetrahydroquinoxaline, indoline, N-diphenylmethanimine, N-benzylbutan-1-amine, methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate was purchased from Sigma-Aldrich. 6-Bromo-1,2,3,4-tetrahydroquinoline, 6-methoxy-1,2,3,4-tetrahydroquinoline, 6-chloro-quinoline, 6-trifluoromethyl-quinoline were purchased from Alfa Aesar. Ar/H_2 (5%) and N_2 was purchased from Linde Gas. All chemicals were used as received without further purification.

Synthesis of ZIF-67

The whole synthetic strategy of catalyst is shown in Figure S1, generally divided into three stages. For synthesis of ZIF-67, in a typical procedure, Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) (5.46 g) and 6.16 g 2-methylimidazole (MeIM) was respectively dissolved in 150 ml methanol under ultrasound for to form a clear solution. Then, MeIM solution was slowly poured into $Co(NO_3)_2$ solution under severe mixing conditions. The mixture was stirred overnight under at room temperature. The as-obtained precipitates were separated by centrifugation, and washed with methanol for three times. After filtering, the purple powder was dried in vacuum at 60 ^oC overnight.

Synthesis of Co NCs/N-C

The powder of ZIF-67 was transferred into a crucible and heated under Ar atmosphere at 4 ^oC min^{-1} (200 min) up to 800 ^oC and then treated at 800 ^oC for 3 h. The as-prepared black powder can be directly used as catalyst.

Acid treatment of Co NCs/N-C

As for acid treatment, Co NCs/N-C was treated by HCl under ultrasound for several minutes to remove those Co particles embedded on the surface. Then, ethanol was added for dilution, and the precipitates were separated by centrifugation. The resultant black powder was washed with HCl for three times and then dried at 60 ºC overnight.

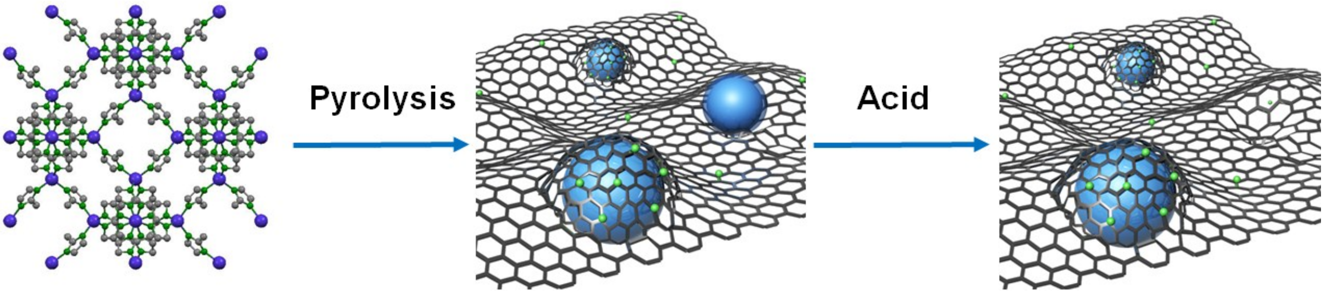


Figure S1. The scheme of Co NCs/N-C obtained from the pyrolysis of ZIF-67 and acid treatment.

Characterization

The crystalline structure and phase purity were determined by Rigaku RU-200b X-ray powder diffractometer with Cu Ka radiation (l = 1.5418 Å).

The size and morphology of as-synthesized samples were determined by using Hitachi-7700 transmission electron microscope working at 100 kV.

The high-angle annular dark-field scanning TEM (HAADF-STEM) were operated at 200 kV by a JEOL-ARM200F. The composition of the product was measured by the inductively coupled plasma-atomic emission spectrometry and energy dispersive X-ray spectrometer.

Photoemission spectroscopy experiments (XPS) were performed on a ULVAC PHI Quantera microscope. For the core-level spectra, the binding energies were calibrated using the C 1s feature located at 284.6 eV as the reference.

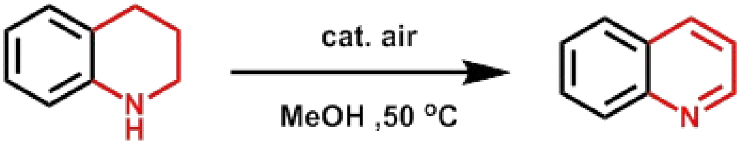
The Co L-edge X-ray absorption spectra were collected at room temperature in fluorescence mode at beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF) using a Si (111) double-crystal monochromator. The storage rings of BSRF were operated at 2.5 GeV with a maximum current of 250 mA in decay mode. The energy was calibrated using Co foil, while the incident and fluorescence x-ray intensities were monitored by using standard 25% Ar and 75% N_2-filled ion chamber and Ar-filled Lytle-type detector, respectively. A detuning of about 20% by misaligning the silicon crystals was also performed to suppress the high harmonic content. The samples were pelletized as disks of 13 mm diameter with 1mm thickness before measurements. Besides, the C K-edge and N K-edge X-ray absorption spectra were measured at beamline BL12B of National Synchrotron Radiation Laboratory (NSRL) of China and the samples were deposited onto double-sided carbon tap.

The XAFS spectra were obtained at 1W1B station in BSRF (Beijing Synchrotron Radiation Facility, P. R. China) operated at 2.5 GeV with a maximum current of 250 mA. All samples were pelletized as disks of 13 mm diameter with 1mm thickness using graphite powder as a binder. Additionally, the C K-edge and N K-edge X-ray absorption spectra were measured at beamline BL12B of National Synchrotron Radiation Laboratory (NSRL) of China and the samples were deposited onto double-sided carbon tap.

The XAFS raw data were background-subtracted, normalized, and Fourier transformed by the standard procedures with the ATHENA program.

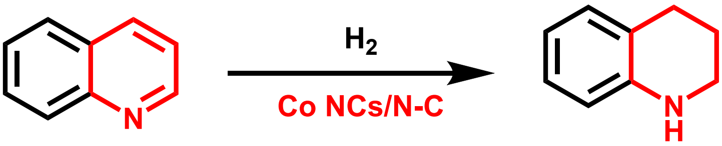
General procedure for the catalytic oxidative dehydrogenation reaction

To a test tube, 0.5 mmol 1,2,3,4-tetrahydroquinoline, 50 mg Co NCs/N-C catalyst, 3 mL MeOH were added. The result mixture was stirred under 50 °C for a proper time, and then the catalyst was removed through magnetic separation. 50 µL supernatant was diluted by 1 mL acetonitrile, and then GC-FID(SP-6890) was used to determine the conversion and selectivity.



General procedure for the catalytic hydrogenation reaction

A stainless steel autoclave reactor with a magnetic stirring bar was charged with Co catalyst (Co NCs/N-C; 50 mg), substrate quinolone (0.5 mmol), and THF (5 mL). Under certain pressure of H_2, the reaction mixture was stirred at different reaction temperature, then cooled to room temperature. After hydrogen was carefully released, the supernatant was diluted by 1 mL THF, and then GC-FID (SP-6890) was used to determine the conversion and selectivity.



Procedure for recovering and reusing the catalyst

After the reaction was over, the reaction mixture was centrifuged under 10000 r/min. The supernatant was removed, and the residue was washed with methanol (3×5 mL). Then, the catalyst powder was dried at 60 °C in a vacuum oven. The regenerated Co NCs/N-C catalyst was used directly for the next run of the model reaction.

Procedure for Electron Paramagnetic Resonance (EPR)

To a test tube, 1 mL 1,2,3,4-tetrahydroquinoline, 50 mg Co NCs/N-C catalyst, 3 mL MeOH were added. The result mixture was stirred under 50 °C for 1 h, and the catalyst was removed through magnetic separation. Solution of 50 mmol/L dmpo in methanol was prepared, and 70 µL dmpo solution was mixed with 70 µL reaction liquid for EPR testing.

RESULTS and DISCUSSION

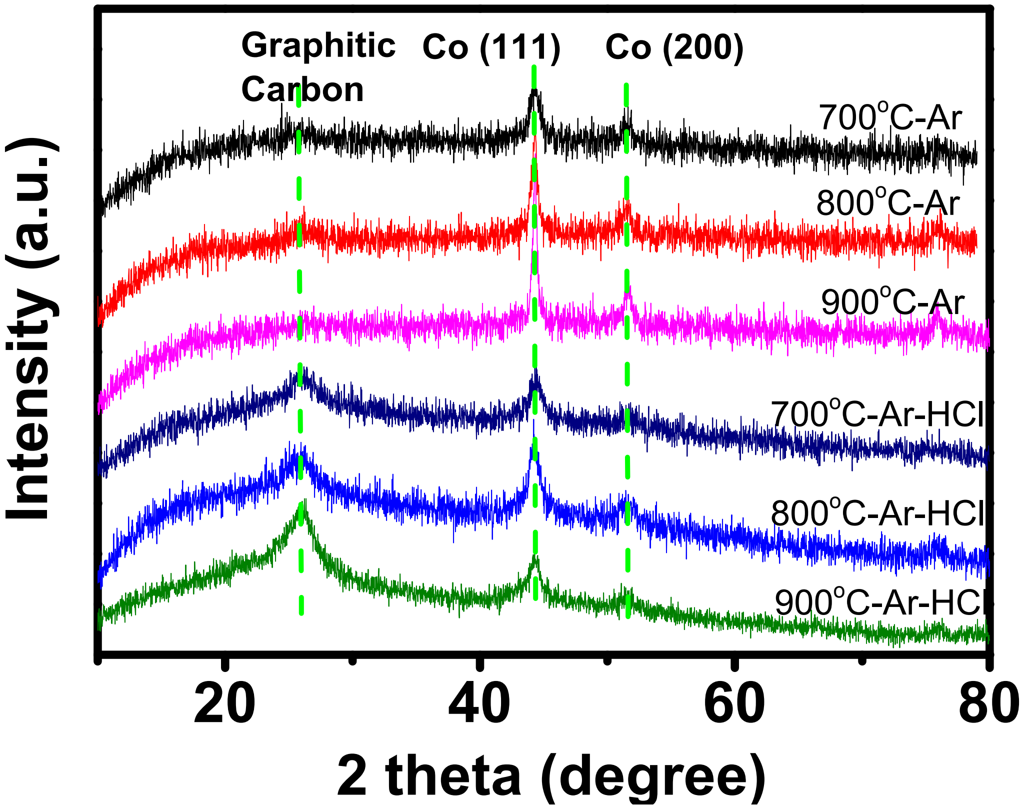


Figure S2. the X-ray diffraction pattern of Co NCs/N-C treated with different conditions.

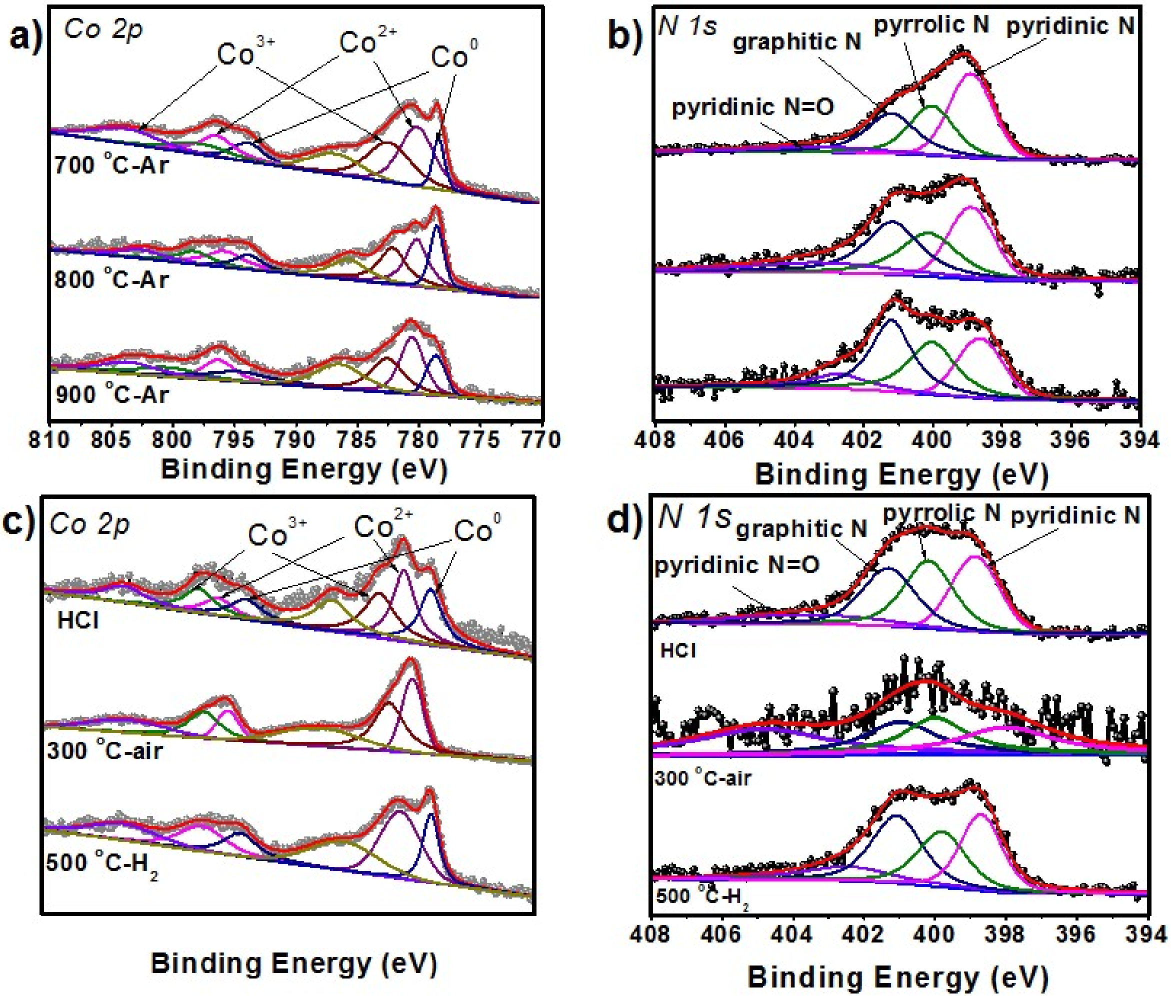


Figure S3. X-ray photoelectron spectra for different catalysts of Co 2p and N 1s.

Table S1. Oxidative dehydrogenation of 1,2,3,4-tetrahydroquinoline with Co NCs/N-C in different solvent at 80 ^oC.[a]

Entry	Solvent	Conversion (%)		Selectivity (%)
		4 h	24 h	
1	DMSO	15.1	33.9	100
2	DMF	33.5	64.1	100
3	DMA	25.4	59.2	100
4	Dioxane	7.0	17.0	100
5	xylene	24.9	46.6	100
6	methylbenzene	22.2	41.2	100
7	N-Methyl pyrrolidone	16.3	31.2	100

[a] Reaction conditions: 0.5 mmol 1,2,3,4-tetrahydroquinoline, 50 mg catalyst, 3 mL solvent, air, 80 ^oC;

Table S2. Oxidative dehydrogenation of 1,2,3,4-tetrahydroquinoline with Co NCs/N-C in different solvent at 50 ^oC.[a]

Entry	Solvent	Conversion (%)		Selectivity (%)
		4 h	15 h	
1	Alcohol	37.0	77.7	100
2	Iso-Propanol	21.8	55.7	100
3	n-butyl alcohol	24.8	59.5	100
4	Phenylcarbinol	10.4	22.9	100
5	Ethyl acetate	12.7	32.4	100
6	Acetonitrile	21.0	48.4	100
7	DMF	8.2	25.5	100

[a] Reaction conditions: 0.5 mmol substrate, 50 mg catalyst, 3 mL solvent, air, 50 ^oC;

Table S3. Oxidative dehydrogenation of 1,2,3,4-tetrahydroquinoline with Co NCs/N-C in MeOH at room temperature.[a]

Entry	Solvent	Conversion(%)	Selectivity(%)
1	Methanol	97.2	100

[a] Reaction conditions: 0.5 mmol 1,2,3,4-tetrahydroquinoline, 50 mg catalyst, 3 mL solvent, air, 25 ^oC;

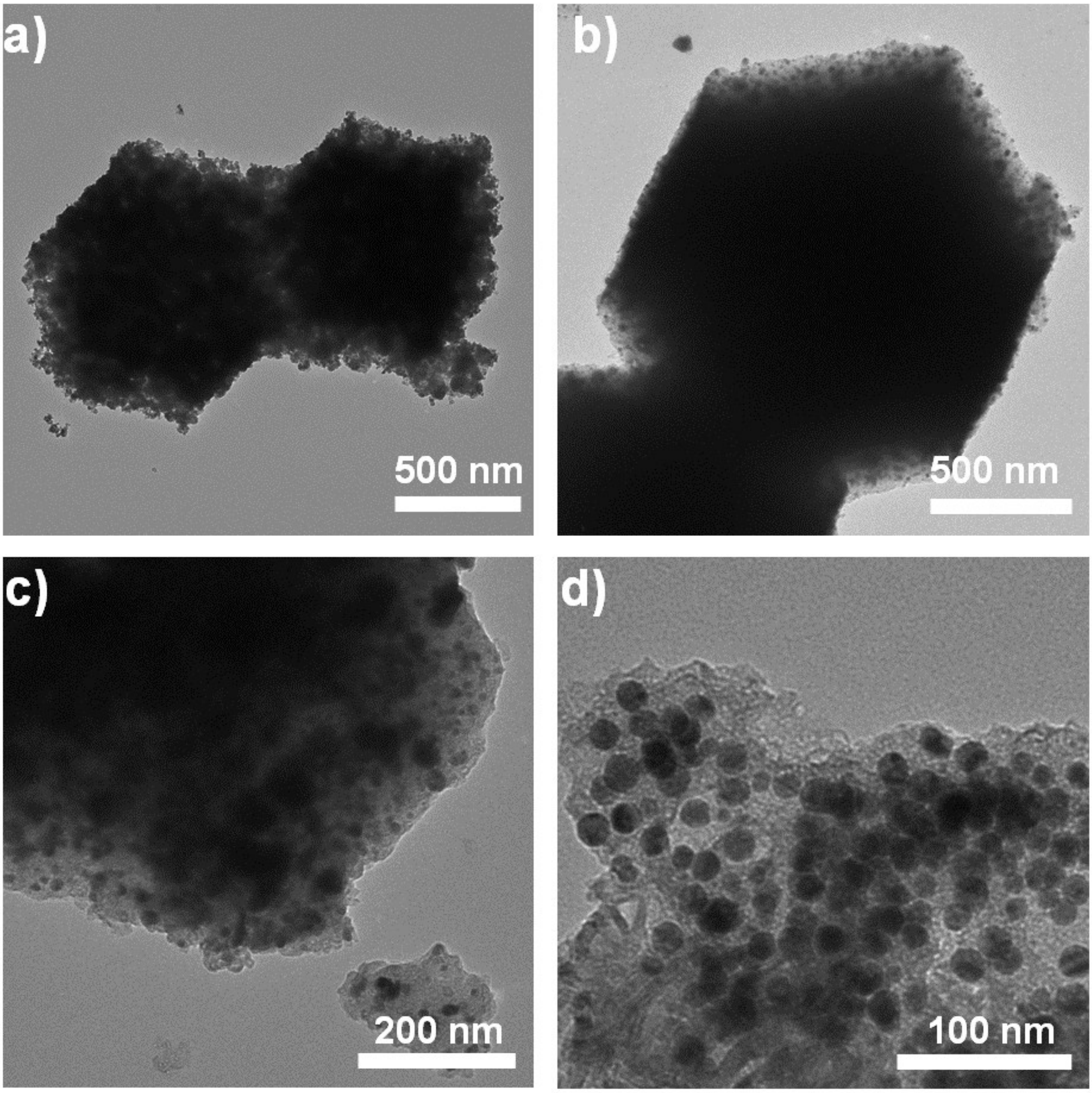


Figure S4. TEM characterizations of a) Co NCs/N-C after treatment at 300 ^{o}C in air, and b) after treatment at 500 ^{o}C in H_2; c) After five-cycle measurement, the Co NCs/N-C could almost maintain its original morphology; d) Co NCs/C by the method modelled on Co NCs/N-C, but the ligands were changed into 1,3,5-benzenetricarboxylic acid (BTC).

Table S4. The Co loadings determined by ICP-OES.

Different catalyst	Co NCs/N-C-800°C	HCl Treatment	Co NCs/C
Actual (wt%)	30.41	4.468	60.04

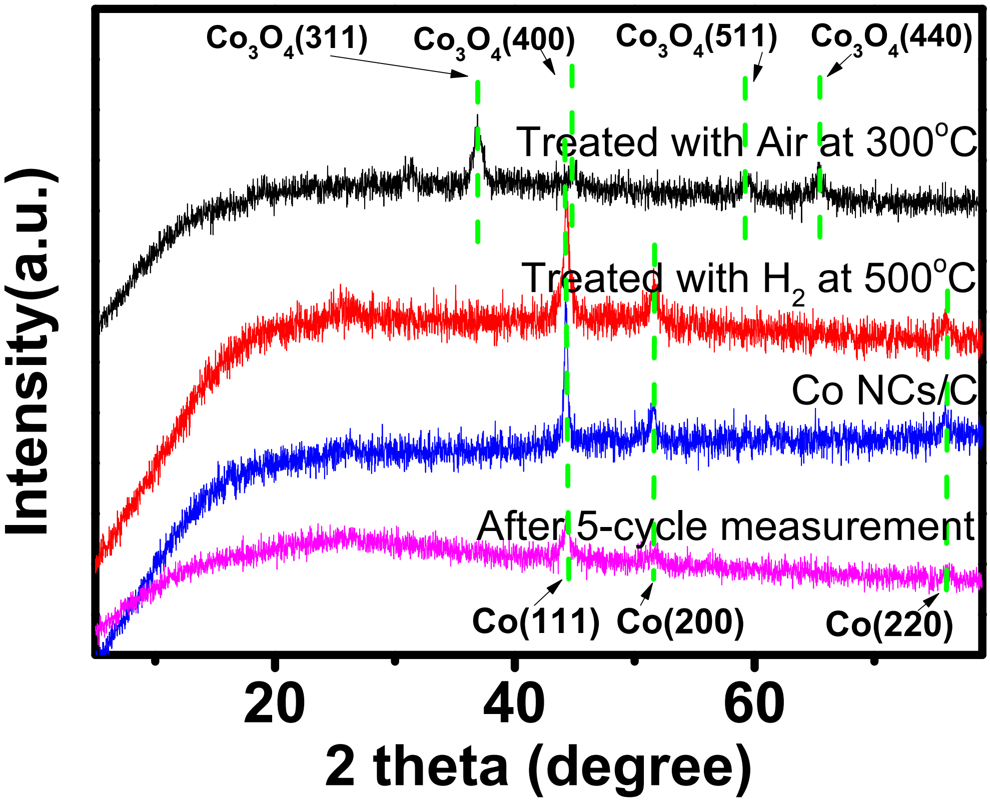


Figure S5. the X-ray diffraction pattern of Co NCs/N-C carbonized at 800 °C subsequently treated with air or H_2, or recycled for 5 times and Co NCs/C.

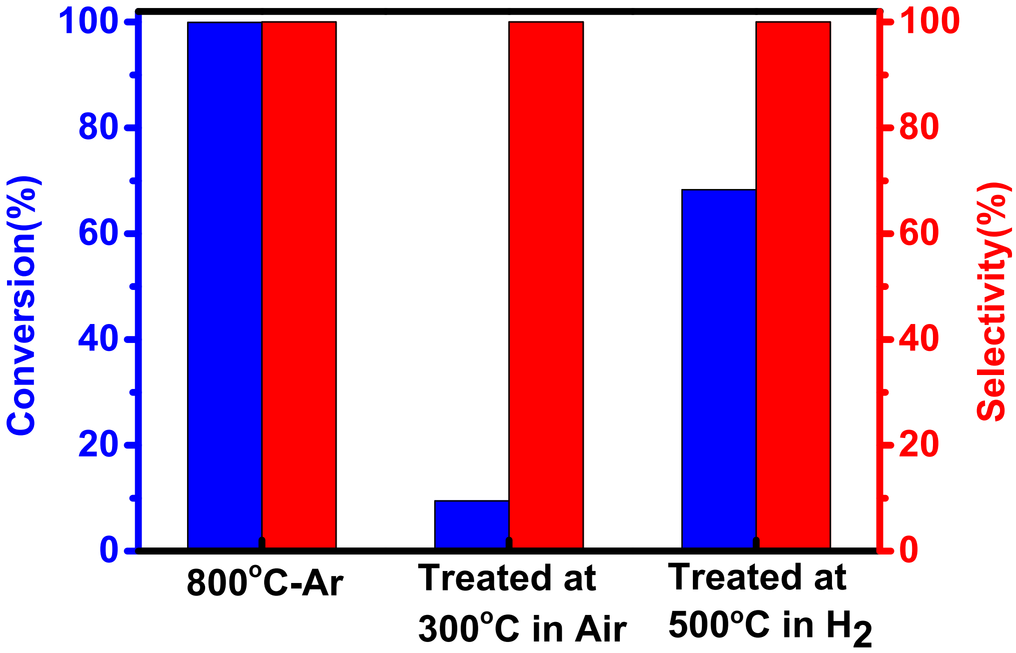


Figure S6. Comparisons of conversion and selectivity for Co NCs/N-C catalysts carbonized at 800°C and aftertreatment in air at 300 °C and in H_2 at 500°C respectively.

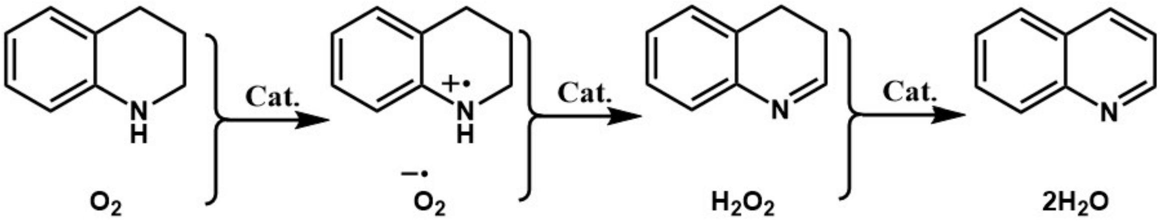


Figure S7. Proposed mechanism for the catalytic oxidative dehydrogenation of 1,2,3,4-tetrahydroquinoline.

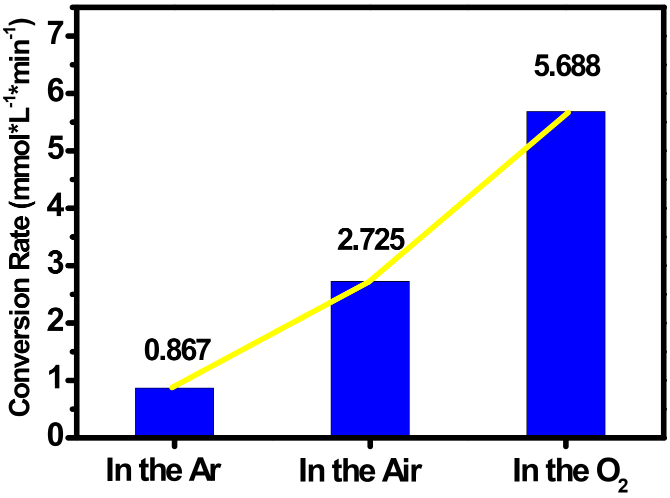


Figure S8. Comparisons of conversion and selectivity for Co NCs/N-C catalysts carbonized at 800°C under different atmospheres (Ar, Air, and O_2 respectively). The initial reaction rate under pure argon (anaerobic conditions), air (about 20% oxygen) and pure oxygen (100% oxygen) at atmospheric pressure were compared, and it turned out that oxygen can significantly promote this reaction. Within first four minutes of initial reaction, the reaction rate $r_{in\,O_2}$: $r_{in\,Air}$: $r_{in\,Ar}$=6.56 : 3.14 : 1..

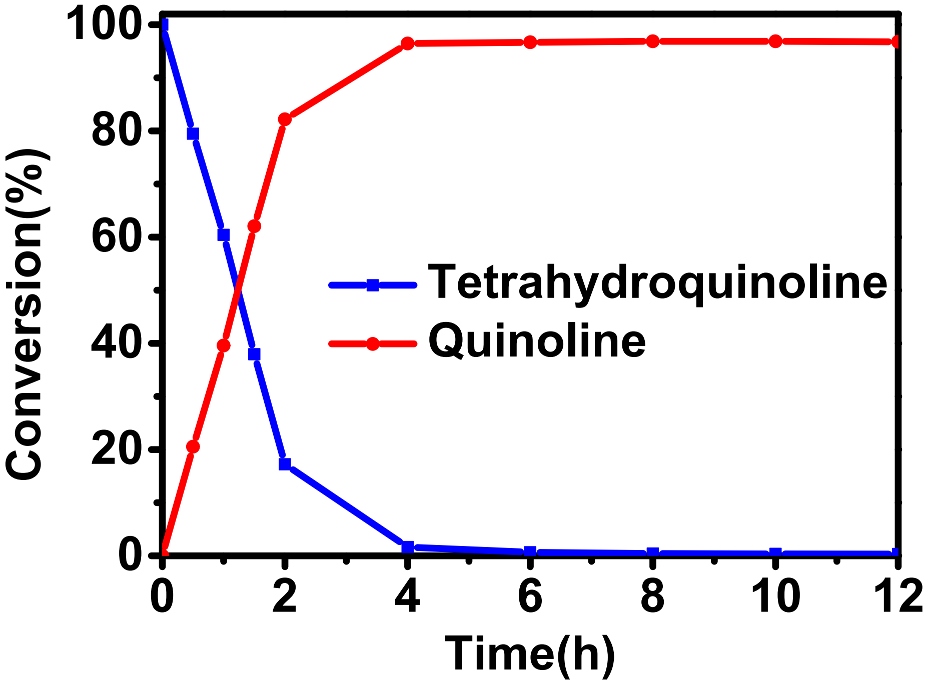


Figure S9. Conversion vs. time results of the Co NCs/N-C catalysts.