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Supporting Information

Structures, dimensions, and particle sizes engineering toward highly efficient supported nanoparticulate metal catalysts

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Experimental section

Chemicals and reagents

Cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$), iron nitrate nonahydrate ($Fe(NO_3)_3·9H_2O$) and dicyandiamide (DCDA) were obtained from Aladdin Industrial Corporation, China. Ethanol, tannic acid (TA), sodium borohydride ($NaBH_4$), *p*-nitrophenol (*p*-NP), and sulfuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All these chemicals in this study were analytical grade and used as received without further purification.

Synthesis of the nitrogen doped carbon supported nanoparticulate metal catalysts

The catalysts were prepared from an easily scalable pyrolysis method and template/activation agent free process. Typically, 0.2 g of tannic acid, 8 g of dicyandiamide and a certain amount of $Co(NO_3)_2·6H_2O$ were dissolved in ethanol, and the resulting homogeneous mixture was stirred at 80℃ for 8h. Subsequently, the solvent was evaporated and the solid was obtained followed by vacuum dried at 75℃ for 12h. After that, the dried solid mixture was grinded for at least 20 min using a mortar-pestle to obtain a fine powder. In the next step, the fine powder was transferred into a quartz boat inside an electrical tube furnace, which was then heat-treated at 800℃ for 3h at a ramping rate of 3℃ min^{-1} under a protective atmosphere of N_2 to generate catalysts. To realize the structural manipulation and particle size engineering, a series of catalysts were prepared by simply changing the amount of $Co(NO_3)_2·6H_2O$ added while keeping other reaction parameters the same, and the catalysts obtained from 0.02 g, 0.1 g, 0.2 g, 0.5 g, 1 g and 2 g $Co(NO_3)_2·6H_2O$ were denoted Co-N-C-0.1, Co-N-C-0.5, Co-N-C-1, Co-N-C-2.5, Co-N-C-5 and Co-N-C-10, respectively. Besides, to evaluate the role of cobalt nanoparticles on the catalytic performance, the catalysts were immersed in 0.5M H_2SO_4 or 3M H_2SO_4 for 24 h to remove the cobalt nanoparticles on the surface. The resulting products were washed to neutral with deionized water and finally vacuum dried at 60℃. For comparative studies, nitrogen doped carbon (NC) was also prepared in a similar way but without the addition of cobalt salt during the preparation process. To verify the universality of this synthetic method, Fe-N-C-X was also obtained by simply replacing the cobalt source of $Co(NO_3)_2 \cdot 6H_2O$ with iron source from $Fe(NO_3)_3 \cdot 9H_2O$ with other synthetic parameters remains the same.

Characterizations

The microstructure of as-prepared products was observed on a JEM-2100 (HR) transmission electron microscope at a working voltage of 200 kV, or Hitachi H-7000FA with an accelerating voltage of 100 kV. The scanning electron microscopy (SEM) measurement was also conducted to study the structure of the catalysts using a Germany Zeiss sigma HD thermal filed of scanning electron microscope at a working voltage of 5.0 kV. The high-resolution transmission electron microscopy (HRTEM) images and the relevant TEM elemental maps were recorded with FEI tecnai G2 F30 operating at 300 kV. The powder X-ray diffraction (XRD) pattern of each sample was identified by a X'pert PRO diffractometer (PANalytical) with Cu Kα radiation (wavelength λ=1.5406 Å). To reveal the surface compositions and elemental state, X-ray photoelectron spectroscopy (XPS) spectra were performed using an Escalab 250XI (Thermo Fisher) spectrometer equipped with a hemispherical energy analyzer. The magnetic property of the catalyst was characterized on a vibrating sample magnetometer (VSM) using a PPMS-9T physical property measurement system (Quantum Design) at 300K. The Raman spectrum was recorded on a Renishaw Raman spectrometer. Nitrogen adsorption and desorption studies were performed at

77 K on a Micromeritics ASAP 2020 adsorption apparatus. The specific surface area was measured using Brunauer-Emmett-Teller (BET) method. All ultraviolet visible (UV－vis) spectra were measured using a Shimadzu UV-2700 spectrophotometer at room temperature.

Catalytic performance evaluation

The hydrogenation of *p*-nitrophenol by $NaBH_4$ in aqueous solution was chosen as the model reaction to evaluate the catalytic performance of as-prepared catalysts. In a typical process, 0.2 mL of 2.5 mM *p*-nitrophenol and 0.2 mL of freshly prepared $NaBH_4$ (0.2 M) were added into 2.5 mL of deionized water in a standard quartz cell at 25℃. Subsequently, 0.08 mL of 0.5 mg mL^{-1} as-obtained catalyst was injected rapidly into the above mixture. As the reaction proceeded, the color of the mixture gradually vanished and the reduction process was monitored by recording the changes of UV-Vis absorption spectra of the mixture in the scanning range of 200-500 nm at a predetermined time interval. To evaluate the recyclability of the catalyst, five consecutive reduction cycles were conducted, and the catalysts were magnetically separated from the mixture with aid of an external magnetic field after each run, followed by washing several times with ethanol and deionized water, and used for the next cycle.

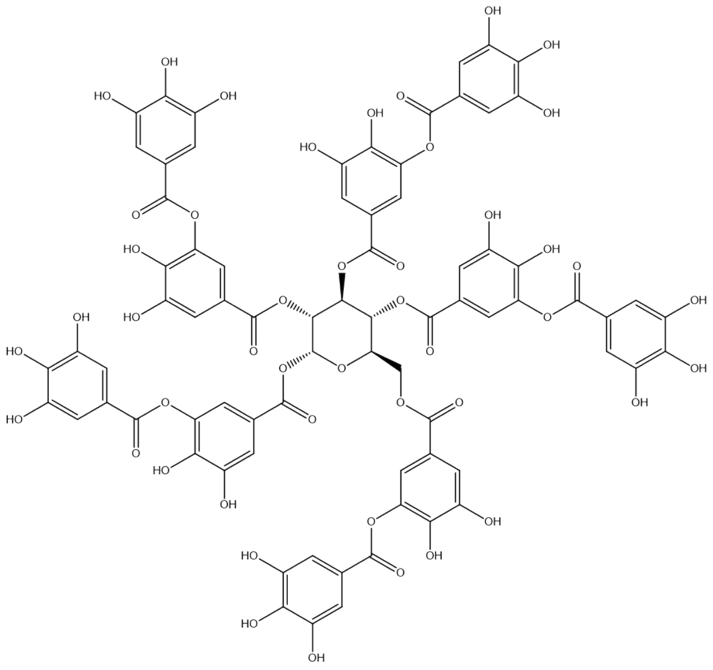

Figure S1. Molecular structure of tannic acid (TA).

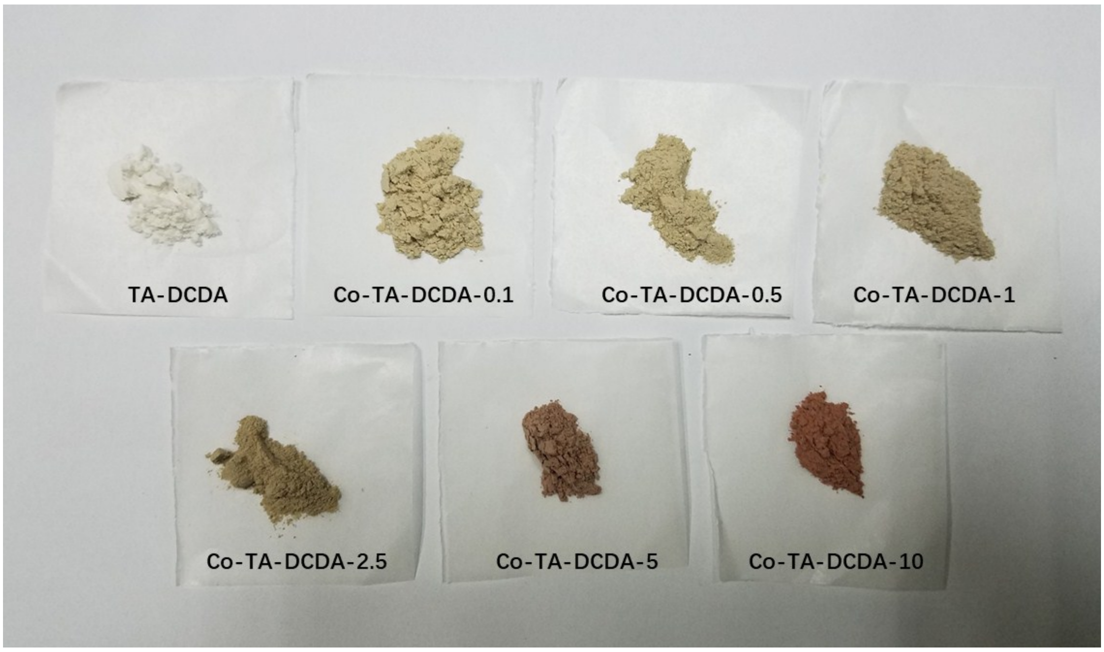

Figure S2. Digital photographs of Co-TA-DCDA powder.

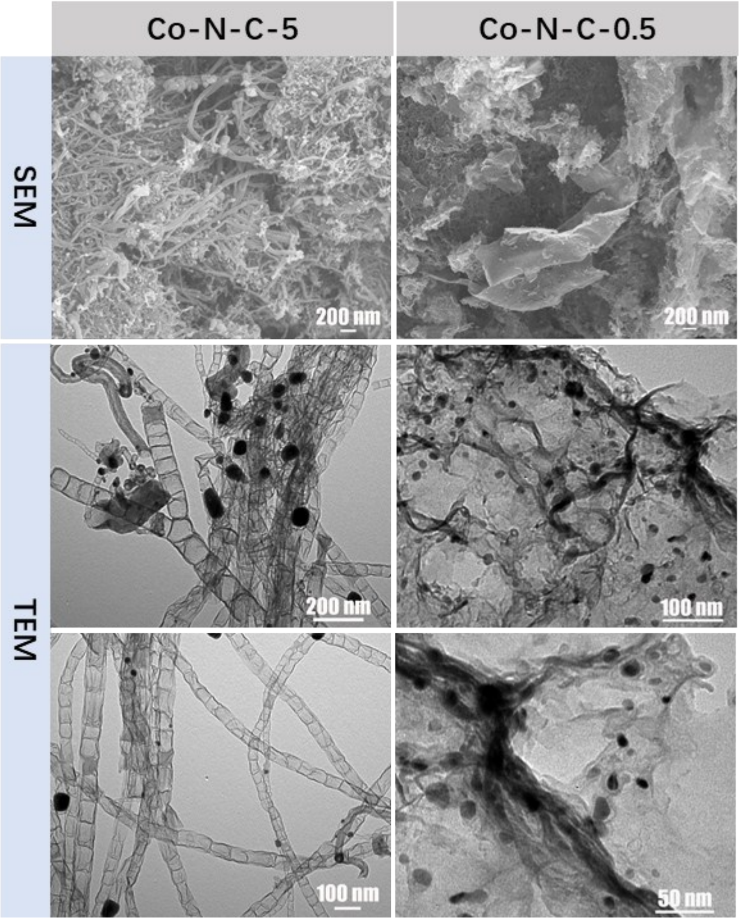

Figure S3. SEM and TEM images of Co-N-C-5 and Co-N-C-0.5.

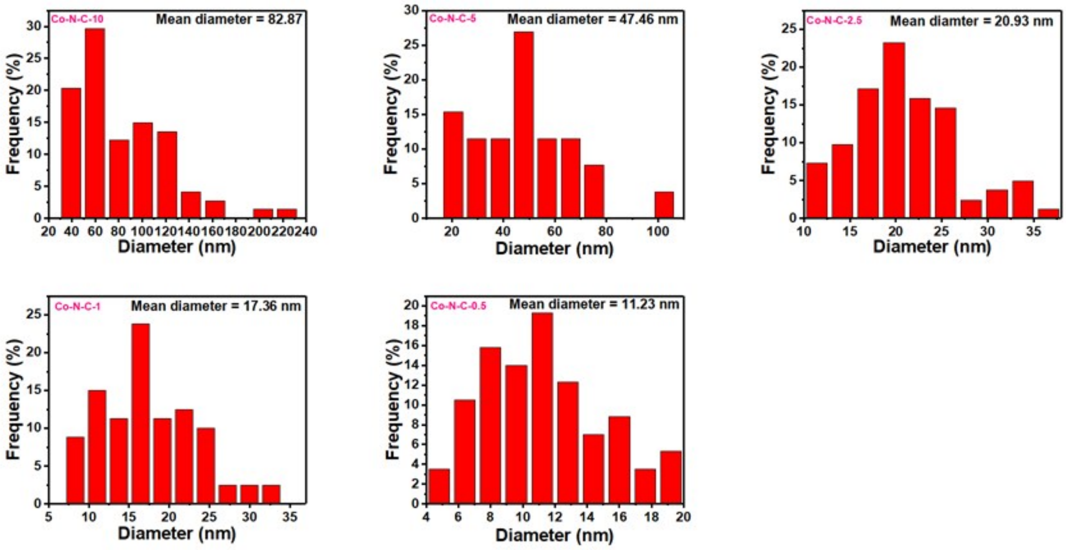

Figure S4. The size distribution curves of Co-N-C-X.

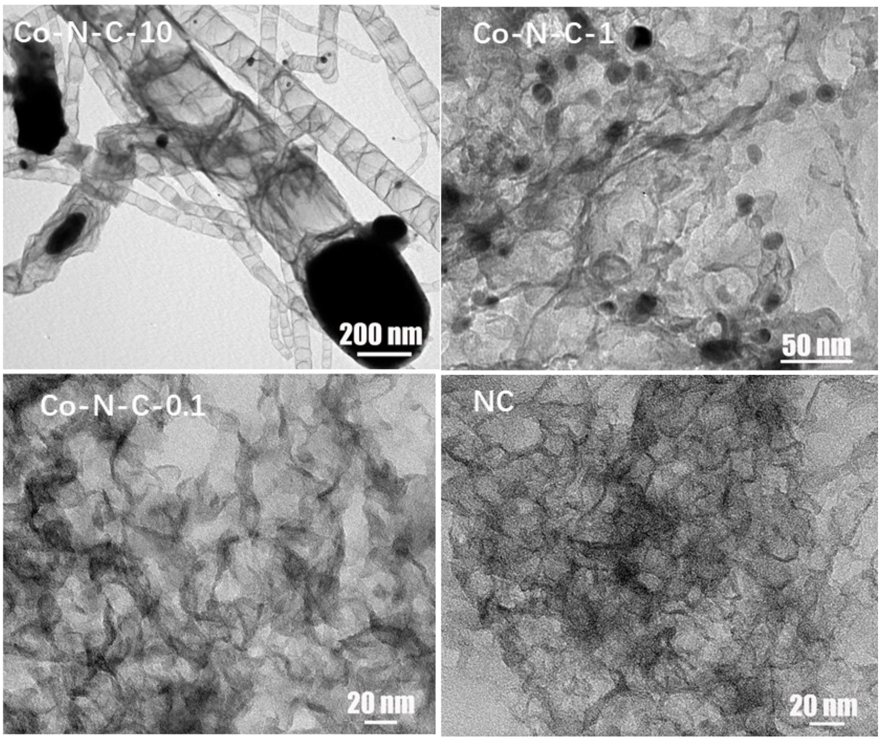

Figure S5. TEM images of Co-N-C-X and NC.

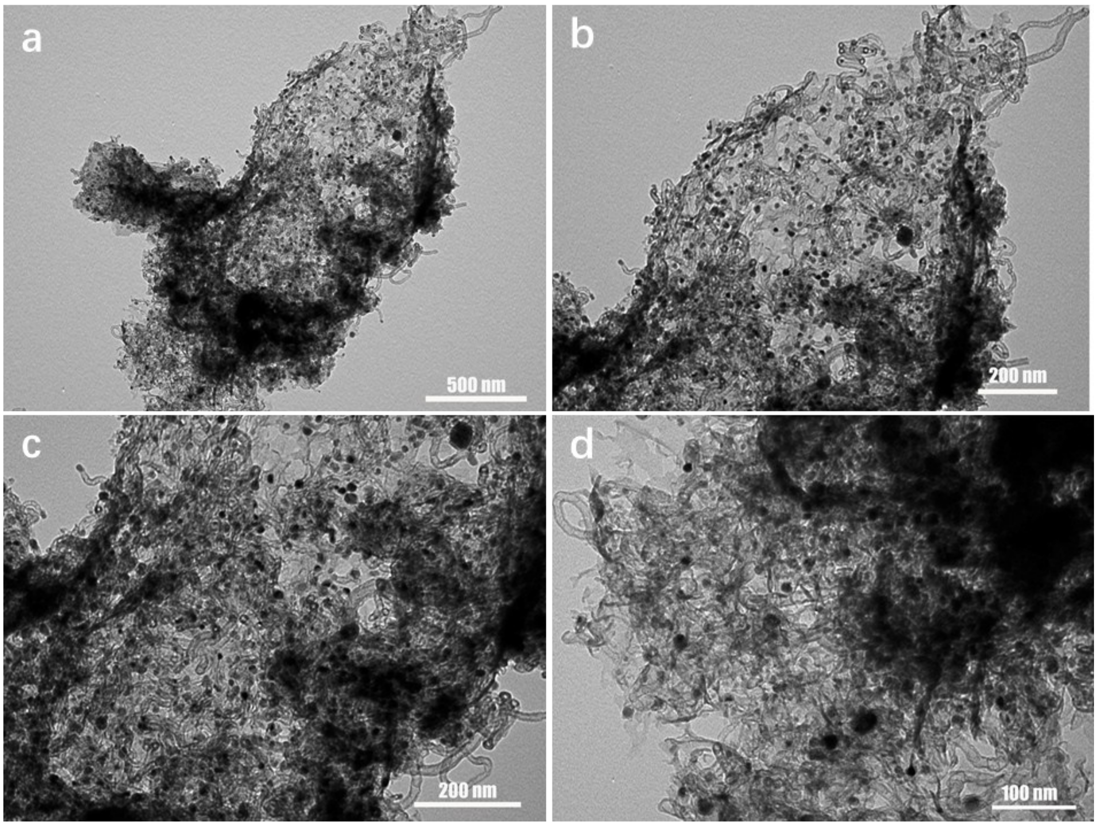

Figure S6. TEM images of Co-N-C-2.5.

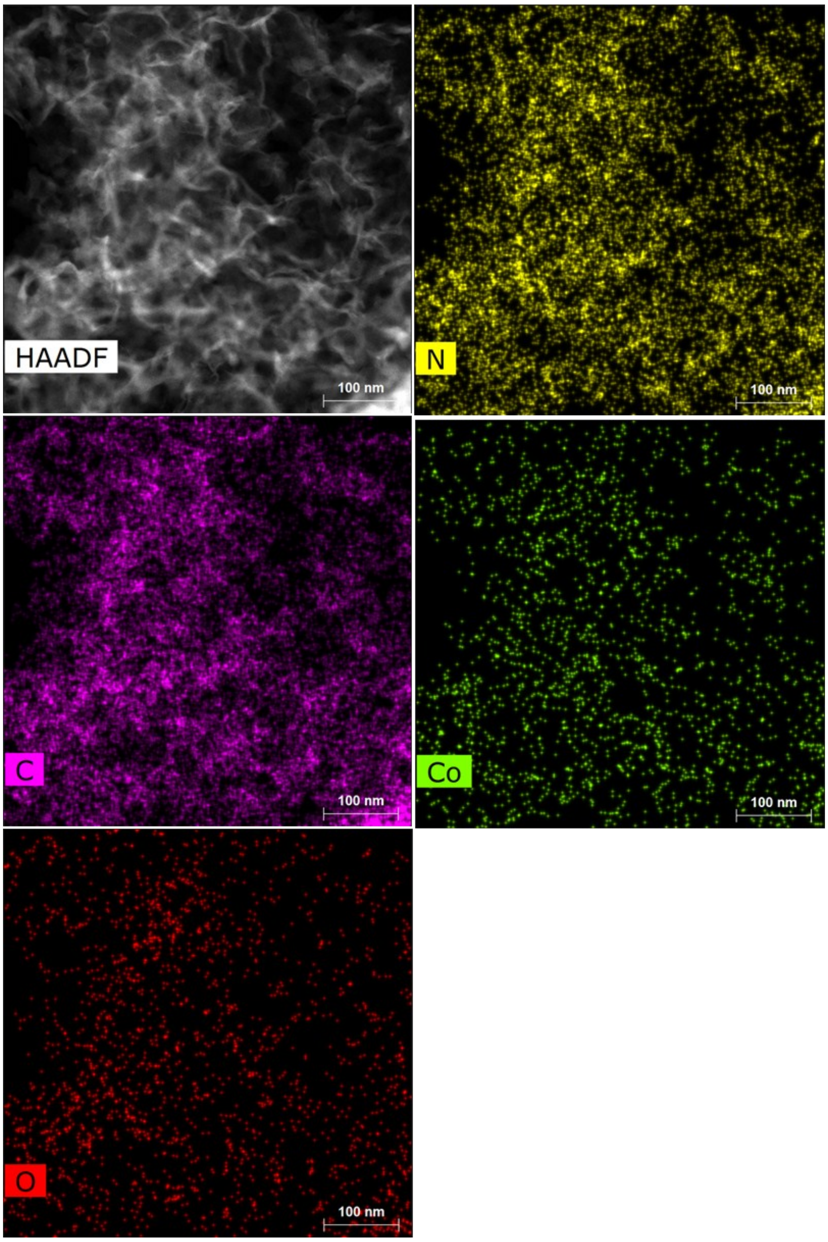

Figure S7. HAADF-STEM images and corresponding EDX elemental mapping images of Co-N-C-0.1.

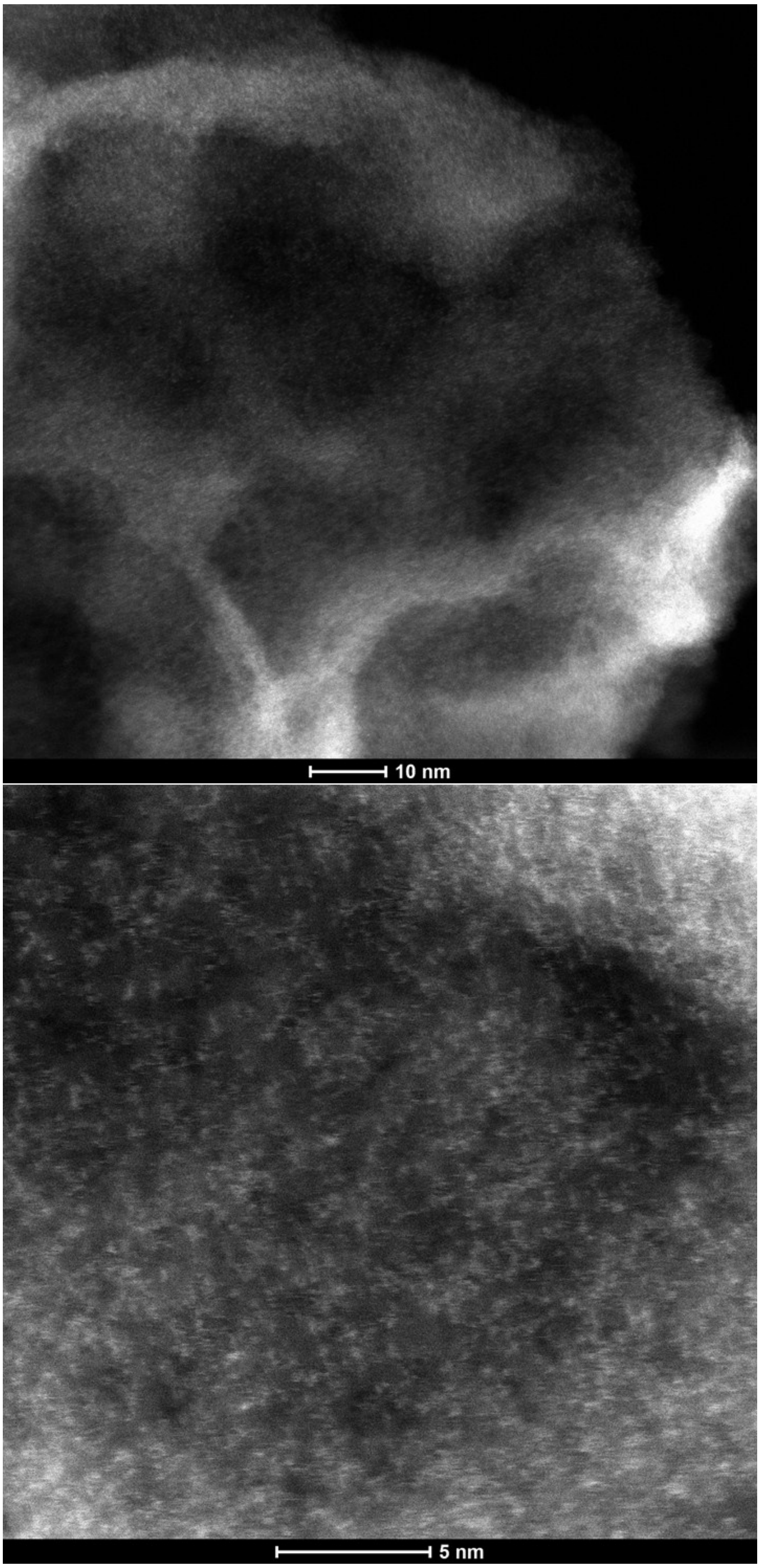

Figure S8. HAADF-STEM images of Co-N-C-0.1.

Table S1 BET surface area and pore properties of the Co-N-C-X.

	Nitrogen sorption analysis		
Samples	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
Co-N-C-0.1	338.50	1.53	18.04
Co-N-C-0.5	344.82	1.46	16.92
Co-N-C-1	289.58	1.34	18.44
Co-N-C-2.5	220.41	1.08	19.62
Co-N-C-5	161.10	0.45	11.11
Co-N-C-10	184.06	0.47	10.12

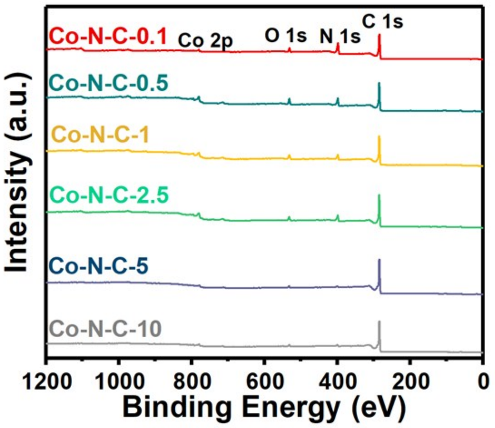

Figure S9. XPS survey spectra of Co-N-C-X.

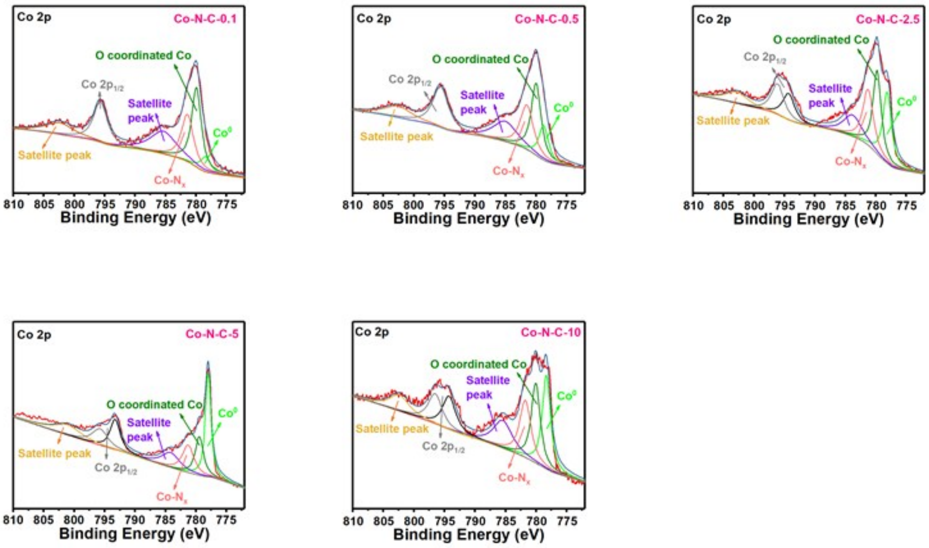

Figure S10. The high-resolution Co 2p spectra of Co-N-C-X.

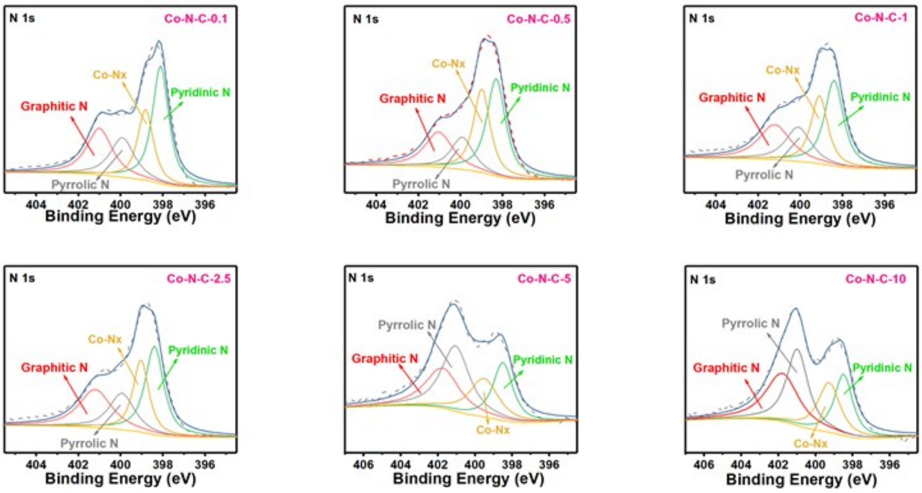

Figure S11. The high-resolution N 1s spectra of Co-N-C-X.

Table S2 Summary of atomic contents of various nitrogen types in the Co-N-C-X. These data are based on the peak intensities of various nitrogen types.

Samples	Nitrogen atomic content (atom %)			
	Pyridinic N	Co-Nx	Pyrrolic N	Graphitic N
Co-N-C-0.1	7.83	4.48	3.85	4.83
Co-N-C-0.5	5.21	4.02	2.02	2.79
Co-N-C-1	3.49	2.46	1.89	2.41
Co-N-C-2.5	3.55	2.46	1.99	2.67
Co-N-C-5	0.62	0.59	0.97	0.73
Co-N-C-10	0.56	0.55	0.79	0.81

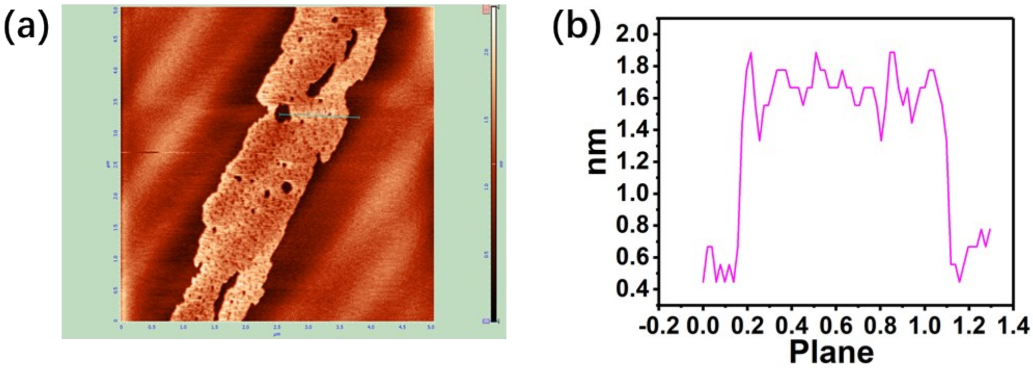

Figure S12. AFM image (a) and height profile (b) of NC.

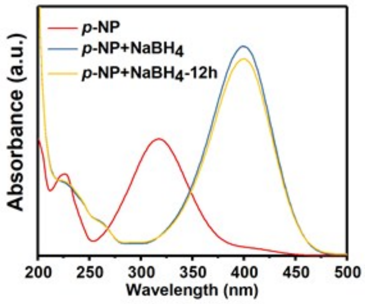

Figure S13. UV-vis spectra of *p*-nitrophenol in the absence and presence of $NaBH_4$.

The characteristic absorption peak of *p*-nitrophenol centered at 317 nm, which shifted to around 400 nm after the addition of $NaBH_4$, due to the formation of *p*-nitrophenolate ions under basic condition. The slight decrease of absorption spectra after 12 h at room temperature indicates an extremely sluggish reaction kinetics in the absence of a catalyst.

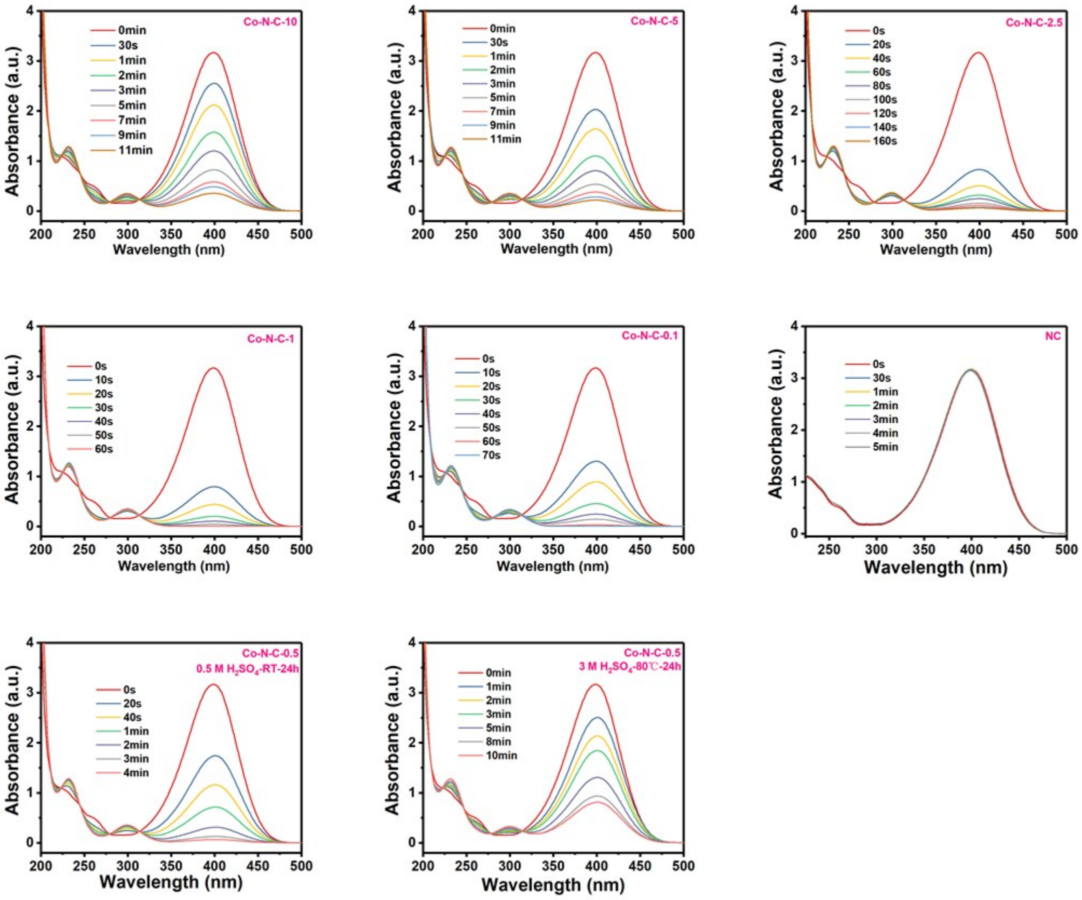

Figure S14. Time-dependent UV-vis absorption spectra during the reduction of *p*-nitrophenol catalyzed by various catalysts.

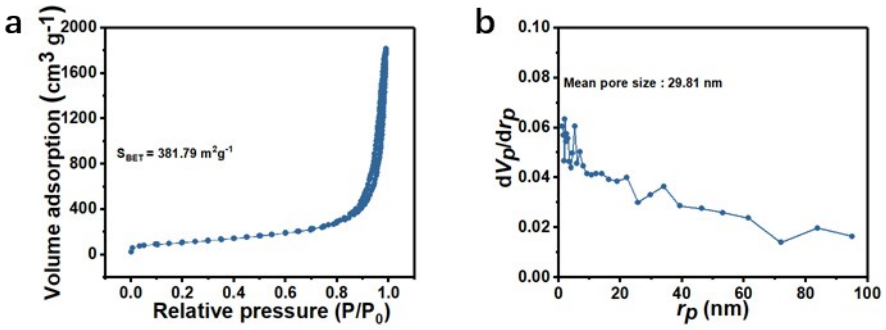

Figure S15. The nitrogen adsorption-desorption isotherms (a) and pore size distribution curve calculated utilizing the Barrett-Joyner-Halenda (BJH) method of NC.

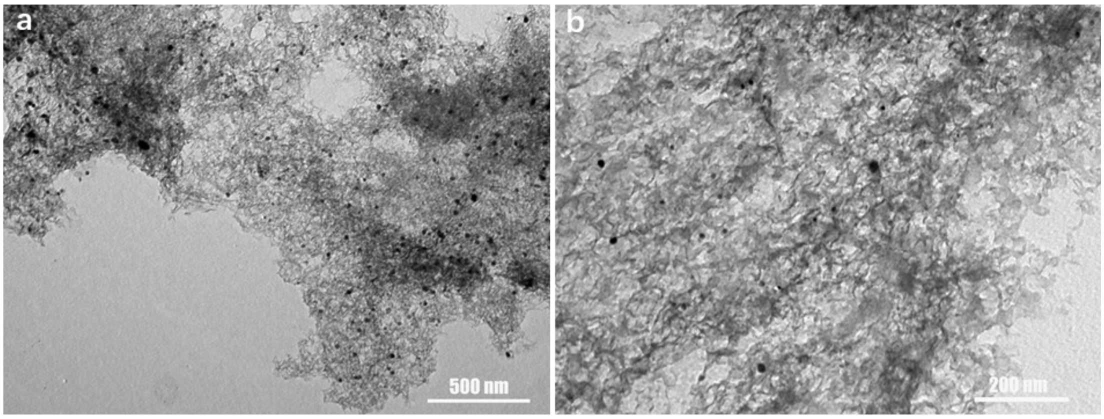

Figure S16. TEM images of Co-N-C-0.5 after treatment with (a) 0.5 M H_2SO_4 at room temperature and (b) 3M H_2SO_4 at 80℃ for 24h.

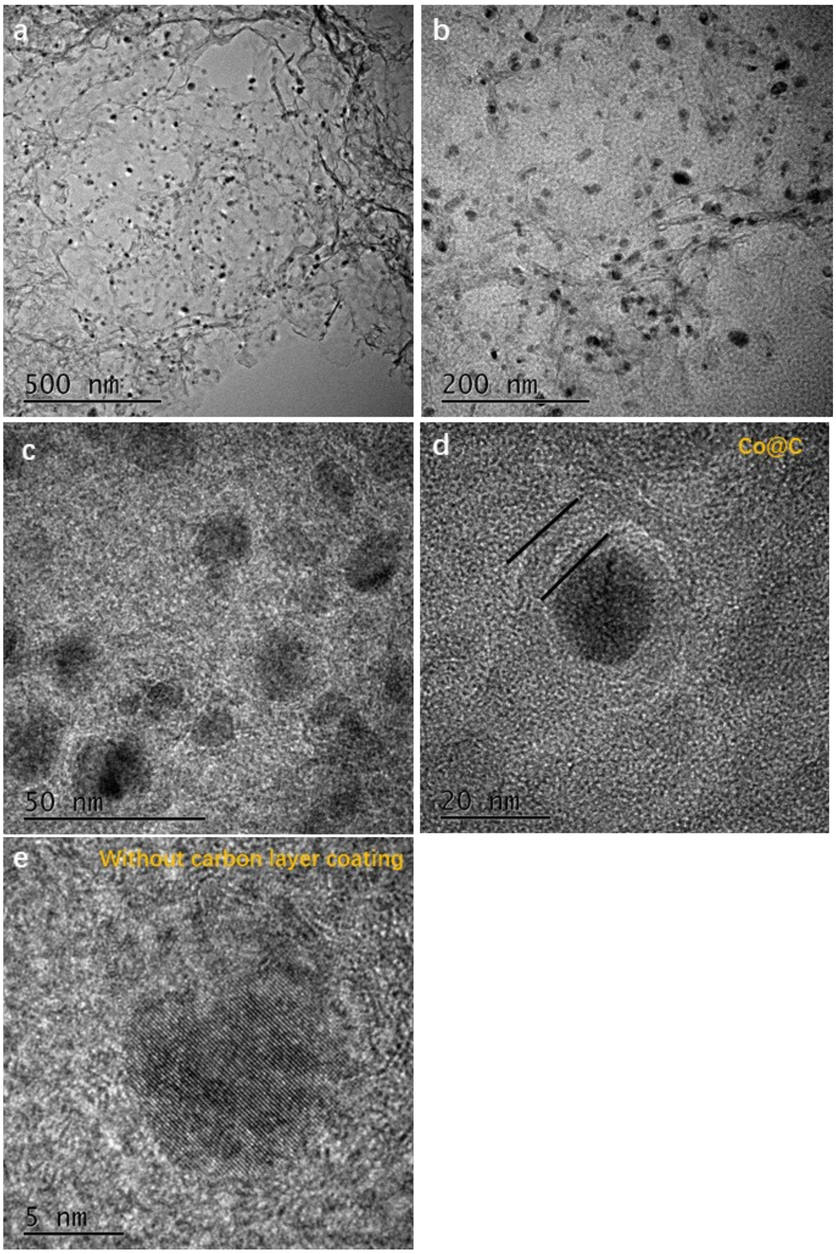

Figure S17. (a-c) TEM images and (d, e) HRTEM images of Co-N-C-0.5 after five consecutive reduction cycles.

As can be seen, there is no structural change of Co-N-C-0.5 after reaction. Highly dispersed cobalt nanoparticles with small size distributions can still be found without aggregation, indicating the high stability of the catalyst. Two types of cobalt nanoparticles including cobalt nanoparticles encapsulated in graphitic carbon layer (Co@C) and bare cobalt nanoparticles without carbon layer coating can be found, which is in line with the catalyst before reaction.

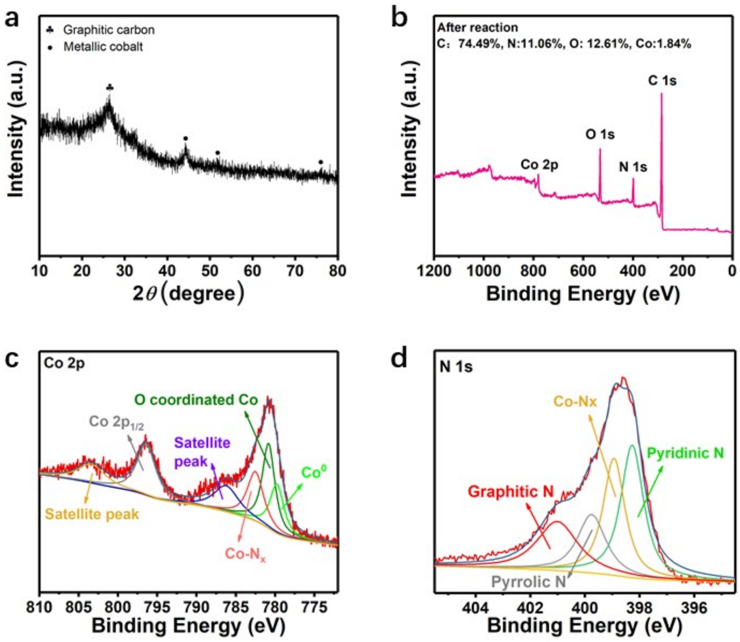

Figure S18. (a) XRD pattern, (b) XPS survey spectrum, (c) high resolution Co 2p spectra and (d) high-resolution N 1s spectra of Co-N-C-0.5 after five consecutive reduction cycles.

After five consecutive reduction cycles, characteristic peaks which are assigned to the graphitic carbon and metallic cobalt nanoparticles can still be found in the XRD pattern, and no peaks ascribed to cobalt oxide or cobalt hydroxide can be found. The XPS spectrum of Co-N-C-0.5 after reaction shows that Co, N, C and O still present on the surface of catalyst. After five consecutive reduction cycles, the catalyst still exhibits a high exposure content of N (11.06 atom%) and Co (1.84 atom%), which explains the excellent catalytic property and high stability of the catalyst even after several cycles. The decrease of atomic content of N and Co can be ascribed to the adsorption of reactants and products, which is confirmed by the increasing atomic content of oxygen.