

Supporting information

N-doped semi-graphitic C loaded with metallic Co: synthesis parameters and catalytic selective reduction of *p*-nitrophenol

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SI. Materials and Instrumentation

Materials

Reagents and materials included $\text{Co}(\text{AC})_2 \cdot 4\text{H}_2\text{O}$ ($\geq 99.5\%$, Aladdin), 95% Ethanol (95%, Shanghai Sinopharm), 3-Nitrophenol (98%, Aladdin), HCOONa ($\geq 99.5\%$, Aladdin), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (AR, Aladdin), Benzimidazole ($\geq 99.0\%$, Aladdin), Cobalt powder ($\geq 99.9\%$, Chengdu Kelong), DMF ($\geq 98.7\%$, Shanghai Sinopharm), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$, Macklin), Nitrobenzene ($>99\%$, Shanghai Sinopharm), 4-Nitrotoluene (CP, Shanghai Sinopharm), Isopropyl alcohol (AR, Shanghai Sinopharm), p-Nitrobenzyl alcohol (98%, Aladdin), 1,2-Propylene oxide ($\geq 99.5\%$, Shanghai Sinopharm), 1,4-Dioxane (AR, Shanghai Sinopharm), Toluene ($\geq 98.5\%$, Shanghai Sinopharm), 3-Nitrophenol (98%, Aladdin), 1-Octanol (AR, Shanghai Sinopharm), p-Aminobenzyl alcohol (98%, Aladdin), p-Aminotoluene (98%, Aladdin), p-Aminophenol (98%, Aladdin), Tetrahydrofuran (99.5%, Shanghai Sinopharm), p-Nitrophenol (98%, Aladdin), o-Nitrophenol (98%, Aladdin), Methanol (100%, Shanghai Sinopharm), Ethyl acetate ($\geq 99.5\%$, Shanghai Sinopharm), Cyclohexane ($\geq 99.5\%$, Shanghai Sinopharm), p-Nitroaniline (AR, Shanghai Sinopharm). All reagents and materials were used without further purification.

Instrumentation

(1) Powder X-ray diffractometer (XRD) Phase analysis was performed using a German Bruker D8 X-ray diffractometer. Test conditions: copper target $\text{K}\alpha$ rays as radiation source ($\lambda = 1.54184\text{\AA}$), voltage 40 kV, current 40 mA, scanning range $2\theta = 5-80^\circ$, scanning speed $10^\circ/\text{min}$. (2) Fourier transform infrared spectrometer (FTIR) was used to test the precursor and the calcined material with Bruker Tensor II infrared spectrometer from Germany, with a scanning range of $400-4000\text{ cm}^{-1}$. (3) Solid UV-Vis Spectrometer (UV-DRS) uses spectral TU-1901 UV spectrometer to characterize materials by UV diffuse reflectance (4) The Raman spectrometer (Raman) employed a 512 nm argon-ion laser (Renishaw Instruments, England) for recordings in the range

of 200–3000 cm^{-1} . (5) Field emission scanning electron microscope (FSEM) used JSM-6510A electron scanning microscope of Japan Electronics Corporation to test and analyze the morphology of the material. The scanning voltage is 15 kV. (6) Thermogravimetric analyzer (TG) The thermal stability of the material was analyzed with a PerkinElmer thermal analyzer under the following conditions: N_2 atmosphere, gas rate of 40 mL/min, heating rate of 10 $^\circ\text{C}/\text{min}$, and temperature range of 30 to 800 $^\circ\text{C}$. (7) The transmission electron microscope (TEM) used the Tecnai G20 transmission electron microscope in the United States to test the structure and morphology of the material, and the test voltage was 200 kV. (8) X-ray photoelectron spectroscopy (XPS) analysis of the materials was performed using a Perkin-Elmer PHI ESCA system with a scan speed set to 0.1 eV and a standard Mg anode at 12 kV and 300 was the X-ray source. (9) The specific surface area and pore size distribution analyzer (BET) used the Quantachrome Autosorb iQ instrument to test the N_2 adsorption of the material. The degassing temperature of the material was 200 $^\circ\text{C}$, the degassing time was 10 h, and the program was a microporous adsorption template with 69 recording points. (10) The chemisorber-temperature-programmed reduction (H_2 -TPR) used the Quantachrome ChemStar instrument to conduct temperature-programmed reduction tests on the materials. The test procedure was as follows: the initial temperature was 30 $^\circ\text{C}$, and the temperature was increased to 200 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$ and maintained for 30 min. After lowering down to 30 $^\circ\text{C}$, it was raised to 800 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$ and held for 1 h. The used gas was a 10% H_2 -Ar mixture. (11) The water contact angles (WCA) of various sample surfaces were detected on a JC2000D1 contact angle meter (DSCHX200 Sony camera); a digital microscope was equipped at room temperature.

S2. Experimental section

Table S1. Elemental content (XPS) and I_D/I_G values of Co/CN-x materials

Catalyst	I_D/I_G	Atomic% (XPS)			
		C	N	O	Co
Co/CN-250	--	72.4	16.22	8.06	3.31
Co/CN-300	0.79	72.53	11.97	12.72	2.82
Co/CN-350	0.93	73.2	2.88	20.86	3.23
Co/CN-400	1.04	73.76	1.62	21.02	3.6

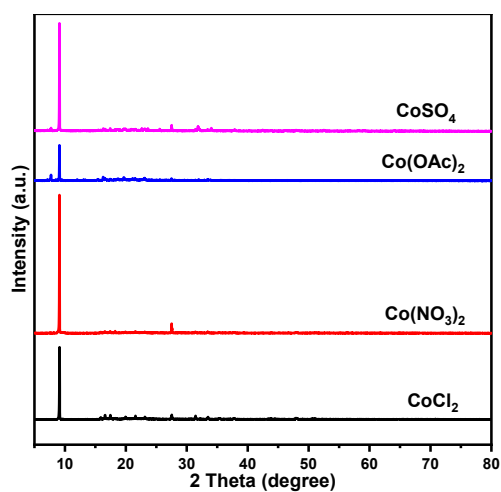


Fig. S1. XRD patterns of Co-ZIF-9 prepared with various cobalt salts.

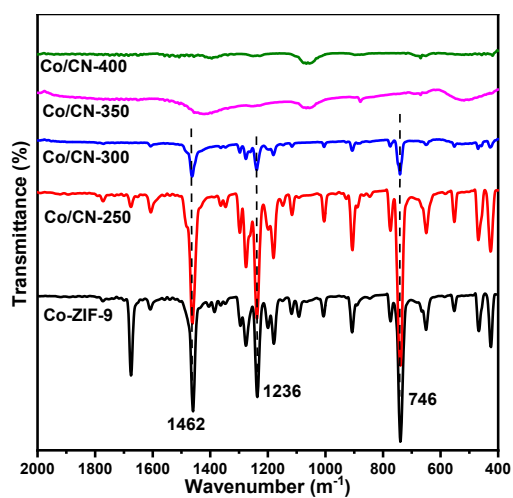


Fig. S2. The IR spectra of Co-ZIF-9 and Co/CN-x materials

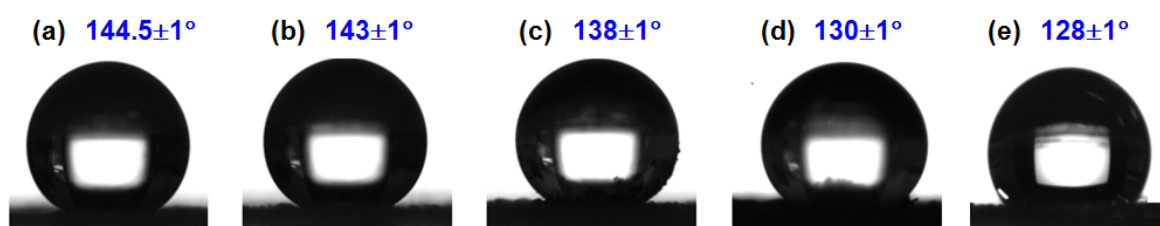


Fig. S3. WCA on the surface of Co-ZIF-9 and Co/CN-x prepared by different pyrolysis temperatures: (a) Co-ZIF-9, (b) Co/CN-250, (c) Co/CN-300, (d) Co/CN-350 and (e) Co/CN-400.

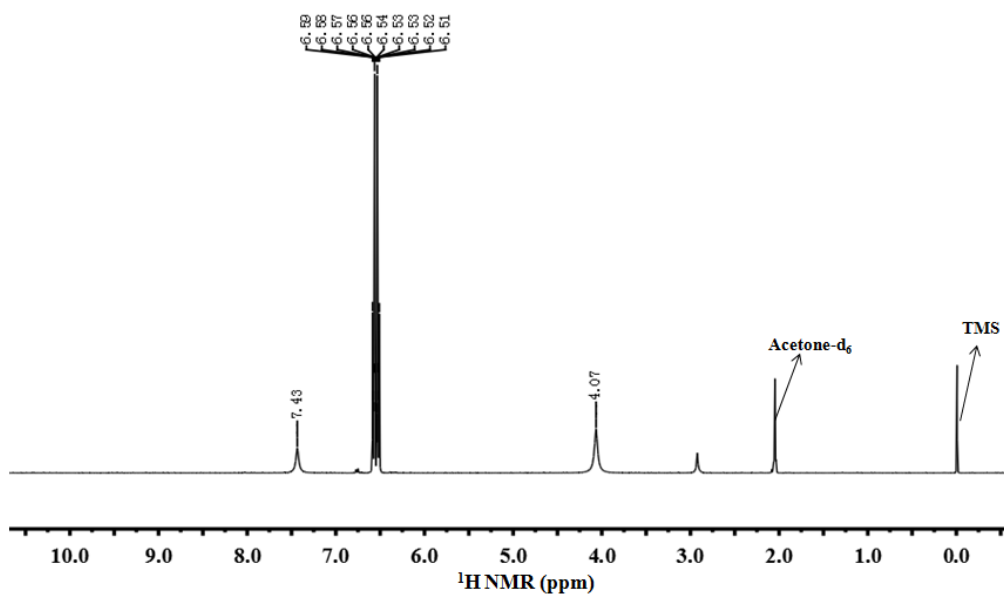


Fig. S4. ^1H NMR (400 MHz, Acetone- d_6) of *p*-aminophenol (PAP). δ 7.43 (s, 1H), 6.72–6.33 (m, 4H), 4.07 (s, 2H).

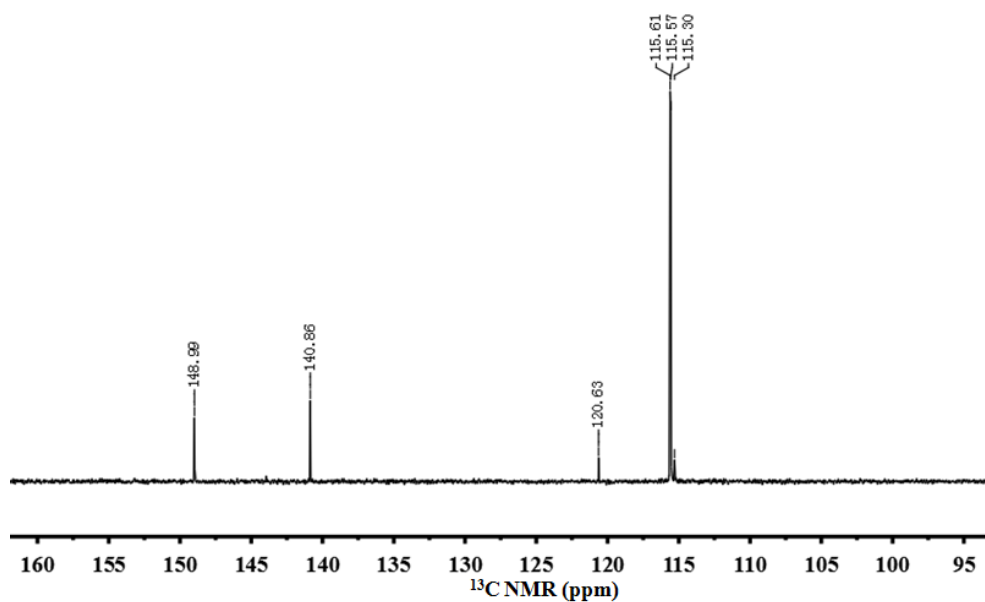


Fig. S5. ^{13}C NMR (100 MHz, Acetone- d_6) of *p*-aminophenol (PAP). δ 148.99 (s), 140.86 (s), 120.63 (s), 115.59 (d, $J = 3.9$ Hz), 115.30 (s).