

Residual metals present in “metal-free” N-doped carbons

Xiuyan Jin, Guoxin Zhang, Yongchao Hao, Zheng Chang* and Xiaoming Sun*

Experimental section

Preparation of the catalysts. The doped carbon materials (DCM) were obtained by the method previously reported by our group. Typically, EDTA (4.0 g) and melamine (2.0 g) was added to KOH powder (2.0 g) by milling. Subsequently, the precursor was transferred into a ceramic boat of a horizontal furnace. The furnace was heated to 800 °C at a rate of 10 °C/min and the temperature was kept for 2 h. The annealing process was performed in Ar atmosphere and the blank sample was denoted as DCM. To study the influence of these transition metals involved into the preparation of nitrogen doped carbons, PR-0.5Fe-DCM, PR-0.5Co-DCM and PR-0.5Ni-DCM were respectively obtained by adding 0.5 mmol of the corresponding metal nitrate into the precursor followed by the same annealing process. All the materials were washed thoroughly with water and ethanol for three times to remove any impurities. Finally, the metal-involved carbons were dispersed in 1 mol L⁻¹ H₂SO₄ solution for one week to remove metals using sonication for one day followed by vigorously stirring. These so-called “metal free” samples after purification were denoted as PU-0.5Fe-DCM, PU-0.5Co-DCM and PU-0.5Ni-DCM, respectively.

To control the metal dosages, 0.05 mmol, 0.1 mmol, 0.2 mmol of cobalt nitrates were used as metal sources in the above synthesis procedure and after purification PU-0.05Co-DCM, PU-0.1Co-DCM and PU-0.2Co-DCM were obtained, respectively.

Electrochemical characterization. Polarization curves were recorded at a rate of 5 mV s⁻¹ and a rotation of 1600 rpm. Linear sweep voltammetry measurements were conducted after every thousand of cyclic voltammetry curves between -0.7 V and +0.1 V (vs. RHE) at 100 mV s⁻¹. All of the electrochemical measurements were carried out on a PARSTAT 2273 electrochemical station using a three-electrode configuration that consisted of a working electrode, a graphite counter electrode, and a SCE reference electrode. The hydrogen evolution reaction (HER) performances were conducted in a hydrogen-saturated 0.5 mol L⁻¹ H₂SO₄ electrolyte on a rotating disk. Glassy carbon was polished with alumina prior to using the catalyst-modified glassy carbon as a working electrode. Catalyst ink was prepared by dispersing 5 mg of the carbon materials into 0.5 mL of ethanol using sonication, and then 20 μL of nafion was added as a binder. 4 μL of the catalyst ink was transferred on the glassy carbon and dried at room temperature. The process led to a catalyst loading of 0.2 mg cm⁻².

Physical and spectroscopic characterization. X-Ray diffraction patterns were recorded on a Shimadzu XRD 6000 diffractometer, using Cu Kα radiation (40 kV, 30 mA, 1.5418 Å) with a scan speed of 5 °/min. Raman spectra were collected on the LabRAM ARAMIS Raman system with a 532 nm argon ion laser as excitation. The morphologies were characterized on scanning electron microscopy (SEM; Zeiss, SUPRA 55) and high resolution transmission electron microscope (HRTEM; JEOL, JEM-2100). X-ray photoelectron spectroscopy (XPS) spectra were measured on a Thermo Electron ESCALAB 250 Spectrometer. Elemental content analysis was carried out on an inductively coupled plasma-atomic emission spectrometry (ICP; Agilent 7700CE).

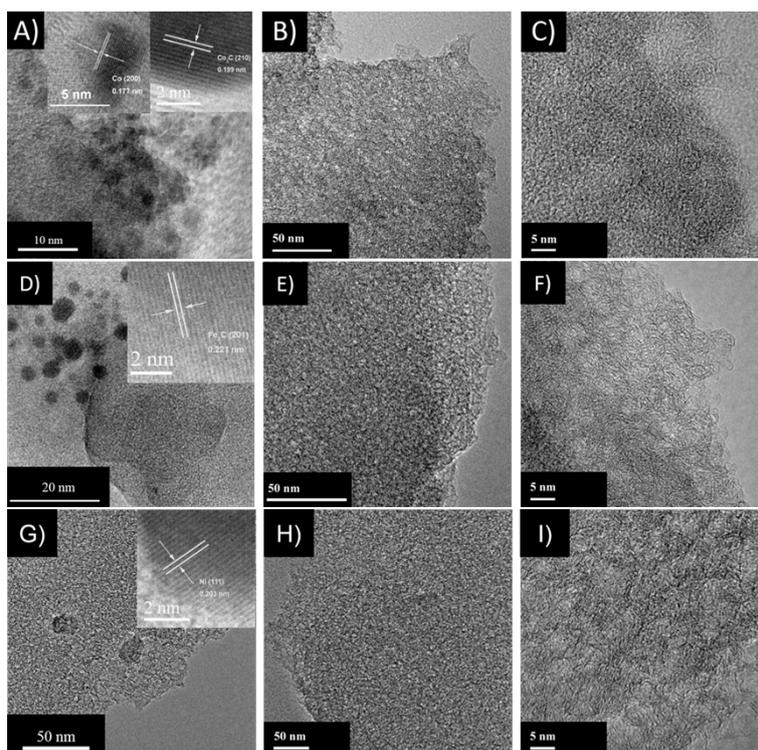


Fig. S1: TEM and HRTEM images of A) PR-0.5Co-DCM, D) PR-0.5Fe-DCM, G) PR-0.5Ni-DCM; TEM and HRTEM images of B,C) PU-0.5Co-DCM, E,F) PU-0.5Fe-DCM and H,I) PU-0.5Ni-DCM.

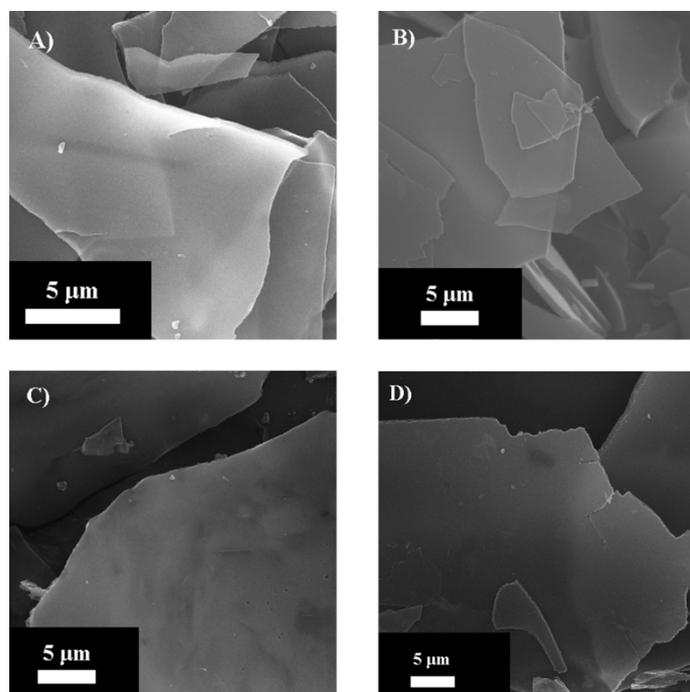


Fig. S2: SEM images of A) DCM, B) PU-0.5Co-DCM, C) PU-0.5Fe-DCM and D) PU-0.5Ni-DCM.

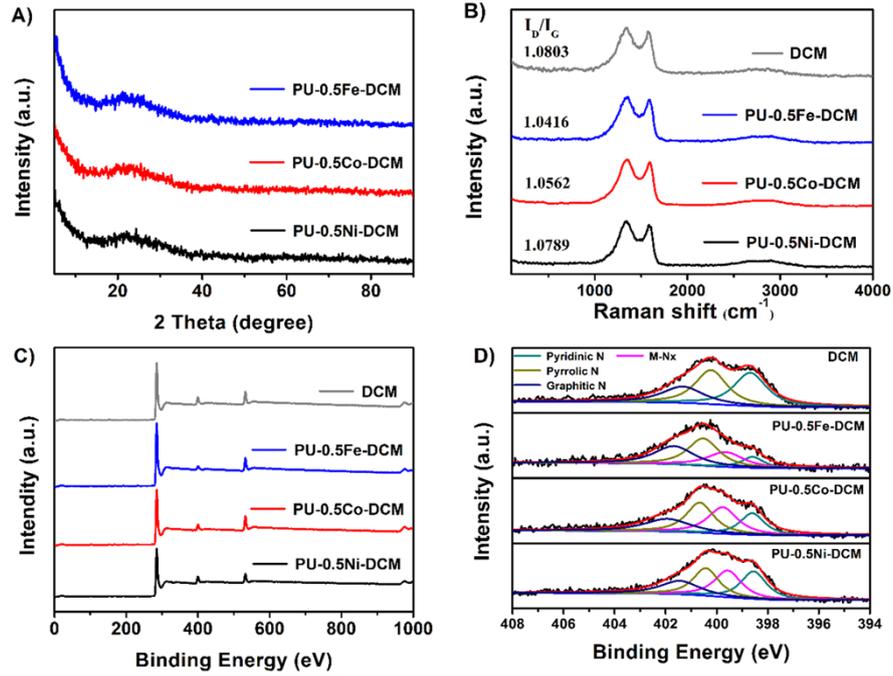


Fig. S3: A) XRD patterns, B) Raman spectra, C) XPS survey and D) N 1s spectra of DCM, PU-0.5Fe-DCM, PU-0.5Co-DCM and PU-0.5Ni-DCM.

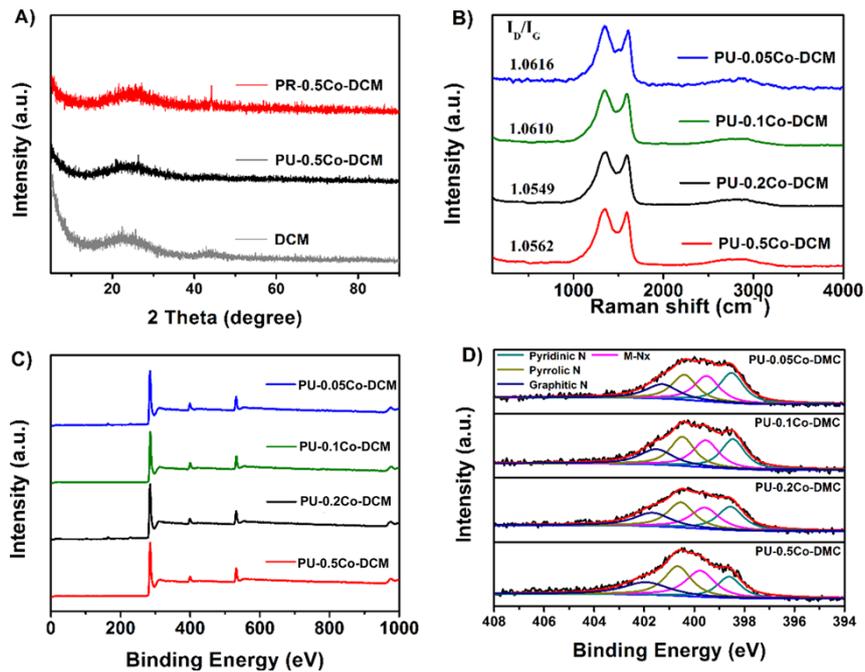


Fig. S4: A) XRD patterns of PR-0.5Co-DCM, PU-0.5Co-DCM and DCM; B) Raman spectra, C) XPS survey and D) N 1s spectra of PU-0.05Co-DCM, PU-0.1Co-DCM, PU-0.2Co-DCM and PU-0.5Co-DCM.

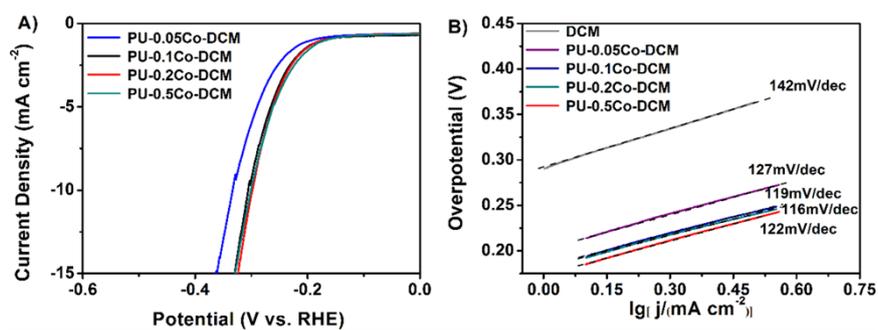


Fig. S5: A) Polarization curves and B) Tafel slopes of PU-0.05Co-DCM, PU-0.1Co-DCM, PU-0.2Co-DCM and PU-0.5Co-DCM.

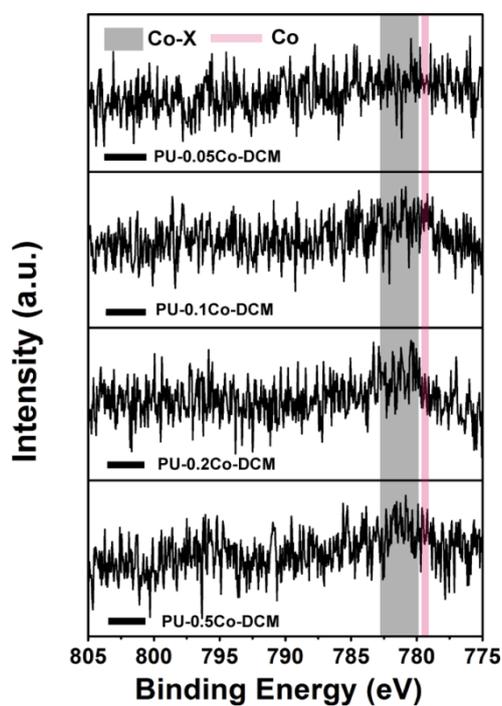


Fig. S6: Co 2p spectra of PU-0.05Co-DCM, PU-0.1Co-DCM, PU-0.2Co-DCM and PU-0.5Co-DCM.