

## Electronic Supporting information

### **Pulsed laser deposition of porous N-carbon supported cobalt (oxide) thin films for highly efficient oxygen evolution**

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#### **I. Experimental section**

##### **Material synthesis**

###### ***Targets and substrate preparation***

High purity (99.99%) pyrolytic graphite and an ultra-high purity cobalt target were used for deposition of carbon films and cobalt nanoparticles, respectively. Silicon wafer and copper foils (1 cm × 1 cm pieces) were used as the substrates for film deposition. All the substrates were cleaned by sonication in isopropanol for 20 minutes, rinsing in isopropanol and drying using N<sub>2</sub> flow before deposition.

###### ***Synthesis of porous nitrogen-doped carbon film***

The porous nitrogen-doped carbon films were deposited at room temperature by reactive PLD using a Nd:YAG pulsed laser ( $\lambda = 532$  nm, duration of 9 ns and repetition rate of 10 Hz), with a pulse energy of 200 mJ. The beam is directed on rotating graphite target with 45° angle of incidence. Laser pulses ablate the target ejecting material in a plasma plume. Ablated species are deposited on the substrates to form the carbon thin film. The ablation process is performed in the presence of a background gas to tune morphology, structure and composition of the deposited film. The distance between the target and the substrate and the laser spot size on the target were kept at 5 cm and 12.5 mm<sup>2</sup>, respectively. The chamber was evacuated first to a base pressure (10<sup>-3</sup> Pa) using a primary scroll pump and a turbo-molecular pump. The chamber was

then fed with nitrogen gas (99.99% purity) within the pressure range of 10-100 Pa to introduce nitrogen to the carbon framework. Ablation in a reactive atmosphere (high purity N<sub>2</sub> gas) was performed to incorporate nitrogen into the carbon framework and create C-N moieties to enhance the electrical conductivity. Porous carbon films (without nitrogen) in Argon flow were also prepared using the same PLD conditions for comparison. Based on desired morphology, the deposition times (i.e. number of laser pulses) were varied to control the film thickness (Figure S1).

Mass loading measurements were obtained using a quartz crystal microbalance (QCM) and keeping other deposition conditions (i.e. chamber pressure, pulse energy, target to substrate distance (QCM in the case of mass loading measurements)) constant.

### ***Synthesis of cobalt (oxide) nanoparticles deposited on porous nitrogen-doped carbon film***

A high purity Cobalt target was used for the deposition of cobalt (oxide) nanoparticles onto nitrogen-doped carbon films deposited on silicon and copper foil substrates. All the deposition conditions were similar to before. Cobalt (oxide) nanoparticles were deposited at three different background gas pressures (1, 10 and 50 Pa) and deposition times were calculated based on a desired cobalt mass percentage of 10 %at. All the calculations were done based on the mass loadings recorded from the quartz crystal microbalance (QCM) at constant PLD conditions (both carbon and cobalt deposition mass loading).

For comparative studies and to obtain some insight into the electrocatalytic activity of Co(Ox)<sub>n</sub>@PNC films, a series of control samples were prepared at a nitrogen background gas pressure of 1 and 10 Pa (to form Co(Ox)<sub>1</sub>@PNC and Co(Ox)<sub>10</sub>@PNC and under an Argon background gas pressure of 50 Pa to form Co(Ox)<sub>50</sub>@PC films. All other deposition conditions were kept the same. To study the effect of cobalt atomic concentration at optimized cobalt deposition pressure, Co(Ox)<sub>50</sub>@PNC films with cobalt concentration of 1 , 5 and 10 at % were prepared. All other deposition conditions were kept the same.

### **Chemical characterization**

The morphology of synthesized samples was characterized by a high resolution transmission electron microscope (TEM, JEM-2100) operating at 200 kV and a scanning electron microscope (SEM, ZEISS Supra40) operating at 10 kV. Elemental mapping was conducted using an EDAX detector attached to the JEM-2100. Raman spectra were collected on Renishaw micro-Raman with 514.5 nm and 325 nm excitation wavelengths and LabRAM (Horiba Ltd) with a 266 nm laser line. X-ray diffraction (XRD) patterns (10-80° in 2θ) were collected on a

powder X-ray diffractometer at 40 kV and 15 mA using Co-K $\alpha$  radiation (Miniflx-600, Rigaku). The X-ray photoelectron spectroscopy (XPS) analysis was conducted on an Axis Ultra spectrometer (Kratos Analytical Ltd.) with monochromated AlK $\alpha$  radiation (1486.6 eV) at ca. 510<sup>-9</sup> Pa.

### **Electrochemical characterization**

All electrochemical tests were performed in a three-electrode glass cell on a 760 workstation (Pine Research Instruments, US). The as-synthesized hybrid films were directly used as the working electrodes, platinum wire as the counter electrode and a standard Ag/AgCl/KCl (4 M) electrode as the reference electrode. A flow of N<sub>2</sub> was maintained over the electrolyte (1 M KOH) during the OER electrochemical measurements to eliminate dissolved oxygen. All potentials were referenced to a reversible hydrogen electrode (RHE) using the equation below:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + (0.059 \times \text{pH} + 0.205)$$

Cyclic voltammogram (CVs) plots were recorded at a scan rate of 100 mV s<sup>-1</sup>, and linear sweep voltammograms (LSVs) at 5 mV s<sup>-1</sup>, to minimize the capacitive current. The working electrodes were scanned several times to achieve stabilization before data collection occurred. The internal resistance of the electrochemical cell was 5  $\Omega$  and all CV and LSV data were corrected for this iR contribution within the cell.

The Tafel slope was calculated according to the Tafel equation as follows:

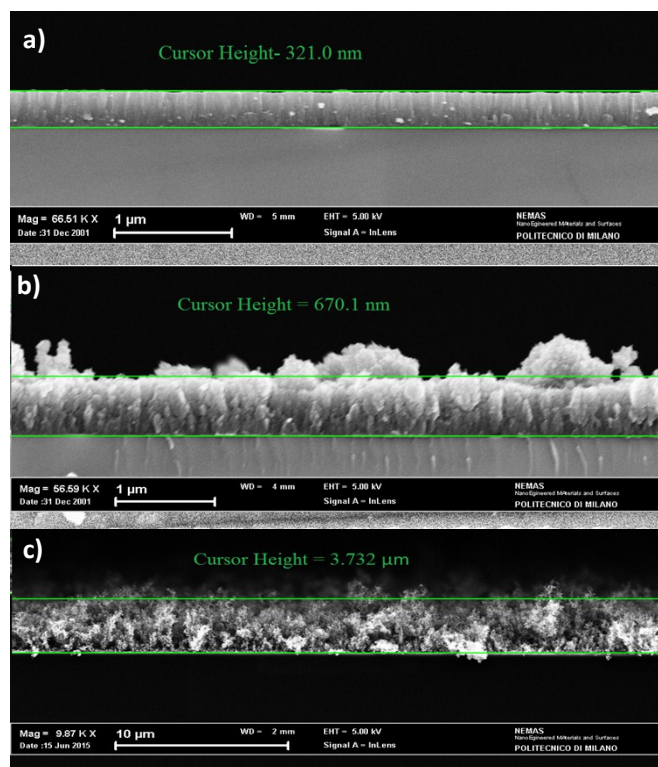
$$\eta = b \log j + a,$$

where  $\eta$  is overpotential (V),  $j$  is the current density (mA cm<sup>-2</sup>), and  $b$  is the Tafel slope (mV dec<sup>-1</sup>).

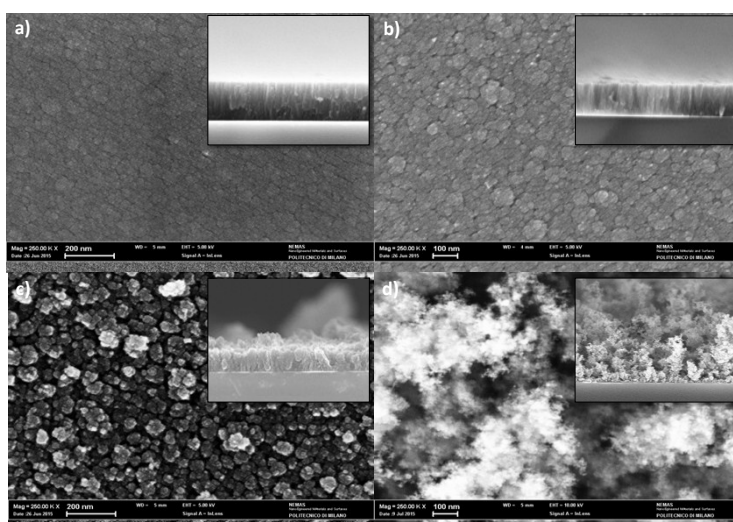
Electrode stability was tested using chronoamperometric response which was conducted at +0.8V (vs. Ag/AgCl) for the OER electrodes. LSVs plots were obtained before and after stability testing for comparison.

The electrical double layer capacitances ( $C_{\text{dl}}$ ,  $\mu\text{F cm}^{-2}$ ) of working electrodes were obtained from double-layer charging-discharging plots using CVs in a small potential range of -0.875 to -0.825 V (vs Ag/AgCl) at scan rates ranging from 10 to 100 mVs<sup>-1</sup>. The plots of the current density (mA cm<sup>-2</sup>) at -0.85V (vs. Ag/AgCl) against the scan rate are nearly linear and the slopes are  $C_{\text{dl}}$  ( $\mu\text{F cm}^{-2}$ ).

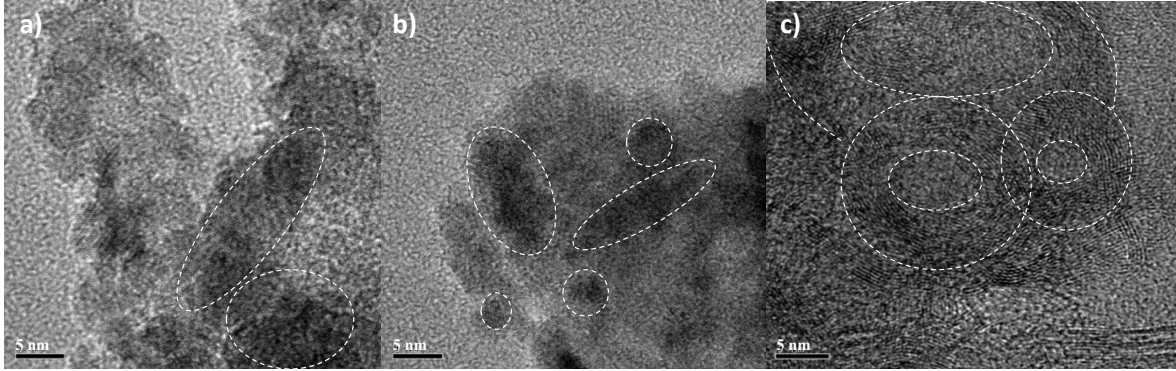
## II. Supporting figures



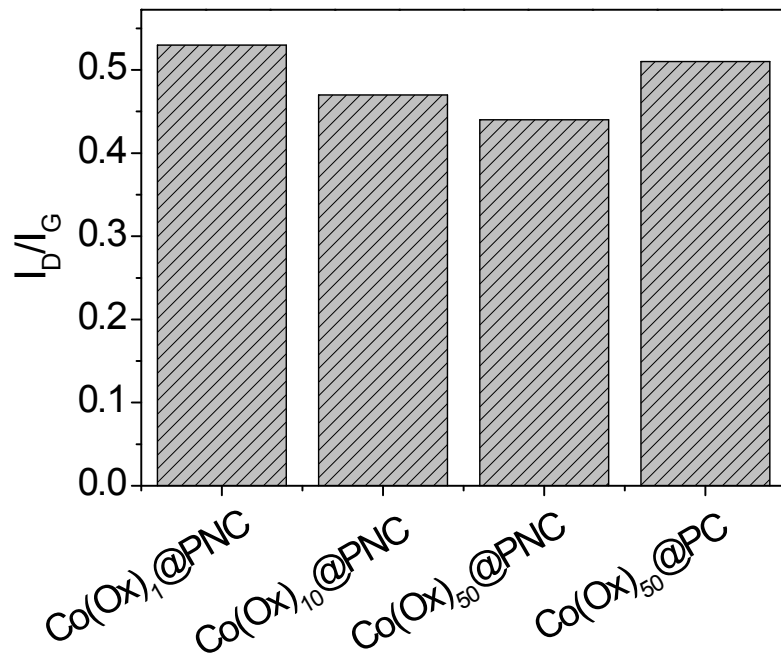
**Figure S1.** Cross sectional SEM image of PNC films prepared with a constant deposition time of 120 seconds and different background gas ( $N_2$ ) pressures (a) 30 Pa, (b) 50 Pa and (c) 100 Pa.



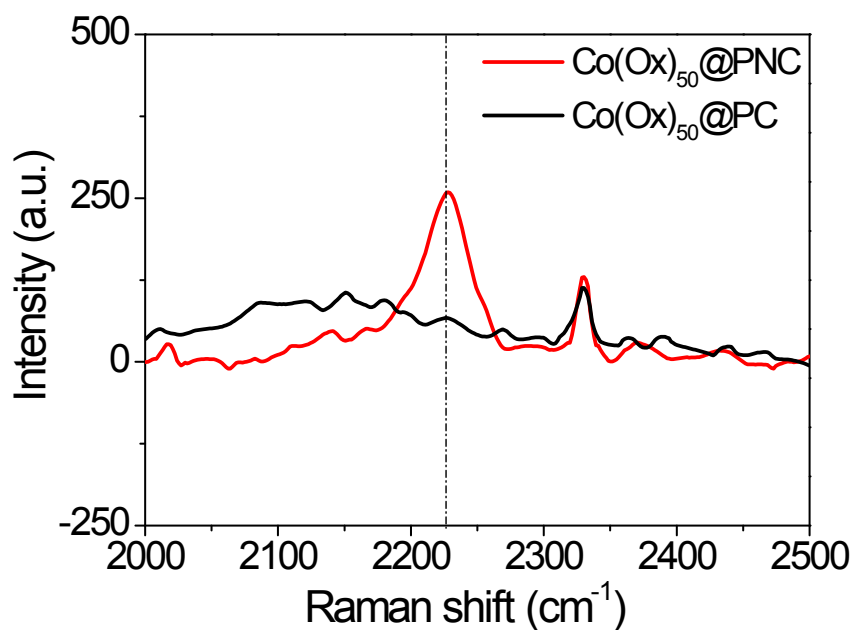
**Figure S2.** Top view SEM image and (insets) cross-sectional image of PNC films deposited at different background gas pressures; (a) 10 Pa, (b) 30 Pa, (c) 50 Pa and (d) 100 Pa.



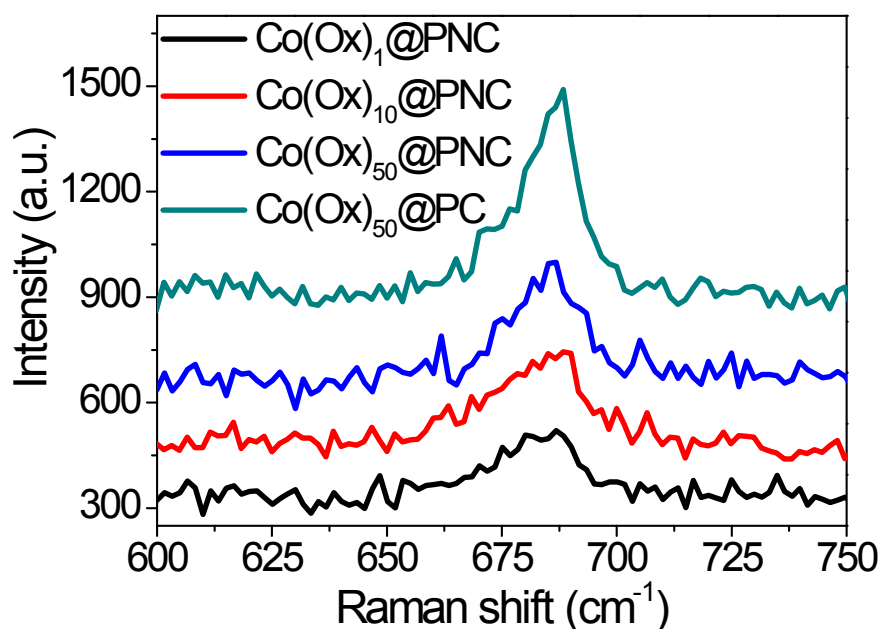
**Figure S3.** HRTEM image of  $\text{Co(Ox)}_p\text{@PNC}$  films prepared at different background gas pressures (for cobalt deposition); (a) 1 Pa, (b) 10 Pa and (c) 50 Pa.



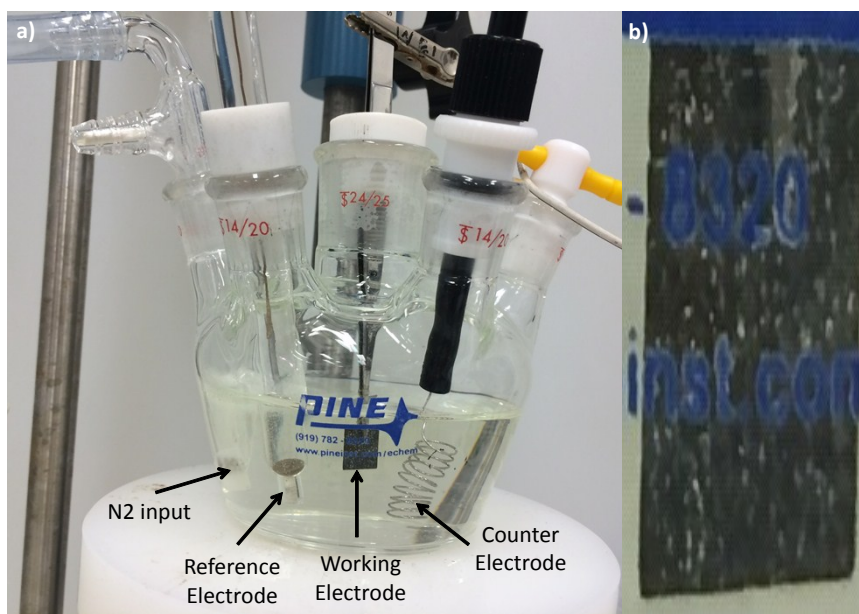
**Figure S4.**  $I_D/I_G$  ratio of  $\text{Co(Ox)}_p\text{@PNC}$  prepared by using three different background gas pressures (for cobalt deposition, i.e. 1, 10 and 50 Pa) and  $\text{Co(Ox)}_{50}\text{@PC}$ .



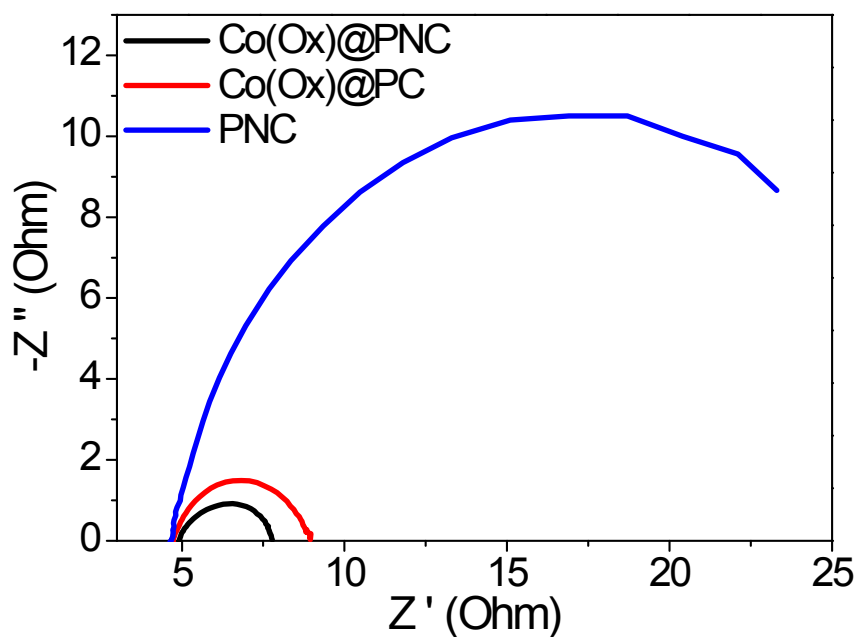
**Figure S5.** Enlarged view of Raman spectra (C-N peak) of  $\text{Co(Ox)}_{50}\text{@PNC}$  (red line) and  $\text{Co(Ox)}_{50}\text{@PC}$  (black line) films in UV range (wavelength=266 nm). The peak at  $2330\text{ cm}^{-1}$  present in both samples originates from adsorbed  $\text{N}_2$  gas molecules.



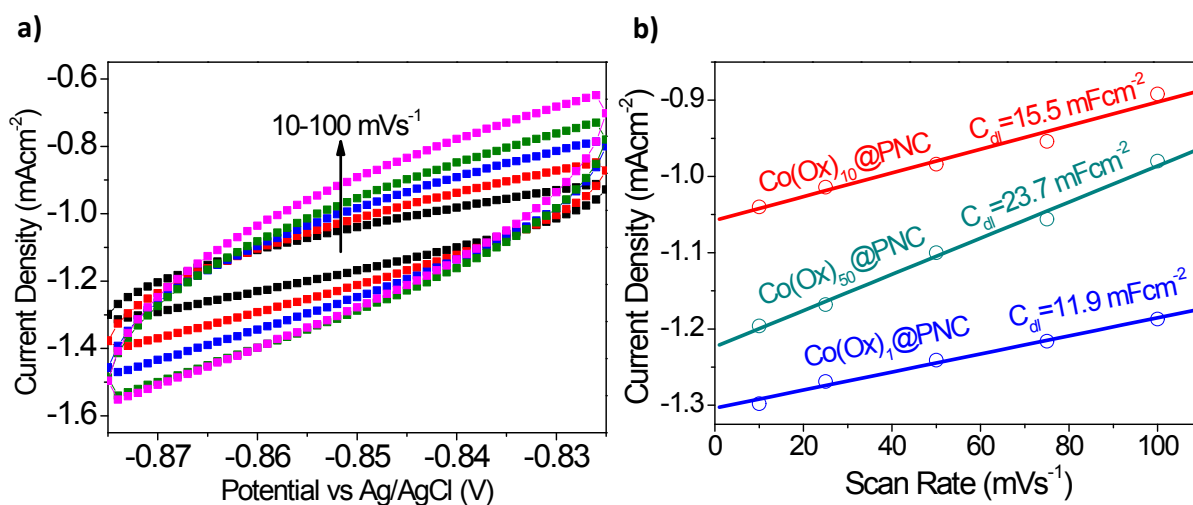
**Figure S6.** Raman spectra of  $\text{Co(Ox)}_p\text{@PNC}$  prepared by using three different background gas pressures for cobalt deposition (i.e. 1, 10 and 50 Pa) and  $\text{Co(Ox)}_{50}\text{@PC}$ .



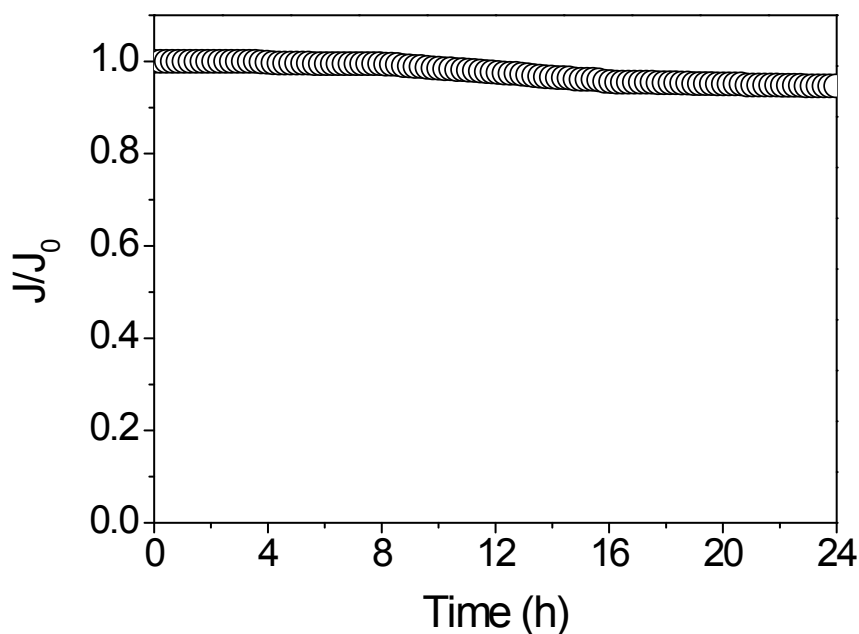
**Figure S7.** (a) Photographs of the applied electrochemical cell. The reference electrode is a standard Ag/AgCl in 4M KCl; the counter electrode is Platinum wire; N<sub>2</sub> was purged during measurements to eliminate dissolved O<sub>2</sub>; working electrodes are the as-prepared films, (b) enlarged view of the working electrode during electrochemical tests.



**Figure S8-** Electrochemical impedance spectra at +0.7 V vs Ag/AgCl of metal-free PNC, Co(Ox)@PC, Co(Ox)@PNC in 1.0 M KOH solution.

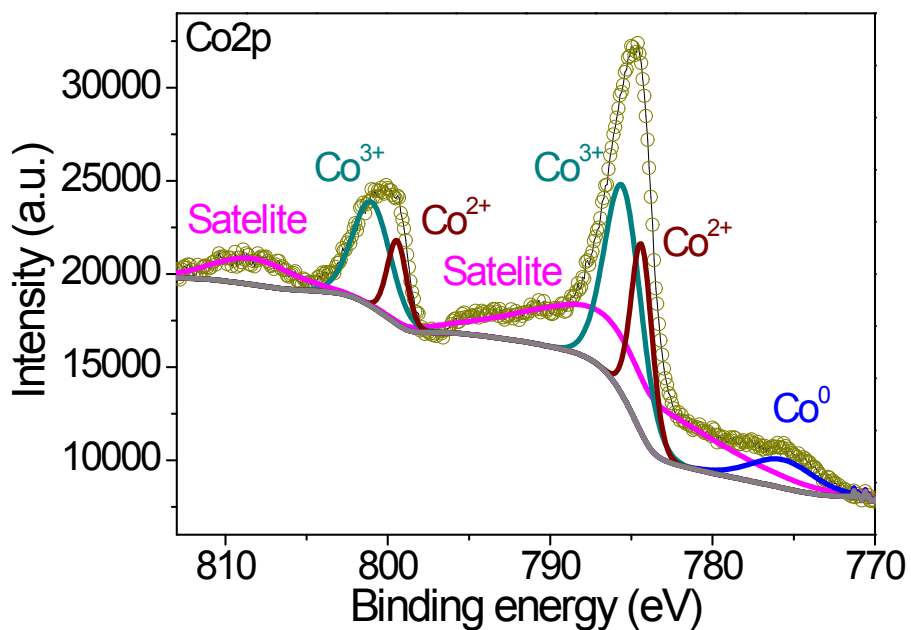


**Figure S9-** a) Cyclic voltammograms (CVs) of Co(Ox)<sub>50</sub>@PNC at background gas pressure of 50 Pa measured at different scan rates from 10 to 100 mV s<sup>-1</sup> and b) Plots of the current density at -0.85 V vs. the scan rate for Co(Ox)<sub>50</sub>@PNC deposited at three background gas pressure (i.e. 1, 10 and 50 Pa).

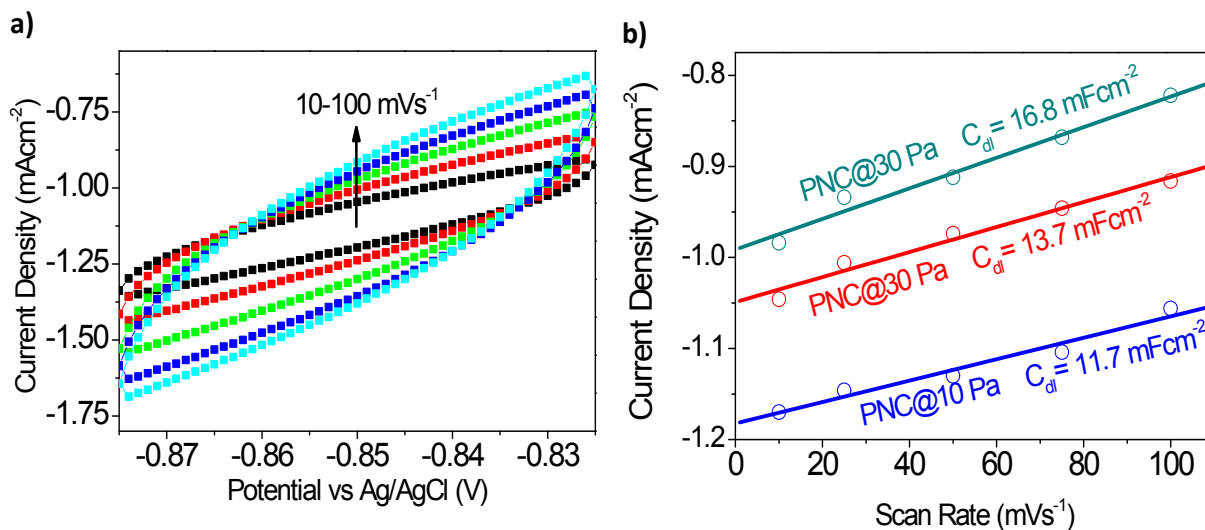


**Figure S10-** The chronoamperometric response of Co(Ox)<sub>50</sub>@PNC at +0.8 V after 24 h in 1.0 M KOH solution.





**Figure S11-** High resolution Co2p spectrum of Co(Ox)@PC.



**Figure S12-** a) Cyclic voltammograms (CVs) of PNC at background gas pressure of 50 Pa measured at different scan rates from 10 to 100 mV s<sup>-1</sup> and b) Plots of the current density at -0.85 V vs. the scan rate for PNC deposited at three background gas pressure (i.e. 10, 30 and 80 Pa).

**Table S1-** Cobalt species contents (obtained from Co2p XPS analysis) for the synthesized electrodes.

<b>Sample</b>	<b>%Co<sup>0</sup></b>	<b>%Co<sup>2+</sup></b>	<b>%Co<sup>3+</sup></b>	<b>Co<sup>2+</sup>/Co<sup>3+</sup></b>
Co(Ox)@PNC	11.8	64.0	24.2	2.64
Co(Ox)@PC	12.6	28.7	58.7	0.49