# Stable Cobalt Nanoparticles and Their Monolayer Array as an Efficient Electrocatalyst for Oxygen Evolution Reaction

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## Experimental Section

**Chemicals**: Cobalt carbonyl ($Co_2(CO)_8$, stabilized with 1-5% hexane) was purchased from Strem Chemicals. Dioctylamine (98%), oleic acid (90%), 1,2,3,4-tetrahydronaphthalene (99%), and Nafion solution (5% in a mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich. The commercial Ir catalyst (10% mass loading on Vulcan carbon, particle diameter ~2 nm) was obtained from Premetek Co.. All chemicals were used without further purification.

**Characterization**: Transmission electron microscopy (TEM) images were collected from a Philips CM20 with operating voltage of 200 kV. High-resolution TEM (HR-TEM) images were

obtained using a JEOL 2010 with an accelerating voltage of 200 kV. SEM images of the monolayer assembly were acquired on a LEO 1530 microscope at an operating voltage of 10 kV. X-ray diffraction (XRD) patterns of the NPs were collected on a Bruker AXS D8-Advanced diffractometer with Cu Kα radiation ($\lambda$ = 1.5418 Å). Magnetic studies were performed on a Lakeshore 7404 high-sensitivity vibrating sample magnetometer (VSM) with fields up to 1.5 T at room temperature. The actual mass loading of Co on the carbon support was determined by elemental analysis using a JY2000 Ultrace ICP Atomic Emission Spectrometer. Ex-situ soft X-ray absorption spectroscopy (XAS) measurements on Co L-edge were done on Beamline 6.3.1.2 (ISAAC) at the Advanced Light Source, Lawrence Berkeley National Laboratory. All the XAS measurements were recorded in the total-electron-yield detection mode to make them sensitive to the surface of the NPs.

**Synthesis of Co NPs**: Uniform Co NPs were synthesized through thermal decomposition of $Co_2(CO)_8$.[1, 2] Briefly, 18 mL of 1,2,3,4-tetrahydrophthalene was mixed with 0.35 mL of oleic acid and 0.5 mL of dioctylamine and heated to 110 ºC for 0.5 h under argon protection and then cooled down to room temperature. 0.54 g of $Co_2(CO)_8$ was quickly added into the above mixture, which was reheated to 100 ºC for 20 min under argon flow. Then the solution was rapidly heated to 210 ºC at the heating rate of 15 ºC/min under the blanket of argon and kept at this temperature for 30 min. After cooling down to room temperature by removing the heating mantle, the obtained Co NPs were precipitated with 60 mL of ethanol and collected by centrifugation (8500 rpm, 8 min). The Co NPs were washed again with hexane and ethanol and then dispersed in hexane for further use.

**Synthesis of carbon supported Co (C-Co) NPs**: To prepare C-Co NPs, 20 mg of Ketjen carbon was dispersed in 10 mL of hexane under ultrasonication. 20 mg of Co NPs dispersed in 5 mL of hexane was added to the carbon support dropwise under sonication. After sonicating for 30 min, the C-Co NPs were collected by centrifugation and washed with ethanol twice and then dried under ambient condition. The acurate NP/C mass ratio is measured to be 42% by ICP-AES. The obtained C-Co NPs were annealed in Ar + 5% $H_2$ at 600 $^o$C for 1 h to obtaine metallic C-Co NPs.

To make C-CoO NPs, the as-synthesized C-Co NPs were annealed in $O_2$ at 150 $^o$C for 12 h.

**Monolayer Assembly of Co NPs**: Large-area monolayer assembly of the 10 nm Co NPs was fabricated through water-air interface self-assembly.[3] Briefly, the NPs were dispersed in a mixture of toluene and hexane (volume ratio of 1:2) at the concentration of 0.5 mg/mL. 150 μL of the dispersion was drop-cast onto the surface of deionized water in a Teflon column, which was then slowly dried at room temperature. After complete evaporation of organic solvent, the monolayer assembly of Co NPs floating on the water surface was transferred onto Cu TEM grids and glassy carbon plate electrode for further characterization.

**Electrochemical Measurements**: Electrochemical measurements were carried out on an Autolab 302 potentiostat with glassy carbon rotating disk (5 mm in diameter) as a working electrode, Ag/AgCl (4 M KCl) as a reference electrode, and platinum wire as a counter electrode. The reference was calibrated vs. reversible hydrogen electrode (RHE) before the measurements and all potentials were converted to the RHE scale. The catalyst was dispersed in a mixture containing water, isopropanol, and Nafion solution (5 wt%) (v/v/v 4:1:0.05, catalyst concentration: 2 mg/mL) by 30 min of sonication to form a homogeneous ink. Then 20 μL of

catalyst ink was casted on the newly polished glassy carbon electrode and dried at ambient condition (loading 0.2 mg/cm$^2$). The catalyst was first subject to cyclic voltammetry (CV) scans between 0 and 1 V at 100 mV/s in N$_2$-saturated 0.1 M KOH until a stable CV was obtained. Then OER polarization curves were recorded by linear-sweep voltammetry (LSV) at a scan rate of 10 mV/s in O$_2$-saturated 0.1 M KOH with the GC-RDE rotating at 1600 rpm. Chronoamperometry data were collected for the annealed Co NPs and commercial Ir NPs at an overpotential of 0.4 V.

**Turnover Frequency (TOF) of the Catalyst**: The TOF value is calculated as following:[4, 5]

$$TOF = \frac{jS}{4nF}$$

Here, $j$ is the measured current density (mA/cm$^2$), $S$ is the surface area of the GC electrode (0.196 cm$^2$ for the GC disk electrode and 0.42 cm$^2$ for the GC plate electrode for the monolayer measurement), $n$ is the moles of active materials deposited on the electrode, $F$ is the Faraday constant (96485 C/mol).

We assume that all the surface metal atoms are involved in the electrocatalysis. The surface atom percentage of the face-centered cubic (fcc) Co NPs is determined using previously reported model for fcc NPs:[6] The diameter of a fcc metallic NPs is illustrated in this equation:

$$d = \frac{(2n_o - 1)a}{\sqrt{2}}$$

Here $n_o$ is the layers of atoms, $a$ is the unit constant of fcc-Co ($a$ = 3.5447 Å). The size of our fcc-Co NPs is 10 nm, so $n_o$ is calculated to be $n_o$ = 21.

Total metal atoms ($N$) of a 10 nm NP:

$$N = \frac{1}{3}(10n_o{}^3 - 15n_o{}^2 + 11n_o - 3) = 28741$$

Surface metal atoms ($N_{surf}$) of a 10 nm NP:

$$N_{surf} = 10n_o{}^2 - 20n_o + 12 = 4002$$

Percentage of atoms on the surface of 10 nm Co NPs:

$$\frac{4002}{28741} \times 100\ \% = 14\ \%$$

<u>TOF and mass activity of the annealed C-Co NPs at the mass loading of 0.2 mg/cm$^2$:</u>

At the overpotential of 0.4 V, $j$ = 10.63 mA/cm$^2$

m(Co) = 0.2 mg/cm$^2$ × 0.196 cm$^2$ × 0.42 = 1.65 × 10$^{-5}$ g  (Co mass loading in C-Co is 42 %)

Moles of surface active Co atoms:

$$n(Co) = \frac{1.65 \times 10^{-5}}{58.933}\ mol \times 14\ \% = 3.92\ \times 10^{-8}\ mol$$

$$TOF = \frac{10.63 \times 0.196\ \text{mA}}{4 \times 3.92 \times 10^{-8} \times 96485\ C} = 0.14\ s^{-1}$$

$$\text{Mass activity} = \frac{10.63 \times 0.196\ \text{mA}}{1.65 \times 10^{-5}\ g} = 126\ A\ g^{-1}$$

<u>TOF and mass activity of the monolayer of Co NPs:</u>

The mass of each NP can be calculated:

$$m\ (NP) = \frac{28741}{6.022 \times 10^{23}} \times 58.933\ g = 2.81 \times 10^{-18} g$$

The monolayer assembly has a packing density of 4000 NPs/$\mu$m$^2$ ($4 \times 10^{11}$ NPs/cm$^2$), the area of the monolayer catalyst is 0.42 cm$^2$, and thus the total mass of Co in the monolayer is estimated to be:

$$M = 0.42 \times 4 \times 10^{11} \times 2.81 \times 10^{-18} \text{ g} = 4.72 \times 10^{-7} \text{ g}$$

Co mass loading in the monolayer catalyst:

$$\text{Mass loading} = \frac{4.72 \times 10^{-7} g_{Co}}{0.42 \; cm^2} = 1.12 \; ug_{Co}/cm^2$$

Moles of surface active Co atoms in the monolayer catalyst:

$$\text{n(Co)} = \frac{4.72 \times 10^{-7}}{58.933} mol \times 14\% = 1.12 \times 10^{-9} \; mol$$

The current density is 2.19 mA/cm$^2$ at the overpotential of 0.4 V, so the TOF for the monolayer catalyst is:

$$\text{TOF} = \frac{2.19 \times 0.42 \text{ mA}}{4 \times 1.12 \times 10^{-9} \times 96485 \; C} = 2.13 \; s^{-1}$$

$$\text{Mass activity} = \frac{2.19 \times 0.42 \text{ mA}}{4.72 \times 10^{-7} \; g} = 1949 \; A \; g^{-1}$$

## References

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6. Owens, F. J.; Poole, C. P., *The Physics and Chemistry of Nanosolids*. Wiley, 2008.
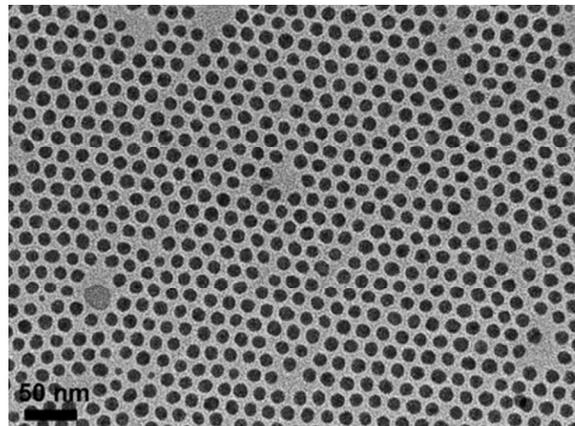
**Figure S1**. TEM image of the as-synthesized 10 nm Co NPs.
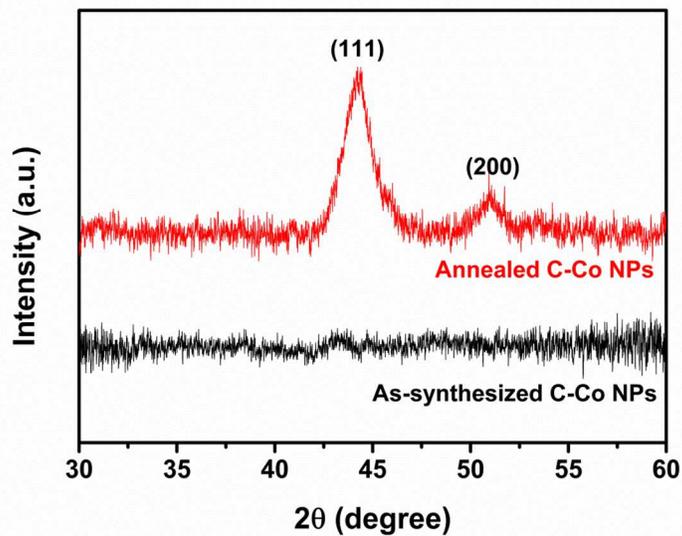


**Figure S2**. XRD patterns of the C-Co NPs before and after reductive annealing in Ar + 5% $H_2$ at 600 $^o$C for 1 h. The as-synthesized C-Co NPs show no obvious diffraction peaks. After annealing, clear diffraction peaks, which can be indexed to fcc-Co, are seen.
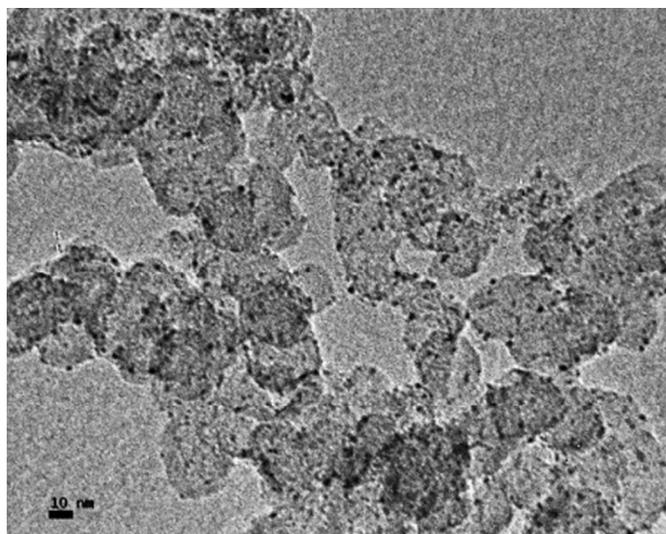
**Figure S3**. TEM image of the commercial C-Ir catalyst with 10 wt% Ir on Vulcan carbon black.
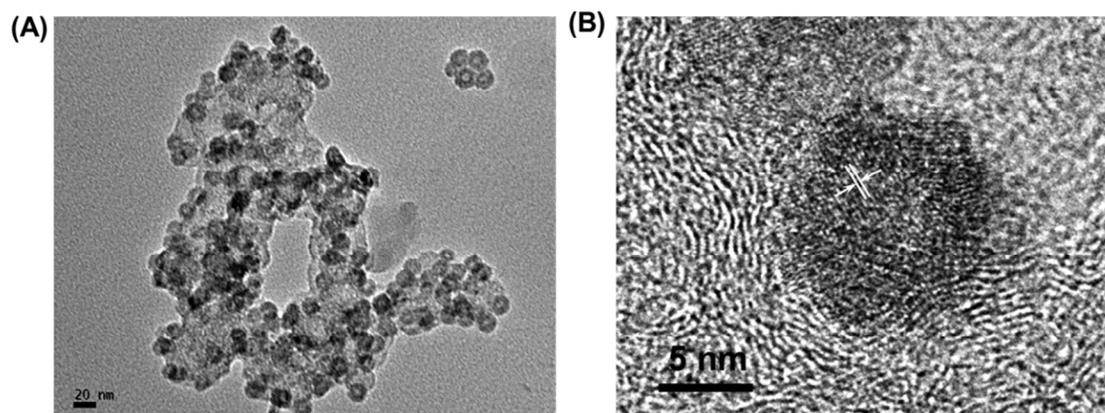


**Figure S4**. (A) TEM image of the C-CoO NPs. (B) HR-TEM of a single CoO NP on carbon support. The interfringe distance is 2.5 Å, corresponding to the lattice spacing of (111) planes of the fcc-CoO.
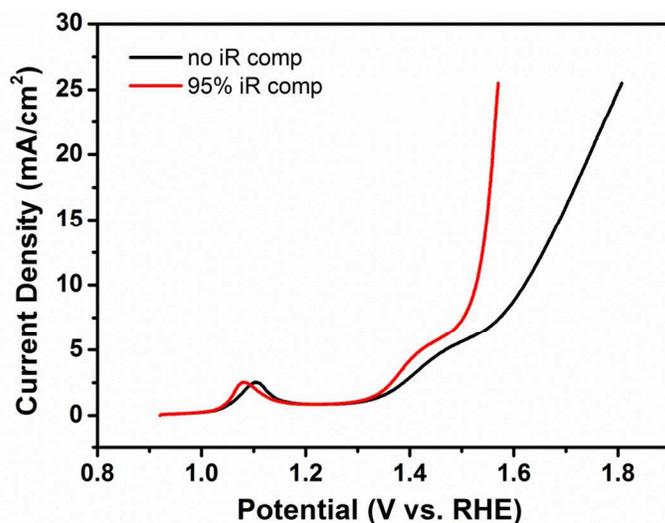
**Figure S5**. Polarization curves of the C-Co NP catalyst on GC electrode in 0.1 M KOH at the mass loading of 0.2 mg/cm$^2$. The black curve is without iR-correction and the red curve is with 95% iR compensation. The uncompensated resistance $R_u$ of our electrochemical cell was determined to be $R_u = \sim50\ \Omega$ by the current interrupt method (i-interrupt).
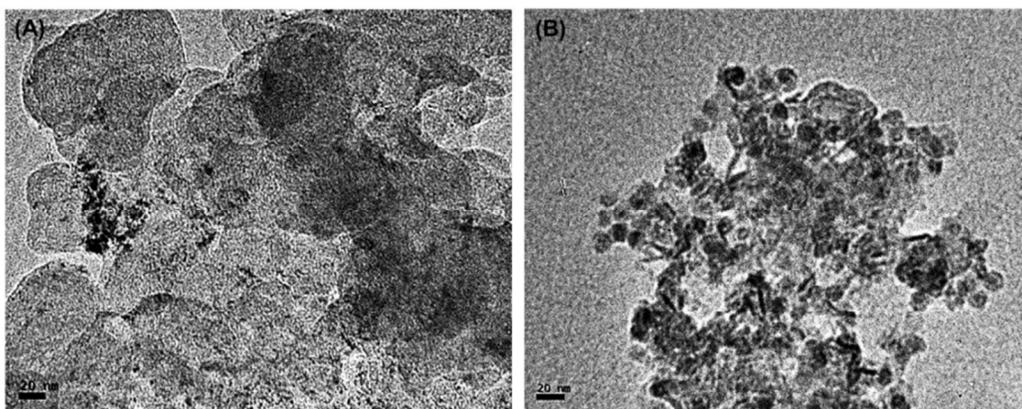


**Figure S6**. TEM images of (A) C-Ir NPs and (B) C-Co NPs after stability test.
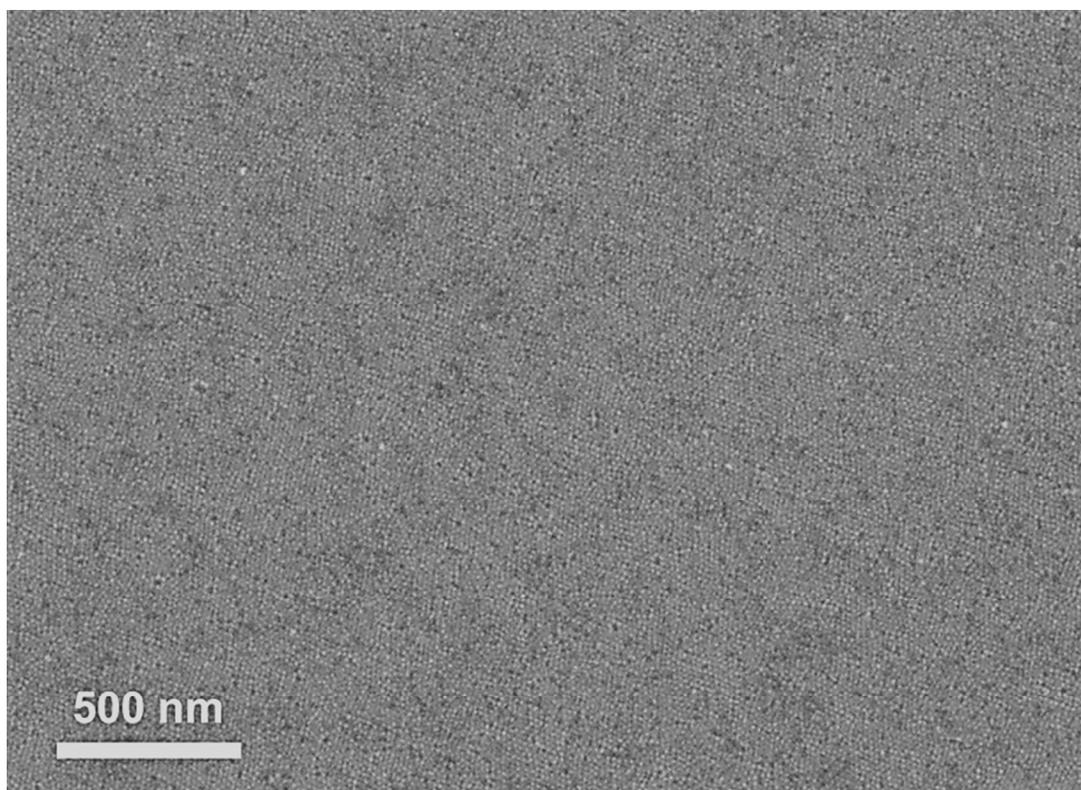
**Figure S7**. SEM image of a representative area of the monolayer assembly of Co NPs on GC plate.