Supporting Information

# In-situ Encapsulated and Well Dispersed Co<sub>3</sub>O<sub>4</sub> Nanoparticles as Efficient and Stable electrocatalysts for High-performance CO<sub>2</sub> reduction

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#### 1. Materials.

2-methylimidazole ( $\geq$ 98%, Aldrich), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O( $\geq$ 98%, Aldrich) and methanol ( $\geq$ 98%, Aldrich), ethanol (AR)were used as received. CO<sub>2</sub> with a purity of 99.99% was purchased from Korea Specialty Gases N<sub>2</sub>/H<sub>2</sub> (90%/10%) was purchased from Korea Specialty Gases. Concentrated H<sub>2</sub>SO<sub>4</sub> (98%).

#### 2. Electrode Synthesis and Structural Characterization

Synthesis of ZIF-67 precursor: In a typical experiment, 16 mmol of 2methylimidazole and 4mmol  $Co(NO_3)_2 \cdot 6H_2O$  were added into 40 mL of methanol, respectively. Then, the 2-methylimidazole solution was quickly poured from one container into another of  $Co(NO_3)_2$  solution to form a purple standardized solution under ultrasonication for 10s. The purple precipitate was collected by filtration, washed 3 times with methanol and placed in a vacuum oven for 6 h, then dried at 60 °C.

Synthesis of Co/C: The ZIF-67 particles (100 mg) obtained above were placed in a porcelain boat and heated to 350 °C and sustained for 1.5 h in tube furnace. Then, the temperature was further increased to 500 °C and sustained for 3.5 h. The ramp rate was constant at 2 °C min<sup>-1</sup> and N<sub>2</sub> flow was filling for these two procedures. Then the N<sub>2</sub> flow was cut off and the temperature was kept at 500 °C under air atmosphere for another 3.5 h. After natural cooling to room temperature, the black powder was obtained as Co/C.

Synthesis of Co/CNTs and CNTs: 100 mg ZIF-67 particles prepared above were placed in a porcelain boat and heated to 350 °C and sustained for 1.5 h in tube furnace. Then, the temperature was further increased to 500 °C and sustained for 3.5 h. The ramp rate was constant at 2 °C min<sup>-1</sup> and N<sub>2</sub>/H<sub>2</sub> flow (90%/10% in volume ratio) was filling the tube furnace for these two steps. Then the N<sub>2</sub>/H<sub>2</sub> flow was cut off and the temperature was kept at 500 °C under air atmosphere for another 3.5 h. After natural cooling to room temperature, the black powder was obtained as Co/CNTs. The synthesized Co/CNTs was put into 0.5 M  $H_2SO_4$  solution, and etched for 12 h. The black precipitate was collected by filtration, washed 3 times with ethanol and put in a vacuum oven for 6 h, then dried at 60 °C overnight. The black powder was obtained as CNTs.

## 3. Materials characterization

Linear sweep voltammograms (LSV) were chronicled with electrochemical workstation (Princeton Applied Research 263A). Potentiostatic electrolysis were performed via a CHI 660C electrochemical station (Shanghai Chenhua). Liquid-phase reduction products were analyzed with <sup>1</sup>H NMR spectra using an Ascend 400 spectrometer (500 MHz, Bruker). Gas-phase reduction products were detected by Gas Chromatography (SRI 8610C).

Field emission scanning electron microscope (FE-SEM) images were acquired with FEI JEOL-7800F. Transmission electron microscopy (TEM) pictures and element mapping analysis (EDS) pictures were taken by JEM-2100F field emission electron microscope conducted at an acceleration voltage of 120 kV. X-ray diffraction (XRD) patterns were taken with a Rigaku MiniFlex 600 powder diffractometer using Cu K $\alpha$  radiation (k= 1.5406 Å). N<sub>2</sub> adsorption-desorption was conducted at 77 K via a Micromeritics ASAP 2460 instrument with outgassing samples under vacuum at 523K for 15 h. X-ray photoelectron spectra analysis (XPS) were performed with ThermoVG Scientific ESCALAB 250 X-ray photoelectron spectra were performed by a Rennishaw InVia spectrometer (INVIA REFLEX) with a 514.5 nm laser excitation.

## 4. Electrochemical measurements

Electrochemical measurements were conducted in a three-electrode system at electrochemical workstation (Princeton Applied Research 263A). Saturated calomel electrode and Pt-foil were used as the reference and counter electrodes in all measurements and the reference electrode was standardized with esteem to a reversible hydrogen electrode.

In a representative method for preparing working electrode, 100  $\mu$ L catalyst ink (2 mg/mL) that was prepared by dispersed 10 mg catalysts in the mixed solution of 5 mL isopropanol and 10  $\mu$ L 5% Nafon was dropped on 1 cm<sup>2</sup> carbon paper. Cyclic voltammetry was implemented in a three-electrode electrochemical cell with a

Ag/AgCl as the counter electrode. The scan rate was  $5mV \cdot s^{-1}$  for all electrochemical measurements.

Measurements at high current densities were performed in a self-made micro flow cell (see **Figure 5a**). Co/CNTs catalyst ink was drop-casted on a gas diffusion layer (SIGRACET) as the cathode compartment in flow cell. A commercial Pt/C electrode was used as anode and an Ag/AgCl were acted as the reference. 0.5 M KHCO<sub>3</sub> aqueous solution was utilized as electrolyte, which were separated by a piece of Nafion®117 membrane. Electrolyte were cycled at with a rate of 50 mL min<sup>-1</sup>. The CO<sub>2</sub> gas was supplied to the cathode and was flown through the gas diffusion layer at rate of 20 mL min<sup>-1</sup>.

All potentials in this paper were transformed to reversible hydrogen electrode (RHE) by the following Nernst equation:

 $E(RHE) = E(Ag/AgCl) + 0.199 + 0.059 \times pH$ 

The electrolyzer outlet was directly connected the gas-sampling loop of the gas chromatograph (SRI-8610C) outfitted with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The Faradaic efficiency(FE) of CO was calculated from the total amount of charge (Q/C) passed through the sample and the total amount of CO ( $n_{CO}$ /mol).  $Q=I\times t$ , where I is the reduction current at a specific applied potential, and t is the time for the constant reduction current. The entire amount of CO produced was measured via gas chromatography (SRI 8610C). As two electrons are needed to produce one CO molecule, the Faradaic efficiency (FE) can be calculated as follows: Faradaic efficiency =  $2F \times n_{CO}/(I \times t)$ , where F is the Faraday constant (96,485 C/mol).



Fig. S1. SEM images of ZIF-67 nanoparticle.



Fig. S2. SEM and TEM images of Co/CNTs.



Fig. S3. SEM images of CNTs.



Fig. S4. TEM images of CNTs.



Fig. S5. SEM images of Co/C.



Fig. S6. TEM images of Co/C.



Fig. S7. N<sub>2</sub> adsorption-desorption isotherms (a) and pore size distribution (b) of

Co/C.



Fig. S8.  $N_2$  adsorption-desorption isotherms (a) and pore size distribution (b) of

CNTs.



Fig. S9. Survey (a) and C *ls* (b) XPS spectra of Co/CNTs.



Fig. S10. C *ls* (a), N *ls* (b) and Co *2p* (c) and survey (d) XPS spectra of Co/C.



Fig. S11. C *ls* (a) and N *ls* (b) XPS spectra of CNTs.



Fig. S12. LSVs of Co/C (a) and CNTs (b) in  $CO_2$ - or  $N_2$ -saturated solution.



Fig. S13. GC spectra of CO<sub>2</sub> reduction products.



Fig. S14. Potential-dependent Faradaic efficiencies of the Co/C (a) and CNTs (b).



Fig. S15. CV curves of three samples modified electrodes in the double layer region.

Table. S1 Comparisons of carbon-based electrocatalysts for CO2 reduction to CO					
Electrode	<i>j</i> co (mA cm <sup>-2</sup> )	CO-FE (%)	Electrolyte	Stability	Capacity (mg/cm <sup>2</sup> )
N-doped CNTs <sup>1</sup>	2.2	80	0.1 M KHCO3	-	0.5
N-doped CNTs <sup>2</sup>	10	80	0.1 M KHCO3	10 h	0.5
CoPc-CN/CNT <sup>3</sup>	15	98	0.1 M KHCO <sub>3</sub>	10 h	0.4
CoTPP-CNT <sup>4</sup>	14	91	0.5 M KHCO3	4 h	0.5
NG-Co <sub>3</sub> O <sub>4</sub> <sup>5</sup>	НСООН 10.5	83	0.1 M KHCO3	8 h	1
Co <sub>3</sub> O <sub>4</sub> single-unit-cell layers <sup>6</sup>	нсоон 2.7	85	0.1 M KHCO3	40 h	0.5
Co <sub>3</sub> S <sub>4</sub> @Co <sub>3</sub> O <sub>4</sub> <sup>7</sup>	НСООН 10	85.3	0.1 M KOH	35000 s	0.1
[Co(L-L)Br <sub>2</sub> ] <sup>8</sup>	0.45	104.3	-	-	-
COF-366-Co <sup>9</sup>	-	87	0.5 M KHCO <sub>3</sub>	12 h	-
CoSA-N-CNTs <sup>10</sup>	6	20		12 h	1
CoPc-P4VP <sup>11</sup>	2.0±0.2	90	0.1 M NaH <sub>2</sub> PO <sub>4</sub>	7000 s	-
CoFPc <sup>12</sup>	6	93	0.5 M NaHCO <sub>3</sub>	10 h	-
[Co(qpy)] <sup>2+</sup> @MWCNTs 13	10	100	0.5 M NaHCO <sub>3</sub>	3.5 h	0.08
Co <sup>II</sup> (Ch) on MWCNTs <sup>14</sup>	0.06	89	1 M Na <sub>2</sub> SO <sub>4</sub>	-	0.18
Co-N <sub>X</sub> <sup>15</sup>	45	94	0.5 M KHCO <sub>3</sub>	60 h	-
CoPPc/CNT <sup>16</sup>	50	90	0.5 M NaHCO <sub>3</sub>	24 h	1
CoPc/CNT <sup>17</sup>	10.2 (MeOH)	32	0.5 M KHCO <sub>3</sub>	12 h	-

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