Supporting Information

Controlled Assembly of Cobalt embedded N-doped Graphene Nanosheets (Co@NGr) Derived by Pyrolysis of Mixed Ligand Co(II) MOF as a Sacrificial Template for High-Performance Electrocatalyst

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Experimental Section

Materials and General Methods: All reagents and solvents were purchased from commercial sources and were used without further purification. Milli-Q water was used for synthetic manipulations. FT-Raman data were collected using a Horiba Scientific LabRAM HR Evolution Raman Spectrometer with 532 nm line of an Ar ion laser at room temperature. Powder X-ray diffraction (PXRD) data were collected using a PANalytical Empyrean (PIXcel 3D detector) system with CuKα radiation. N₂ adsorption-desorption isotherm and BET surface area was measured on a Micromeritics, 3 Flex instrument. Field Emission-Scanning Electron Microscopy (FE-SEM) micrographs were recorded using a JEOL JSM-7100F instrument employing an 15-kV accelerating
voltage. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100 microscope with an acceleration voltage of 200 kV using lacy carbon-coated 300-mesh copper grids. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Fisher Scientific ESCALAB Xi+ instrument.

**Synthesis of CoMOF-2:** Bulk powder of CoMOF-2 was synthesized via RT Stirring method according to our previous report.\(^1\) 10 mmol of Co(NO\(_3\))\(_2\).6H\(_2\)O, 10 mmol 1,4-benzenedicarboxylic acid (H\(_2\)BDC), 20 mmol NaOH and 10 mmol (E)-N'-(pyridin-4-ylmethylene) isonicotinohydrazide (L) in 100 mL H\(_2\)O:MeOH:EtOH (5:4:1/v:v) solvent were stirred in a 200 mL round bottom flask at room temperature for 8 h. The resulting precipitate was filtered and washed with H\(_2\)O:MeOH (1:1/v:v) followed by acetone and then air dried. Yield ca. 90 %.

**Synthesis of Co@NGr nanomaterials:** 1.5 gm of CoMOF-2 was placed in a tube furnace and pyrolyzed at set temperature (700, 800, 900 °C) for 5 hr under N\(_2\) gas condition at a heating rate of 5 °C min\(^{-1}\). After completion of pyrolysis, furnace was cooled to room temperature and the collected electrocatalysts material at the respective temperature is labeled as Co@NGr-700, Co@NGr-800 and Co@NGr-900 respectively and thoroughly characterized.

**Electrochemical Measurements**

**Materials and General Methods:** All the electrochemical activity/measurements, i.e., Oxygen Evolution Reaction (OER), Hydrogen Evolution Reaction (HER), Cyclic Voltammetry (CV), of the synthesized materials were performed by using Metrohm Autolab PGSTAT204 potentiostat/galvanostat electrochemical workstation under room temperature and ambient atmospheric pressure. The electrochemical impedance spectroscopy measurements were
carried out using Princeton applied research potentiostat-galvanostat (PARSTAT 2273) by the three-electrode system. For the measurements, the Glassy carbon electrode (GCE) of 3 mm diameter was used as a working electrode while Pt foil and Ag/AgCl (saturated KCl) were used as a counter and reference electrodes, respectively.

**Electrode Preparation:** To prepare a working electrode, GCE was mirror polished on nylon pad using alumina powder (0.3 μ) and washed with milli-Q (MQ) water. The polished and washed GCE was then ultrasonicated into 1:1 acetone and water mixture for 30 minutes and dried properly at room temperature. A fixed amount of 5 mg electrocatalyst material was dispersed in 1 ml isopropanol (IPA) solvent and 10 μl Nafion was mixed separately with 90 μl MQ water. Both the solutions were separately ultrasonicated for 30 minutes. After proper dispersion, 10 μl was taken from each solution and mixed together in a separate vial and ultrasonicated for 30 min to form a homogenous ink. 10 μl of the completely dispersed catalyst ink was then loaded over the cleaned and dried surface of the bare GCE through drop-casting and kept overnight at 25 °C for drying. 1M KOH and 0.5M H₂SO₄ solutions were used as electrolytes for OER and HER process, respectively. Linear sweep voltammetry (LSV) was performed at 5mV/s scan rate in the potential range of 0.0 V to +2.0 V and 0.1 V to -1.2 V for the OER and HER process, respectively. Cyclic voltammetry was recorded from 0.0 V to +2.0 V potential at the scan rate of 25 mV/S to see the stability of the catalyst. Electrochemical impedance spectroscopy (EIS) was carried out in 1M KOH at the frequency range of 50 kHz to 100 mHz. The electrochemical active surface area (EASA) of the electrocatalyst was calculated from the curves which were obtained after performing cyclic voltammetry (CV) at different scan rates, i.e., 1, 2, 3, 4, and 5 mV/s.
Figure S1. Comparison of PXRD data of CoMOF-2 synthesized by RT stirring with simulated SXRD.

Figure S2. FE-SEM images recorded for CoMOF-2 synthesized by RT stirring.
Figure S3. 3D framework in CoMOF-2, viewed down the c-axis.
Figure S4. TEM images, HR-TEM images, SAED and TEM-EDX pattern of Co@NGr-700.
Figure S5. TEM images, HR-TEM images, SAED and TEM-EDX pattern of Co@NGr-800.
Figure S6. TEM-EDX pattern of Co@NGr-900.

Figure S7. FT-Raman shift for Co@NGr-700 and Co@NGr-800.
**Figure S8.** XPS survey spectrum of Co@NGr-700, Co@NGr-800 and Co@NGr-900 shows the peaks of C, N, O, and Co elements.

**Table S1.** Elemental composition of Co@NGr nanomaterials calcined at different temperature obtained from XPS analysis.

|                | XPS                |                |                |
|----------------|--------------------|----------------|----------------|
|                | Co@NGr-700         | Co@NGr-800     | Co@NGr-900     |
| Co             | 6.3                | 5.5            | 4.03           |
| C              | 80.27              | 84.94          | 87.21          |
| N              | 3.27               | 0.75           | 0.69           |
| O              | 10.15              | 8.8            | 8.07           |
Figure S9. N$_2$ adsorption isotherm of Co@NGr-700/800/900 nanomaterials at 77 K.

Figure S10. (a,b) BJH Desorption dV/dD Pore Volume plot for the mesopore determination in Co@NGr-600/700/900 nanomaterials.
Figure S11. Horvath-Kawazoe Differential Pore Volume Plot for the micropore size determination in Co@NGr-700/800/900 nanomaterials.

Table S2. Summary of BET surface area, average pore diameter and micropore size obtained from N₂ adsorption for Co@NGr-700/800/900 nanomaterials.

| Co@NGr nanomaterials | BET Surface Area (m²/g) | Average Pore Diameter (Å) | Micropore Size (Å) |
|-----------------------|-------------------------|---------------------------|-------------------|
| Co@NGr-700            | 127.4                   | 38                        | 6.92              |
| Co@NGr-800            | 58.2                    | 86                        | 6.89              |
| Co@NGr-900            | 54.9                    | 77                        | 6.94              |

Table S3. Summary of overpotential to achieve current density of 50 mA/cm² in OER and -50 mA/cm² in HER for different Co@NGr nanomaterials.

| Co@NGr nanomaterials | Overpotential (mV) for OER at 10 mA/cm² | Overpotential (mV) for HER at -10 mA/cm² |
|-----------------------|----------------------------------------|-----------------------------------------|
| Co@NGr-700            | 700                                    | 908                                     |
| Co@NGr-800            | 590                                    | 625                                     |
| Co@NGr-900            | 520                                    | 628                                     |
Figure S12. Cyclic voltammetry (CV) performed up to 200 cycles at 5 mV/s for Co@NGr-900.

Figure S13. TEM images and HR-TEM images of recycled Co@NGr-900.
Figure S14. Nyquist Plot for Co@NGr-700/800/900 nanomaterials.
**Table S4.** Comparison of the oxygen evolution reaction (OER) activities of recently reported electrocatalysts in respect of overpotential@10 mA/cm².

| Sr No. | OER Electrocatalysts                     | Electrolytes | Overpotential@10 mA/cm² (mV) | Ref. |
|--------|-----------------------------------------|--------------|------------------------------|------|
| 1      | CoMOF-1 @900                            | 1 M KOH      | 210                          | S2   |
| 2      | Co₃O₄/N-rmGO                            | 1 M KOH      | 310                          | S3   |
| 3      | Ultrathin CoSe₂ nanosheets              | 0.1 M KOH    | 320                          | S4   |
| 4      | Annealed C–Co NPs                       | 0.1 M KOH    | 390                          | S5   |
| 5      | CoP/C                                   | 0.1 M KOH    | 360                          | S6   |
| 6      | Co₂B-500/NG                             | 0.1 M KOH    | 380                          | S7   |
| 7      | CoP/rGO-400 (MOF-derived)               | 1 M KOH      | 340                          | S8   |
| 8      | NCNTFs obtained at 700 °C (MOF-derived) | 0.1 M KOH    | 370                          | S9   |
| 9      | PNC/Co (MOF-derived)                    | 1 M KOH      | 370                          | S10  |
| 10     | Co-NC/CNT (MOF-derived)                 | 1 M KOH      | 354                          | S11  |
| 11     | Co@NCNT (MOF-derived)                   | 1 M KOH      | 429                          | S12  |
| 12     | CoZn-NC-700 (MOF-derived)               | 0.1 M KOH    | 390                          | S13  |
| 13     | Co-N-CNTs (MOF-derived)                 | 0.1 M KOH    | 460                          | S14  |
| 14     | GNCNTs-4 (MOF-derived)                  | 0.1 M KOH    | 370                          | S15  |
| 15     | Co@N-CNTF-2 (MOF-derived)               | 1 M KOH      | 350                          | S16  |
| 16     | Pt-SCFP/C-12                            | 0.1 M KOH    | 370                          | S17  |
| 17     | Co@NGr-900                              | 1 M KOH      | **390**                      | This Work |
Table S5. Comparison of the hydrogen evolution reaction (HER) activities of recently reported electrocatalysts in respect of overpotential@-10 mA/cm$^2$.

| Sr No. | HER Electrocatalysts          | Electrolytes | Overpotential@-10 mA/cm$^2$ (mV) | Ref. |
|--------|-------------------------------|--------------|----------------------------------|------|
| 1      | Co@N-CNTF-2 (MOF-derived)    | 0.5 M H$_2$SO$_4$ | 220                              | S16  |
| 2      | NENU-500                      | 0.5 M H$_2$SO$_4$ | 237                              | S18  |
| 3      | NENU-501                      | 0.5 M H$_2$SO$_4$ | 397                              | S18  |
| 4      | Co@N–C-600                    | 0.5 M H$_2$SO$_4$ | 339                              | S19  |
| 5      | Co@NCNTs-800                  | 0.5 M H$_2$SO$_4$ | 280                              | S20  |
| 6      | CTGU-5                        | 0.5 M H$_2$SO$_4$ | 388                              | S21  |
| 7      | CTGU-6                        | 0.5 M H$_2$SO$_4$ | 425                              | S21  |
| 8      | THAT-Co                       | 0.5 M H$_2$SO$_4$ | 283                              | S22  |
| 9      | S-600                         | 0.5 M H$_2$SO$_4$ | 262                              | S23  |
| 10     | Ni$_2$P polyhedron            | 0.5 M H$_2$SO$_4$ | 158                              | S24  |
| 11     | CoP NRAs                      | 0.5 M H$_2$SO$_4$ | 181                              | S25  |
| 12     | NiMo$_2$C@C                   | 0.5 M H$_2$SO$_4$ | 169                              | S26  |
| 13     | Fe$_x$P@NPC                   | 0.5 M H$_2$SO$_4$ | 227                              | S27  |
| 14     | CoMOF-1@900                   | 0.5 M H$_2$SO$_4$ | 580                              | S2   |
| 15     | Co@NGr-900                    | 0.5 M H$_2$SO$_4$ | **340**                          | This work |
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