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Supporting Information

Metal-Organic Framework on Fullerene (MOFOF) Derived Co-anchored Hierarchical Carbon Nanocomposite for Catalytic Nitroarene Reduction

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1. Materials

All chemicals used in this study were sourced from commercial suppliers and utilized without further purification. Pristine fullerene C_{60} (pC_{60}: 99.9%) was obtained from BBS Chemicals, USA. Methanol (99.7%), triethylamine (TEA), mesitylene (C_9H_{12}: 99.8%), nitric acid (HNO_3: 65%), sulfuric acid (H_2SO_4: 98%), were purchased from Wako Chemical Corporation, Tokyo, Japan. Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$: 99%), methylimidazole (Mim: 99.8%) para nitrophenol ($C_6H_5NO_3$: 98%), nitrobenzene ($C_6H_5NO_2$: 98%), ortho-nitrophenol ($C_6H_5NO_3$: 98%), para-methyl nitrobenzene ($C_7H_7NO_2$: 98%), para-chloro nitrobenzene ($C_6H_4ClNO_2$: 99%) and sodium borohydride ($NaBH_4$: 98%) were acquired from Tokyo Chemical Industry Co., Ltd., Japan.

2. Experimental

2.1 Synthesis and carbonization of MOFOF

The synthesis of MOF-on-fullerene composites (MOFOFs) followed methods similar to our recent work.[1] The FNT crystals were first prepared using the liquid-liquid interphase precipitation (LLIP) method, with mesitylene as the good solvent and methanol as the poor solvent. A solution of pristine C_{60} (pC_{60}) in mesitylene (1.0 mg/mL) was sonicated for 1 hour and filtered to remove undissolved particles. To induce FNT crystallization, methanol (90 mL) was rapidly added to the pC_{60} solution (30 mL) and hand-shaken for 5 seconds. The resulting precipitates, after undisturbed incubation at 25 °C for 2 hours, were collected by centrifugation, washed with methanol, and dried under vacuum at 80 °C for 6 hours. The dried FNT was oxidized by immersing 100 mg of FNT in a 1:1 mixture of concentrated HNO_3 and H_2SO_4 (10 mL) followed by sonication for 20 minutes. The oxidized FNT (FNT_{ox}) was then centrifuged, washed with water until the pH was neutral, and dried under vacuum at 80 °C for 12 hours.

The MOFOF composites were obtained via in-situ growth of ZIF-67 onto FNT_{ox} under sonication. $Co(NO_3)_2{\cdot}6H_2O$ (2 mM, 10 mL) and a ligand-modulator mixture of methylimidazole (Mim) and triethylamine (TEA) (16 mM, 10 mL) were dissolved in water. The Co^{2+} solution was added to a dispersion of FNT_{ox} (100 mg/mL) and sonicated for 5 minutes with periodic hand-shaking. The Mim and TEA solution was then added, and sonication/hand-shaking was continued for an additional 15 minutes. The resulting MOFOF solids were collected by centrifugation, washed with water and methanol, and dried under vacuum at 80 °C for 12 hours. MOFOF composites with different FNT_{ox}/MOF or C_{60}/Co^{2+} ratios (0.5, 1.0, 1.5, 2.0) were labeled MOFOF-0.5, MOFOF-1.0, MOFOF-1.5, and MOFOF-2.0, respectively.

The dried FNT_{ox}, pZIF-67, MOFOF-0.5, MOFOF-1.0, MOFOF-1.5, and MOFOF-2.0 samples were subjected to carbonization at 800 °C in a tube furnace under an inert nitrogen atmosphere to produce hierarchically porous carbon nanocomposites. The carbonization process involved a heating ramp of 10 °C/min, a hold time of 4 hours, and a nitrogen gas flow rate of 120 cc/min. The resulting carbonized products were labelled as FDC, Co@ZDC, Co@HC-0.5, Co@HC-1.0, Co@HC-1.5, and Co@HC-2.0, respectively.

2.2 Characterisations

The synthesized MOFOF composites and carbon nanocomposites were characterized using a range of analytical techniques, including scanning electron microscopy (SEM, 10 kV, Hitachi S-4800, Tokyo, Japan), scanning transmission electron microscopy (STEM, 30 kV, Hitachi S-4800, Tokyo, Japan), powder X-ray diffraction (PXRD, 40 kV, Cu-Kα radiation, λ = 0.1541 nm, RINT2000 diffractometer, Rigaku, Tokyo, Japan), Raman spectroscopy (NRS-3100 Raman spectrometer, JASCO, Tokyo, Japan), and X-ray photoelectron spectroscopy (XPS; Thermo Electron Co., Karlsruhe, Germany, with monochromatic Al-Kα radiation at 15 keV). Nitrogen adsorption-desorption measurements were conducted using a Quantachrome Instrument Autosorb-1 (USA). Samples for electron microscopy were prepared by depositing a suspension of the materials in isopropyl alcohol onto carbon-coated copper grids and drying them under vacuum at 70 °C.

2.2 Evaluation of catalytic activities

The catalytic reduction of nitroarenes was measured using a Shimadzu UV2550 spectrophotometer in a 4 mL quartz cell. Typically, a freshly prepared aqueous $NaBH_4$ solution (2.5 mL, 0.05 M) was mixed with an aqueous nitroarene solution (25 µL, 10 mM) in the quartz cell, resulting in a colour change from light yellow to yellow-green. Then, a suspension of the catalysts Co@HCs, FDC, or Co@ZDC (20 µL, 1 mg/mL) was added to the mixture. The reduction process was monitored by recording the UV-Vis absorbance at 400 nm at 1-minute intervals.[2,3]

Recycling of catalysts. To assess catalyst recyclability, the performance of Co@HC-1.0 in 4-NP reduction was evaluated after regeneration. After each catalytic reaction, the Co@HC-1.0 catalyst was separated from the reaction mixture using a magnet, thoroughly washed with ethanol, and dried under vacuum at 100 °C overnight for subsequent reuse.

3. Additional data

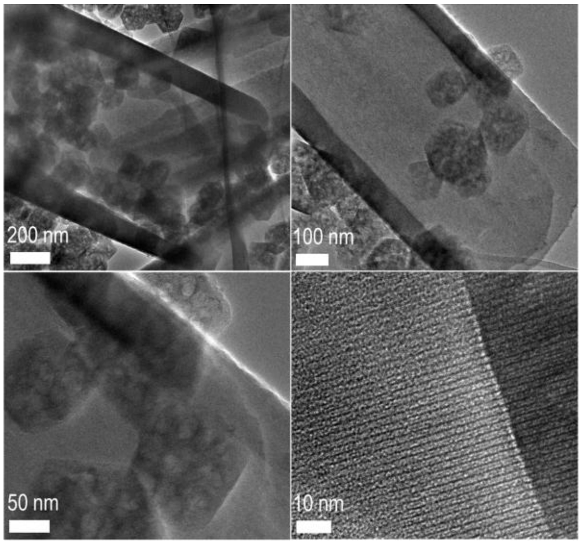

Fig. S1. TEM images of MOFOF-1.0.

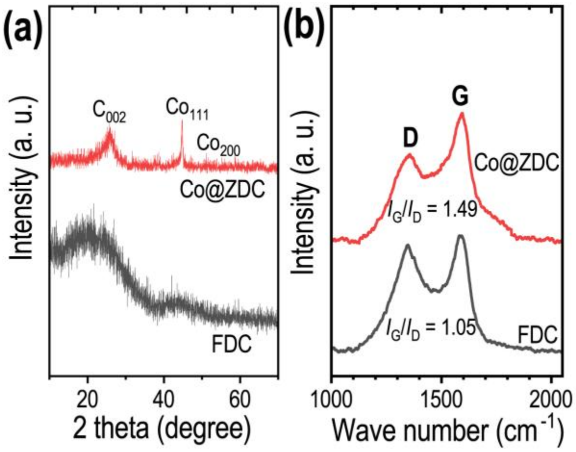

Fig. S2. (a) XRD patterns and Raman spectrum of FDC (FNT_{ox}-derived carbon) and Co@ZDC (ZIF-67-derived Co@carbon) materials.

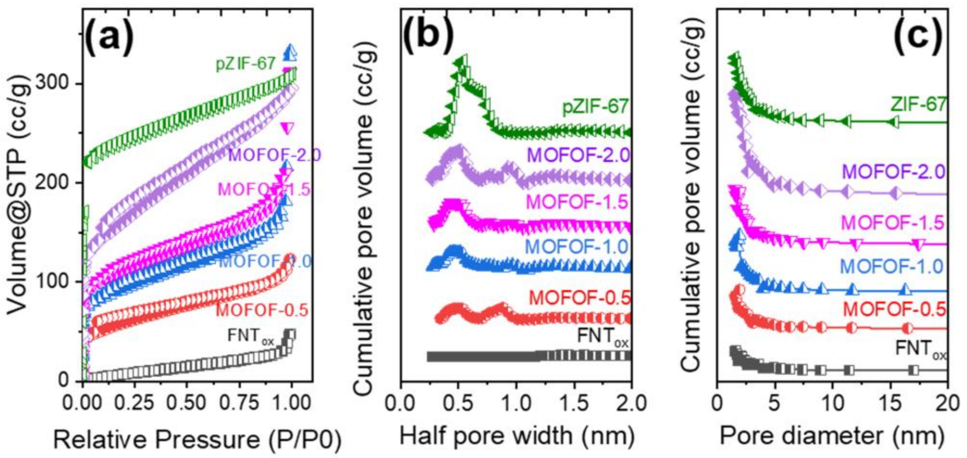

Fig. S3. (a) Nitrogen adsorption-desorption isotherms of the FNT$_{ox}$, MOFOF, and pZIF-67 samples, pore size distribution curves using (b) the DFT method and (c) the BJH method.

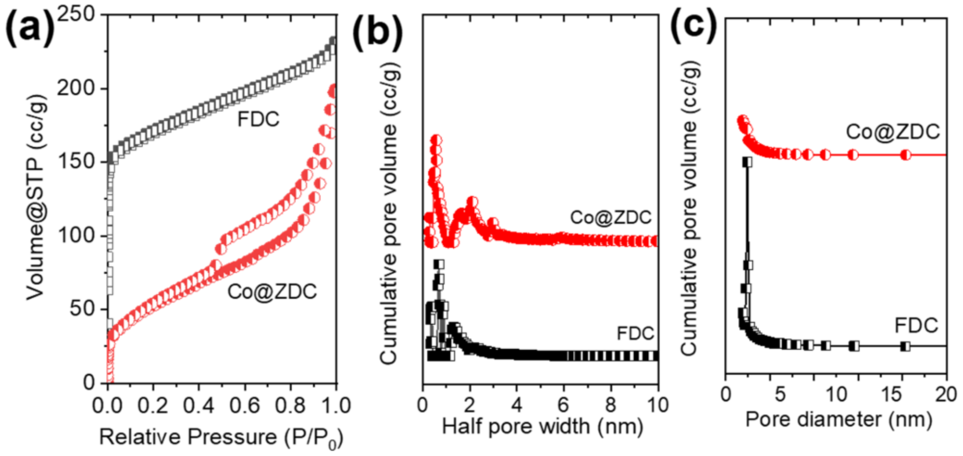

Fig. S4. (a) Nitrogen adsorption-desorption isotherms of the FDC and Co@ZDC samples, pore size distribution curves using (b) the DFT method and (c) the BJH method.

Table S1: Comparative analysis of the catalytic efficiency of Co@HCs versus reported Co-based and remarkable reported catalysts in the reduction of 4-NP using $NaBH_4$.

Entry	Catalyst	K (min-1)	TOF (h^{-1})	Reference
1	Co@HC-0.5	1.63×10^{-1}	231	This study
2	Co@HC-1.0	9.25×10^{-1}	486	
3	Co@HC-1.5	4.16×10^{-1}	285	
4	Co@HC-2.0	3.09×10^{-1}	142	
5	Co@ZDC	7.24×10^{-1}	55	
6	MDC-6(75Zn25Co)-900	3.8×10^{-1}	325	4
7	Co/AC	1.1×10^{-1}	42	
8	Co/rGO	1.6×10^{-1}	93	
9	Co@NC	1.02×10^{-1}	45	5
10	N-Co@C-800-3	3.5×10^{0}	–	6
11	Co-NCC	2.82×10^{0}	–	7
12	Co-Ni-rGO	1.14×10^{0}	–	8
13	Co@BrNC	8.82×10^{-1}	–	9
14	Co@CN/CM	–	2556	10
15	C@Co	2.52×10^{0}	0.17	11
16	Co-W-P/CC	7.14×10^{-1}	–	12
17	Co@SiO2	8.2×10^{-1}	–	13
18	reduced Co3O4	14.9×10^{-1}	–	14
19	ZnCo2O4	1.02×10^{-0}	–	15
20	Co/ZnO/N-C	4.2×10^{-2}	–	16
21	Co-NB	5.4×10^{-2}	–	17
22	Co_1/NC-800	1.28×10^{-0}	73668	18
23	Co–N_4/TiN–rGO	1.20×10^{-0}	300	19
24	Co_3O_4/HNTs	2.7×10^{-1}	264	20
25	Cu/Co@NCF-15	4.16×10^{0}	438	21
26	Rh@ZrO_2/NC	–	2136	22
27	PtNiCo/C	–	2616	23
28	Pt-PMo@UiO-66	–	1498	24
29	Ni-SiW POMOF	–	255.5	25

[a]Co-content was analyzed by EDS analysis; [b]Relative k was estimated by considering the k of FDC as 1; [b]relative Co@ZDC

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