Electronic Supplementary Information for

Organometallic Approach for Microporous Organic Network (MON)-Co_3O_4 Composites: Enhanced Stability as Anode Materials for Lithium Ion Batteries

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Experimental Section

All SEM images were taken using a FE-SEM (JSM6700F). The TEM and EDS-mapped images were taken using a JEOL 2100F unit operated at 200kV. Solid phase ^{13}C-NMR spectrum was recorded on a Varian 600 MHz solid state NOVA600 spectrometer at Korea Basic Science Institute (Daegu) operated at 150.9 MHz Larmor frequency. The spinning speed of 9.5 kHz was applied and the repetition delay time was 6.5 sec. Adsorption-desorption isotherm for N_2 (77 K) was recorded by using BELSORP II-mini volumetric adsorption equipment. The TGA curve was obtained by Seiko Exstar 7300. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku MAX-2200 and filtered Cu-Ka radiation. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) experiment was performed by Shimadzu ICPS-1000IV. Electrochemical studies were performed using WBCS3000 automatic battery cycler system.

Preparation of MON-Co_3O_4 composites: **1,3-Bis(4-iodophenyl)benzene** was prepared from 1,3-diiodobenzene following the literature method.(ref. 10 in text) Briefly, 4-(trimethylsilyl)phenyl magnesium bromide (Grignard reagent) was prepared by reaction of 4-(trimethylsilyl)bromobenzene (0.504g, 2.20 mmol) with Mg (80 mg, 3.3 mmol) in anhydrous ether (20 ml) for 12 hours at room temperature. Then, Kumada coupling was performed in ether with refluxing for 48 hours between the prepared Grignard reagent and 1,3-dichlorobenzene (0.181 g, 0.549 mmol) with nickel catalyst, dichloro[1,3-bis(diphenyl-phosphino)propane] nickel(II) (2.9 mg, 0.0053 mmol). After quenching the reaction mixture with 2M aqueous HCl solution, the product was extracted with ether and dried over anhydrous $MgSO_4$. After evaporating the solvent, the product, 4,4''-bis(trimethylsilyl-m-terphenyl was purified by silica gel column chromatography. Then, 4,4''-bis(trimethylsilyl)-m-terphenyl (0.126 g, 0.335 mmol) was reacted with iodine monochloride (0.42 ml of 1.0 M solution of CH_2Cl_2) in in carbon tetrachloride (3.5 ml) at -20 ^{o}C. The reaction mixture was heated at 50 ^{o}C for 2 hours. After quenching the remained iodine monochloride with aqueous $Na_2S_2O_3$ solution, the organic layer was dried over $MgSO_4$. After evaporating the solvent, the product, 1,3-Bis(4-iodophenyl)benzene was recrystallized using pentane and methylene dichloride. ^{1}H NMR (300 MHz, $CDCl_3$): δ = ^{1}H NMR 7.79 (d, J=6.6 Hz, 4H), 7.70 (s, 1H), 7.54 (m, 3H), 7.37 (d, J=6.6 Hz, 4H) ppm. **Tetrakis(4-ethynylphenyl)methane** was prepared by following the method in literature (Yuan, S.; Kirklin, S.; Dorney, B.; Liu, D.-J.; Yu, L. *Macromolecules* **2009**, *42*, 1554.) For preparation of **MON**, in flame-dried 50 mL Schlenk flask, 1,3-bis(4-iodophenyl)benzene (0.12 g, 0.24 mmol) and tetrakis(4-ethynylphenyl)-methane (50 mg, 0.12 mmol) were dissolved in mixture of toluene (5 mL) and diisopropylamine (2 mL). After adding bis(triphenylphosphine)palladium dichloride (10 mg, 0.014 mmol) and copper iodide (10 mg, 0.053 mmol), the reaction mixture was heated at 90 ^{o}C under nitrogen for 1 day. Then, the formed yellow precipitates were retrieved by centrifugation, washed with methanol, methylene dichloride, toluene and hexane. The resultant powder was dried under vacuum. For the control experiment, sub-micropolystyrene beads were prepared by the literature method and used instead of **MON**. (Wang, H.; Zhang, S.; Wang, M.; Ge, X. *Chem. Lett.* **2008**, 37, 1158) For preparation of **MON-Co_3O_4**, in flame-dried 20 mL Schlenk flask, **MON** (30 mg) and $Co_2(CO)_8$ (30 mg, 0.035 mmol) were dispersed in toluene (5 mL) under nitrogen. Then, the temperature was gradually increased from room temperature to 90 ^oC. During the heating, the yellow solid became slowly black. After aging overnight, the reaction mixture was cooled to room temperature and the black solid was retrieved by centrifugation, washed with toluene and dried under vacuum. To transform the metallic cobalt to cobalt oxides, the black powder was heated at 225 ^oC for 2 hours under oxygen and aged for 5 hours under argon.

Fabrication of coin cells: For electrochemical studies, **MON-**Co_3O_4 composites (80 mg), Super P carbon black (10 mg) and polyvinylidene fluoride binder (10 mg) were mixed in N-methylpyrrolidone (NMP). After coating the copper foil with this mixture, the electrode was dried under vacuum at 120 ^oC overnight. The diameter of copper electrode was 14 mm. The average loading amount of electrode materials was 0.95 mg/cm^2. Cell tests were conducted using coin-type half cells (CR2016 type) with Li metal as the counter electrode and 1M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1 v/v) as the electrolyte. The discharge/charge cycle tests were performed using WBCS3000 automatic battery cycler system.

Figure S1. TEM images of **MON**-Co_3O_4 composites and **MON** (a), Co_3O_4 nanoparticles (b) prepared without use of **MON** at same reaction conditions of composites and the mixture materials (c) prepared by use of polystyrene instead of **MON** .

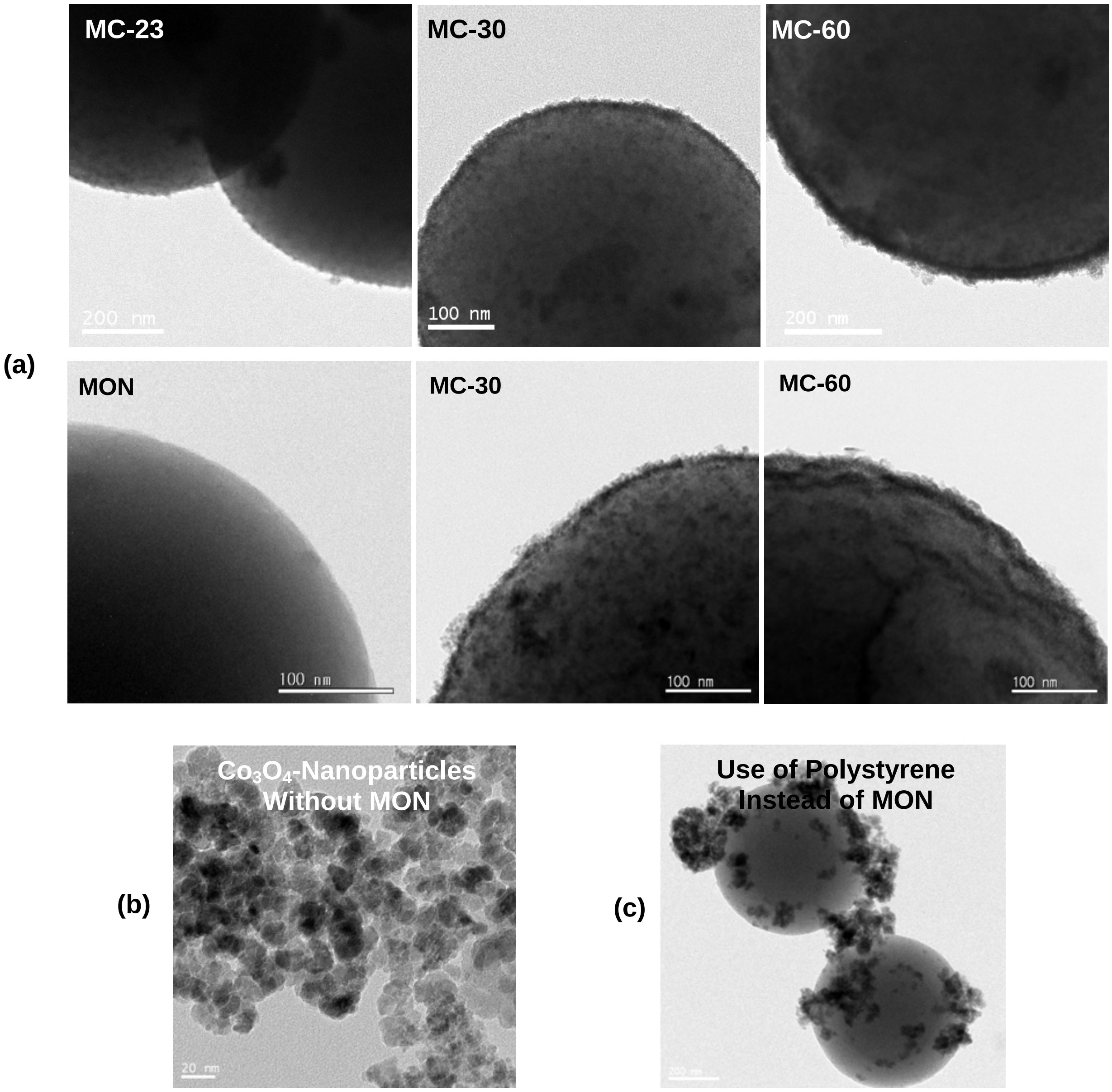

Figure S2. PXRD patterns of amorphous-**MON** (a) and **MON**-ε-Co (b).

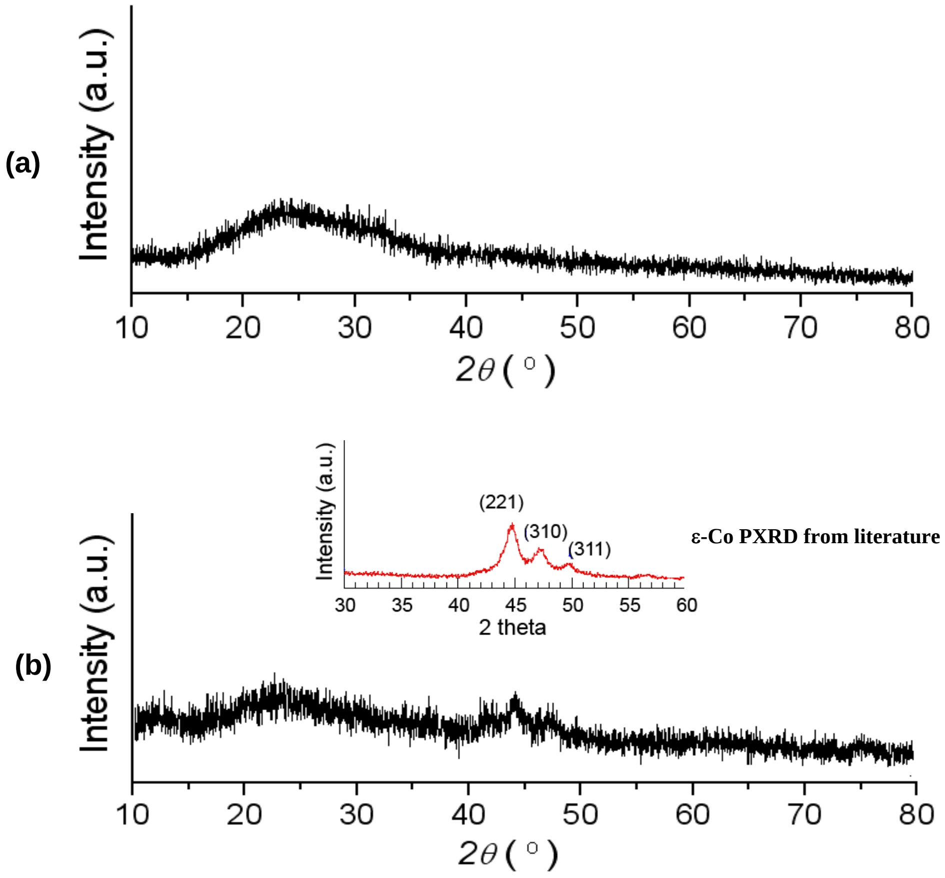

Figure S3. BET analysis for **MON** and **MC-60**.

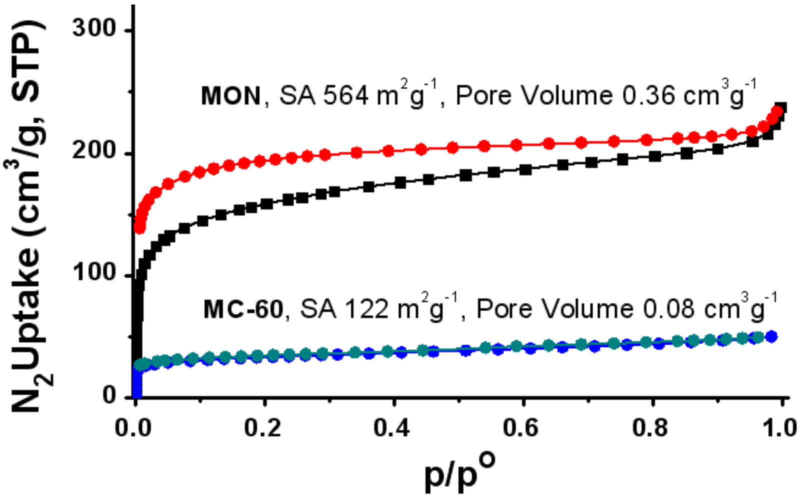

Figure S4. Rate performance (a), charge-discharge profiles (b) and columbic efficiencies (c) of **MC-60**; The first five discharge capacities in (a) correspond to the last five cycles in Figure 4 in text. Then, the discharge capacities with 100, 200, and 500 mA/g were obtained successively.

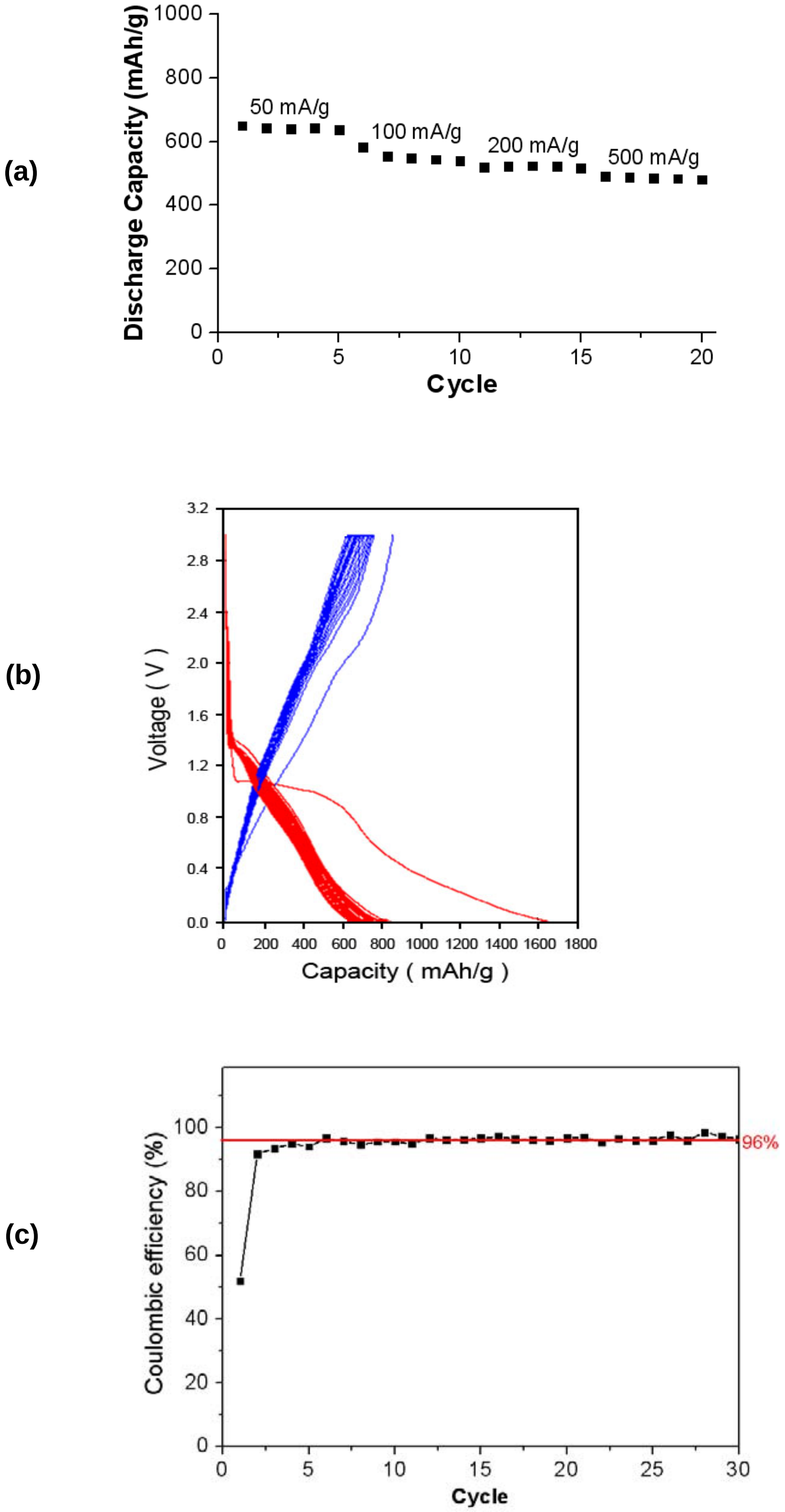

Figure S5. Cell cycle performance (a) and charge-discharge curves (b) of **MON** without Co_3O_4.