

**Electronic Supplementary Information for**  
**Hollow Co@C prepared from Co-ZIF@microporous organic network:**  
**Magnetic adsorbents for aromatic pollutants in water**

SeokJo Hong,<sup>a</sup> Jin Yoo,<sup>a</sup> Nojin Park,<sup>a</sup> Sang Moon Lee,<sup>a</sup> Je-Geun Park,<sup>b</sup> Ji Hoon Park,<sup>c</sup> and Seung Uk Son<sup>\*,a</sup>

<sup>a</sup>Department of Energy Science and Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea

<sup>b</sup>Department of Physics & Astronomy, Seoul National University, Seoul 151-747, Korea

<sup>c</sup>Korea Research Institute of Chemical Technology, Daejeon 305-600, Korea

**Experimental Sections**

SEM images were obtained using a FE-SEM (JSM6700F). TEM images were obtained using a JEOL 2100F instrument. N<sub>2</sub> sorption isotherms (77 K) were measured using a BELSORP II-mini equipment. For pore size analysis, the DFT method was applied. PXRD patterns were obtained using a Rigaku MAX-2200 which was operated with filtered Cu-K $\alpha$  radiation. Solid phase <sup>13</sup>C-NMR spectra were obtained on a Bruker 400 MHz Solid State DSX NMR spectrometer at the Korea Basic Science Institute (Seoul, South Korea). Elemental analysis was performed using a CE EA1110 elemental analyzer. Magnetic properties were measured using a Quantum Design MPMS XL SQUID magnetometer. UV/vis absorption spectra were obtained with a JASCO V-630.

**Synthetic procedure for ZIF-67 particles**

ZIF-67 nanoparticles were prepared by the synthetic procedure in the literature. (J. Shao *et al.* *J. Mater. Chem. A*, 2014, **2**, 12194-12200.) Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.87 g, 3.0 mmol) and 2-methylimidazole (0.99 g, 12 mmol) were dissolved in methanol (30 mL), separately. The cobalt solution was added to 2-methylimidazole solution. The reaction mixture was left without stirring for 24 hours at room temperature. Deep purple ZIF-67 nanoparticles with a ~560 nm diameter were separated by centrifugation, washed with methanol four times, and dried under vacuum.

**Synthetic procedure for ZIF-67@MON and hollow MON**

In a flame-dried 100 mL Schlenk flask, ZIF-67 (0.18 g) was added to a mixture of triethylamine (20 mL) and methanol (10 mL). After Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (6.3 mg, 9.0  $\mu$ mol) and CuI (2.0 mg, 11  $\mu$ mol) were added, the reaction mixture was sonicated for 5 minutes and stirred for 30 minutes at room temperature. Tetrakis(4-ethynyl phenyl)methane (40 mg, 0.096 mmol) and 1,4-diiodobenzene (63 mg, 0.19 mmol) were added. The reaction mixture was heated at 80 °C for 24 hours. After being cooled to room temperature, precipitates were retrieved by centrifugation, washed with methanol, methylene chloride, and acetone, and dried under vacuum. The resultant ZIF-67@MON was used as precursor materials for Co@C-600-2. For the preparation of precursor materials for Co@C-600-1, tetrakis(4-ethynylphenyl)methane (20 mg, 0.048 mmol) and 1,4-diiodobenzene (32 mg, 0.096 mmol) were used. For the preparation of precursor materials for Co@C-600-3, tetrakis(4-ethynylphenyl)methane (60 mg, 0.14 mmol) and 1,4-diiodobenzene (95 mg, 0.29 mmol) were used.

For the preparation of hollow MON, ZIF-67@MON was treated with acetic acid solution (99.5% solution, 30ml) for 1 hour at room temperature. After inner ZIF-67 was completely etched, the resultant hollow MON materials were separated by centrifugation, washed with water, methanol, and acetone, and dried under vacuum.

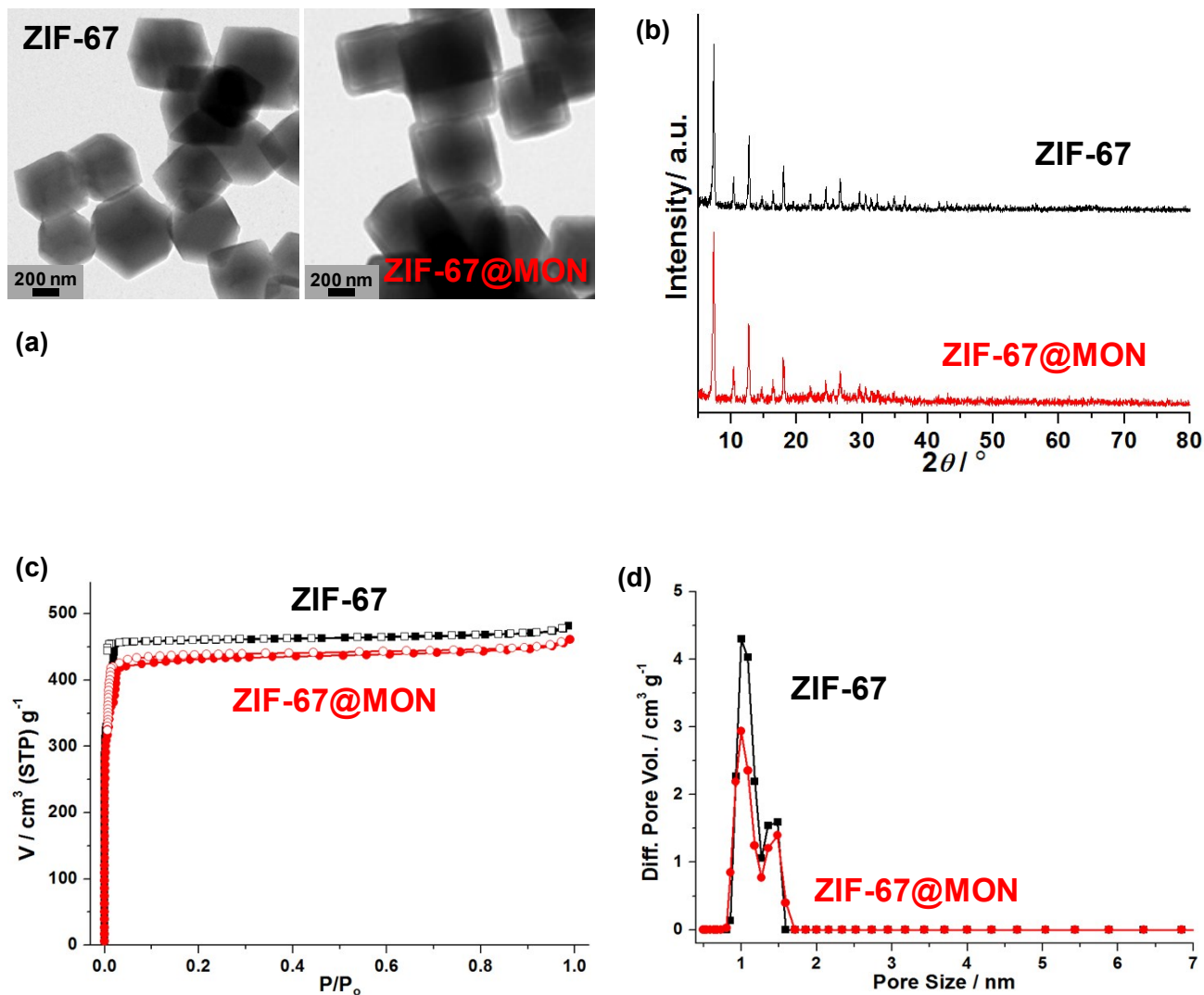
### ***Synthetic procedure for Co@C and Co-C materials***

Co@C-500, Co@C-600, and Co@C-700 were prepared by the heat-treatment of ZIF-67@MON for 3 hours under argon at 500°C, 600°C, and 700°C, respectively. For the preparation of control materials (Co-C), ZIF-67 nanoparticles without MON coating were heated at 600 °C for 3 hours under argon.

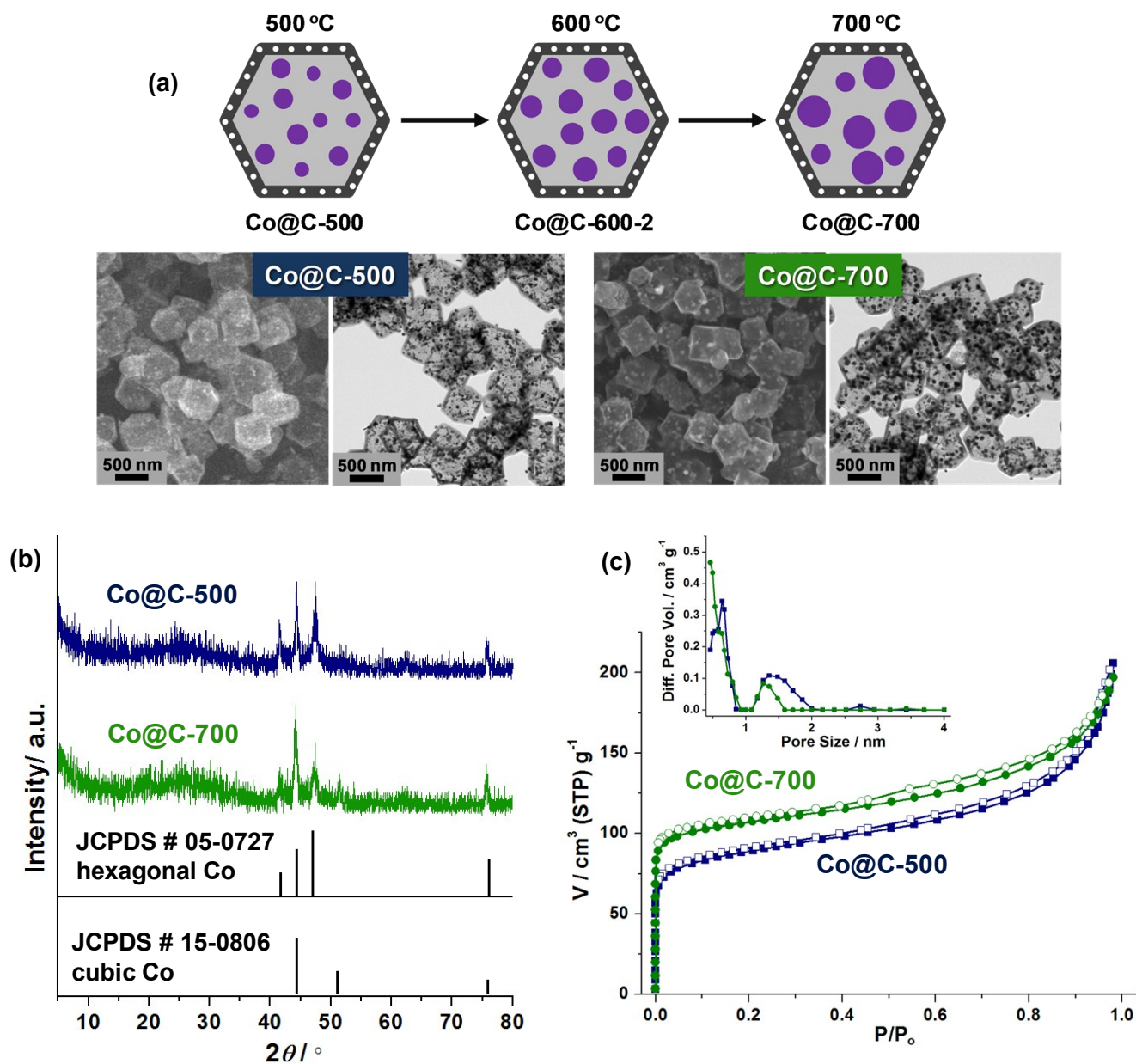
### ***Procedure for batch adsorption tests***

Calibration curves of the concentration of adsorbates versus the intensity of UV/vis absorption were obtained for the calculation of adsorbate concentration in water. For adsorption studies displayed in Fig. 4a and b in text, adsorbents (20 mg) were added to adsorbate solution (30 mL, 100 mg/L). After samples were taken in each adsorption time, adsorbents in samples were removed by magnetic separation. The concentration of the adsorbates remained in water was measured by UV/vis absorption spectroscopy. For phenol, aniline, and 4-nitrobenzene, the intensities of UV/vis absorption peaks at 270 nm, 230 nm, and 268 nm, respectively were used for the calculation of concentration.  $C_e$  and  $q_e$  values in Fig. 4 and Table 1 are the concentration (mg/L) of adsorbates at equilibrium and the adsorbed quantity (mg/g) at equilibrium, respectively. The  $q_e$  values was calculated by the following equation:  $q_e = [(C_0 - C_e) \times V] / m$ ,  $V$ : volume of solution,  $m$ : mass of adsorbent,  $C_0$ : initial concentration. For obtaining the Langmuir isotherm and the Freundlich isotherm parameters in Table 1 and Fig. 4, the following equations and corresponding plotting were applied, respectively;  $C_e / q_e = 1 / [q_{\max} K_L] + C_e / q_{\max}$  for Langmuir isotherm,  $q_{\max}$  (mg/g): monolayer adsorption capacity,  $K_L$  (L/mg): Langmuir isotherm constant,  $\log q_e = \log K_F + (1/n) \log C_e$  (Freundlich isotherm),  $K_F$  (mg/g): Freundlich isotherm constant,  $n$ : adsorption intensity. For reuse experiments, the adsorbents separated using a magnetic bar were washed by stirring in acetone (30 mL), ethanol (30 mL), and methanol (30 mL $\times$ 2) for 30 min each. The adsorbents dried under vacuum were used for the next runs.

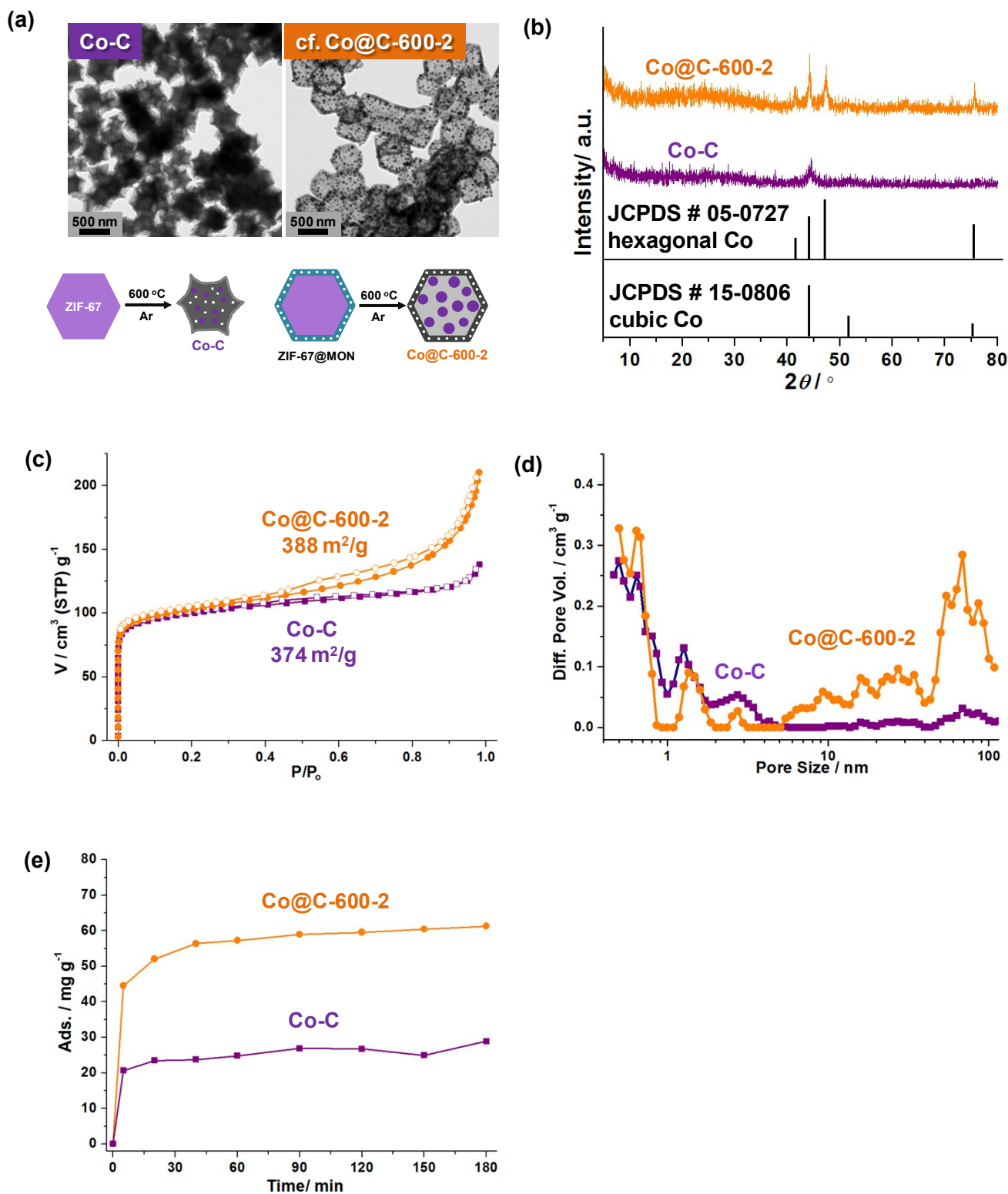
**Fig. S1** Characterization of ZIF-67 and ZIF-67@MON: (a) TEM images; (b) PXRD patterns; (c) N<sub>2</sub> adsorption-desorption isotherm curves at 77K; (d) pore size distribution diagram based on the DFT method.



**Fig. S2** Characterization of Co@C-500 and Co@C-700 (For the characterization data of Co@C-600, refer to Figs. 2-3 in text: (a) Illustration, SEM, and TEM images; (b) PXRD patterns; (c) N<sub>2</sub> adsorption-desorption isotherm curves at 77K and pore size distribution diagram based on the DFT method.

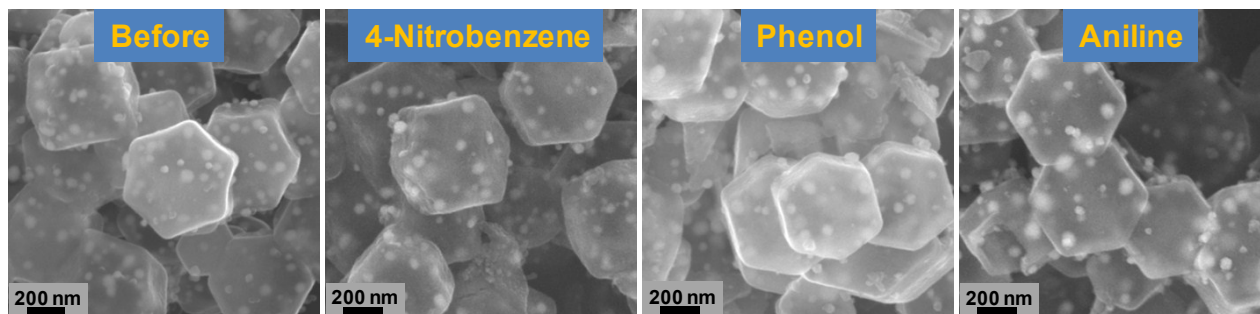


**Fig. S3** Characterization of Co-C control materials obtained by the thermolysis of ZIF-67 without MON coating at 600 °C: (a) Illustration, SEM, and TEM images; (b) PXRD patterns; (c) N<sub>2</sub> adsorption-desorption isotherm curves at 77K; (d) pore size distribution diagram based on the DFT method; (e) phenol adsorption (C<sub>0</sub>: 100 mg/L).

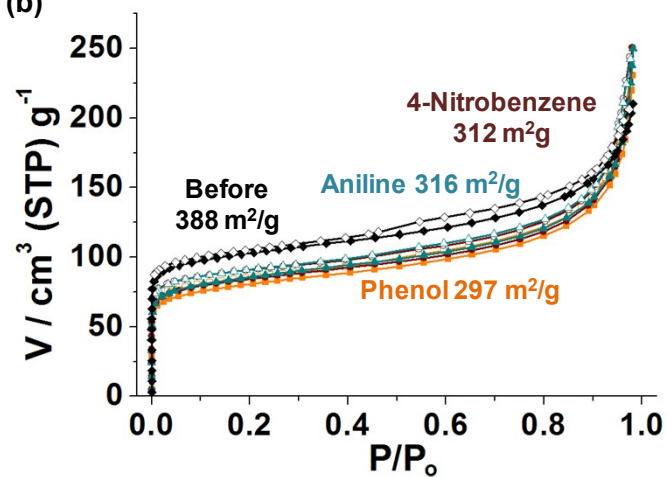


**Fig. S4** Characterization of Co@C-600-2 recovered via magnetic separation after five adsorption processes: (a) SEM images; (b) N<sub>2</sub> adsorption-desorption isotherm curves at 77K; (c) PXRD patterns.

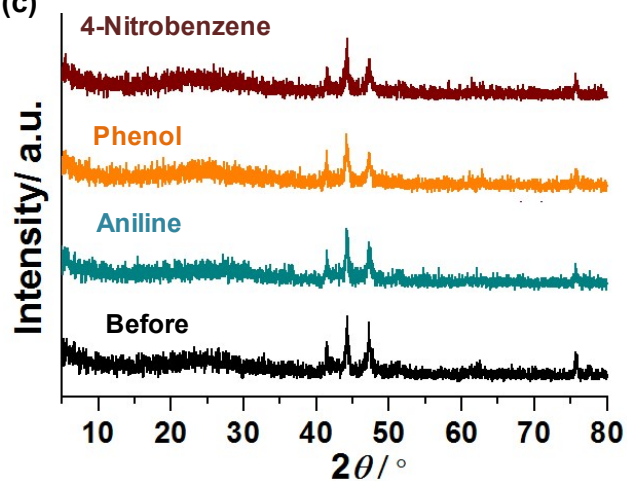
(a)



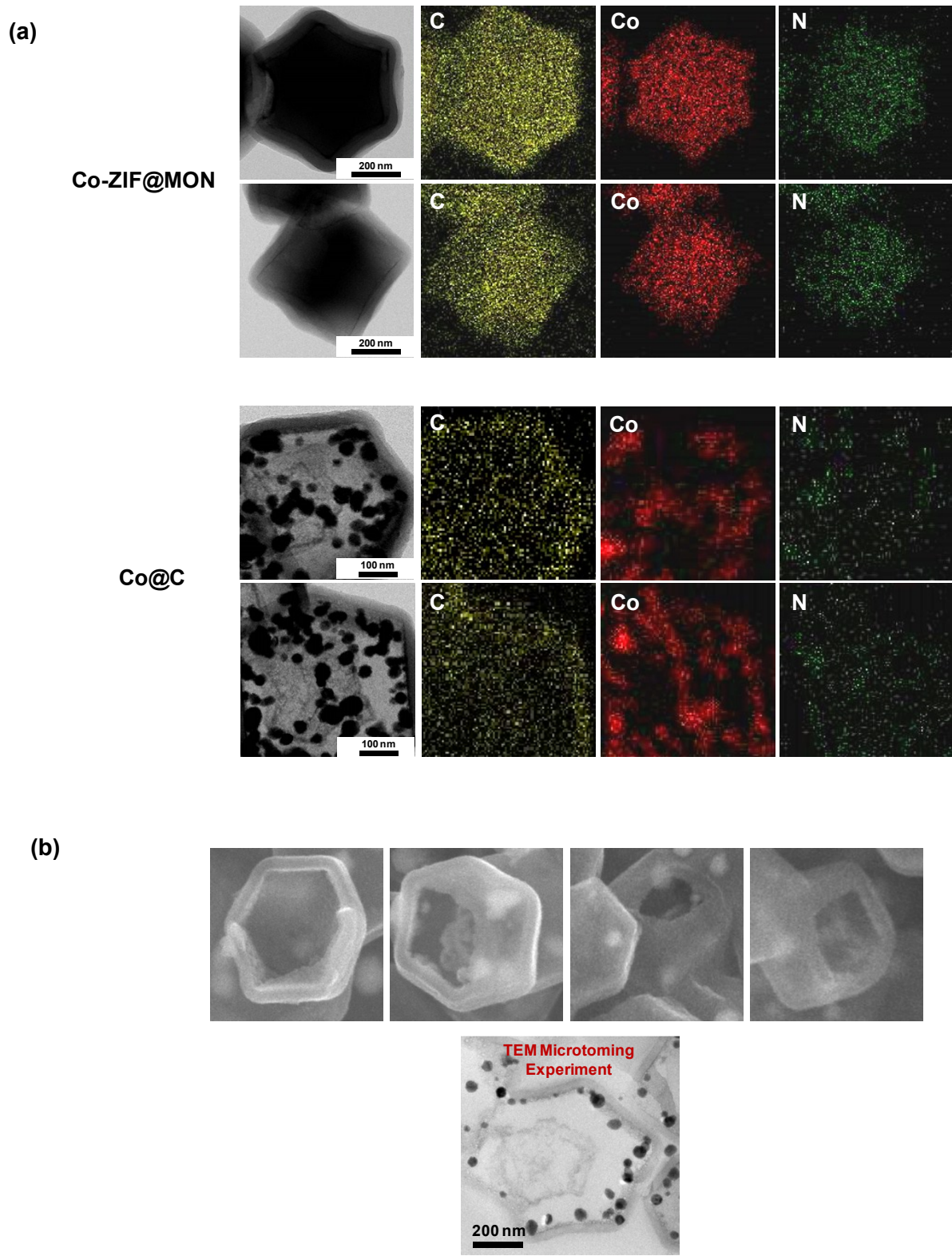
(b)



(c)

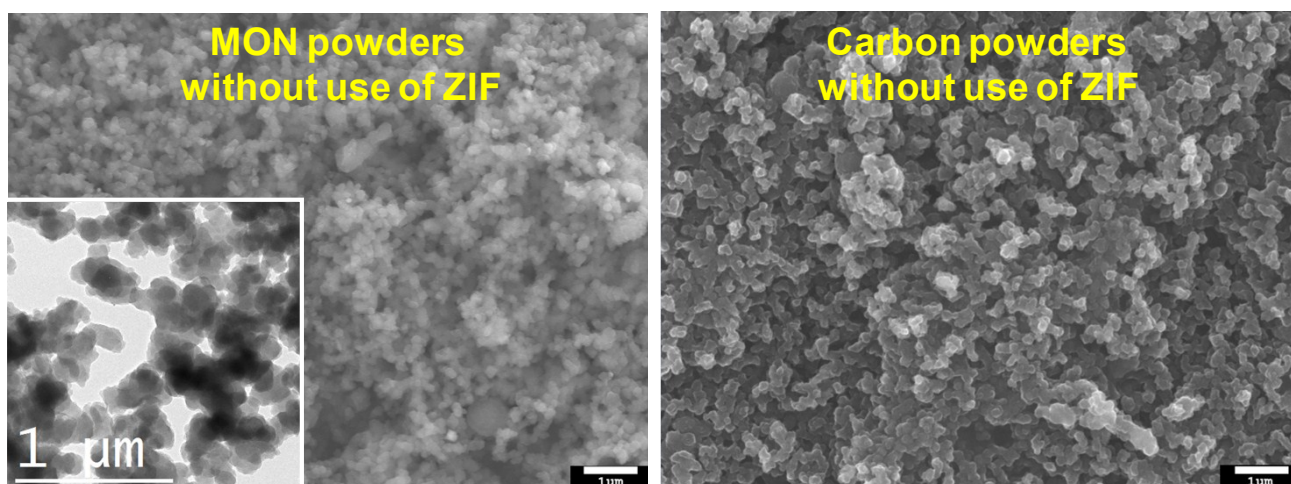


**Fig. S5** (a) EDS elemental mapping images of ZIF-67@MON and Co@C-600-2; (b) SEM images of partially broken Co@C-600-2 and TEM images of cross section of Co@C-600-2 obtained via microtoming technique.

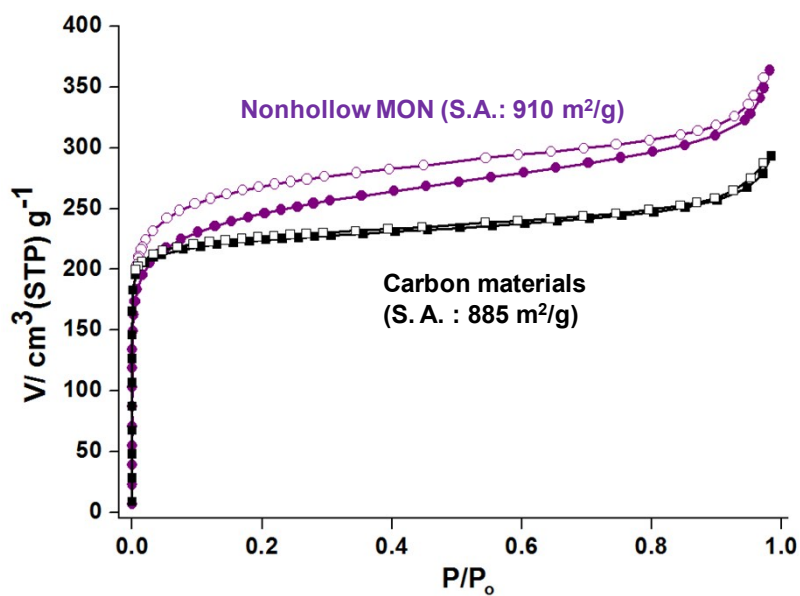


**Fig. S6** Characterization data of nonhollow MON powders and carbon materials (carbonization temperature: 600°C) obtained without use of ZIF templates: (a) SEM and TEM images; (b) N<sub>2</sub> adsorption-desorption isotherm curves at 77K.

(a)



(b)





**Fig. S7** (a) XPS analysis of N 1s orbital and (b) Raman spectra of Co@C-600-2.

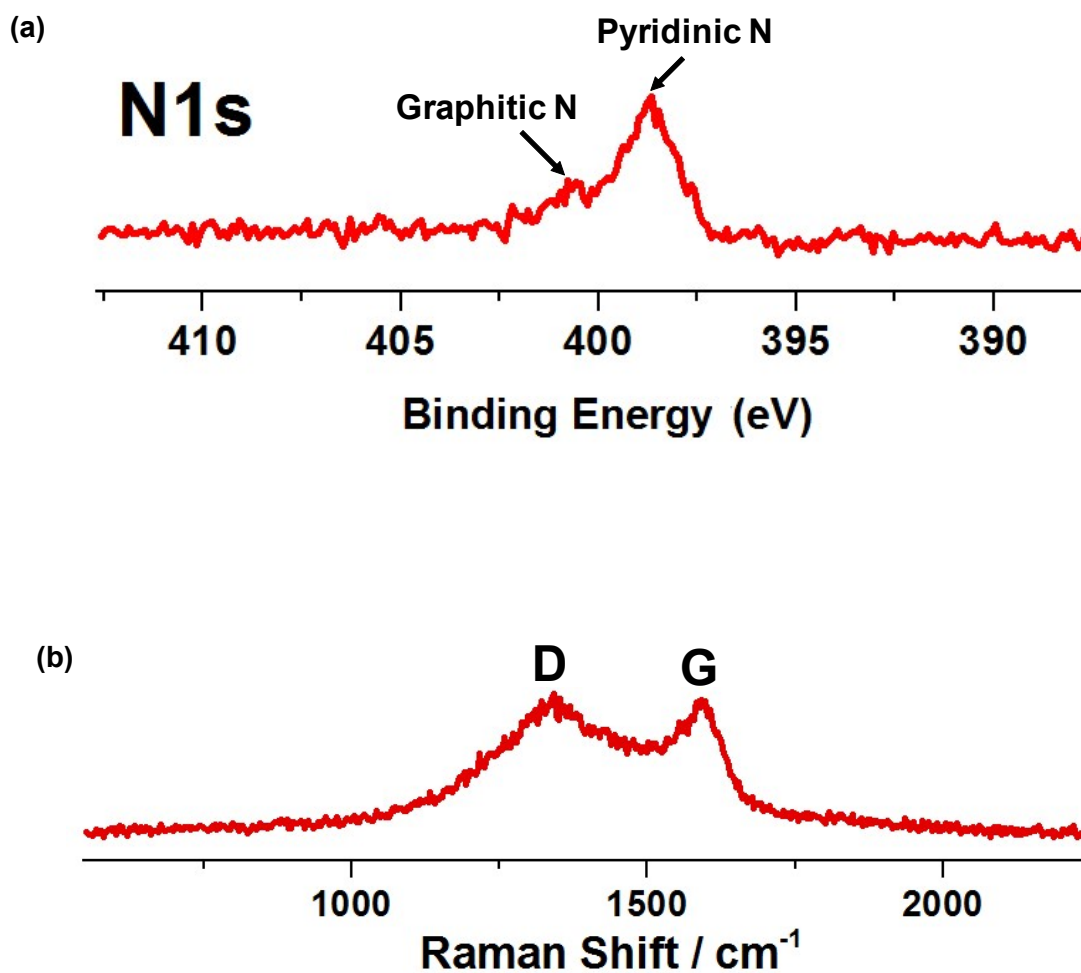
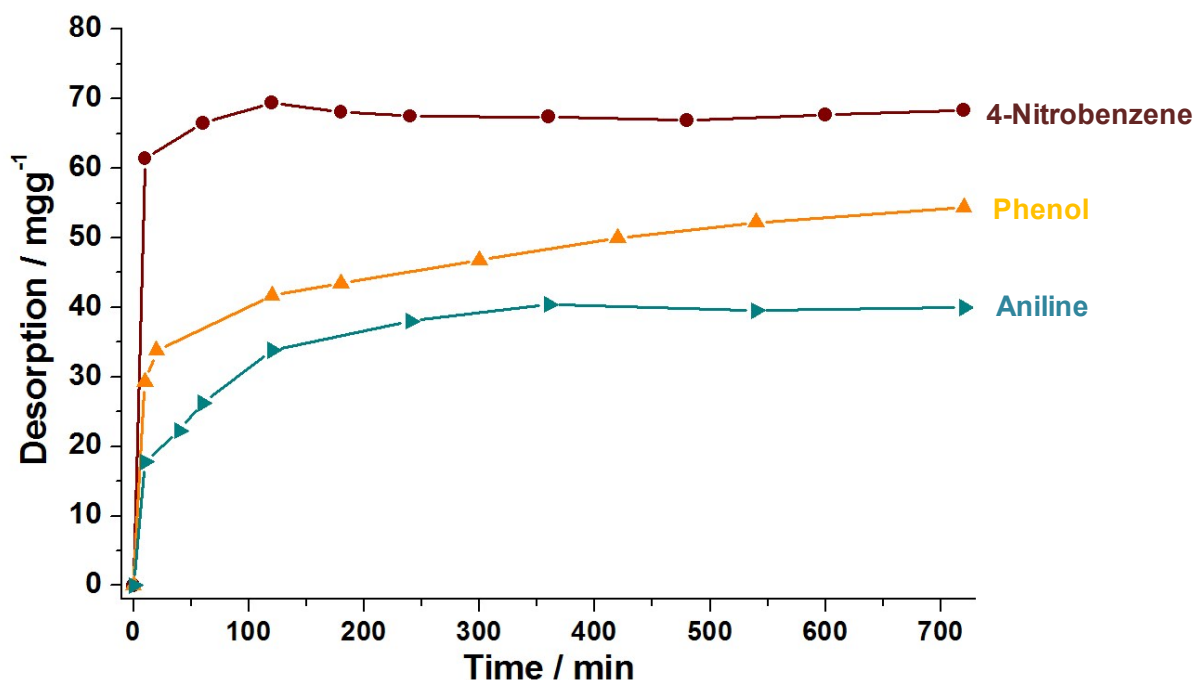


Fig. S8 Desorption behaviors of Co@C-600-2 in ethanol.



We conducted desorption branch experiment in ethanol (60 mL) using adsorbed materials (The 40 mg of Co@C-600-2 was used for adsorption.) in which the adsorbate-dependent desorption equilibrium behavior was observed. 4-Nitrobenzene showed fast desorption and reached equilibrium clearly, which implies the relatively weak interaction of adsorbate with adsorbent. Aniline showed relatively slow desorption and reached equilibrium clearly, which is attributable to the interaction of adsorbate with cobalt particles. Phenol showed fast desorption in early stage and very slow desorption followed. The slow desorption behavior is attributable to the chemical reactivity of carbon adsorbents with phenols as commented in the literature (ref. 17 in the text). This desorption behavior of phenol can be related to relatively poor recycle performance of adsorbents toward phenols.

**Table S1.** Adsorption parameters (at 298K) of Co@C-600-2 toward 4-nitrobenzene, phenol, and aniline based on Langmuir and Freundlich isotherm models.

Parameters	Adsorbates		
	4-nitrobenzene	phenol	aniline
<b>Langmuir constants<sup>a</sup></b>			
$q_{\max}$ (mg/g)	87.2	75.6	56.7
$K_L$ (L/mg)	0.28	0.044	0.032
$R^2$	0.99	0.99	0.99
<b>Freundlich constants<sup>b</sup></b>			
$K_F$ (mg/g)	55.9	11.3	6.2
n	10.7	2.6	2.3
$R^2$	0.96	0.96	0.77

<sup>a</sup>The values were obtained by the equation,  $C_e/q_e = 1/(q_{\max}K_L) + C_e/q_{\max}$ .  $C_e$ : equilibrium concentration of adsorbates in solution,  $q_e$ : adsorption capacity at equilibrium,  $q_{\max}$ : maximum adsorption capacity,  $K_L$ : Langmuir constant. <sup>b</sup>The values were obtained by the equation,  $\log q_e = (1/n) \log C_e + \log K_F$ .  $C_e$ : equilibrium concentration of adsorbates in solution,  $q_e$ : adsorption capacity at equilibrium,  $K_F$ : Freundlich isotherm constant, n: adsorption intensity.