Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supplementary Information for
Microporous organic networking and calcination on Fe_3O_4 nanospheres for enhanced anode performances in lithium ion batteries

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Experimental Sections

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were conducted using a FE-SEM (JSM6700F) and a JEOL 2100F unit. The adsorption-desorption isotherms for N_2 (77 K) were recorded using the BELSORP II-mini volumetric adsorption equipment. Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku MAX-2200. The solid phase ^{13}C-NMR spectrum was obtained on a Bruker 400 MHz DSX NMR spectrometer at the Korea Basic Science Institute (Daegu). The thermogravimetic analysis (TGA) curve was obtained by Seiko Exstar 7300. Elemental analysis was performed on a CE EA1110 instrument.

Preparation of bare Fe_3O_4 nanospheres

Bare Fe_3O_4 nanospheres were prepared by the modified method described in the literature (J. Ge, Y. Hu, M. Maurizio, W. P. Beyermann and Y. Yin, *Angew. Chem. Int. Ed.* 2007, **46**, 4342). In a 50 mL Schlenk flask, $FeCl_3 \cdot 6H_2O$ (0.54 g, 2.0 mmol) and NaOAc (1.5 g, 18 mmol) were added to a mixture of ethylene glycol (5 mL, EG) and diethylene glycol (15 mL, DEG, a polyhydric alcohol with a boiling point of 244–245°C). The solution was vigorously stirred for 30 min. The resultant gel like solution was transferred to a Teflon container in an 80 mL autoclave. The autoclave was heated at 200°C for 10 hours. After cooling to room temperature, the black solution was poured into a Falcon tube. Resultant black precipitates were retrieved by centrifugation, washed with water and ethanol, and dried under vacuum.

Preparation of Fe_3O_4 @MON-10

In a flame-dried 50 mL Schlenk flask, Fe_3O_4 nanospheres (0.10 g), $Pd(PPh_3)_2Cl_2$ (1.7 mg, 2.4 μmol) and CuI (0.50 mg, 2.6 μmol) were dispersed in triethylamine (15 mL) under argon. The mixture was sonicated for 1 hour at room temperature. Tetra(4-ethynyl phenyl)methane (10 mg, 0.024 mmol) and 1,4-diiodobenzene (16 mg, 0.048 mmol) were added. The reaction mixture was heated at 90 °C for 24 hours. After cooling to room temperature, the resultant precipitates were retrieved by centrifugation, washed with acetone, methanol, methylene chloride, and diethylether, and dried under vacuum. For the preparation of Fe_3O_4 @MON-25, tetra(4-ethynyl phenyl)methane (25 mg, 0.060 mmol) and 1,4-diiodobenzene (40 mg, 0.12 mmol) were used with the same synthetic procedure.

Preparation of Fe_3O_4 @C-700, hollow MON and hollow carbon materials

For the preparation of Fe_3O_4@C-700, the Fe_3O_4@MON-10 (0.10 g) was heated at 700°C for 2 hours under argon. For the preparation of Fe_3O_4@C-600 and Fe_3O_4@C-800, the Fe_3O_4@MON-10 (0.10 g) was heated at 600 °C and 800°C, respectively, for 2 hours under argon.

For the preparation of hollow MON, Fe_3O_4@MON-10 (50 mg) was treated with concentrated HCl solution for 45 min. The resultant yellow precipitates were retrieved by centrifugation, washed with water and acetone, and then dried under vacuum. For the preparation of hollow carbon materials, Fe_3O_4@C-700 (50 mg) was treated with concentrated HCl solution (5 mL) for 45 min. The resultant black precipitates were retrieved by centrifugation, washed with water and acetone, and then dried under vacuum.

Fabrication of electrochemical cells

For the preparation of working electrodes, Fe_3O_4@C-700 (80 mg), polyvinylidene fluoride binder (10 mg) and Super P carbon black (10 mg) were well mixed in N-methylpyrrolidone (NMP). Copper foil was then coated with this mixture, dried under a vacuum overnight at 120 °C. The Fe_3O_4@C-700 coated copper electrodes were cut into a circular shape with a 1.4 cm diameter. The loading weight of Fe_3O_4@C-700 was calculated as 1.12 mg/cm^2. Electrochemical cells were assembled in a glove box filled with argon. Coin-type half cells (CR2016 type) were used. Li metal was used as the counter electrode. 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1 v/v) was used as the electrolyte. For the electrochemical tests shown in the text in Fig. 4, the coin cells were discharged from an open circuit potential to 1 mV and then, cycled between 1 mV and 3 V with a 50 mAg^{-1} current density. The discharge/charge cycle tests were conducted using a WBCS3000 automatic battery cycler system.

Figure S1. Solid phase ^{13}C NMR (CPMAS-TOSS) spectrum of hollow MON.

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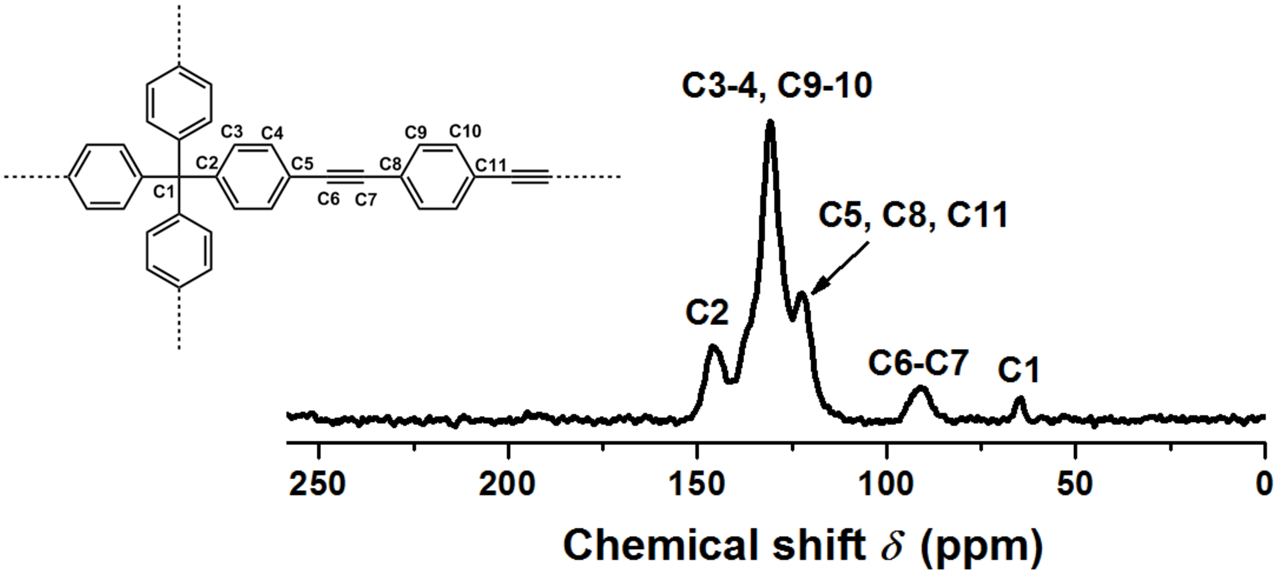


Figure S2. Powder XRD patterns of hollow MON and hollow carbon materials.

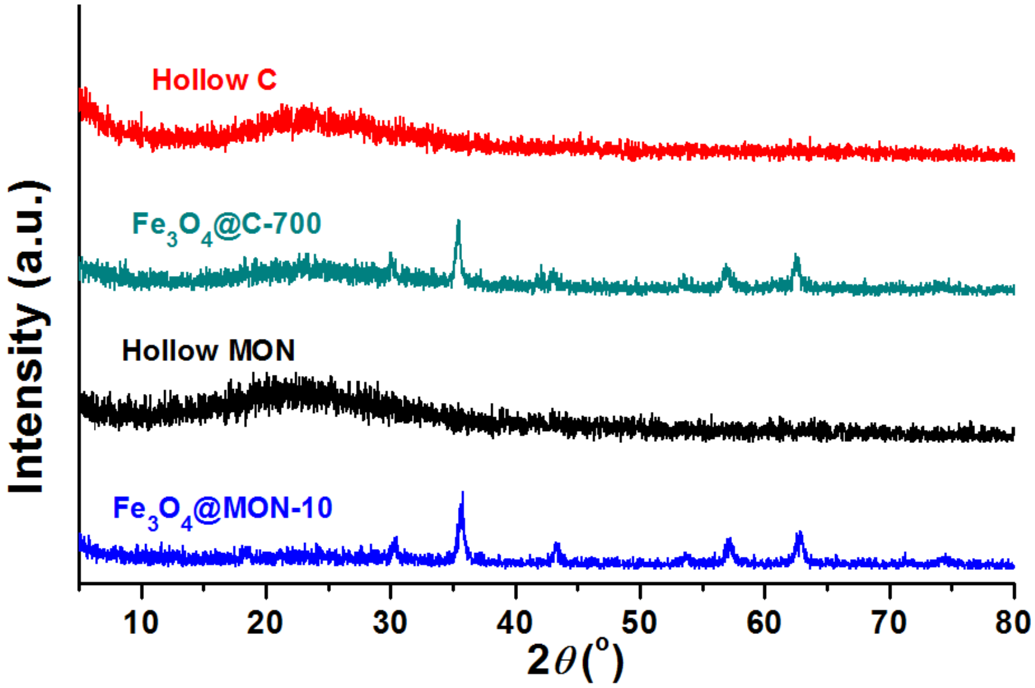


Figure S3. TGA curve of hollow MON under N_2.

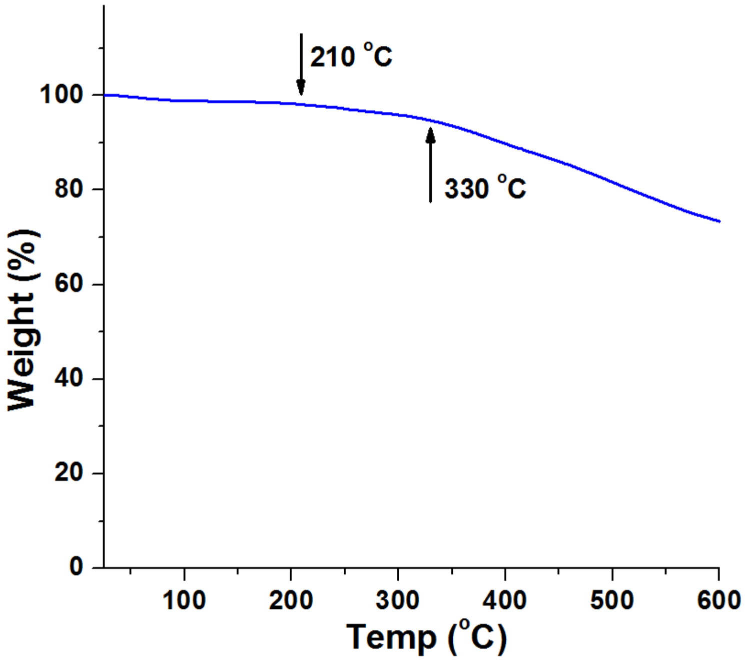


Figure S4. Comparison of cycling performance of Fe_3O_4@C-700 composites prepared by calcination of Fe_3O_4@MON-10 (green line, carbon coating thickness was 4~6 nm) and Fe_3O_4@MON-25 (red line, carbon coating thickness was 15 nm) at 700°C.

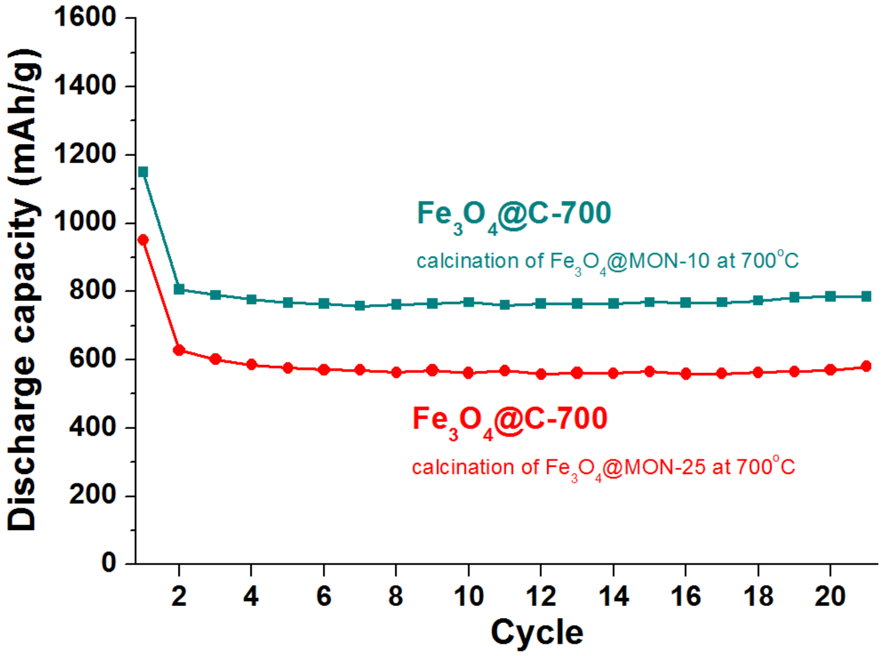


Figure S5. SEM (a-b) and TEM (c-d) images of Fe_3O_4@C-700 after 50 cycles (The materials for SEM studies were obtained through disassembly of electrochemical cell after 50 cycles. Interestingly, as shown in TEM images, nano-porosity of inner iron oxide materials was observed.).

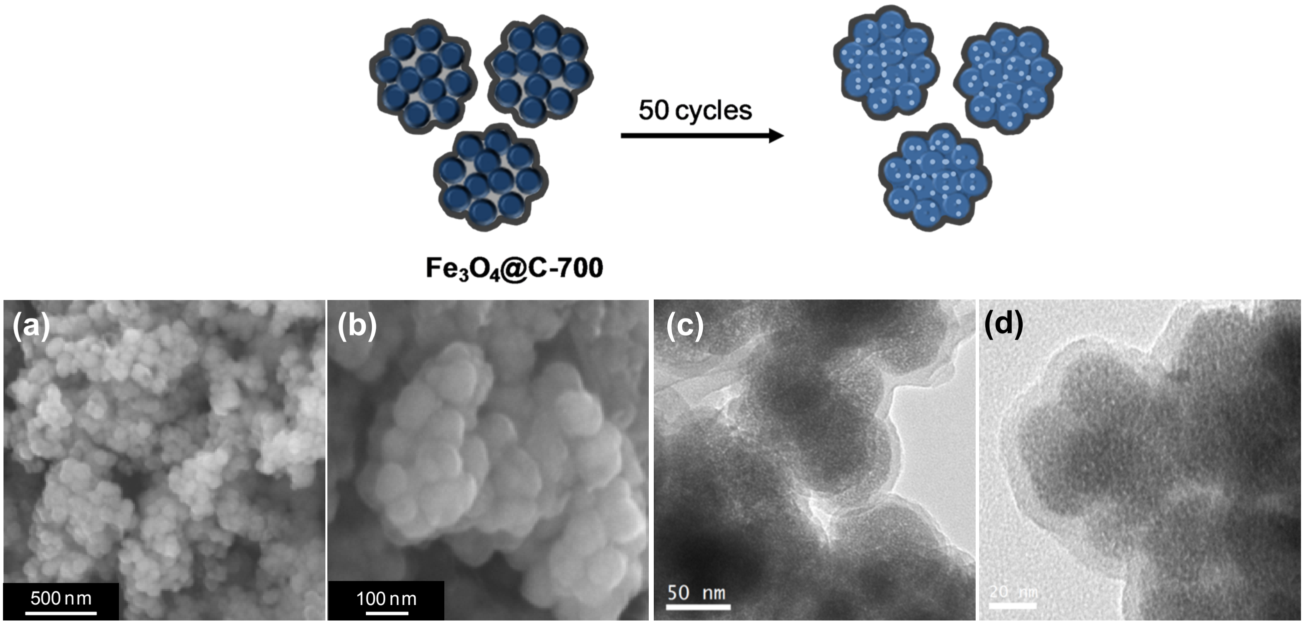


Figure S6. (a) charge/discharge curves of Fe_3O_4@C-700 with a 50 mA/g current density and (b) current density-dependent discharge capacities of Fe_3O_4@C-700.

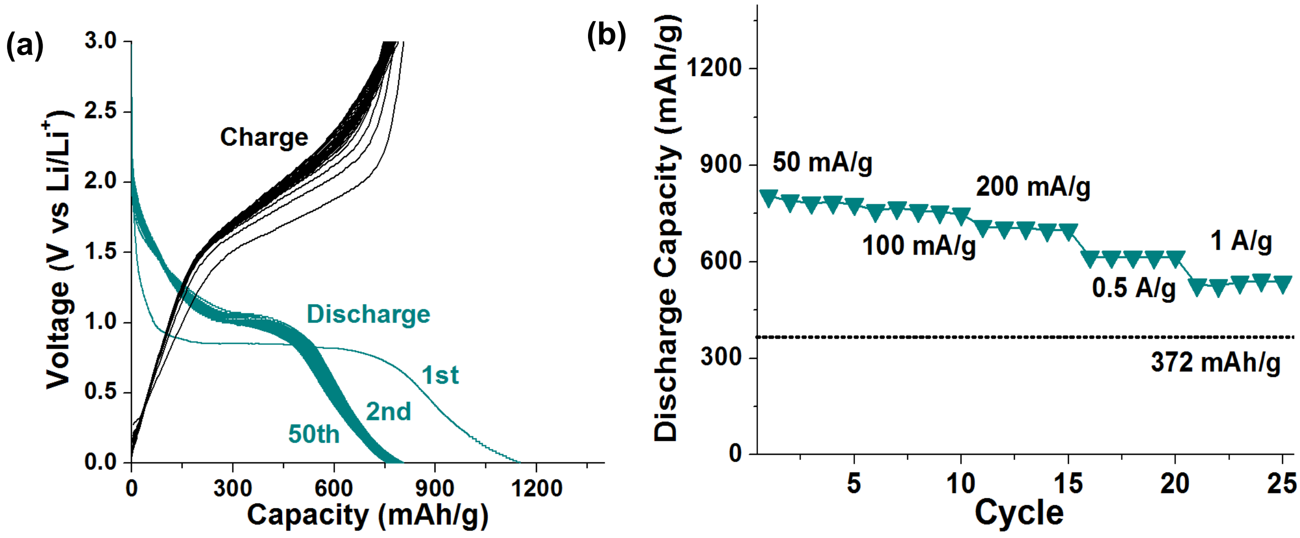
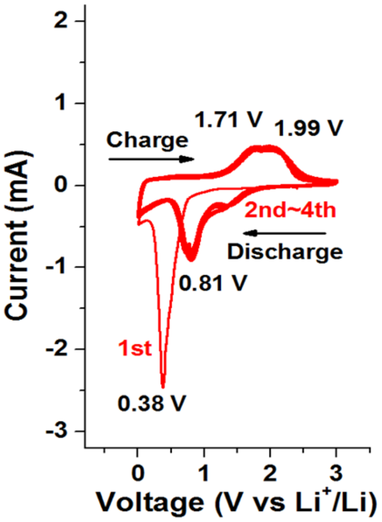
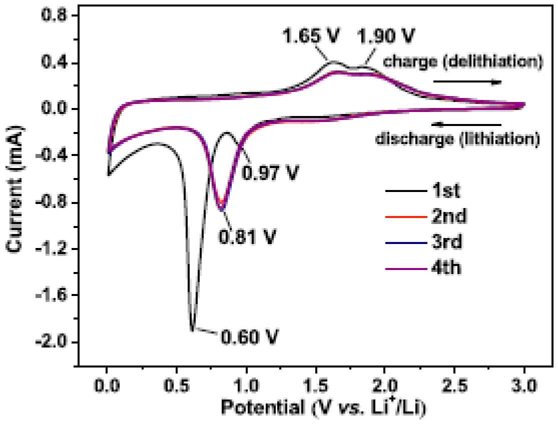


Figure S7. Typical cyclovoltammogram of electrochemical cell (scan rate = 0.1 mV/s) prepared by Fe_3O_4@C-700.





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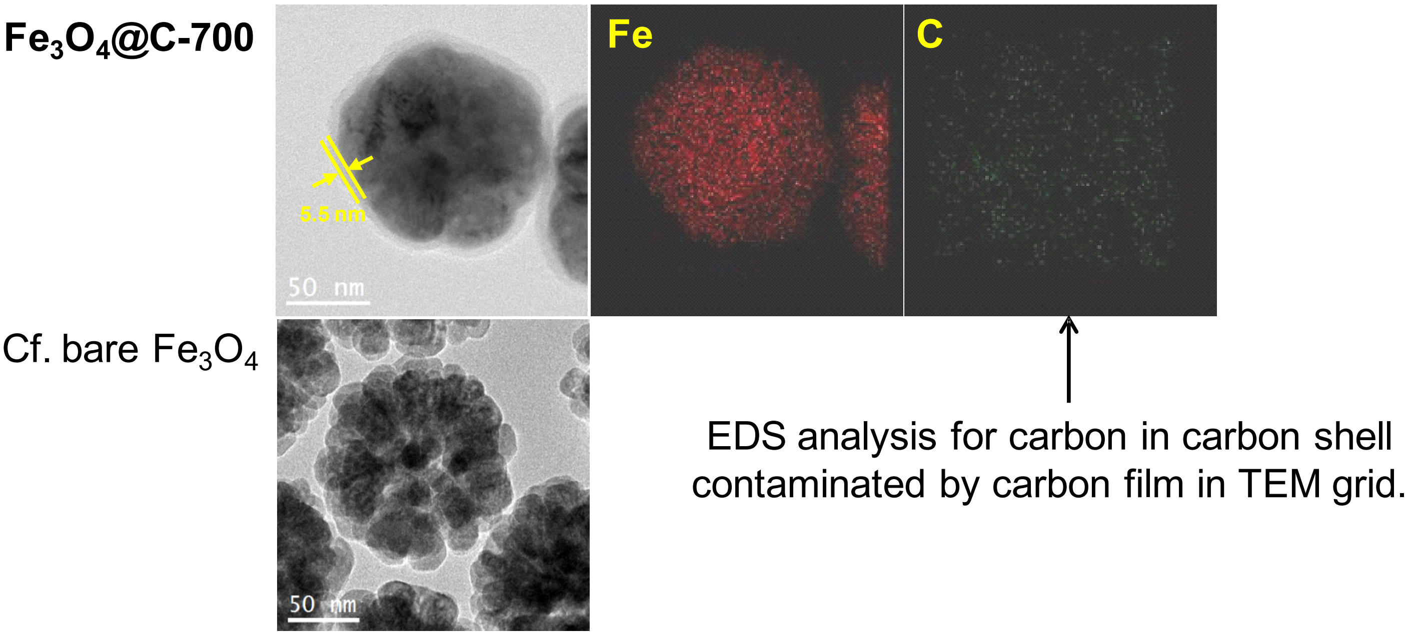
ACS Nano, 2013, **7**, 4459

Figure S8. EDS mapping of Fe_3O_4@C-700.



EDS analysis for carbon in carbon shell contaminated by carbon film in TEM grid.

Figure S9. Pore size distribution (DFT method) of **Fe_3O_4@C-700**.

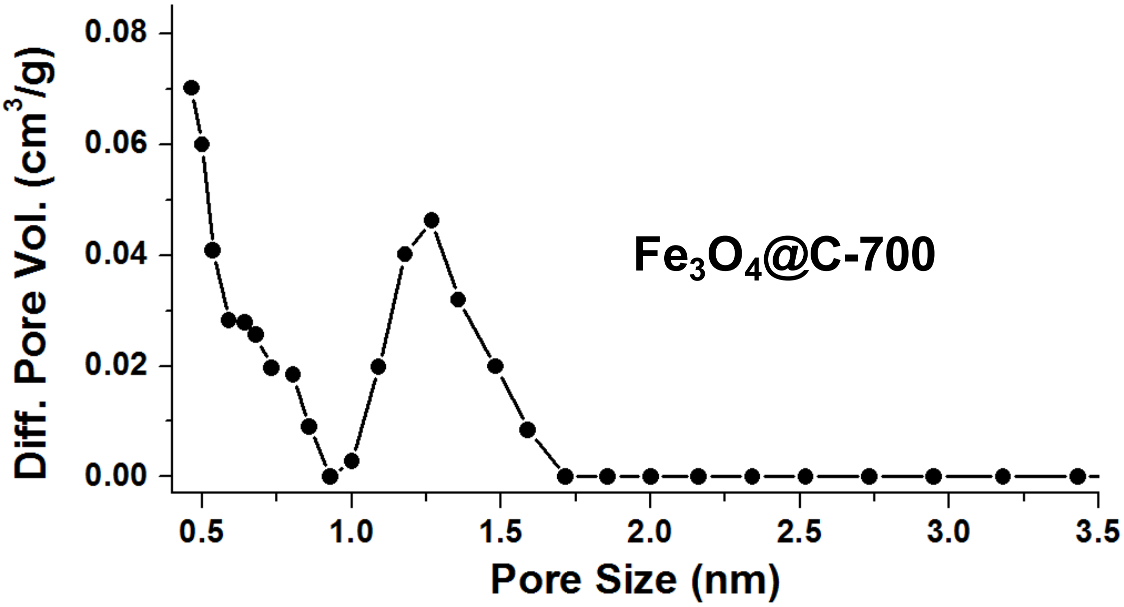


Figure S10. Extended cycling performances of **Fe_3O_4@C-700** at a 5 A/g current density.