Supporting Information

Hetero-Structured Fe-Cr-O Hollow Multishelled Spheres for Stable Sodium Storage

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Experimental Section

Sample Synthesis

The spray drying method is applied to synthesized metal salts/sucrose composite microspheres. Iron (III) citrate ($FeC_6H_5O_7$), chromium (III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$) with different molar ratios (4:0, 3:1, 2:2, 1:3, 0:4) are added into 100 mL 0.1 M sucrose solutions and stirred overnight. The metal salts/sucrose solution is pumped into the spray drying machine with a pump rate of 5% and an inlet temperature of 220 ^oC. The colors of collected power vary from red to green. The Fe-Cr-O HoMS are obtained after the following calcination in air under 400 ^oC for 2h at a ramp rate of 2 $^oC\ min^{-1}$.

Structural and Morphological Characterization

The crystallographic structure information was collected on a Bruker D8 Advance X-ray diffractometer equipped with a Cu Kα radiation source (λ = 0.15418 nm). The microstructure information was obtained using a JEOL-7100F field emission SEM at 15 kV and a JEM-2100F TEM at 200 kV. EDS was collected by an Oxford IE250 system. XPS analysis was carried on a VG Multi Lab 2000. Thermo gravimetric

analysis was performed using a Netzsch STA 449 simultaneous analyzer. Brunauer–Emmett–Teller surface areas were calculated from nitrogen sorption isotherms measured at 77 K using a Tristar II 3020 instrument.

Electrode Fabrication and Electrochemical Measurements

To conduct the electrochemical measurements, 2016 coin cells were assembled in a glove box filled with pure Ar gas. The working electrodes were prepared by mixing 70% active material, 20% acetylene black, and 10% carboxyl methyl cellulose binder, and spreading the slurry onto a copper foil. The electrodes were cut into small wafers with a diameter of 1.0 cm. Na discs were used as both the counter and reference electrodes. The electrolyte was composed of 1.0 M $NaClO_4$ dissolved in a mixture of ethylene carbonate/dimethyl carbonate (1:1 w/w) with 5% fluoroethylene carbonate, and a Whatman glass microfiber filter (Grade GF/A) was used as the separator. Galvanostatic charge/discharge measurements were performed with a multi-channel battery testing system (LAND CT2001A). CV and EIS were recorded with an electrochemical workstation (Bio-Logic VMP3).

Table S1. The preparation parameters for the synthesis of Fe-Cr-O HoMS with different Fe/Cr molar ratios.

Samples	Chromic nitrate nonahydrate (mmol)	Iron citrate (mmol)	Sucrose (mmol)	Deionized water (mL)
Fe-Cr-O-4/0 or Fe_2O_3	0	10	10	100
Fe-Cr-O-3/1	2.5	7.5	10	100
Fe-Cr-O-2/2	5	5	10	100
Fe-Cr-O-1/3	7.5	2.5	10	100
Fe-Cr-O-0/4 or Cr_2O_3	10	0	10	100

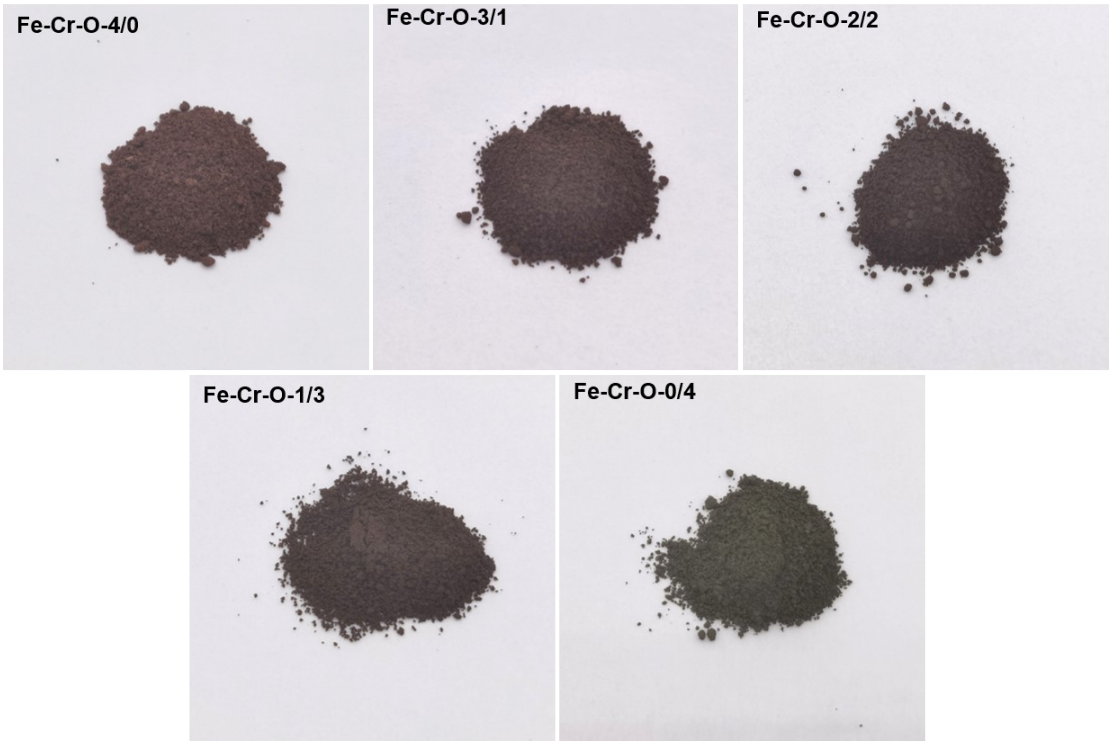

Figure S1. Digital photos showing the color of Fe-Cr-O HoMS with different Fe/Cr molar ratios.

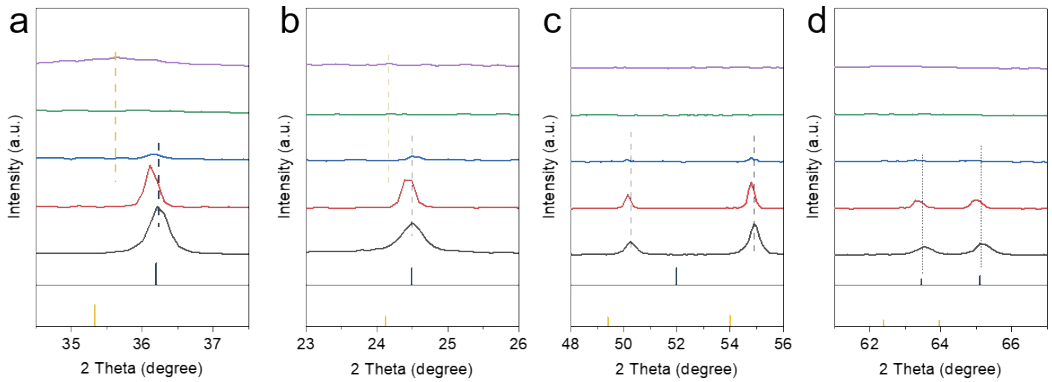

Figure S2. Magnified XRD patterns of the Fe-Cr-O HoMS with various Fe/Cr molar ratios.

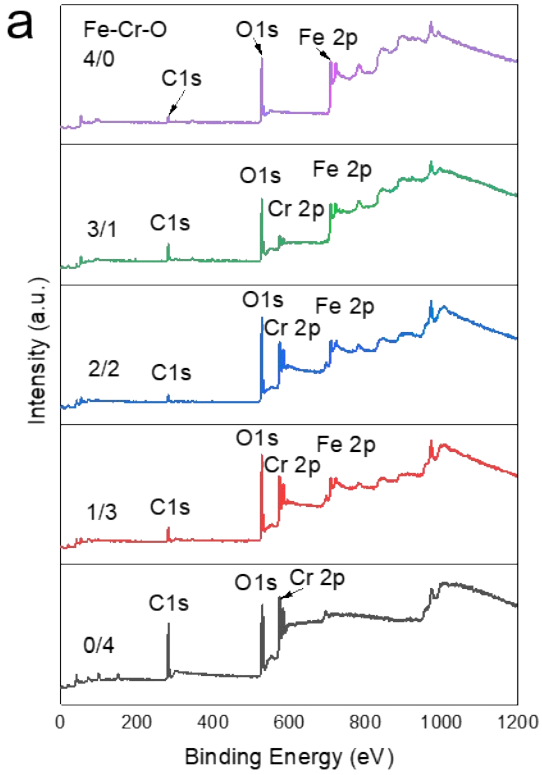

Figure S3. XPS survey spectra of the Fe-Cr-O HoMS with the variation of Fe/Cr molar ratio.

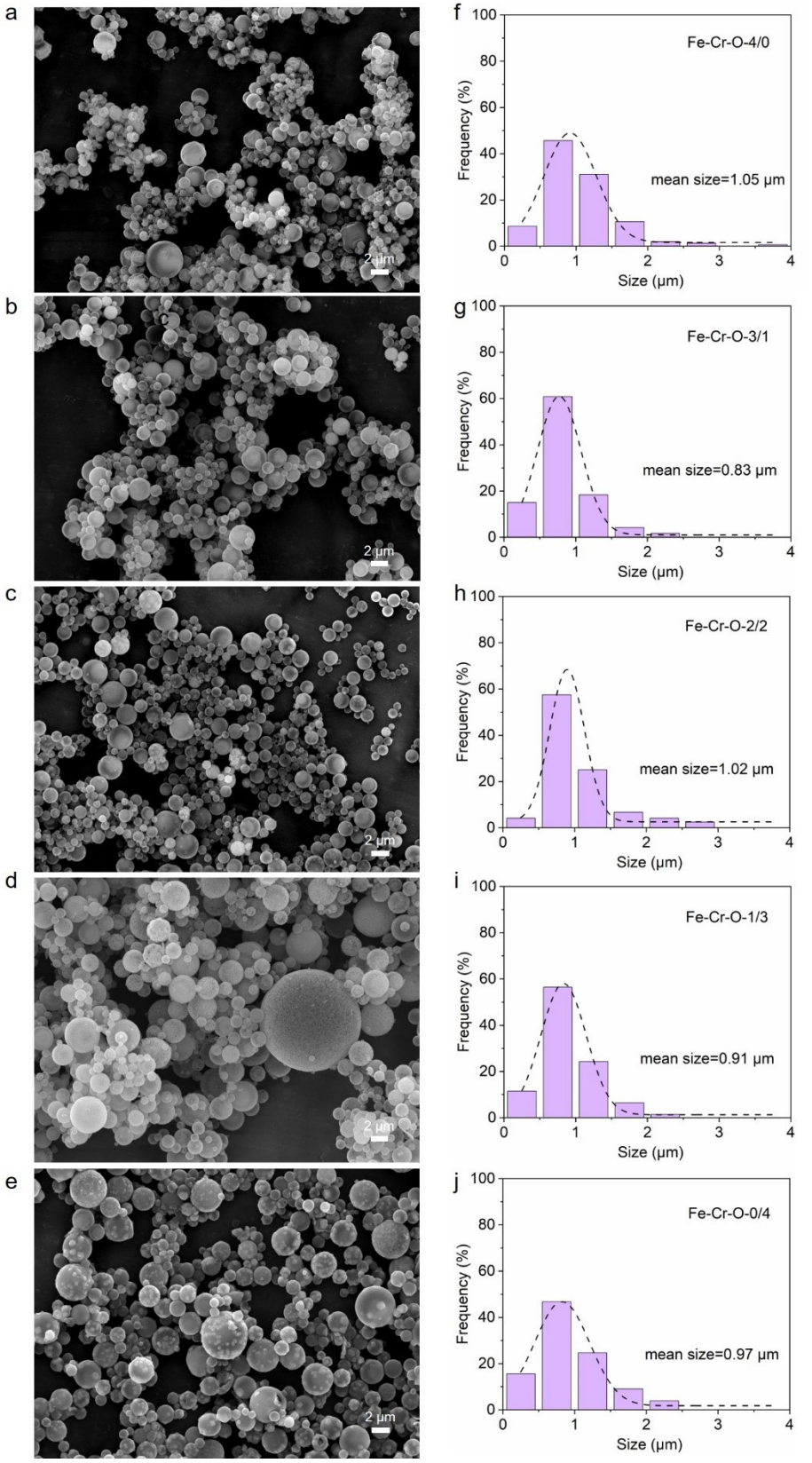

Figure S4. (a)-(e) The SEM images of the Fe-Cr-O HoMS and (f)-(j) the corresponding particle size distribution histograms (100 particles total for each sample).

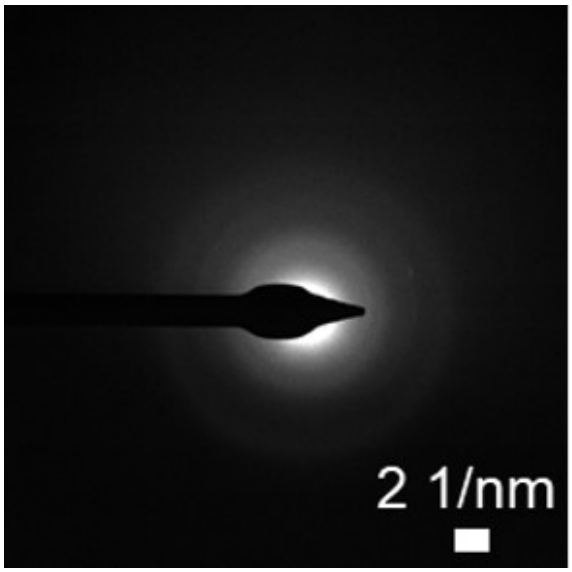

Figure S5. SAED patterns of Fe-Cr-O-3/1.

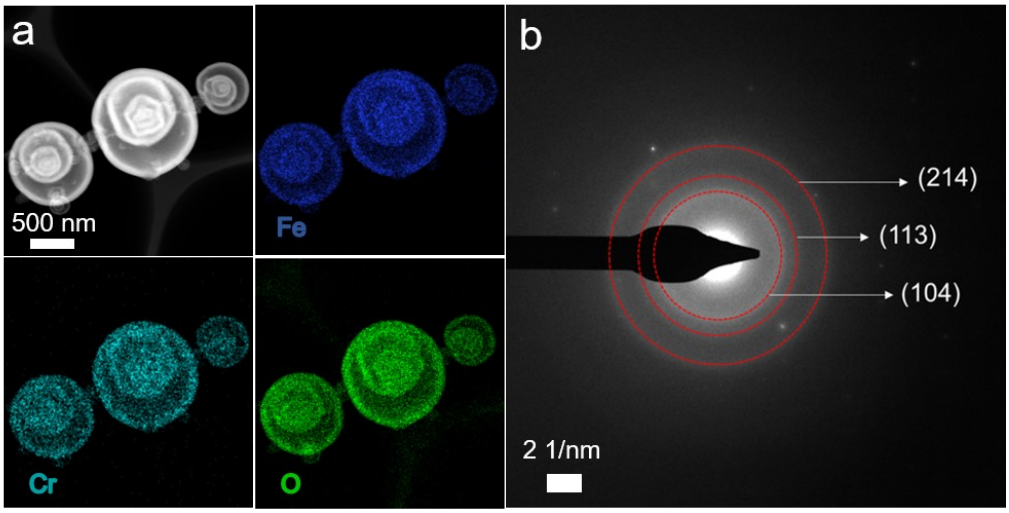

Figure S6. (a) HAADF-STEM images and EDS elemental mappings, (b) SAED patterns of Fe-Cr-O-2/2.

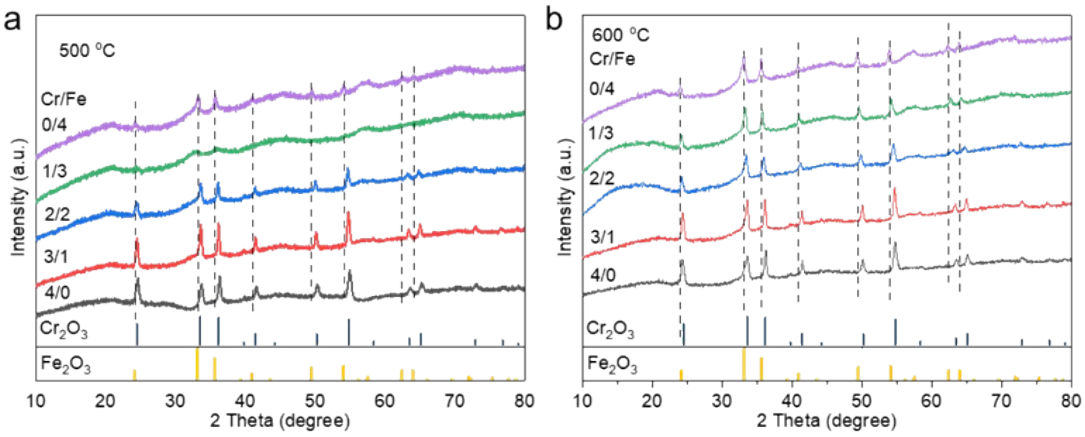

Figure S7. XRD patterns of the Fe-Cr-O HoMS prepared at (a) 500 °C, (b) 600 °C.

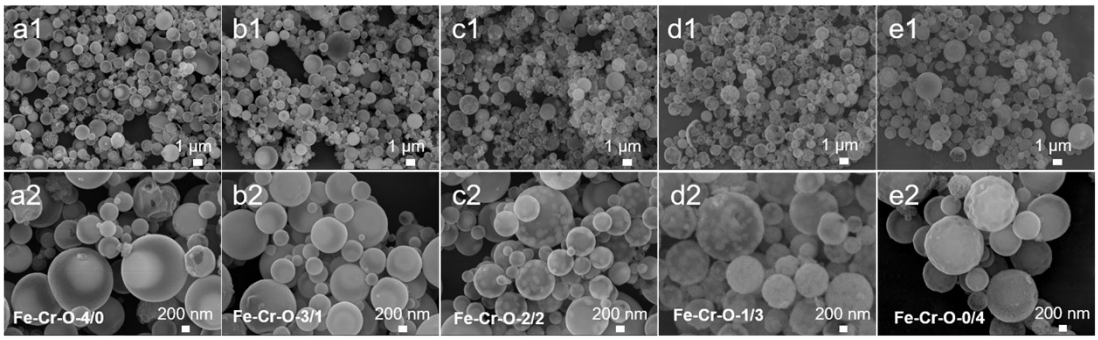

Figure S8. SEM images of the Fe-Cr-O HoMS prepared at 500 °C with the variation of Fe/Cr molar ratio from 4/0 to 0/4.

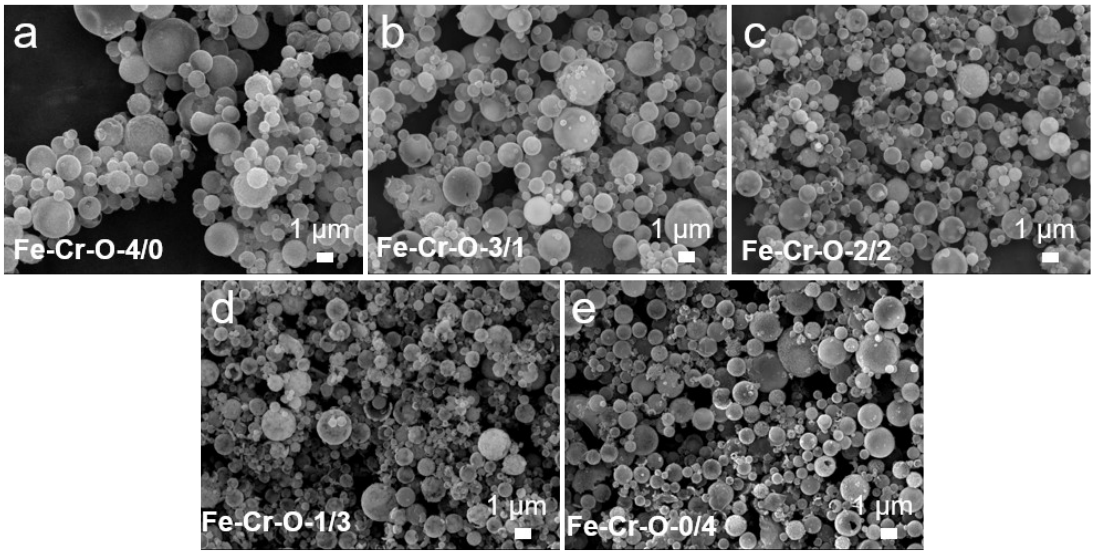

Figure S9. SEM images of the Fe-Cr-O HoMS prepared at 600 °C with the variation of Fe/Cr molar ratio from 4/0 to 0/4.

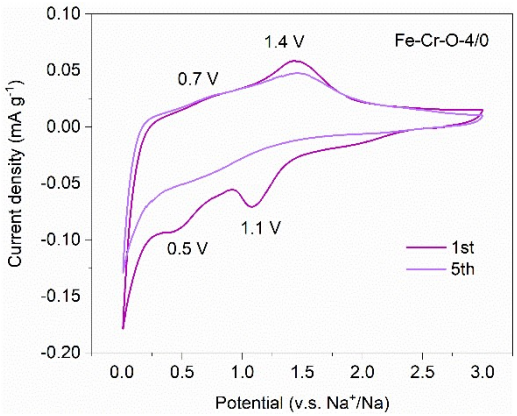

Figure S10. CV curves of Fe-Cr-O-4/0 HoMS.

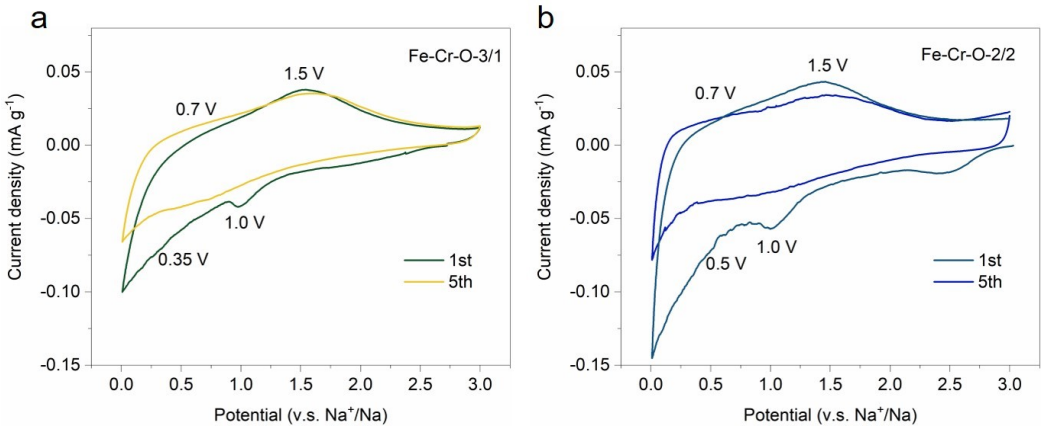

Figure S11. CV curves of (a) Fe-Cr-O-3/1 and (b) Fe-Cr-O-2/2 HoMS.

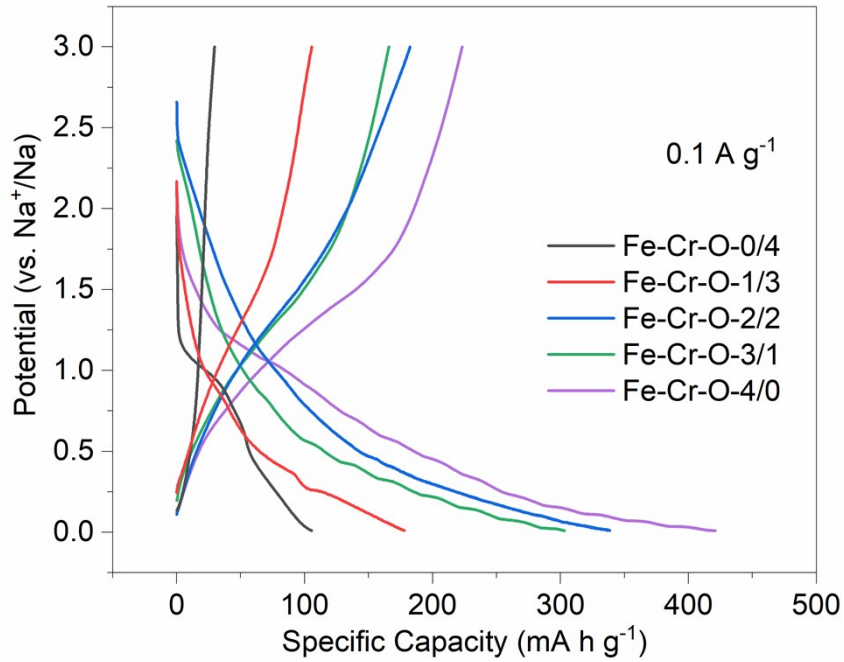

Figure S12. Discharge/charge curves at 0.1 A g^{-1} for the 1st cycle.

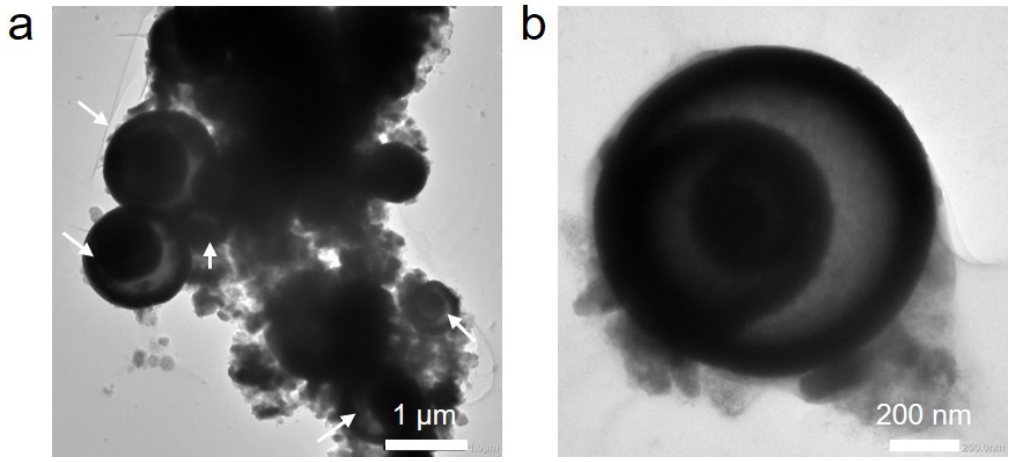

Figure S13. (a)-(b) TEM images of the Fe-Cr-O-2/2 HoMS after 200 times cycling at 0.1 A g^{-1}.

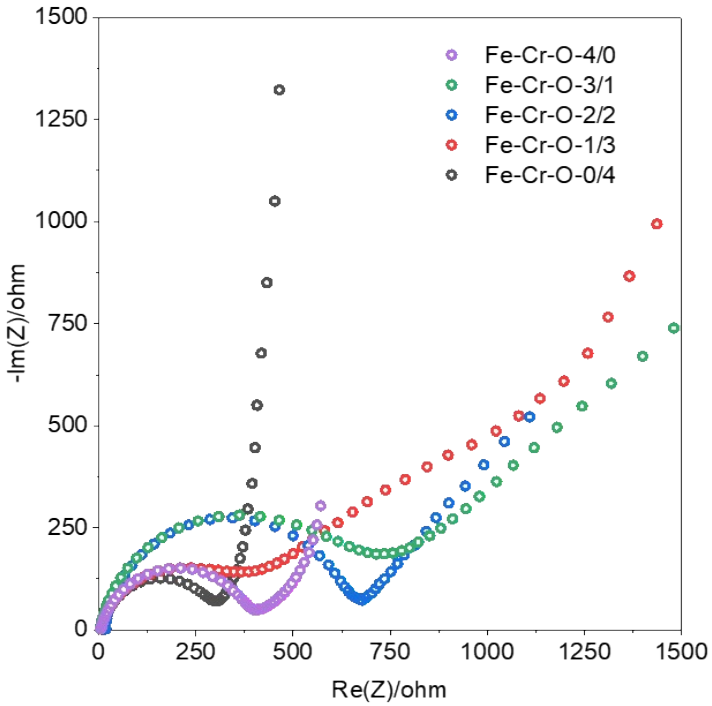

Figure S14. EIS spectra of the Fe-Cr-O HoMS with the variation of Fe/Cr molar ratio.

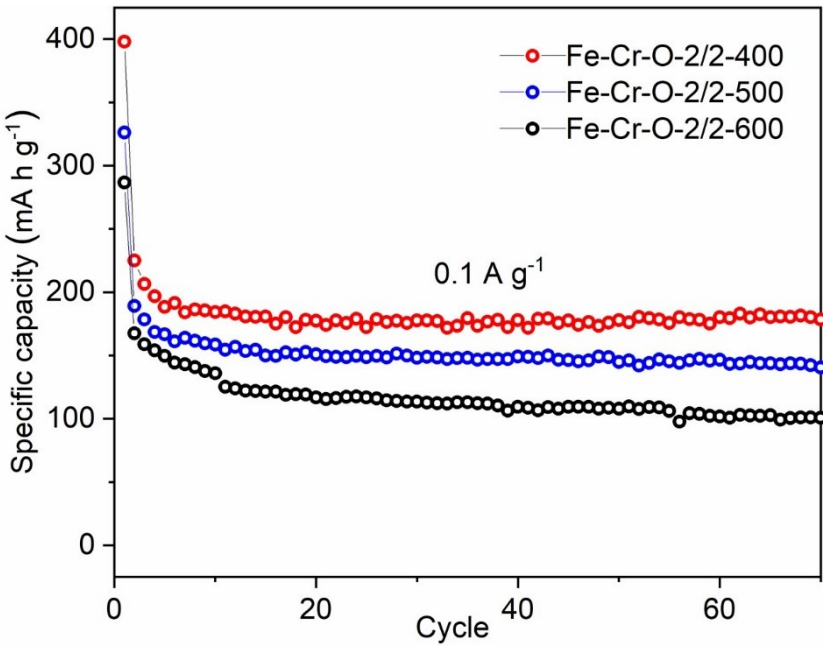

Figure S15. Cycling performances of the Fe-Cr-O HoMS prepared at different temperatures at 0.1 A g^{-1}.