Supplementary Information

Synthesis, Structural Characterization, and Electrochemical Performance of Nanocast Mesoporous Cu-/Fe-based Oxides

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Synthesis of mesoporous silica MCM-48: The MCM-48 nanospheres were synthesized using a mixture of cetyltetramethylammonum bromide (CTAB) and ethanol as a structure-directing mixture.[S1] Tetraethyl orthosilicate (TEOS) and triblock copolymer F127 (Pluronic F127, $EO_{106}PO_{70}EO_{106}$) were applied as a silica source and a particle dispersion agent, respectively. The molar composition of the reaction mixture was of 1 TEOS/ 0.16 CTAB/ 10.4 NH_3/ 89 EtOH/ 676 H_2O/ 0.017 F127. A typical preparation of the MCM-48 nanospheres is as follows: 1g of CTAB and 4g of F127 are dissolved in 85ml of EtOH, and 212.8 ml of 2.9 wt% ammonium hydroxide solution at room temperature. After complete dissolution, 3.6g of TEOS is added into the mixture at once. After 1 min of mechanical stirring at 1000 rpm, the mixture was kept at a static condition for 24 h at RT for further silica condensation. The white solid product is recovered by ultrahigh speed centrifuge, washed with water, and dried at 70°C in air. The final template free MCM-48 nanosphere materials are obtained after calcination at 550°C for 5h in the air.

Synthesis of mesoporous silica SBA-15:[S2] The synthesis was performed with the following initial molar gel composition: 1 TEOS/ 0.55 HCl/ 0.017 P123/ 100 H_2O. In a typical synthesis, 8.0 g of Pluronic P123 was dissolved in 145.4 g of deionized water and 4.4 g of hydrochloric acid (37%) at 35°C under magnetic stirring. Then, 17.2 g of TEOS was rapidly added to the initial homogeneous solution. The resulting mixture was stirred for 24 h at 35°C and subsequently hydrothermally treated for an additional 24h at 100°C to ensure further framework condensation. The solid product was filtered without washing and dried for 24h at 100°C. For template removal, the as-synthesized silica powders were first shortly slurried in an ethanol-HCl mixture and subsequently calcined at 550 °C for 3 h.

Synthesis of mesoporous silica KIT-6:[S3] Briefly, 8.0 g of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Sigma-Aldrich) was dissolved in 290 g of distilled water and 14.75 g of HCl (37%) under vigorous stirring. After complete dissolution, 8.0 g of 1-butanol was added. The mixture was left under stirring at 35 °C for 1 h, after which 20.63 g of tetraethoxysilane (TEOS) was added to the homogeneous clear solution. The synthesis is carried out in a closed polypropylene bottle. The molar composition of the starting reaction mixture is 1 TEOS/ 0.014 P123/ 1.54 HCl/ 165.6 H_2O/ 1.11 BuOH. This mixture was left under stirring at 35°C for 24 h, followed by an aging step at 100°C or 40°C for 24 h under static. The resulting solid products were then filtered and dried for 24h at 100°C. The solid product was then filtered, dried, and finally calcined at 550°C for 3h.

References

S1. (a) T.-W. Kim, P.-W. Chung, V. S.-Y. Lin, *Chem. Mater.* 2010, **22**, 5093-5104. (b) R. Guillet-Nicolas, J.-L. Bridot, Y. Seo, M.-A. Fortin and F. Kleitz, *Adv. Func. Mater.*, 2011, **21**, 4653-4662.

S2. M. Choi, W. Heo, F. Kleitz and R. Ryoo, *Chem. Commun.*, 2003, 1340-1341.

S3. (a) F. Kleitz, S. H. Choi and R. Ryoo, *Chem. Commun.*, 2003, 2136-2137; (b) F. Kleitz, F. Bérubé, R. Guillet-Nicolas, C. M. Yang and M. Thommes, *J. Phys. Chem. C* 2010, **114**, 9344-9355.

Supplementary Table

Table S1 Estimated crystal sizes from PXRD results using the Scherrer formula for mesoporous CFOs.

Material	Size (nm, spinel phase)	Size (nm, α-Fe_2O_3)	Size (nm, CuO)
CFO-MCM-48	8.2±0.4	N/A	N/A
CFO-SBA-15	N/A	23.0±0.4	19.1±0.3
CFO-KIT-6-100	N/A	21.8±0.4	18.3±0.3
CFO-KIT-6-40	N/A	19.7±0.3	24.8±0.4

Supplementary Figures

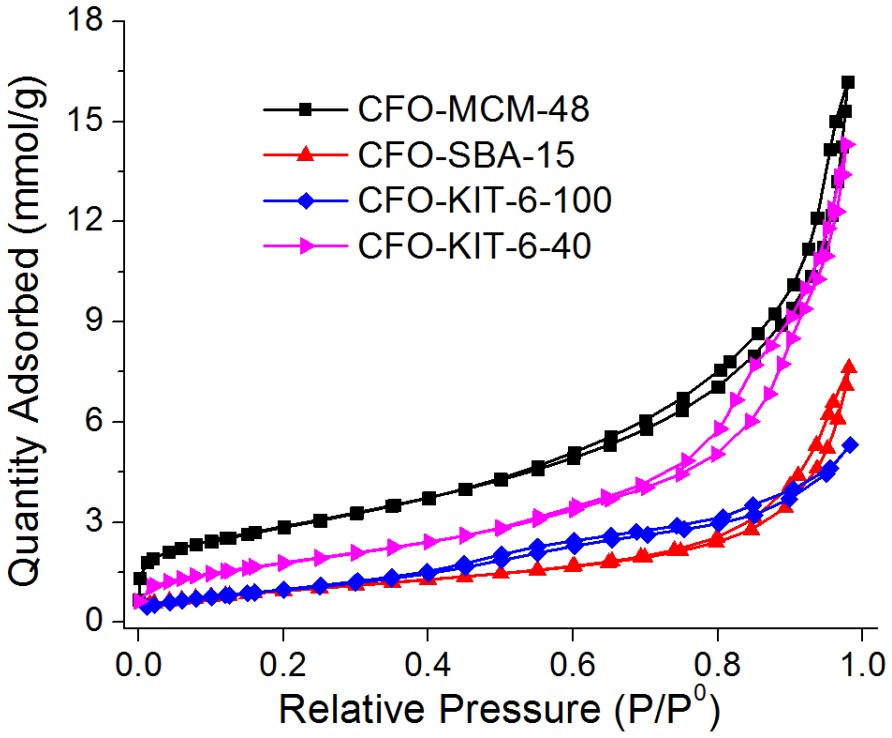

Figure S1. N_2 adsorption-desorption isotherms for mesoporous CFOs (-196°C).

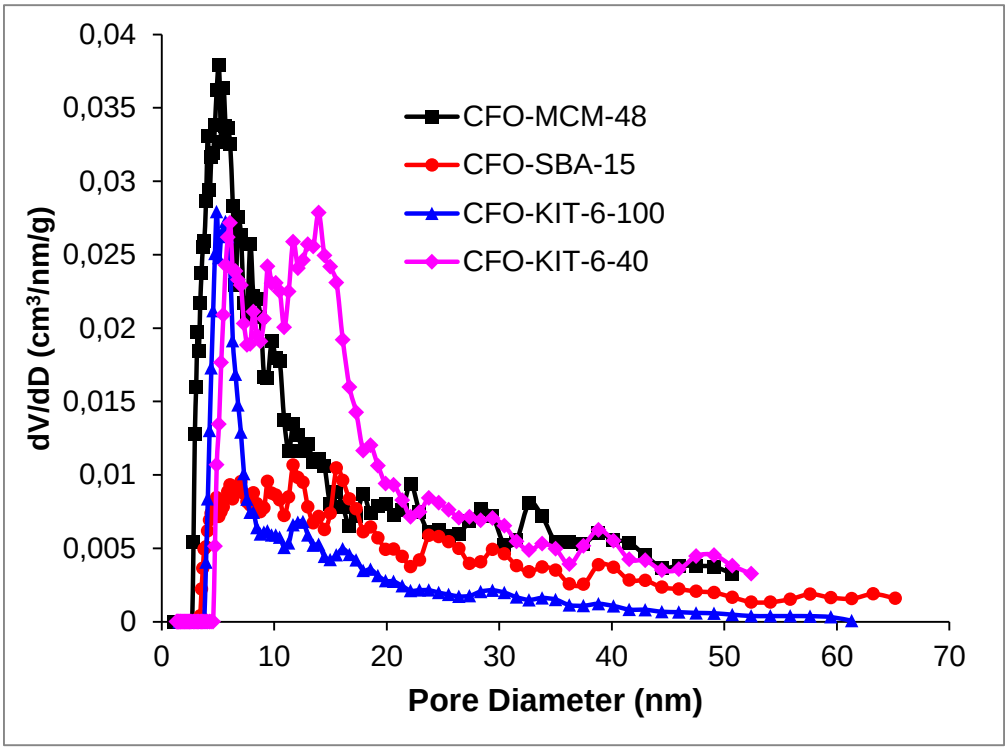

Figure S2. Pore size distributions for mesoporous CFOs calculated using NLDFT method (adsorption branch).

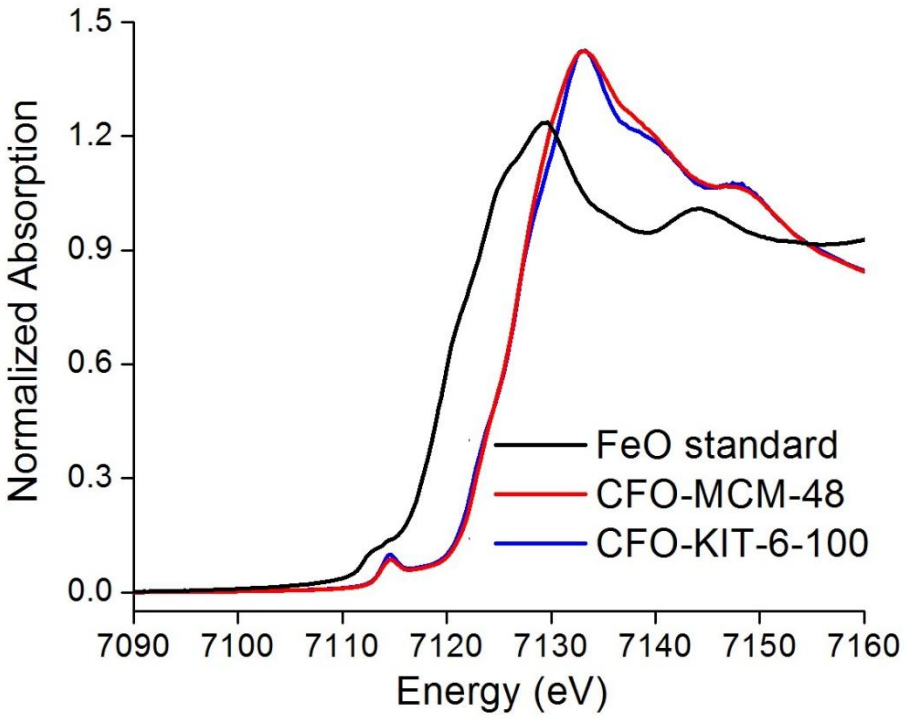

Figure S3. Fe K-edge XANES data for mesoporous CFOs. Data for bulk FeO are also included as a reference.

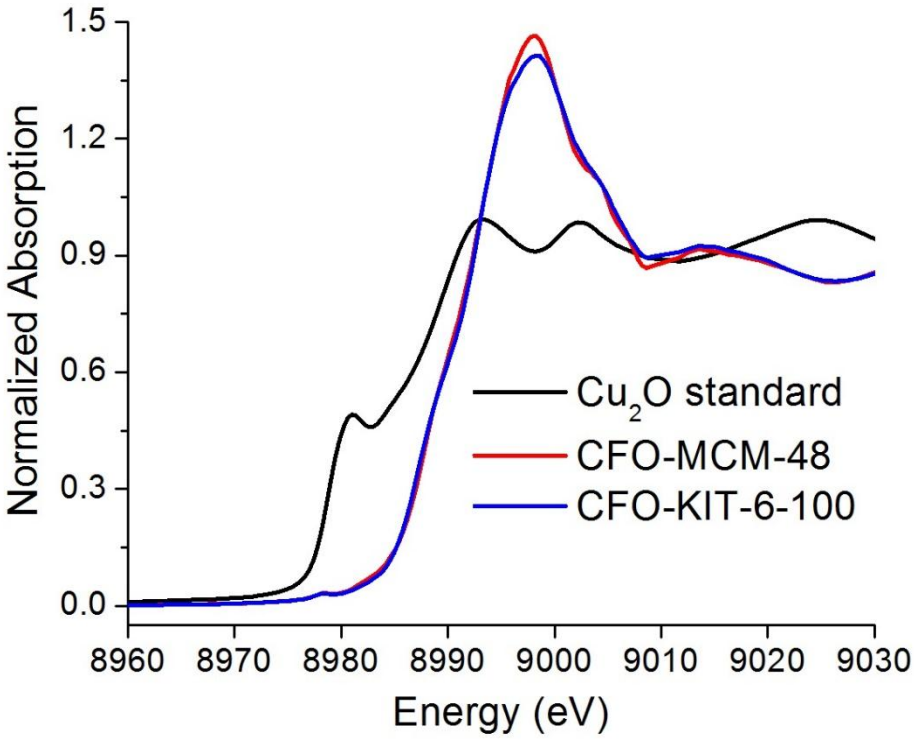

Figure S4. Cu K-edge XANES data for mesoporous CFOs. Data for bulk Cu_2O are also included as a reference.

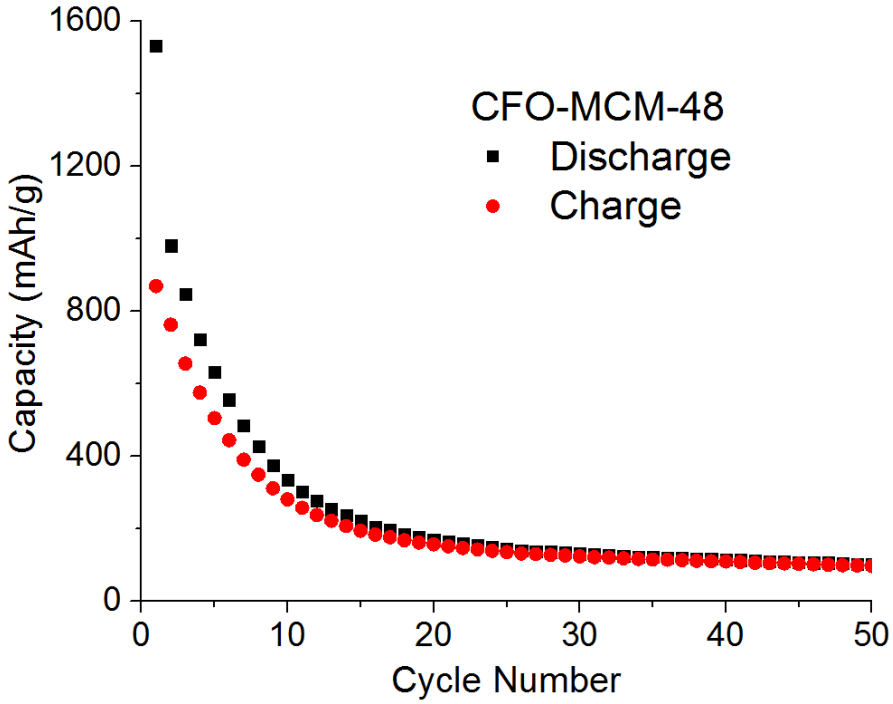

Figure S5. Cycling data for CFO-MCM-48 between 0.005-3V at a current density of 100 mA g^{-1}.