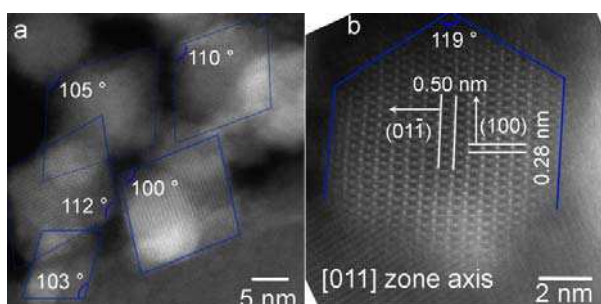


### Pseudocapacitive Mn<sub>3</sub>O<sub>4</sub> Octahedral Nanoparticles: Synthesis, Characterizations and Study of Charge-Transfer using in situ XANES and XRD

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In addition to clean and renewable energy generation, the subsequent storage and delivery is likewise a critical facet to achieving long-term sustainable energy practices. The principal means for storing energy generated off-peak for later on-peak usage currently leaves a void between overall storage capability and power delivery. As a promising technological candidate for efficient and reversible energy storage, pseudocapacitors are a sub-technology of electrochemical capacitors (so-called supercapacitors or ultra capacitors) that utilize fast and reversible Faradaic redox reactions. Although manganese oxides (MnOX) possess a theoretical capacitance of 1233 F/g based on one-electron charge-transfer reactions between Mn<sup>3+</sup> and Mn<sup>4+</sup>, they have systematically exhibited much lower specific capacitances (~100 F/g). Intensive research activities have been reported to increase the capacitance of MnO<sub>x</sub> materials, including the design nanostructured materials to shorten diffusion distance of ions and electrons or the incorporation with other conductive materials (e.g., active carbon, carbon nanotube, graphene, or conductive polymer) to improve the electrical conductivity and stability of MnO<sub>x</sub>.

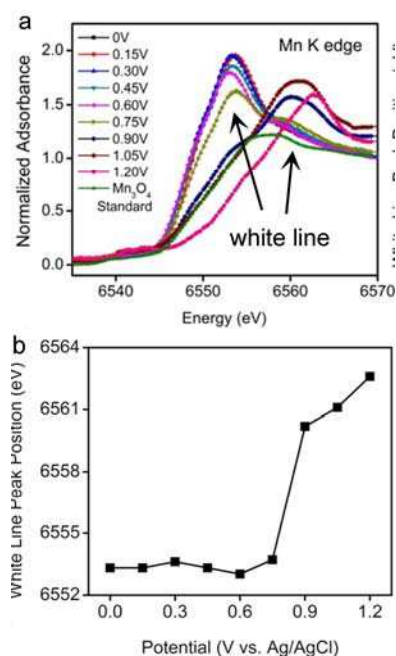


**Figure 1.** High angle annular dark field images of Mn<sub>3</sub>O<sub>4</sub> faceted nanoparticles with a high percentage of {101} facets via controlled oxidation method obtained from aberration-corrected STEM, showing an octahedron morphology with a [011] zone axis. The Mn<sub>3</sub>O<sub>4</sub> nanoparticles had an average size of 18 nm, made by reacting MnCl<sub>2</sub> with KOH in aqueous solution.

In this study, we show that Mn<sub>3</sub>O<sub>4</sub> octahedra nanoparticles (18.3 ± 7.0 nm in diagonal width) can be synthesized through a simple controlled oxidation method (**Figure 1**). The electrochemical properties of Mn<sub>3</sub>O<sub>4</sub> particles as a pseudocapacitive cathode were characterized in both half-cells and button-cells. Mn<sub>3</sub>O<sub>4</sub> nanoparticles exhibited a high mass specific capacitance of 261 F/g from cyclic voltammetry analyses in half-cell, and superb a capacitive retention of 78% after 10,000-cycle galvanostatic charge/discharge analyses in button-cell. The charge-transfer mechanisms of Mn<sub>3</sub>O<sub>4</sub> nanoparticles were further studied via synchrotron-based in situ X-ray absorption near edge spectroscopy (XANES) and X-ray diffraction (XRD) spectroscopy (**Figure 2**). Both measurements showed concurrently that throughout

the potential window between 0 V and 1.2 V (vs. Ag/AgCl), a stable spinel structure of Mn<sub>3</sub>O<sub>4</sub> remained, while a reversible electrochemical conversion between [Mn(II)O<sub>4</sub>] tetrahedral and [Mn(III)O<sub>6</sub>] octahedral units was accounted for the redox reactions, in contrast to charge-transfer mechanism observed in MnO<sub>2</sub> materials where Mn<sup>3+</sup> and Mn<sup>4+</sup> conversion accounts for the capacitance. Density functional theory calculations further corroborated this mechanism by confirming the enhanced redox stability afforded by the abundantly exposed {101} facets of Mn<sub>3</sub>O<sub>4</sub> octahedra.

Our findings underscore the intriguing structure-property relationship of Mn<sub>3</sub>O<sub>4</sub> nanoparticles and will provide a new insight into the design new type of metal oxides for supercapacitor devices with high capacitance and a stable electrolyte/electrode interface.



**Figure 2.** a) *In situ* XANES spectra (Mn K edge) of Mn<sub>3</sub>O<sub>4</sub> nanoparticles at potentials from 0 V to 1.20 V (vs. Ag/AgCl), (b) the shifting of white line peaks as a function of potentials.

Reference:

1. Yeager, M.; Du, W. X.; Xu, W.; Bishop, B.; Sullivan, M.; Su, D.; Si, R.; Deskins, N. A.; Jonason, H.; Teng, X. W., *Pseudocapacitive Hausmannite Nanoparticles with (101) Facets: Synthesis, Characterization, and Charge-Transfer Mechanism*, **ChemSusChem** 2013, 10.1002/cssc.201300027.