Hierarchical Porosity Tailoring of δ-MnO_2 Nanosheet Assemblies through the Layer-Tunnel Conversion

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Layer-tunnel conversion of alkali free 2-D δ-MnO_2 nanosheet agglomerates derived from highly crystalline potassium birnessite has been systematically investigated via synchrotron X-ray total scattering techniques, Raman spectroscopy, and scanning electron microscopy. High specific surface areas between 90-130 m^2g^{-1} were obtained for flocculated material treated between room temperature and 400°C, which microstructurally resemble a crumpled newspaper-like morphology. On the atomic and local scale, pore walls comprising the nanosheet stacks condense, forming fragments suggesting a 1-D of a tunnel motif. These tunnel fragments reminiscent of α-MnO_2 nucleate below 100°C, and increase in volume faction with increasing temperature, while the flocculated microstructure remains intact. We correlate the increasing interconnectivity, up to ≈30%, from structural changes to the kinetic barriers for Na^+ intercalation by cyclic voltammetry. Overall, the results demonstrate that the conversion can be tailored for applications ranging from sequestering of nanosolids or aqueous ions to kinetically accessible Na^+ ion intercalation.