

# Hollow Mn<sub>2</sub>O<sub>3</sub> Nanoparticles for Supercapacitor Electrodes via Solvothermal and High-Temperature Processing

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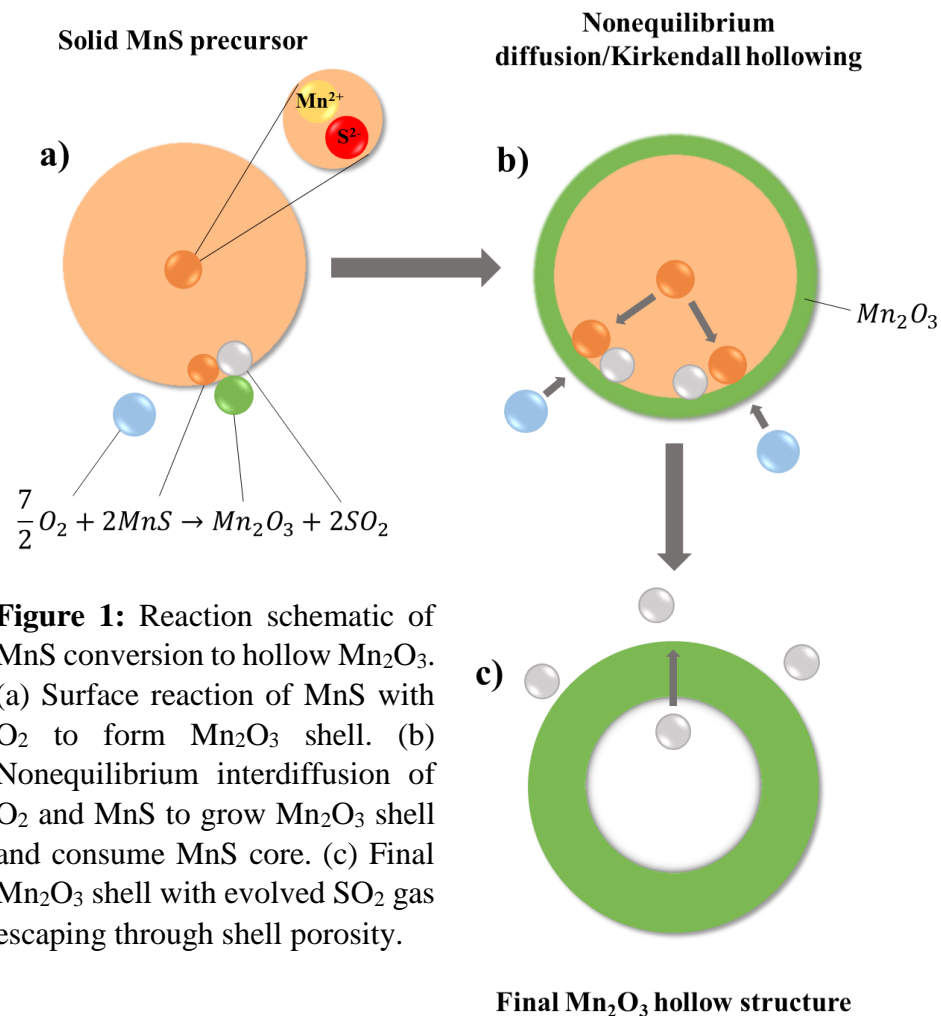
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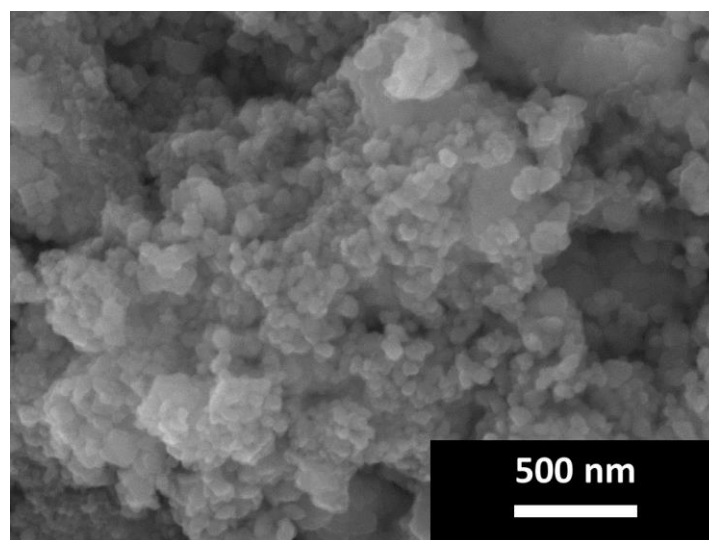
Manganese oxides, including Mn<sub>2</sub>O<sub>3</sub>, are promising supercapacitor electrode materials due to their high theoretical capacitances, low-cost, natural abundance, and environmental benignity.<sup>1</sup> Electrodes fabricated from nanostructured materials have the additional benefit of high surface-area-to-volume ratios, further increasing theoretical storage capacities. Nanostructured electrodes demonstrate decreased cycling stability when compared to bulk electrodes, but the stability issue may be mitigated through use of hollow electrode micro- nanostructures.<sup>2</sup> Hollow nanostructures demonstrate improved cycling stability as compared to solid nanostructures, as the interior void acts as a volume buffer to allow for volume expansion and contraction. Preparation of hollow Mn<sub>2</sub>O<sub>3</sub> micro- and nanoparticles has been previously demonstrated by several research groups. However, thermally produced hollow Mn<sub>2</sub>O<sub>3</sub> structures have remained in the micro-scale, and electrochemical characterization of hollow Mn<sub>2</sub>O<sub>3</sub> nano- and microstructures for supercapacitor electrode applications require more work to measure cycling stabilities and capacities. Increases in both storage capacity and cycling stability of the electrochemical capacitor electrodes can be realized by smaller nanoparticle size with a hollow structure.

In this work, MnS nanocrystals are synthesized via a facile solvothermal route utilizing inexpensive and nontoxic reagents. The MnS crystals are calcined to induce Kirkendall hollowing, in which nonequilibrium diffusion during oxidation results in the formation of a hollow Mn<sub>2</sub>O<sub>3</sub> shell (Fig. 1). Because the MnS precursor is consumed during the hollowing reaction, post-processing to isolate the oxide shells is unnecessary. Sulfide nanocrystals are examined with thermogravimetry to elucidate calcination temperatures necessary for conversion to Mn<sub>2</sub>O<sub>3</sub>. X-ray diffraction is used to confirm phases of the sulfide nanocrystals and oxide nanoshells, and Scherrer's equation is used to calculate crystallite size. Size and morphology of the precursor crystals and calcined shells are assessed with scanning electron microscopy. Finally, the oxide nanoshells are processed into electrodes for electrochemical characterization including cyclic voltammetry and galvanostatic charge/discharge. The electrochemical performance of hollow nanostructured electrodes is compared to electrodes fabricated from bulk-processed Mn<sub>2</sub>O<sub>3</sub> powder (Fig. 2), and changes in capacity and stability are quantified.

1. W. Wei, *et al.* Manganese oxide-based materials as electrochemical supercapacitor electrodes. *Chem. Soc. Rev.*, 40, 1697-1721, (2011).
2. Z. Wang, *et al.* Metal oxide hollow nanostructures for lithium-ion batteries. *Adv. Mater.*, 24, 1903-1911, (2012).



**Figure 1:** Reaction schematic of MnS conversion to hollow  $Mn_2O_3$ . (a) Surface reaction of MnS with  $O_2$  to form  $Mn_2O_3$  shell. (b) Nonequilibrium interdiffusion of  $O_2$  and MnS to grow  $Mn_2O_3$  shell and consume MnS core. (c) Final  $Mn_2O_3$  shell with evolved  $SO_2$  gas escaping through shell porosity.



**Figure 2:** Scanning electron micrograph of powder-processed  $Mn_2O_3$  nanoparticle electrode. Fabricated with 80:10:10 active material:acetylene black:PTFE binder by weight on Ni mesh.