

## Electronic supplementary information

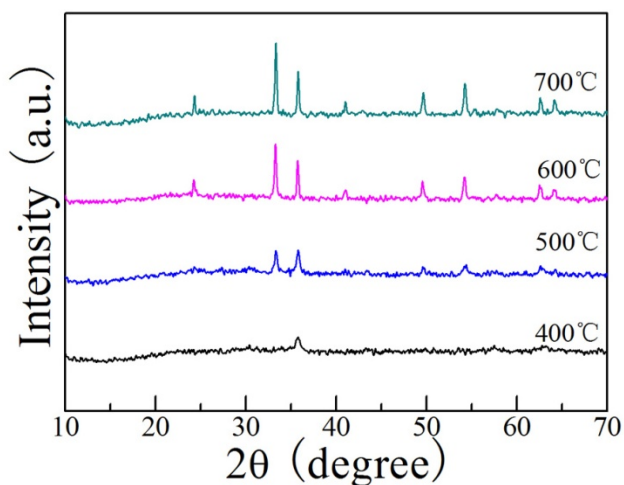
### The controlling synthesis and improved electrochemical cycleability of Mn-doped $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hollow porous quadrangular prisms as lithium-ion battery anodes

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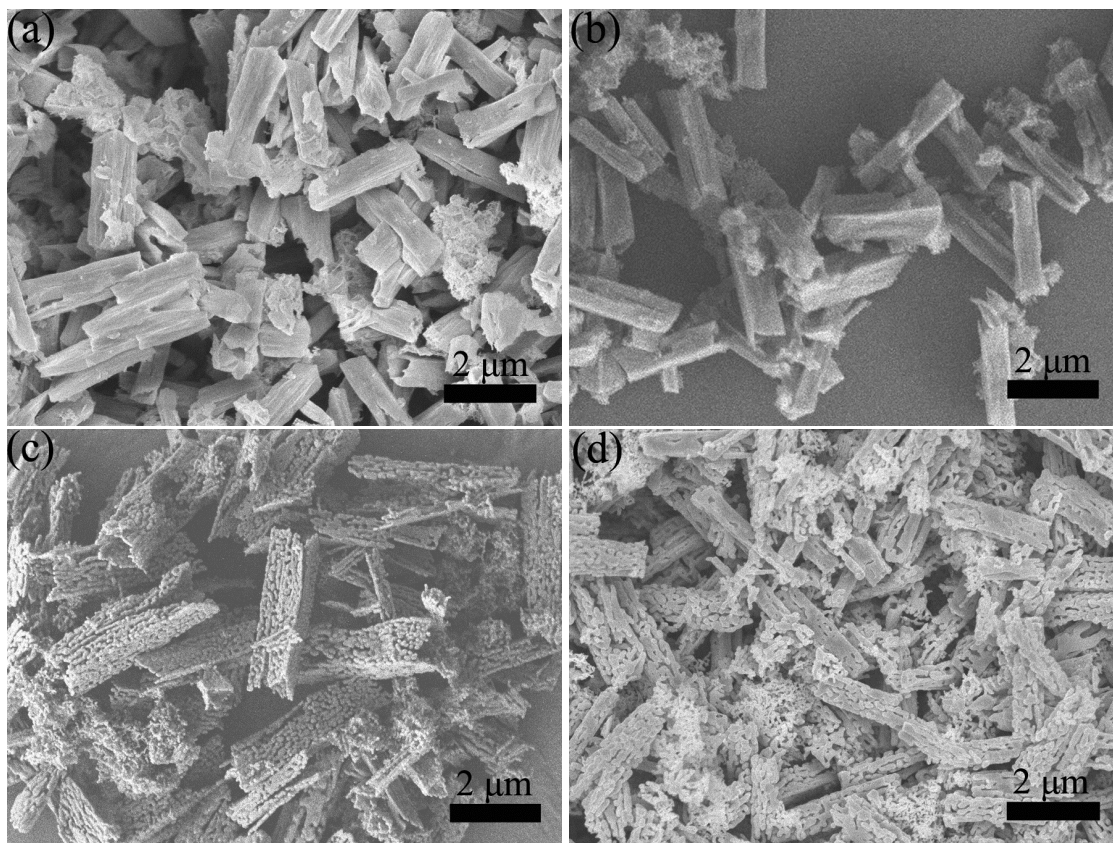
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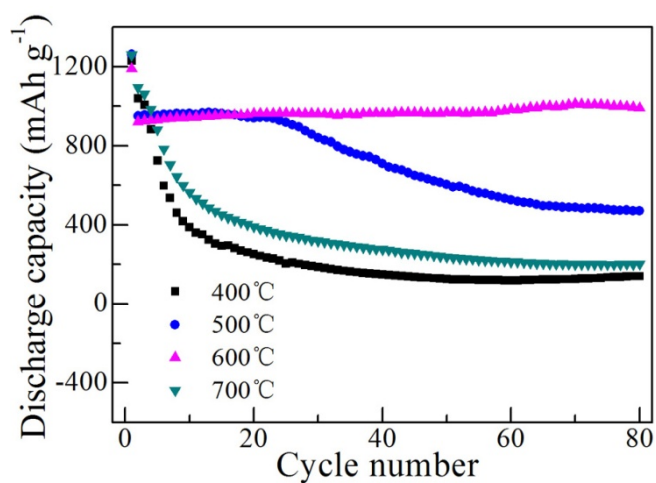
**Fig. S1** XRD patterns of Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> samples obtained at various calcination temperatures.

Comparing the crystallinity of each sample shown above, the calcination temperature of oxalate precursors should be selected at 600 °C or higher.



**Fig. S2** SEM images of  $\text{Fe}_{1.7}\text{Mn}_{0.3}\text{O}_3$  samples obtained at a calcination temperature of (a) 400, (b) 500, (c) 600 and (d) 700 °C.

The solid-state transformation of  $\text{MC}_2\text{O}_4$  to  $\text{M}_2\text{O}_3$  ( $\text{M} = \text{Fe-Mn}$ ) mainly replicates the skeletons of precursor, however, the release of gaseous  $\text{CO}_2$  and  $\text{CO}$  could hardly endow the oxides with a porous feature when operated at a low calcination temperature of 400 or 500 °C (Fig. S2-a, b). Furthermore, when calcined at 700 °C, parts of resulting quadrangular prisms become cracked and their porous skeletons became vague in appearance owing to crystal fusion probably (Fig. S2-d). Therefore, the optimal calcination temperature of Mn-doped  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  precursor was selected at 600 °C.



**Fig. S3** Cycling performances of  $\text{Fe}_{1.7}\text{Mn}_{0.3}\text{O}_3$  samples, obtained at various calcination temperatures, operated at  $200 \text{ mA g}^{-1}$  in the voltage range of 0.01-3.0 V.

When used as the active substances of a Li-ion battery anode, the initial specific discharge capacities of these oxides obtained at 400, 500, 600 and 700 °C are 1231.2, 1262.6, 1189.9 and 1260.6  $\text{mAh g}^{-1}$ . By comparison, the sample sintered at 400 or 700 °C shows rapid capacity decay and gives the 80<sup>th</sup> reversible value of 139.9 or 202.1  $\text{mAh g}^{-1}$ ; the discharge capacity of the powdered oxide obtained at 500 °C is nearly stable from the 2<sup>nd</sup> to 20<sup>th</sup> cycles and then gradually reduces to 470.1  $\text{mAh g}^{-1}$  at the 80<sup>th</sup> cycle; while the  $\text{M}_2\text{O}_3$  (M = Fe-Mn) product collected at 600 °C exhibits a high cycling durability and retains a high reversible capacity of 1000.0  $\text{mAh g}^{-1}$  over 80 discharge-charge cycles.

In a word, the comparative cycling performances of  $\text{Fe}_{1.7}\text{Mn}_{0.3}\text{O}_3$  samples furthermore confirm that the optimal calcination temperature of Mn-doped  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  precursor is 600 °C.