Electronic Supplementary information for
A new CaCO$_3$-template method to synthesize nanoporous manganese oxides hollow structures and their transformation to high-performance LiMn$_2$O$_4$ cathode for Lithium-ion batteries

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Figure S1. XRD patterns for the coprecipitated carbonates.

- S1: MnCO$_3$
- S2: Mn$_3$Ca$_1$(CO$_3$)$_4$
- S3: MnCa(CO$_3$)$_2$
- S4: MnCa$_2$(CO$_3$)$_3$
- S5: CaCO$_3$
Figure S2. SEM images and EDS analysis for the as-prepared carbonates.
(a). S1, MnCO$_3$;
(b). S2, Mn$_3$Ca$_1$(CO$_3$)$_4$;
(c). S3, Mn$_1$Ca$_1$(CO$_3$)$_2$;
(d). S4, Mn$_1$Ca$_2$(CO$_3$)$_3$.
(e). S5, CaCO$_3$
Figure S2-(a)
Figure S2-(b)  
S2, 3:1, Mn$_3$Ca$_1$(CO$_3$)$_4$
Figure S2-(c)  

S3, 1:1, Mn$_1$Ca$_1$(CO$_3$)$_2$
Figure S2-(d)  S4, 1:2, Mn₁Ca₂(CO₃)₃
Figure S2-(e)  

S5, CaCO$_3$
Figure S3. XRD patterns for the carbonates after thermal decomposition at 400 °C for 4 h.
Figure S4. XRD patterns for the carbonates after the treatment of thermal decomposition at 400 °C for 4 h and HCl wash.
Figure S5. SEM images for the carbonates after thermal decomposition at 400 °C for 4 h and HCl wash.

(a). S1, from MnCO$_3$, no HCl wash;
(b). S2, from Mn$_3$Ca$_1$(CO$_3$)$_4$;
(c). S3, from Mn$_1$Ca$_1$(CO$_3$)$_2$;
(d). S4, from Mn$_1$Ca$_2$(CO$_3$)$_3$. 
Figure S5-(a)

S1, from MnCO₃, 400 °C-4h
Figure S5-(b) S2, from Mn$_3$Ca$_1$(CO$_3$)$_4$, 400 °C-4h, HCl wash
Figure S5-(c)

S3, from $\text{Mn}_1\text{Ca}_1(\text{CO}_3)_2$, 400 °C-4h, HCl wash
Figure S5-(d)

S4, from Mn\textsubscript{1}Ca\textsubscript{2}(CO\textsubscript{3})\textsubscript{3}, 400 °C-4h, HCl wash
S2, from Mn$_3$Ca$_1$(CO$_3$)$_4$, 400 °C-4h, HCl wash

Figure 6. TEM images for the carbonate of Mn$_3$Ca$_1$(CO$_3$)$_4$ after thermal decomposition at 400 °C for 4 h and HCl wash.
Figure 7. TG curves for the four samples after thermal decomposition at 400 °C for 4 h and HCl wash. (a). S1, from MnCO$_3$, no HCl wash was used; (b). S2, from Mn$_3$Ca$_1$(CO$_3$)$_4$; (c). S3, from Mn$_1$Ca$_1$(CO$_3$)$_2$; (d). S4, from Mn$_1$Ca$_2$(CO$_3$)$_3$. The analysis were carried out under ambient atmosphere at a heating rate of 5 °C/min.
Figure S8. XRD patterns for the carbonates after a series of treatment of thermal decomposition at 400 ºC for 4 h, HCl wash, and thermal decomposition at 600 ºC for 3 h. S1 was obtained by directly decomposition at 600 ºC for 3 h.
Figure S9. SEM images for the carbonates after a series of treatment of thermal decomposition at 400 °C for 4 h, HCl wash, and thermal decomposition at 600 °C for 3 h.

(a). S1, from MnCO$_3$, directly decomposed at 600 °C for 3 h;
(b). S2, from Mn$_3$Ca$_1$(CO$_3$)$_4$;
(c). S3, from Mn$_1$Ca$_1$(CO$_3$)$_2$;
(d). S4, from Mn$_1$Ca$_2$(CO$_3$)$_3$. 

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Figure S9-(a)

S1, from MnCO$_3$, 600 ºC-3h
Figure S9-(b)  S2, from Mn₃Ca₁(CO₃)₄, 400 °C-4h, HCl wash, 600 °C-3h
Figure S9-(c) S3, from Mn$_1$Ca$_1$(CO$_3$)$_2$, 400 °C-4h, HCl wash, 600 °C-3h
Figure S9-(d)  S4, from Mn$_1$Ca$_2$(CO$_3$)$_3$, 400 °C-4h, HCl wash, 600 °C-3h
Figure S10. TEM images for the manganese oxide (Mn$_2$O$_3$) porous structures obtained from (a). S1, directly from MnCO$_3$ (b). S2, from Mn$_3$Ca$_1$(CO$_3$)$_4$; (c). S3, from Mn$_1$Ca$_1$(CO$_3$)$_2$. 
Figure S11. SEM and TEM images for LiMn$_2$O$_4$ prepared from solid-state reaction of the porous Mn$_2$O$_3$ with LiOH·H$_2$O at 750 ºC for 20 h. S1, porous Mn$_2$O$_3$ directly from MnCO$_3$
Figure S12. SEM, TEM images and EDS analysis for LiMn$_2$O$_4$ prepared from solid-state reaction of the porous hollow Mn$_2$O$_3$ with LiOH·H$_2$O at 750 ºC for 20 h. S2, porous Mn$_2$O$_3$ hollow spheres from Mn$_3$Ca$_1$(CO$_3$)$_4$. 

No Ca peaks
Figure S13. Cycling performance for the porous LiMn$_2$O$_4$ hollow spheres.
Figure S14. Charge-discharge curves at 1-C rate.
Figure S15. Cycling performance and the charge-discharge curves for the porous LiMn$_2$O$_4$ hollow spheres (S2) at different C-rates.