

Supporting information for

## Synergistic Effect for the Preparation of $\text{LiMn}_2\text{O}_4$ Microspheres with High Electrochemical Performance

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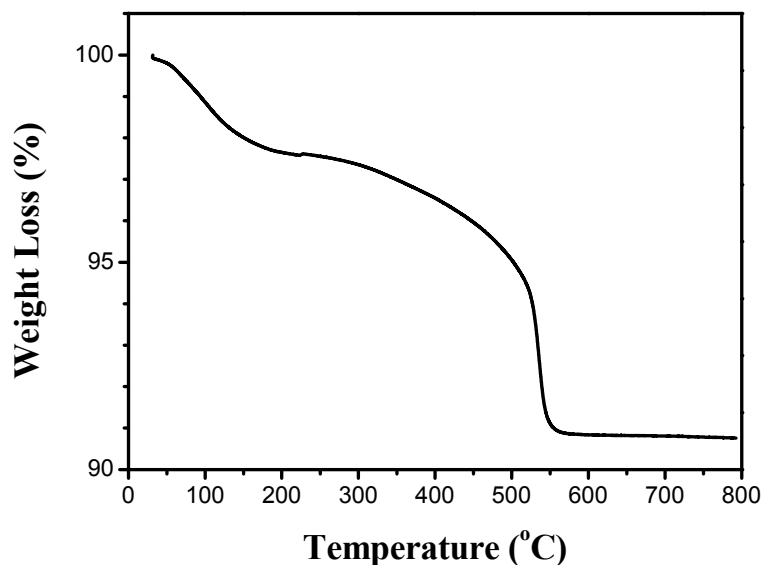
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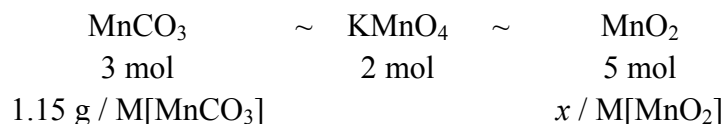
**Fig. S1.** Photographs of (a) the reaction bottle after adding HCl with 2 min for routine method (left) and 60 min (right), (b,c) below filtrate of the routine method and synergistic method, respectively.

## Calculation of the yield of MnO<sub>2</sub>



**Fig. S2.** Thermo gravimetric analysis (TGA) curve of MnO<sub>2</sub> microspheres recorded from ambient to 800 °C with a heating rate of 10 °C·min<sup>-1</sup> under air flow.

Theoretical total weight of MnO<sub>2</sub> is calculated based on the chemical reaction equation (1) in the main body of this article. The stoichiometric relationship between MnCO<sub>3</sub> and MnO<sub>2</sub> are as follows:

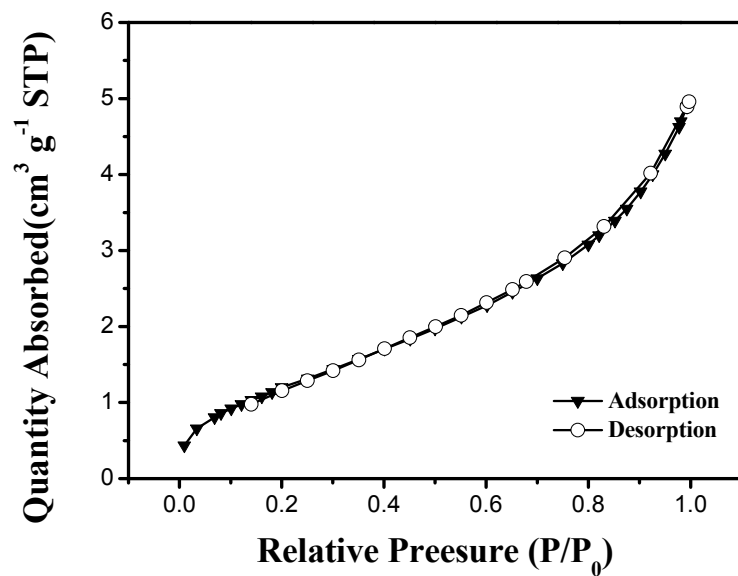


Where M[MnCO<sub>3</sub>] and M[MnO<sub>2</sub>] is the molecular weight of MnCO<sub>3</sub> (114.95 g mol<sup>-1</sup>) and MnO<sub>2</sub> (86.94 g mol<sup>-1</sup>).

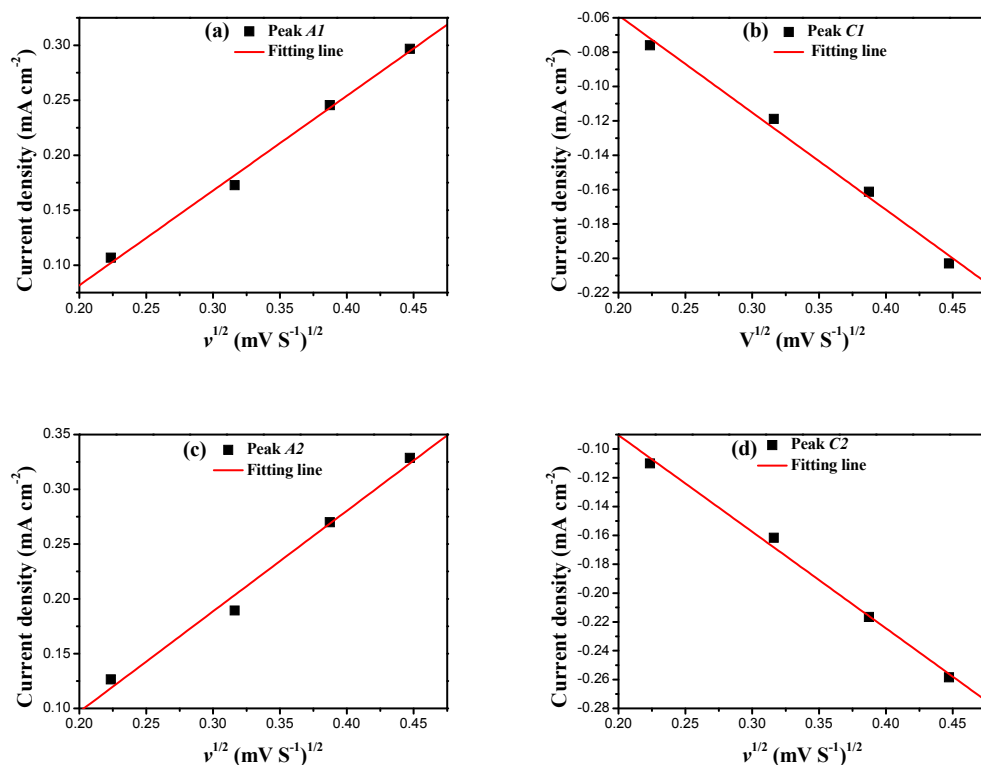
In the TGA curve of MnO<sub>2</sub> microspheres, as shown in Fig. S2, we observed a weight loss of 9.2 wt% upon heating, which involves the volatilization of free or crystal water (normally below 200 °C) and the decomposition and release of O<sub>2</sub> from MnO<sub>2</sub>: 4MnO<sub>2</sub> → 2Mn<sub>2</sub>O<sub>3</sub> + O<sub>2</sub>. So when using 1.15 g of MnCO<sub>3</sub>, the theoretical weight of MnO<sub>2</sub> is  $x = 1.45 \text{ g}$ . If further minus the water (2~3 wt%) part, the experimental weight of MnO<sub>2</sub> would approximately equal to 1.49 g. The yield of the obtained MnO<sub>2</sub> powders prepared via the routine method and our method is calculated in Table S1, it can be seen that the yield in our experiment is nearly 99%, indicating the completely conversion of MnCO<sub>3</sub> and KMnO<sub>4</sub>.

**Table S1** The weight and yield of obtained MnO<sub>2</sub> powders.

Reaction time after adding HCl	Routine method	synergistic method
Experimental weight (g)	1.25 g	1.47 g
Yield	~ 84 %	~ 99 %



**Fig. S3** N<sub>2</sub> adsorption/desorption isotherms plots of the LiMn<sub>2</sub>O<sub>4</sub> microspheres.



**Fig. S4** Plots of the peak current density versus the square root of potential scan rate derived from the CV curves of  $\text{LiMn}_2\text{O}_4$  microspheres. (a) Peak A1, (b) Peak C1, (c) Peak A2 and (d) Peak C2, respectively.

**Table S2** Summary of  $\text{Li}^+$  diffusion coefficient determined by CV method.

$v$ (mV/s)	<i>Peak A1</i>			<i>Peak C1</i>		
	$E$ (V)	$I_p$ (mA/cm <sup>2</sup> )	$D_{\text{Li}}$ (cm <sup>2</sup> s <sup>-1</sup> )	$E$ (V)	$I_p$ (mA/cm <sup>2</sup> )	$D_{\text{Li}}$ (cm <sup>2</sup> s <sup>-1</sup> )
0.05	4.067	1.07E-01	5.56E-09	3.95	-7.60E-02	8.04E-10
0.10	4.090	1.73E-01	7.30E-09	3.932	-1.19E-01	2.06E-09
0.15	4.109	2.45E-01	9.81E-09	3.914	-1.61E-01	3.41E-09
0.20	4.119	2.97E-01	1.08E-08	3.908	-2.03E-01	4.81E-09
$v$ (mV/s)	<i>Peak A2</i>			<i>Peak C2</i>		
	$E$ (V)	$I_p$ (mA/cm <sup>2</sup> )	$D_{\text{Li}}$ (cm <sup>2</sup> s <sup>-1</sup> )	$E$ (V)	$I_p$ (mA/cm <sup>2</sup> )	$D_{\text{Li}}$ (cm <sup>2</sup> s <sup>-1</sup> )
0.05	4.187	1.26E-01	4.83E-10	4.072	-1.10E-01	5.55E-10
0.10	4.208	1.89E-01	1.29E-09	4.055	-1.62E-01	1.51E-09
0.15	4.224	2.70E-01	2.04E-09	4.042	-2.17E-01	2.54E-09
0.20	4.231	3.29E-01	2.97E-09	4.035	-2.58E-01	3.78E-09

**Table S3** Summary of the Lithium ion diffusion coefficient in references

Morphology	Measurement method	Lithium ion diffusion coefficient ( $D \text{ cm}^2 \text{ S}^{-1}$ )	References
Porous nanorods	CV	$1.74 \times 10^{-9} \sim 1.30 \times 10^{-8}$	[23]
Spherical	CITT	$0.9 \times 10^{-10} \sim 16.3 \times 10^{-10}$	[29]
	PITT	$10^{-9.5} \sim 10^{-11.5}$	
Porous spheres	CV	$4.61 \times 10^{-10}$	[30]
Porous nanoscaled	CV	$1.40 \times 10^{-8} \sim 3.6 \times 10^{-10}$	[31]

CV: cycling voltammetry

CITT: capacity intermittent titration technique

PITT: potential intermittent titration technique