## **Supplementary Information**

## Simple Synthesis of double-shell hollow structured MnO<sub>2</sub>@TiO<sub>2</sub>

## composite as anode materials for lithium ion battery



Fig. S1 TEM images of C@MnO<sub>2</sub> (a), the product of sample (a) treated with 350 °C for 1h (b), the product of sample (a) treated with 450 °C for 2 h (c), magnification of (c) (d)



Fig. S2 TG-DSC curves of carbon spheres with a heating rate of 10 °C /min. It shows that the temperature of thermal decomposition of carbon spheres ranges from 300 °C  $\sim$ 500 °C.



Fig. S3 The EDS of Fig. 4b. It confirms the presence of Ti and Mn.



Fig. S4 (a) The cycling performance of MnO<sub>2</sub>@TiO<sub>2</sub>, MnO<sub>2</sub>-350 and MnO<sub>2</sub>-450 in the range of 0.01~3 V vs. Li+/Li at a current rate of 200 mA/g after 200 cycles; (b) electrochemical impedance spectra of MnO<sub>2</sub>@TiO<sub>2</sub>, MnO<sub>2</sub>-350 and MnO<sub>2</sub>-450;

The first-cycle Coulombic Efficiency could be calculated as 28.1% for M-450, 36.7% for M-350 and 42.9% for MT-450. M-350 exhibits a relatively higher first Coulombic Efficiency of 36.7% and a more stable cyclic performance than M-450, however its electrochemical performances lose to MT-450, as is figured in Fig. S4. Because there still exists much non-activity carbon in M-350 owing to a relatively low temperature. This part of carbon occupied some of the weight while perform bad capacity as well as electron and ion conductivity. Therefore, we need to improve the calcination temperature to 450 °C. And further improve its electrochemical performance via coating it with  $TiO_2$ .

| a<br>EDS 2<br>MinO <sub>2</sub> @<br>TiO <sub>2</sub><br>200 nm |       |       |         |        |       |         |       |       |
|---|-------|-------|---------|--------|-------|---------|-------|-------|
|   |       |       |         |        |       | Element | %wt   | %atom |
| EDS I   |       |       | EDS 2   |        |       | СК      | 52.70 | 82.15 |
| Element   | %wt   | %atom | Element | %wt    | %atom | FK      | 4.49  | 4.43  |
| ск  | 50.30 | 69.11 | СК      | 10.39  | 26.57 | КК      | 1.37  | 0.65  |
| ок  | 23.16 | 23.89 | ок      | 18.18  | 34.91 | Ti K    | 2.33  | 0.91  |
| TiK   | 0.40  | 0.14  | TiK     | 7.01   | 4.50  | MnK     | 11.22 | 3.82  |
| MnK   | 1.86  | 0.56  | MnK     | 38.13  | 21.32 | CuK     | 26.90 | 7.93  |
| CuK   | 24.27 | 6.30  | CuK     | 26.28  | 12.71 | ТаМ     | 1.00  | 0.10  |
| -   |       |       |         | 100.00 |       |         |       |       |

Fig. S5 The SEM images of MnO<sub>2</sub>@TiO<sub>2</sub> after 200 cycles (a, b in different regions) and the EDS results corresponding to different certain positions.

According to EDS, region 1 is mainly SEI, and region 3 is super P and binder. From EDS 2, the atom percent ratio of Mn:Ti is about 5:1. So, the content of  $TiO_2$  is calculated as around 15.5 wt.%.