

Fig.S1 SEM images of commercial V_2O_5 powder with irregular appearance under different amplifications.

We can find from the above SEM images (Fig. S1) that the commercial V_2O_5 powder displays irregular appearance, whose size ranges from a few microns to dozens of microns.

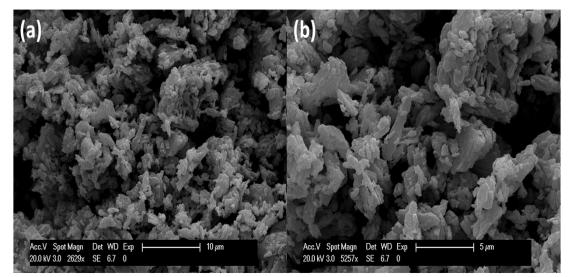


Figure S2. SEM images of commercial V₂O₅ powder after mechanical ball milling at different magnifications.

Microscopic morphology of commercial V_2O_5 powder after mechanical ball milling is illustrated in Fig. S2. It can be found that the size of irregular V_2O_5 particles after milling become smaller than the raw one when we compare Fig. S2 (a) with Fig. S1 (b) at the same magnification. Besides, the number of "little pieces" of V_2O_5 powder with dimension less than 1 µm become more through ball milling. When the sintering process is conducted, these small "little pieces" would get closer to the large particle in the vicinity of them and develop into a larger V_2O_5 particle with smooth surface as time goes on. This is because that the microscopic particles always tend to gather together and form larger particles under high temperature in order to reduce the overall surface energy. The agglomeration phenomena for many particulate materials are caused by this principle of minimum surface energy. Nevertheless, the extent of agglomeration is limited by treating temperature and physical property of material itself. So, here the appropriate treating temperature and heating rate could lead to the generation of smooth particle with proper size as shown in Fig. 1 of original manuscript.

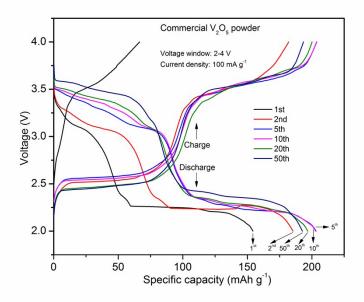


Figure S3. Selected charge-discharge curves of commercial V_2O_5 powder cathode material without sintering and ball milling.

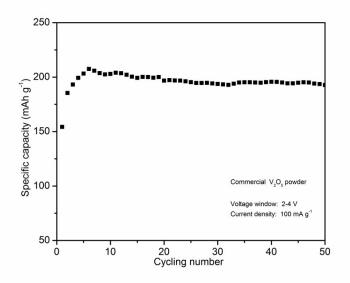


Figure S4. Cycling performance of commercial V_2O_5 powder cathode material without sintering and ball milling between 2-4 V under the current density of 100 mA g⁻¹.

Fig. S3 gives the 1st, 2nd, 5th, 10th, 20th and 50th charge-discharge curves of raw V₂O₅ powder cathode material without sintering and ball milling. The profile of these curves is similar to that of bare V₂O₅ particle with milling and sintering as well as TiO₂-coated one. The cycling performance of raw V₂O₅ powder without sintering and milling is presented in Fig. S4. It can be seen that raw V₂O₅ powder shows an initial specific capacity of 154.3 mAh g⁻¹. After that, an obvious activation process happens, which leads to the increase of specific capacity from 154.3 mAh g⁻¹ (for the 1st cycle) to 207.5 mAh g⁻¹ (for the 6th cycle) and then gradually decrease to 192.7 mAh g⁻¹ for the 50th cycle. Although the raw V₂O₅ powder displays stable discharge specific capacity during the subsequent cycles, the absolute value of its capacity is much lower than that of the sample with milling and sintering (218.2 mAh g⁻¹ for the 1st cycle; highest value 247.8 mAh g⁻¹ for the 3rd; 212.6 mAh g⁻¹ for the 50th) as well as the TiO₂-coated one (212.3 mAh g⁻¹ for the 1st cycle; highest value 246.6 mAh g⁻¹ for the

5th; 229.1 mAh g⁻¹ for the 50th). The lower discharge capacity of raw V_2O_5 powder may be owing to its larger particle size and irregular morphology which could not be fully utilized upon electrochemical reaction. It is noteworthy that the raw V_2O_5 undergoes a distinct activation process, which is due to its large and irregular particle size. During electrochemical reaction, lithium ions migrate into active material from electrolyte and diffuse within it. If the contact between active material and electrolyte is not so good or the size of active particle is too large, lithium ions cannot insert into active material and occupy the active site adequately in the early stage [1-4]. Consequently, the highest specific capacity value will not reach at the first cycle but a certain one at the subsequent cycles.

References:

[1] X. Feng, Y.R. Gao, L.B. Ben, Z.Z. Yang, Z.X. Wang and L.Q. Chen, *J. Power Sources*, 2016, 317, 74.

- [2] G.R. Li,X. Feng,Y. Ding,S.H. Ye,X.P. Gao, Electrochim. Acta, 2012, 78, 308.
- [3] X.P. Gao and H.X. Yang, Energy Environ. Sci., 2010, 3, 174.
- [4] C. Lai, X.P. Gao, B. Zhang, T.Y. Yan and Z. Zhou, J. Phys. Chem. C, 2009, 113, 4712.