

## Electronic Supplementary Information

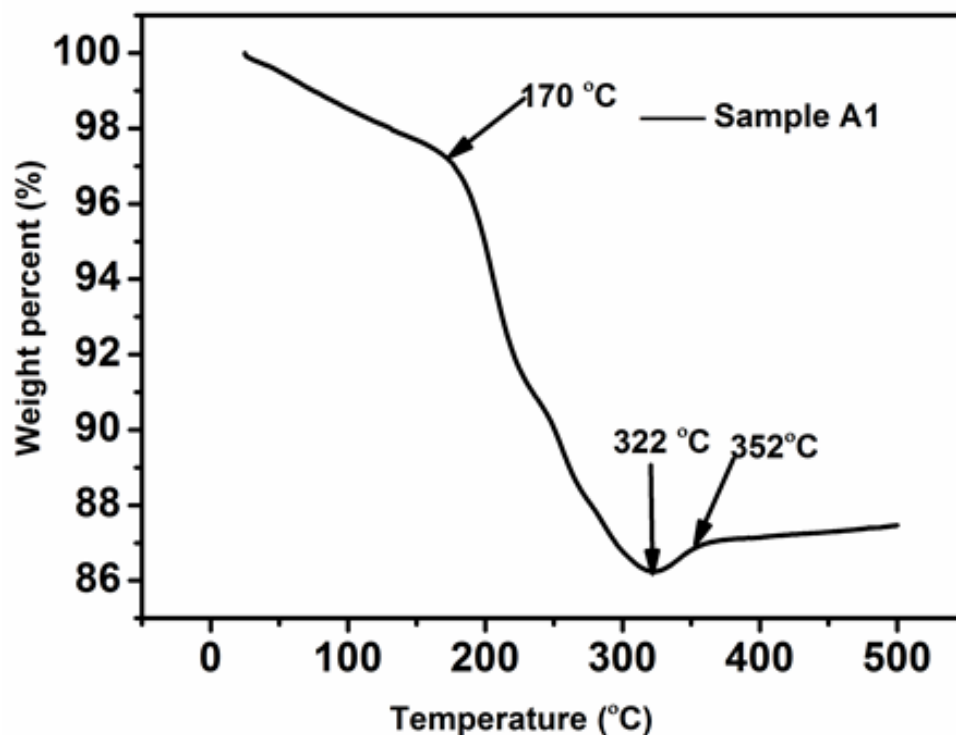
### Synthesis of $V_2O_5$ Hierarchical Structures for Long Cycle-Life Lithium-Ion Storage

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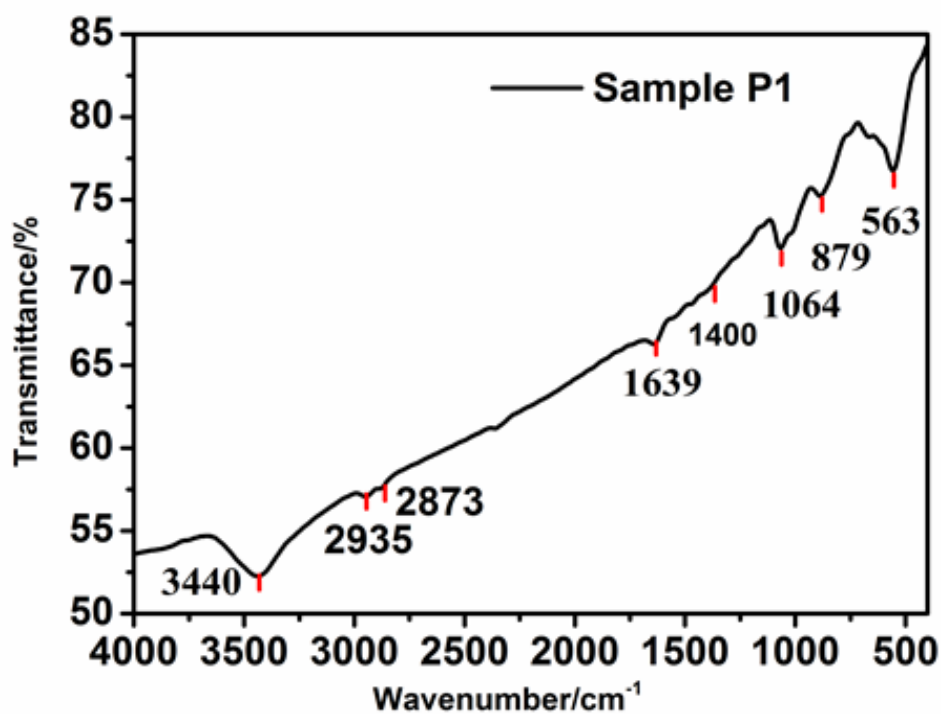
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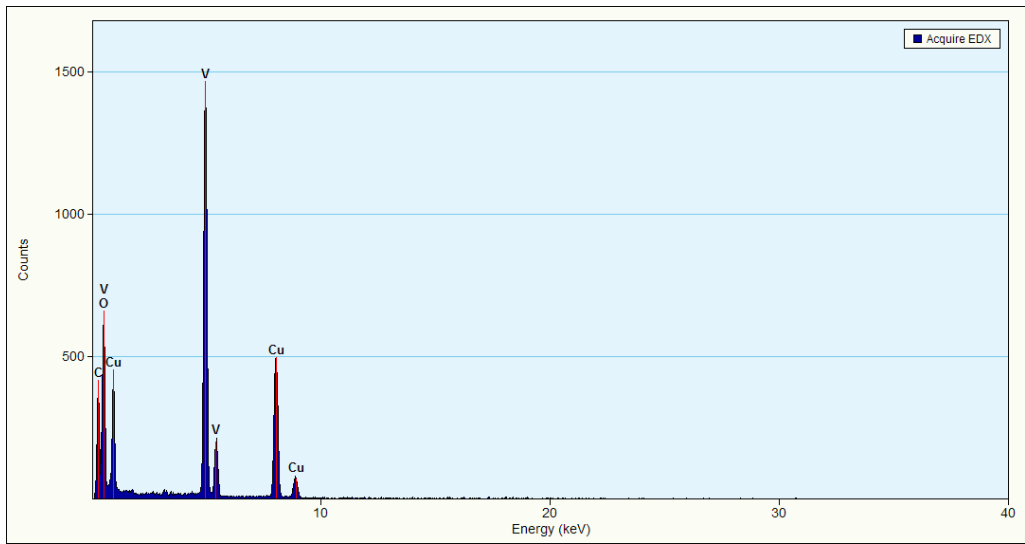


**Figure S1.** TGA trace of the bilayered  $V_2O_5$  precursor sample P1.

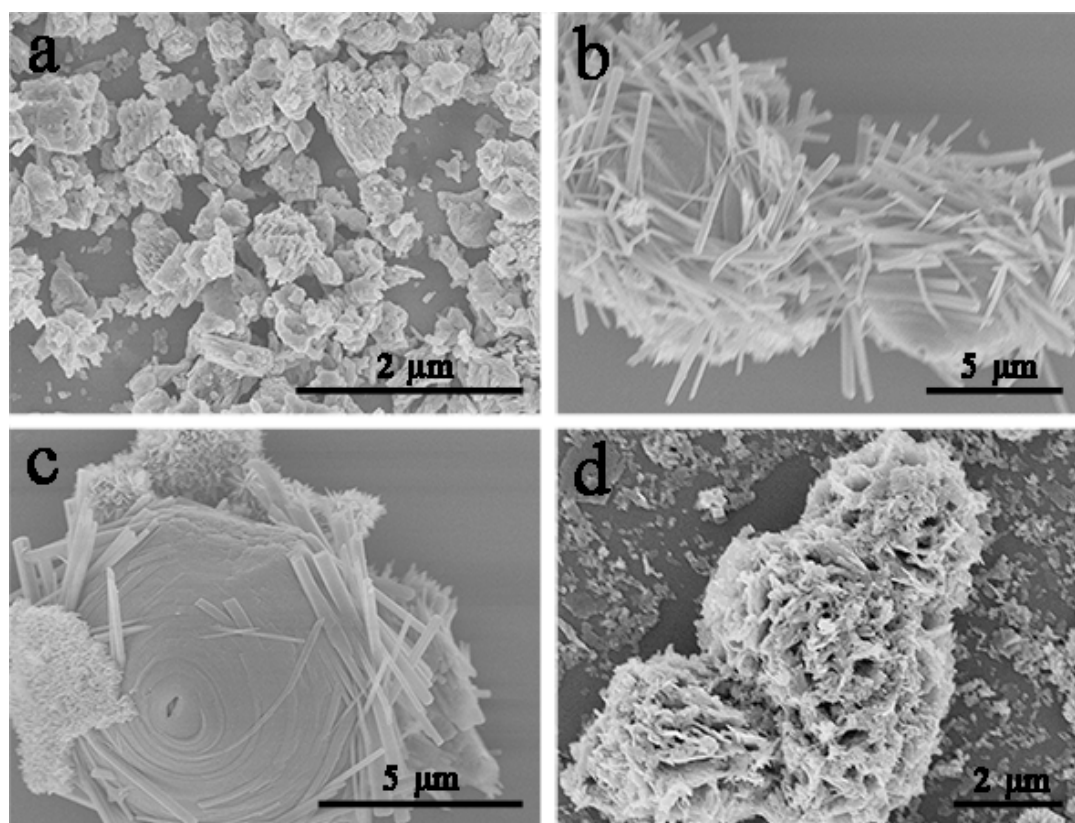


**Figure S2.** FT-IR spectrum of the bilayered  $V_2O_5$  precursor sample P1.

The broad band centered at  $3448\text{ cm}^{-1}$  and the peak at  $1639\text{ cm}^{-1}$  corresponds to the stretching and bending modes of the OH groups of water and ethylene glycol. The minor peaks at  $2935$  and  $2873\text{ cm}^{-1}$  are assigned to the asymmetric and symmetric stretching of ( $\nu_{as}(CH_2)$ ,  $\nu_s(CH_2)$ ) ethylene glycol. The peaks at  $1400$ ,  $1064$  and  $879\text{ cm}^{-1}$  are assigned to the  $\nu_3$ ,  $\nu_1$  and  $\nu_2$  mode of the  $CO_3^{2-}$  group, respectively. The band at  $563\text{ cm}^{-1}$  is assigned to the vibration of V-O bonds.<sup>1-4</sup>



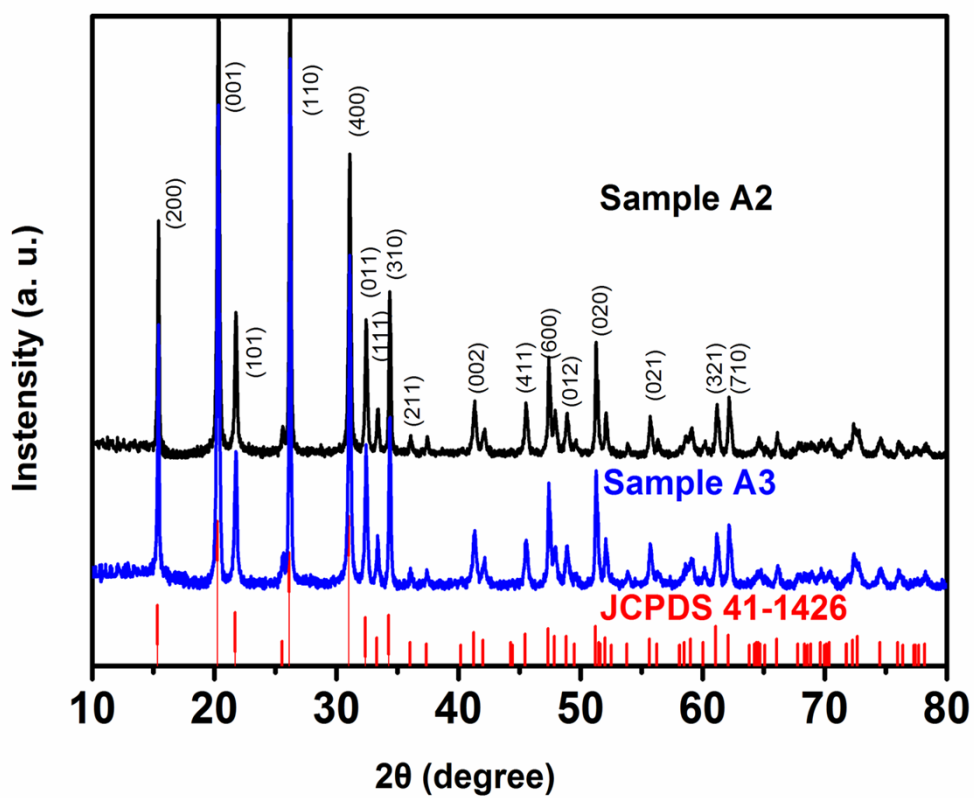
**Figure S3.** EDX of spectrum the sample A1.



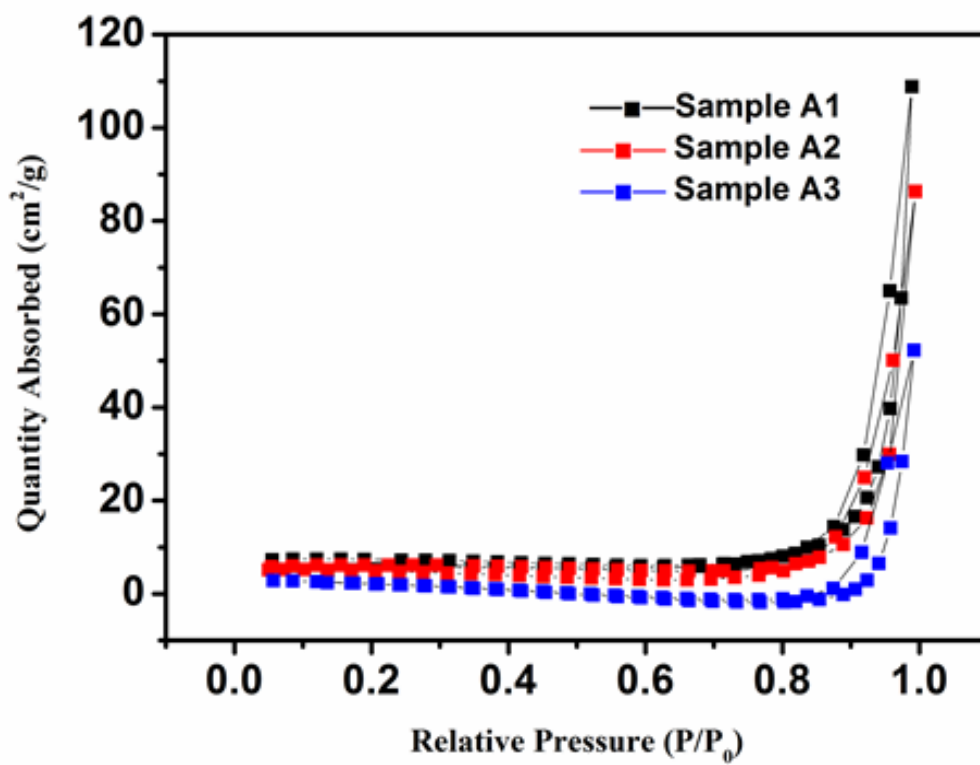
**Figure S4.** FESEM images of (a) irregular bulks (urea dose: 0 mmol), (b,c) the micro-cakes comprising of ribbons and sheets (urea dose: 0.5 mmol), and (d) irregular bulks consisting of nanosheets (urea dose: 2 mmol) of the  $V_2O_5$  precursor.

By changing the reaction conditions during the crystal growth process, it is feasible to control the morphology and structure of the final  $V_2O_5$  products. Urea is chosen as the morphology controlling agent because it is proved that the morphological structures of transition metal oxide could be effectively tuned via the concentration of urea.<sup>5</sup> To demonstrate the critical role of urea in morphology control, we performed three control experiments in which 0.0 mmol urea, 0.5 mmol urea, and 2.0 mmol urea were used for the reaction, respectively. Except for the urea amount, the rest of the experimental parameters were the same as the sample P1. As clearly shown in Figure S4a, irregular particles without nanosheets are obtained in the absence of urea. When

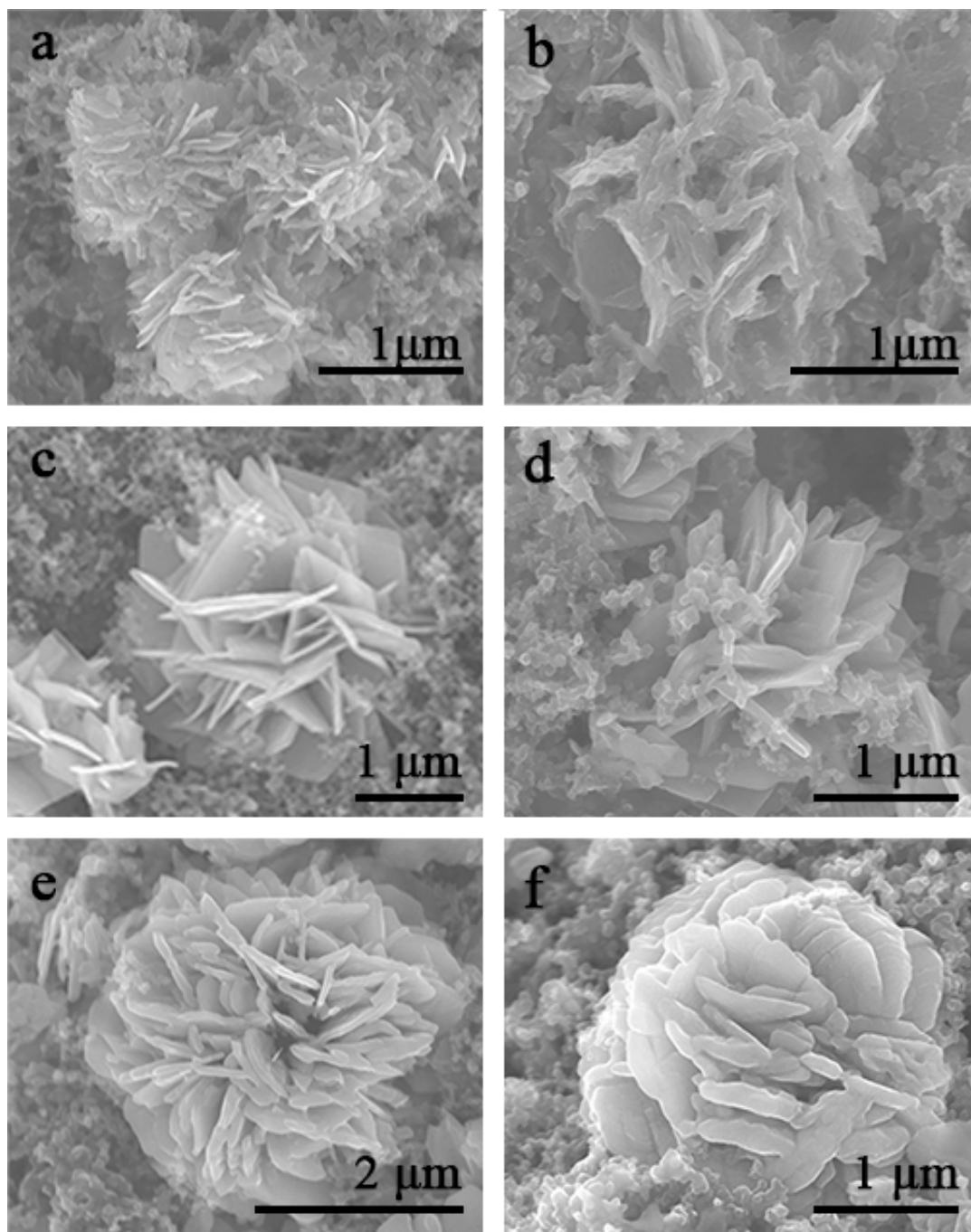
0.5 mmol urea is used into the reaction system, the initial product is an assembly of nanoribbons (Figure S4b). However, the circumjacent ribbons can gradually develop into sheet-shaped structures (Figure S4c). When the amount of urea is further increased to 1 mmol, the flower-like hierarchical structures consisted of ultra-thin nanosheets are obtained (Figure 1b-c). If the amount of urea continues to increase to 2 mmol, the flower-like hierarchical structures cannot be generated; instead, the produced nanosheets are randomly assembled into large aggregates (Figure S4d). Based on the above experiments, urea plays an important role in growth of the sheet-like nanocrystals, and an appropriate amount of urea is critical for the formation of ordered hierarchical structures. Although the exact mechanism how urea tailors the morphology is unclear at this moment, the coordination effect between vanadium and urea or its decomposition products, such as  $\text{CO}_3^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{OH}^-$ , would facilitate the initial seed crystallites to develop into nanosheets and finally grow into flower-like hierarchical structures.



**Figure S5.** XRD patterns of the orthogonal  $V_2O_5$  sample A2 and A3 obtained by annealing the sample P2 and P3, respectively.



**Figure S6.** N<sub>2</sub> adsorption–desorption isotherms of the orthogonal V<sub>2</sub>O<sub>5</sub> sample A1, A2 and A3.



**Figure S7.** SEM images of the electrodes of the sample A1 before (a) and after (b), the sample A2 before (c) and after (d), and the sample A3 before (e) and after (f) discharge/charge for 80 cycles at a current density of 100 mA g<sup>-1</sup> in the range of 2.0-4.0 V.