**Supplementary material**

**Study on the optical and electrochemical performance of V2O5 with various morphologies**

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**Fig. S1**

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**Fig. S1.** SEM image of commercial V2O5.



**Fig. S2.** CV curves of V2O5 hollow spheres at various scan rates.



**Fig. S3.** Galvanostatic discharge curves of V2O5 hollow spheres at different current densities.



**Fig. S4.** Cycling performance of V2O5 hollow spheres at 20 mV·s-1.

**Formation Mechanism:**

According previous literatures [*Current Applied Physics 15(2015), 493-498*; *Applied Surface Science 399(2017), 151-159;* *Inorganic Chemistry 48(2009), 6044-6054*], the possible formation mechanism of V2O5 was discussed. Nanowires were synthesized from commercial V2O5, which converted to [VO(O2)(OH2)3]+ by adding H2O2 and deionized water. Then the species released oxygen to form [HnV10O28]n-6 in hydrothermal reaction. Next, [HnV10O28]n-6 was dissociated to vanadium pentoxide gel, which was changed to V2O5·nH2O sheet with increase of reaction time. V2O5·nH2O sheets continued to dehydrated and formed nanowires because they had the tendency to one-dimensionally grow. For layer-by-layer, the addition of carbon spheres was important. Brick-liked particles were firstly formed, then converted to sheet, finally self-assembly constructed layer-by-layer due to the influence of carbon spheres. The function of carbon spheres acted as a structure-oriented agent, such as adhesives, to guide the formation of layer-by-layer structure. Whereas hollow spheres evolved from solid spheres to core/shell structures and then completely became hollow structure. As the reaction proceeded, the solid inner cores shrank and then gradually formed more core-shell space. Finally, the inner cores completely disappeared, leading to hollow spheres. Detailed formation mechanism was further investigated.