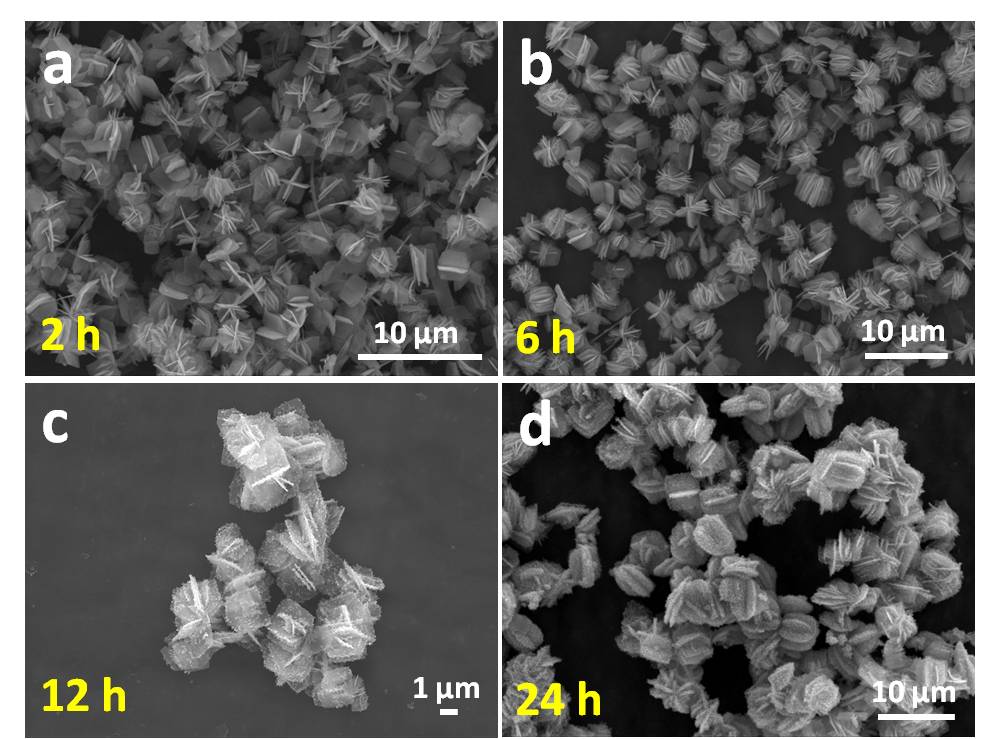
**Supplementary material**

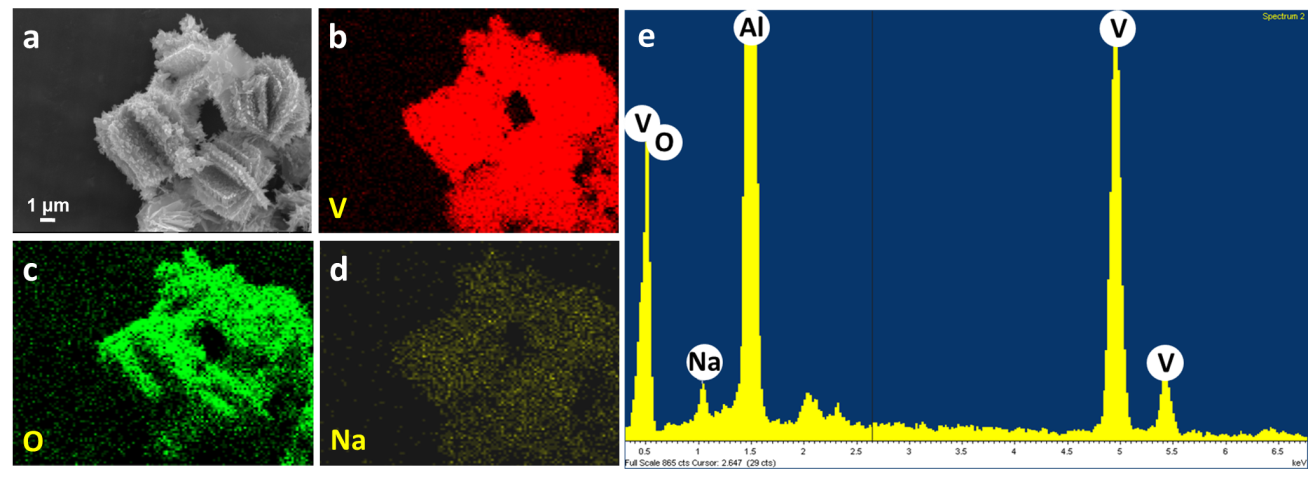
**Three Dimensional** **V2O5/NaV6O15 Hierarchical Heterostructures: Controlled Synthesis and Synergistic Effect Investigated by *in Situ* X-ray Diffraction**

Chaojiang Niu#, Xiong Liu#, Jiashen Meng#, Lin Xu\*, Mengyu Yan, Xuanpeng Wang, Guobin Zhang, Ziang Liu, Xiaoming Xu, Liqiang Mai\*

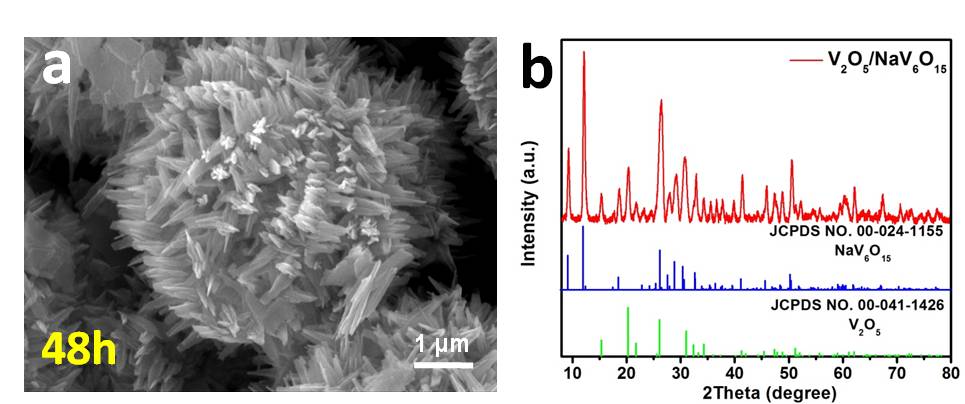
#These authors contributed equally to this work.



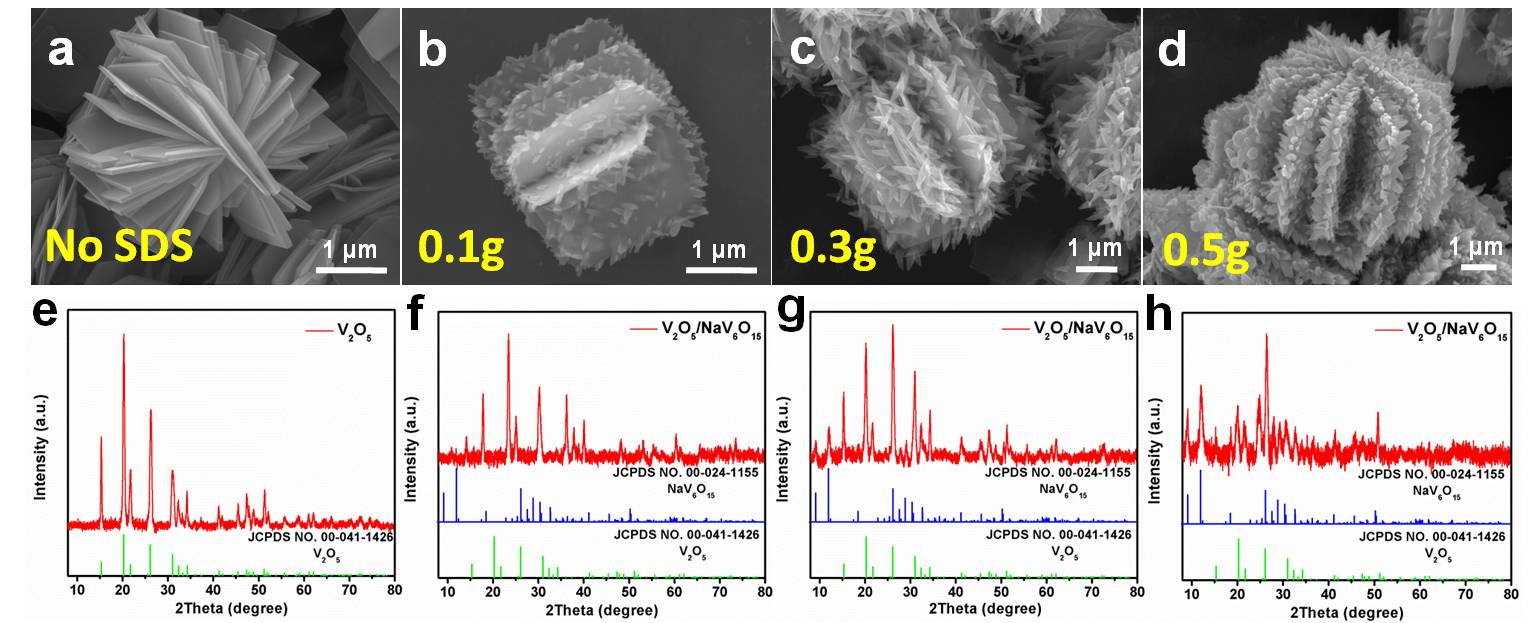
**Figure S1.** (**a-d**) Low-magnification SEM images of 3D V2O5/NaV6O15 hierarchical heterogeneous microspheres prepared at 2 (**a**), 6 (**b**), 12 (**c**) and 24 h (**d**), respectively.



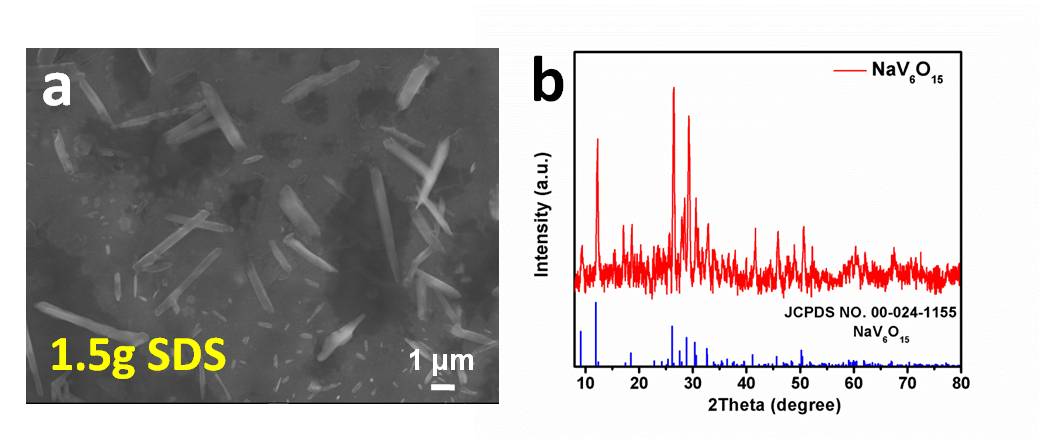
**Figure S2.** SEM image (**a**) and EDS mapping images of V (**b**), O (**c**), and Na (**d**) in 3D V2O5/NaV6O15 hierarchical heterogeneous microspheres. (e) The corresponding EDS spectrum of 3D V2O5/NaV6O15hierarchical heterogeneous microspheres.



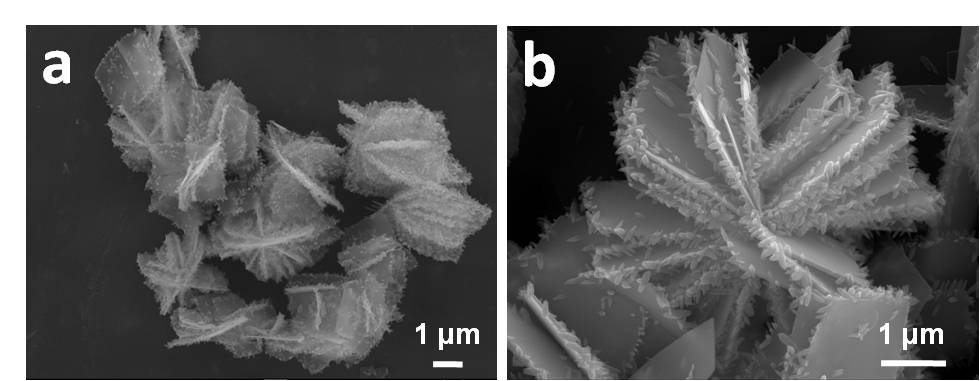
**Figure S3.** SEM image and the corresponding XRD pattern of 3D V2O5/NaV6O15 hierarchical heterogeneous microspheres prepared over a period of 48 h.



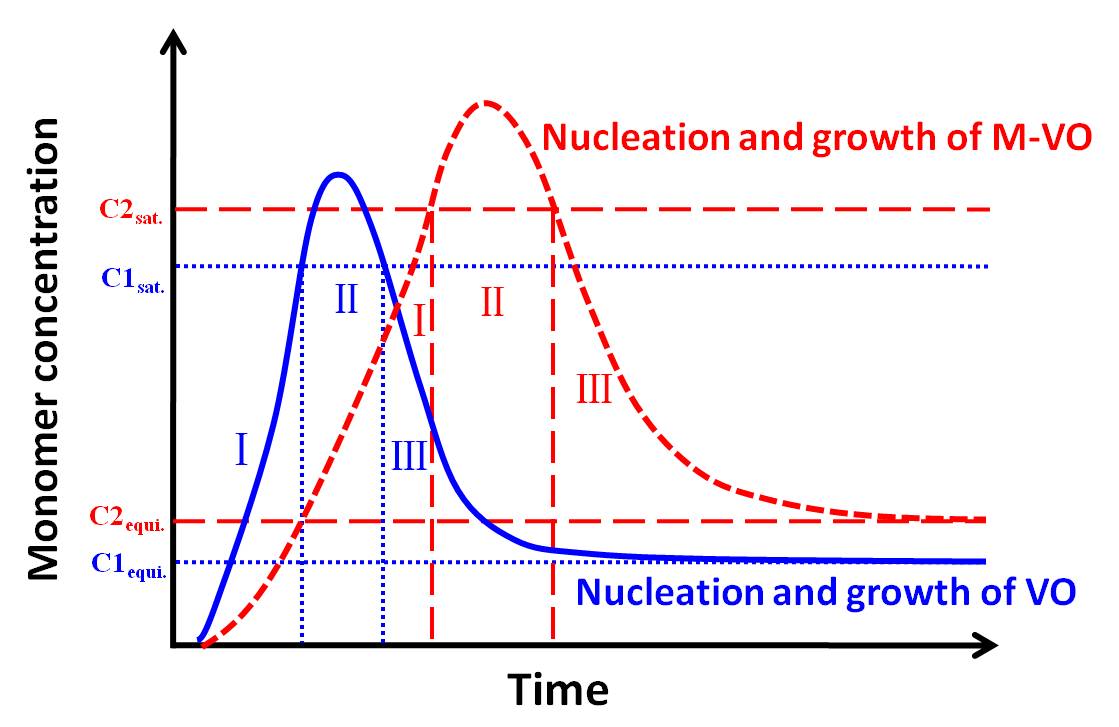
**Figure S4.** SEM images of samples prepared with 0 (**a**), 0.1 (**b**), 0.3 (**c**) and 0.5 g (**d**) of C12H25SO4Na (SDS) over a period of 24 h, and their corresponding XRD patterns (**e-h**) after annealing in air for 5 h at 450 °C.



**Figure S5.** SEM image of NaV6O15 nanorods prepared with 1.5 g of SDS (**a**)and the corresponding XRD pattern (**b**) after annealing in air for 5 h at 450 °C.



**Figure S6**. SEM images of 3D V2O5/NaV6O15 hierarchical heterogeneous microspheres synthesized by substituting SDS with C18H29NaO3S (SDBS).

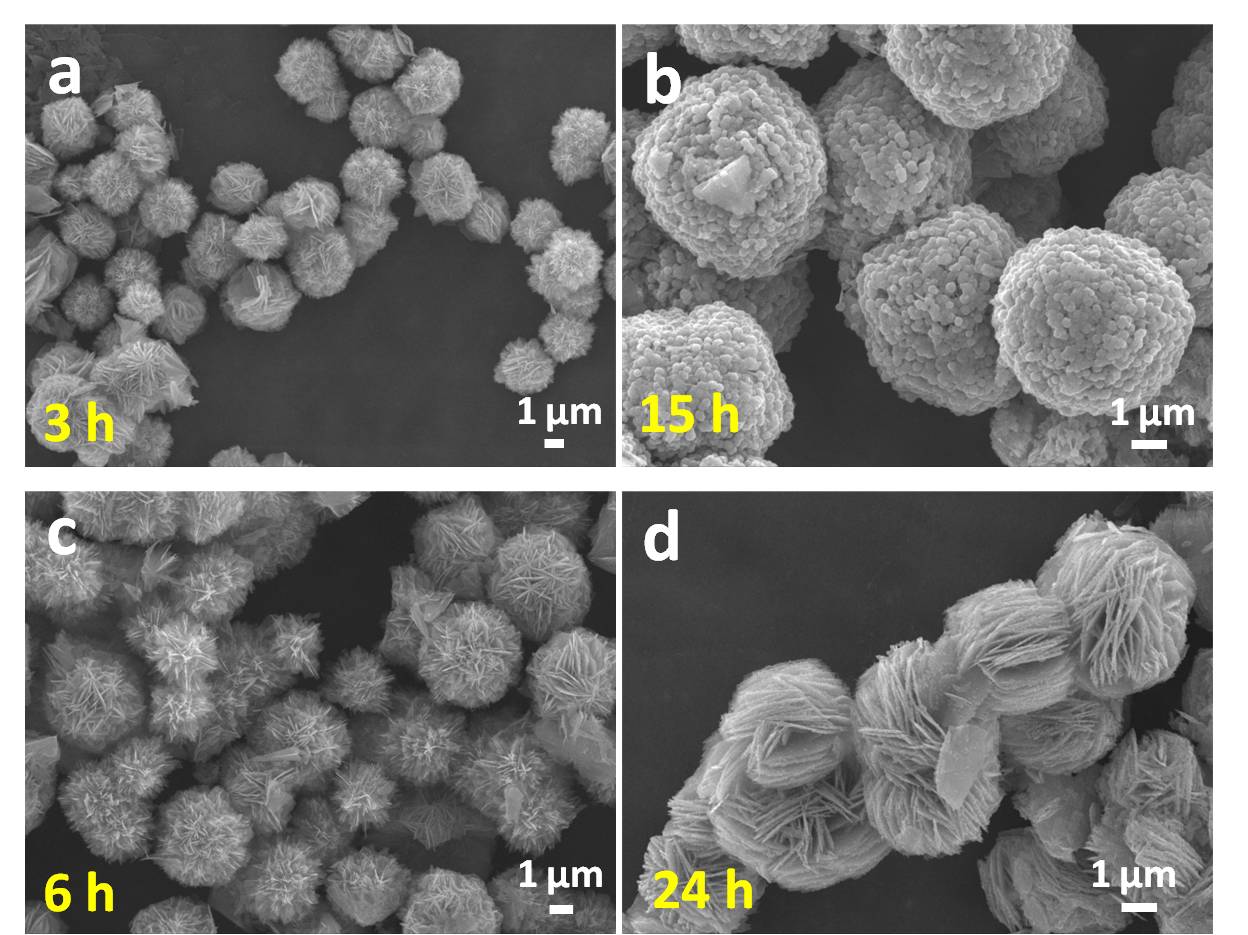


**Figure S7.** Crystal nucleation and growth diagrams of hierarchical heterostructures. C1sat. and C2sat. represent the saturation concentrations of different monomers (VO and M-VO); C1equi. and C2equi. represent the corresponding equilibrium concentrations.

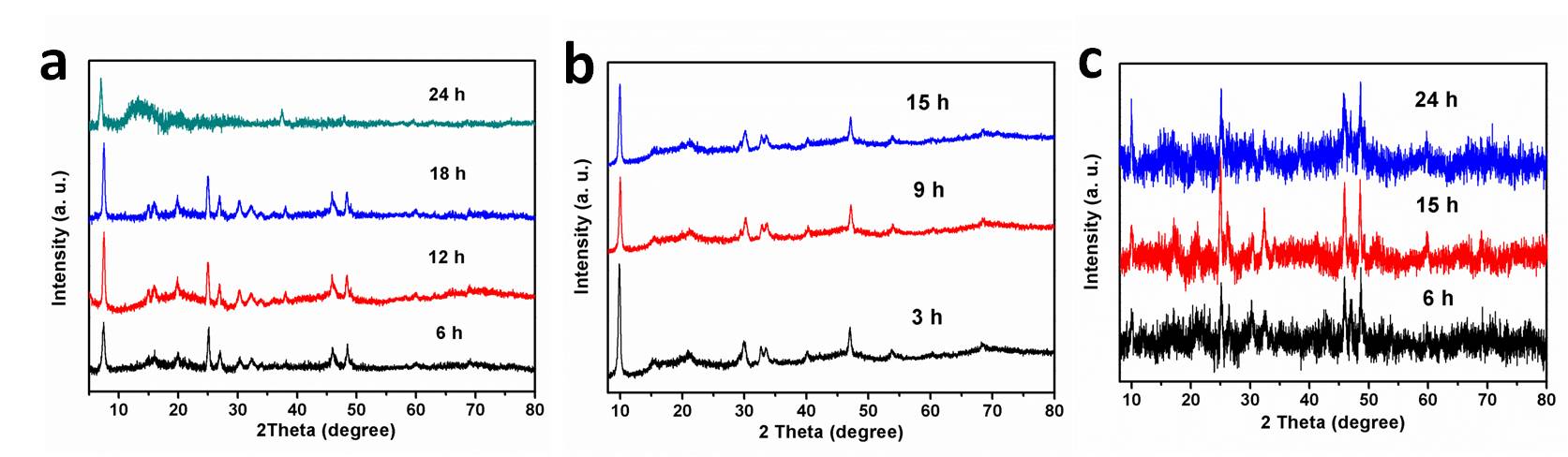
Table S1 Different morphologies of hydrothermal products in different reaction systems

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Vanadium source** | **Sodium**  **source** | **6 h** | **12 h** | **24 h** |
| 1.2 mmol NH4VO3 | 0 mmol SDS | V2O5 nanogears | V2O5  nanogears | V2O5  nanogears |
| 1.2 mmol NH4VO3 | 1 mmol SDS | V2O5 nanogears | **3D**  **V2O5/NaV6O15** | **3D**  **V2O5/NaV6O15** |
| 1.2 mmol NH4VO3 | 1.5 mmol SDS | V2O5 nanogears | **3D**  **V2O5/NaV6O15** | **3D**  **V2O5/NaV6O15** |
| 1.2 mmol NH4VO3 | 5 mmol SDS | -- | -- | NaV6O15 Nanorods |
| 1.2 mmol NH4VO3 | 1 mmol SDBS | V2O5 nanogears | **3D**  **V2O5/NaV6O15** | **3D**  **V2O5/NaV6O15** |
| 1 mmol NH4VO3 | 0.1 mmol Zn(CH3COO)2 | V2O5 microspheres | **3D**  **V2O5/ZnV2O6** | **3D**  **V2O5/ZnV2O6** |
| 1 mmol NH4VO3 | 0.1 mmol Co(CH3COO)2 | V2O5 microspheres | V2O5 microspheres | **3D**  **V2O5/CoV2O6** |

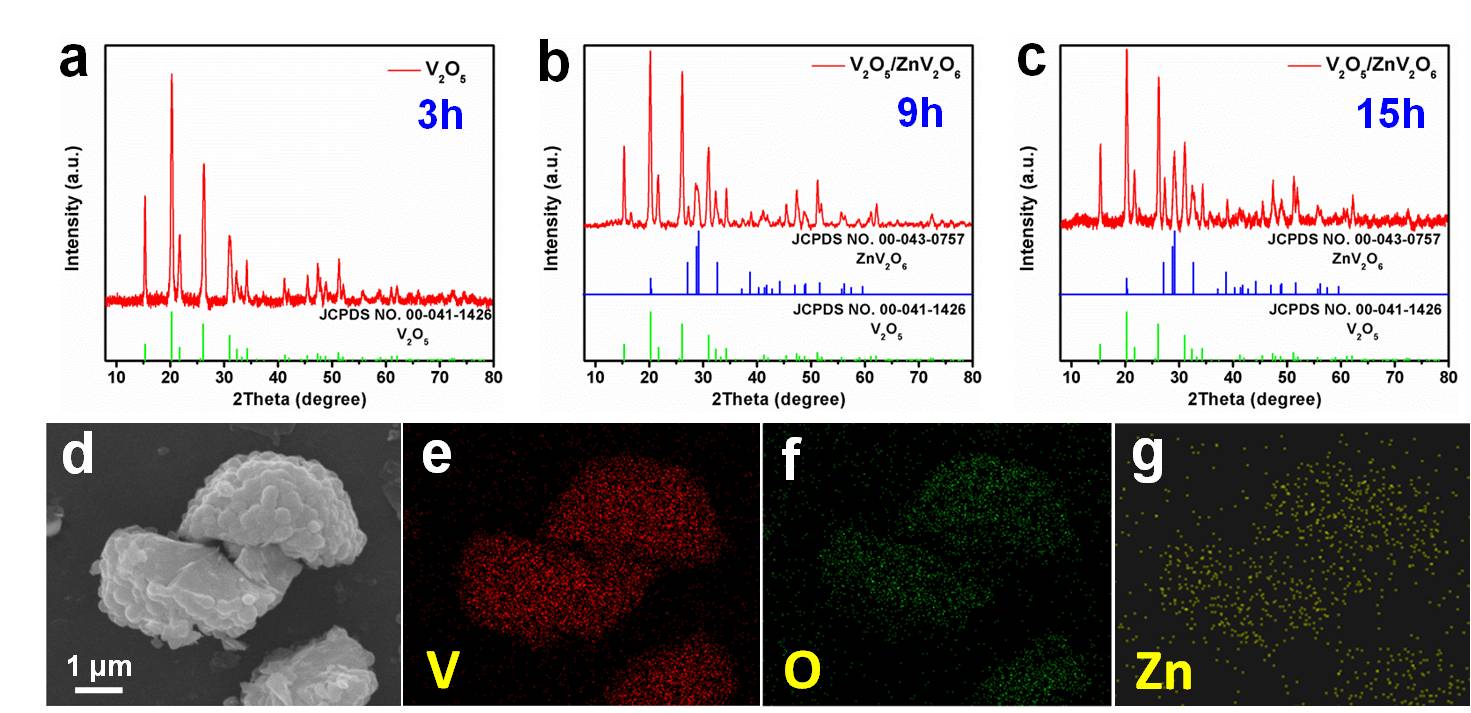
Where SDS is C12H25SO4Na, SDBS is C18H29NaO3S, and 3D refers to the three-dimensional hierarchical heterostructure.



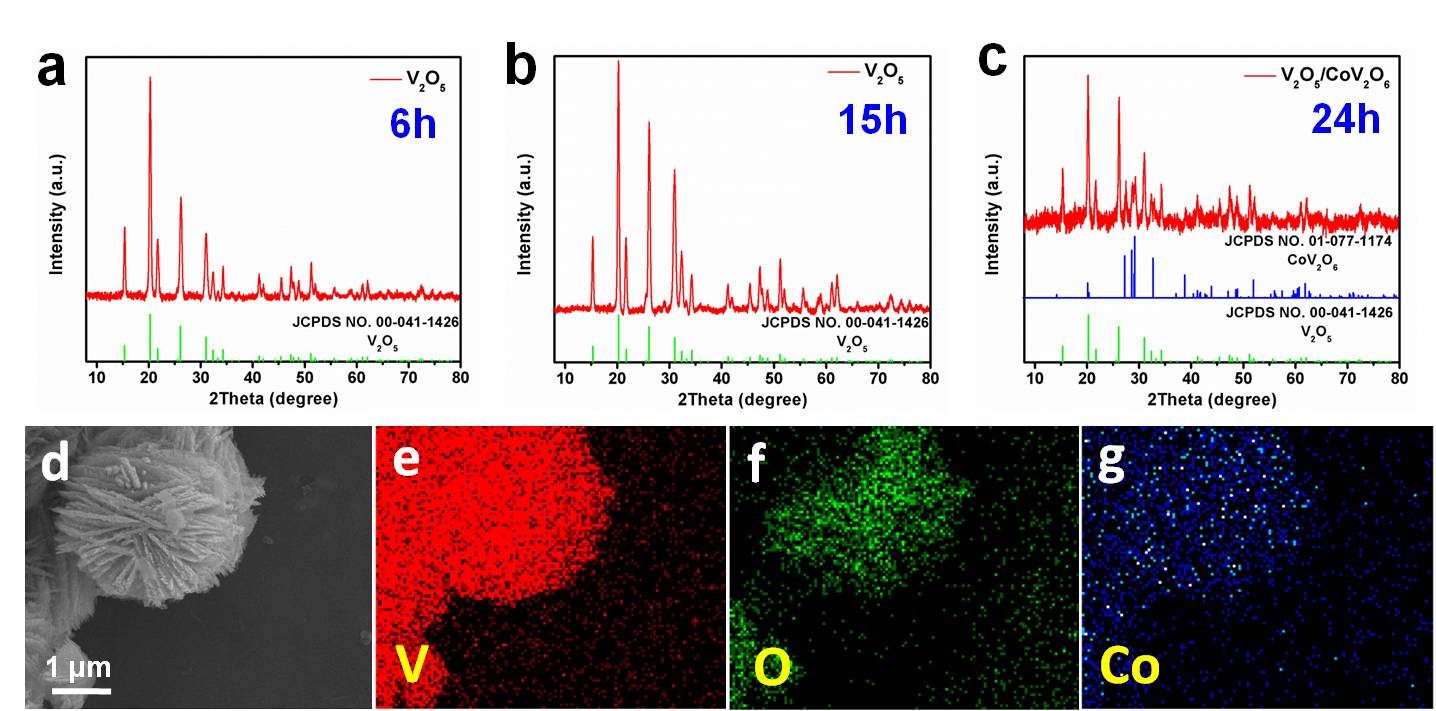
**Figure S8.** (**a-b**) Low-magnification SEM images of 3D V2O5/ZnV2O6 hierarchical heterogeneous microspheres prepared at 3 and 15 h, respectively. (**c-d**) Low-magnification SEM images of 3D V2O5/CoV2O6 hierarchical heterogeneous microspheres prepared at 6 and 24 h, respectively.



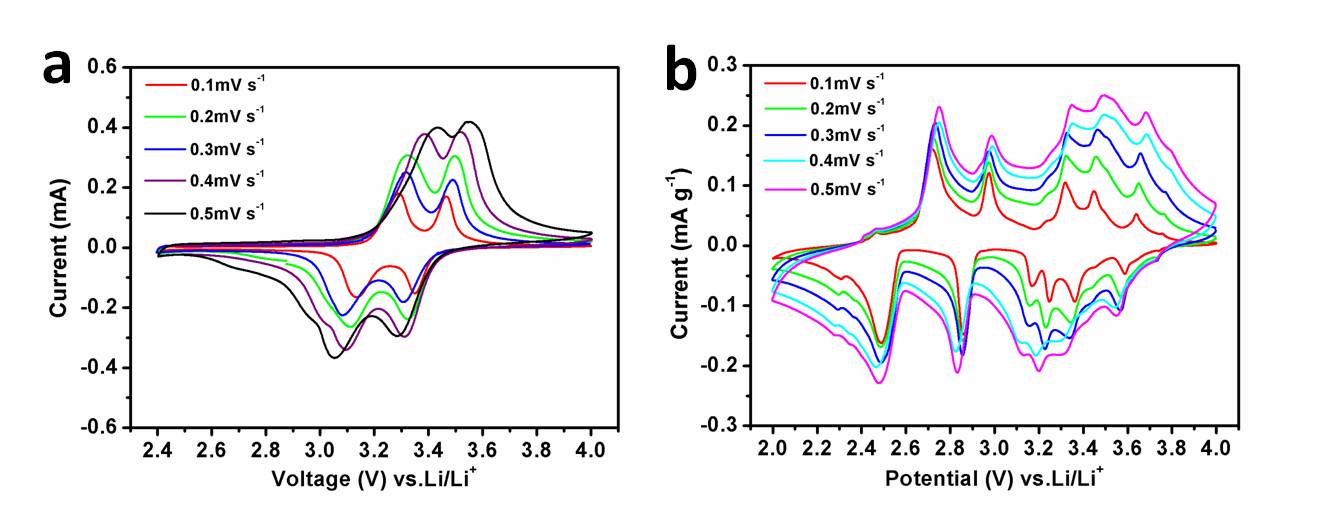
**Figure S9.** XRD patterns of the precursors for V2O5/NaV6O15 (**a**), V2O5/ZnV2O6 (**b**) and V2O5/CoV2O6 (**c**) heterogeneous microspheres prepared at different reaction times.



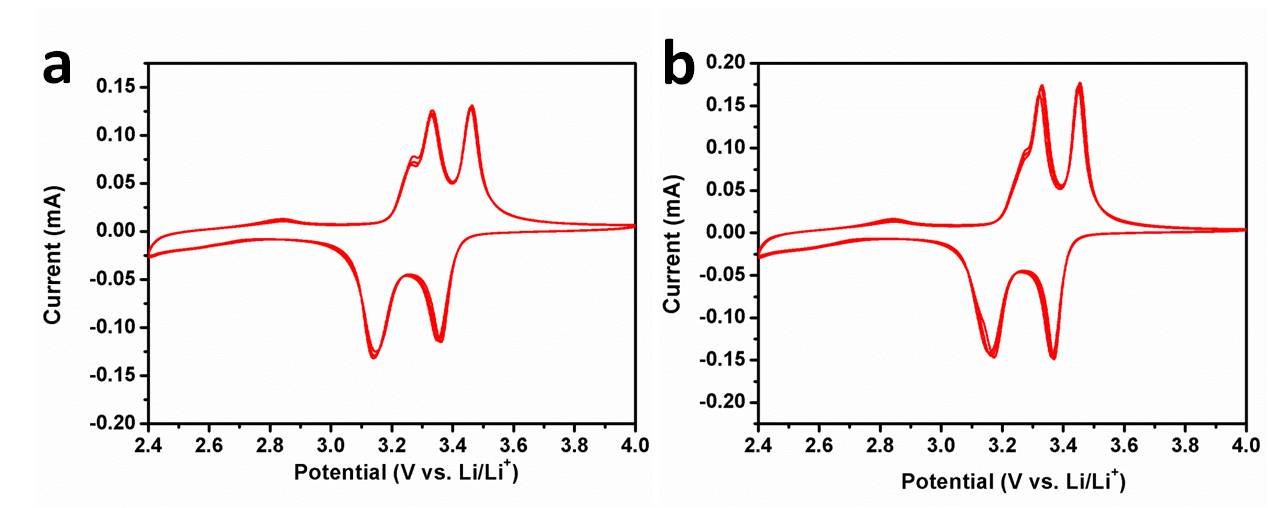
**Figure S10.** XRD patterns (**a-c**) of 3D V2O5/ZnV2O6 hierarchical heterogeneous microspheres prepared over 3, 9 and 15 h, respectively, after annealing in air for 5 h at 450 °C. SEM image (**d**) and EDS mapping images of V (**e**), O (**f**) and Zn (**d**) in 3D V2O5/ZnV2O6 hierarchical heterogeneous microspheres prepared at 15 h.



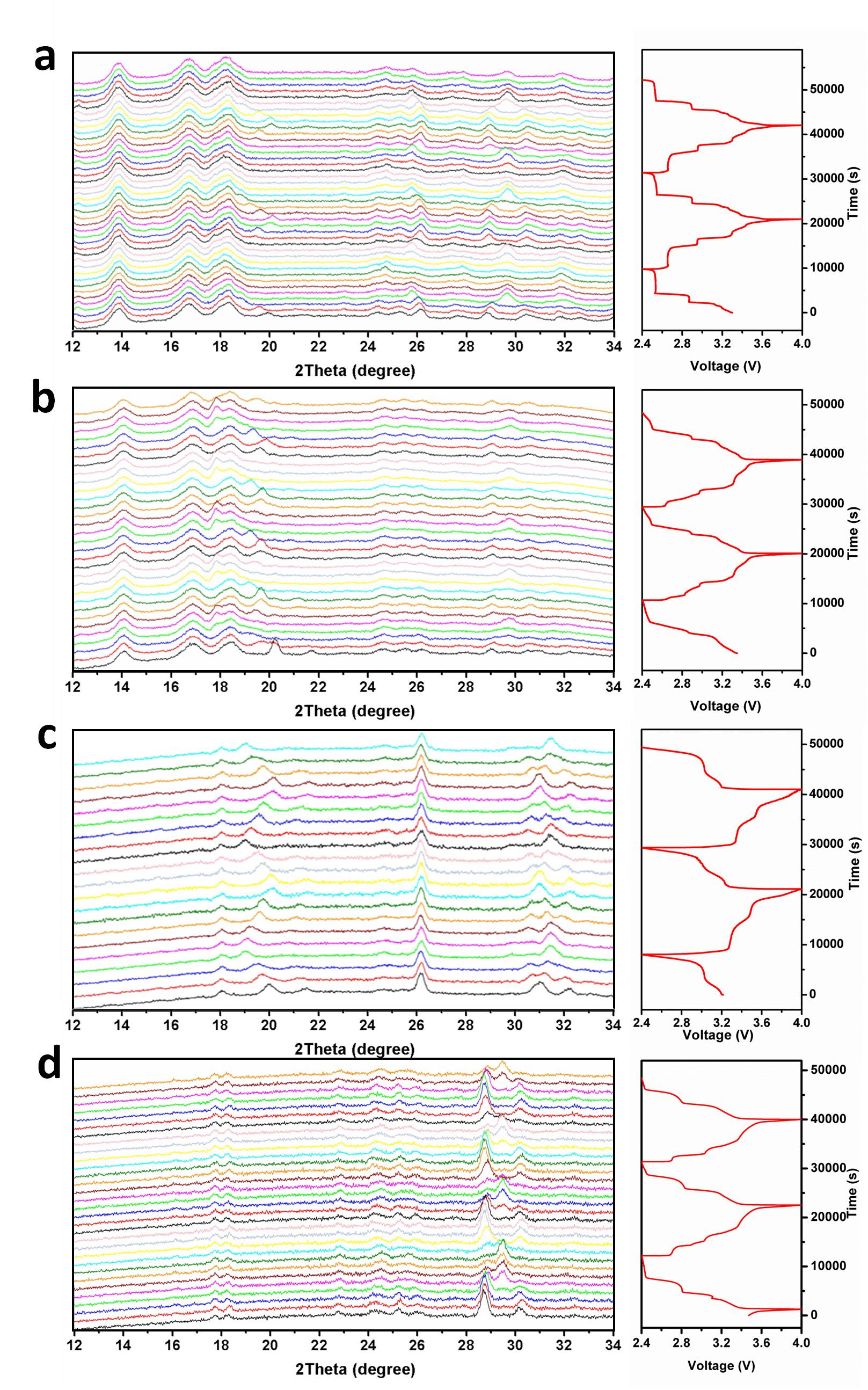
**Figure S11.** XRD patterns (**a-c**) of 3D V2O5/CoV2O6 hierarchical heterogeneous microspheres prepared over 6, 15 and 24 h, respectively, after annealing in air for 5 h at 450 °C. SEM image (**d**) and EDS mapping images of V (**e**), O (**f**) and Co (**g**) in 3D V2O5/CoV2O6 hierarchical heterogeneous microspheres prepared at 24 h.



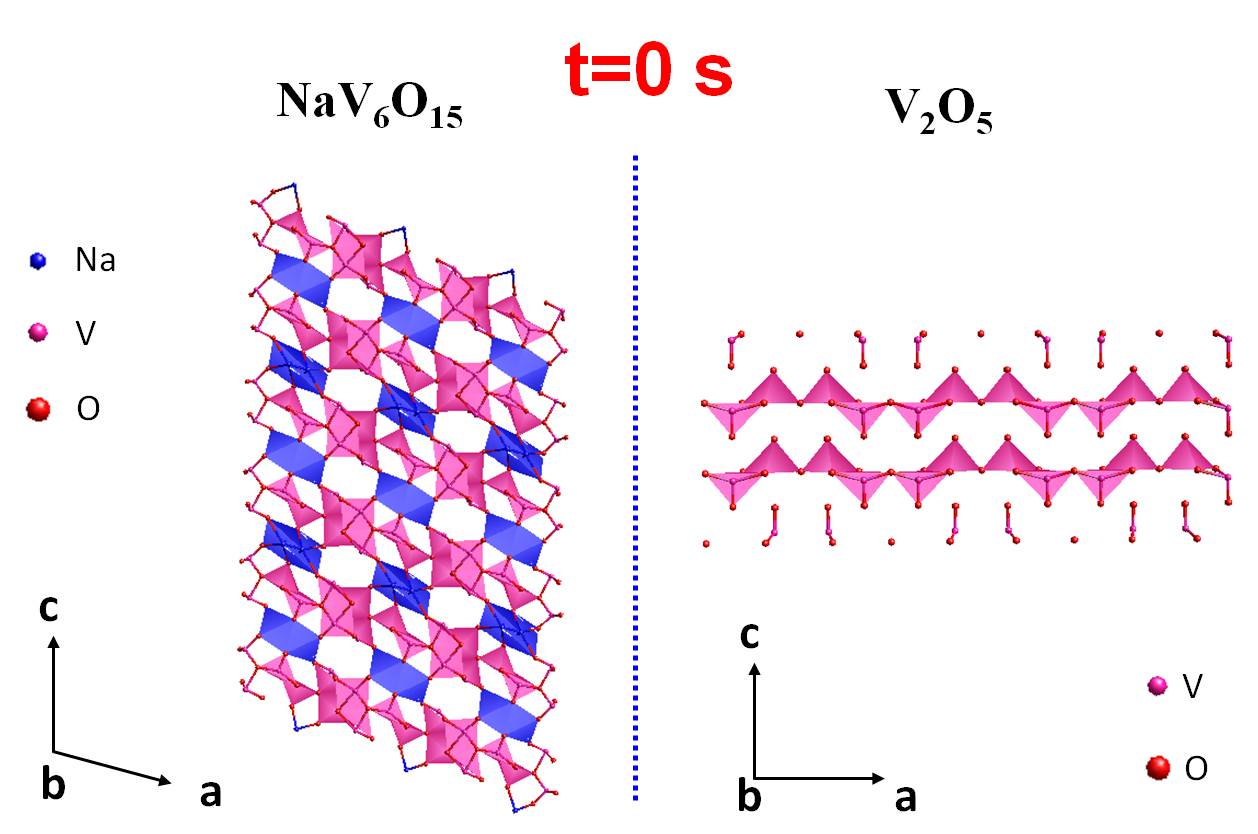
**Figure S12**. The CV curves of pure V2O5 nanogears (**a**) and 3D V2O5/NaV6O15 hierarchical heterogeneous microsphere (**b**) tested at different scan rates ranging from 0.1 to 0.2, 0.3, 0.4 and 0.5 mV s-1, respectively. 3D V2O5/NaV6O15 hierarchical heterogeneous microspheres exhibit smaller peaks shift and polarization than pure V2O5 nanogears.



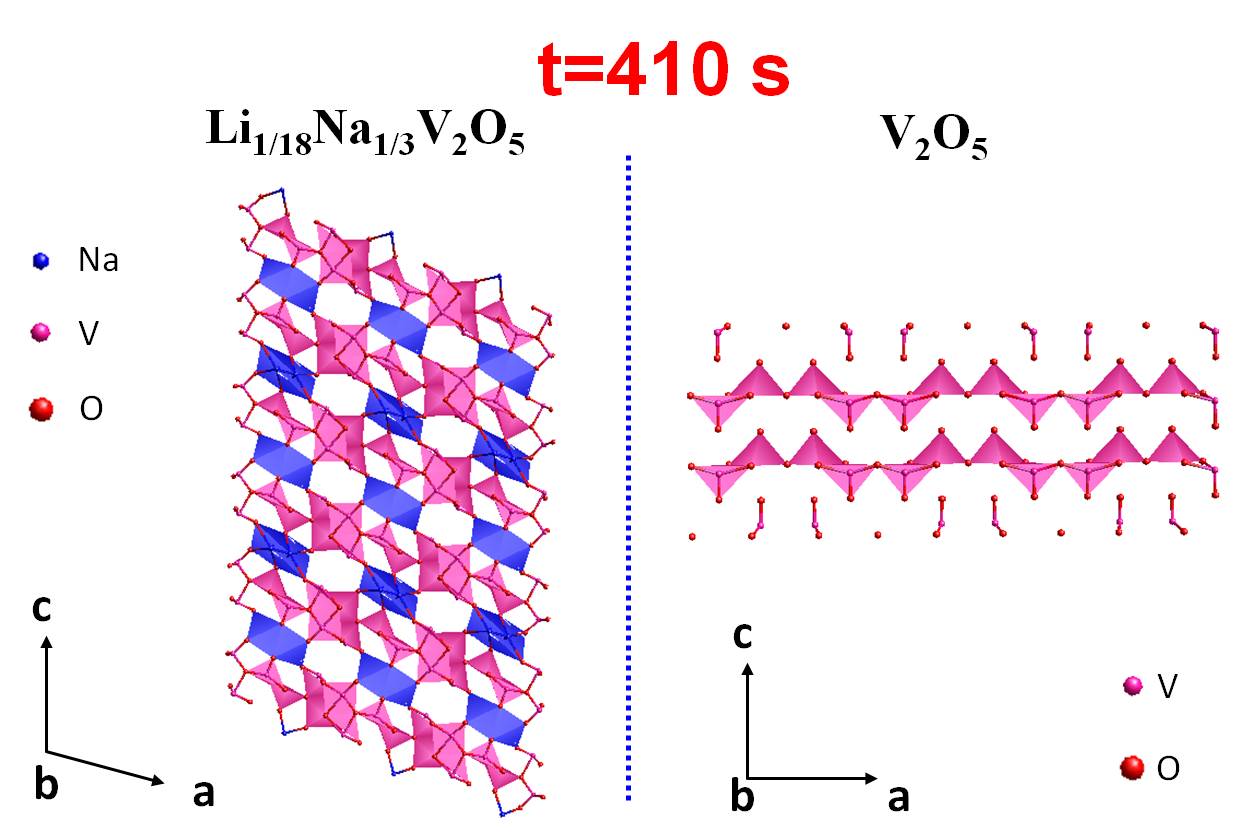
**Figure S13.** CV curves of 3D V2O5/ZnV2O6 (a) and V2O5/CoV2O6 (b) hierarchical heterogeneous microspheres.

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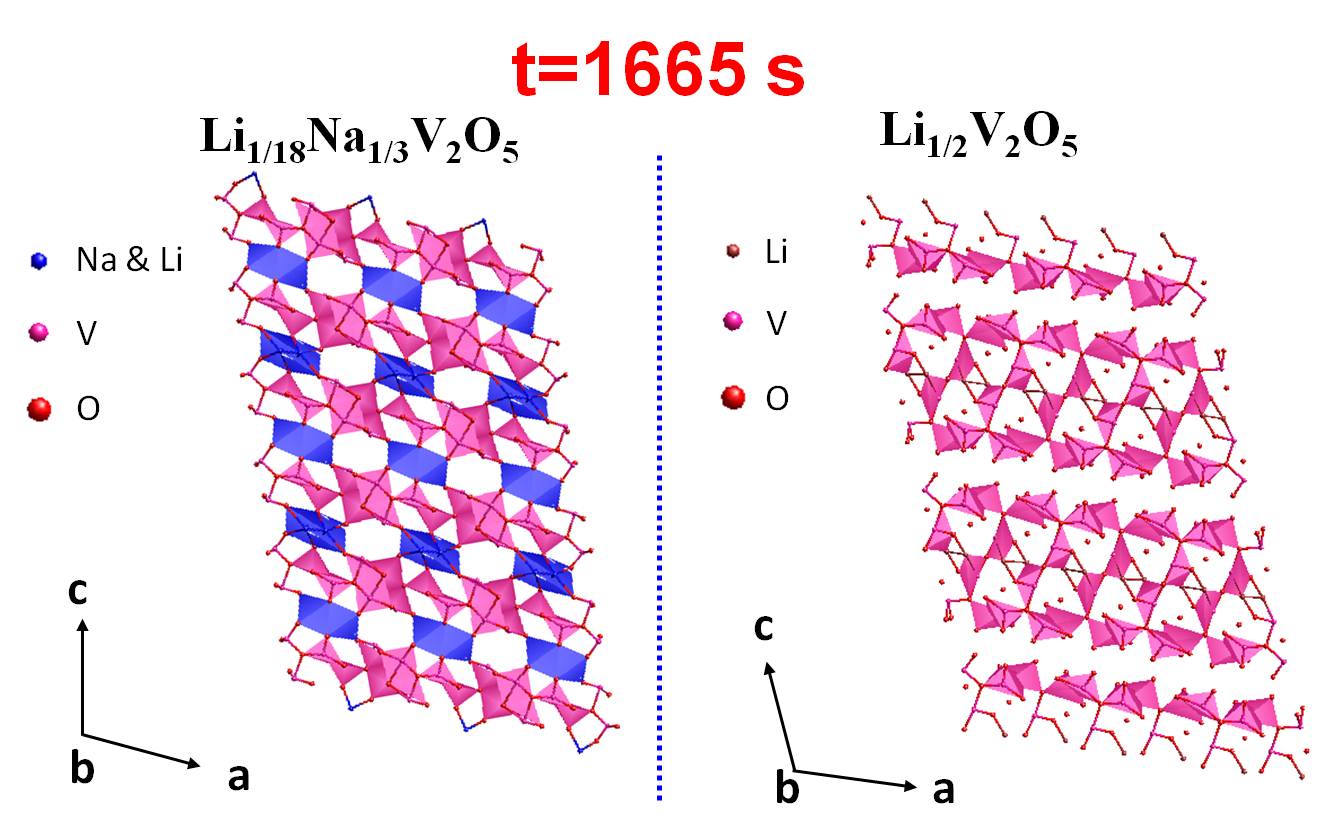
**Figure S14.** The corresponding **s**elected individual diffraction patterns of 3D V2O5/NaV6O15 hierarchical heterogeneous microspheres (**a**), V2O5/NaV6O15 physical mixture (**b**), pure V2O5 nanogears (**c**) and pure NaV6O15 nanospindles (**d**), during galvanostatic charge and discharge at 50 mA g-1. The horizontal axis represents the selected 2θ regions from 12° to 34°, and time is plotted on the vertical axis.



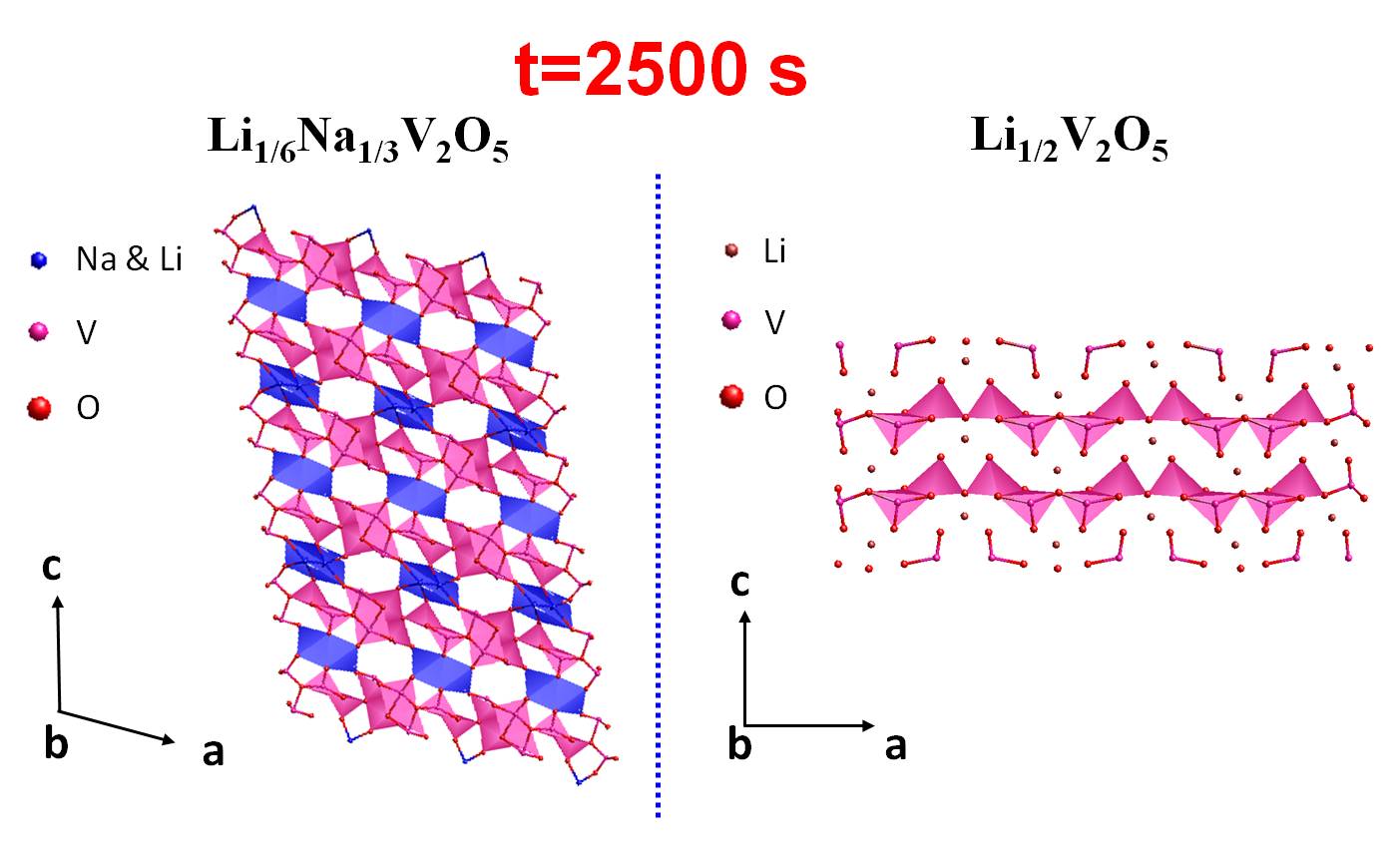
**Figure S15.** Illustration of the initial crystal structures of NaV6O15 and V2O5 along the *b*-axis.



**Figure S16.** Illustration of the crystal structures of Li1/18Na1/3V2O5 and V2O5 at 410 s along the *b*-axis.

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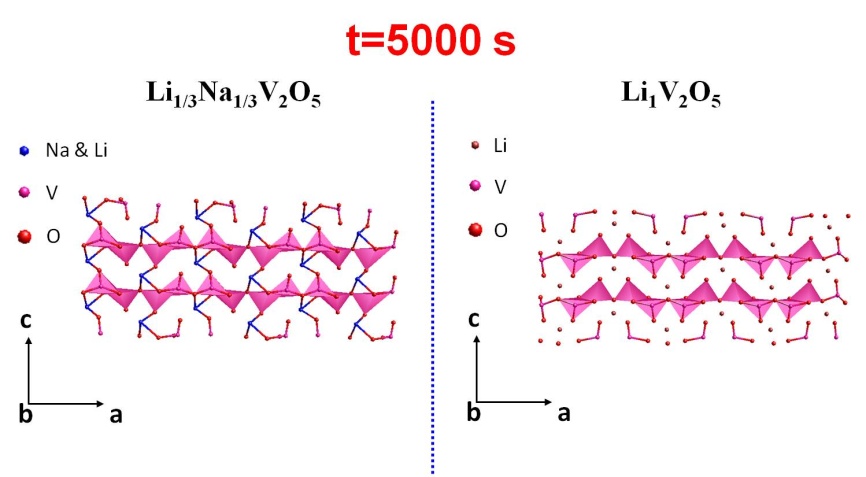
**Figure S17.** Illustration of the crystal structures of Li1/18Na1/3V2O5 and Li1/2V2O5 at 1665 s along the *b*-axis.



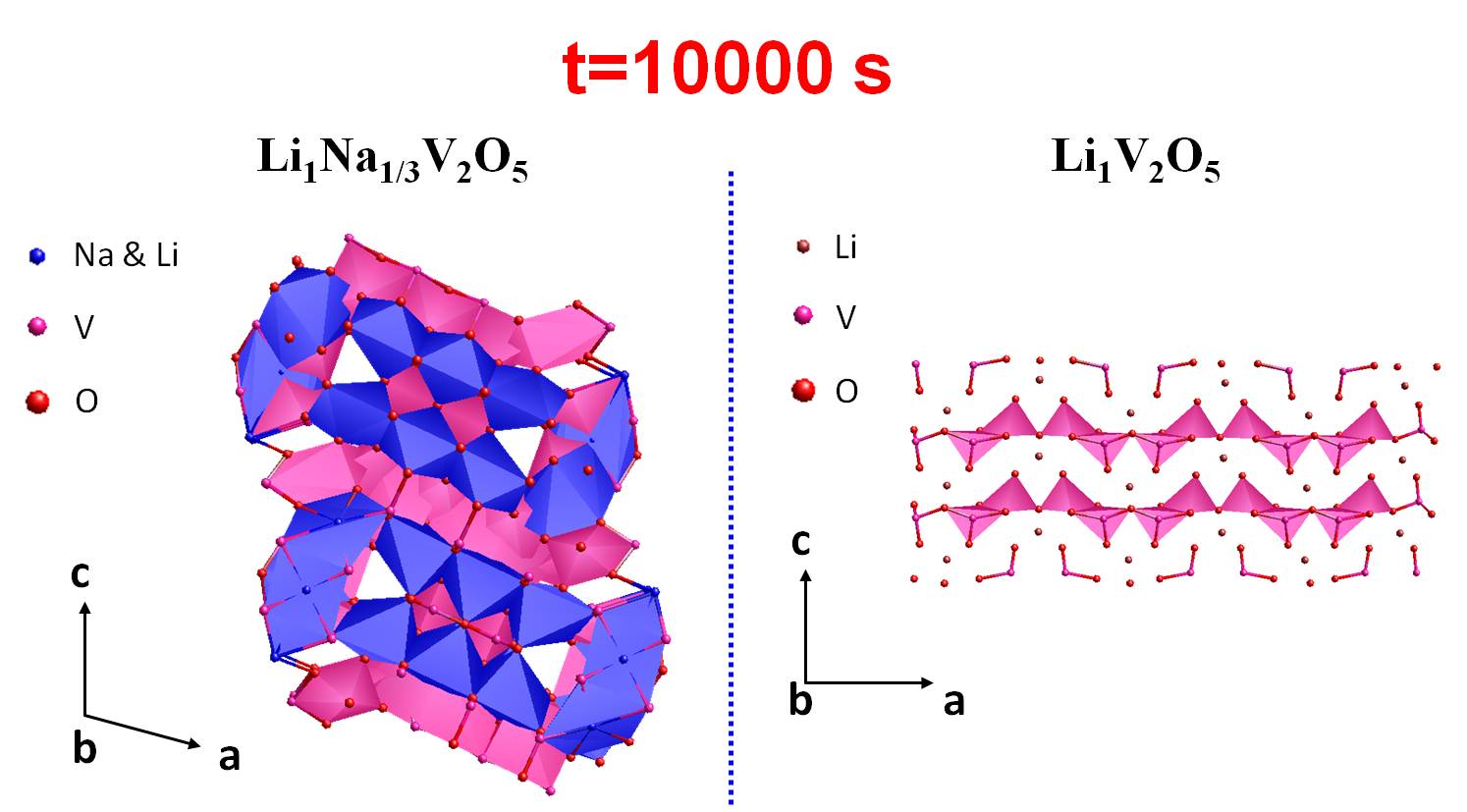
**Figure S18.** Illustration of the crystal structures of Li1/6Na1/3V2O5 and Li1/2V2O5 at 2500 s along the *b*-axis.



**Figure S19.** Illustration of the crystal structures of Li1/6Na1/3V2O5 and Li1V2O5 at 3745 s along the *b*-axis.



**Figure S20.** Illustration of the crystal structures of Li1/3Na1/3V2O5 and Li1V2O5 at 5000 s along the *b*-axis.



**Figure S21.** Illustration of the crystal structures of Li1Na1/3V2O5 and Li1V2O5 at 10,000 s along the *b*-axis.

These illustrations from Figure S12 to Figure S18 are analyzed by Total pattern solution (TOPAS) structure refinement.

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**Figure S22.** Kinetics calculations based on the frequency (ω-1/2) and Z′ values at low frequency region of 3D V2O5/NaV6O15 hierarchical heterogeneous microspheres, V2O5 nanogears and V2O5/NaV6O15 physical mixture before cycling.

Calculation of the Lithium-ion Diffusion Kinetics

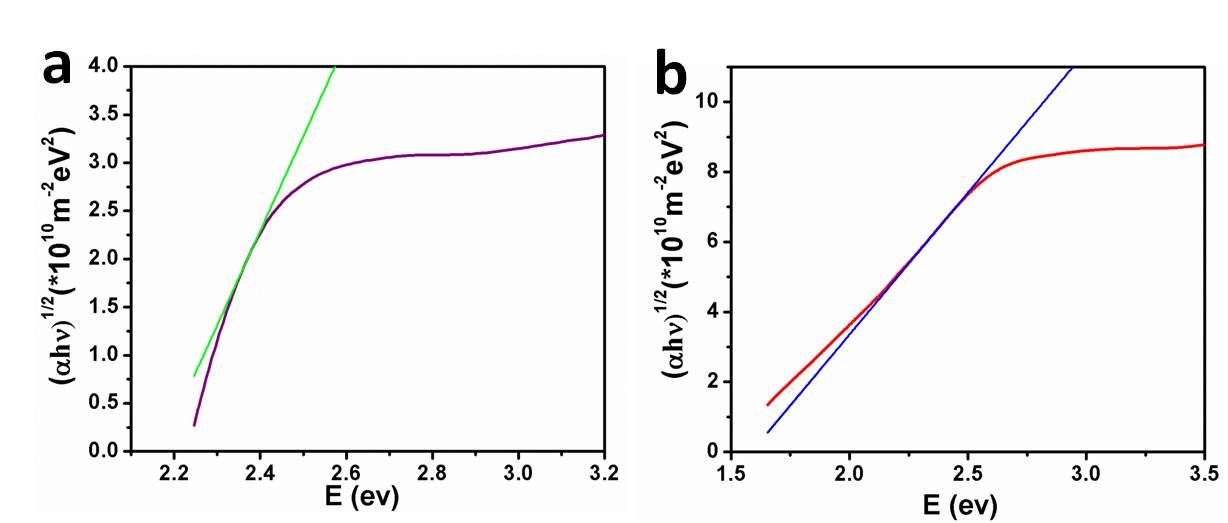
*D*Na=*R* 2*T* 2/2*A* 2*n* 4*F* 4*C* 2*σ* 2 (1)

*Z'* =*R*D+*R*L+*σω -1/2* (2)

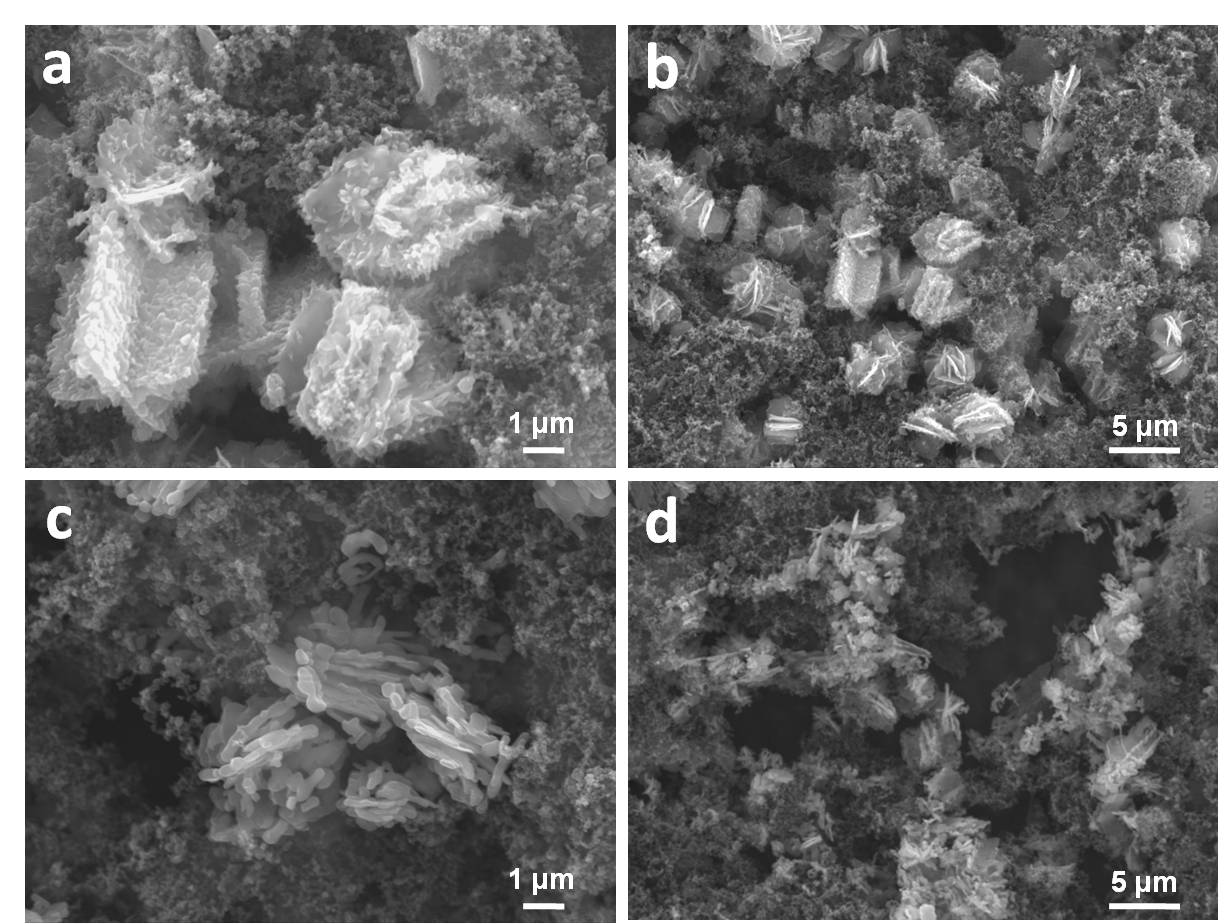
Where ***D*Na** is the sodium-ion diffusion coefficient, ***R*** is the gas constant, ***T*** is the absolute temperature, ***A*** is the surface area of cathode, ***n*** is the number of electrons per molecule during oxidization, ***F*** is the number of electrons per molecule during oxidization, ***C*** is the concentration of sodium-ion and ***σ*** is the Warburg factor which could be obtained by equation (2). By linear fitting of ***Z'***and ***ω* -1/2**, the slope is described as ***σ*** value. Combining with equation (1), the square of *σ* value has an inverse relationship with *D*Na. According to equations (1) and (2), the slope in fitting line of***ω* -1/2** (*ω* is frequency) and ***Z'*** is defined as Warburg factor and its square values have an inverse relationship with ***D*Na**.

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**Figure S23.** EIS curves of 3D V2O5/NaV6O15 hierarchical heterogeneous microspheres under different depth during the discharge process.



**Figure S24.** UV-VIS diffuse reflectance spectra of V2O5 (**a**) and NaV6O15 (**b**).



**Figure S25**. SEM images of 3D V2O5/NaV6O15 hierarchical heterogeneous microspheres (**a-b**) and pure V2O5 nanogears (**c-d**) after cycling 50 times at the current density of 500 mA g-1.