Supporting Information

**Synergistic Effect of Core-Shell Heterogeneous V2O5@MV6O15 (M=Na, K) Nanoparticles for Enhanced Lithium Storage Performance**

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**Figure S1.** The discharge/charge curves of (a) pure NaV6O15 and (b) KV6O15 NPs at the current density of 200 mA g-1. The cycling performance of (c) pure NaV6O15 and (d) KV6O15 NPs at the current density of 500 and 200 mA g-1, respectively.



**Figure S2**. XRD pattern of the as-prepared VO2 nanorod precursors.



**Figure S3**. (a) SEM image and (b) XRD pattern of VO2@NaxV2O5 before calcining.



**Figure S4**. (a) SEM image and (b) XRD pattern of VO2@KxV2O5 before calcining.



**Figure S5.** (a) SEM image and (b) XRD pattern of as-prepared V2O5@KV6O15.

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**Figure S6.** (a-d) EDS elemental mapping and (e) energy dispersive spectrum image of as-prepared V2O5@KV6O15 NPs, the magnified labels are added by the side of the original labels.



**Figure S7**. SEM images of as-prepared (a) bare V2O5 NPs, (c) pure NaV6O15 NPs and (e) pure KV6O15 NPs. XRD patterns of as-prepared (b) bare V2O5 NPs, (d) pure NaV6O15 NPs and (f) pure KV6O15 NPs.



**Figure S8.** HAADF energy dispersive spectrum of as-prepared V2O5@NaV6O15 NPs.



**Figure S9.** The positions of redox peaks in the first CV curve of V2O5@NaV6O15 NPs.



**Figure S10.** First three cycles of CV curves of (a) V2O5 and (b) V2O5@KV6O15 NPs at the scan rate of 0.1 mV s-1 of 2.4-4 V. Electrochemical performances of V2O5@KV6O15 NPs (blue triangles): (c) cycling performance at 200 mA g-1 and (d) rate performance at different current densities from 100 to 200, 300, 500, 1000 and 2000 mA g-1.



**Figure S11.** The corresponding discharge/charge curves at different rates from 100 to 200, 300, 500, 1000 and 2000 mA/g of V2O5@KV6O15 NPs.

**Table S1:** The comparison of the electrochemical performances between V2O5@MV6O15 NPs and other previously reported results.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Electrode material | Capacity (mAh g-1) | Current density | Cycles | References |
| V2O5@NaV6O15 nanoparticles | 133 | 200 mA g-1 | 200 | This work |
| V2O5@KV6O15 nanoparticles | 119 | 200 mA g-1 | 100 | This work |
| V2O5 hollow microclews | 137.2 | 0.67 C (100 mA g-1) | 50 | [1] |
| interconnected V2O5 nanonetworks | 145 | 100 mA g-1 | 100 | [2] |
| 3D porous V2O5 octahedrons | 141 | 100 mA g-1 | 60 | [3] |
| mesoporous V2O5 nanosheets | 144 | 100 mA g-1 | 100 | [4] |
| 3D porous  V2O5 hierarchical microplates | 137 | 100 mA g-1 | 50 | [5] |
| Hierarchical and porous V2O5 microspheres | 102 | 0.5 C (73.5 mA g-1) | 100 | [6] |
| V2O5 hollow microspheres | 128.8 | 1 C (147 mA g-1) | 200 | [7] |
| Ultrathin V2O5 nanosheets | 140 | 1 C (147 mA g-1) | 50 | [8] |
| V2O5 film | Coulombic efficiency=100% | 1 C (147 mA g-1) | 105 | [9] |

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**Figure S12.** The GITT curves of (a) V2O5@NaV6O15 NPs, (b) V2O5 NPs, (c) V2O5@KV6O15 NPs, (d) pure NaV6O15 NPs and (e) pure KV6O15 NPs. (f) Li+ diffusivity versus the state of discharge of bare V2O5 NPs (black squares), pure NaV6O15 (dark yellow pentagons) and pure KV6O15 (magenta hexagons) NPs.



**Figure S13.** GITT potential response curve with time. The experiment was conducted at constant current pulse of 15 mA g-1 for 5 min followed by a relaxation period of 10 min.

**Scheme 1.** Where τ refers to constant current pulse time, mB, VM, MB, and S are the mass, molar volume, molar mass of the cathode material, and electrode-electrolyte interface area, respectively. △ES is voltage difference during a single-step experiment, and △Eτ is the total change of cell voltage during a constant current pulse excluding the IR drop.

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**Figure S14.** SEM images of (a) V2O5@NaV6O15 NPs, (b) V2O5@KV6O15 NPs and (c) bare V2O5 NPs, respectively, after 500 cycles at the current density of 1 A g-1. Red dash circles mark out the cathode materials, blue dash circles mark out the acetylene black and in the insets of (a) and (b), red arrows point out the cracks.



**Figure S15.** Schematic illustration showing the synergistic effect between the two components in the lithiation processes, and delithiation process takes the reverse direction. Our group has calculated the amount of Li+ insertion in NaV6O15[10].

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