Supporting Information

Hierarchical Orthorhombic V_2O_5 Hollow Nanospheres as High Performance Cathode Materials for Sodium-Ion Batteries

Dawei Su,[a,b] *Shixue Dou**[b] *and Guoxiu Wang**[a]

[a] Centre for Clean Energy Technology, School of Chemistry and Forensic Science, Faculty of Science, University of Technology, Sydney, NSW 2007, Australia.

[b] Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia

Crystallographic Data

Table S1. Crystallographic data and Rietveld refinement of vanadyl acetylacetonate ($VO(acac)_2$).

Crystal information	**Crystallographic data**
Crystal system	Triclinic
Space group	$P\bar{2}$ (No. 2)
a / Å	7.5258
b / Å	8.2242
c / Å	11.2321
α / °	73.0599
β /°	71.3566
γ /°	66.6140
Cell volume / Å^3	593.7
Z	2
χ^2	7.3
R_{wp}	8.76 %
R_p	8.46 %

Table S2. Atomic coordinates and occupancies with atomic displacement parameters of $VO(acac)_2$.

Atom	**x**	**y**	**z**	**g**
V	0.14364	0.29028	0.22359	1.00
O1	0.94067	0.41418	0.36046	1.00
O2	0.99809	0.12126	0.26991	1.00
O3	0.14724	0.53608	0.13733	1.00
O4	0.22006	0.23025	0.05358	1.00
O5	0.33170	0.18871	0.27989	1.00
O6	0.27538	0.53735	0.44054	1.00
C1	0.82264	0.35208	0.45730	1.00
C2	0.78383	0.19642	0.46715	1.00
C3	0.86745	0.09227	0.37096	1.00
C4	0.79023	0.94101	0.38409	1.00
C5	0.77673	0.21653	0.01324	1.00
C6	0.22156	0.59188	0.02015	1.00
C7	0.70410	0.50906	0.07607	1.00
C8	0.70721	0.68623	0.05760	1.00
C9	0.63088	0.78568	0.16710	1.00

***Table S3*.** Selected interatomic distances in $VO(acac)_2$.

Atoms		Distance / Å
V	O1	1.978
V	O2	1.956
V	O3	1.978
V	O4	1.960
V	O5	1.558
O1	V	1.978
O1	C1	1.285
O2	V	1.956
O2	C3	1.275
O3	C6	1.279
O4	C8	1.301
O6	C1	1.491
C1	O6	1.491
C1	C2	1.389
C2	C3	1.405
C3	C4	1.523
C4	C3	1.523
C5	C6	1.514
C6	C5	1.514
C6	C7	1.392
C7	C6	1.392
C7	C8	1.419
C8	O4	1.301
C8	C9	1.508

Table S4. Crystallographic data and Rietveld refinement of vanadyl ethylene glycolate (VEG).

Crystal information	**Crystallographic data**
Crystal system	Monoclinic
Space group	C2/C (No. 15)
a / Å	9.2717
b / Å	9.7350
c / Å	9.9179
α / °	90.0000
β /°	105.9814
γ /°	90.0000
Cell volume / Å^3	860.592
Z	8
χ^2	8.6
R_{wp}	9.98%
R_p	7.21 %

Table S5. Atomic coordinates and occupancies of VEG.

Atom	**x**	**y**	**z**	**g**
V	-0.01650	0.12390	0.09170	1.00
C1	0.27100	0.03000	0.27000	1.00
C2	0.27900	0.01600	0.13200	1.00
O1	-0.01150	0.26730	0.01920	1.00
O2	0.14260	0.10020	0.27850	1.00
O3	0.12850	0.02320	0.03200	1.00
H1	0.25175	-0.08639	0.27265	1.00
H2	0.37207	0.03481	0.33776	1.00
H3	0.33618	0.12836	0.12806	1.00
H4	0.37036	-0.03659	0.11670	1.00

Table S6. Selected interatomic distances in VEG.

Atoms		Distance / Å
V	O1	1.577
V	O2	1.976
V	O3	1.983
C1	C2	1.398
C1	O2	1.395
C1	H1	1.148
C1	H2	0.993
C2	O3	1.474
C2	H3	1.221
C2	H4	1.036
O2	V	1.976
O3	V	1.983

Table S7. Crystallographic data and Rietveld refinement of V_2O_5 nanospheres.

Crystal information	**Crystallographic data**
Crystal system	orthorhombic
Space group	Pmmn (No. 59)
a / Å	11.4914
b / Å	3.5577
c / Å	4.3696
α / °	90.0000
β /°	90.0000
γ /°	90.0000
Cell volume / Å^3	178.643
Z	2
χ^2	5.71
R_{wp}	5.48%
R_p	7.42 %

Table S8. Atomic coordinates and occupancies of V_2O_5 nanosphere.

Atom	**x**	**y**	**z**	**g**
V	0.60120	0.25000	0.10860	1.00
O1	0.43090	0.25000	-0.00200	1.00
O2	0.60450	0.25000	0.46970	1.00
O3	0.75000	0.25000	0.00080	1.00

Table S9. Selected interatomic distances in V_2O_5 nanosphere.

Atoms		Distance / Å
V	O1	2.016
V	O2	1.578
V	O3	1.774
V	O1	1.875
V	O1	1.875
O1	V	1.875
O1	V	1.875
O3	V	1.774

Table S10. Elastic constants for polycrystalline V_2O_5.

Axis	Young's Modulus (GPa)	Poisson Ratios	
X	115.43402	E_{xy} =.03361	E_{xz} = 0.4964
Y	187.04257	E_{yx} = 0.5445	E_{yz} = 0.0032
Z	56.36276	E_{zx} = 0.2424	E_{zy} = 0.0010

Table S11. Crystallographic data and Rietveld refinement of discharged NaV_2O_5 nanospheres.

Crystal information	**Crystallographic data**
Crystal system	orthorhombic
Space group	Pmmn (No. 59)
a / Å	11.2616
b / Å	3.6073
c / Å	4.8810
α / °	90.0000
β /°	90.0000
γ /°	90.0000
Cell volume / $Å^3$	198.285
Z	2
χ^2	9.94
R_{wp}	12.53%
R_p	9.57 %

Table S12. Atomic coordinates and occupancies of discharged NaV_2O_5.

Atom	**x**	**y**	**z**	**g**
V	0.40210	0.25000	0.39210	1.00
Na	0.75000	0.25000	0.13990	1.00
O1	0.38540	0.25000	0.05860	1.00
O2	0.57310	0.25000	0.48780	1.00
O3	0.25000	0.25000	0.51950	1.00

Table S13. Selected interatomic distances in discharged NaV_2O_5.

Atoms	**Distance / Å**	**Atoms**
V	O1	1.639
V	O2	1.982
V	O3	1.822
V	O2	1.917
V	O2	1.917
O2	V	1.917
O2	V	1.917
O3	V	1.822

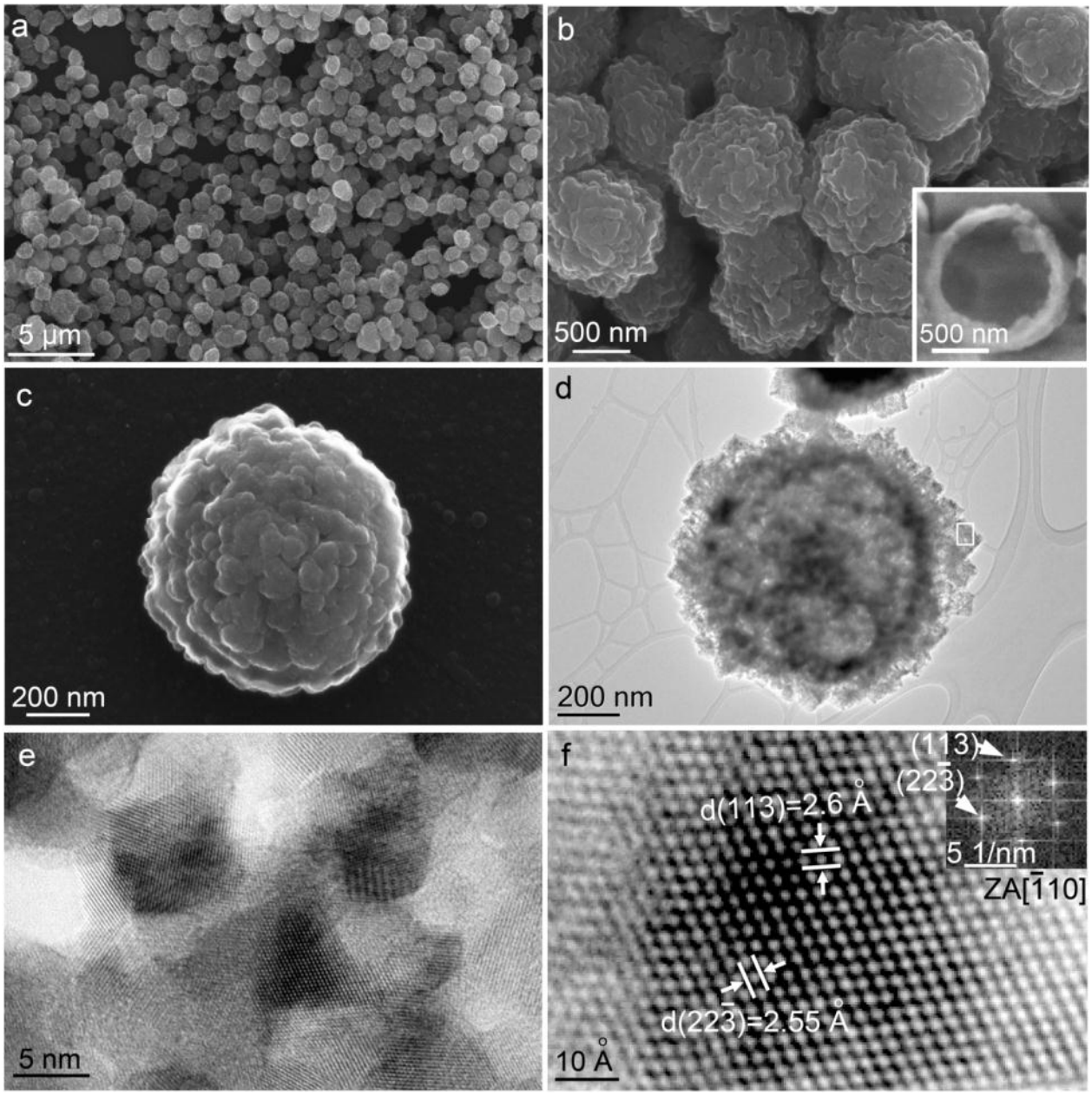

Figure S1. Low (a, b) and high (c) magnification FESEM images of VEG nanospheres. The inset in (b) shows the magnified view of hollow feature. (c) Features of an individual VEG nanosphere. (d) Corresponding TEM image of a single VEG nanosphere. (e) Lattice resolution HRTEM image taken from the marked region in (d). (f) Atomic resolution HRTEM image. Inset in (f) is the fast Fourier-transform (FFT) pattern along the [$\bar{1}$10] zone axis of VEG.

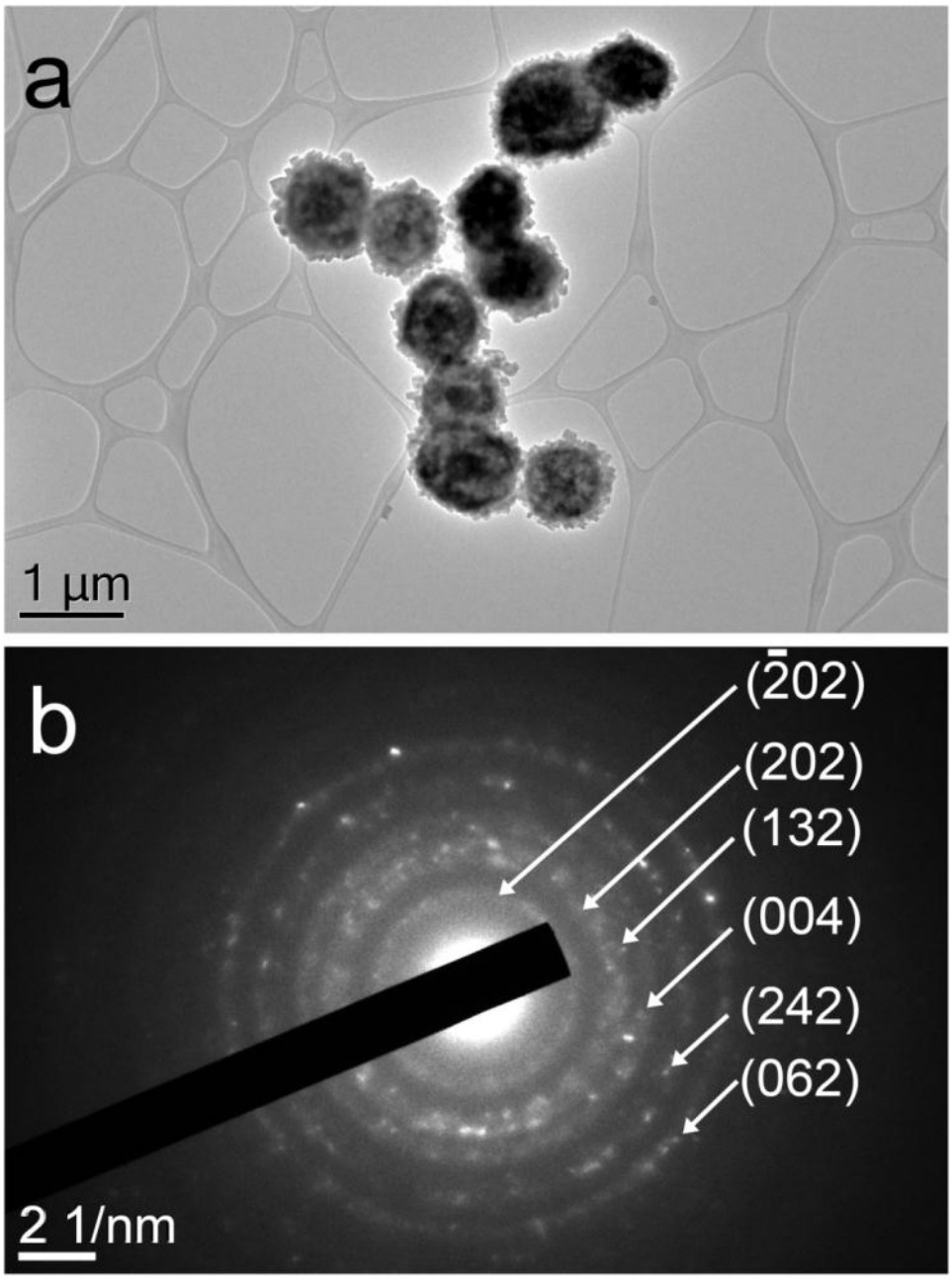

Figure S2. Low magnification TEM image (a) and corresponding selected area electron diffraction (SAED) ring pattern (b) of the VEG hollow nanospheres.

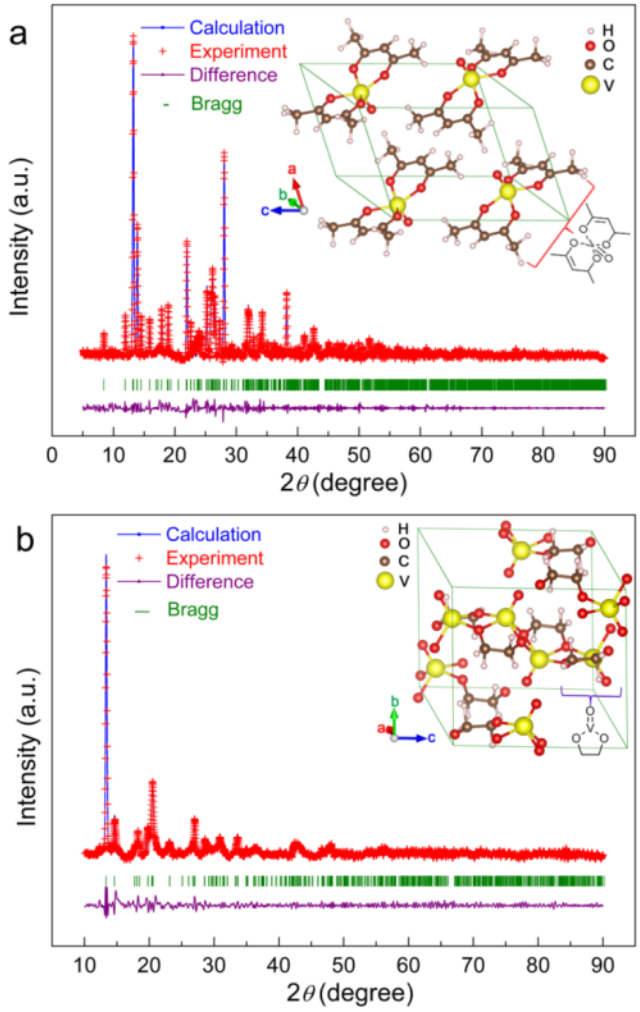

Figure S3. Rietveld refinement patterns of X-ray diffraction data for vanadyl acetylacetonate ($VO(acac)_2$) (a) and vanadyl ethylene glycolate (VEG) (b) crystals. The observed and calculated intensities are represented by red crosses and the blue solid line, respectively. The bottom purple line shows the fitting residual difference. Bragg positions are represented as light-green ticks. The insets in (a) and (b) are refined structural models of triclinic $VO(acac)_2$ and monoclinic VEG, respectively. The diffraction symmetry confirms that $VO(acac)_2$ crystals are triclinic, with the $P\bar{1}$ space group. The lattice parameters of $VO(acac)_2$ were calculated as: a = 7.5258 Å, b = 8.2242 Å, c = 11.2321 Å, and α = 73.0599˚, β = 71.3566˚, γ = 66.6140˚, with satisfactory convergence factors (χ^2 = 7.3, R_{wp} = 8.76 %, R_p = 8.46 %), which is consistent with previously reported $VO(acac)_2$.[1] Detailed crystallographic data on $VO(acac)_2$ are listed in Tables S1-S3. All diffraction peaks of VEG can be indexed to the monoclinic phase with space group C2/C. The lattice parameters were calculated to be a = 9.2717 Å, b = 9.7350 Å, c = 9.9179 Å, and β = 105.9814˚ (χ^2 = 8.6, R_{wp} = 9.98 %, R_p = 7.21 %). No impurity phases were observed. The refined crystal structure is shown as the inset in Figure S3(b), from which the chain structure of $VO(OCH_2\text{-}CH_2O)$ is visible. More crystallographic data on VEG are listed in Tables S4-S6.

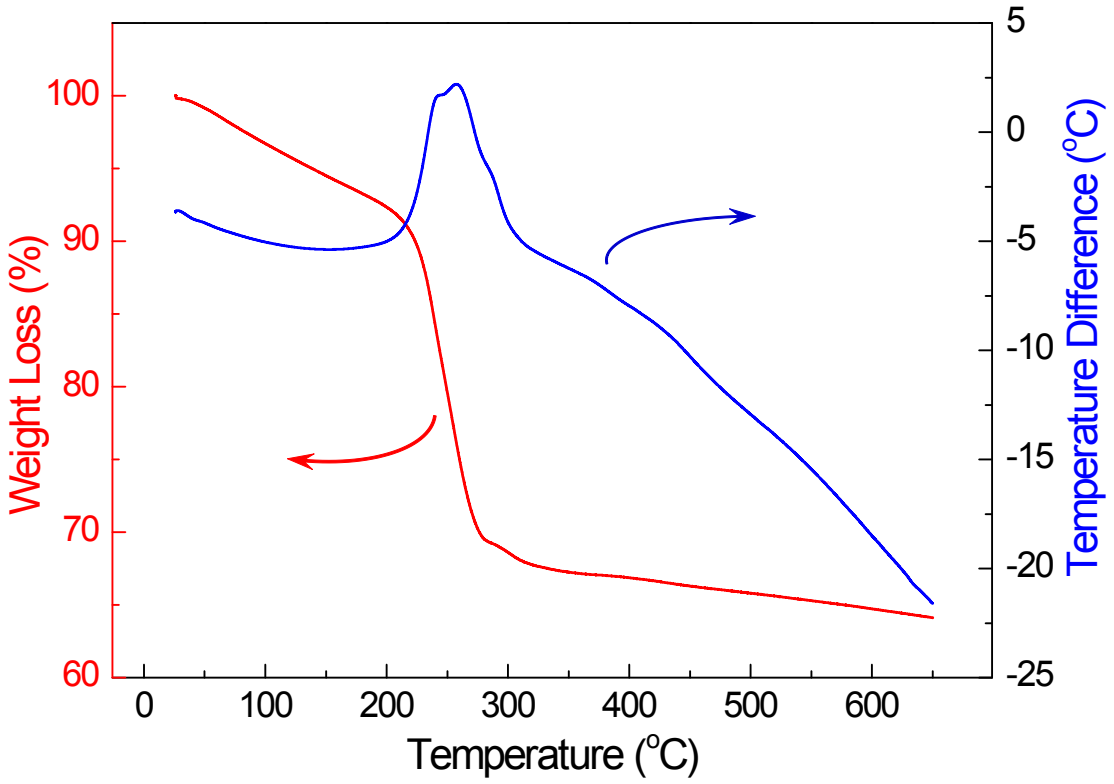

Figure S4. TG/DTA curves of VEG. Two regions with different slopes can be observed in the weight loss curve. The first, ~ 10 % weight loss below 220 ˚C, should correspond to the evaporation of moisture or gaseous contents in the porous material, as well as hydrous groups attached to the VEG crystals, while the main weight loss (~ 20 %) that took place between 220 and 340 °C is likely to be related to the phase transition of VEG.

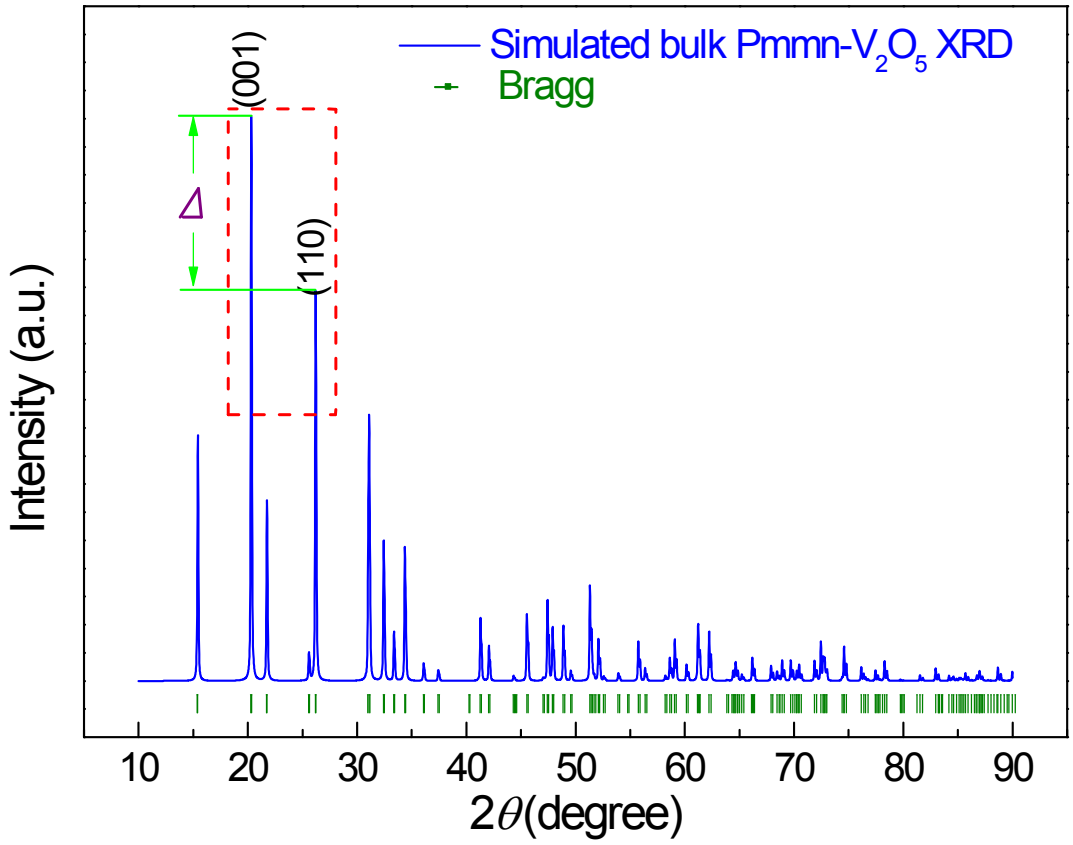

Figure S5. Simulated bulk Pmmn-V_2O_5 XRD pattern, in which the (001) and (110) diffraction peaks are indexed for comparison of the relative intensity.

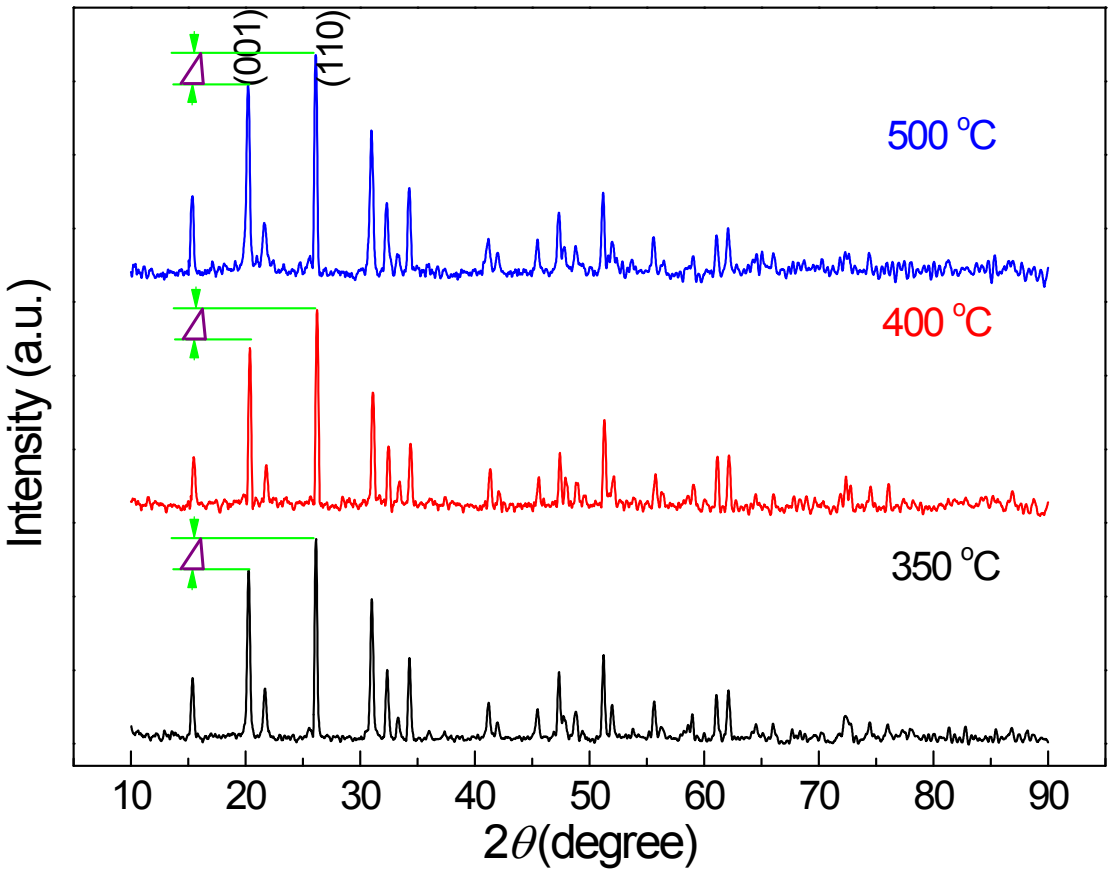

Figure S6. XRD patterns of V_2O_5 synthesized at different sintering temperatures (350, 400, and 500 ˚C).

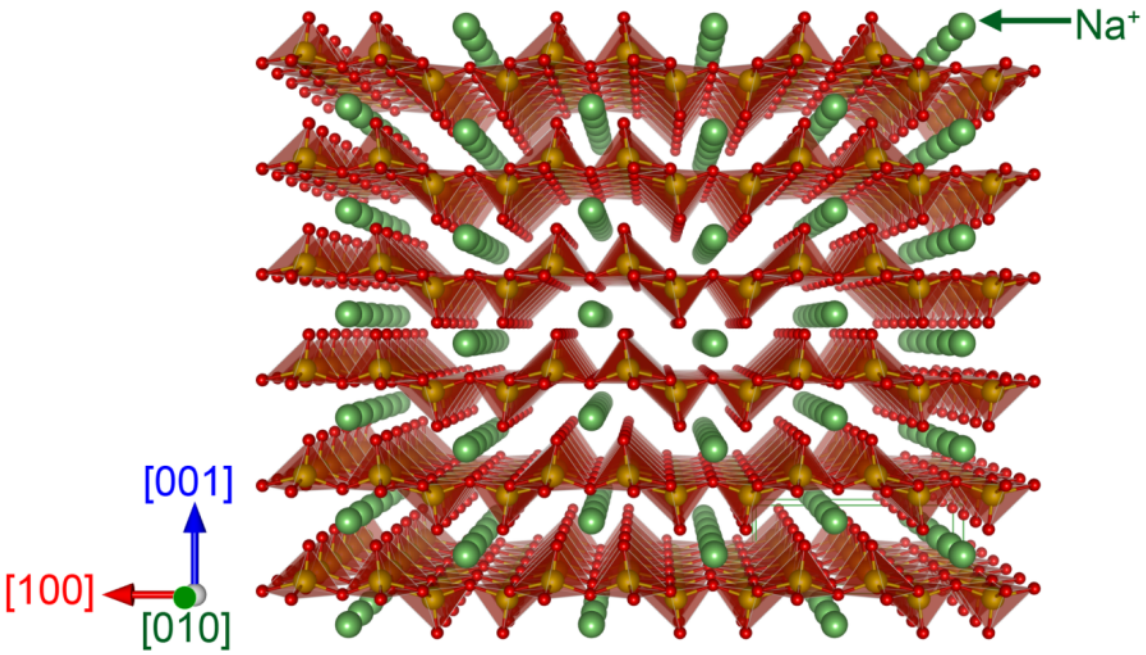

Figure S7. Schematic diagram of Na^+ ions inserted into V_2O_5 along the [010] direction. V, O, and Na atoms are coloured in tan, green, and red, respectively.

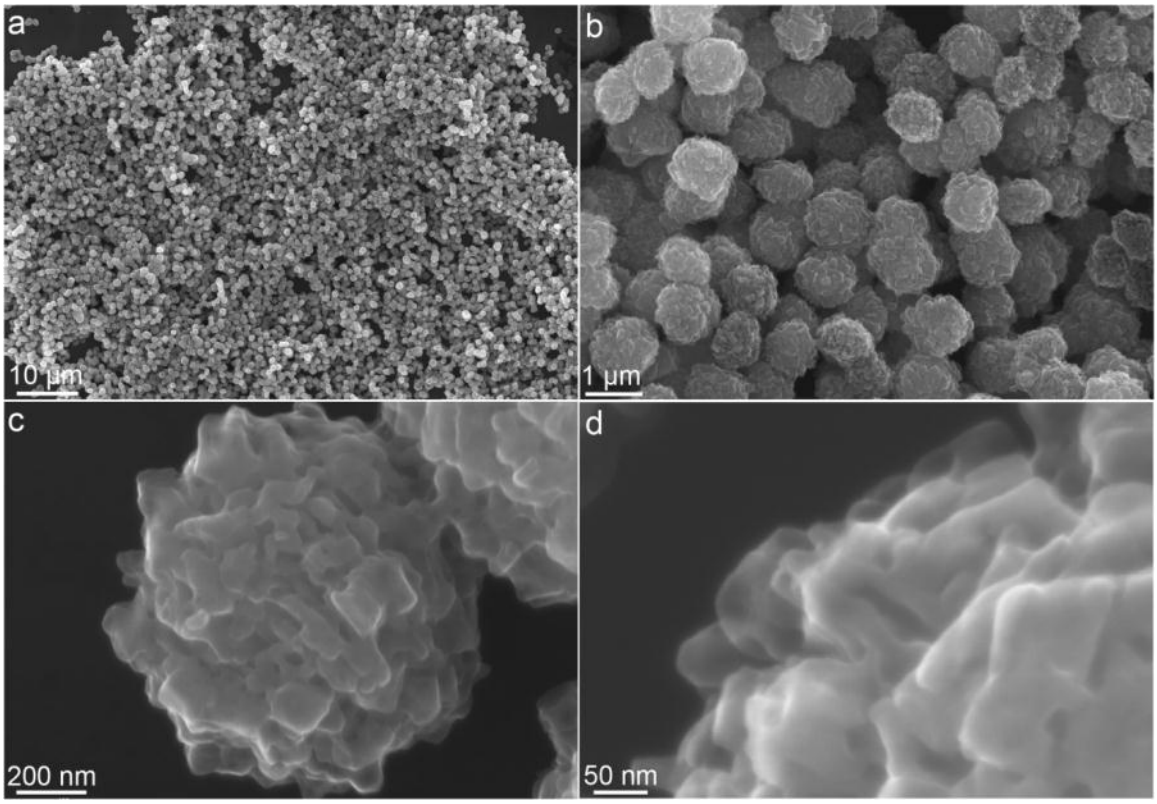

Figure S8. FESEM images of the as-prepared V_2O_5 hollow nanospheres at different magnifications.

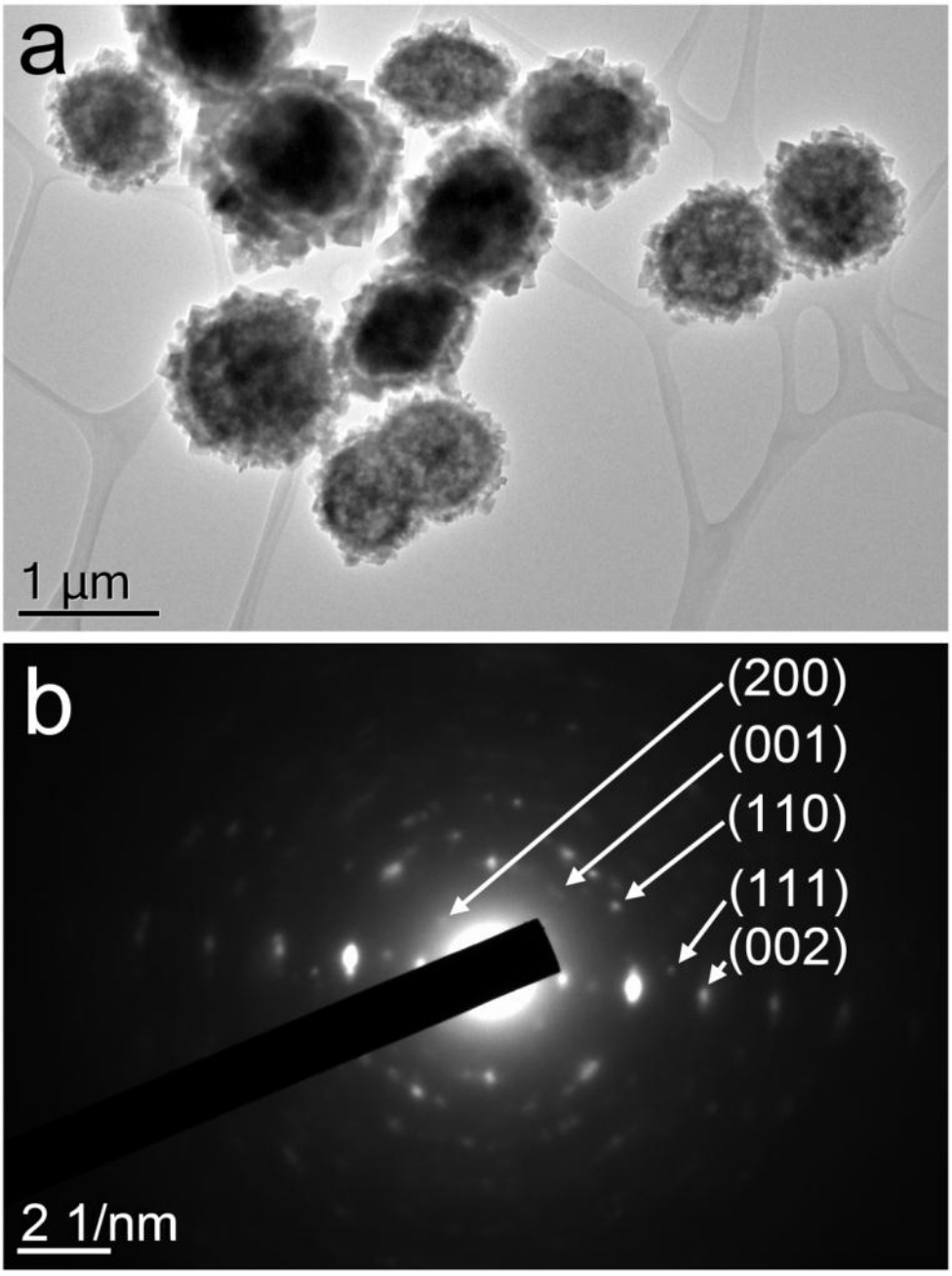

Figure S9. Low magnification TEM image (a) and corresponding selected area electron diffraction (SAED) ring pattern (b) of the as-prepared V_2O_5 hollow nanospheres.

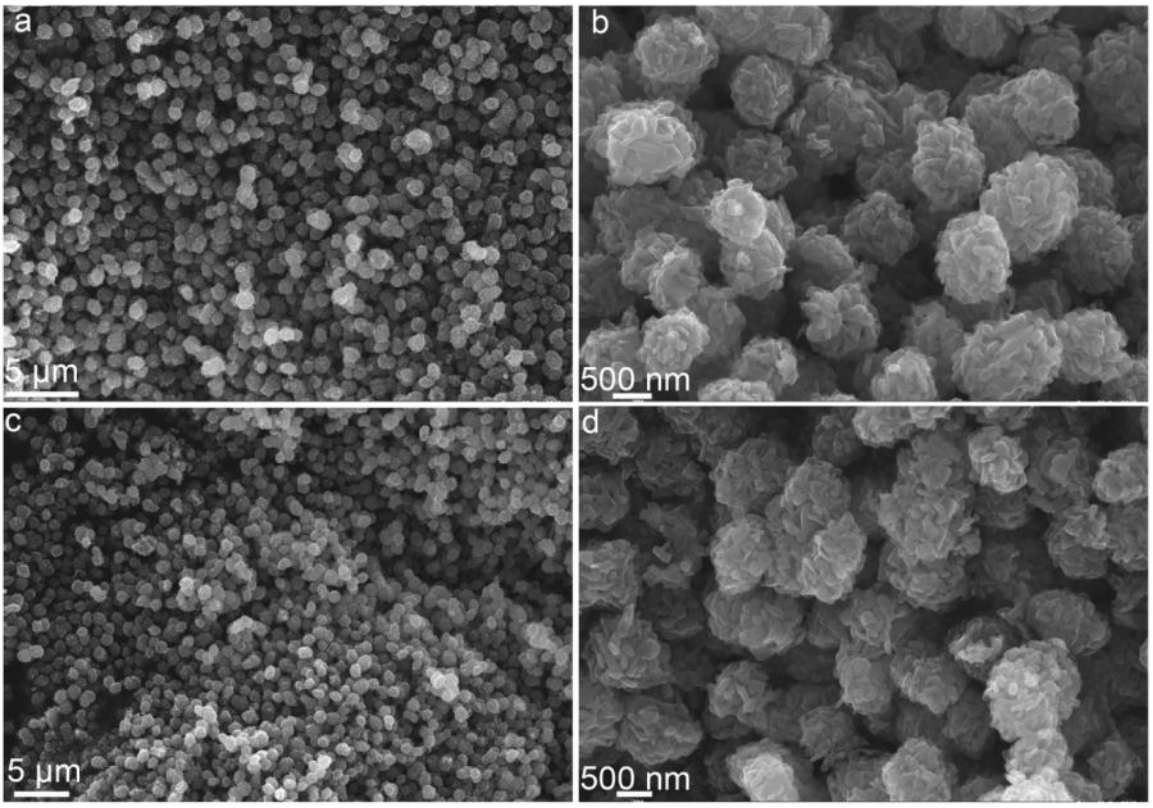

Figure S10. Low (a, c), and high (b, d) magnification FESEM images of the as-prepared V_2O_5 hollow nanospheres obtained by sintering the VEG precursor at 400 ˚C (a, b), and 500 ˚C (c, d).

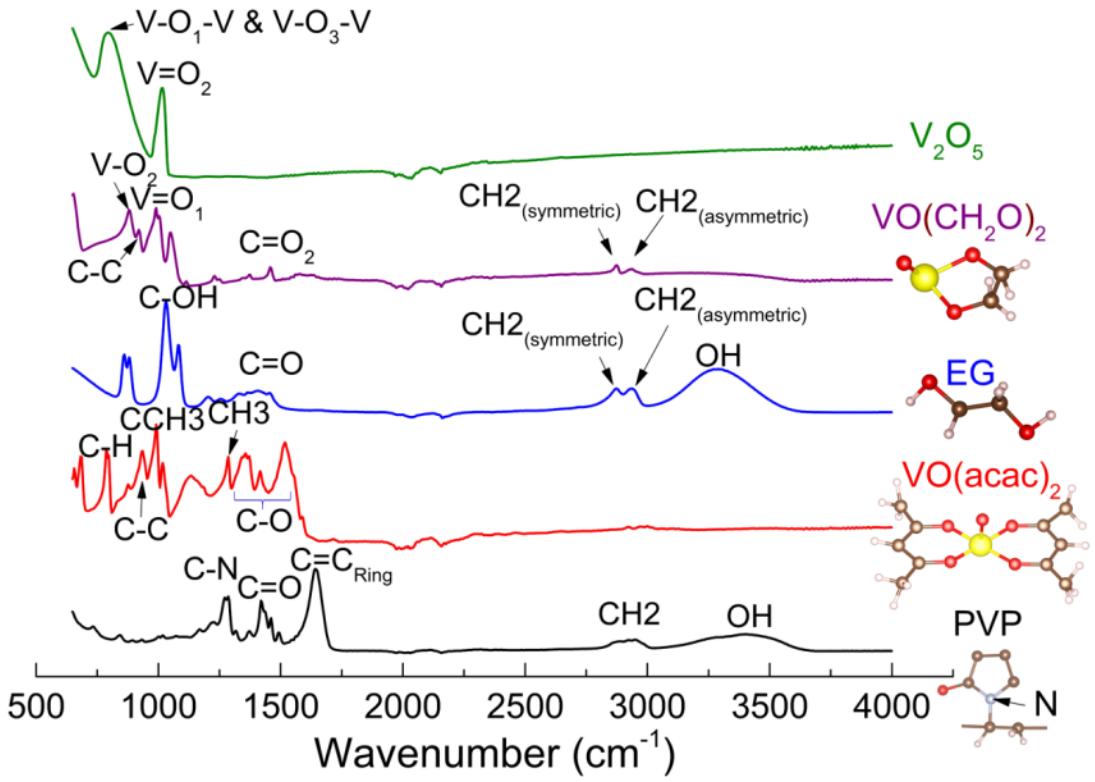

Figure S11. FT-IR spectra of PVP, $VO(acac)_2$, EG, VEG, and V_2O_5.

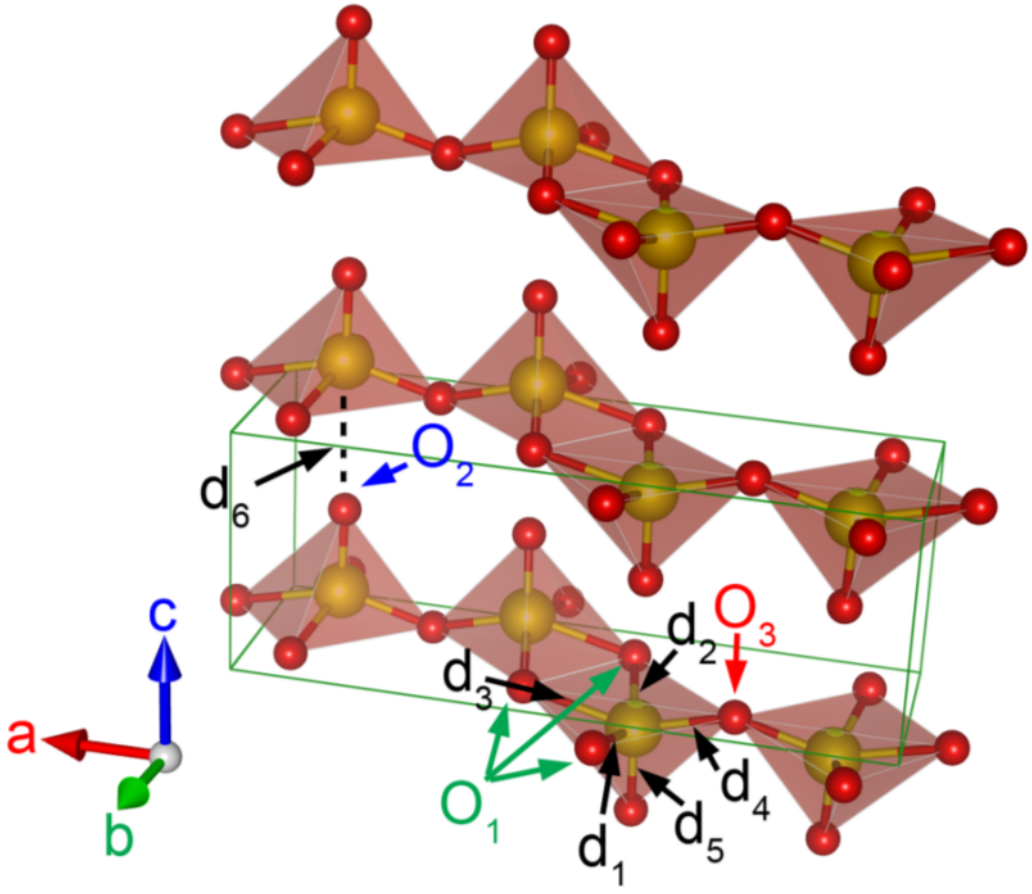

Figure S12. Orthorhombic V_2O_5 crystal structure, in which the six-fold coordinated V and three types of structurally different oxygen atoms are present.

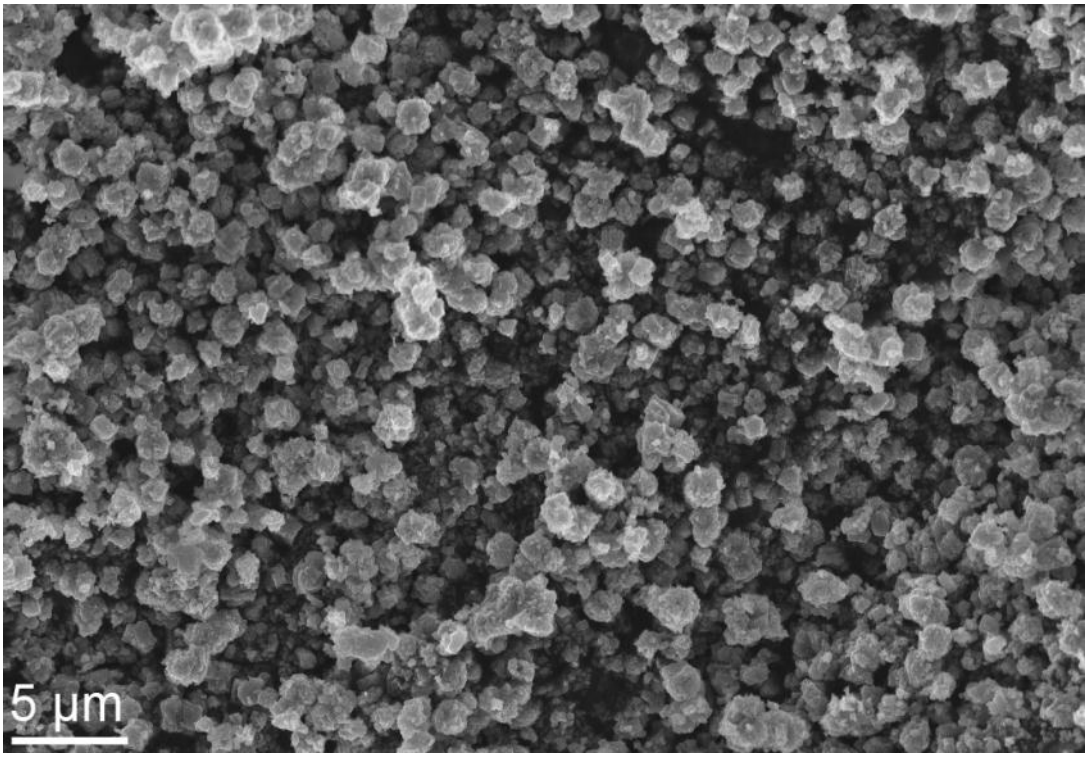

Figure S13. The as-prepared VEG without the addition of PVP.

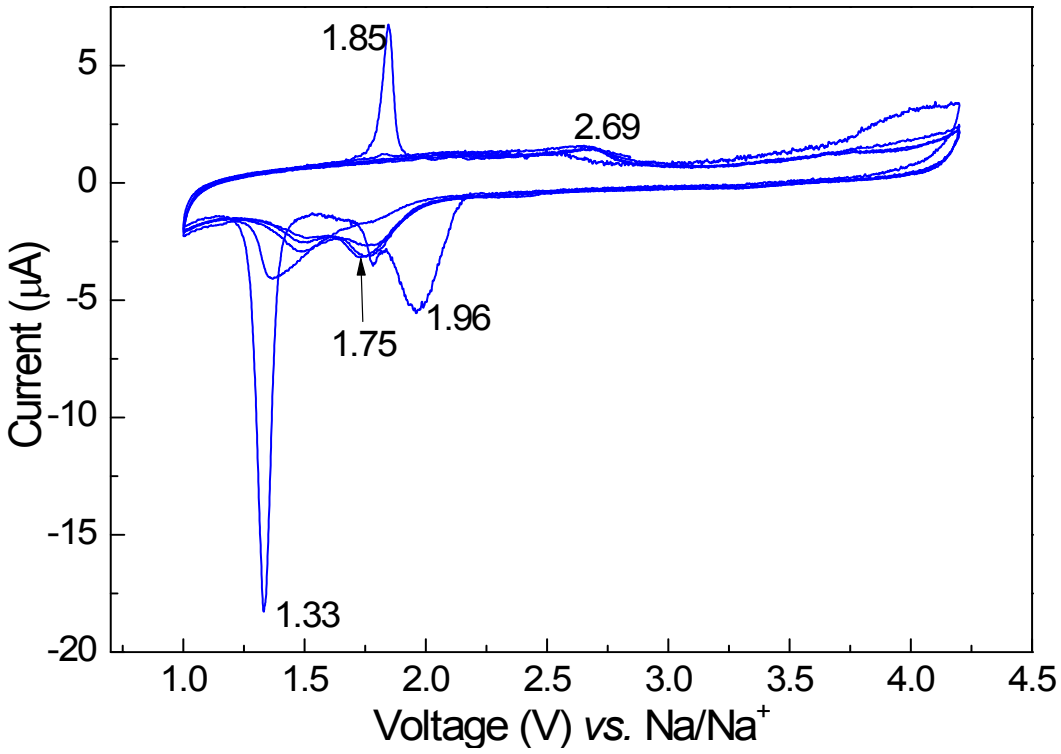

Figure S14. 1st – 5th cyclic voltammograms of V_2O_5 hollow nanosphere cathodes in sodium ion cells.

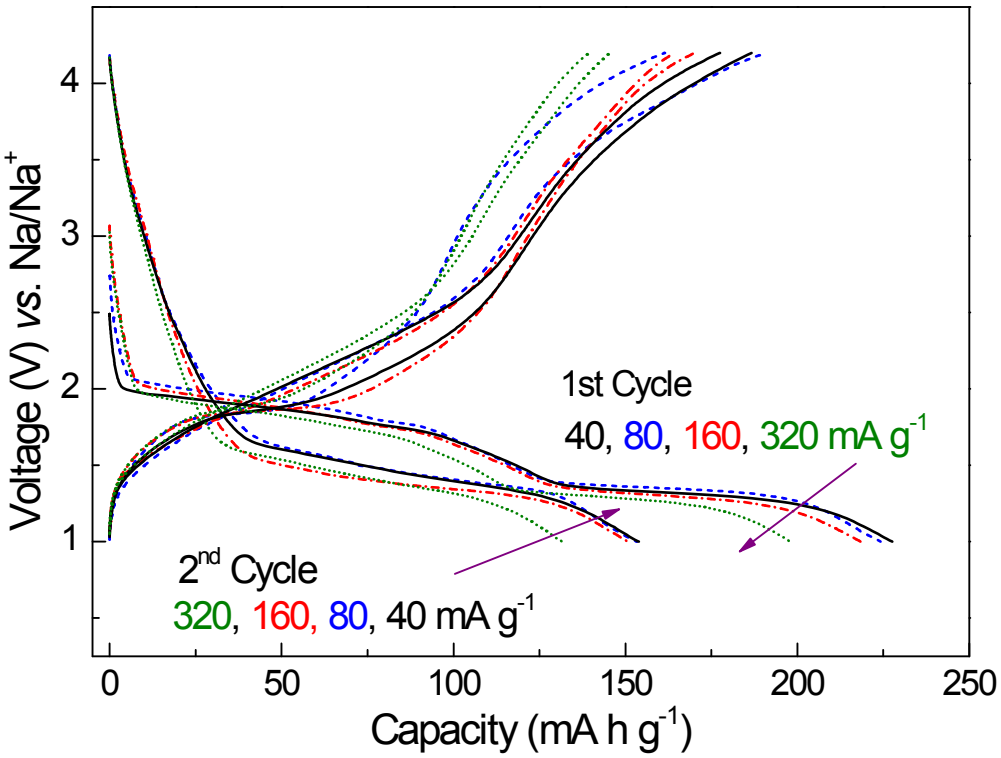

Figure S15. 1st and 2nd cycle charge and discharge profiles of V_2O_5 hollow nanospheres at current densities of 40, 80, 160, and 320 mA g^{-1}.

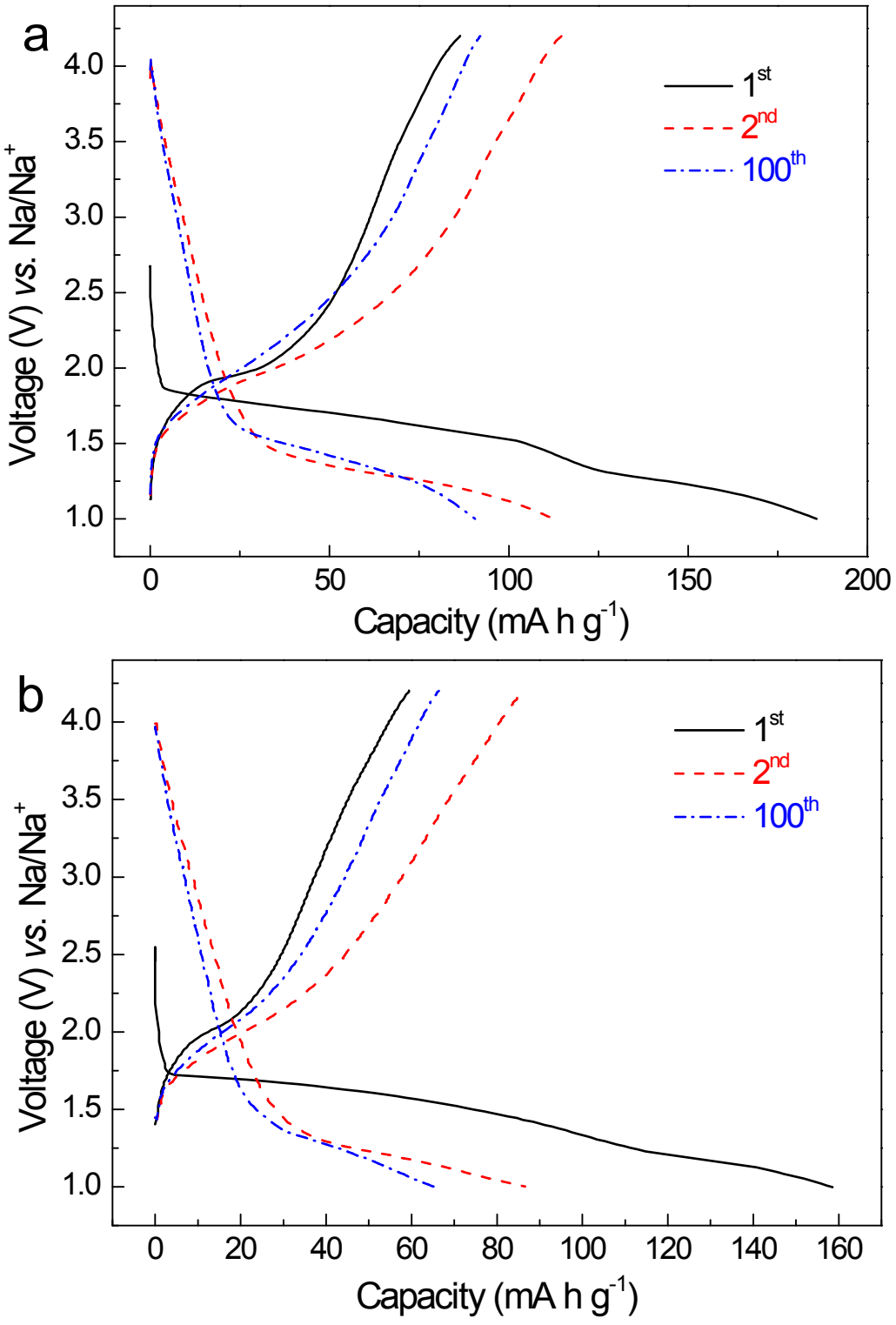

Figure S16. 1st, 2nd, and 100th cycle discharge and charge profiles of V_2O_5 hollow nanospheres at current densities of 640 mA g^{-1} (a), and 1280 mA g^{-1} (b).

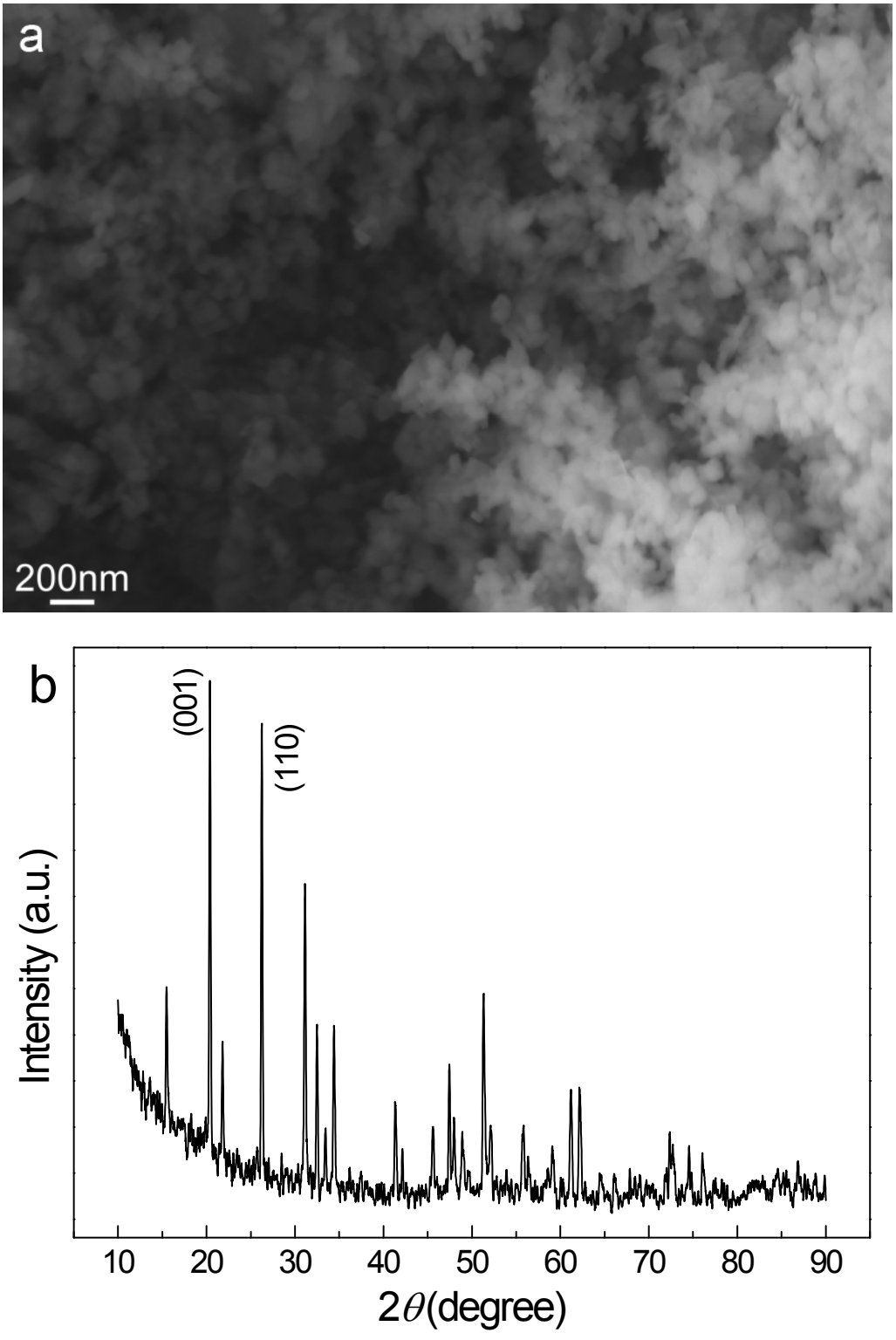

Figure S17. FESEM image (a) and XRD pattern (b) of solid Pmmn V_2O_5 nanocrystals.

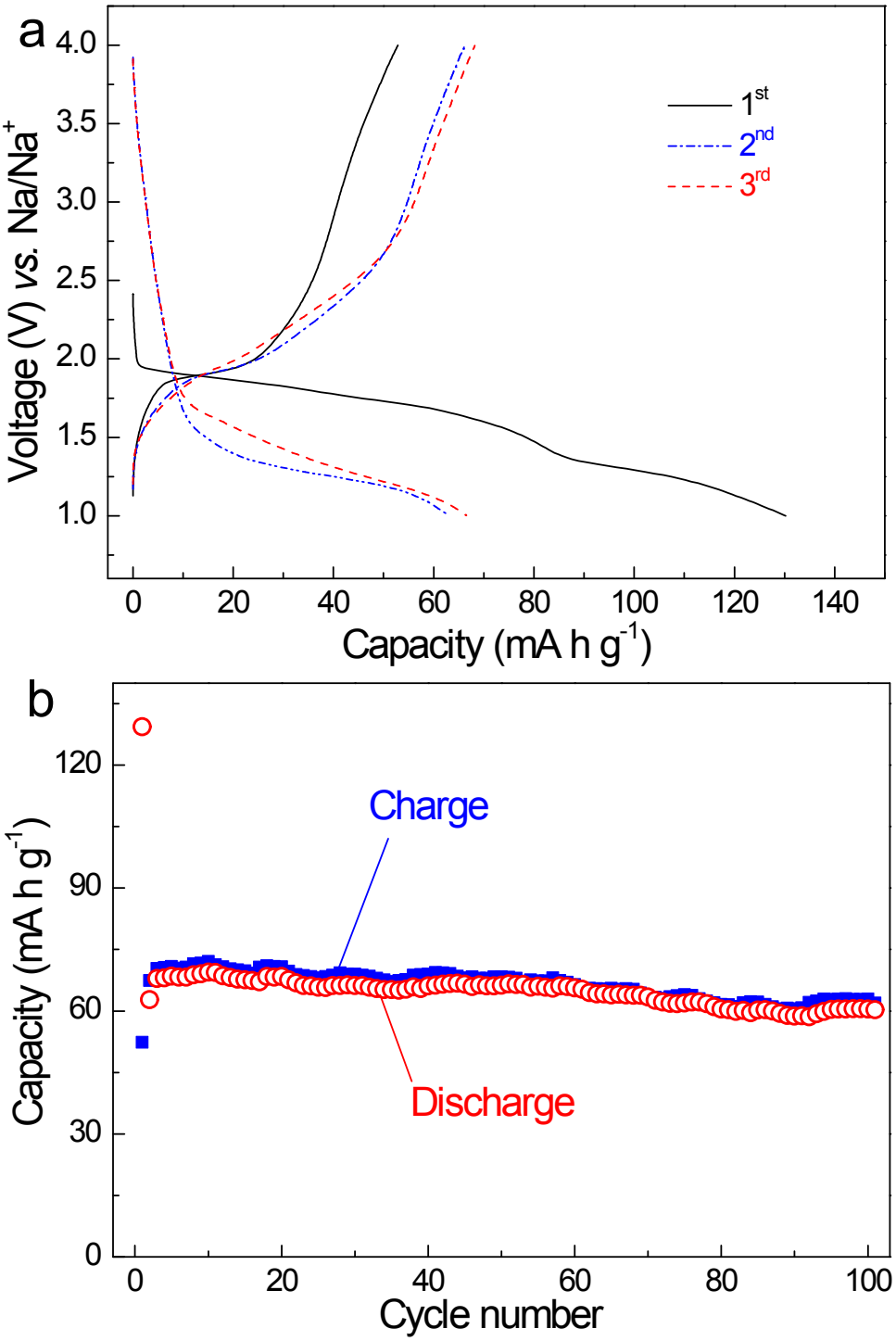

Figure S18. 1st, 2nd, and 3rd cycle discharge and charge profiles (a) and cyclability (b) of solid V_2O_5 nanocrystals at current density of 80 mA g^{-1}.

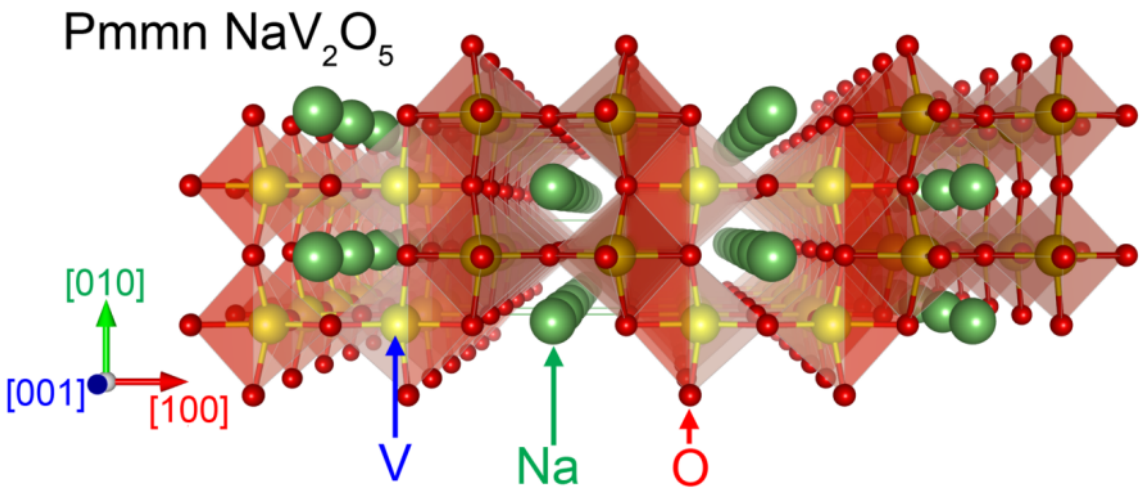

Figure S19. Refined structural model of Pmmn NaV_2O_5, viewed along the [001] direction. The brown base-faced square-pyramidal VO_5 unit is composed of one vanadium atom and five oxygen atoms, which are coloured yellow and red, respectively, while the Na^+ ions are coloured in green.

Reference:

(1) Dodge, R. P.; Templeton, D. H.; Zalkin, *J. Chem. Phys.* **1961,** *35*, 55.