Electronic Supplementary Information

Experimental section

Materials:

$Ca(CH_3COO)_2$ (99%) and *N*-Methyl-2-pyrrolidone (NMP, anhydrous) were obtained from Sigma Aldrich. Zinc foil (thickness: 25 μm, >99.99%.) and stainless steel (thickness: 50 μm) were purchased from Goodfellow. Polyvinylidenedifluoride (PVdF, Solef 6020), carbon black (Super C65), V_2O_5, glass fiber separator, and $Zn(CF_3SO_3)_2$ (99.5%) were purchased from Arkema Group, IMERYS, Pechiney, Whatman and Solvionic, respectively. The chemicals were directly used without further purification.

Preparation of CVO via microwave reaction

First, 1 mmol of $Ca(CH_3COO)_2$ was dissolved in 20 mL ultrapure water in the glass reactor (30 mL, Anton Paar). After dissolution of $Ca(CH_3COO)_2$, 2 mmol of V_2O_5 powder was added to the reactor. The suspension was heated in a "Monowave 300" microwave oven (Anton Paar) up to 180 °C using the "Heat as fast as possible" mode, and held at such a temperature for 2 h upon stirring rate of 300 rpm. The obtained product was centrifuged, and the red precipitate was thoroughly washed with water and acetone. After evaporation of the residual acetone in an oven at 80 °C, 0.430 g of CVO powder was obtained. Based on the amount of V_2O_5, the yield of the product was 98.4%.

Phisical-chemical characterization

X-ray diffraction was conducted using a Bruker D8 Advance diffractometer (Bruker, Germany) with Cu-Kα radiation in the 2θ range from 7° to 80° while the step length and time for every step were 0.0205° and 6 seconds, respectively. For ex-situ XRD, the 2θ range and step time were changed to 4-55° and 1 second, respectively. The electrodes for the ex-situ XRD were taken from the coin cells, which were disassembled in ambient atmosphere. The obtained electrodes were immersed in 5 mL ultrapure water and further flushed with 1 mL ultrapure water. After drying at 80 °C, the electrodes were ready for ex-situ XRD test. Thermogravimetric

analysis was carried out on TA Q2000 apparatus heating the powder up to 400 °C with a heating rate of 5 °C min^{-1} under oxygen flow. Scanning electron microscope of as-prepared sample was performed on a Zeiss LEO 1550 microscope, equipped with an EDX spectrometer (Oxford Instruments X-MaxN, 50 mm^2, 15kV). The high resolution transmission electron microscopy (HRTEM) analysis was performed using the image Cs-corrected TEM, FEI Titan 80-300 kV, operated at 300 kV.

Electrochemical characterization

Electrochemical measurements were performed in 2032 type coin cells. The CVO electrodes were prepared by doctor-blade casting slurries with 70 wt. % CVO, 20 wt. % C65, and 10 wt. % PVdF on stain steel substrate. NMP was used as the solvent to prepare the slurry. After drying at 60 °C, electrodes with a diameter of 14 mm were punched and further dried at 120 °C under high vacuum to fully remove the NMP. The average mass loading of the active material was around 3.5 mg cm^{-2}. To assemble the zinc battery, 12 mm zinc disc, 3 m $Zn(CF_3SO_3)_2$ aqueous solution, glass fiber film disk (Whatman GF/F), and the as-fabricated CVO electrodes were used as anode, electrolyte, separator, and cathode, respectively. Before use, the electrolyte was de-aerated bubbling N_2 for 1 h. A Maccor 4000 Battery system (Maccor, USA) was used for the galvanostatic charge/discharge tests. Cyclic voltammetry tests were carried out with a galvanostat/potentiostat VMP3 (Bio-Logic, France).

Table S1. A summary of layer spacing of different alkali metal-based vanadium bronzes.

Formula	PDF number	Crystal plane	Interlayer distance (Å)
LiV_3O_8	72-1193	(100)	6.36
$Li_{0.3}V_2O_5$	73-1670	(002)	7.19
$Na_{1.1}V_3O_{7.9}$	45-0498	(002)	6.89
NaV_6O_{15}	24-1155	(002)	7.25
$Na_2V_6O_{16}\cdot 3H_2O$	16-0601	(001)	7.90
$K_{0.25}V_2O_5$	39-0889	(002)	7.41
KV_3O_8	22-1247	(100)	7.58
$K_2V_6O_{16}\cdot 2.7H_2O$	54-0602	(001)	7.60

Table S2. Structural data and refinement parameters for as-prepared CVO via Rietveld refinement of experimental XRD powder pattern.

Formula		$CaV_6O_{16}·3H_2O$	
Space group		C2/m	
a		12.2117	
b		3.6011	
c		18.3953	
beta		118.48	
Atom	x / Å	y / Å	z / Å
Ca1	0.5338	0.0000	0.0052
Ca2	0.1440	0.5000	0.0754
V1	0.0165	0.5000	0.1919
V2	0.4044	0.0000	0.1724
V3	0.3126	0.5000	0.2779
O1	-0.0967	0.5000	0.1129
O2	0.2960	0.0000	0.0958
O3	0.3420	0.5000	0.0000
O4	0.1750	0.5000	0.1730
O5	0.5255	0.0000	0.1466
O6	0.3274	0.0000	0.2775
O7	0.0336	0.0000	0.2293
O8	0.3951	0.5000	0.1939
OW1	0.7204	0.5000	0.0884
OW2	0.0185	0.0950	0.0003
R_{wp}		11.14%	

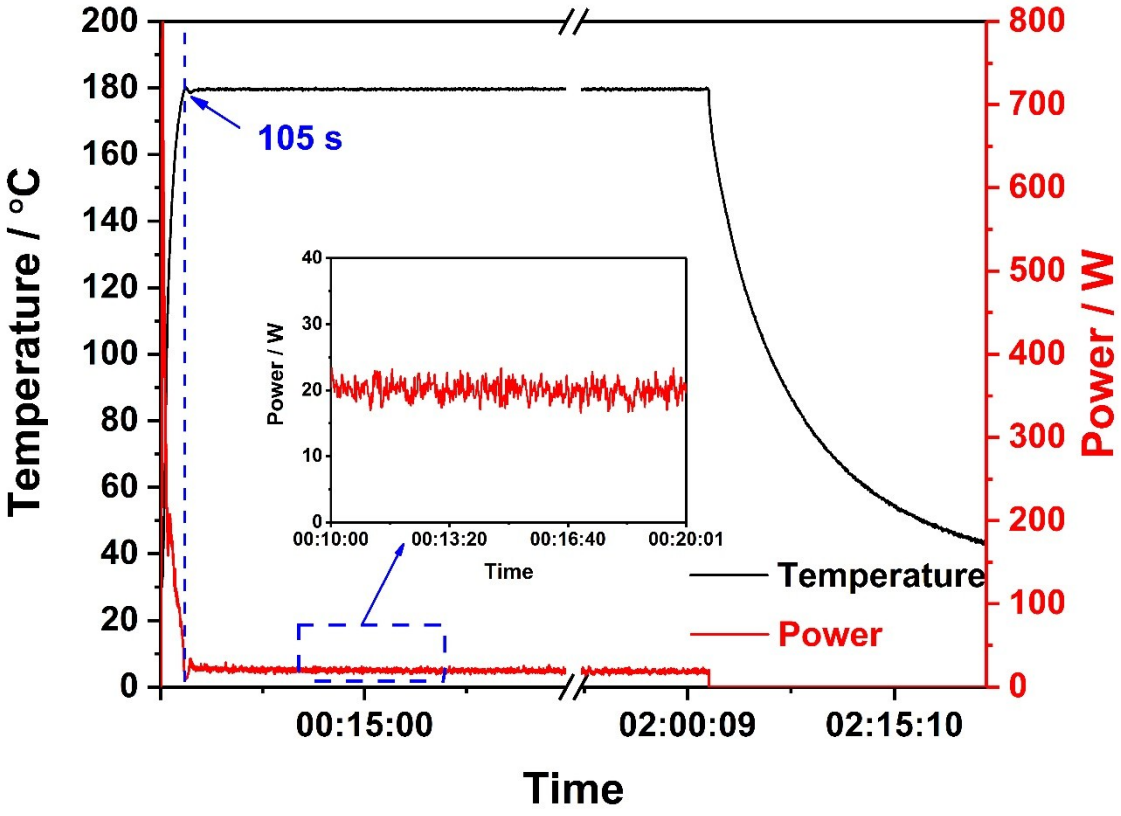

Figure S1. Evolution of temperature and power during the microwave reaction. The data was directly recorded by the microwave oven. The inset shows the power needed to keep the temperature constant from 10 to 20 min.

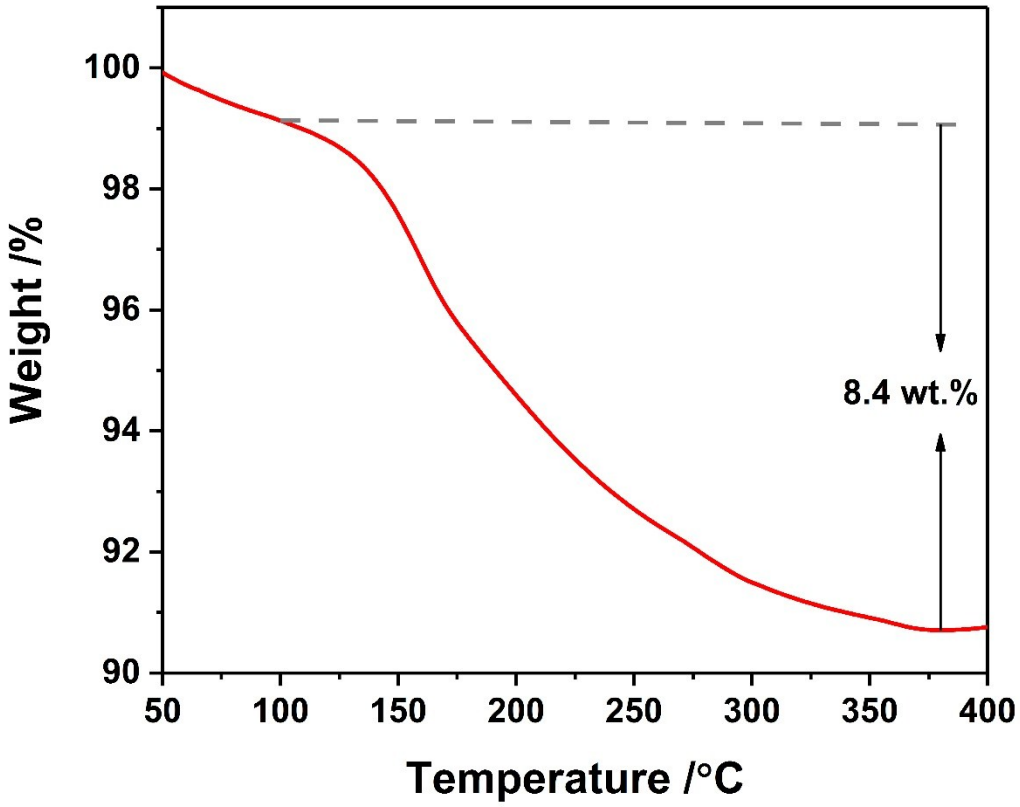

Figure S2. TGA curve of as-prepared CVO.

The curve can be divided into two parts. Up to 100 °C, little weight variation is registered that can be attributed to the absorbed surface water. Above 100 °C, the weight loss of 8.4 wt. % is assigned to water molecules trapped in the interlayer space and matches well with the theoretical content in the formula $CaV_6O_{16}\cdot 3H_2O$ (8.2 wt. %).

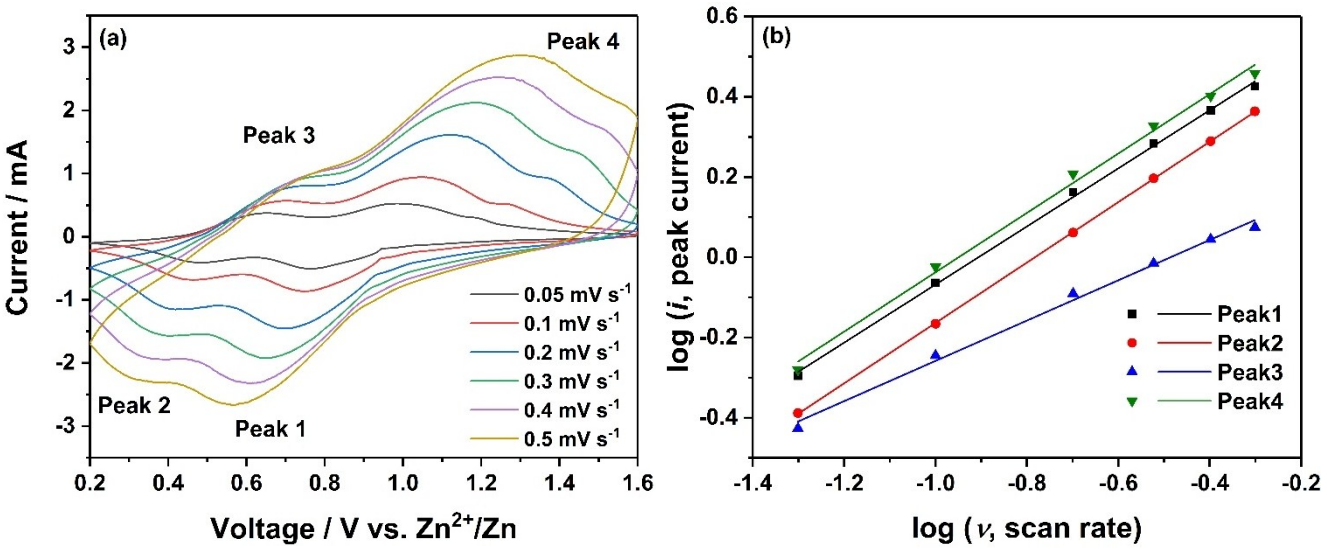

Figure S3. (a) CV curves of CVO at different scan rates of 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mV s^{-1}.

(b) log (*i*) versus log (*v*) plots of the peaks marked in (a).

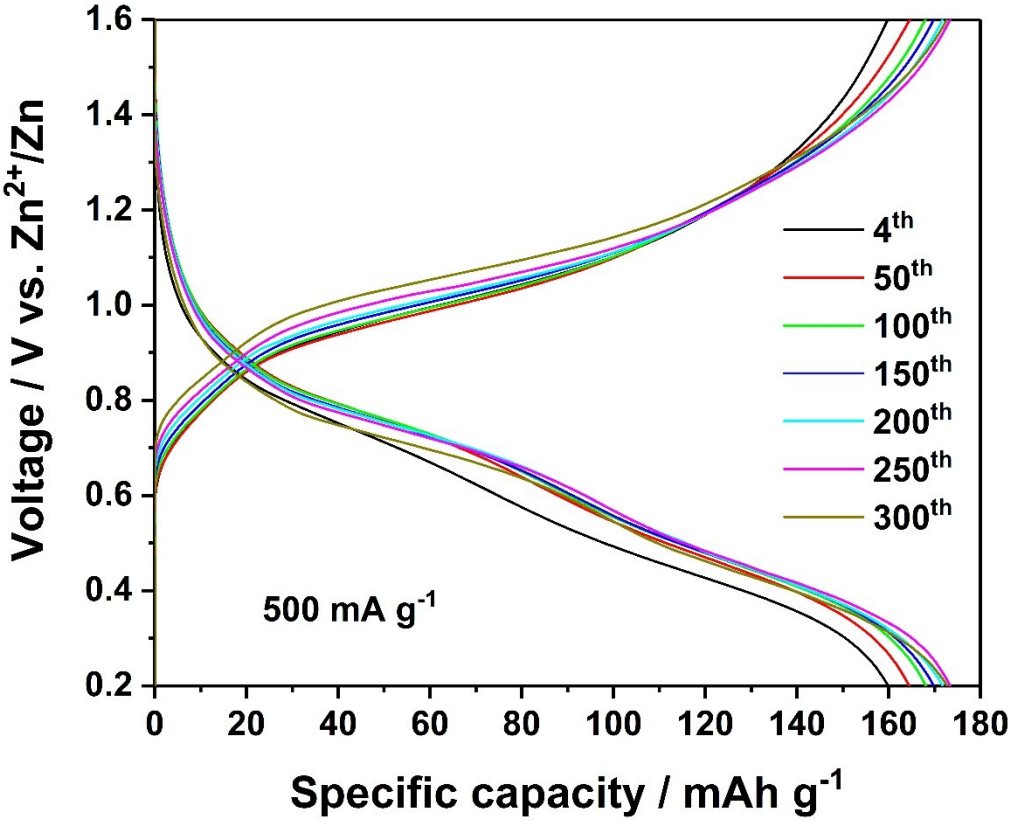

Figure S4. Selected voltage profiles at 500 mA g^{-1} of CVO electrode.

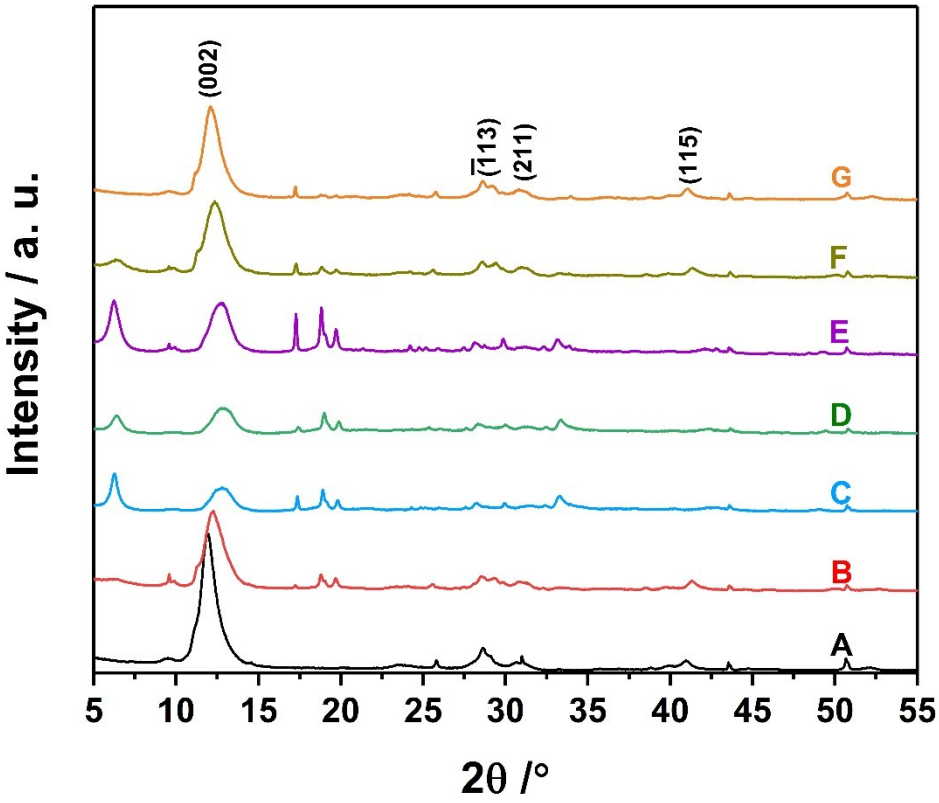

Figure S5. Ex-situ XRD spectra up to 55°.

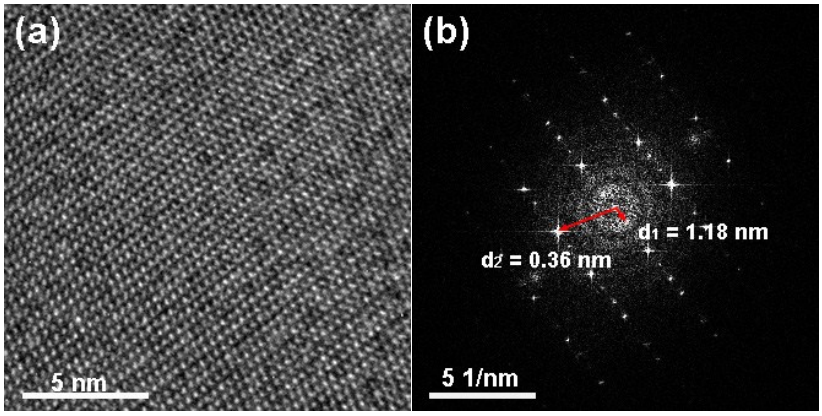

Figure S6. (a) HRTEM of fully discharged CVO, and (b) corresponding FFT image (diffractogram).

The HRTEM exhibits the well-developed crystal fringes. Based on the corresponding FFT image, the interplanar spacings were calculated to be 1.18 and 0.36 nm. Obviously, the plane with a d value of 1.18 nm does not belong to the pristine CVO.

Table S3. Properties of reported cathode materials for aqueous zinc batteries.

Materials	Electrolyte	Specific capacity at x mA g^{-1}	Capacity retention after n cycles at y mA g^{-1}	Ref.
$Na_3V_2(PO_4)_3$	0.5 M $Zn(Ac)_2$	97 (x = 50)	74% (n = 100, y = 50)	1
$Na_3V_2(PO_4)_3$/C	0.5 M $Zn(Ac)_2$ NaAc	92 (x = 50)	74% (n = 100, y = 50)	2
$Na_3V_2(PO_4)_2F_3$	2 M $Zn(OTF)_2$	65 (x = 80)	No fading (n = 600, y = 200)	3
$ZnMn_2O_4$	3 M $Zn(OTF)_2$	150 (x = 50)	94% (n = 500, y = 500)	4
MnO_2	3 M $Zn(OTF)_2$ 0.1 M $Mn(OTF)_2$	275 (x = 200)	94% (n = 2000, y = 2000)	5
ZnHCFs	1 M $ZnSO_4$	65 (x = 60)	80% (n = 100, y = 300)	6
CuHCFs	0.02 M $ZnSO_4$	55 (x = 60)	96% (n = 100)	7
$VO_{1.52}(OH)_{0.77}$	1 M $ZnSO_4$	140 (x = 15)	70% (n = 50, y =15)	8
VS_2	1 M $ZnSO_4$	190 (x = 50)	75% (n = 200, y =500)	9
LiV_3O_8	1 M $ZnSO_4$	256 (x = 16)	No fading, (n = 70, y = 133)	10
$Zn_{0.25}V_2O_5$	1 M $ZnSO_4$	300 (x = 50)	80% (n = 1000, y = 2400)	11
$Ca_{0.25}V_2O_5$	1 M $ZnSO_4$	340 (x = 60)	78% (n = 5000, y = 2400) Curve is not smooth	12
$Zn_2V_2O_7$	1 M $ZnSO_4$	248 (x = 50)	86% (n = 200, y = 300)	13
$Zn_3V_2O_7(OH)_2 \cdot 2H_2O$	1 M $ZnSO_4$	200 (x = 50)	68% (n = 300, y = 200)	14
VO_2	3 M $Zn(OTF)_2$	274 (x = 100)	94% (n = 350, y = 500)	15
$Na_{1.1}V_3O_{7.9}$/graphene	1 M $Zn(OTF)_2$	238 (x = 50)	78% (n = 100, y = 300)	16
V_2O_5 (crystalline)	3 M $ZnSO_4$	224 (x = 100)	81% (n = 30, y = 100)	17
$K_2V_8O_{21}$	2 M $ZnSO_4$	210 (x = 500)	≈ 95% (n = 50, y =500)	18
$K_2V_6O_{16} \cdot 1.57H_2O$		175 (x = 500)	≈ 43% (n = 50, y =500)	
$K_{0.25}V_2O_5$		80 (x = 500)	≈ 100% (n = 50, y =500)	
KV_3O_8		80 (x = 500)	≈ 65% (n = 50, y =500)	
$Na_2V_6O_{16} \cdot 1.63H_2O$	3 M $Zn(OTF)_2$	352 (x = 50)	76% (n = 500, y = 1000)	19
$Fe_5V_{15}O_{39}(OH)_9 \cdot 9H_2O$	0.3 M $Zn(TFSI)_2$	385 (x = 100)	80% (n = 300, y = 5000)	20
$V_2O_5 \cdot nH_2O$/GO	3 M $Zn(OTF)_2$ 0.1 M vanadium sol	381 (x = 60)	71% (n = 900, y = 6000)	21
$H_2V_3O_8$	3 M $Zn(OTF)_2$	423 (x = 100)	83% (n = 100, y =1000)	22
$Na_{0.33}V_2O_5$	3 M $Zn(OTF)_2$	367 (x = 100)	91% (n = 100, y =200)	23
$V_3O_7 \cdot H_2O$	1 M $ZnSO_4$	375 (x = 375)	80% (n = 200, y =3000)	24
$Na_2V_6O_{16} \cdot 3H_2O$	1 M $ZnSO_4$	361 (x = 105)	94% (n = 400, y =1875)	25
$H_2V_3O_8$/Graphene	3 M $Zn(OTF)_2$ 5 vol% diethyl ether	350 (x = 100)	96% (n = 150, y =300)	26
VO_2	3 M $Zn(OTF)_2$	357 (x = 100)	91% (n = 300, y =1500)	27
$K_2V_6O_{16} \cdot 2.7H_2O$	1 M $ZnSO_4$	239 (x = 100)	82% (n = 500, y =6000)	28
$CaV_6O_{16} \cdot 3H_2O$	3 m $Zn(OTF)_2$	367 (x = 50) 265 (x = 100) 179 (x = 500)	No fading (n = 300, y = 500)	This work

*Ac means CH_3COO^- anion.
** OTF means $CF_3SO_3^-$ anion.

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