Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

New Anatase Phase $VTi_{2.6}O_{7.2}$ Ultrafine Nanocrystals for High-Performance Rechargeable Magnesium-Based Batteries

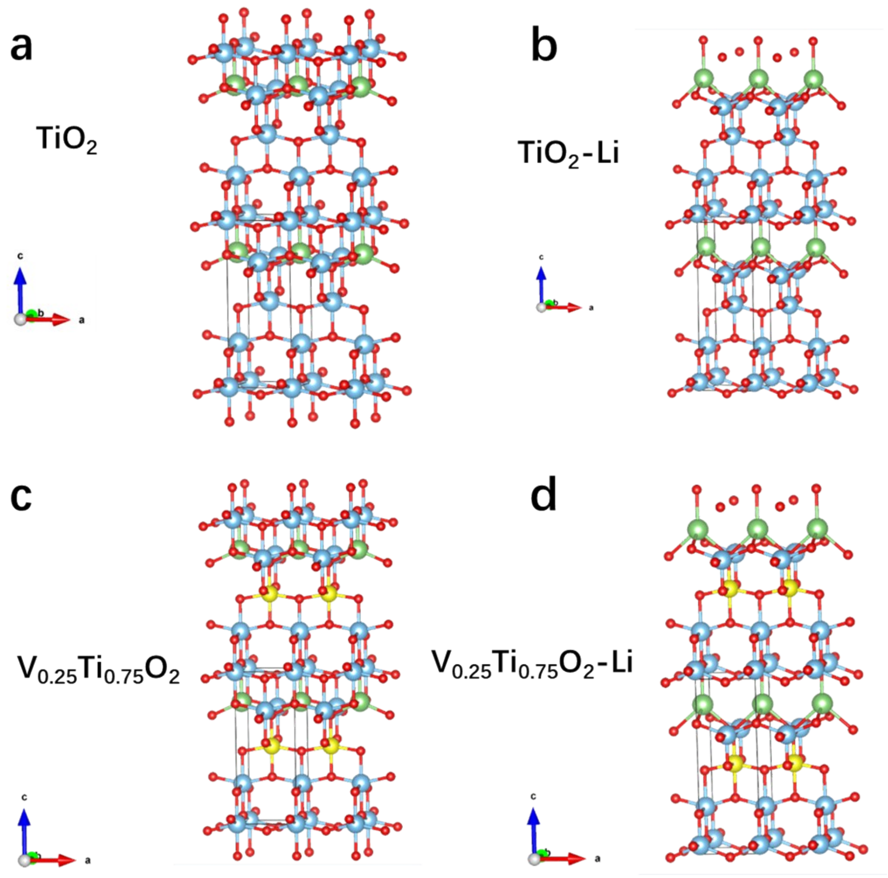

Fig. S1 (a, b) The unit cell of anatase TiO_2 before and after Li^+ intercalation. (c, d) The unit cell of anatase $V_{0.25}Ti_{0.75}O_2$ with one forth titanium atoms replaced by vanadium atoms before and after Li^+ intercalation.

DFT caculation process

The DFT was performed within the framework of Cambridge Serial Total Energy Package plane wave code.[S1-S2] Ultrasoft pseudopotentials were used to describe the interaction of ionic core and valence electrons. The generalized gradient approximation of Perdew–Burke–Ernzerhof method parameterized by Perdew was used to calculate the exchange and correlation terms.[S3-S4] Brillouin-zone integrations were performed using Monkhorst and Pack k-point meshes.[S5] To calculate the intercalation energy in $V_{0.25}Ti_{0.75}O_2$, of, the central Ti atom in the cellular is replace with V atom. The Li^+ intercalation energy (E_i) is defined as $E_i = E_{Li+V} - E_{Li} - E_V$, where E_{Li+V} and E_V are total energies of intercalated Li^+ and pristine VTO unit cell respectively, while E_{Li} is the energy of isolated lithium.[S6]

S 1 W. Kohn, L. J. Sham, *Phys. Rev.*, 1965, **140**, 1133.

S 2 V. Milman, B. Winkler, J. White, C. Pickard, M. Payne, E. Akhmatskaya, R. Nobes, *Int. J. Quantum Chem.*, 2000, **77**, 895.

S 3 M. Marlo, V. Milman, *Phys. Rev. B*, 2000, **62**, 2899.

S 4 J. White, D. Bird, *Phys. Rev. B*, 1994, **50**, 4954.

S 5 J. D. Pack, H. J. Monkhorst, *Phys. Rev. B*, 1977, **16**, 1748.

S 6 P. M. Harris, E. MackJr., F. Blake, *J. Am. Chem. Soc.*, 1928, **50**, 1583.

Table S1 The calculations of intercalation energy and volume expand after Li^+ intercalating into TiO_2 and $V_{0.25}Ti_{0.75}O_2$ crystal lattice by the DFT results.

	Energy	**Intercalation energy**	**Volume**	**Volume expand**
TiO_2	-107.7034	/	140.14	/
TiO_2-Li	-109.0828	-1.3794	155.56	11.00%
$V_{0.25}Ti_{0.75}O_2$	-106.1338	/	137.42	/
$V_{0.25}Ti_{0.75}O_2$-Li	-107.8681	-1.7343	150.13	9.25%

Table S2 Lattice constants and Rietveld refinement results of $VTi_{2.6}O_{7.2}$

GOF	0.86
a (Å)	3.79959
b (Å)	3.79959
c (Å)	9.51160
Rexp	1.36
Rwp	1.18
Rp	0.90
Rexp-dash	14.85
Rwp-dash	12.83
Rp-dash	20.25
Weighted Durbin Watson	0.16

Table S3 Refined peak list of $VTi_{2.6}O_{7.2}$

No.	h	k	l	m	d	th2	F^2
1	0	1	1	8	3.52847	25.21948	204.407
2	0	1	3	8	2.43434	36.89426	23.688
3	0	0	4	2	2.3779	37.80278	84.314
4	1	1	2	8	2.33924	38.45193	37.476
5	0	2	0	4	1.89979	47.84044	218.303
6	0	2	2	8	1.76424	51.77663	0

7	0	1	5	8	1.70103	53.85221	180.764
8	2	1	1	16	1.67274	54.83873	186.413
9	2	1	3	16	1.49769	61.90451	34.74
10	0	2	4	8	1.48426	62.5275	169.788
11	1	1	6	8	1.36532	68.69204	114.154
12	2	2	0	4	1.34336	69.97713	113.246
13	0	1	7	8	1.27945	74.03453	10.994
14	2	1	5	16	1.26728	74.86658	197.158
15	0	3	1	8	1.25545	75.69537	54.005
16	0	2	6	8	1.21717	78.52272	0
17	0	0	8	2	1.18895	80.76402	7.404
18	0	3	3	8	1.17616	81.82831	12.583
19	2	2	4	8	1.16962	82.38474	102.328
20	3	1	2	16	1.16493	82.78892	43.448
21	3	1	4	16	1.07241	91.82695	0
22	2	1	7	16	1.06122	93.08081	16.685
23	0	3	5	8	1.05425	93.88389	62.283
24	3	2	1	16	1.04741	94.68773	70.688
25	0	1	9	8	1.01819	98.31941	39.887
26	0	2	8	8	1.00785	99.68907	21.642
27	3	2	3	16	1.00002	100.7581	18.694
28	3	1	6	16	0.95757	107.111	101.078
29	0	4	0	4	0.9499	108.3735	47.274
30	0	4	2	8	0.9315	111.5725	0
31	0	3	7	8	0.92648	112.4915	6.446
32	3	2	5	16	0.92182	113.3619	86.594
33	4	1	1	16	0.91724	114.238	50.221
34	2	1	9	16	0.89743	118.2613	57.003
35	1	1	10	8	0.89663	118.4322	78.984
36	2	2	8	8	0.89032	119.8086	16.464
37	4	1	3	16	0.88491	121.0285	14.368
38	0	4	4	8	0.88212	121.6739	49.795
39	3	3	2	8	0.8801	122.1461	12.71
40	0	2	10	8	0.85052	129.8306	0
41	4	2	0	8	0.84961	130.0917	69.074
42	3	1	8	16	0.84513	131.4148	0
43	0	1	11	8	0.84313	132.0191	16.117
44	4	2	2	16	0.83637	134.1453	0

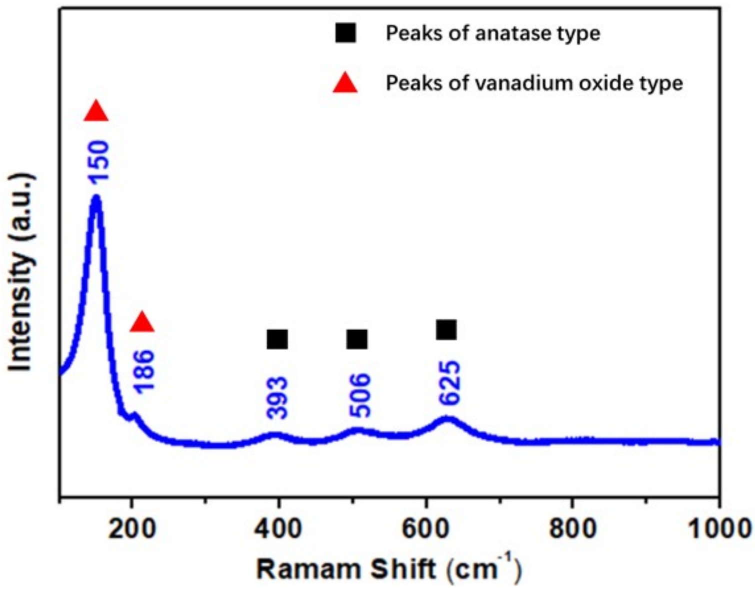

Fig. S2 Raman spectrum of $VTi_{2.6}O_{7.2}$.

Equation S1

$$C = \frac{\frac{1}{3.6} \times \mathrm{n} \times F}{M}$$

C ---- Specific capacity;

n ---- Transfer electronic number in a molecular;

F ---- Faraday constant;

M ---- The molecular weight

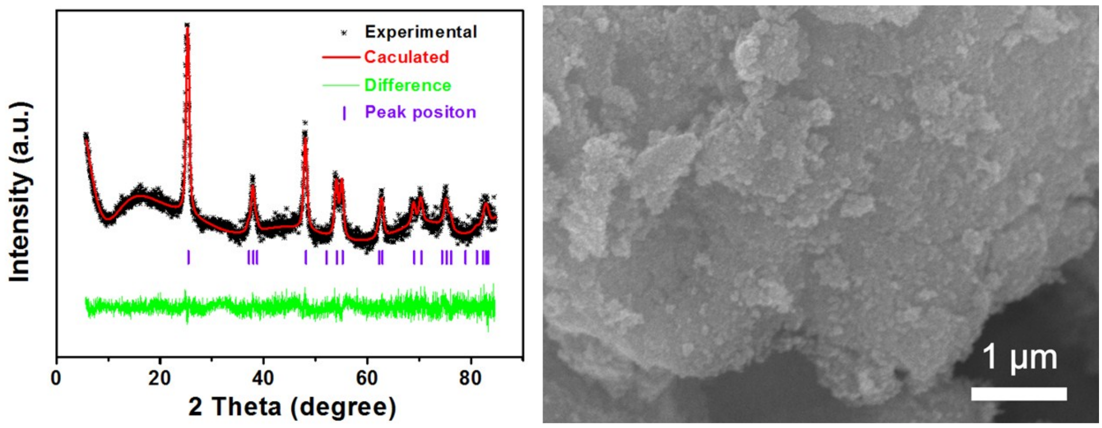

Fig. S3 (a) The Rietveld plot for the refined TiO_2 XRD pattern. (b) SEM image of the as prepared TiO_2.

Table S4 Lattice constants and Rietveld refinement results for TiO_2

GOF	0.78
Rexp	7.33
a (Å)	3.78489
b (Å)	3.78489
c (Å)	9.48892
Rwp	5.73
Rp	4.27
Rexp-dash	32.48
Rwp-dash	25.37
Rp-dash	23.89
Weighted Durbin Watson	0.29

Table S5 Refined peak list for TiO_2

No.	h	k	l	m	d	th2	F^2
1	0	1	1	8	3.51554	25.31378	53.36
2	0	1	3	8	2.42705	37.00908	7.995
3	0	0	4	2	2.37223	37.89657	25.609
4	1	1	2	8	2.33103	38.59273	10.295
5	0	2	0	4	1.89244	48.03791	61.084
6	0	2	2	8	1.75777	51.98127	0
7	0	1	5	8	1.69647	54.0088	50.63

8	2	1	1	16	1.66635	55.06697	52.818
9	2	1	3	16	1.49239	62.14867	12.33
10	0	2	4	8	1.47937	62.75737	55.02
11	1	1	6	8	1.36154	68.90955	29.94
12	2	2	0	4	1.33816	70.28891	34.131
13	0	1	7	8	1.27618	74.25584	3.361
14	2	1	5	16	1.26321	75.14938	59.599
15	0	3	1	8	1.25062	76.03925	16.64
16	0	2	6	8	1.21353	78.80431	0
17	0	0	8	2	1.18612	80.99716	3.261
18	0	3	3	8	1.17185	82.19409	4.821
19	2	2	4	8	1.16551	82.73849	35.686
20	3	1	2	16	1.16053	83.1727	14.885

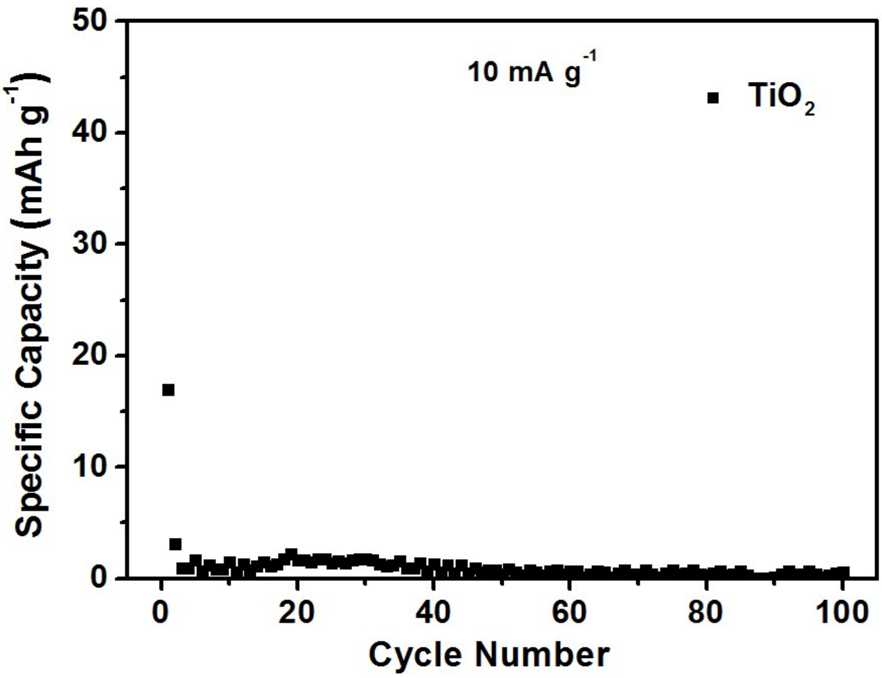

Fig. S4 Cycling performance of the as prepared TiO_2 in MBs at 10 mA g^{-1}.

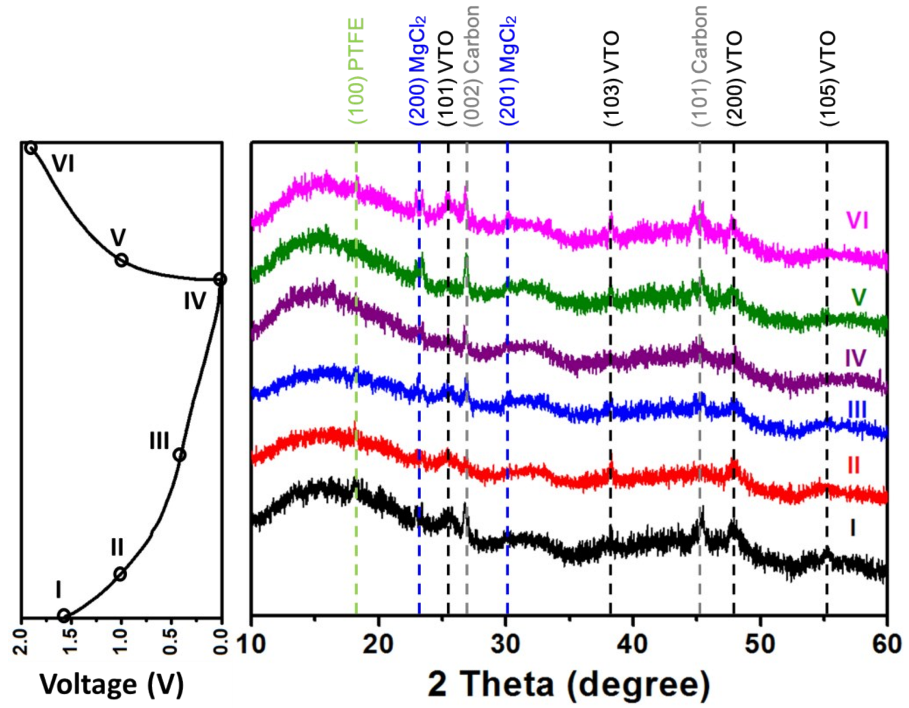

Fig. S5 Ex situ XRD measurement of VTO in MBs.

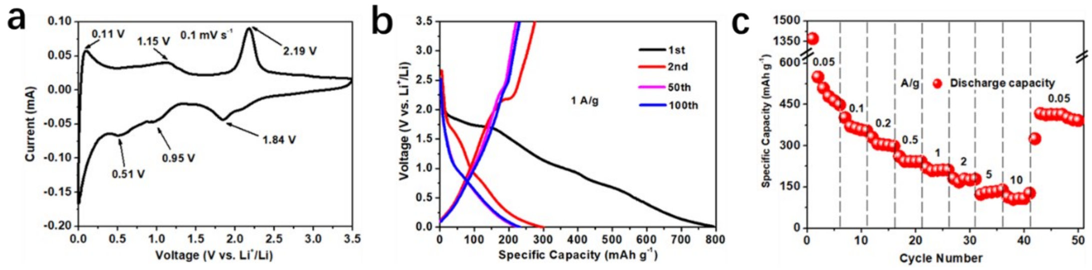

Fig. S6 Electrochemical performance of $VTi_{2.6}O_{7.2}$ in LIBs. (a) Cyclic voltammogram curve of LIBs (scan rate, 0.1 mV s^{-1}). (b) Charge-discharge curves of different cycles at 1 A g^{-1} in the voltage window of 0.01-3.5 V. (c) Rate performances.

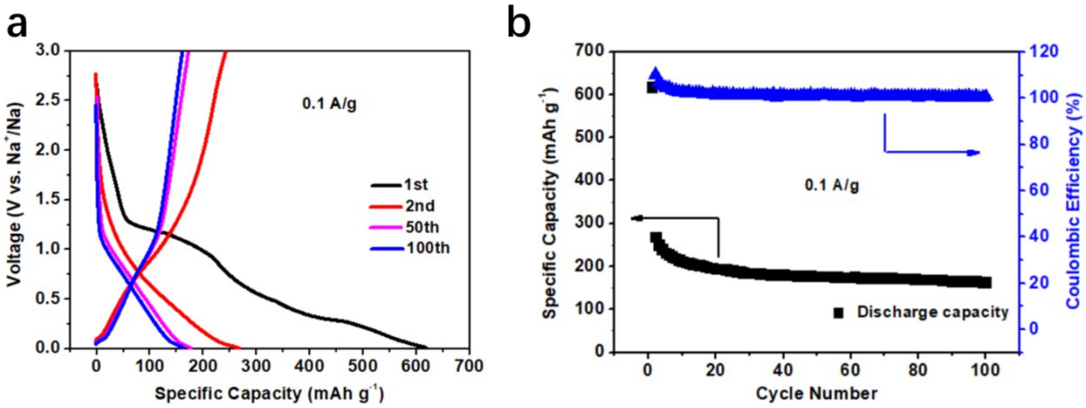

Fig. S7 Electrochemical performance of $VTi_{2.6}O_{7.2}$ in SIBs. (a) Charge-discharge curves of different cycles at 0.1 A g^{-1} in the voltage window of 0.01-3 V. (b) Cycling performance at 0.1 A g^{-1}.

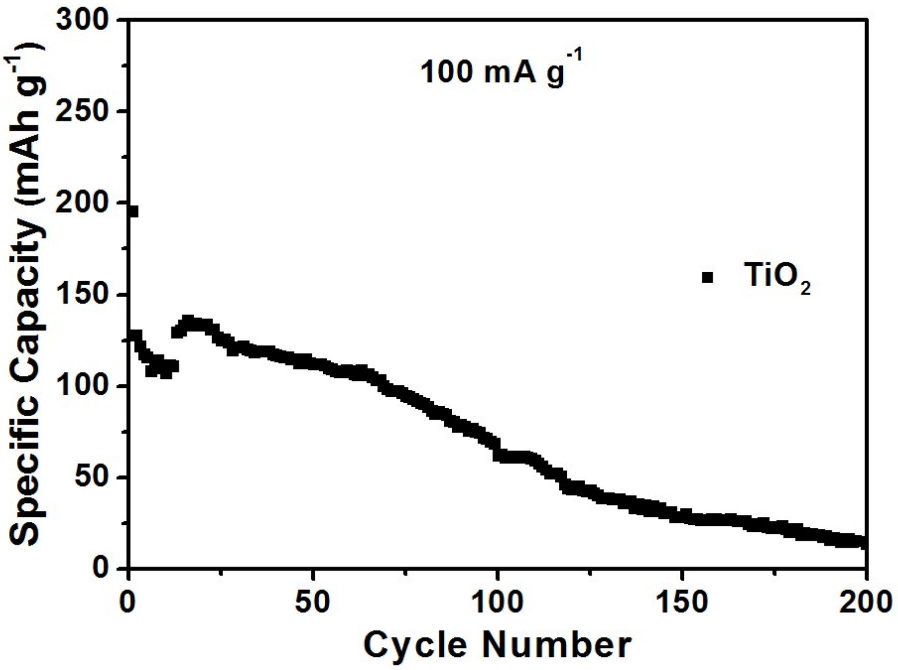

Fig. S8 Cycling performance of the as prepared TiO_2 in MLHBs at 100 mA g^{-1}.

Table S6 Comparison of the reported different cathode materials in specific energy density for coin-type batteries.

Cathode materials	Electrolyte	Voltage window (V)	Current density (mA/g)	Discharged capacity (mA h/g)	Average Working voltage (V)	Specific energy density (Wh/kg)	Ref.
TiO_2 (B)	0.5 mol/L $Mg(BH_4)_2$ + 1.5 mol/ L $LiBH_4$/TG	0.5-1.7	33.5	180	~0.7 V	126	13
TiO_2 (B)	0.4 M LiCl in 0.4 M APC/THF	0.01-2	20	236	~0.75 V	177	14
VO_2	1M LiCl in 0.25 M APC/THF	0.5-2	20	244.4	1.75	427	15
TiS_2	0.4 M LiCl in 0.4 M APC/THF	0.5-2	24	161	1.3	209.3	16
TiS_2	0.5 M LiCl in 0.25 M APC/THF	0.5-2	24.1	220	1.4	308	17
FeS	1.5 M $LiBH_4$ in 0.1 M $Mg(BH_4)_2$	0.1-1.7	60.9	458	0.7	320.6	18
FeS_2	1.5 M $LiBH_4$ in 0.1 M $Mg(BH_4)_2$	0.1-1.7	89.4	566	0.7	396.2	18
$Li_4Ti_5O_{12}$	0.5 M LiCl in 0.25 M $Mg(AlCl_2BuEt_2)_2$/THF	0-1.8	60	175	0.5	87.5	39
Mo_6S_8	0.5 M LiCl in 0.2 M APC/THF	0.5-1.7	30.5	120	1.28	153.6	51
Mo_6S_8	1 M LiCl in 0.4 M APC/THF	0.5-2	12.3	126	1.3	163.8	52
MoS_2	0.5 M LiCl in APC/THF	0.1-1.8	25	160	~0.95	152	53
MoO_2	1 M LiCl in 0.4 M APC/THF	0.5-2	20	191	0.75	143.3	54
$LiCrTiO_4$	1 M LiCl in 0.3 M APC/THF	0.01-1.8	20	178	~0.66	117.5	55
$VTi_{2.6}O_{7.2}$	1M LiCl in 0.25 M APC/THF	0.01-1.9	100	265.2	~1	265.5	This work