Supplementary information

Synthesis, characterization and structure of $(NH_4)_4[Zn_5V^{IV}_4V^{V}_{16}O_{56}H_2(H_2O)_4]$ with a novel V_5O_{14} layer

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Supplementary figure and table lists

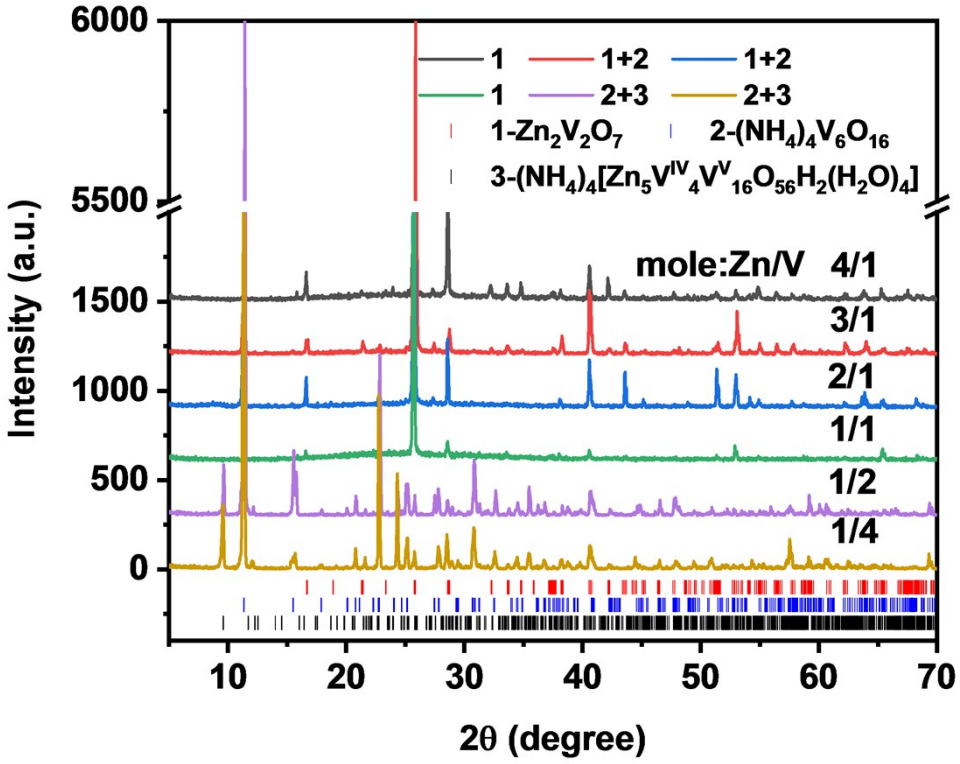

Fig. S1 The hydrothermal powder products with different Zn/V ratio at 473K (24h)

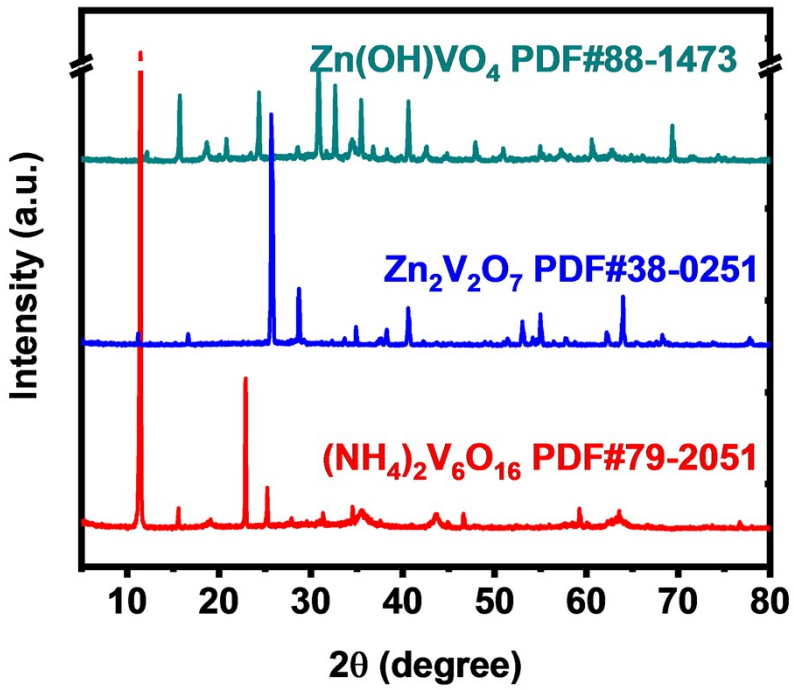

Fig. S2 the XRD patterns of the products at different time and pH.

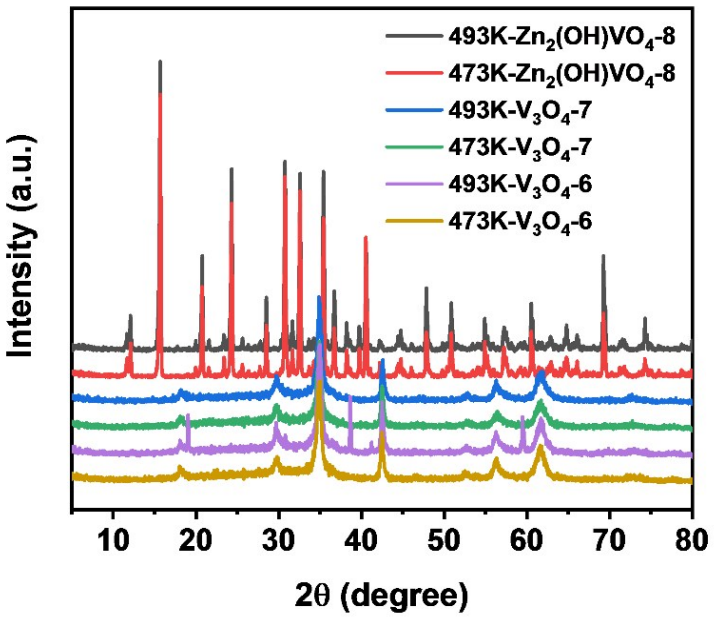

Fig. S3 XRD patterns of the products when $(NH_4)_2V_6O_{16}$ was used as the raw materials with different pH and reaction temperature.

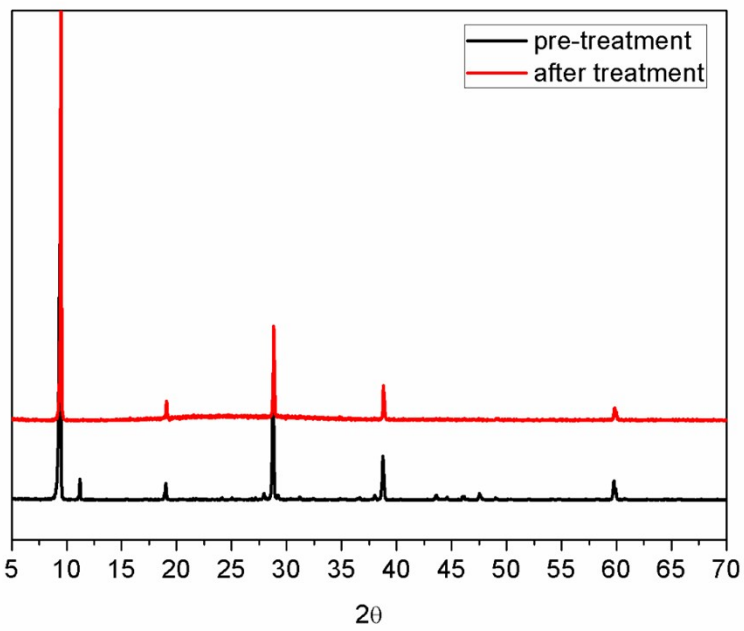

Fig. S4 XRD patterns of $(NH_4)_4[Zn_5V^{IV}_4V^{V}_{16}O_{56}H_2(H_2O)_4]$ before and after treatment in ammonium solution.

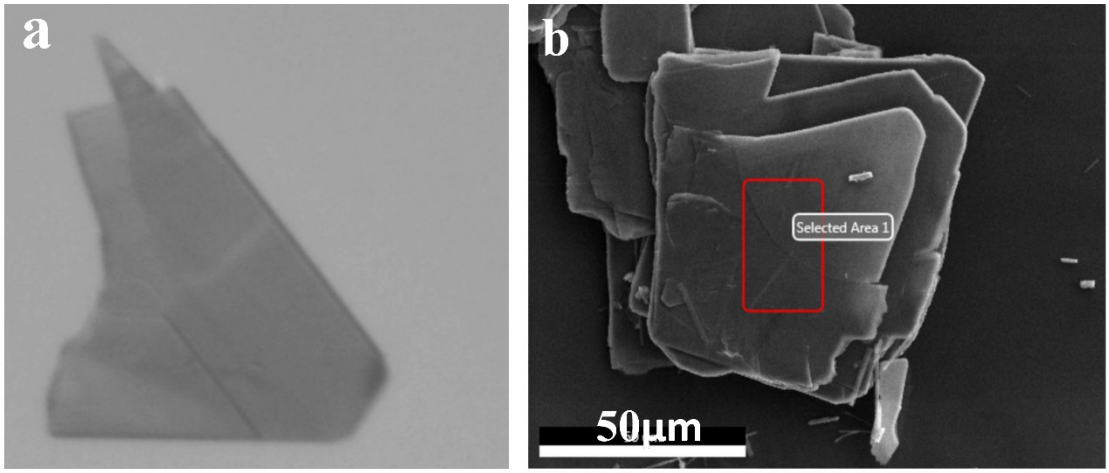

Fig S5 The morphologies of $(NH_4)_4[Zn_5V^{IV}_4V^{V}_{16}O_{56}H_2(H_2O)_4]$ obtained in (a) optical and (b) scanning electron microscopy.

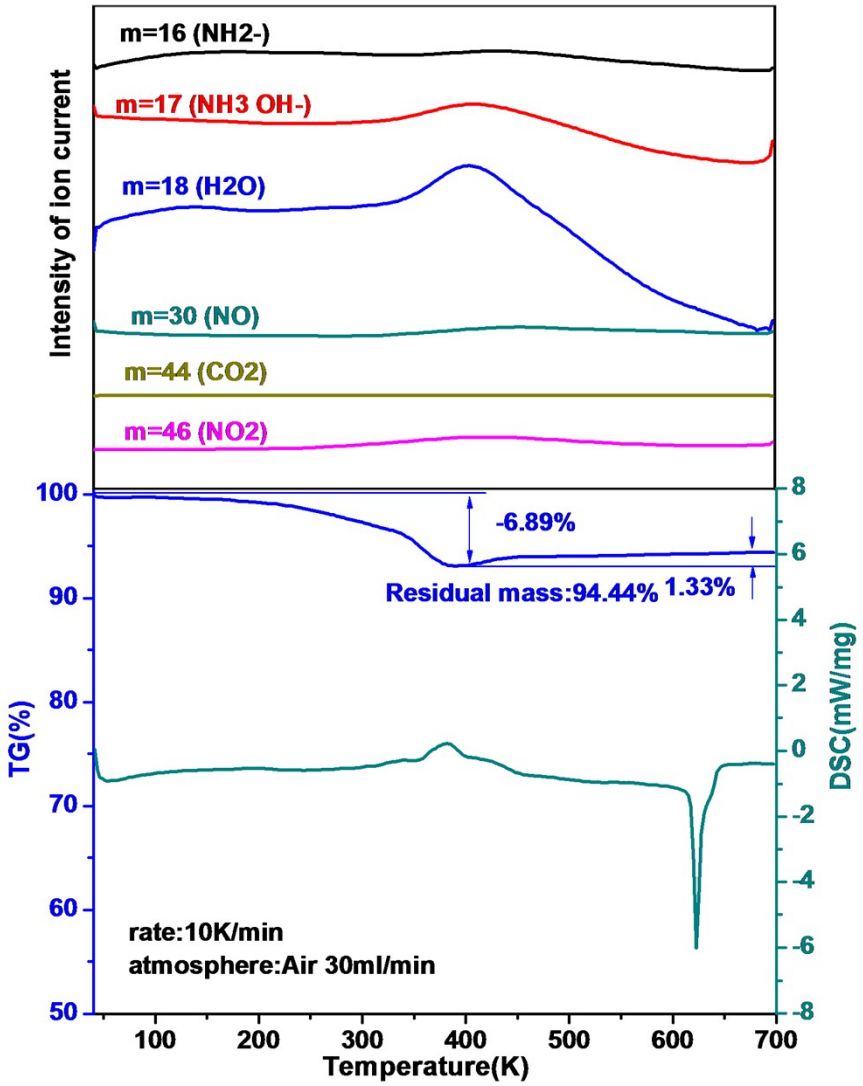

Fig. S6 TG-DSC-MS result of $(NH_4)_4[Zn_5V^{IV}_4V^{V}_{16}O_{56}H_2(H_2O)_4]$.

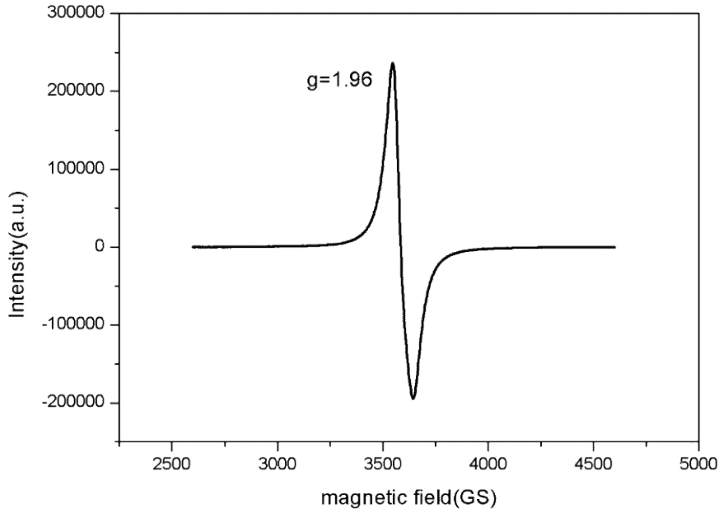

Fig. S7 EPR data of $(NH_4)_4[Zn_5V^{IV}_4V^{V}_{16}O_{56}H_2(H_2O)_4]$ indicating the valence of V^{4+}.

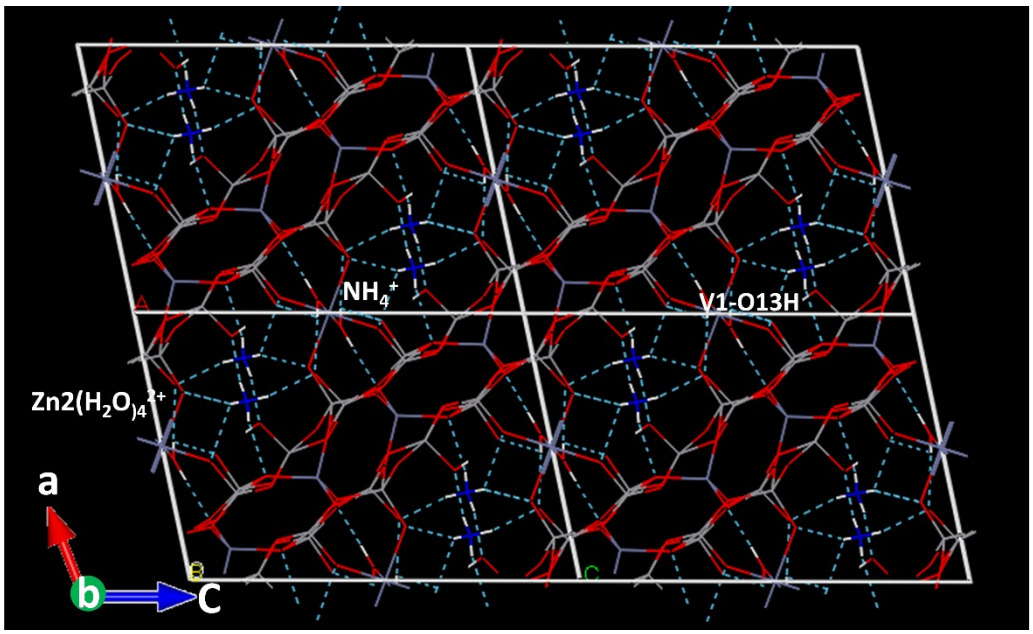

Fig. S8 The hydrogen atom positions in $(NH_4)_4[Zn_5V^{IV}_4V^{V}_{16}O_{56}H_2(H_2O)_4]$.

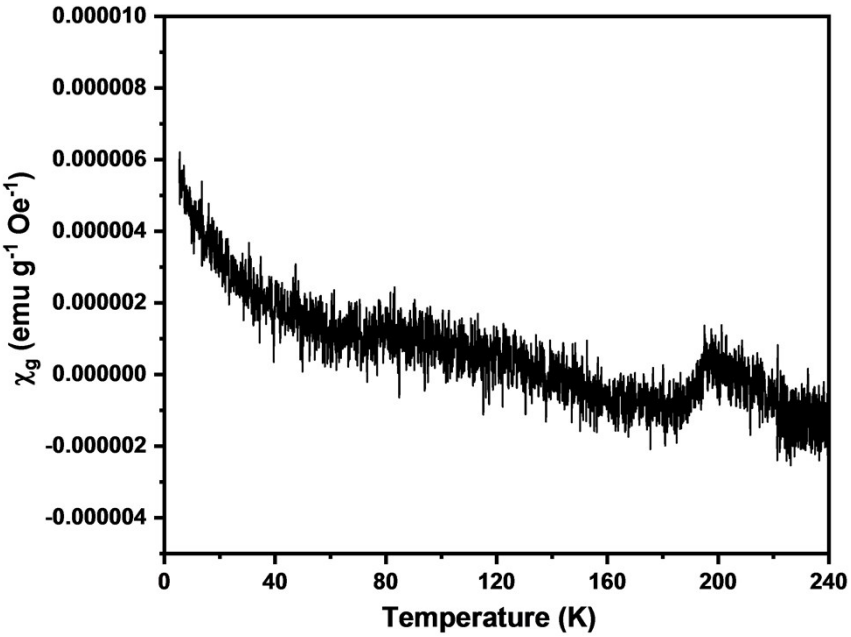

Fig. S9 The paramagnetic property of $(NH_4)_4[Zn_5V^{IV}_4V^{V}_{16}O_{56}H_2(H_2O)_4]$

Table S1 Bond lengths of V-O and Zn-O in $(NH_4)_4[Zn_5V^{IV}_4V^{V}_{16}O_{56}H_2(H_2O)_4]$

Bond name	Bond length (Å)	Bond name	Bond length (Å)	Bond name	Bond length (Å)
V1-O4	1.940(5)	V2-O1	1.995(5)	V3-O1	2.012(5)
V1-O6	1.931(5)	V2-O7	1.767(5)	V3-O4	1.738(5)
V1-O7	1.925(5)	V2-O10	1.905(5)	V3-O9	1.970(5)
V1-O8	1.992(5)	V2-O11	1.605(5)	V3-O10	1.905(5)
V1-O13	1.613(6)	V2-O12	1.938(5)	V3-O14	1.618(5)
		V2-O4	2.399(5)	V3-O7	2.315(5)
BVS	**4.17**		**5.02**		**5.02**
V4-O2	1.647(6)	V5-O1	1.986(5)	Zn1-O3	1.968(5)
V4-O3	1.799(5)	V5-O3	1.998(5)	Zn1-O9	1.982(5)
V4-O8	1.667(5)	V5-O5	1.615(5)	Zn1-O10	1.946(5)
V4-O9	1.786(5)	V5-O6	1.755(5)	Zn1-O12	1.941(5)
		V5-O12	1.907(5)		
BVS	**5.01**		**4.77**		**2.00**

Table S2 Hydrogen Bonds in $(NH_4)_4[Zn_5V^{IV}_4V^{V}_{16}O_{56}H_2(H_2O)_4]$

D-H (Å)	H...A(Å)	D...A(Å)	<(DHA)(degree)	Hydrogen bond
0.97(2)	2.29(2)	3.202(8)	156(4)	O15-H15A...O5_$1
0.97(2)	2.29(2)	2.831(8)	115(2)	O15-H15A...O11_$2
0.96(2)	2.02(2)	2.969(8)	170(8)	O15-H15B...O12_$3
0.91(2)	2.17(4)	3.013(9)	153(6)	N16-HN1...O10_$4
0.91(2)	2.54(5)	3.279(9)	138(6)	N16-HN1...O11_$5
0.91(2)	2.06(3)	2.960(10)	170(7)	N16-HN2...O5_$6
0.91(2)	1.92(4)	2.754(9)	153(7)	N16-HN3...O13_$7
0.92(2)	2.27(4)	3.131(10)	156(6)	N16-HN4...O2_$8
0.92(2)	2.32(7)	2.796(8)	112(5)	N16-HN4...O14_$9
0.96(2)	2.22(2)	3.122(7)	156(7)	O13-H13A… O14_$10

EQIV $1 -x-1, -y, -z $2 x, y-1, z $3 -x, -y, -z $4 x+1/2, -y+1/2, z+1/2
$5 x+1, y, z+1 $6 x+1/2, -y+1/2, z+1/2 $7 x, y, z+1 $8 -x, -y, -z+1 $9 x+1, y, z+1
$10 -x-1/2, y+1/2, -z-1/2