

ACCESSORY PUBLICATION

Novel doped tungstovanadate and molybdovanadate with bi-antimony-capped Keggin structure

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S-Fig. 10 XRD and EDX-SEM of **1-3**.

S-Table 1 Selective bond lengths (Å) in **1-3**

Compound 1	(i= -x,y,-z+3/2; ii= -x+1,y,-z+3/2)		
W(1)-O(13)	1.730(14)	V(7)-O(3)	2.030(11)
W(1)-O(14)	1.797(11)	V(7)-O(4)	2.224(11)
W(1)-O(12)	1.842(11)	V(7)-O(21 ⁱ)	2.47(3)
W(1)-O(4)	2.020(10)	Sb(2)-O(16)	2.011(12)
W(1)-O(5)	2.058(11)	Sb(2)-O(17)	2.309(12)
W(1)-O(1)	2.338(10)	Sb(3)-O(11)	2.021(11)
V(1)-O(1)	1.713(10)	Sb(3)-O(10)	2.216(12)
V(1)-O(2)	1.693(10)	Sb(2)-V(4 ⁱⁱ)	3.022(2)
V(7)-O(21)	1.670(10)	Sb(2)-W(3 ⁱⁱ)	3.162(3)
V(7)-O(5)	2.001(11)	Sb(3)-W(5 ⁱⁱ)	3.144(2)
V(7)-O(6)	2.021(11)	Sb(3)-W(6 ⁱⁱ)	3.206(2)
Compound 2			
Mo(1)-O(10)	1.653(8)	Sb(1)-O(19)	2.035(9)
Mo(1)-O(11)	1.784(11)	Sb(1)-O(8)	2.036(9)
Mo(1)-O(9)	1.799(11)	Sb(1)-O(20)	2.055(9)
Mo(1)-O(20)	2.071(9)	Co(1)-N(5)	2.063(10)
Mo(1)-O(8)	2.083(10)	Co(1)-N(4)	2.070(10)
Mo(1)-O(1')	2.461(14)	Co(1)-N(2)	2.103(10)
V(1)-O(2)	1.642(15)	Co(1)-N(3)	2.118(10)
V(1)-O(2')	1.657(13)	Co(1)-N(1)	2.119(9)
V(1)-O(1')	1.706(15)	Co(1)-N(6)	2.120(10)
V(1)-O(1)	1.712(15)	Mo(3)-Sb(1)	3.2640(13)
Sb(1)-O(18)	2.025(8)	Mo(4)-Sb(1)	3.2658(13)
Compound 3 (i= -x,-y+2,-z+2)			

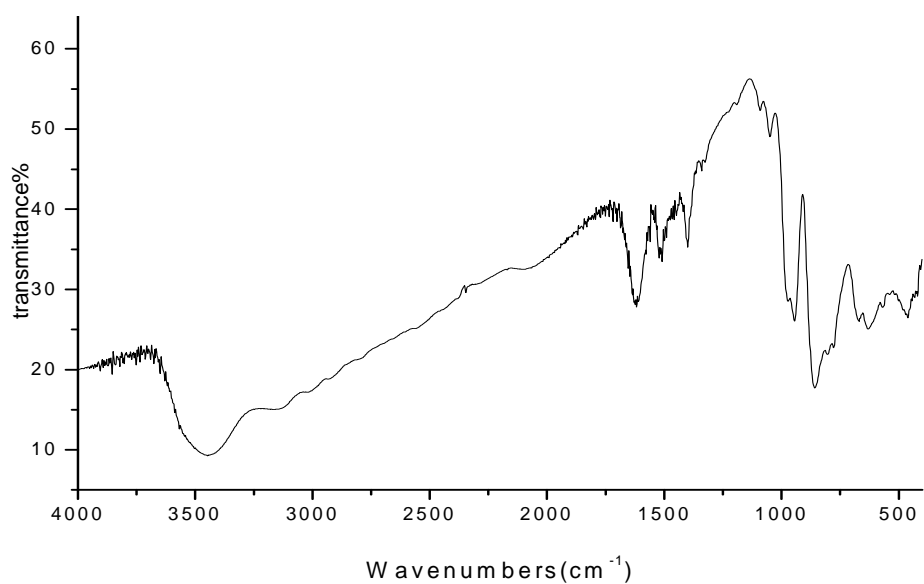
Mo(1)-O(14)	1.675(12)	V(2)-O(10)	1.962(13)
Mo(1)-O(9)	1.776(12)	V(2)-O(2')	2.36(2)
Mo(1)-O(4)	1.777(13)	V(2)-O(2)	2.41(2)
Mo(1)-O(20 ⁱ)	2.067(10)	Sb(1)-O(20)	2.039(11)
Mo(1)-O(16)	2.072(13)	Sb(1)-O(16 ⁱ)	2.040(10)
Mo(1)-O(1')	2.44(2)	Sb(1)-O(13 ⁱ)	2.044(13)
Mo(1)-O(2)	2.44(3)	Sb(1)-O(17)	2.054(14)
V(1)-O(1')	1.64(2)	Ni(1)-OW1	2.055(10)
V(1)-O(2)	1.66(3)	Ni(1)-N(2)	2.064(11)
V(1)-O(1)	1.70(2)	Ni(1)-N(1)	2.071(10)
V(1)-O(2')	1.73(2)	Ni(1)-N(3)	2.070(12)
V(2)-O(18)	1.584(11)	Ni(1)-N(4)	2.082(11)
V(2)-O(9)	1.900(13)	Ni(1)-O(18)	2.122(11)
V(2)-O(7)	1.940(14)	Mo(1)-Sb(1 ⁱ)	3.2562(14)
V(2)-O(3)	1.941(15)		

S-Table 2 Hydrogen bond distances in **1-3** involving O-H...O and C-H...O interactions.

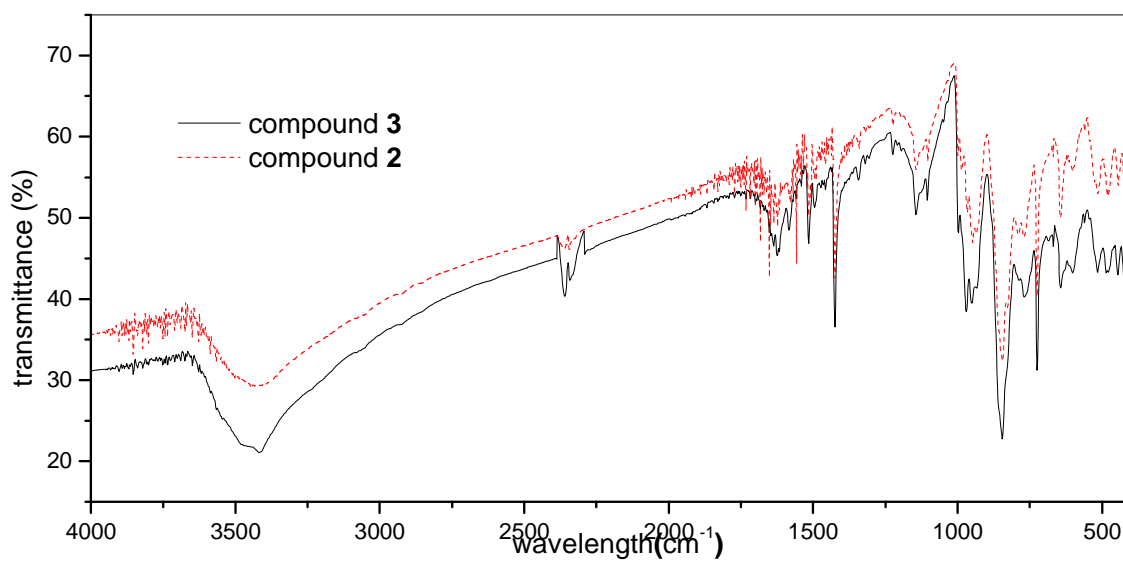
D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	∠D-H...A (°)
Compound 1				
O(23)-H(23C)...O(3 ⁱ)	0.85	1.80	2.65(3)	178
O(23)-H(23D)...O(6 ⁱⁱ)	0.85	1.88	2.73(3)	177
O(24)-H(24C)...O(5 ⁱⁱⁱ)	0.85	1.97	2.81(3)	175
O(25)-H(25C)...O(10 ⁱ)	0.79	2.09	2.88(3)	175
O(25)-H(25D)...O(19 ^{iv})	0.87	1.96	2.82(3)	178
C(2)-H(2A)...O(16 ^v)	0.97	2.19	3.12(4)	162
C(2)-H(2B)...O(14 ^{vi})	0.96	2.28	3.15(4)	150
C(2)-H(2C)...O(15 ^v)	0.96	2.25	3.05(5)	141
C(3)-H(3B)...O(18 ^{vii})	0.96	1.94	2.86(5)	161
C(3)-H(3C)...O(8 ^{viii})	0.96	2.19	3.08(5)	152
Symmetry code: i=x,1-y,-1/2+z; ii=3/2-x,1/2-y,1-z; iii=x,1-y,1/2+z; iv: 1-x,1-y,1-z; v=1-x,y,3/2-z; vi=-1/2+x,1/2+y,z; vii=-1/2+x,3/2-y,1/2+z; viii=3/2-x,3/2-y,2-z				
Compound 2				
C(2)-H(2)...O(12 ⁱ)	0.93	2.48	3.193(18)	134
C(10)-H(10)...O(22 ⁱⁱ)	0.93	2.52	3.24(3)	134
C(13)-H(13)...O(22 ⁱⁱⁱ)	0.93	2.56	3.34(2)	142
C(22)-H(22A)...O(14 ^{iv})	0.93	2.50	3.313(18)	146
C(23)-H(23A)...O(3 ⁱⁱⁱ)	0.93	2.24	3.040(17)	144
C(32)-H(32)...O(14 ^v)	0.93	2.38	3.27(2)	160
C(36)-H(36)...O(3 ^{vi})	0.93	2.38	3.165(18)	142
Symmetry code: i=1-x,2-y,1-z; ii=2-x,1-y,2-z; iii=x,1+y,z; iv=1-x,1-y,1-z; v=x,y,1+z; vi= 2-x,1-y,1-z				

Compound 3				
O(W1)-H(W1B)...O(15 ⁱ)	0.90	2.16	2.826(14)	130
O(W2)-H(W2B)...O(11 ⁱⁱ)	0.90	2.18	2.984(17)	148
C(2)-H(2A)...O(7 ⁱⁱⁱ)	0.90	2.56	3.47(2)	163
C(9)-H(9A)...O(14 ^{iv})	0.93	2.47	3.33(2)	154
C(11)-H(11A)...O(10 ⁱ)	0.93	2.53	3.33(2)	144
C(13)-H(13A)...O(9)	0.93	2.55	3.38(2)	150
C(20)-H(20A)...O(W2 ^v)	0.93	2.51	3.38(2)	156
C(21)-H(21A)...O(15 ^{vi})	0.93	2.57	3.46(2)	161

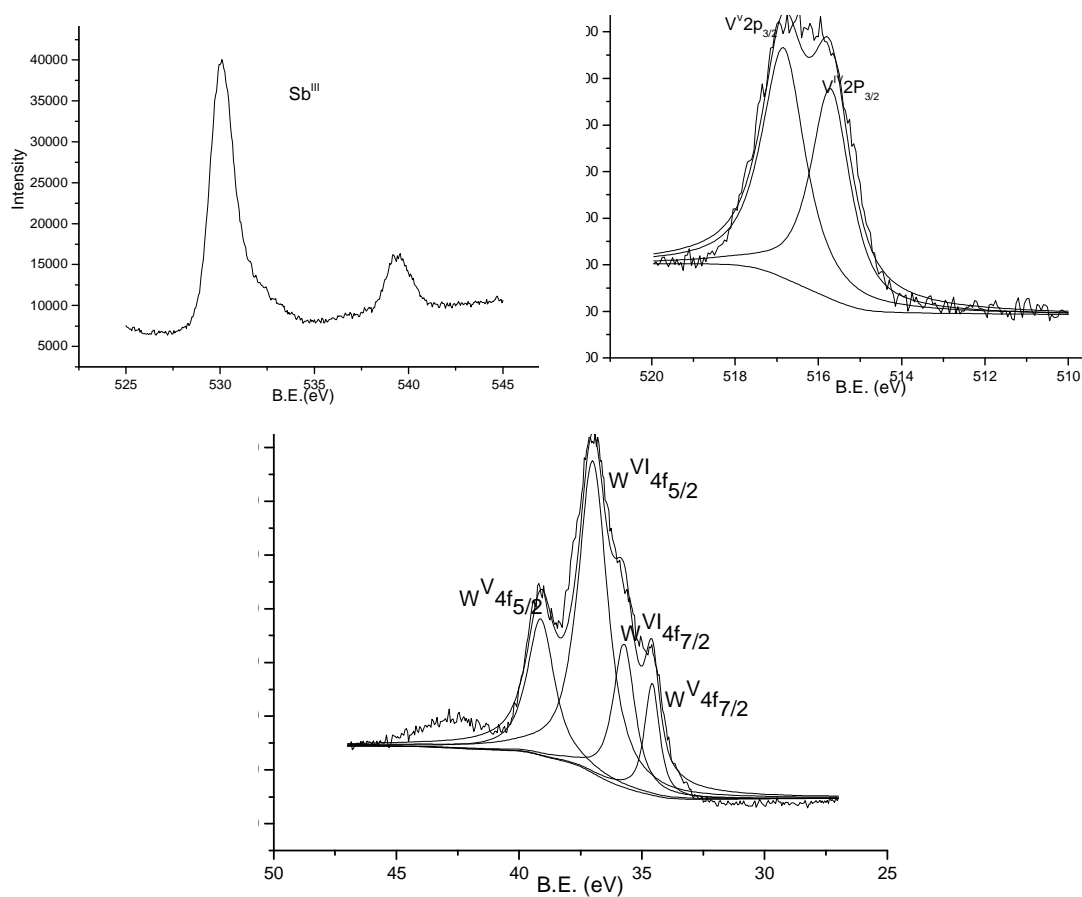
Symmetry code: i=-x,2-y,1-z; ii=1-x,2-y,1-z; iii=-x,1-y,2-z; iv=-1+x,y,z; v=1-x,1-y,1-z; vi= 1+x,-1+y,z



S-Fig. 1 IR spectra of **1**.

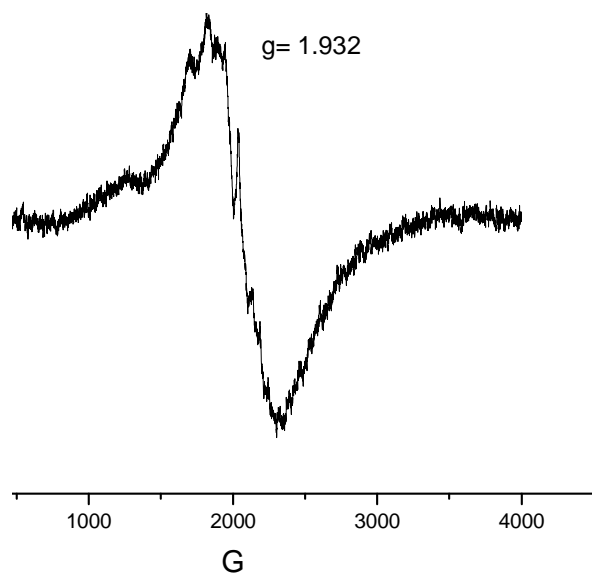


S-Fig. 2 IR spectra of **2** and **3**.

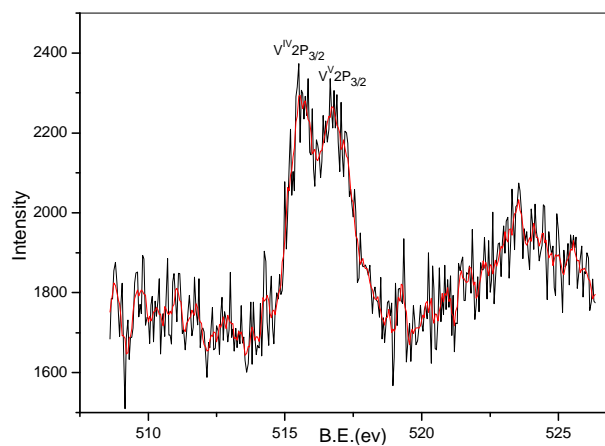
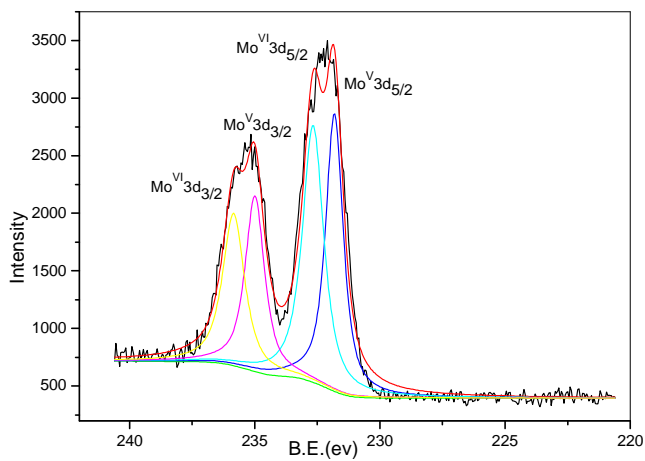


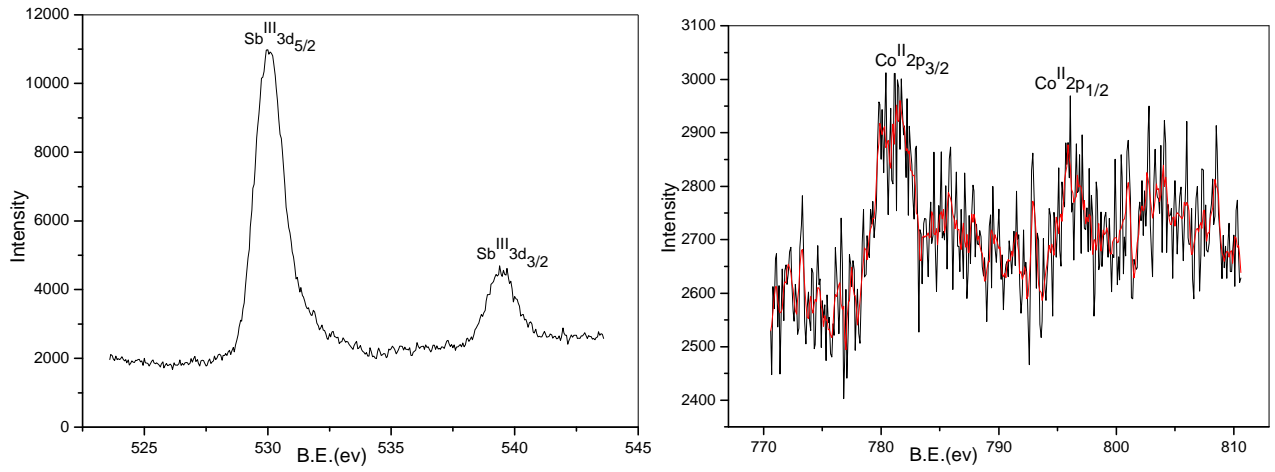
(c)

S-Fig. 3 XPS spectra of Sb, V and W of **1**.

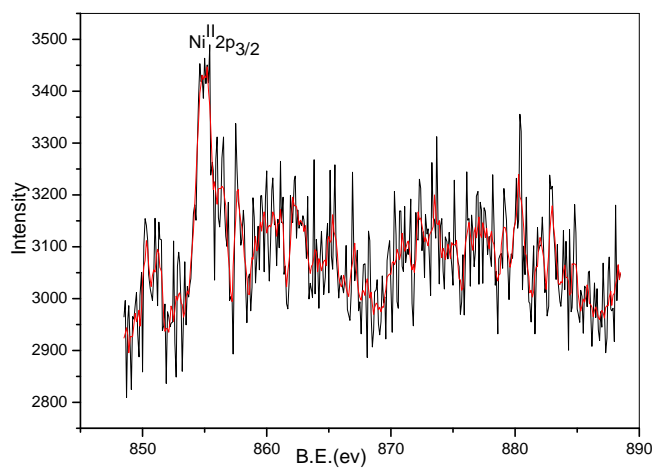
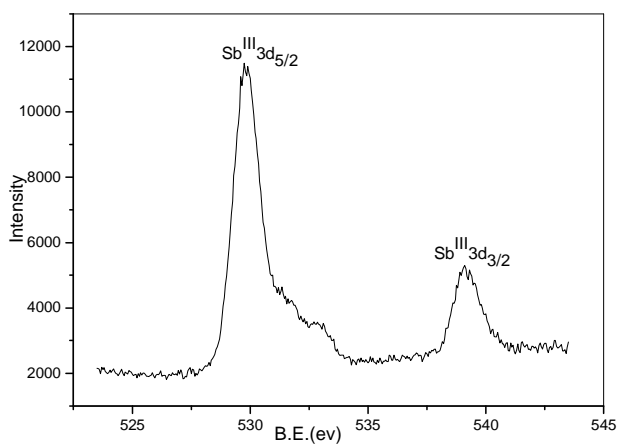
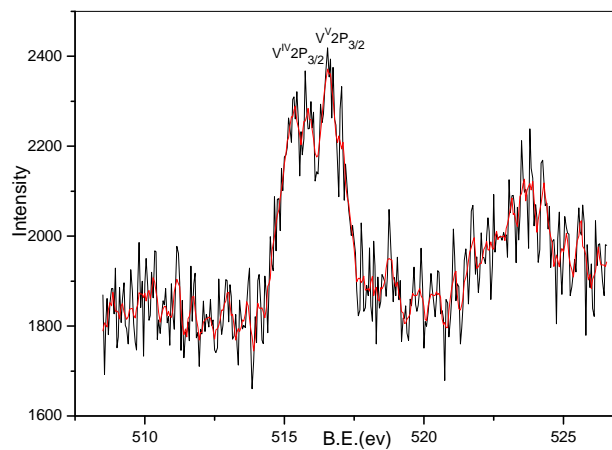
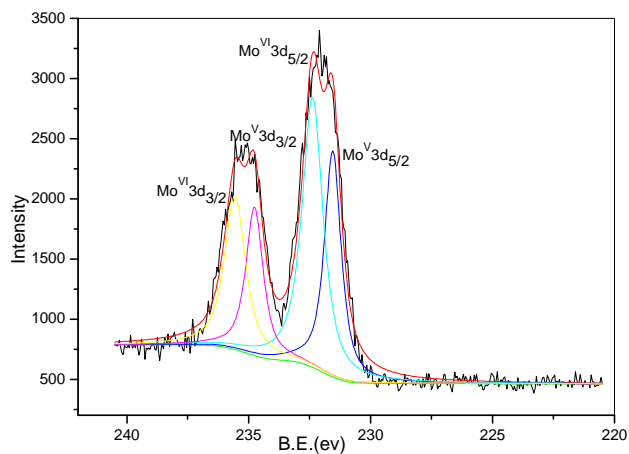


S-Fig. 4 EPR curve of **1**.

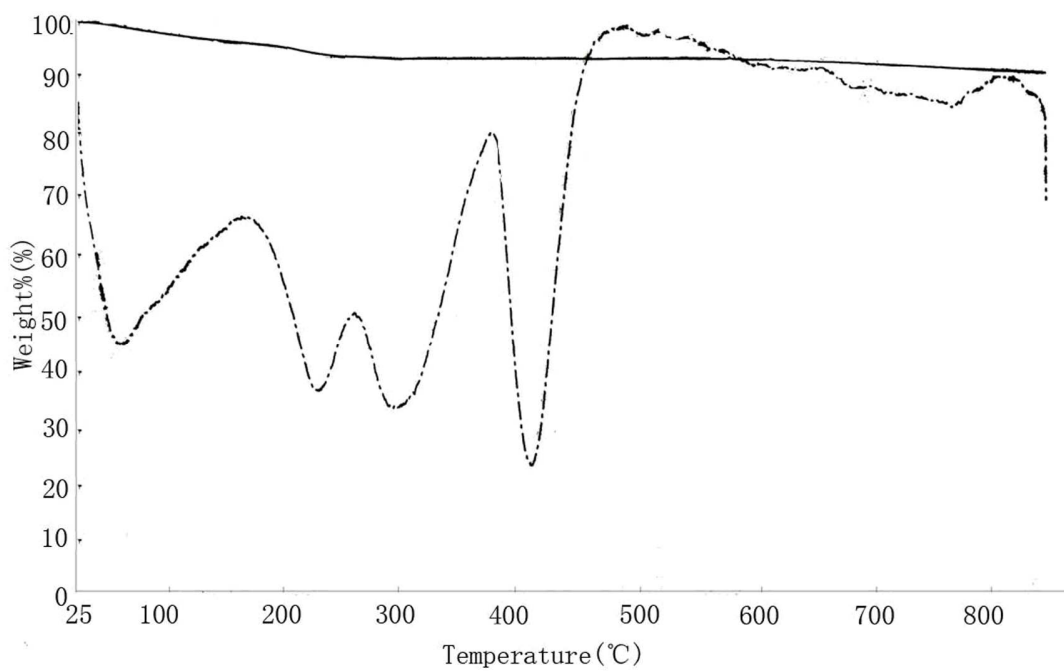




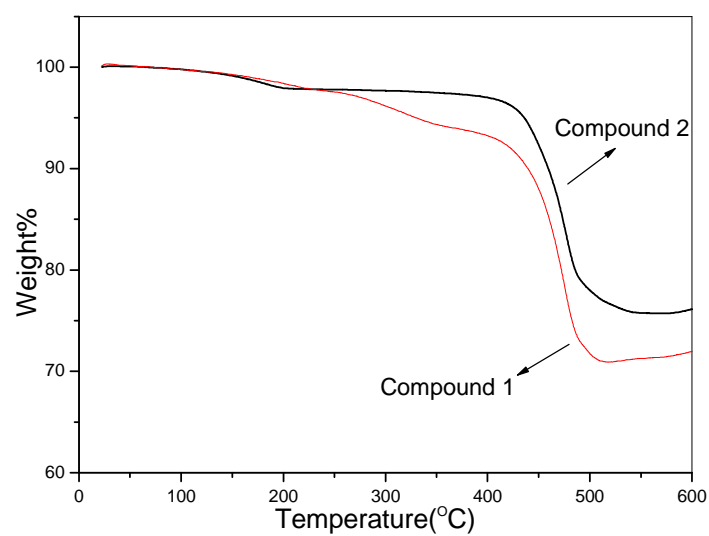
S-Fig. 5 XPS spectra of Mo, V, Sb and Co of **2**.



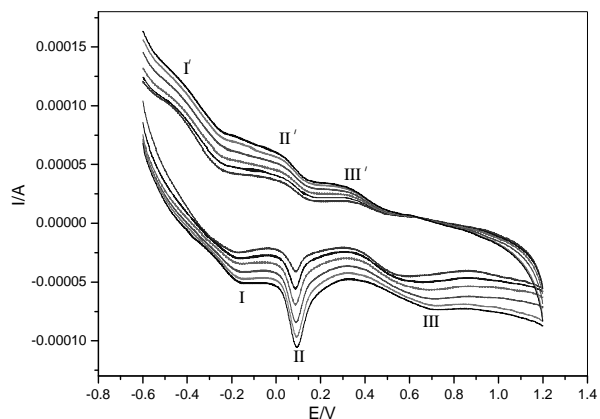
S-Fig. 6 XPS spectra of Mo, V, Sb and Ni of **3**.



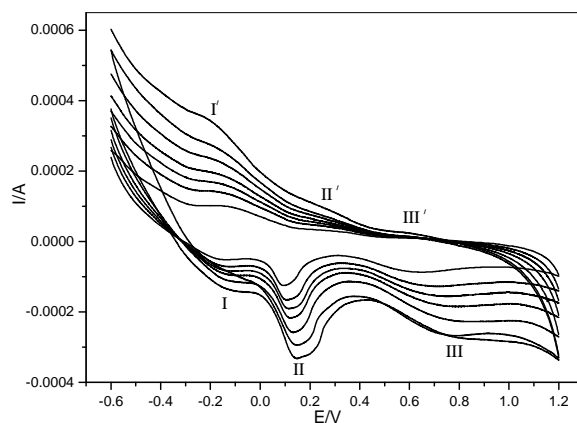
S-Fig. 7 TG curve of **1**.



S-Fig. 8 TG curves of **2-3**.



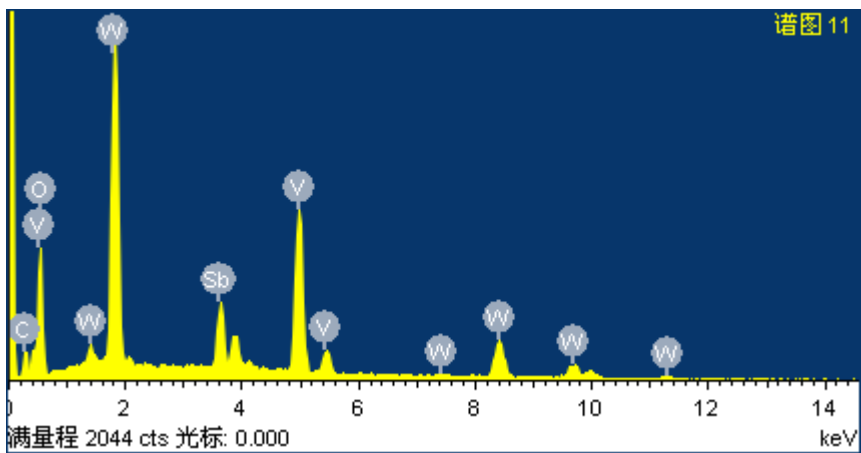
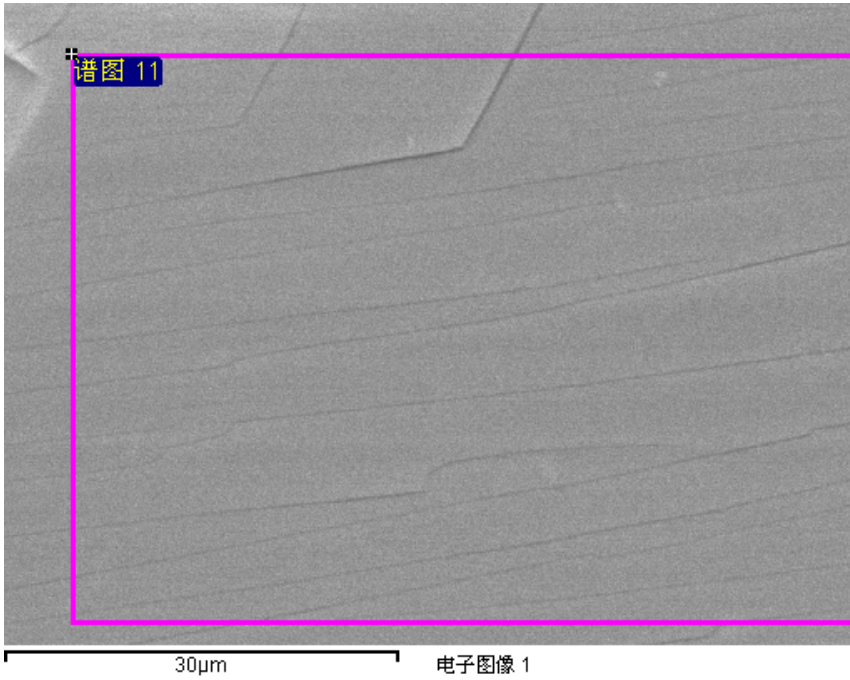
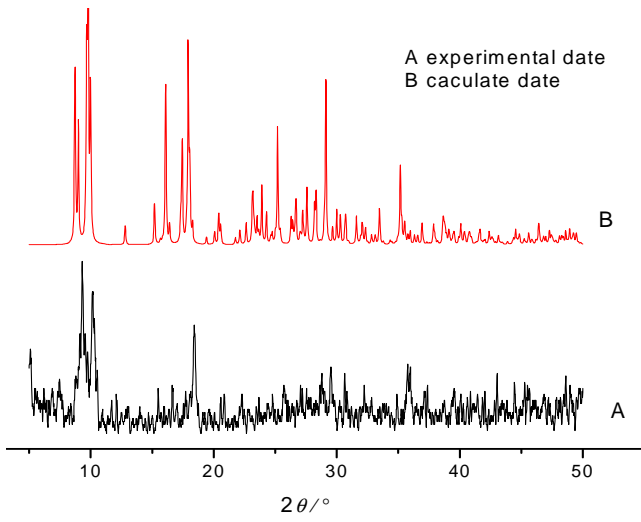
(a)



(b)

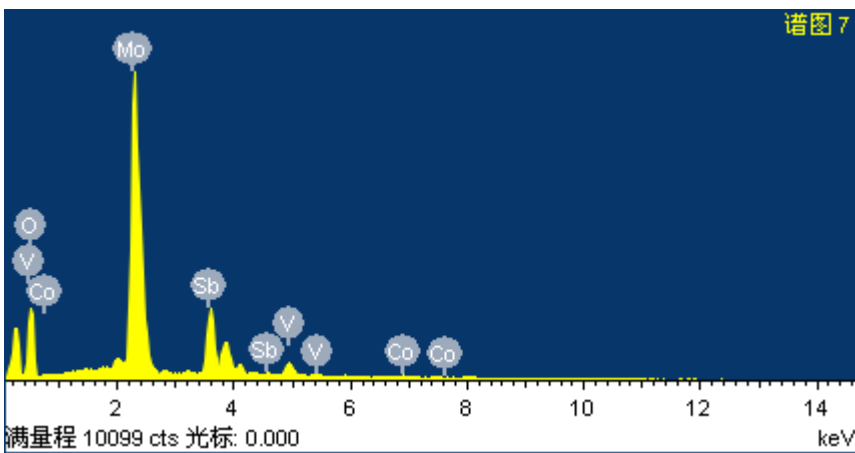
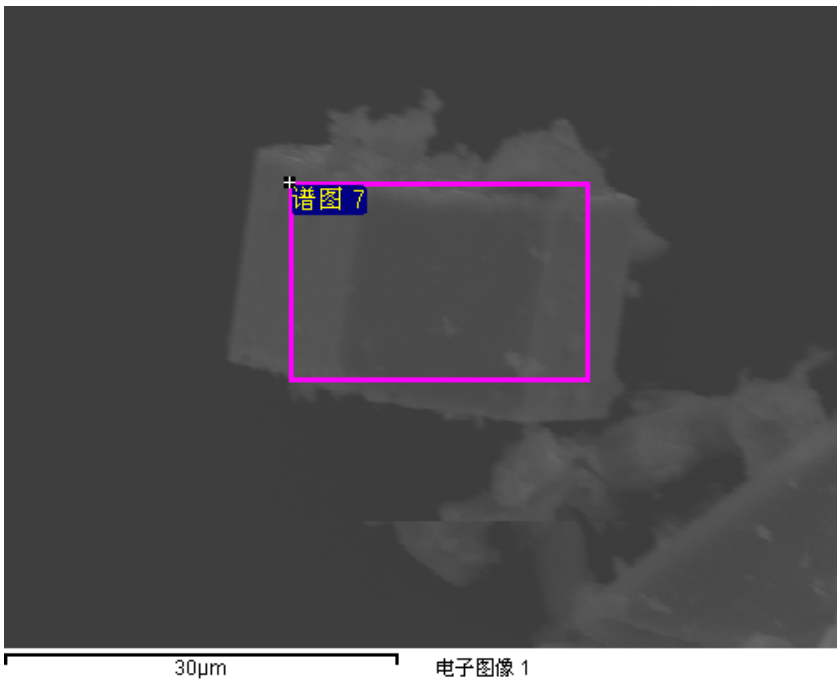
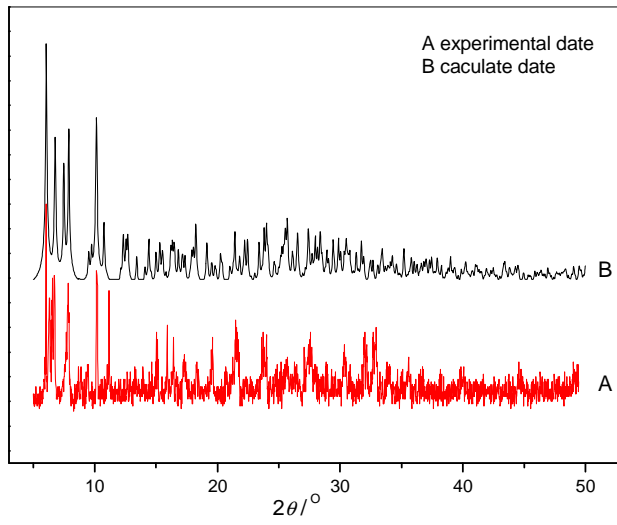
S-Fig. 9 Cyclic voltammograms of **2-CPE**(a) and **3-CPE**(b) in 1 M H_2SO_4 aqueous solution at different scan rates (from inner to outer: 50, 80, 110, 140, 170, 190 (for **3-CPE**) and 200 mV s^{-1}).

Compound **1**:



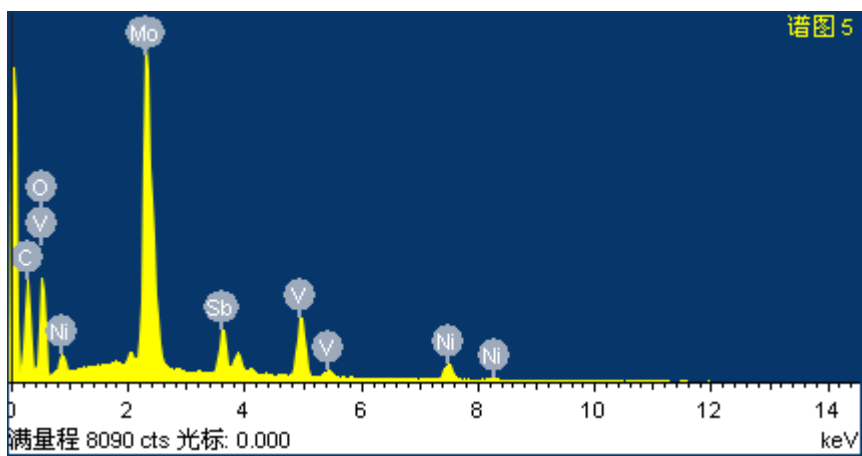
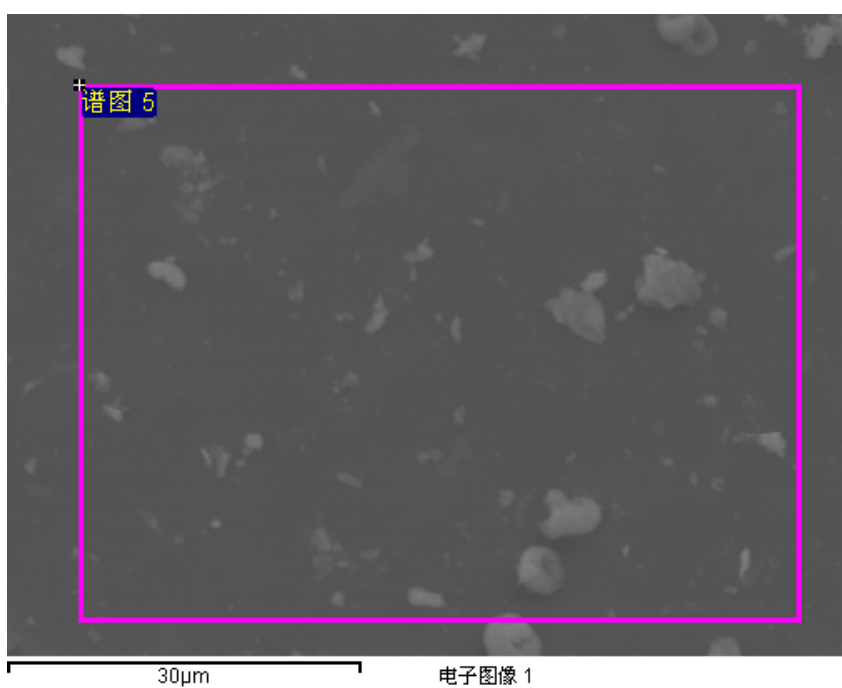
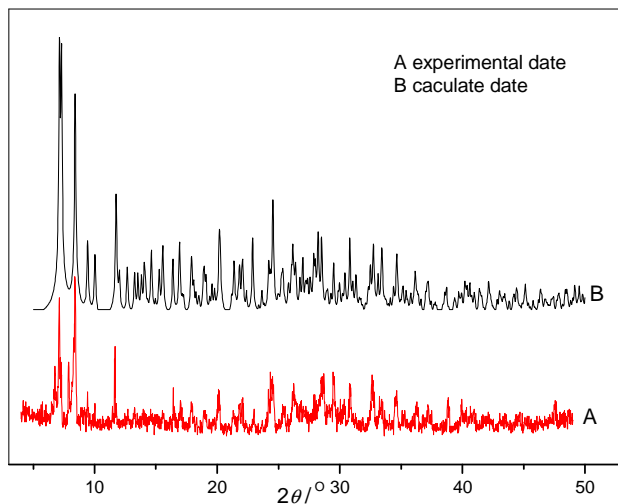
V : Sb : W = 8.84 : 2.74 : 5.65

Compound 2:



V : Co : Mo : Sb = 3.40 : 2.01 : 9.51 : 2.05

Compound 3:



V : Ni : Mo : Sb = 5.07 : 2.06 : 8.11 : 2.08

S-Fig. 10 XRD and EDX-SEM of **1-3**