Supporting Information

Carboxyethyltin and transition metal co-functionalized tungstoantimonates composited with polypyrrole for enhanced electrocatalytic methanol oxidation

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Contents

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1. Crystal structure figures ……..Page 2-3

2. Selected bond lengths and angles of SbW_9-TM-SnR (TM = Mn, Co, Ni, Zn)……Page 4-11

3. Physical characterizations ……Page 12-14

4. CV of the original material……Page 15

5. Catalytic oxidation activity of different catalysts……Page 16

6. Characterization and electrocatalytic performance of PPy-SbW_9-TM-SnR/Pt composite film……Page 17-19

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1. Crystal structure figures

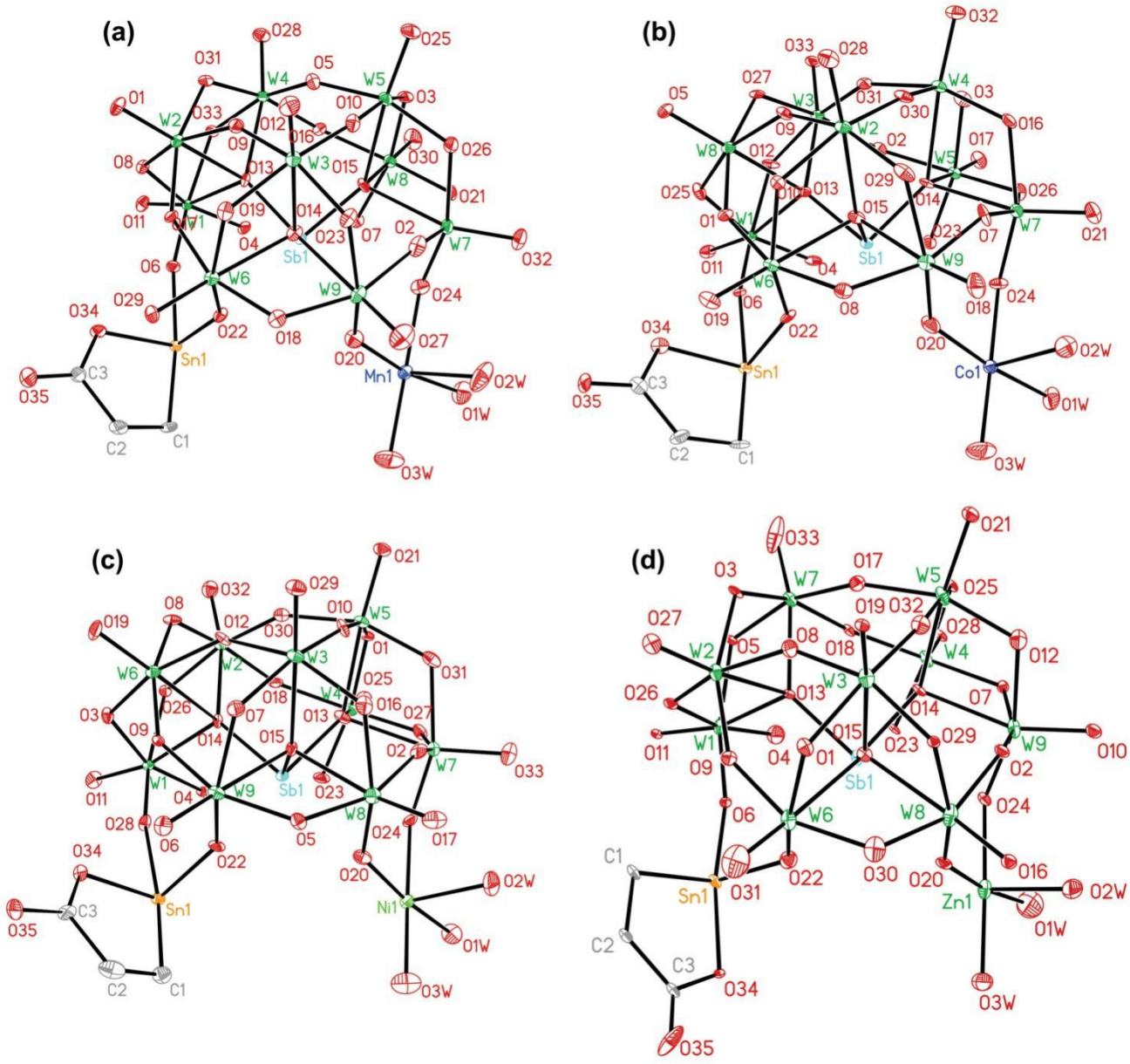

Fig. S1 ORTEP drawing of the polyoxoanion of **SbW_9-TM-SnR** (TM = Mn (a); Co (b); Ni (c); Zn (d)) with thermal ellipsoids at 30% probability (H, K, Na atoms, and free water molecules have been omitted for clarity).

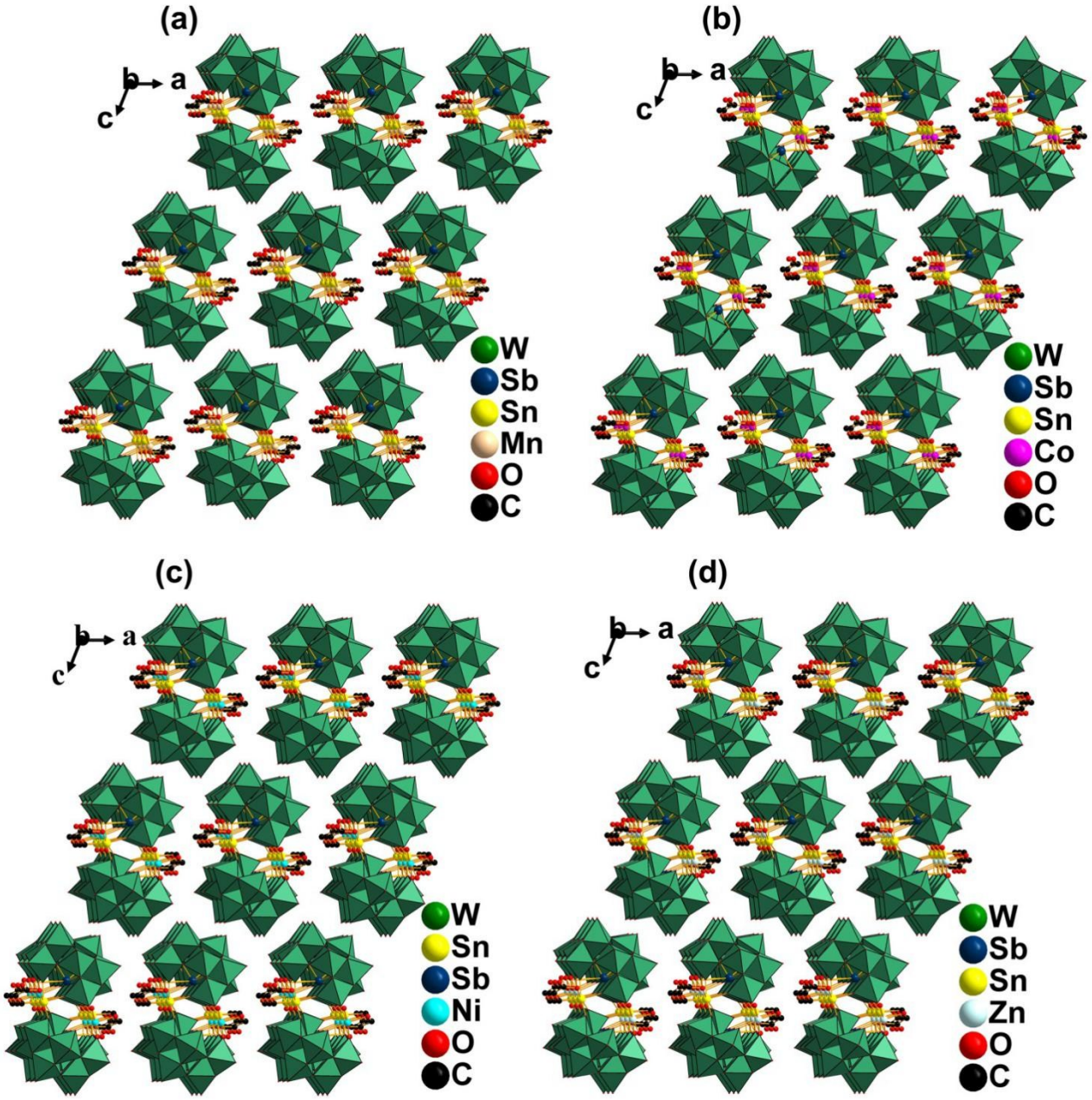

Fig. S2 The packing arrangement of the polyoxoanion in **SbW_9-TM-SnR** (TM = Mn (a); Co (b); Ni (c); Zn (d)) (all H, K, Na atoms, and water molecules existed in the interspaces are omitted for clarity).

2. Selected bond lengths and angles of SbW_9-TM-SnR (TM = Mn, Co, Ni, Zn)

Table S1 Selected bond lengths (Å) and angles (°) for **SbW_9-Mn-SnR**

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
W1–O24	1.725(9)	W5–O26	1.911(9)	W9–O11	1.774(10)
W1–O4	1.823(9)	W5–O5	1.915(9)	W9–O2	1.939(10)
W1–O6	1.831(8)	W5–O10	1.928(9)	W9–O18	1.972(9)
W1–O8	2.020(9)	W5–O3	1.957(10)	W9–O7	2.092(9)
W1–O33	2.036(8)	W5–O15	2.294(9)	W9–O14	2.257(8)
W1–O13	2.288(8)	W6–O29	1.732(8)	Sb1–O13	2.007(8)
W2–O1	1.718(9)	W6–O23	1.810(9)	Sb1–O15	2.019(8)
W2–O9	1.915(9)	W6–O18	1.932(9)	Sb1–O14	2.028(8)
W2–O8	1.916(8)	W6–O17	1.943(7)	Sn1–O6	2.046(8)
W2–O17	1.923(8)	W6–O19	2.006(9)	Sn1–O4#2	2.054(9)
W2–O31	1.928(9)	W6–O14	2.277(8)	Sn1–O22#2	2.126(8)
W2–O13	2.324(9)	W7–O32	1.742(9)	Sn1–O23	2.141(9)
W3–O12	1.726(10)	W7–O20	1.762(10)	Sn1–C1	2.145(11)
W3–O7	1.871(8)	W7–O2	1.929(9)	Sn1–O34	2.185(9)
W3–O10	1.907(9)	W7–O21	2.020(9)	Mn1–O11	2.139(11)
W3–O19	1.939(9)	W7–O26	2.050(10)	Mn1–O20	2.148(9)
W3–O9	1.963(8)	W7–O15	2.285(8)	Mn1–O3W	2.150(12)
W3–O14	2.316(9)	W8–O30	1.743(10)	Mn1–O24#2	2.203(9)
W4–O28	1.741(9)	W8–O22	1.832(9)	Mn1–O1W	2.240(13)
W4–O16	1.877(10)	W8–O21	1.897(9)	Mn1–O2W	2.207(12)
W4–O33	1.878(9)	W8–O3	1.967(9)	C3–O34	1.295(15)
W4–O31	1.959(9)	W8–O16	1.996(9)	C3–O35	1.230(17)
W4–O5	1.970(9)	W8–O15	2.296(9)	C1–C2	1.536(18)
W4–O13	2.351(8)	W9–O27	1.741(10)	C2–C3	1.572(19)
W5–O25	1.726(10)				
Bond	**Angle(°)**	**Bond**	**Angle(°)**	**Bond**	**Angle(°)**
O6–W1–O33	159.3(4)	O10–W5–O3	163.0(4)	O20–W9–O7	160.4(4)
O24–W1–O13	163.3(4)	O25–W5–O15	171.9(4)	O27–W9–O14	165.0(5)
O8–W1–O13	72.7(3)	O26–W5–O15	73.5(3)	O18–W9–O14	73.4(3)
O33–W1–O13	71.3(3)	O3–W5–O15	76.1(3)	O7–W9–O14	71.9(3)
O9–W2–O8	160.8(4)	O18–W6–O17	158.0(3)	O13–Sb1–O15	93.3(3)
O1–W2–O13	169.5(4)	O29–W6–O14	169.5(4)	O13–Sb1–O14	91.8(3)
O8–W2–O13	73.7(3)	O18–W6–O14	73.7(3)	O15–Sb1–O14	89.0(4)
O31–W2–O13	75.3(3)	O19–W6–O14	75.1(3)	O6–Sn1–O23	82.6(3)
O10–W3–O19	160.4(4)	O20–W7–O26	159.5(4)	O6–Sn1–C1	167.5(5)
O12–W3–O14	172.7(4)	O32–W7–O15	162.7(4)	O4–Sn1–C1#2	105.2(4)
O7–W3–O14	74.5(3)	O21–W7–O15	73.5(3)	O23–Sn1–C1	90.7(4)
O19–W3–O14	75.4(3)	O26–W7–O15	71.3(3)	O20–Mn1–O3W	176.3(5)
O16–W4–O31	159.6(4)	O21–W8–O16	157.3(4)	O11–Mn1–O2W	171.1(5)

O28–W4–O13	168.3(4)	O30–W8–O15	173.6(4)	O11–Mn1–O20	80.7(4)
O33–W4–O13	72.5(3)	O21–W8–O15	75.4(3)	O24–Mn1–O2W#2	83.6(4)
O31–W4–O13	74.2(3)	O3–W8–O15	75.8(3)		

Symmetry transformations used to generate equivalent atoms: #2 -x+2,-y,-z

Table S2 Selected bond lengths (Å) and angles (°) for **SbW_9-Co-SnR**

Bond	**Length (Å)**	**Bond**	**Length (Å)**	**Bond**	**Length (Å)**
W1–O11	1.742(9)	W5–O23	1.839(9)	W9–O20	1.781(10)
W1–O4	1.803(9)	W5–O26	1.883(9)	W9–O7	1.924(8)
W1–O6	1.808(8)	W5–O3	1.951(9)	W9–O8	1.952(9)
W1–O25	1.997(9)	W5–O2	1.984(9)	W9–O29	2.084(10)
W1–O12	2.018(8)	W5–O14	2.297(8)	W9–O15	2.227(9)
W1–O13	2.281(8)	W6–O19	1.727(9)	Sb1–O13	1.991(9)
W2–O33	1.724(10)	W6–O22	1.800(9)	Sb1–O14	2.005(8)
W2–O29	1.869(10)	W6–O8	1.931(9)	Sb1–O15	2.020(8)
W2–O30	1.910(8)	W6–O1	1.966(9)	Sn1–O6	2.043(9)
W2–O9	1.933(9)	W6–O10	1.971(8)	Sn1–O4#3	2.053(9)
W2–O10	1.936(8)	W6–O15	2.310(8)	Sn1–O23#3	2.096(8)
W2–O15	2.282(9)	W7–O21	1.738(10)	Sn1–O22	2.122(9)
W3–O28	1.723(9)	W7–O24	1.770(9)	Sn1–C1	2.148(12)
W3–O2	1.862(9)	W7–O7	1.915(8)	Sn1–O34	2.182(9)
W3–O12	1.890(8)	W7–O26	1.985(8)	Co1–O20	2.055(10)
W3–O27	1.942(8)	W7–O16	2.067(10)	Co1–O3W	2.038(11)
W3–O31	1.944(8)	W7–O14	2.258(9)	Co1–O24	2.066(9)
W3–O13	2.348(8)	W8–O5	1.702(9)	Co1–O1W	2.073(11)
W4–O32	1.731(9)	W8–O1	1.895(9)	Co1–O11#3	2.123(9)
W4–O16	1.865(10)	W8–O9	1.918(8)	Co1–O2W	2.136(11)
W4–O30	1.912(8)	W8–O25	1.921(8)	C3–O34	1.280(15)
W4–O31	1.916(9)	W8–O27	1.929(8)	C3–O35	1.246(15)
W4–O3	1.939(8)	W8–O13	2.309(8)	C1–C2	1.523(18)
W4–O14	2.291(8)	W9–O18	1.726(10)	C2–C3	1.49(2)
W5–O17	1.722(9)				
Bond	**Angle(°)**	**Bond**	**Angle(°)**	**Bond**	**Angle(°)**
O6–W1–O12	159.9(4)	O23–W5–O3	157.4(4)	O20–W9–O29	162.0(4)
O11–W1–O13	165.4(4)	O17–W5–O14	172.5(4)	O18–W9–O15	164.1(4)
O25–W1–O13	72.9(3)	O26–W5–O14	74.5(3)	O8–W9–O15	74.7(3)
O12–W1–O13	71.9(3)	O3–W5–O14	75.8(3)	O29–W9–O15O13–S	71.7(3)
O30–W2–O10	160.4(3)	O8–W6–O1	157.6(4)	O13–Sb1–O14	93.7(3)
O33–W2–O15	173.4(4)	O19–W6–O15	170.8(4)	O13–Sb1–O15	91.5(3)
O29–W2–O15	74.2(3)	O8–W6–O15	73.2(3)	O14–Sb1–O15	88.2(3)
O10–W2–O15	75.7(3)	O10–W6–O15	74.4(3)	O6–Sn1–O23#3	84.3(4)
O2–W3–O27	158.8(4)	O24–W7–O16	161.4(4)	O6–Sn1–C1	168.0(5)
O28–W3–O13	168.5(4)	O21–W7–O14	163.5(4)	O4–Sn1–C1#3	105.5(5)

O12–W3–O13	72.5(3)	O26–W7–O14	73.6(3)	O23–Sn1–C1#3	99.6(5)
O27–W3–O13	73.6(3)	O16–W7–O14	71.3(3)	O3W–Co1–O24	175.2(5)
O30–W4–O3	163.0(4)	O9–W8–O25	161.0(4)	O20–Co1–O1W	174.5(4)
O32–W4–O14	172.4(4)	O5–W8–O13	169.3(4)	O20–Co1–O24	82.7(4)
O16–W4–O14	74.1(3)	O25–W8–O13	73.6(3)	O1W–Co1–O11#3	84.0(4)
O3–W4–O14	76.1(3)	O27–W8–O13	74.7(3)		

Symmetry transformations used to generate equivalent atoms: #3 -x+1,-y,-z+1

Table S3 Selected bond lengths (Å) and angles (°) for **SbW_9-Ni-SnR**

Bond	**Length (Å)**	**Bond**	**Length (Å)**	**Bond**	**Length (Å)**
W1–O11	1.739(11)	W5–O31	1.846(13)	W9–O22	1.806(11)
W1–O4	1.802(11)	W5–O30	1.922(11)	W9–O5	1.930(11)
W1–O6	1.829(10)	W5–O10	1.925(10)	W9–O9	1.965(10)
W1–O3	2.013(11)	W5–O1	1.922(11)	W9–O7	1.980(11)
W1–O26	2.042(10)	W5–O13	2.269(11)	W9–O15	2.302(10)
W1–O14	2.288(10)	W6–O19	1.714(12)	Sn1–O6	2.033(10)
W2–O32	1.748(12)	W6–O9	1.908(10)	Sn1–O4#3	2.058(11)
W2–O18	1.871(11)	W6–O8	1.910(10)	Sn1–O23#3	2.095(11)
W2–O26	1.879(10)	W6–O3	1.921(11)	Sn1–C1	2.113(16)
W2–O8	1.952(11)	W6–O12	1.923(11)	Sn1–O22	2.118(11)
W2–O30	1.953(11)	W6–O14	2.321(10)	Sn1–O34	2.188(10)
W2–O14	2.343(10)	W7–O33	1.749(12)	Sb1–O14	1.994(10)
W3–O29	1.719(12)	W7–O24	1.781(11)	Sb1–O15	2.016(10)
W3–O25	1.880(12)	W7–O2	1.919(11)	Sb1–O13	2.034(10)
W3–O10	1.907(10)	W7–O27	1.989(11)	Ni1–O3W	2.040(16)
W3–O7	1.950(11)	W7–O31	2.086(12)	Ni1–O1W	2.048(13)
W3–O12	1.951(11)	W7–O13	2.255(11)	Ni1–O20	2.059(12)
W3–O15	2.302(11)	W8–O17	1.708(13)	Ni1–O24	2.056(11)
W4–O16	1.716(11)	W8–O20	1.772(11)	Ni1–O11#3	2.102(11)
W4–O23	1.847(11)	W8–O2	1.927(11)	Ni1–O2W	2.107(14)
W4–O27	1.888(11)	W8–O5	1.957(10)	C3–O34	1.264(19)
W4–O1	1.974(11)	W8–O25	2.072(12)	C3–O35	1.28(2)
W4–O18	1.984(11)	W8–O15	2.232(10)	C1–C2	1.51(2)
W4–O13	2.308(10)	W9–O28	1.733(10)	C2–C3	1.54(2)
W5–O21	1.732(11)				
Bond	**Angle(°)**	**Bond**	**Angle(°)**	**Bond**	**Angle(°)**
O6–W1–O26	159.6(5)	O10–W5–O1	163.8(5)	O5–W9–O9	158.0(4)
O11–W1–O14	165.4(5)	O21–W5–O13	172.6(5)	O28–W9–O15	170.9(5)
O3–W1–O14	72.9(4)	O31–W5–O13	73.7(5)	O5–W9–O15	73.3(4)
O26–W1–O14	71.3(4)	O1–W5–O13	76.5(4)	O7–W9–O15	75.1(4)
O18–W2–O8	158.2(4)	O3–W6–O12	161.3(5)	O14–Sb1–O15	91.9(4)
O32–W2–O14	168.1(5)	O19–W6–O14	169.5(5)	O15–Sb1–O13	88.1(4)
O26–W2–O14	72.7(4)	O8–W6–O14	74.4(4)	O14–Sb1–O13	93.4(4)
O8–W2–O14	73.2(4)	O3–W6–O14	73.7(4)	O6–Sn1–O22	83.9(4)

O10–W3–O7	161.5(5)	O24–W7–O31	161.1(5)	O6–Sn1–C1	167.4(6)
O29–W3–O15	171.9(4)	O33–W7–O13	162.9(5)	C1–Sn1–O22	91.7(6)
O25–W3–O15	73.8(4)	O27–W7–O13	73.9(4)	O34–Sn1–O4#3	170.7(4)
O7–W3–O15	75.6(4)	O31–W7–O13	69.9(4)	O1W–Ni1–O20	173.6(5)
O27–W4–O18	157.0(5)	O20–W8–O25	161.1(5)	O3W–Ni1–O24	175.1(6)
O16–W4–O13	171.5(5)	O17–W8–O15	164.3(5)	O20–Ni1–O24	83.0(4)
O27–W4–O13	74.5(4)	O5–W8–O15	74.5(4)	O1W–Ni1–O11#3	84.0(5)
O1–W4–O13	74.7(4)	O25–W8–O15	72.0(4)		

Symmetry transformations used to generate equivalent atoms: #3 -x+1,-y,-z+1

Table S4 Selected bond lengths (Å) and angles (°) for **SbW_9-Zn-SnR**

Bond	**Length (Å)**	**Bond**	**Length (Å)**	**Bond**	**Length (Å)**
W1–O11	1.78(4)	W5–O32	1.87(5)	W9–O24	1.80(5)
W1–O4	1.80(5)	W5–O12	1.89(6)	W9–O2	1.89(5)
W1–O6	1.84(4)	W5–O17	1.92(4)	W9–O7	1.97(5)
W1–O5	2.03(4)	W5–O25	1.93(4)	W9–O12	2.02(6)
W1–O26	2.05(5)	W5–O14	2.25(4)	W9–O14	2.25(4)
W1–O13	2.28(4)	W6–O31	1.73(6)	Sb1–O15	2.03(4)
W2–O27	1.72(4)	W6–O22	1.83(5)	Sb1–O14	2.03(4)
W2–O8	1.87(4)	W6–O30	1.92(5)	Sb1–O13	2.03(4)
W2–O26	1.94(5)	W6–O9	1.92(5)	Sn1–O6	2.02(4)
W2–O9	1.94(5)	W6–O1	1.92(5)	Sn1–O4#3	2.06(5)
W2–O3	2.01(4)	W6–O15	2.31(4)	Sn1–O23#3	2.11(4)
W2–O13	2.38(4)	W7–O33	1.73(7)	Sn1–C1	2.14(6)
W3–O19	1.66(4)	W7–O5	1.90(4)	Sn1–O22	2.12(5)
W3–O29	1.90(4)	W7–O3	1.93(4)	Sn1–O34	2.17(4)
W3–O8	1.94(4)	W7–O17	1.91(4)	Zn1–O1W	2.00(8)
W3–O1	1.97(5)	W7–O18	1.93(4)	Zn1–O24	2.04(5)
W3–O32	1.98(5)	W7–O13	2.25(4)	Zn1–O20	2.06(5)
W3–O15	2.24(4)	W8–O16	1.74(4)	Zn1–O3W	2.08(5)
W4–O28	1.69(4)	W8–O20	1.74(5)	Zn1–O11#3	2.09(4)
W4–O23	1.84(4)	W8–O30	1.84(5)	Zn1–O2W	2.15(6)
W4–O18	1.94(4)	W8–O2	2.01(4)	C3–O34	1.34(7)
W4–O7	1.93(4)	W8–O29	2.00(4)	C3–O35	1.16(8)
W4–O25	2.11(4)	W8–O15	2.28(4)	C1–C2	1.520(10)
W4–O14	2.31(4)	W9–O10	1.74(5)	C2–C3	1.520(10)
W5–O21	1.85(5)				
Bond	**Angle(°)**	**Bond**	**Angle(°)**	**Bond**	**Angle(°)**
O4–W1–O26	161(2)	O32–W5–O25	167(2)	O24–W9–O12	160(2)
O11–W1–O13	163.7(17)	O21–W5–O14	171.3(18)	O10–W9–O14	161(2)
O5–W1–O13	71.0(16)	O12–W5–O14	73(2)	O7–W9–O14	74.3(16)
O26–W1–O13	74.5(16)	O25–W5–O14	79.9(17)	O12–W9–O14	70(2)
O9–W2–O3	159.3(18)	O22–W6–O1	158(2)	O13–Sb1–O15	93.9(17)
O27–W2–O13	167.1(18)	O31–W6–O15	172(2)	O13–Sb1–O14	89.9(16)

O26–W2–O13	74.0(16)	O30–W6–O15	69(2)	O15–Sb1–O14	87.0(17)
O3–W2–O13	73.0(16)	O1–W6–O15	75.2(17)	O6–Sn1–O34	170.3(16)
O1–W3–O32	163.7(19)	O3–W7–O18	159.8(18)	O22–Sn1–O34	83.8(17)
O19–W3–O15	170.5(18)	O33–W7–O13	169(3)	O4–Sn1–C1#3	167(2)
O29–W3–O15	72.1(17)	O5–W7–O13	73.7(16)	C1–Sn1–O34	83.2(16)
O1–W3–O15	75.8(17)	O3–W7–O13	77.4(16)	O1W–Zn1–O20	172(3)
O7–W4–O18	156.9(18)	O20–W8–O29	162.1(19)	O24–Zn1–O3W	173(2)
O28–W4–O14	171.1(18)	O16–W8–O15	163.5(17)	O24–Zn1–O20	80.1(19)
O7–W4–O14	73.4(17)	O30–W8–O15	71(2)	O3W–Zn1–O11#3	83.6(19)
O25–W4–O14	75.0(16)	O29–W8–O15	69.7(15)		

Symmetry transformations used to generate equivalent atoms: #3 -x+2,-y+1,-z

Table S5 Hydrogen bonds for **SbW_9-Mn-SnR**

D–H...A	d(D–H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)
O1W–H1WB...O35#6	0.852(10)	2.02(11)	2.720(16)	139(14)
O1W–H1WA...O3W	0.852(10)	2.62(19)	3.12(2)	118(17)
O2W–H2WA...O21#8	0.850(10)	2.64(12)	3.138(15)	119(11)
O2W–H2WA...O8W#2	0.850(10)	2.14(4)	2.97(2)	166(14)
O2W–H2WB...O4W#6	0.850(10)	1.89(7)	2.678(17)	153(15)
O3W–H3WA...O12W#9	0.848(10)	2.09(18)	2.67(2)	125(18)
O3W–H3WB...O6W#2	0.848(10)	2.10(15)	2.73(2)	130(17)
O3W–H3WB...O12W#2	0.848(10)	2.34(12)	3.04(3)	140(15)
O4W–H4WB...O2W#2	0.849(10)	2.19(4)	3.023(17)	166(11)
O4W–H4WA...O20#2	0.850(10)	2.47(9)	3.098(15)	131(10)
O4W–H4WA...O22#2	0.850(10)	2.23(7)	2.944(14)	142(11)
O5W–H5WA...O19#1	0.851(10)	2.04(7)	2.832(15)	155(15)
O5W–H5WB...O19#4	0.851(10)	2.57(17)	2.860(14)	102(13)
O5W–H5WB...O15W#1	0.851(10)	2.39(12)	3.08(3)	139(15)
O6W–H6WA...O33	0.851(10)	2.23(15)	2.757(13)	120(14)
O6W–H6WB...O35#4	0.851(10)	2.08(12)	2.711(14)	131(14)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z-1 #2 -x+2,-y,-z #4 x+1,y,z #6 x,y-1,z #8 -x+2,-y-1,-z #9 x-1,y-1,z

Table S6 Hydrogen bonds for **SbW_9-Co-SnR**

D–H...A	d(D–H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)
O1W–H1WA...O5W#3	0.850(10)	2.54(4)	2.997(16)	115(4)
O1W–H1WA...O9W#7	0.850(10)	2.29(7)	2.795(18)	119(7)
O1W–H1WB...O5W#2	0.850(10)	1.89(5)	2.656(15)	149(9)
O2W–H2WA...O21	0.851(10)	2.58(5)	3.369(16)	155(12)
O2W–H2WB...O35#2	0.851(11)	1.95(6)	2.762(15)	158(14)
O3W–H3WA...O4W	0.852(10)	1.89(3)	2.727(19)	168(13)
O3W–H3WB...O15W	0.851(11)	1.98(8)	2.78(2)	157(19)
O4W–H4WA...O35#8	0.850(10)	2.03(12)	2.730(15)	139(16)
O4W–H4WB...O12#3	0.850(10)	2.00(7)	2.782(14)	153(14)
O5W–H5WA...O23#3	0.849(10)	2.18(4)	2.959(14)	152(8)

O5W–H5WB...O24#3	0.848(10)	2.40(4)	3.077(13)	138(5)
O5W–H5WB...O1W#3	0.848(10)	2.28(4)	2.997(16)	142(5)
O6W–H6WA...O10#6	0.847(11)	2.046(18)	2.863(13)	162(5)
O6W–H6WB...O10	0.847(10)	2.23(2)	2.845(15)	130(2)
O7W–H7WA...O8W	0.850(10)	2.23(3)	2.814(19)	125.5(14)
O7W–H7WB...O6W	0.851(10)	2.211(19)	2.912(16)	140(3)
O8W–H8WA...O18#4	0.849(10)	2.39(3)	3.017(17)	131(3)
O8W–H8WB...O29#6	0.848(10)	2.37(2)	2.791(14)	111.3(16)
O9W–H9WA...O4W#7	0.850(11)	2.65(8)	3.253(18)	129(8)
O9W–H9WB...O25#2	0.849(11)	2.05(8)	2.860(16)	158(20)
O10W–H10A...O3#1	0.851(10)	2.05(10)	2.831(17)	152(20)
O10W–H10B...O8#6	0.851(11)	2.07(3)	2.816(14)	146(6)
O11W–H11A...O18#9	0.852(11)	2.57(10)	3.18(2)	130(11)
O11W–H11A...O2W#9	0.852(11)	2.40(6)	3.133(19)	144(7)
O11W–H11B...O4W#10	0.852(10)	2.44(8)	3.15(2)	141(9)
O11W–H11B...O17W#1	0.852(10)	1.51(3)	2.24(4)	142(4)
O12W–H12A...O18#6	0.849(11)	2.13(7)	2.932(17)	157(16)
O12W–H12B...O29#4	0.851(10)	2.52(6)	3.272(18)	148(9)
O12W–H12B...O30#4	0.851(10)	2.43(12)	3.078(17)	133(14)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2 #2 x,y+1,z #3 -x+1,-y,-z+1 #4 x,y-1,z #6 -x+2,-y,-z+2 #7 -x+1,-y+1,-z+1 #8 -x+2,-y,-z+1 #9 -x+2,-y+1,-z+2 #10 x,y,z+1

Table S7 Hydrogen bonds for **SbW_9-Ni-SnR**

D–H...A	**d(D–H) (Å)**	**d(H...A) (Å)**	**d(D...A) (Å)**	**<(DHA) (°)**
O1W–H1WA...O12W#3	0.850(11)	2.38(8)	2.81(3)	113(7)
O1W–H1WA...O17W#9	0.850(11)	2.02(10)	2.87(10)	175(10)
O1W–H1WB...O4W#2	0.851(10)	1.92(3)	2.678(19)	147(5)
O2W–H2WA...O35#2	0.850(11)	1.91(6)	2.735(19)	164(20)
O2W–H2WB...O17	0.850(11)	2.56(9)	3.33(2)	151(16)
O2W–H2WB...O6W#10	0.850(11)	2.66(10)	3.22(3)	124(9)
O3W–H3WA...O11#3	0.851(11)	2.5(2)	2.937(19)	113(17)
O3W–H3WB...O15W#11	0.850(11)	1.99(9)	2.79(4)	156(20)
O3W–H3WB...O17W#8	0.850(11)	2.7(2)	3.14(9)	117(18)
O3W–H3WB...O18W#11	0.850(11)	2.32(16)	2.96(10)	132(15)
O4W–H4WA...O23#3	0.852(10)	2.40(5)	2.972(18)	125(6)
O4W–H4WA...O24#3	0.852(10)	2.33(4)	3.067(18)	145(5)
O4W–H4WB...O1W#3	0.851(10)	2.29(3)	2.950(19)	134(2)
O5W–H5WA...O28	0.851(10)	2.34(2)	3.113(19)	151.8(13)
O5W–H5WB...O7W	0.850(10)	2.32(4)	2.76(2)	113(3)
O5W–H5WB...O9W	0.850(10)	2.44(3)	2.97(2)	120.6(18)
O6W–H6WA...O2W#10	0.851(11)	2.57(8)	3.22(3)	133(9)
O6W–H6WB...O17#10	0.851(11)	2.58(9)	3.20(3)	131(9)
O6W–H6WB...O8W#2	0.851(11)	2.59(8)	3.30(3)	142(11)
O7W–H7WA...O2#5	0.850(10)	2.66(4)	3.18(2)	121(3)

O7W–H7WA...O17#5	0.850(10)	2.66(3)	3.06(2)	110(3)
O7W–H7WB...O8W	0.849(10)	2.44(3)	2.98(3)	122(2)
O8W–H8WA...O13W#4	0.850(10)	2.52(6)	3.11(4)	128(4)
O8W–H8WB...O17#6	0.849(11)	2.18(3)	3.02(2)	168(3)
O9W–H9WA...O7#6	0.850(11)	2.08(4)	2.841(18)	149(6)
O9W–H9WB...O5W	0.849(10)	2.390(18)	2.97(2)	126(3)
O10W–H10A...O1#1	0.851(10)	2.21(3)	2.83(2)	130(3)
O10W–H10B...O5#6	0.852(10)	2.061(18)	2.845(19)	153(2)
O12W–H12B...O15W	0.850(11)	2.51(5)	3.28(4)	150(6)
O12W–H12B...O16W	0.850(11)	1.79(6)	2.24(3)	112(5)
O12W–H12B...O17W#5	0.850(11)	1.80(9)	2.59(9)	154(6)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+2 #2 x,y+1,z #3 -x,-y+1,-z+1 #4 -x,-y,-z+2 #5 x,y-1,z #6 -x+1,-y+1,-z+2 #8 x+1,y,z #9 -x,-y+2,-z+1 #10 -x+1,-y+2,-z+2 #11 x+1,y+1,z

Table S8 Hydrogen bonds for **SbW_9-Zn-SnR**

D–H...A	**d(D–H) (Å)**	**d(H...A) (Å)**	**d(D...A) (Å)**	**<(DHA) (°)**
O1W–H1WA...O7W	0.850(11)	2.29(16)	2.68(11)	108(13)
O1W–H1WB...O15W#11	0.850(11)	1.750(11)	2.48(9)	143(14)
O2W–H2WA...O4W#6	0.850(11)	2.6(5)	3.29(8)	142(64)
O2W–H2WB...O13W#6	0.850(11)	2.4(5)	3.07(11)	133(56)
O3W–H3WA...O8W	0.850(11)	2.2(3)	2.92(11)	137(37)
O3W–H3WB...O20	0.850(10)	2.5(3)	3.00(7)	118(25)
O3W–H3WB...O5W	0.850(10)	2.2(3)	2.70(8)	117(26)
O3W–H3WB...O5W#7	0.850(10)	2.38(19)	2.98(8)	128(19)
O4W–H4WA...O18#5	0.850(10)	2.40(7)	3.22(6)	163(15)
O4W–H4WA...O28#5	0.850(10)	2.63(7)	3.15(7)	121(5)
O4W–H4WB...O12W#6	0.850(11)	2.22(15)	2.68(11)	114(9)
O5W–H5WA...O11#8	0.850(11)	2.39(10)	3.23(7)	167(26)
O5W–H5WA...O3W#7	0.850(11)	2.4(2)	2.98(8)	122(20)
O5W–H5WB...O22#7	0.850(11)	2.13(18)	2.94(8)	159(38)
O6W–H6WA...O25#12	0.850(10)	2.11(8)	2.83(7)	141(5)
O6W–H6WB...O4W#12	0.850(11)	2.22(14)	2.91(8)	139(17)
O7W–H7WA...O35#13	0.850(12)	2.13(16)	2.78(9)	133(18)
O7W–H7WB...O26#3	0.850(11)	2.06(16)	2.73(8)	136(18)
O8W–H8WA...O16#7	0.850(10)	2.6(2)	3.26(9)	136(24)
O8W–H8WA...O30#7	0.850(10)	2.16(13)	2.96(10)	157(25)
O8W–H8WB...O5#3	0.850(11)	2.01(17)	2.83(9)	161(45)
O9W–H9WA...O32#9	0.850(11)	2.30(15)	3.14(10)	171(60)
O9W–H9WB...O12W#9	0.850(10)	2.42(14)	3.08(13)	135(8)
O10W–H10A...O7#12	0.850(10)	2.06(16)	2.83(9)	151(23)
O10W–H10B...O1	0.850(10)	2.3(2)	2.85(10)	126(17)
O12W–H12A...O12#6	0.850(11)	2.39(14)	2.93(11)	122(13)
O12W–H12B...O9W#9	0.850(10)	2.58(8)	3.08(13)	119(11)
O13W–H13A...O14W	0.850(10)	1.75(15)	2.30(12)	120(16)

O13W–H13B...O10#6	0.850(11)	2.39(7)	3.16(11)	151(14)
O14W–H14A...O15W#14	0.850(11)	1.749(11)	2.49(9)	144(15)
O14W–H14B...O7W#14	0.851(11)	1.97(17)	2.56(10)	126(16)

Symmetry transformations used to generate equivalent atoms: #3 -x+2,-y+1,-z #5 -x+1,-y+1,-z-1 #6 -x+1,-y,-z-1 #7 -x+2,-y,-z #8 x,y-1,z #9 -x+2,-y,-z-1 #11 -x+1,-y,-z #12 x+1,y,z #14 x,y,z-1

3. Physical characterizations

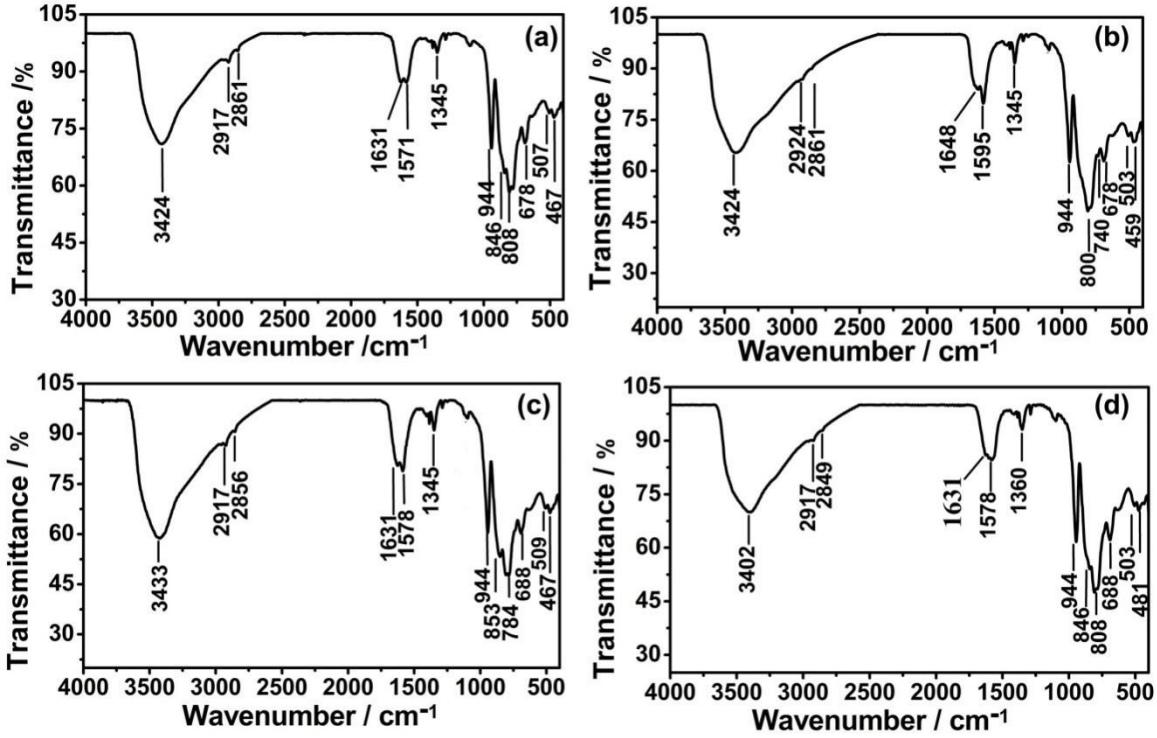

Fig. S3 IR spectra of **SbW_9-TM-SnR** (TM = Mn (a); TM = Co (b); TM = Ni (c); TM = Zn (d)).

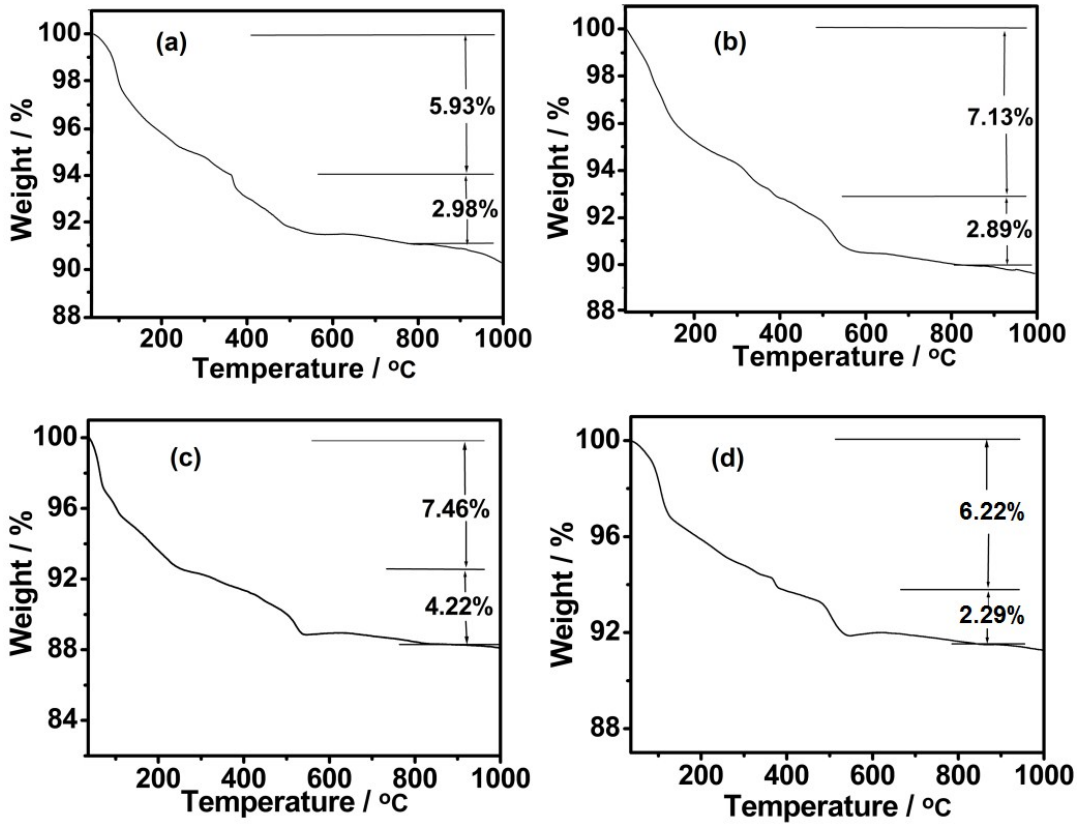

Fig. S4 TG curves of **SbW_9-TM-SnR** (TM = Mn (a); TM = Co (b); TM = Ni (c); TM = Zn (d)).

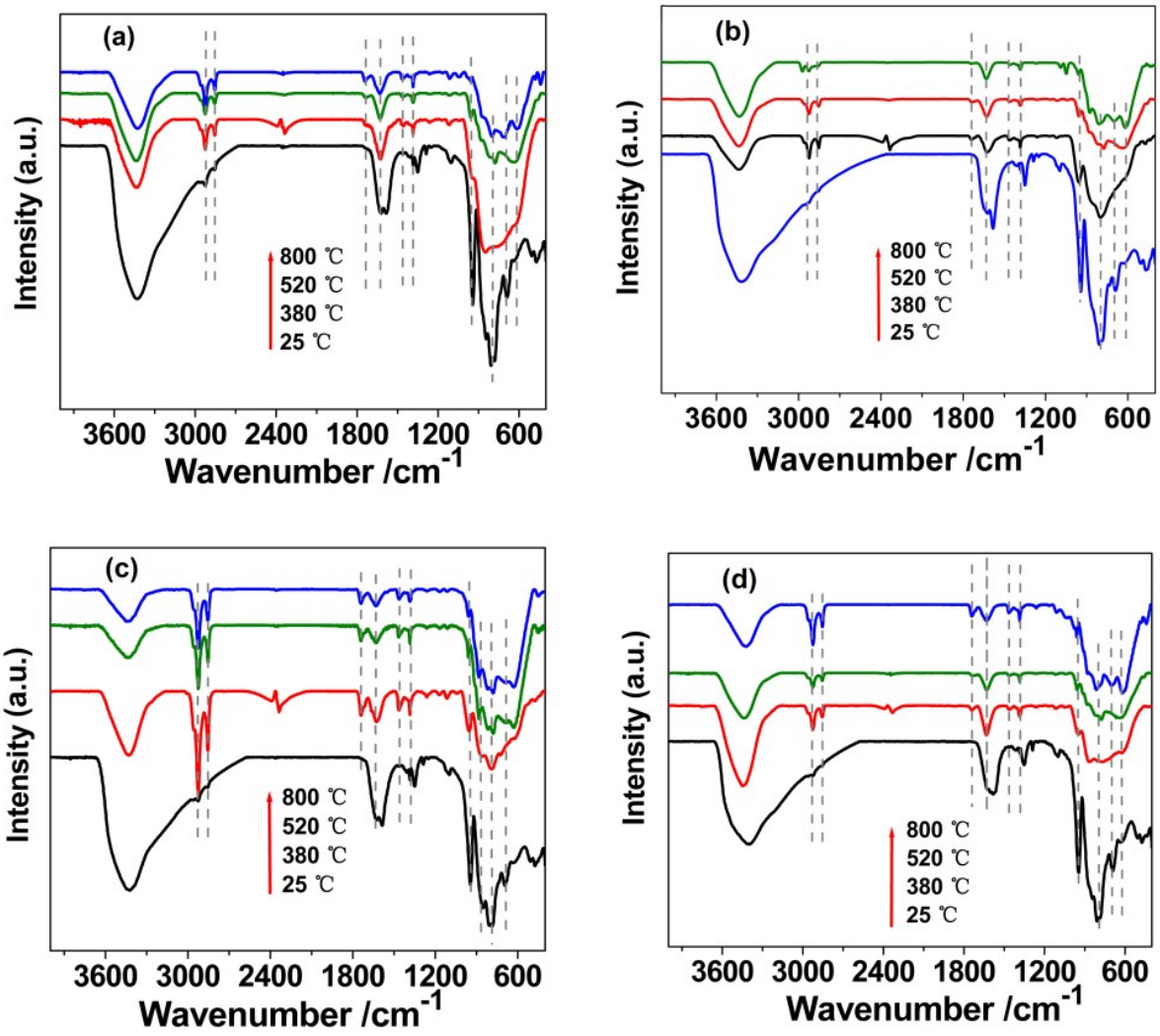

Fig. S5 IR spectra of **SbW_9-TM-SnR** (TM = Mn (a); TM = Co (b); TM = Ni (c); TM = Zn (d)) after heating at 380, 520 and 800 °C in air.

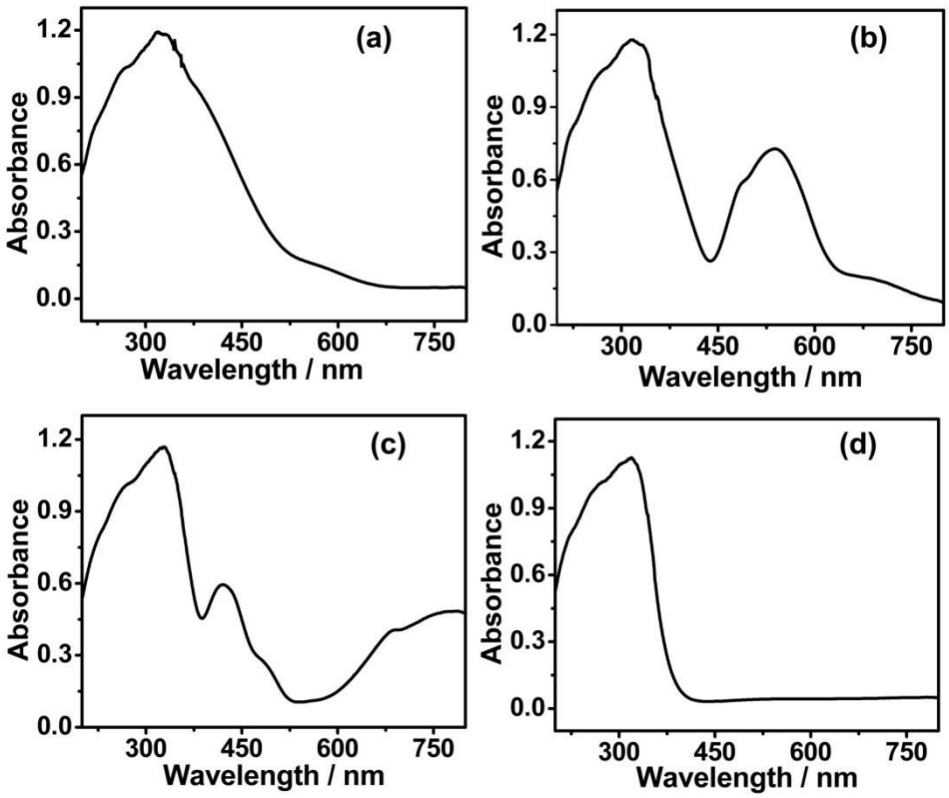

Fig. S6 Solid diffuse reflection absorption spectra of **SbW_9-TM-SnR** (TM = Mn (a); TM = Co (b); TM = Ni (c); TM = Zn (d)).

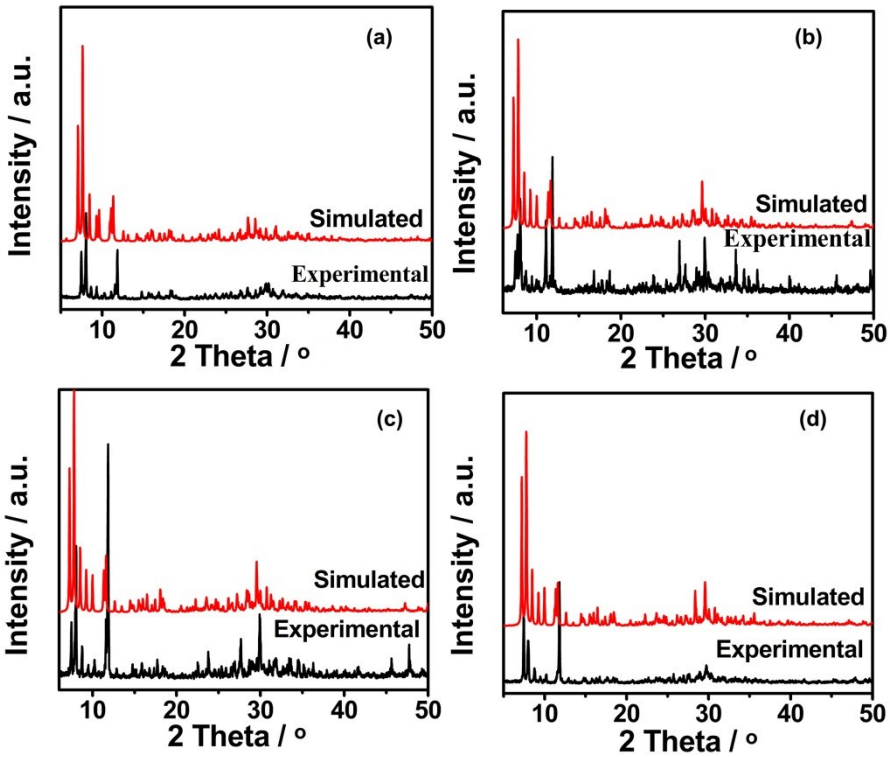

Fig. S7 The simulated and experimental XRPD patterns of **SbW_9-TM-SnR** (TM = Mn (a); TM = Co (b); TM = Ni (c); TM = Zn (d)).

4. **CV of the original material**

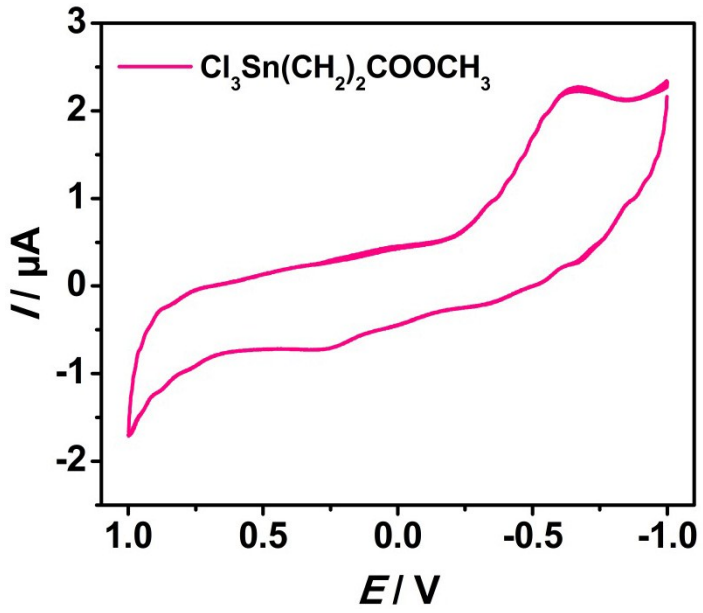

Fig. S8 CV curves of $Cl_3Sn(CH_2)_2COOCH_2$ in 0.4 mol L^{-1} NaAc-HAc solution (pH = 5), scan rate is 50 mV s^{-1}..

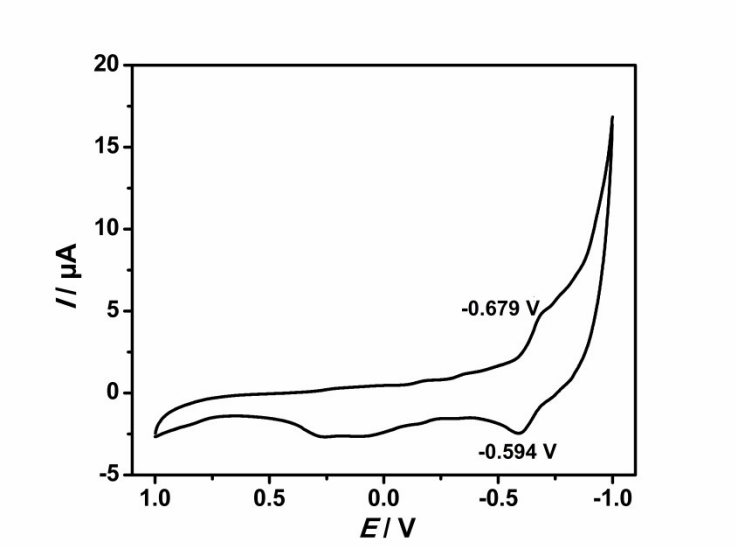

Fig. S9 CV curve of **Na-SbW**$_9$ in 0.4 mol L^{-1} NaAc-HAc solution (pH = 5), scan rate is 50 mV s^{-1}.

5. Catalytic oxidation activity of different catalysts

Table S9 Catalytic performance of various catalysts for the oxidation of cyclohexanol to cyclohexanone with H_2O_2

Entry	Catalyst	H_2O_2 (equiv.)	Solvent	Solubility	T (°C)	Time (h)	Conversion (%)
1	**SbW_9-Mn-SnR**	2.2	MeCN	soluble	88	3.0	88.7
2	**SbW_9-Co-SnR**	2.2	MeCN	soluble	88	3.0	92.1
3	**SbW_9-Ni-SnR**	2.2	MeCN	soluble	88	3.0	94.6
4	**SbW_9-Zn-SnR**	2.2	MeCN	soluble	88	3.0	91.2
5	**Na-SbW_9**	2.2	MeCN	soluble	88	3.0	27.6
6	$Co(NO_3)_2{\cdot}6H_2O$	2.2	MeCN	soluble	88	3.0	15.1
7	$ZnSO_4{\cdot}7H_2O$	2.2	MeCN	soluble	88	3.0	10.1
8	$Cl_3Sn(CH_2)_2COOCH_3$	2.2	MeCN	soluble	88	3.0	7.5
9	$MnCl_2{\cdot}4H_2O$	2.2	MeCN	soluble	88	3.0	11.2
10	$Ni(NO_3)_2{\cdot}6H_2O$	2.2	MeCN	soluble	88	3.0	6.5

6. Characterization, and electrocatalytic performance of PPy-SbW_9-TM-SnR/Pt composite film

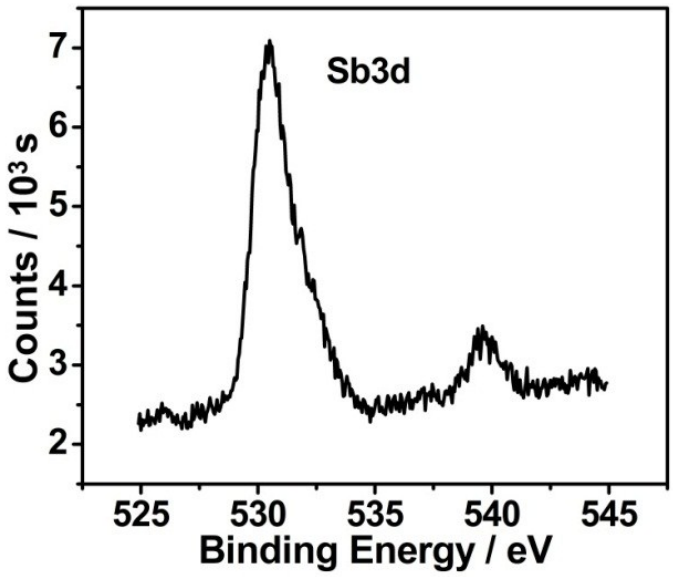

Fig. S10 XPS of Sb 3d of PPy-**SbW_9-Co-SnR**/Pt on FTO electrode.

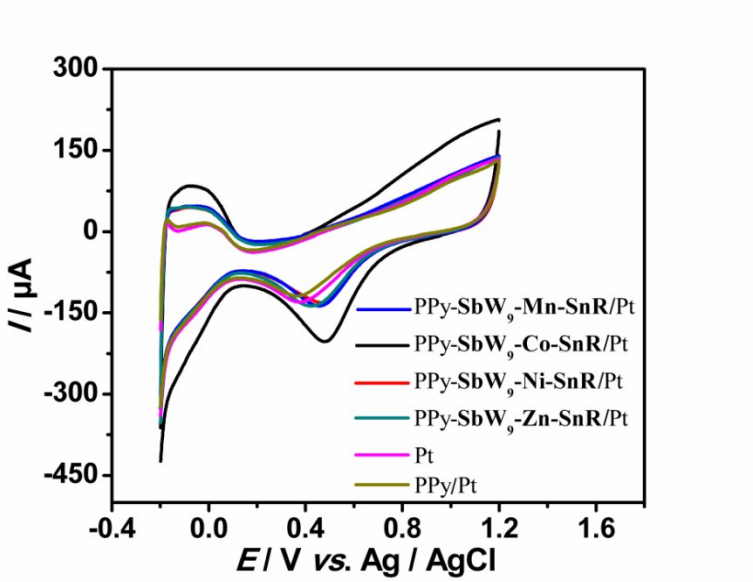

Fig. S11 CV curves of different composites modified FTO electrodes: PPy-**SbW_9-TM-SnR**/Pt, Pt, PPy/Pt, in 0.5 mol L^{-1} H_2SO_4, scan rate is 50 mV s^{-1}.

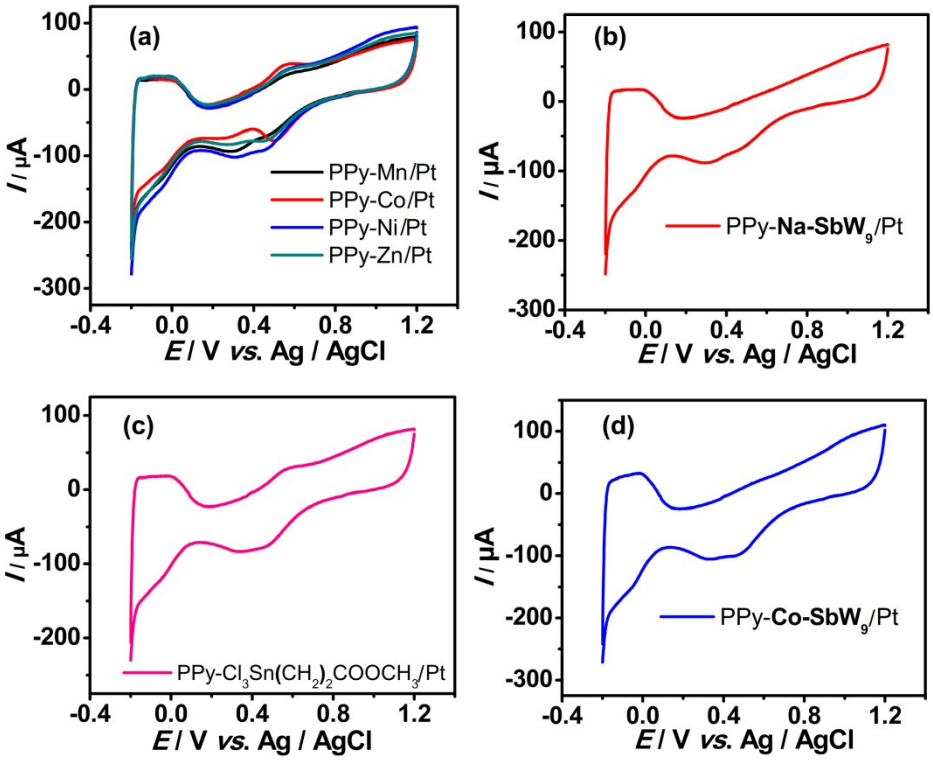

Fig. S12 CV curves of different composites modified FTO electrodes: PPy-TM/Pt, TM presents simple TM (Mn, Co, Ni, Zn) salts (a), PPy-**Na-SbW$_9$**/Pt (b), PPy-$Cl_3Sn(CH_2)_2COOCH_3$/Pt (c), PPy-**Co-SbW$_9$**/Pt (d) in 0.5 mol L^{-1} H_2SO_4, scan rate is 50 mV s^{-1}.

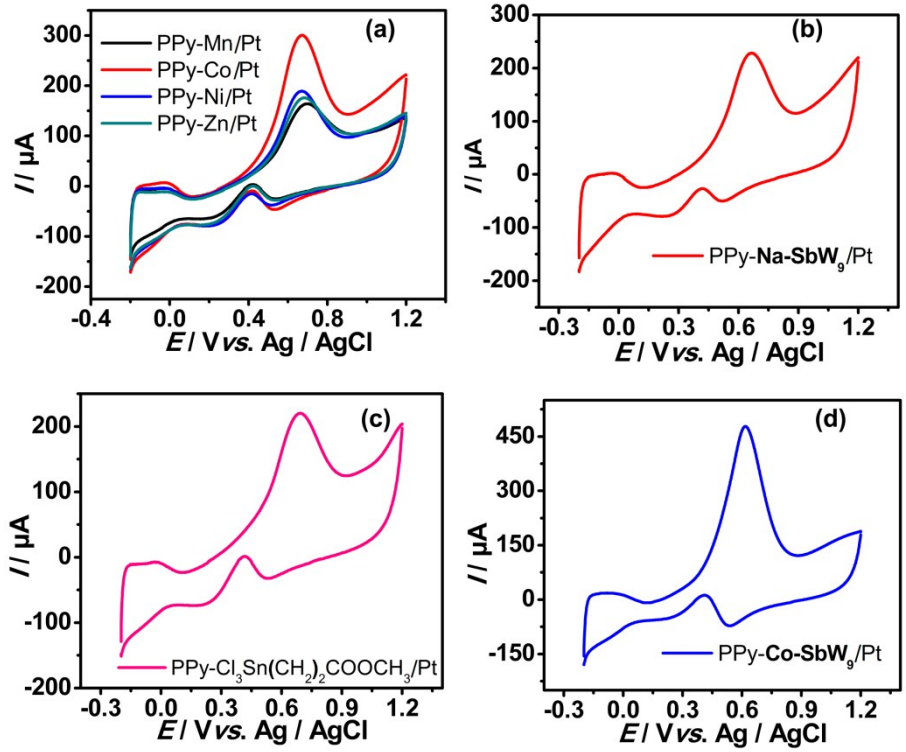

Fig. S13 CV curves of different composites modified FTO electrodes: PPy-TM/Pt, TM presents simple TM (Mn, Co, Ni, Zn) salts (a), PPy-**Na-SbW$_9$**/Pt (b), PPy-$Cl_3Sn(CH_2)_2COOCH_3$/Pt (c), PPy-**Co-SbW$_9$**/Pt (d) in 0.5 mol L^{-1} H_2SO_4 and 1 mol L^{-1} CH_3OH, scan rate is 50 mV s^{-1}.

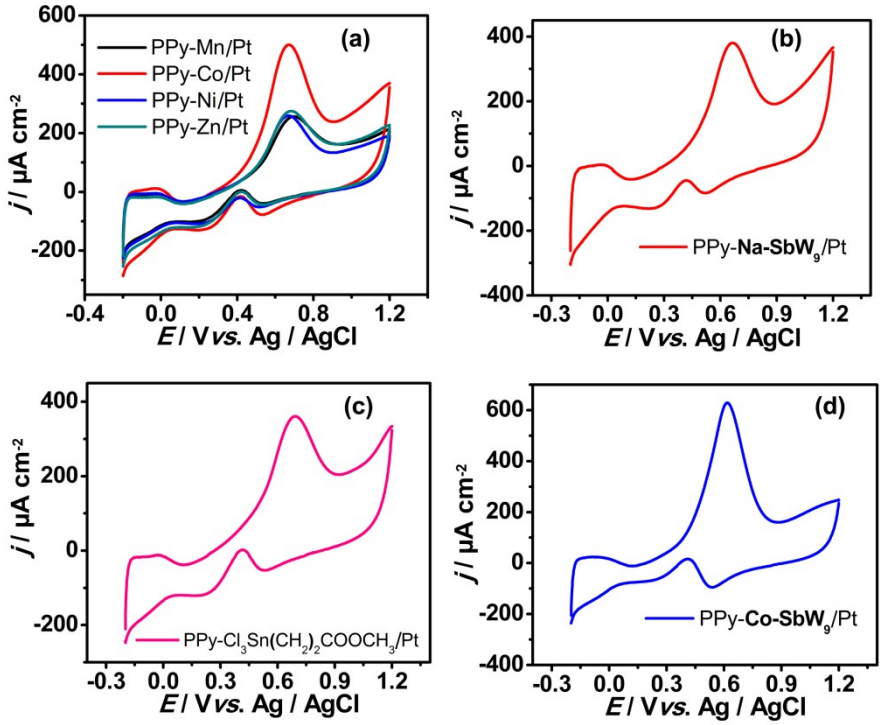

Fig. S14 CV curves of different composites modified FTO electrodes: PPy-TM/Pt, TM presents simple TM (Mn, Co, Ni, Zn) salts (a), PPy-**Na-SbW$_9$**/Pt (b), PPy-$Cl_3Sn(CH_2)_2COOCH_3$/Pt (c), PPy-**Co-SbW$_9$**/Pt (d) in 0.5 mol L^{-1} H_2SO_4 and 1 mol L^{-1} CH_3OH, scan rate is 50 mV s^{-1}.

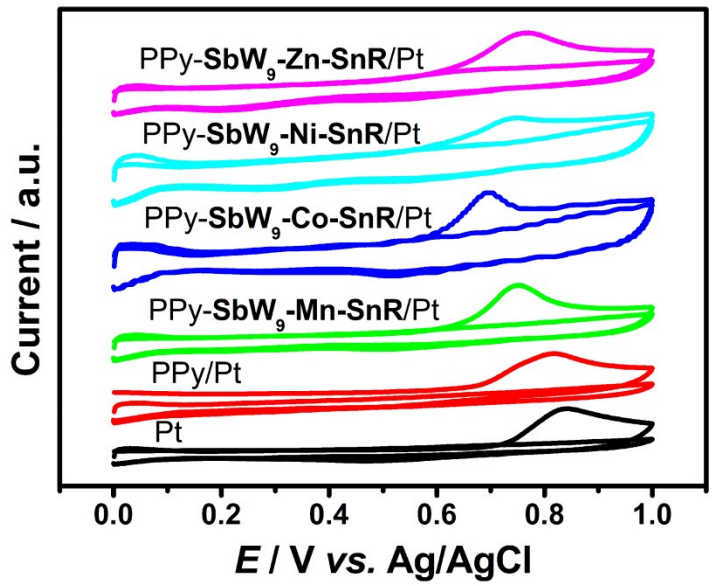

Fig. S15 CO stripping voltammograms of different catalysts modified FTO electrodes: Pt, PPy/Pt and PPy-**SbW$_9$ - TM- SnR**/Pt in 0.5 mol L^{-1} H_2SO_4, scan rate is 50 mV s^{-1}.