Electronic Supplementary Information (ESI†)

Two Ni/Co-substituted sandwich-type germanomolybdates based on unprecedented trivacant polyanion [α-$GeMo_{10}O_{36}$]$^{8-}$

Hui Xu,[a] Xing-Man Liu,[c] Tan Su,*[a,b] Wei-Chao Chen,[c] and Zhong-Min Su*[a]

[a]*College of Chemistry, Jilin University, Changchun, 130012, PR China*

[b]*Institute of Theoretical Chemistry, Jilin University, Changchun 130021, PR China*

[c]*College of Chemistry, Northeast Normal University, Changchun 130024, PR China*

*Corresponding author：

E-mail address: sutan_jlu@jlu.edu.cn; zmsu@nenu.edu.cn

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Section 1 Synthesis, Crystal Data, and Structure of 1 and 2

1.1 Materials and Methods

All the reagents were purchased from commercial sources and used without further purification. The C, H, and N elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded in the range of 4000–400 cm^{-1} using an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) patterns were collected using a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å). TG analyses were performed using a Perkin-Elmer TG-7 analyzer under flowing nitrogen with the heating rate of 10 °C·min^{-1}. X-ray photoelectron spectroscopy (XPS) analyses were performed using a VG ESCALABMKII spectrometer with an Al-Kα (1486.6 eV) achromatic X-ray source. UV–Vis absorption spectra were obtained by using a Shimadzu UV-2550 spectrometer. The gas product in photocatalytic reaction was measured by Shimadzu Gas Chromatography.

1.2 Synthesis

(1) Synthesis of $\{[Ni_3(NH_2\text{-trz})_6(H_2O)_6][Ni_4(H_2O)_2(HGeMo_{10}O_{36})_2]\}\cdot 10H_2O$ (**1**)

GeO_2 (0.01 g, 0.096 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.2 g, 0.16 mmol), $NiCl_2\cdot 6H_2O$ (0.01 g, 0.04 mmol), $Ni(CH_3COO)_2\cdot 4H_2O$ (0.01 g, 0.04 mmol), and NH_2-trz (0.02 g, 0.24 mmol), were mixed in distilled water (3 mL). The mixture was stirred for 30 min and the pH of the reaction mixture was maintained at 2.0-3.0 by addition of 1M HCl (aq). The solution was transferred to a Teflon-lined steel autoclave kept at 180 °C for three days, and then cooled to room temperature. Pale green block were collected by filtration, washed with distilled water, and dried in air. Yield: 32% (based on Mo). Elemental analysis calcd (found %) for $C_{12}H_{62}Ge_2Mo_{20}N_{24}Ni_7$: C, 3.23 (3.18); H, 1.39 (1.28); N, 7.54 (7.47).

(2) Synthesis of $\{[Co_3(NH_2\text{-trz})_6(H_2O)_6][Co_4(H_2O)_2(HGeMo_{10}O_{36})_2]\}\cdot 11H_2O$ (**2**).

The synthetic methods of **2** are similar to **1**, except that use $CoCl_2\cdot 6H_2O$. (0.01g, 0.04 mmol) and $Co(CH_3COO)_2\cdot 4H_2O$ (0.01g, 0.04 mmol) instead of $NiCl_2\cdot 6H_2O$ and $Ni(CH_3COO)_2\cdot 4H_2O$. Pale orange-yellow block crystals were collected. Yield: 34% (based on Mo). Elemental analysis calcd (found %) for $C_{12}H_{64}Co_7Ge_2Mo_{20}N_{24}O_{91}$: C, 3.22 (3.16); H, 1.43 (1.32); N, 7.50 (7.42).

1.3 Crystal Data

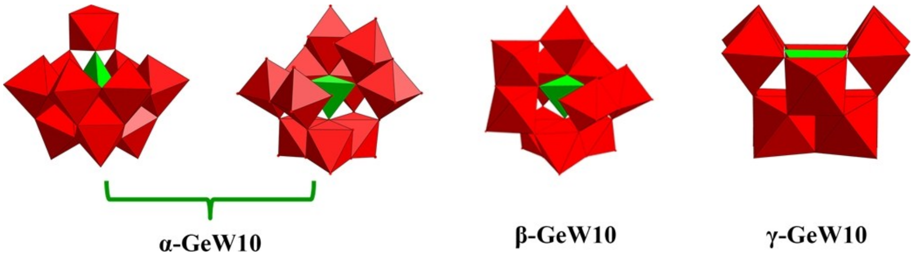
Table S1. Crystal data and structure refinements for **1** and **2.**

	1	**2**
Empirical formula	$C_{12}H_{62}Ge_2Mo_{20}N_{24}Ni_7\,O_{90}$	$C_{12}H_{64}Co_7Ge_2Mo_{20}N_{24}O_{91}$
M	4457.79	4477.34
λ/Å	0.71073	1.54178
T/K	296.15	173.0
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a, Å	13.9330(19)	13.9114(12)
b, Å	14.2147(19)	14.1874(12)
c, Å	14.591(2)	14.6356(13)
α/°	110.716(2)	110.550(4)
β/°	98.574(2)	98.559(4)
γ/°	112.773(2)	112.651(4)
V ($Å^3$)	2351.3(6)	2357.5(4)
Z	1	1
Dc/Mg m^{-3}	3.147	3.152
F(000)	2120.0	2123
θ Range/°	1.680-28.322	1.708-33.427
Reflections collected /unique/ *R*int	17517/11563/0.0243	31585/11563/ 0.0243
Data/restraints/parameters	11563/36/720	8291/18/732
$R_1/\ wR_2$ [$I \geq 2\sigma(I)$]^a	0.0351/0.0824	0.0310/0.0675
$R_1/wR_2{}^b$(all data)	0.0483/0.0893	0.0405/0.0716
GoF on F^2	1.039	1.050

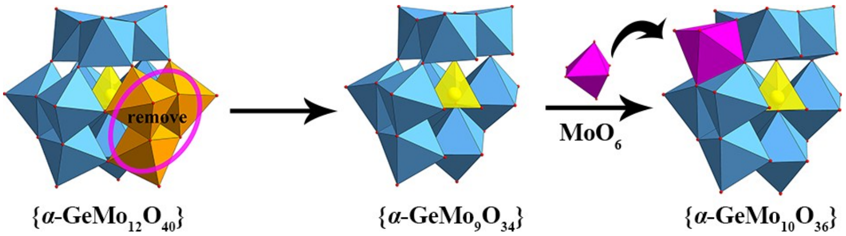
$^aR_1 = \sum||F_0|-|F_C||/\sum|F_0|$; $^bwR_2 = \sum[w(F_0{}^2-F_C{}^2)^2]/\sum[w(F_0{}^2)^2]^{1/2}$

Single-crystal X-ray Crystallography. The single-crystal diffraction for **1** was collected on a Bruker Apex CCD II area-detector diffractometer equiped with graphite-monochromated Mo K*α* radiation (λ = 0.71073 Å) and Data of **2** was collected on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Cu K*α* radiation, λ = 1.5418Å), respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. All structures were solved by the direct method and refined with the full-matrix least-squares technique on F^2 using the SHELX-2018 program package. Selected bond lengths for **1** and **2** are listed in Tables S2 and S3†. The X-ray crystallographic data of **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1961645 and 1961646, respectively. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1.4 Structure



Scheme S1. Summary Keggin {GeW$_{10}$} units in the reported germantungstates.



Scheme S2. The unprecedented {*α*-GeMo$_{10}$O$_{36}$} unit derives from the well-known {α-GeMo$_{12}$O$_{40}$}.

1.5 Selected Bond Lengths for 1 and 2

Table S2. Selected bond lengths (Å) of **1.**

Mo(1)-O(7)	1.692(4)	Mo(2)-O(15)#1	2.298(3)	Mo(3)-O(9)	1.689(4)
Mo(1)-O(8)	1.807(4)	Mo(2)-O(18)	1.832(4)	Mo(3)-O(10)	2.006(4)
Mo(1)-O(11)	1.957(3)	Mo(2)-O(20)	1.693(4)	Mo(3)-O(14)	1.745(4)
Mo(1)-O(12)	1.813(3)	Mo(2)-O(26)	2.180(3)	Mo(3)-O(27)	2.103(3)
Mo(1)-O(15)#1	2.387(3)	Mo(2)-O(31)	1.799(3)	Mo(3)-O(28)	1.909(3)
Mo(1)-O(26)	2.141(4)	Mo(2)-O(33)	1.964(3)	Mo(3)-O(37)#1	2.297(3)
Mo(4)-O(6)	1.692(4)	Mo(5)-O(3)	1.678(4)	Mo(6)-O(4)	1.697(4)
Mo(4)-O(13)	1.815(4)	Mo(5)-O(8)	2.011(4)	Mo(6)-O(19)	1.970(4)
Mo(4)-O(22)#1	2.170(4)	Mo(5)-O(27)	1.804(4)	Mo(6)-O(21)	1.754(4)
Mo(4)-O(24)	2.306(3)	Mo(5)-O(30)	1.844(3)	Mo(6)-O(28)#1	1.948(3)
Mo(4)-O(33)#1	1.986(3)	Mo(5)-O(32)	2.064(4)	Mo(6)-O(30)#1	2.079(3)
Mo(4)-O(34)	1.799(3)	Mo(5)-O(37)#1	2.396(3)	Mo(6)-O(37)	2.285(3)

Mo(7)-O(13)	2.105(4)	Mo(8)-O(2)	1.687(4)	Mo(9)-O(5)	1.706(4)
Mo(7)-O(19)	1.854(4)	Mo(8)-O(11)	1.966(3)	Mo(9)-O(10)	1.839(4)
Mo(7)-O(23)	1.690(4)	Mo(8)-O(22)	2.170(4)	Mo(9)-O(12)	2.106(3)
Mo(7)-O(24)	2.245(3)	Mo(8)-O(24)#1	2.384(3)	Mo(9)-O(15)#1	2.230(3)
Mo(7)-O(29)#1	2.082(3)	Mo(8)-O(29)	1.812(4)	Mo(9)-O(18)	2.087(4)
Mo(7)-O(36)	1.767(4)	Mo(8)-O(32)	1.796(4)	Mo(9)-O(25)	1.743(3)
Mo(10)-O(1)	1.737(4)	Ni(1)-O(25)	2.038(3)	Ni(2)-O(14)#1	2.050(4)
Mo(10)-O(11)	2.156(4)	Ni(1)-O(31)	2.065(4)	Ni(2)-O(10W)	2.045(4)
Mo(10)-O(17)	1.704(4)	Ni(1)-O(34)	2.056(4)	Ni(2)-O(21)	2.037(4)
Mo(10)-O(22)	1.991(4)	Ni(1)-O(35)	2.077(3)	Ni(2)-O(31)	2.086(4)
Mo(10)-O(26)	1.982(4)	Ni(1)-O(35)#1	2.083(3)	Ni(2)-O(34)#1	2.075(3)
Mo(10)-O(33)	2.189(3)	Ni(1)-O(36)	2.042(3)	Ni(2)-O(35)	2.060(3)
Ni(3)-N(7)	2.103(4)	Ni(4)-O(1W)	2.067(4)	Ge(1)-O(15)	1.757(3)
Ni(3)-N(7)#2	2.103(4)	Ni(4)-O(2W)	2.097(4)	Ge(1)-O(24)	1.749(3)
Ni(3)-N(8)#2	2.098(4)	Ni(4)-O(3W)	2.103(4)	Ge(1)-O(35)	1.753(3)
Ni(3)-N(8)	2.098(4)	Ni(4)-N(6)	2.077(5)	Ge(1)-O(37)	1.755(3)
Ni(3)-N(11)#2	2.068(4)	Ni(4)-N(9)	2.037(4)		
Ni(3)-N(11)	2.068(4)	Ni(4)-N(12)	2.084(5)		

Table S3. Selected bond lengths (Å) of **2.**

Mo(1)-O(5)	2.106(4)	Mo(2)-O(6)	1.802(4)	Mo(3)-O(1)	1.793(4)
Mo(1)-O(13)	2.096(4)	Mo(2)-O(10)	1.834(4)	Mo(3)-O(2)	1.976(4)
Mo(1)-O(17)	2.226(4)	Mo(2)-O(14)	2.416(4)	Mo(3)-O(3)	2.185(4)
Mo(1)-O(18)	1.746(4)	Mo(2)-O(21)	2.015(4)	Mo(3)-O(13)	1.826(4)
Mo(1)-O(24)	1.844(4)	Mo(2)-O(23)	2.055(4)	Mo(3)-O(17)	2.313(4)
Mo(1)-O(30)	1.709(4)	Mo(2)-O(29)	1.681(4)	Mo(3)-O(26)	1.691(4)
Mo(4)-O(2)	1.984(4)	Mo(5)-O(3)	2.141(4)	Mo(6)-O(7)	2.090(4)
Mo(4)-O(4)	1.791(4)	Mo(5)-O(5)	1.819(4)	Mo(6)-O(12)	1.680(4)
Mo(4)-O(11)	2.178(4)	Mo(5)-O(8)	1.952(4)	Mo(6)-O(15)	1.762(4)
Mo(4)-O(20)	1.818(4)	Mo(5)-O(17)	2.401(3)	Mo(6)-O(19)	1.854(4)
Mo(4)-O(28)	1.700(4)	Mo(5)-O(21)	1.806(4)	Mo(6)-O(20)	2.103(4)
Mo(4)-O(36)	2.305(4)	Mo(5)-O(32)	1.683(4)	Mo(6)-O(36)	2.249(4)

Mo(7)-O(7)	1.808(4)	Mo(8)-O(10)	2.087(4)	Mo(9)-O(6)	2.112(4)
Mo(7)-O(8)	1.968(4)	Mo(8)-O(14)	2.287(4)	Mo(9)-O(14)	2.301(4)
Mo(7)-O(11)	2.170(4)	Mo(8)-O(19)	1.973(4)	Mo(9)-O(16)	1.747(4)
Mo(7)-O(23)	1.807(4)	Mo(8)-O(22)	1.749(4)	Mo(9)-O(24)	2.013(4)
Mo(7)-O(35)	1.693(4)	Mo(8)-O(27)	1.950(4)	Mo(9)-O(25)	1.692(4)
Mo(7)-O(36)	2.399(3)	Mo(8)-O(33)	1.687(4)	Mo(9)-O(27)	1.907(4)
Mo(10)-O(2)	2.186(4)	Co(1)-O(1)#1	2.114(4)	Co(2)-O(1)#1	2.112(4)
Mo(10)-O(3)	1.987(4)	Co(1)-O(1W)	2.066(4)	Co(2)-O(4)	2.098(4)
Mo(10)-O(8)	2.160(4)	Co(1)-O(4)#1	2.113(4)	Co(2)-O(9)#1	2.131(4)
Mo(10)-O(11)	1.981(4)	Co(1)-O(9)	2.097(4)	Co(2)-O(9)	2.111(4)
Mo(10)-O(31)	1.699(4)	Co(1)-O(16)	2.084(4)	Co(2)-O(15)	2.063(4)
Mo(10)-O(34)	1.733(5)	Co(1)-O(22)	2.075(4)	Co(2)-O(18)#1	2.046(4)
Co(3)-O(2W)	2.132(5)	Co(4)-N(10)#2	2.146(5)	Ge(1)-O(9)	1.759(3)
Co(3)-O(3W)	2.137(5)	Co(4)-N(10)	2.146(5)	Ge(1)-O(14)	1.750(4)
Co(3)-O(4W)	2.095(5)	Co(4)-N(5)	2.116(5)	Ge(1)-O(17)	1.753(4)
Co(3)-N(9)	2.136(5)	Co(4)-N(5)#2	2.116(5)	Ge(1)-O(36)	1.753(3)
Co(3)-N(6)#2	2.145(5)	Co(4)-N(2)#2	2.148(5)		
Co(3)-N(1)	2.076(5)	Co(4)-N(2)	2.148(5)		

1.6 Selected Hydrogen Bond Lengths and Bond Angles for 1 and 2

Table S4. Selected hydrogen bond lengths ( ) and bond angles (°) of **1.**

D-H…A	**d(D…H)nm**	**d(H…A)nm**	**d(D…A)nm**	**∠(DHA)°**
O(1W)-H(1WB)...O(1)#3	0.85	1.86	2.673(6)	158.5
O(3W)-H(3WB)...O(7W)	0.89	1.89	2.672(9)	146.1
O(4W)-H(4WA)...O(10W)	0.85	1.83	2.603(6)	150.7
O(4W)-H(4WB)...O(30)#4	0.85	1.96	2.724(6)	148.9
O(5W)-H(5WB)...O(20)#3	0.85	2.08	2.893(8)	161.3
O(7W)-H(7WB)...O(5)	0.84	2.02	2.841(9)	167.1
O(7WA)-H(7WC)...O(13)#5	0.85	2.07	2.871(15)	156.9
O(7WA)-H(7WD)...O(5)	0.85	1.99	2.835(15)	176.6
O(8W)-H(8WA)...O(5W)#3	0.81	2.11	2.833(12)	148.8
O(8W)-H(8WB)...O(9W)	0.85	2.03	2.81(2)	152.8

O(9W)-H(9WB)	O(6)	0.88	1.97	2.818(4)	161

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z+1, #2 -x+1,-y+2,-z+2, #3 -x,-y+1,-z+1, #4 x,y,z+1, #5 -x+1,-y+2,-z+1.

Table S5. Selected hydrogen bond lengths ( ) and bond angles (°) of **2.**

D-H…A	**d(D…H)nm**	**d(H…A)nm**	**d(D…A)nm**	**∠(DHA)°**
O(1W)-H(1WA)...O(5W)#3	0.85	1.79	2.595(7)	156.6
O(2W)-H(2WB)...O(7W)	0.87	1.90	2.680(12)	149.8
O(2W)-H(2WB)...O(7WA)	0.87	1.86	2.703(16)	164.5
O(5W)-H(5WA)...O(10)#4	0.82	2.07	2.741(7)	139.3
O(6W)-H(6WA)...O(9W)#5	0.85	1.99	2.82(3)	163.7
O(6W)-H(6WA)...O(9WA)#5	0.85	1.85	2.70(5)	170.4
O(7W)-H(7WA)...O(3W)#6	0.75	2.12	2.855(15)	167.7
O(7W)-H(7WB)...O(30)#7	0.84	2.06	2.808(11)	148.5
O(7WA)-H(7WC)...O(20)#8	0.85	2.04	2.822(13)	152.6
O(7WA)-H(7WD)...O(30)#7	0.89	1.97	2.833(13)	164.2
O(9WA)-H(9WD)...O(8W)#4	0.87	2.00	2.85(4)	165.4

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y-2,-z, #2 -x+2,-y,-z+1, #3 -x+1,-y-1,-z+1, #4 x,y+1,z, #5 -x+1,-y,-z+1, #6 -x+2,-y,-z+2, #7 x+1,y+1,z+1, #8 x,y+1,z+1.

1.7 BVS Calculation

Table S6. The BVS calculation results of Mo and Ni atoms in **1.**

Code	**Bond Valence**	**Code**	**Bond Valence**
Ni1	1.902	Mo4	6.062
Ni2	1.907	Mo5	6.052
Ni3	2.352	Mo6	6.022
Ni4	2.1	Mo7	6.025
Mo1	5.802	Mo8	6.082
Mo2	6.143	Mo9	6.111
Mo3	6.067	Mo10	5.917

Table S7. The BVS calculation results of Mo and Co atoms in **2.**

Code	Bond Valence	Code	Bond Valence
Co1	1.978	Mo4	6.037
Co2	1.969	Mo5	6.102
Co3	2.147	Mo6	6.089
Co4	2.35	Mo7	6.02
Mo1	6.055	Mo8	6.054
Mo2	6.069	Mo9	6.007
Mo3	6.048	Mo10	5.961

Table S8. A detailed summary of sandwich-type germanomolybdates.

Year	Compound Formula	Characteristics	Raw materials	Reaction solvent	Reaction conditions	Crystal growth time	Synthetic Method	Ref
2009	$[Na_{12}(H_2O)_{36}][Cu_2(\beta\text{-}Y\text{-}GeMo_9O_{33})_2]\ 3H_2O$ $[Na_6(H_2O)_{24}][Cr_2(\beta\text{-}Y\text{-}GeMo_9O_{33})_2]\ 7H_2O$ $[Na_{11}(H_2O)_{25}]H[M_4(H_2O)_2(\alpha\text{-}B\text{-}GeMo_9O_{34})_2]$ $6H_2O$ (M = Ni^{II}, Mn^{II}, Co^{II})	the first di-/tetra-nuclear transition-metal clusters and trivacant Keggin Germanomolybdate	Na_2MoO_4, GeO_2	HAc-NaAc	water bath 80℃	1-2 weeks	evaporation solvent	1
2010	$(Him)_8Na_7H_7[Cu(im)_4(CuGeMo_9O_{33})_2][(CuGeMo_9O_{33})_2]\cdot 41H_2O$	di-Cu^{II}-substituted $[(CuGeMo_9O_{33})_2]^{12-}$ 1D chain-like framework	Na_2MoO_4, GeO_2	HAc-NaAc	heated 80℃	8 days	evaporation solvent	2
2012	$H(H_2en)_5[Cu(en)_2]\ [Eu(GeMo_{11}O_{39})_2]\cdot 11H_2O$	Europium substituted monovacant germanomolybdate	Na_2MoO_4, GeO_2, KCl, ,	HAc-NaAc, en, CH_3COOH, HCl	heated 50℃	2 weeks	conventional aqueous solutions	3
2012	$(H_2en)_2H_7\{[Na_{0.5}(H_2O)_{3.5}]_2[Cu_2(\beta\text{-}Y\text{-}GeMo_9O_{33})_2]\}\cdot 6H_2O$ $(H_2en)_2H\{[Na_{2.5}(H_2O)_{12}]_2[Cu(en)_2][Cu_2(\beta\text{-}Y\text{-}GeMo_9O_{33})_2]\}\cdot 8H_2O$ $[Na_4(H_2O)_{12}]_2H_4[Cu_2(\beta\text{-}Y\text{-}GeMo_9O_{33})_2]\}\cdot 11H_2O$ $[Cu(en)_2]_2[Cu(en)_2(H_2O)]_2\{[Cu(en)_2]_2[Cu_2(\beta\text{-}Y\text{-}GeMo_9O_{33})_2]\}\cdot 8H_2O$	di-Cu^{II}-substituted $[Cu_2(\beta\text{-}Y\text{-}GeMo_9O_{33})_2]^{12-}$	Na_2MoO_4, GeO_2	HAc-NaAc, en	water bath 80℃	1-5 days	evaporation solvent hydrothermal condition	4
2013	$[C_3H_5N_2]_6[GeMo_{11}Co(H_2O)O_{39}]\cdot 9H_2O$ $[C_3H_5N_2]_6[GeMo_{11}Ni(H_2O)O_{39}]\cdot 9H_2O$ $[C_3H_5N_2]_6[GeMo_{11}Mn(H_2O)O_{39}]\cdot 6H_2O$	the first examples of transition-metal-mono substituted germanomolybdates	$H_4[\alpha\text{-}GeMo_{12}O_{40}]\cdot 14H_2O$	HAc, NaOH	heated 100℃	15 days	evaporation solvent a	5
2017	$[(CH_3)_4N]_6H_6\{Mn^{II}(GeMo_8O_{31})[Mn^{I}(CO)_3]_2\}_2\cdot 12H_2O$	Tetravacant germanomolybdates	$(NH_4)_6Mo_7O_{24}$,GeO_2, ammonia	CH_3CN/H_2O	refluxed 70℃	—	evaporation solvent	6
2017	$(C_4H_{10}ON)_8H_5[Er(GeMo_{11}O_{39})_2]\cdot 14H_2O$ $(C_4H_{10}ON)_8H_5[Gd(GeMo_{11}O_{39})_2]\cdot 13H_2O$ $(C_4H_{10}ON)_8H_5[Dy(GeMo_{11}O_{39})_2]\ 15H_2O$ $(C_4H_{10}ON)_8H_5[Tb(GeMo_{11}O_{39})_2]\cdot 14H_2O$	the first examples of the heavy rare earth metal substituted germanomolybdates	$(NH_4)_6Mo_7O_{24}$,GeO_2,	Morpholine HCl, NaOH	heated 90℃	1-7 days	evaporation solvent	7
2019	**$\{[M_3(NH_2\text{-}trz)_6(H_2O)_6][M_4(H_2O)_2(HGeMo_{10}O_{36})_2]\}\cdot 10H_2O$ (M = Ni/Co)**	**the first tetra-nuclear transition-metal clusters substituted trivacant Keggin $[GeMo_{10}O_{36}]^{8-}$**	$(NH_4)_6Mo_7O_{24}$,GeO_2	**H_2O HCl**	room temperatue	**3 days**	**hydrothermal conditions**	**This work**

Section 2 Materials characterization

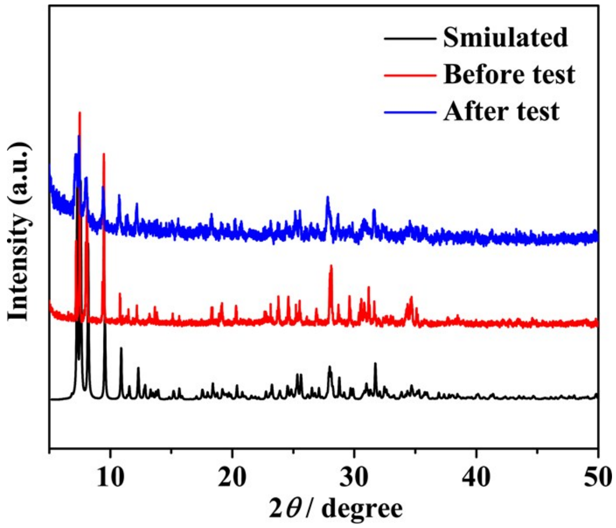


Fig. S1 Comparison of the simulated and synthesized XRD patterns of **1.**

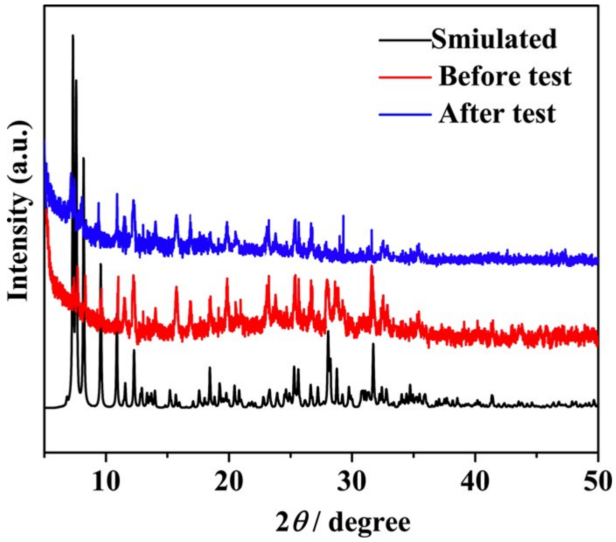


Fig. S2 Comparison of the simulated and synthesized XRD patterns of **2.**

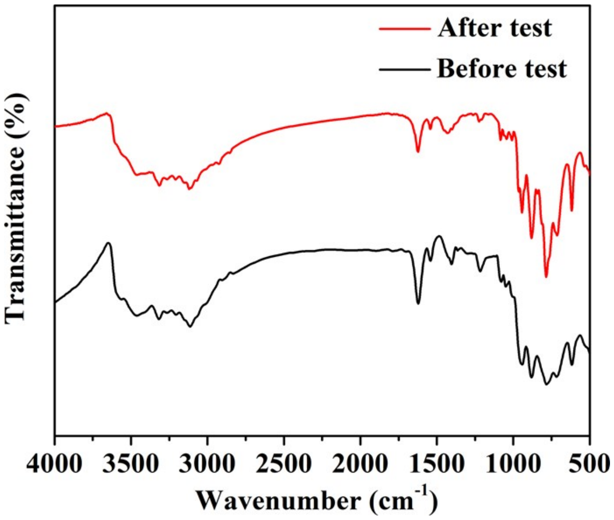


Fig. S3 IR spectrum of **1.**

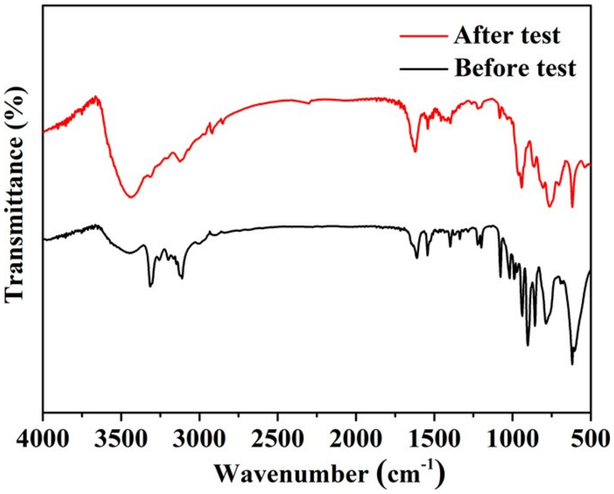


Fig. S4 IR spectrum of **2.**

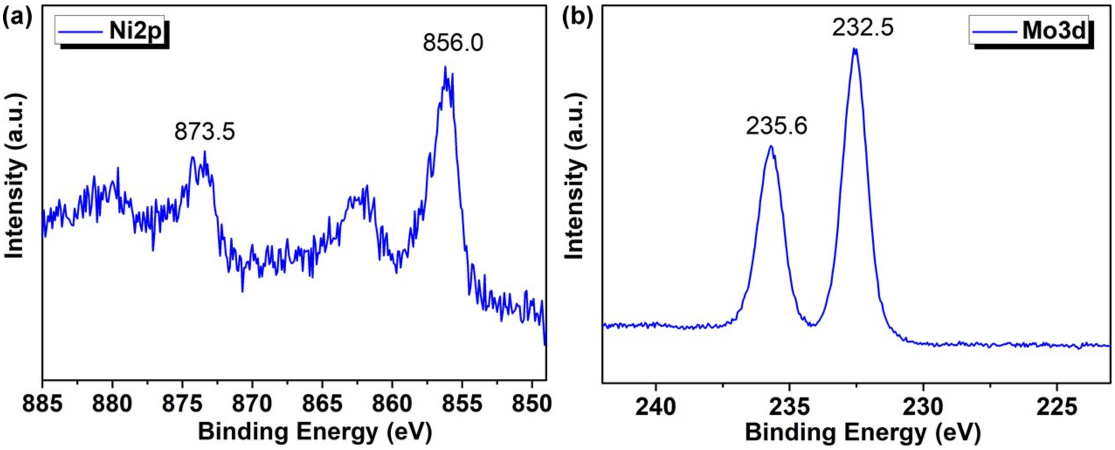


Fig. S5 (a) XPS spectra of **1** for Ni $2p_{3/2}$ and Ni $2p_{1/2}$; (b) XPS spectra of **1** for Mo $3d_{5/2}$ and Mo $3d_{3/2}$.

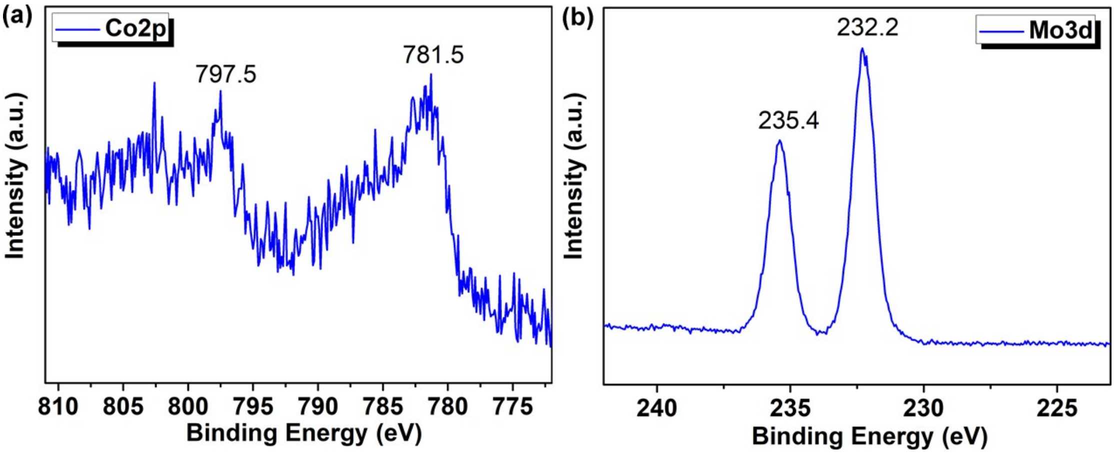


Fig. S6 (a) XPS spectra of **2** for Co $2p_{3/2}$ and Co $2p_{1/2}$; (b) XPS spectra of **2** for Mo $3d_{5/2}$ and Mo $3d_{3/2}$.

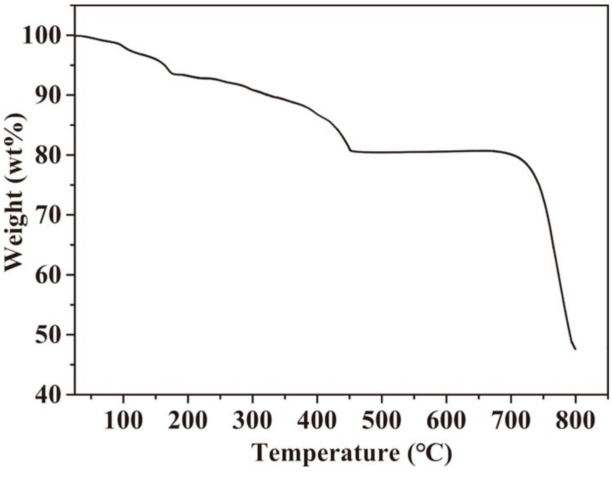


Fig. S7 The TG curve of **1.**

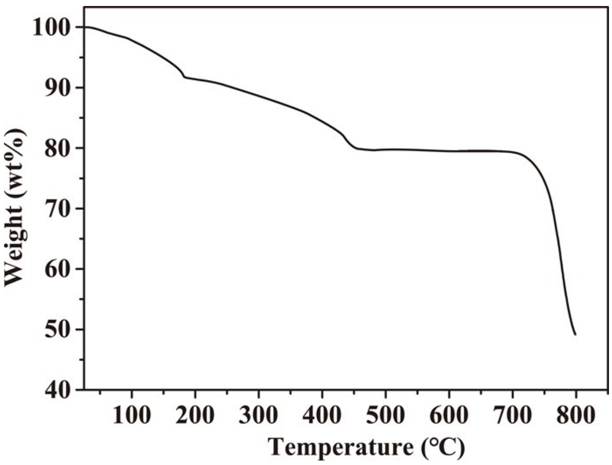


Fig. S8 The TG curve of **2.**

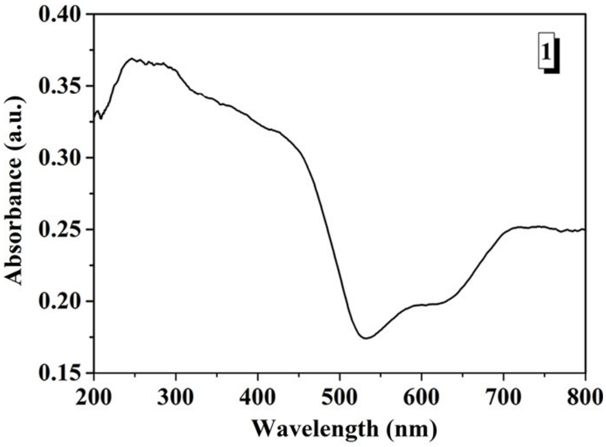


Fig. S9 The diffuse reflectance UV-Vis absorption spectrum of the powder samples of **1**.

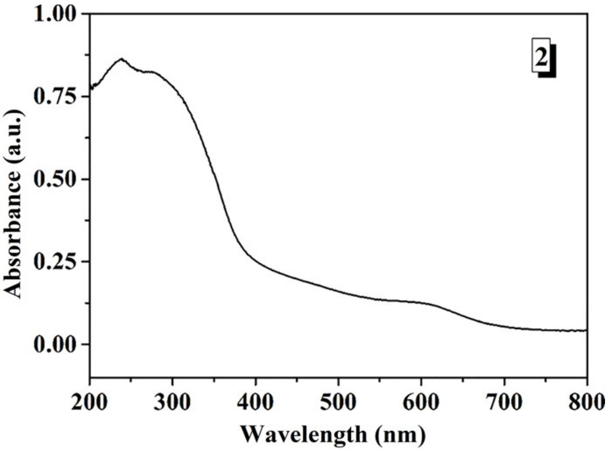


Fig. S10 The diffuse reflectance UV-Vis absorption spectrum of the powder samples of **2.**

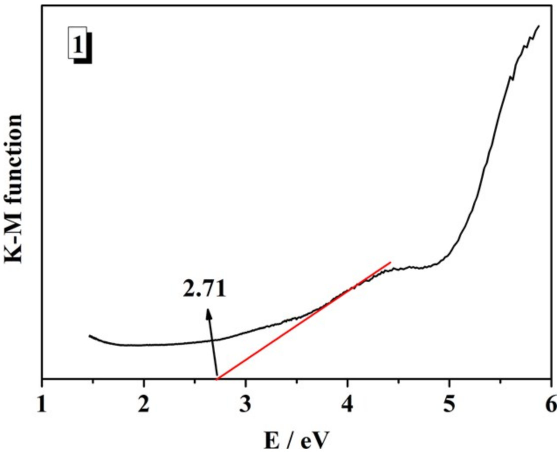


Fig. S11 The plot of K-M function against energy E of **1**.

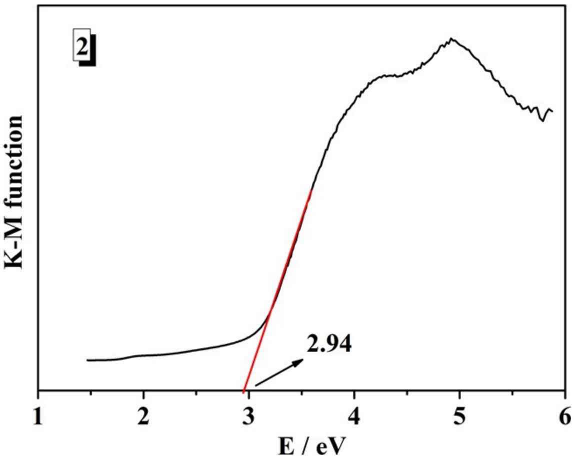


Fig. S12 The plot of K-M function against energy E of **2**.

Section 3 Photocatalytic Activity Measurements

Photocatalytic tests were performed in a quartz tube under 1 atm pressure of CO_2. A mixture of acetonitrile (4 mL), H_2O (1 mL), triethanolamine (TEOA, 1 mL), compound **1** or **2** and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ was put into the quartz tube. The reaction system was purified by bubbling pure carbon dioxide to remove oxygen for 15 min. Then, the mixture system was irradiated by a 300W Xenon lamp with a 420 nm cutoff filter under constant stirring. The temperature of the system was controlled at 20 ^{o}C. To detect the gas product of CO, 500 mL gas in the middle of the test tube was taken out by syringe and injected into FID detector, using argon as carrier gas. The volume of the CO produced was calculated by comparing the integrated area of the signals of CO with a calibration curve. The injector and detector temperatures were set to 60^{o}C. To detect the formation of hydrogen from the reaction mixture, 1000 mL of the headspace of the test tube was taken out by syringe and injected into a TCD detector, using a 5 Å molecular sieve column and argon as the carrier gas and reference gas.

Table S9. Comparison of our samples with the reported heterogeneous catalysts with $Ru^{II}(bpy)_3^{2+}$ participation for CO generation in pure CO_2 condinaton.

Catalyst	Light absorber	Light source	Reaction medium	Products	TON (CO)	$TOF_{(CO)}$ (min^{-1})	Selectivity (%)	Reference
1	**$Ru^{II}(bpy)_3^{2+}$**	**λ > 420 nm**	**MeCN/H_2O/TEOA**	**CO, H_2**	**44.3**	**0.25**	**82**	**This Work**
2	**$Ru^{II}(bpy)_3^{2+}$**	**λ > 420 nm**	**MeCN/H_2O/TEOA**	**CO, H_2**	**76.5**	**0.42**	**62**	**This Work**
Co-ZIF-9	$Ru^{II}(bpy)_3^{2+}$	λ > 420 nm	MeCN/H_2O/TEOA	CO, H_2	52.3	1.74	58.3	8
Co-ZIF-67	$Ru^{II}(bpy)_3^{2+}$	λ>420 nm	MeCN/H_2O/TEOA	CO, H_2	112	—	66.7	9
Co1-G nanosheets	$Ru^{II}(bpy)_3^{2+}$	λ>420 nm	MeCN/H_2O/TEOA	CO, H_2	678	3.77	79.4	10
MOF-253–$Ru(CO)_2Cl_2$	$Ru^{II}(bpy)_3^{2+}$	420-800 nm	MeCN/TEOA	CO, $HCOO^-$, H_2	7.3	0.015	13.3	11
$[Co_{2.67}(SiW_{12}O_{40})(H_2O)_4(Htrz)_4]\cdot Cl_{1.33}$	$Ru^{II}(bpy)_3^{2+}$	λ>420 nm	MeCN/H_2O/TEOA	CO, H_2	53.3	0.29	50.5	12
$\{Co_3[SiW_{12}O_{40}](H_2O)_3(Htrz)_6Cl\}Cl\cdot 6H_2O$	$Ru^{II}(bpy)_3^{2+}$	λ>420 nm	MeCN/H_2O/TEOA	CO, H_2	61.67	0.34	50.4	12

Table S10. The research of various reaction conditions.

	POMs	Reaction conditions	CO (μmol)	H_2 (μmol)	Sel. (CO) (%)
1	a	all	10.2	2.3	82
2	b	all	17.6	10.8	62
3	a/b	all	n.d	n.d	—
4	a/b	Without $[Ru(bpy)_3]Cl_2$	n.d	n.d	—
5	a/b	Without TEOA	n.d	n.d	—
6	Without a/b	all	n.d	0.5	—
7	a	all	n.d	0.2	—
	b	all	n.d	0.5	—
8	a	all	4.6	16.3	22.3
	b	all	6.0	24.2	20

9	a	all	6.7	2.8	70.2
	b	all	12.8	8.7	59.6

Reaction conditions: POMs (a = **1**, b = **2**) (1 mg), $[Ru(bpy)_3]Cl_2·6H_2O$ (7 mg), MeCN(4 ml), TEOA (1 ml), H_2O (1 ml), CO_2 (1 atm), λ ≥ 420 nm, 20 °C, 3 h. n.d. = Not detectable. Selectivity = $n(CO)/n(CO+H_2) \times 100$. 3 In the dark. 4 Without $[Ru(bpy)_3]Cl_2·6H_2O$. 5 Without TEOA. 6 Without a or b. 7 Using Ar to replace CO_2. 8 Using DMF to replace MeCN. 9 Using TEA to replace TEOA.

Section 4 Electrochemical and Electrocatalytic Properties

Cyclic voltammetry measurements of **1** and **2** were performed using an electrochemical workstation (CHI 660e, China) with a three-electrode system. The working electrode was a modified carbon paste electrode (CPE) with a twisted platinum wire as the counter electrode and an Ag/AgCl (saturated KCl) electrode as the reference electrode. The electrochemical measurements were tested in 0.5M H_2SO_4 and Na_2SO_4 electrolyte solution. The preparation of the CPE were as follows: 0.5 g of graphite powder and 50 mg of **1** or **2** were mixed and ground together with an agate mortar and pestle to achieve a uniform and dry mixture, then 0.35 mL of paraffin oil was added and stirred with a glass rod. The homogenized mixture was packed into a 3 mm inner diameter glass tube. The surface was wiped with weighing paper, and an electrical contact was established with a copper rod through the back of the electrode.

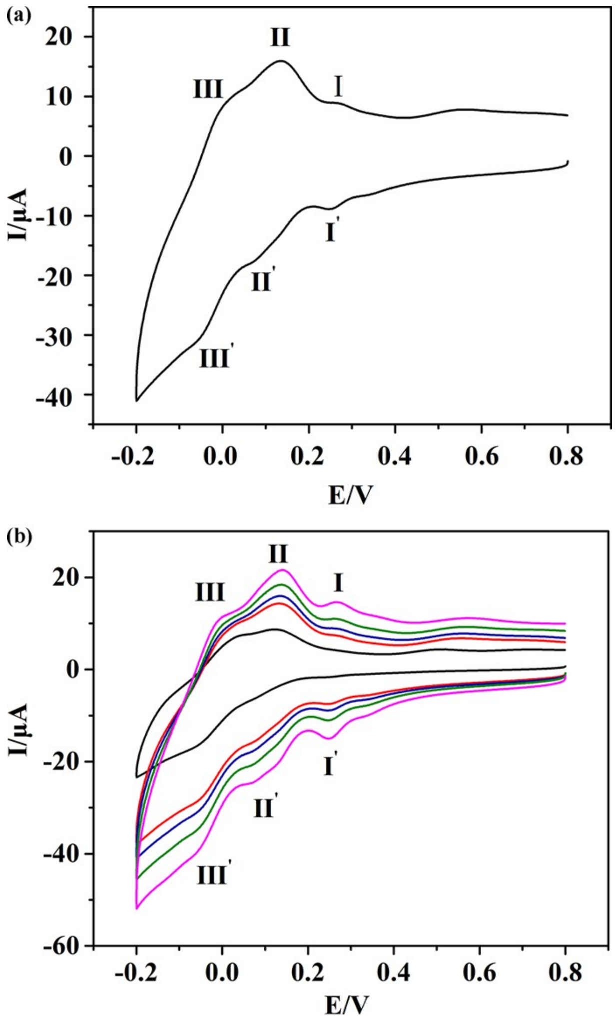


Fig. S13 The solid-state cyclic voltammograms of **1** in 0.5 M Na_2SO_4/H_2SO_4 aqueous solution (pH = 2.5, scan rate: 100 mV s^{-1}, top). CV of **1** at different scan rates (50, 100, 200, 300 and 400 mV s^{-1}, down).

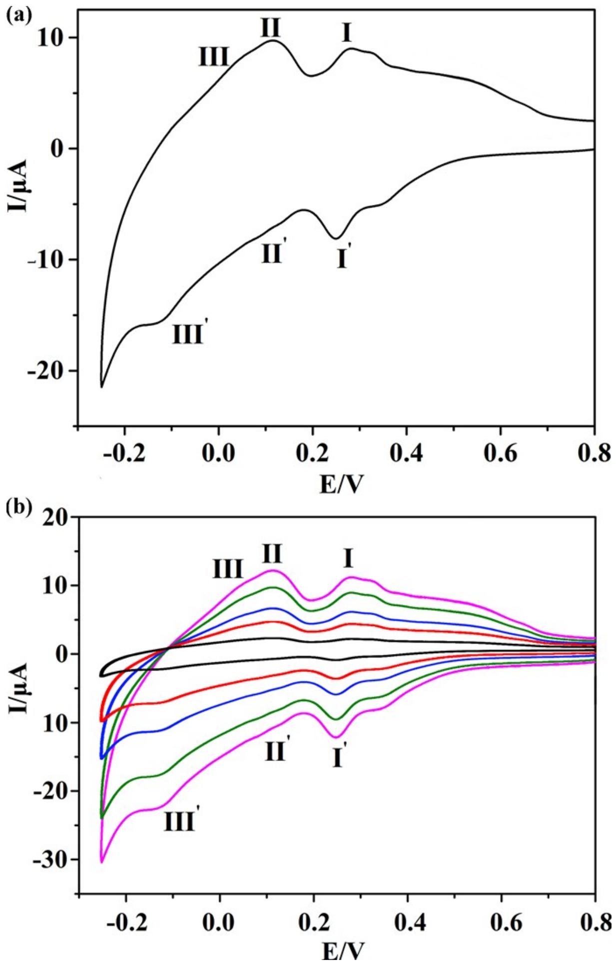


Fig. S14 The solid-state cyclic voltammograms of **2** in 0.5 M Na_2SO_4/H_2SO_4 aqueous solution (pH = 2.5, scan rate: 100 mV s^{-1}, top). CV of **2** at different scan rates (50, 100, 200, 300 and 400 mV s^{-1}, down).

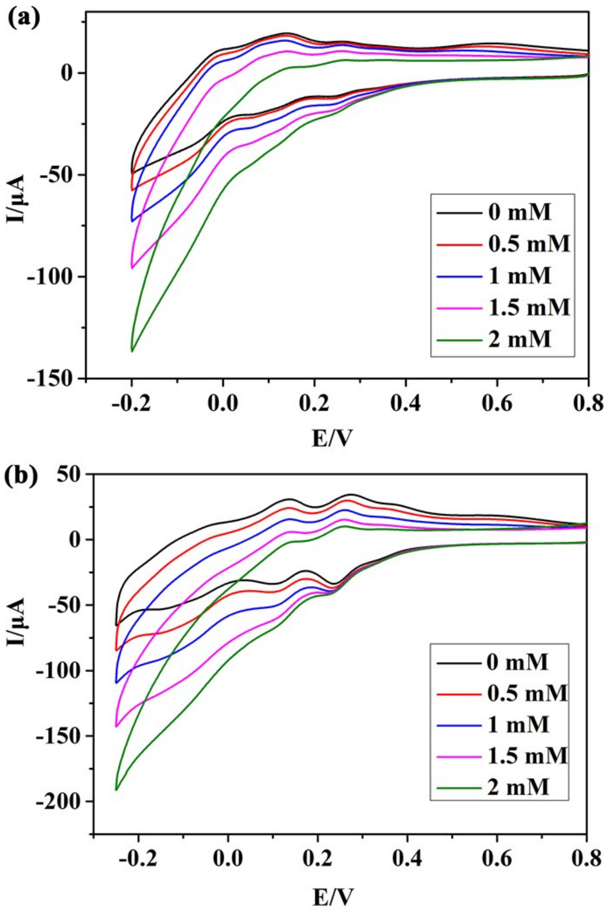


Fig. S15 Cyclic voltammograms of **1** (a) and **2** (b) with adding H_2O_2 different concentrations at the scan rate of 500 mV·s^{-1}.

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