

## Supporting Information

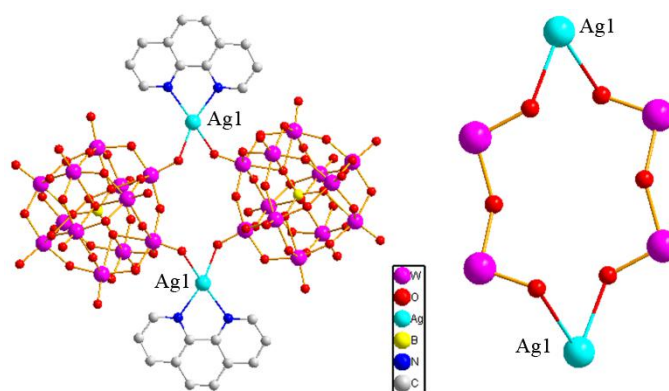
### {BW<sub>12</sub>O<sub>40</sub>} Hybrid decorated by Ag<sup>+</sup> for using as the material of Supercapacitor and Photocatalyst

Qiu-Lan Liang<sup>a</sup>, Na-Na Du<sup>a</sup>, Li-Ge Gong<sup>a,b\*</sup>, Chun-Xiao Wang<sup>a</sup>, Chun-Mei Wang<sup>a</sup>, Kai Yu<sup>a,b\*</sup>, Bai-Bin Zhou<sup>a,b\*</sup>

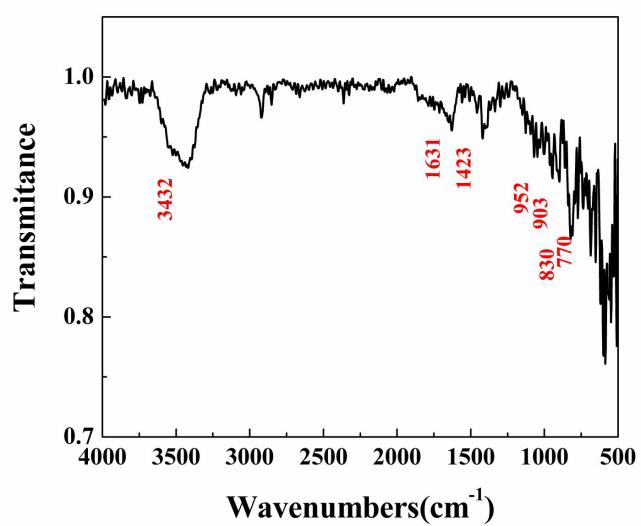
**Materials and General Characterization.** All reagents are purchased without further purification. The infrared spectroscopy (IR) of the compound is carried out on a VER TEX 80 infrared Raman spectrometer from the Bruker Germany, adopting KBr pellets in the range 4000-400 cm<sup>-1</sup>. X-ray powder diffraction (XRPD) were conducted by a Bruker D8 ADVANCE instrument using Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at room temperature. Scanning electron microscope (SEM) was performed on Hitachi SU-70. The content analysis of C, H, and N were tested by the American Flash EA1112 CHN elemental analyzer, and B, W, and Ag were tested by the US 7500CX inductively coupled plasma mass spectrometer. The Diamond 6300 differential thermal analyzer from Perkin-Elmer company in the United States is used, with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as the reference, platinum crucible, heating rate is 10 °C min<sup>-1</sup>, static air atmosphere.

**X-ray crystallography.** The compound was fastened to the glass filament for collecting the diffraction data at 296(2) Bruker SMART CCD detector with graphite monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Crystal structure of compound is determined by direct methods and refined by means of full-matrix least-squares on F<sup>2</sup> (Table S3). Selected bond lengths (Å) and angles were listed in Table S4.

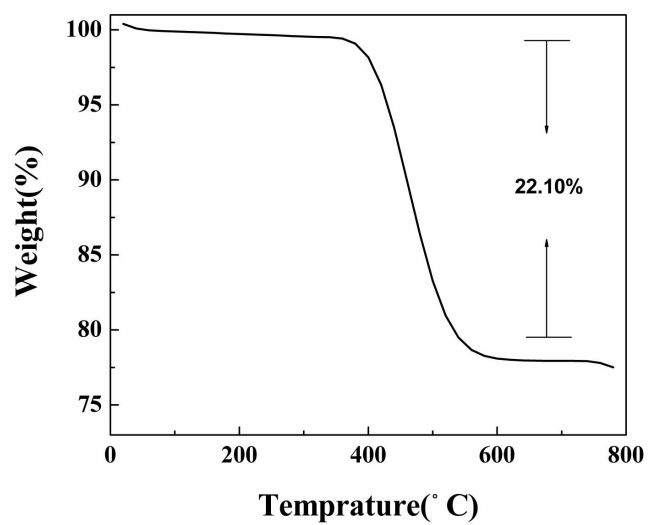
**electrochemical characterization for Supercapacitor.** The electrochemical performance of the prepared electrode materials were carried out on the CHI660E electrochemical workstation by using a three-electrode system in 1 M H<sub>2</sub>SO<sub>4</sub> solution. A Pt plate and the Ag/AgCl (3M KCl) electrode were used as the counter electrode and reference electrode, respectively. The as-prepared glassy carbon electrode was employed as the working electrode. The main methods used are cyclic voltammetry, galvanostatic charge-discharge measurement and electrochemical impedance spectroscopy.



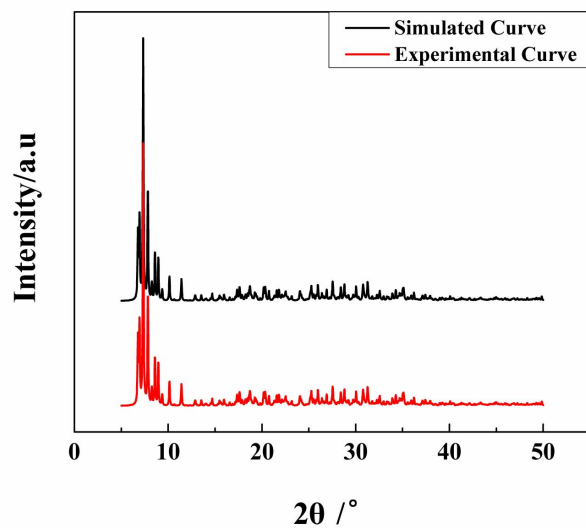
**Fig. S1** The twelve-membered ring view of compound.



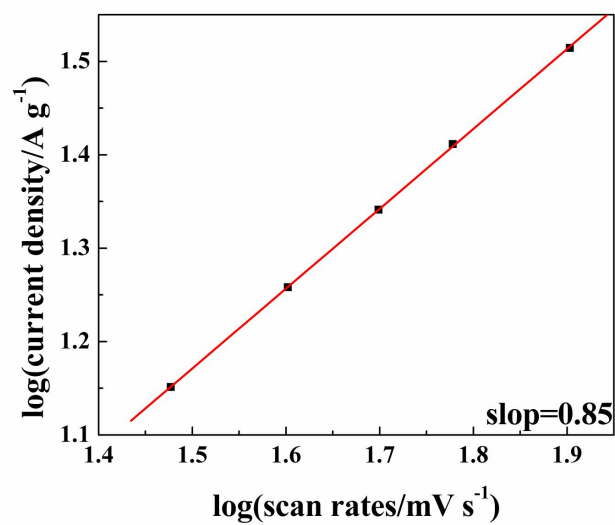
**Fig. S2** IR spectra of compound.



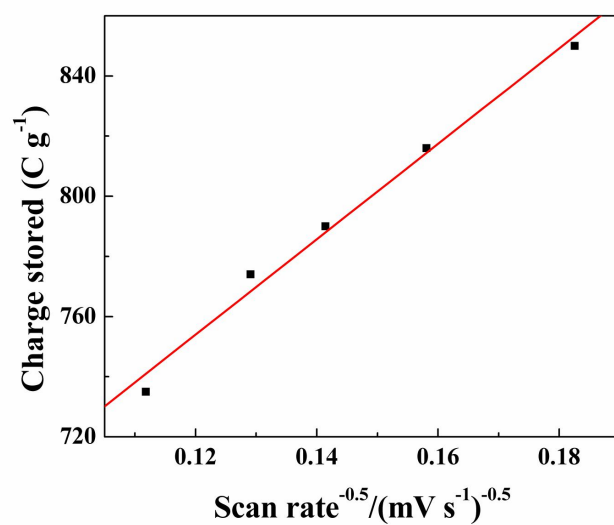
**Fig. S3** TG curve of compound.



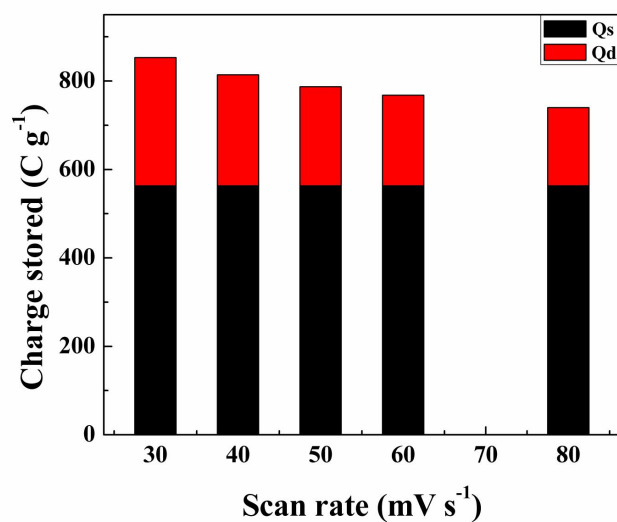
**Fig. S4** XRD spectra of compound.



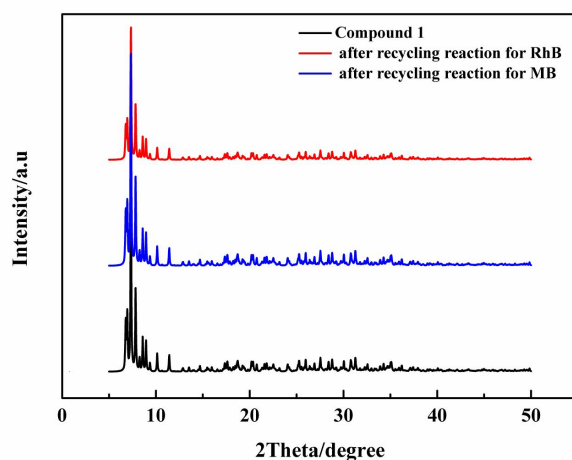
**Fig. S5** The plot of log of current density vs. the log of scan rate in the scan rate range of 30-80  $\text{mV s}^{-1}$  for 1-GCE.



**Fig. S6** The plot of the total charge stored( $q$ ) vs. the reciprocal of the square root of the scan rate for 1-GCE.



**Fig. S7** illustration of the contribution from the capacitive( $Q_s$ ) and diffusion-controlled( $Q_d$ ) charge to the total charge stored at different scan rates for 1-GCE.



**Fig. S8** XRD patterns before and after recycling reactions.

**Table S1** Crystal data and structure refinement data for **1**

Compound	<b>1</b>
Chemical formula	C <sub>120</sub> H <sub>80</sub> Ag <sub>6</sub> B <sub>2</sub> N <sub>20</sub> O <sub>80</sub> W <sub>24</sub>
Formula weight	8163.05
T/K	296(2)
Crystal system	Triclinic
Space group	P-1
a/Å	14.3019(10)
b/Å	14.9420(11)
c/Å	21.4307(15)
α/°	74.0570(10)
β/°	86.3790(10)
γ/°	65.4190(10)
V/Å <sup>3</sup>	3997.6(5)
Z	1
Dcalc/Mg m <sup>-3</sup>	3.391
μ/mm <sup>-1</sup>	17.996
F(000)	3648.0
θ range/°	2.335-28.332
Reflections	38592/19323
collected/ unique	[R(int) = 0.0331]
Data/restraints/paramtrs	19323/12/1135
GOF on F <sup>2</sup>	1.022
R <sub>1</sub> <sup>a</sup> /wR <sub>2</sub> [I > 2σ(I)] <sup>b</sup>	0.0415/0.1248
Δρfin (max/min), e Å <sup>-3</sup>	3.396/-7.023

$${}^a R_1 = \sum ||F_0| - |F_c|| / \sum |F_0| \cdot {}^b wR_2 = \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]^{1/2}.$$

**Table S2** Selected bond lengths (Å) and bond angles (°) of **1**

B(1)-O(9)	1.528(11)	B(1)-O(11)#1	1.528(12)	B(1)-O(12)	1.544(11)
B(1)-O(14)	1.517(12)	W(1)-O(1)	1.926(7)	W(1)-O(3)	1.904(7)
W(1)-O(12)	2.367(6)	W(1)-O(15)	1.877(7)	W(1)-O(25)	1.710(8)

W(1)-O(31)	1.927(7)	W(2)-O(1)	1.932(7)	W(2)-O(2)	1.884(7)
W(2)-O(4)	1.871(7)	W(2)-O(6)	1.757(7)	W(2)-O(8)	1.919(7)
W(2)-O(12)	2.285(7)	W(3)-O(8)	1.916(8)	W(3)-O(10)	1.914(7)
W(3)-O(12)	2.392(7)	W(3)-O(23)	1.893(7)	W(3)-O(31)	1.905(7)
W(3)-O(32)	1.704(7)	W(4)-O(14)	2.354(7)	W(4)-O(16)	1.910(7)
W(4)-O(23)	1.908(7)	W(4)-O(26)	1.906(8)	W(4)-O(29)	1.910(8)
W(4)-O(39)	1.709(9)	W(5)-O(3)	1.897(7)	W(5)-O(7)	1.728(8)
W(5)-O(11)	2.353(7)	W(5)-O(22)	1.887(8)	W(5)-O(24)	1.902(8)
W(5)-O(40)	1.921(7)	W(6)-O(2)	1.933(7)	W(6)-O(9)	2.381(7)
W(6)-O(19)	1.904(7)	W(6)-O(20)	1.907(8)	W(6)-O(30)	1.708(8)
W(6)-O(33)	1.901(7)	W(7)-O(5)	1.903(7)	W(7)-O(9)	2.395(6)
W(7)-O(17)	1.919(7)	W(7)-O(21)	1.900(7)	W(7)-O(33)	1.928(8)
W(7)-O(34)	1.713(7)	W(8)-O(5)	1.895(7)	W(8)-O(11)	2.389(6)
W(8)-O(13)	1.880(8)	W(8)-O(18)	1.931(8)	W(8)-O(28)	1.725(8)
W(8)-O(40)	1.912(7)	W(9)-O(4)	1.922(7)	W(9)-O(11)	2.348(7)
W(9)-O(18)	1.898(7)	W(9)-O(19)	1.894(7)	W(9)-O(24)	1.922(7)
W(9)-O(35)	1.707(8)	W(10)-O(14)	2.376(7)	W(10)-O(15)	1.906(7)
W(10)-O(22)	1.903(8)	W(10)-O(26)	1.917(8)	W(10)-O(27)	1.916(7)
W(10)-O(36)	1.706(8)	W(11)-O(9)	2.316(6)	W(11)-O(10)	1.874(7)
W(11)-O(17)	1.916(7)	W(11)-O(20)	1.931(8)	W(11)-O(29)	1.881(8)
W(11)-O(37)	1.749(8)	W(12)-O(13)	1.911(8)	W(12)-O(14)	2.393(7)
W(12)-O(16)	1.905(8)	W(12)-O(21)	1.889(7)	W(12)-O(27)	1.916(7)
W(12)-O(38)	1.713(8)	Ag(1)-N(8)	2.357(11)	Ag(1)-N(10)	2.326(11)
Ag(2)-N(2)	1.997(10)	Ag(2)-N(3)	2.032(9)	Ag(2)-N(5)	2.014(9)
Ag(2)-N(7)	1.987(10)	Ag(3)-N(1)	1.970(9)	Ag(3)-N(4)	1.963(9)
Ag(3)-N(6)	2.154(10)	Ag(3)-N(9)	2.043(10)	Ag(1)-O(7)	2.298(8)
Ag(1)-O(25)	2.638	Ag(2)-O(37)	2.136(8)	Ag(3)-O(6)	2.077(8)
O(1)-W(1)-O(12)	74.9(3)	O(1)-W(1)-O(31)	88.3(3)	O(3)-W(1)-O(1)	89.9(3)
O(3)-W(1)-O(12)	85.9(3)	O(3)-W(1)-O(31)	161.4(3)	O(15)-W(1)-O(1)	161.1(3)
O(15)-W(1)-O(3)	86.8(3)	O(15)-W(1)-O(12)	86.3(3)	O(15)-W(1)-O(31)	89.0(3)
O(25)-W(1)-O(1)	97.6(4)	O(25)-W(1)-O(3)	101.8(3)	O(25)-W(1)-O(12)	169.4(3)
O(25)-W(1)-O(15)	101.3(4)	O(25)-W(1)-O(31)	96.9(3)	O(31)-W(1)-O(12)	75.7(3)
O(1)-W(2)-O(12)	76.8(3)	O(2)-W(2)-O(1)	164.7(3)	O(2)-W(2)-O(8)	88.9(3)
O(2)-W(2)-O(12)	87.9(3)	O(4)-W(2)-O(1)	89.9(3)	O(4)-W(2)-O(2)	88.4(3)
O(4)-W(2)-O(8)	161.4(3)	O(4)-W(2)-O(12)	85.2(3)	O(6)-W(2)-O(1)	92.8(3)
O(6)-W(2)-O(2)	102.5(3)	O(6)-W(2)-O(4)	99.2(3)	O(6)-W(2)-O(8)	99.3(3)
O(6)-W(2)-O(12)	168.8(3)	O(8)-W(2)-O(1)	87.9(3)	O(8)-W(2)-O(12)	76.3(3)
O(8)-W(3)-O(12)	73.8(3)	O(10)-W(3)-O(8)	88.4(3)	O(10)-W(3)-O(12)	84.2(3)
O(23)-W(3)-O(8)	159.3(3)	O(23)-W(3)-O(10)	85.9(3)	O(23)-W(3)-O(12)	85.9(3)
O(23)-W(3)-O(31)	89.1(3)	O(31)-W(3)-O(8)	89.4(3)	O(31)-W(3)-O(10)	159.4(3)
O(31)-W(3)-O(12)	75.5(3)	O(32)-W(3)-O(8)	98.9(4)	O(32)-W(3)-O(10)	101.1(3)
O(32)-W(3)-O(12)	170.9(3)	O(32)-W(3)-O(23)	101.8(4)	O(32)-W(3)-O(31)	99.5(3)
O(16)-W(4)-O(14)	76.2(3)	O(23)-W(4)-O(14)	85.1(3)	O(23)-W(4)-O(16)	160.9(3)
O(23)-W(4)-O(29)	85.7(3)	O(26)-W(4)-O(14)	76.4(3)	O(26)-W(4)-O(16)	88.4(3)
O(26)-W(4)-O(23)	91.1(3)	O(26)-W(4)-O(29)	160.8(3)	O(29)-W(4)-O(14)	84.5(3)

O(29)-W(4)-O(16)	88.5(3)	O(39)-W(4)-O(14)	173.2(3)	O(39)-W(4)-O(16)	98.2(4)
O(39)-W(4)-O(23)	100.7(4)	O(39)-W(4)-O(26)	99.8(4)	O(39)-W(4)-O(29)	99.3(4)
O(3)-W(5)-O(11)	86.8(3)	O(3)-W(5)-O(24)	90.7(3)	O(3)-W(5)-O(40)	162.0(3)
O(7)-W(5)-O(3)	101.9(3)	O(7)-W(5)-O(11)	170.5(3)	O(7)-W(5)-O(22)	99.1(4)
O(7)-W(5)-O(24)	100.2(4)	O(7)-W(5)-O(40)	96.0(3)	O(22)-W(5)-O(3)	86.4(3)
O(22)-W(5)-O(11)	85.1(3)	O(22)-W(5)-O(24)	160.6(3)	O(22)-W(5)-O(40)	89.0(3)
O(24)-W(5)-O(11)	75.6(3)	O(24)-W(5)-O(40)	87.9(3)	O(40)-W(5)-O(11)	75.4(3)
O(2)-W(6)-O(9)	84.8(3)	O(19)-W(6)-O(2)	85.3(3)	O(19)-W(6)-O(9)	84.8(3)
O(19)-W(6)-O(20)	159.4(3)	O(20)-W(6)-O(2)	89.2(3)	O(20)-W(6)-O(9)	74.9(3)
O(30)-W(6)-O(2)	98.8(3)	O(30)-W(6)-O(9)	173.3(3)	O(30)-W(6)-O(19)	101.1(4)
O(30)-W(6)-O(20)	99.4(4)	O(30)-W(6)-O(33)	100.7(4)	O(33)-W(6)-O(2)	160.5(3)
O(33)-W(6)-O(9)	76.1(3)	O(33)-W(6)-O(19)	89.1(3)	O(33)-W(6)-O(20)	89.4(3)
O(5)-W(7)-O(9)	85.6(3)	O(5)-W(7)-O(17)	160.2(3)	O(5)-W(7)-O(33)	88.9(3)
O(17)-W(7)-O(9)	74.7(3)	O(17)-W(7)-O(33)	87.9(3)	O(21)-W(7)-O(5)	86.5(3)
O(21)-W(7)-O(9)	84.3(3)	O(21)-W(7)-O(17)	89.6(3)	O(21)-W(7)-O(33)	159.3(3)
O(33)-W(7)-O(9)	75.2(3)	O(34)-W(7)-O(5)	100.2(3)	O(34)-W(7)-O(9)	172.3(3)
O(34)-W(7)-O(17)	99.5(4)	O(34)-W(7)-O(21)	101.0(4)	O(34)-W(7)-O(33)	99.6(4)
O(5)-W(8)-O(11)	84.6(3)	O(5)-W(8)-O(18)	87.3(3)	O(5)-W(8)-O(40)	159.3(3)
O(13)-W(8)-O(5)	88.4(3)	O(13)-W(8)-O(11)	85.5(3)	O(13)-W(8)-O(18)	160.2(3)
O(13)-W(8)-O(40)	89.5(3)	O(18)-W(8)-O(11)	74.8(3)	O(28)-W(8)-O(5)	100.8(4)
O(28)-W(8)-O(11)	171.9(3)	O(28)-W(8)-O(13)	100.6(4)	O(28)-W(8)-O(18)	99.2(4)
O(28)-W(8)-O(40)	99.8(4)	O(40)-W(8)-O(11)	74.7(3)	O(40)-W(8)-O(18)	87.7(3)
O(4)-W(9)-O(11)	83.3(3)	O(4)-W(9)-O(24)	87.2(3)	O(18)-W(9)-O(4)	159.7(3)
O(18)-W(9)-O(11)	76.4(3)	O(18)-W(9)-O(24)	89.2(3)	O(19)-W(9)-O(4)	86.0(3)
O(19)-W(9)-O(11)	86.2(3)	O(19)-W(9)-O(18)	91.1(3)	O(19)-W(9)-O(24)	161.0(3)
O(24)-W(9)-O(11)	75.4(3)	O(35)-W(9)-O(4)	100.1(4)	O(35)-W(9)-O(11)	173.4(3)
O(35)-W(9)-O(18)	100.2(4)	O(35)-W(9)-O(19)	99.6(4)	O(35)-W(9)-O(24)	99.1(4)
O(15)-W(10)-O(14)	84.1(3)	O(15)-W(10)-O(26)	89.3(3)	O(15)-W(10)-O(27)	159.8(3)
O(22)-W(10)-O(14)	84.3(3)	O(22)-W(10)-O(15)	86.7(3)	O(22)-W(10)-O(26)	159.8(3)
O(22)-W(10)-O(27)	88.9(3)	O(26)-W(10)-O(14)	75.6(3)	O(27)-W(10)-O(14)	75.9(3)
O(27)-W(10)-O(26)	88.1(3)	O(36)-W(10)-O(14)	173.5(3)	O(36)-W(10)-O(15)	100.7(4)
O(36)-W(10)-O(22)	100.3(4)	O(36)-W(10)-O(26)	99.8(4)	O(36)-W(10)-O(27)	99.5(4)
O(10)-W(11)-O(9)	85.9(3)	O(10)-W(11)-O(17)	162.6(3)	O(10)-W(11)-O(20)	88.7(3)
O(10)-W(11)-O(29)	88.5(3)	O(17)-W(11)-O(9)	76.8(3)	O(17)-W(11)-O(20)	87.6(3)
O(20)-W(11)-O(9)	76.1(3)	O(29)-W(11)-O(9)	86.6(3)	O(29)-W(11)-O(17)	90.0(3)
O(29)-W(11)-O(20)	162.7(3)	O(37)-W(11)-O(9)	172.5(3)	O(37)-W(11)-O(10)	98.5(3)
O(37)-W(11)-O(17)	98.8(3)	O(37)-W(11)-O(20)	97.9(3)	O(37)-W(11)-O(29)	99.5(4)
O(13)-W(12)-O(14)	85.6(3)	O(13)-W(12)-O(27)	88.8(3)	O(16)-W(12)-O(13)	160.8(3)
O(16)-W(12)-O(14)	75.3(3)	O(16)-W(12)-O(27)	88.2(3)	O(21)-W(12)-O(13)	86.1(3)
O(21)-W(12)-O(14)	84.3(3)	O(21)-W(12)-O(16)	90.1(3)	O(21)-W(12)-O(27)	159.4(3)
O(27)-W(12)-O(14)	75.4(3)	O(38)-W(12)-O(13)	100.7(4)	O(38)-W(12)-O(14)	172.5(3)
O(38)-W(12)-O(16)	98.5(4)	O(38)-W(12)-O(21)	100.0(4)	O(38)-W(12)-O(27)	100.5(4)
N(10)-Ag(1)-N(8)	71.5(4)	N(2)-Ag(2)-N(3)	82.5(4)	N(2)-Ag(2)-N(5)	99.8(4)
N(5)-Ag(2)-N(3)	141.4(4)	N(7)-Ag(2)-N(2)	171.3(4)	N(7)-Ag(2)-N(3)	101.7(4)
N(7)-Ag(2)-N(5)	81.8(4)	N(1)-Ag(3)-N(6)	81.1(4)	N(1)-Ag(3)-N(9)	93.2(4)

N(4)-Ag(3)-N(1)	174.8(4)	N(4)-Ag(3)-N(6)	98.2(4)	N(4)-Ag(3)-N(9)	82.0(4)
N(9)-Ag(3)-N(6)	104.1(4)	N(8)-Ag(1)-O(7)	121.6(3)	N(10)-Ag(1)-O(7)	156.2(3)
N(8)-Ag(1)-O(25)	146.4	N(10)-Ag(1)-O(25)	109.6	N(2)-Ag(2)-O(37)	84.5(3)
N(3)-Ag(2)-O(37)	93.6(3)	N(5)-Ag(2)-O(37)	125.0(4)	N(7)-Ag(2)-O(37)	87.5(4)
N(1)-Ag(3)-O(6)	94.1(3)	N(4)-Ag(3)-O(6)	91.1(4)	N(6)-Ag(3)-O(6)	104.4(4)
N(9)-Ag(3)-O(6)	151.3(4)	O(7)-Ag(1)-O(25)	71.4		

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

**Table S3** Keggin-based electrode materials

	Electrode material	Electrolyte	Scan rate / Current density	Specific capacitance	Ref.
1	Compound 1	1 M H <sub>2</sub> SO <sub>4</sub>	2.16 A g <sup>-1</sup>	1647 F g <sup>-1</sup>	<b>This work</b>
2	NENU-5/PPy /60	1 M H <sub>2</sub> SO <sub>4</sub>	2 mA cm <sup>-2</sup>	508.6 F g <sup>-1</sup>	1
3	[PW <sub>11</sub> CuO <sub>39</sub> ] <sup>5-</sup> @Ru-rGO	0.5 M HOAC	0.2 A g <sup>-1</sup>	705 F g <sup>-1</sup>	2
4	[Ag <sub>5</sub> (brtmb) <sub>4</sub> ][VW <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	1 M H <sub>2</sub> SO <sub>4</sub>	110 A g <sup>-1</sup>	206 F g <sup>-1</sup>	3
5	(PMo <sub>12</sub> /PANI/TiN NWA)	1 M H <sub>2</sub> SO <sub>4</sub>	1 A g <sup>-1</sup>	469 F g <sup>-1</sup>	4
6	[H(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> )Cu <sub>2</sub> ][PMo <sub>12</sub> O <sub>40</sub> ]	0.5 M H <sub>2</sub> SO <sub>4</sub>	1 A g <sup>-1</sup>	287 F g <sup>-1</sup>	5
7	[H(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> )Cu <sub>2</sub> ][PW <sub>12</sub> O <sub>40</sub> ]	0.5 M H <sub>2</sub> SO <sub>4</sub>	1 A g <sup>-1</sup>	153.4 F g <sup>-1</sup>	5
8	[Cu <sup>I</sup> H <sub>2</sub> (C <sub>12</sub> H <sub>12</sub> N <sub>6</sub> )(PMo <sub>12</sub> O <sub>40</sub> )]·[(C <sub>6</sub> H <sub>15</sub> N)(H <sub>2</sub> O) <sub>2</sub> ]	1 M H <sub>2</sub> SO <sub>4</sub>	3 A g <sup>-1</sup>	249 F g <sup>-1</sup>	6
9	HPW/rGO	5 M H <sub>2</sub> SO <sub>4</sub>	5 mV s <sup>-1</sup>	337.5 F g <sup>-1</sup>	7
10	PAni/H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	1 M HClO <sub>4</sub>		120 F g <sup>-1</sup>	8
11	SWCNT-TBA-PV <sub>2</sub> Mo <sub>10</sub>	1 M H <sub>2</sub> SO <sub>4</sub>	0.1 A g <sup>-1</sup>	444 F g <sup>-1</sup>	9
12	[Cu <sup>I</sup> (btx)] <sub>4</sub> [SiW <sub>12</sub> O <sub>40</sub> ]	1 M H <sub>2</sub> SO <sub>4</sub>	3 A g <sup>-1</sup>	110.3 F g <sup>-1</sup>	10
13	AC/PW <sub>12</sub> O <sub>40</sub>	1 M H <sub>2</sub> SO <sub>4</sub>	10 mV s <sup>-1</sup>	254 F g <sup>-1</sup>	11
14	[Ag <sub>5</sub> (C <sub>2</sub> H <sub>2</sub> N <sub>3</sub> ) <sub>6</sub> ][H <sub>5</sub> SiW <sub>12</sub> O <sub>40</sub> ]	0.5 M H <sub>2</sub> SO <sub>4</sub>	6 A g <sup>-1</sup>	29.8 F g <sup>-1</sup>	12
15	[Ag <sub>5</sub> (C <sub>2</sub> H <sub>2</sub> N <sub>3</sub> ) <sub>6</sub> ][H <sub>5</sub> SiMo <sub>12</sub> O <sub>40</sub> ]	0.5 M H <sub>2</sub> SO <sub>4</sub>	0.5A g <sup>-1</sup>	155.0 F g <sup>-1</sup>	12
16	[Ag <sub>5</sub> (C <sub>2</sub> H <sub>2</sub> N <sub>3</sub> ) <sub>6</sub> ][H <sub>5</sub> SiMo <sub>12</sub> O <sub>40</sub> ]@1 5%GO-based electrode	0.5 M H <sub>2</sub> SO <sub>4</sub>	0.5A g <sup>-1</sup>	230.2 F g <sup>-1</sup>	12
17	[Cu <sup>I</sup> <sub>4</sub> H <sub>2</sub> (btx) <sub>5</sub> (PMo <sub>12</sub> O <sub>40</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O	1 M H <sub>2</sub> SO <sub>4</sub>	2 A g <sup>-1</sup>	237.0 F g <sup>-1</sup>	13
18	[Cu <sup>I</sup> <sub>4</sub> H <sub>2</sub> (btx) <sub>5</sub> (PW <sub>12</sub> O <sub>40</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O	1 M H <sub>2</sub> SO <sub>4</sub>	2 A g <sup>-1</sup>	100.0 F g <sup>-1</sup>	13
19	RGO/PIL/PMo <sub>12</sub> O <sub>40</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	10 mV s <sup>-1</sup>	456 F g <sup>-1</sup>	14
20	HT-RGO-PMo <sub>12</sub> O <sub>40</sub>	1 M H <sub>2</sub> SO <sub>4</sub>	10 mV s <sup>-1</sup>	276 F g <sup>-1</sup>	15



21	AC/PMo <sub>12</sub>	1 M H <sub>2</sub> SO <sub>4</sub>	2 A g <sup>-1</sup>	160 F g <sup>-1</sup> ( for the Positive Electrode) and 183 F g <sup>-1</sup> (for the negative hybrid Electrode)	16
22	AC@PMo <sub>12</sub> O <sub>40</sub>	1 M [Bmim] H <sub>2</sub> SO <sub>4</sub>	1 mV s <sup>-1</sup>	223 F g <sup>-1</sup>	17
23	PC 5-1-PMo <sub>12</sub>	1 M H <sub>2</sub> SO <sub>4</sub>	200 mV s <sup>-1</sup>	361F g <sup>-1</sup>	18
24	PMo <sub>10</sub> V <sub>2</sub> @ZIF-67	3M KOH	2 A g <sup>-1</sup>	475 F g <sup>-1</sup>	19

**Table S4** Other POMs-based electrode materials

	Electrode material	Electrolyte	Scan rate / Current density	Specific capacitance	Ref.
1	(H <sub>2</sub> bpe)(Hbpe) <sub>2</sub> {[Cu(pzta)(H <sub>2</sub> O)[P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ]} · 5H <sub>2</sub> O	1 M H <sub>2</sub> SO <sub>4</sub>	5 A g <sup>-1</sup>	168 F g <sup>-1</sup>	20
2	[{K(H <sub>2</sub> O) <sub>2</sub> }{Cu <sub>2</sub> (biiim) <sub>2</sub> }(P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> )]	1 M H <sub>2</sub> SO <sub>4</sub>	0.2 A g <sup>-1</sup>	95.7 F g <sup>-1</sup>	21
3	AC/P <sub>2</sub> Mo <sub>18</sub>	1 M H <sub>2</sub> SO <sub>4</sub>	6 A g <sup>-1</sup>	275F g <sup>-1</sup>	22
4	[Cu <sup>II</sup> <sub>2</sub> (bipy)(H <sub>2</sub> O) <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> PO <sub>3</sub> ) <sub>2</sub> Mo <sub>5</sub> O <sub>15</sub> ]	0.5 M H <sub>2</sub> SO <sub>4</sub>	2 A g <sup>-1</sup>	160.9F g <sup>-1</sup>	23
5	{Mo <sub>132</sub> } -rGO	1 M Li <sub>2</sub> SO <sub>4</sub>	A g <sup>-1</sup>	617.3F g <sup>-1</sup>	24
6	[Cu <sup>I</sup> <sub>2</sub> (bnie) <sub>2</sub> ] <sub>2</sub> (β-Mo <sub>8</sub> O <sub>26</sub> )	4.0 M KOH	1 A g <sup>-1</sup>	828F g <sup>-1</sup>	25
7	[Cu <sup>I</sup> <sub>2</sub> (β-Mo <sub>8</sub> O <sub>26</sub> )(bnie) <sub>2</sub> ][Cu <sub>2</sub> (bnie) <sub>2</sub> ]	4.0 M KOH	1 A g <sup>-1</sup>	800F g <sup>-1</sup>	25
8	MoS/rGO	0.5 M Na <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub>	10 mV s <sup>-1</sup>	870 F g <sup>-1</sup>	26
9	[Ru(bpy) <sub>3</sub> ] <sub>3.33</sub> P <sub>2</sub> Mo <sub>18</sub> O <sub>62</sub> · mH <sub>2</sub> O	pH=7 (0.25 M total salt containing 0.05 M KH <sub>2</sub> PO <sub>4</sub> , 0.05 M K <sub>2</sub> HPO <sub>4</sub> , 0.1 M NaCl, 0.025 M MgCl <sub>2</sub> and 0.025 M CaCl <sub>2</sub> )	0.2 A g <sup>-1</sup>	125 F g <sup>-1</sup>	27
10	[Ru(bpy) <sub>3</sub> ] <sub>3</sub> P <sub>2</sub> Mo <sub>18</sub> O <sub>62</sub> · nH <sub>2</sub> O	—	0.2 A g <sup>-1</sup>	68 F g <sup>-1</sup>	27

11	Na <sub>6</sub> V <sub>10</sub> O <sub>28</sub>	1M LiClO <sub>4</sub> in propylene carbonate	0.1 A g <sup>-1</sup>	354 F g <sup>-1</sup>	28
12	{Ag <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> }@Ag-MOF	1 M Na <sub>2</sub> SO <sub>4</sub>	1 A g <sup>-1</sup>	320.8 F g <sup>-1</sup>	29
13	Ni(OH) <sub>2</sub> -POV thin films (LNHV-1)	2 M KOH	1 A g <sup>-1</sup>	1440 F g <sup>-1</sup>	30
14	LNHV-2.5	2 M KOH	1 A g <sup>-1</sup>	637 F g <sup>-1</sup>	30
15	LNHV-3	2 M KOH	1 A g <sup>-1</sup>	536 F g <sup>-1</sup>	30

## Reference

- (1) Z. Liu, W. Yao, H. Gan, C. Sun, Z. Su and X. Wang, *Chem. Eur. J.*, 2019, **25**, 16617–16624. DOI:10.1002/chem.201903664
- (2) A. Ensafi, E. Heydari Soureshjani and B. Rezaei, *Chem. Eng. J.*, 2017, **330**, 1109–1118. DOI: 10.1016/j.cej.2017.08.062
- (3) G. Wang, T. Chen, X. Wang, H. Ma and H. Pang, *Eur. J. Inorg. Chem.*, 2017, **45**, 5350–5355. DOI: 10.1002/ejic.201701031
- (4) L. Lu, Y. Xie, *New J. Chem.*, 2017, **41**, 335–346. DOI:10.1039/C6NJ02368A
- (5) S. Roy, V. Vemuri, S. Maiti, K. Manoj, *Inorg. Chem.*, 2018, **57**, 12078–12092. DOI: 10.1021/acs.inorgchem.8b01631
- (6) D. Chai, J. Xin, B. Li, H. Pang, H. Ma, K. Li, B. Xiao, X. Wang and L. Tan, *Dalton Trans.*, 2019, **48**, 13026–13033. DOI: 10.1039/C9DT02420D
- (7) R. Li, C. He, L. Cheng, G. Lin, G. Wang, D. Shi, R. Kowk Yiulic and Y. Yang, *Composites Part B: Engineering*, 2017, **121**, 75–82. DOI:10.1016/j.compositesb.2017.03.026
- (8) A. Cuentas Gallegos, M. Lira Cantú, N. Casañ Pastor and P. Gómez Romero, *Adv. Funct. Mater.*, 2005, **15**, 1125–1133. DOI:https://doi.org/10.1002/adfm.200400326
- (9) H. Chen, R. Oweini, J. Friedl, C. Lee, L. Li, U. Kortz, *Nanoscale*, 2015, **7**, 7934–7941. DOI:10.1039/c4nr07528e
- (10) D. Chai, Y. Hou, K. O'Halloran, H. Pang, H. Ma, G. Wang and X. Wang, *Chem Electro Chem*, 2018, **5**, 3443–3450. DOI: 10.1002/celec.201801081
- (11) J. Guevar, V. Ruiz and P. Romero, *J. Mater. Chem. A*, 2014, **2**, 1014–102. DOI:10.1039/c3ta14455k
- (12) Y. Hou, D. Chai, B. Li, H. Pang, H. Ma, X. Wang and L. Tan, *ACS Appl. Mater. Interfaces*, 2019, **11**, 20845–20853. DOI: 10.1021/acsami.9b04649
- (13) D. Chai, C. Gómez García, B. Li, H. Pang, H. Ma, X. Wang and L. Tan, *Chem Eng J*, 2019, **373**, 587–597. DOI:10.1016/j.cej.2019.05.084
- (14) M. Yang, B. Choi, S. Jung, Y. Han, Y. Huh and S. Lee, *Adv. Funct. Mater.*, 2014, **24**, 7301–7309. DOI:10.1002/adfm.201401798
- (15) J. Guevara, V. Ruiza, and P. Romero, *Phys. Chem. Chem. Phys.*, 2014, **16**, 20411–20414. DOI:10.1039/C4CP03321C

- (16) V. Ruiz, J. Guevara and P. Romero, *Electrochem Commun*, 2012, **24**, 35–38. DOI:10.1016/j.elecom.2012.08.003
- (17) C. Hu, E. Zhao, N. Nitta, A. Magasinski, G. Berdichevsky and G. Yushin, *J. Power Source*, 2016, **326**, 569–574. DOI:10.1016/j.jpowsour.2016.04.036
- (18) M. Genovese, K. Lian, *J. Mater. Chem. A.*, 2017, **5**, 3939–3947. DOI:10.1039/C6TA10382K
- (19) A. Mohamed, M. Ramadan, N. Ahmed, A. Abo. ElNaga, H. Alalawy, T. Zaki, S. Shaban, H. Hassan and N. Allam, *J. Energy Storage*, 2020, **28**, 101292. DOI:10.1016/j.est.2020.101292
- (20) G. Wang, T. Chen, S. Li, H. Pang and H. Ma, *Dalton Trans.*, 2017, **46**, 13897–13902. DOI:10.1039/C7DT02230A
- (21) J. Gao, L. Gong, X. Fan, K. Yu, Z. Zheng and B. Zhou, *ACS Appl. Nano Mater.*, 2020, **3**, 1497–1507. DOI: 10.1021/acsanm.9b02312
- (22) A. Mu, J. Li, W. Chen, X. Sang, Z. Su, E. Wang, *Inorg. Chem. Commun.*, 2015, **46**, 149–152. DOI: 10.1016/j.inoche.2015.03.032
- (23) B. R. Lu, S. B. Li, J. Pan, L. Zhang, J. J. Xin, Y. Chen and X. G. Tan, *Inorg. Chem.*, 2020, **59**, 1702–1714. DOI:10.1021/acs.inorgchem.9b02858
- (24) Y. Dong, L. Chen, W. Chen, X. Zheng, X. Wang and E. Wang, *Chem Asian J.*, 2018, **13**, 3304–3313. DOI: 10.1002/asia.201801018
- (25) K. Wang, Z. Wang, S. Wang, Y. Chu, R. Xi, X. Zhang and H. Wu, *Chem. Eng. J.*, 2019, **367**, 239–248. DOI:10.1016/j.cej.2019.02.145
- (26) S. Zhang, R. Liu, S. Li, A. Dolbecq, P. Mialane, L. Suo, L. Bi, B. Zhang, T. Liu, C. Wu, L. Yan, Z. Su, G. Zhang and B. Keita, *J. Colloid Interf. Sci.*, 2018, **514**, 507–516. DOI:10.1016/j.jcis.2017.12.039
- (27) S. Chinnathambi, M. Ammam, *J. Power Sources*, 2015, **284**, 524–535. DOI:10.1016/j.jpowsour.2015.03.034
- (28) H. Chen, G. Wee, R. Al Oweini, J. Friedl, K. Tan, Y. Wang, C. Wong, *ChemPhysChem*, 2014, **15**, 2162–2169. DOI:10.1002/cphc.201400091
- (29) X. Zhao, L. Gong, C. Wang, C. Wang, K. Yu and B. Zhou, *Chem. Eur. J.*, 2020, **26**, 4613–4619. DOI:10.1002/chem.201905689
- (30) J. Gunjekar, A. Inamdar, B. Hou, S. Cha, S. Pawar, A. Abu Talha, H. Chavan, J. Kim, S. Cho, S. Lee, Y. Jo, H. Kim and H. Im, *Nanoscale*, 2018, **10**, 8953–8961. DOI: 10.1039/c7nr09626g