# Transition-Metal-Modified Vanadoborate Clusters as Stable and Efficient Photocatalysts for CO<sub>2</sub> Reduction

Xiang Yu,<sup>§</sup> Cong-Cong Zhao,<sup>§</sup> Jian-Xia Gu, Chun-Yi Sun,<sup>\*</sup> Hai-Yan Zheng, Li-Kai Yan,<sup>\*</sup> Min Sun, Xin-Long Wang,<sup>\*</sup> and Zhong-Min Su

Cite This: https:/	//doi.org/10.1021/acs.inorgche	m.1c00499	Read Online	
ACCESS	III Metrics & More		Article Recommendations	s Supporting Information

**ABSTRACT:** Photocatalytic carbon dioxide reduction (CO<sub>2</sub>RR) is considered to be a promising sustainable and clean approach to solve environmental issues. Polyoxometalates (POMs), with advantages in fast, reversible, and stepwise multiple-electron transfer without changing their structures, have been promising catalysts in various redox reactions. However, their performance is often restricted by poor thermal or chemical stability. In this work, two transition-metal-modified vanadoborate clusters,  $[Co(en)_2]_6[V_{12}B_{18}O_{54}(OH)_6]\cdot17H_2O$  ( $V_{12}B_{18}-Co$ ) and  $[Ni(en)_2]_6[V_{12}B_{18}O_{54}-(OH)_6]\cdot17H_2O$  ( $V_{12}B_{18}-Co$ ) and  $[Ni(en)_2]_6[V_{12}B_{18}O_{54}-(OH)_6]\cdot17H_2O$  ( $V_{12}B_{18}-Ni$ ), are reported for photocatalytic CO<sub>2</sub> reduction.  $V_{12}B_{18}-Co$  and  $V_{12}B_{18}-Ni$  can preserve their structures to 200 and 250 °C, respectively, and remain stable in polar organic solvents and a wide range of pH solutions. Under visible-light irradiation, CO<sub>2</sub> can be converted into syngas and HCOO<sup>-</sup> with  $V_{12}B_{18}-Co$  or  $V_{12}B_{18}-Ni$  as catalysts. The total amount of gaseous products and liquid products for  $V_{12}B_{18}-Co$  is up to 9.5 and 0.168 mmol g<sup>-1</sup> h<sup>-1</sup>.



Comparing with  $V_{12}B_{18}$ -Co, the yield of CO for  $V_{12}B_{18}$ -Ni declines by 1.8-fold, while that of HCOO<sup>-</sup> increases by 35%. The AQY of  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni is 1.1% and 0.93%, respectively. These values are higher than most of the reported POM materials under similar conditions. The density functional theory (DFT) calculations illuminate the active site of CO<sub>2</sub>RR and the reduction mechanism. This work provides new insights into the design of stable, high-performance, and low-cost photocatalysts for CO<sub>2</sub> reduction.

# 1. INTRODUCTION

Excessive carbon dioxide emissions from fossil fuel combustion have led to numerous energy and environmental problems.<sup>1–3</sup> Converting CO<sub>2</sub> into valuable fuels and chemical feedstocks through photochemical reduction is an appealing approach to promote CO<sub>2</sub> fixation and sustainable energy generation.<sup>4,5</sup> Two-electron-reduction products of syngas (made of CO and H<sub>2</sub>) and formic acid are important raw materials and liquid fuel in the organic industry or oxidized fuel cells.<sup>6,7</sup> Transition metals with multiple redox couples, which can facilitate electron transfer and overcome the unfavorable high-energy intermediates, have presented a unique activity toward CO<sub>2</sub> photoreduction.<sup>8–10</sup> It is worth noting that not only the reduction reactivity but also the kinds of products are strongly affected by the transition-metal sites.<sup>11,12</sup>

Currently, transition-metal- (such as Co, Ni, Zn, and Fe) modified polyoxometalates (POMs) have received increasing attention for their potential applications in various fields.<sup>13,14</sup> Especially, the properties of fast, reversible, and stepwise multiple-electron transfer without changing of structures endow POMs' highly catalytic activity for numerous redox reactions, such as CO<sub>2</sub> photoreduction.<sup>15–23</sup> Besides, the specific crystalline structures will help to understand the structure–activity relationship in photochemical CO<sub>2</sub> reduc-

tion, while the tunability in structures facilitates the modification of active centers and incorporation of functional groups to adjust the yield and selectivity in  $CO_2$  reduction.<sup>2,24–27</sup> However, most POM clusters have a major limitation in catalytic durability, as structural stability is the prerequisite for POM chemistry to be applied in any catalysis.<sup>28–30</sup>

Herein, two transition-metal-modified wheel-type vanadoborate clusters,  $[Co(en)_2]_6[V_{12}B_{18}O_{54}(OH)_6] \cdot 17H_2O$  $(V_{12}B_{18}-Co)$  and  $[Ni(en)_2]_6[V_{12}B_{18}O_{54}(OH)_6] \cdot 17H_2O$  $(V_{12}B_{18}-Ni)$ , were reported. Both of them have excellent thermal and chemical stabilities. Under visible-light irradiation,  $CO_2$  can be converted into syngas and HCOO<sup>-</sup> by  $V_{12}B_{18}-Co$ and  $V_{12}B_{18}-Ni$ . The syngas product (CO and H<sub>2</sub>) of  $V_{12}B_{18}-Co$ co reaches up to 9.5 mmol  $g^{-1}h^{-1}$  that is 2.7-fold higher than that of  $V_{12}B_{18}-Ni$ , while for the liquid products, the yield of  $V_{12}B_{18}-Co$  is 0.168 mmol  $g^{-1}h^{-1}$  that is lower than that of

Received: February 23, 2021





Figure 1. (a) Schematic representation of the  $V_6O_{18}$  cluster. (b) Ball-and-stick representation of the  $V_{12}O_{60}$  cluster connected by the  $B_{18}$  ring. (c) Ball-and-stick view of the whole structural arrangement of  $V_{12}B_{18}$ -Co showing the situation of six Co(en)<sub>2</sub> connected to the  $V_{12}B_{18}$  cluster. (d) Polyhedral representation of  $V_{12}B_{18}$ -Co.

 $V_{12}B_{18}$ –Ni, by 35%. The AQY of them is 1.1% and 0.93%, respectively. The value of  $V_{12}B_{18}$ –Co climbs to the top of the reported POM materials that are under similar conditions. The calculations of charge decomposition analysis (CDA) and density functional theory (DFT) illuminate the active site of  $CO_2RR$  and the reduction mechanism.

## 2. EXPERIMENTAL SECTION

**2.1.** Syntheses of  $V_{12}B_{18}$ -Co. NaVO<sub>3</sub> (0.085 g, 0.7 mmol), H<sub>3</sub>BO<sub>3</sub> (1.625 g, 0.026 mol), and Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.623 g, 2.5 mmol) were added to water (10 mL), the formed solution was stirred uniformly at room temperature for 2 h, and then ethylenediamine (en) (1 mL) was slowly added to the stirring solution. After that, the solution was transferred into a Teflon-lined reactor, heated at 160 °C for 60 h, and gradually cooled to room temperature. Red cubic crystals were obtained by ultrasound, washed with H<sub>2</sub>O, and dried in air (yield: ~40%, based on NaVO<sub>3</sub>). Elemental analysis (%) for [Co(en)<sub>2</sub>]<sub>6</sub>[V<sub>12</sub>B<sub>18</sub>O<sub>54</sub>(OH)<sub>6</sub>]·17H<sub>2</sub>O: Calcd: C, 9.14; H, 4.31; N, 10.65. Found: C, 9.13; H, 4.30; N, 10.64. IR (KBr, cm<sup>-1</sup>): 3259(w), 2890(w), 1642(m), 1396(s), 1353(s), 1066(s), 950(s), 792(m), 727(m), 663(m).

**2.2. Syntheses of V<sub>12</sub>B<sub>18</sub>–Ni.** The preparation of V<sub>12</sub>B<sub>18</sub>–Ni was similar to the method of V<sub>12</sub>B<sub>18</sub>–Co except for replacing cobalt acetate with nickel acetate (yield: ~40%, based on NaVO<sub>3</sub>). Elemental analysis (%) for  $[Ni(en)_2]_6[V_{12}B_{18}O_{54}(OH)_6]\cdot17H_2O$ : Calcd: C, 9.14; H, 4.32; N, 10.66. Found: C, 9.13; H, 4.31; N, 10.65. IR (KBr, cm<sup>-1</sup>): 3268(w), 2960(w), 1627(m), 1389(s), 1350(s), 1064(s), 962(s), 789(m), 724(m), 669(m).

**2.3.** Photocatalytic Reaction. 2.3.1. Photocatalytic Test. The experiment of photocatalytic reduction of carbon dioxide was performed in a 50 mL quartz tube with a cover and irradiated under a 300W xenon lamp with a 420 nm cut off filter. The reaction was kept at about 20  $^{\circ}$ C by condensate circulating water. Specifically, the as-prepared catalyst (1 mg) was dispersed in deionized water (1 mL), acetonitrile (4 mL), and triethanolamine (1 mL). After that, a

high-purity CO<sub>2</sub> gas was bubbled into the mixed solution for 15 min until the CO<sub>2</sub> concentration became saturated and the oxygen in the device was removed. After reacting under visible light ( $420 \le \lambda \le 780$  nm) for 3 h, the generated gases (CO and H<sub>2</sub>) were collected by a 1 mL syringe, then immediately tested, and analyzed by a GC-9800. To ensure data reliability, all photocatalytic experiments were repeated three times.

2.3.2. Isotopic Experiment. Isotope experiments were performed in a 50 mL quartz tube with a catalyst (1 mg), acetonitrile (4 mL), triethanolamine (1 mL), and water (1 mL) as the solvent. Before the photocatalytic reaction, <sup>13</sup>CO<sub>2</sub> (98%) gas was bubbled into the mixed solution for 20 min until the dissolved oxygen was removed completely. A 300W xenon lamp with a CUT420 filter ( $420 \le \lambda \le$ 780 nm) was used as the light source. After 3 h, the <sup>13</sup>C-labeled product was tested by a gas chromatography–mass spectrometer (GC-MS) and a 500 MHz nuclear magnetic resonance spectrometer (NMR), respectively.

## 3. RESULTS AND DISCUSSION

**3.1. Structural Description and Characterization.** Single-crystal X-ray diffraction reveals that  $V_{12}B_{18}$ —Co and  $V_{12}B_{18}$ —Ni are isostructural and crystallize in trigonal form with the  $R\overline{3}$  space group (Table S4). Therefore, only the crystal structure of  $V_{12}B_{18}$ —Co is described here. The asymmetric unit of  $V_{12}B_{18}$ —Co includes 1 Co ion, 2 V ions, 3 B ions, and 2 ethylenediamine ligands. Two V atoms have the same coordination environment bridged by five O atoms with square-pyramidal geometries, and six VO<sub>5</sub> square pyramids are edge-sharing to form a  $V_6O_{18}$  cluster (Figure 1a). Two  $V_6$  clusters are bridged by boron and oxygen atoms to form a  $V_{12}O_{60}$  cluster, as shown in Figure 1b. The bond lengths of V–O are in the range of 1.607–2.007 Å. Outside the  $V_{12}$  cluster, there is a  $B_{18}$  ring. B atoms in the  $B_{18}$  ring show two different coordination geometries. One type of B atom



Figure 2. PXRD patterns of  $V_{12}B_{18}$ —Co in different manual variable temperatures (a), solvents (b), and aqueous solutions of pH = 5-13 (c) and PXRD patterns of  $V_{12}B_{18}$ —Ni in different manual variable temperatures (d), solvents (e), and aqueous solutions of pH = 5-13 (f).

coordinates with four oxygen atoms and forms tetrahedral coordination with the B–O distance of 1.425-1.527 Å. Another type of B atom is connected to three oxygen atoms showing a triangular geometry with B–O lengths from 1.352 to 1.368 Å. As shown in Figures 1c and 1d, six cobalt atoms are modified on the outer ring of the V<sub>12</sub>B<sub>18</sub> cluster. Each Co cation is coordinated with four N atoms from two independent ethylenediamine ligands (Co–N 2.036–2.141 Å) and two O atoms with a distorted octahedral geometry (Co–O 2.08–2.26 Å).

The phase purities of V12B18-Co and V12B18-Ni are characterized by powder X-ray diffraction (PXRD) patterns (Figure S1). The PXRD patterns of the synthesized  $V_{12}B_{18}$ -Co and V<sub>12</sub>B<sub>18</sub>-Ni match well with the simulated patterns, indicating the synthetic samples are pretty pure. The catalysts are characterized by Fourier transform infrared (FTIR) spectroscopy using KBr pellets in the range of 4000-400 cm<sup>-1</sup> on a Nicolet 6700 FT/IR spectrophotometer (Figure S2). In the IR spectrum of  $V_{12}B_{18}$ –Co and  $V_{12}B_{18}$ –Ni, there are strong bands at 950 and 962 cm<sup>-1</sup> attributable to the V–O bond stretching.<sup>31</sup> Due to the symmetrical and asymmetrical stretching of V-O-V, there are strong peaks at 792, 727, and 663 cm<sup>-</sup> <sup>1</sup> for  $V_{12}B_{18}$ -Co and 789, 724, and 669 cm<sup>-1</sup> for V<sub>12</sub>B<sub>18</sub>-Ni.<sup>32</sup> In addition, two peaks located at 1350-1400 cm<sup>-1</sup> and 1060–1070 cm<sup>-1</sup> are ascribed to the B–O stretching of [BO<sub>3</sub>] and [BO<sub>4</sub>] units, respectively.<sup>33,34</sup> The peaks at 1650-1600 and 3250-3300 cm<sup>-1</sup> are the stretch of N-H.<sup>35</sup> The symmetric and asymmetric stretching of the C-H bond results in peaks at 2960 for  $V_{12}B_{18}$ -Ni and 2890 cm<sup>-1</sup> for  $V_{12}B_{18}$ -Co.<sup>36</sup> The light absorption capabilities of  $V_{12}B_{18}$ -Co and V<sub>12</sub>B<sub>18</sub>-Ni are studied by UV-vis absorption spectroscopy, which displays three intense absorption bands (Figure S3). The higher energy bands are at 233 (5.32 eV) and 312 nm (3.97 eV), which can be assigned to  $O \rightarrow V$  and  $O \rightarrow B$  charge transfers of the  $[V_{12}B_{18}]$  cluster. The weak absorption at 555 nm (2.23 eV) presumably arises from the d-d electronic

transition.  $^{37}$  In addition,  $V_{12}B_{18}-Co$  and  $V_{12}B_{18}-Ni$  clusters both absorb ultraviolet and visible light.

Bond valence sum (BVS) calculations (Tables S1 and S2) show the oxidation states of Co atoms of  $V_{12}B_{18}$ —Co and Ni atoms of  $V_{12}B_{18}$ —Ni are +2. The V and B atoms in  $V_{12}B_{18}$ —Co and  $V_{12}B_{18}$ —Ni are +4 and +3, respectively, which is consistent with X-ray photoelectron spectroscopy (XPS) (Figures S4 and S5). The peaks at 191.9 eV can be assigned to the B 1s signals of  $V_{12}B_{18}$ —Co and  $V_{12}B_{18}$ —Ni, indicating that the B species in the  $V_{12}B_{18}$ —Co and  $V_{12}B_{18}$ —Ni exist as  $B^{3+}$ .<sup>38</sup> The V 2p peak can be fitted with two peaks at 515.9 and 523.5 eV, which are assignable to  $V^{4+}$ .<sup>39</sup> The peaks located at 856.0 and 873.5 eV correspond to Ni<sup>2+</sup> (2p<sub>3/2</sub>) and Ni<sup>2+</sup> (2p<sub>1/2</sub>) of  $V_{12}B_{18}$ —Ni.<sup>40</sup> The weak peaks are located at approximately 802.5 and 789.7 eV, and the strong peaks located at 796.2 and 781.3 eV originate from the Co<sup>2+</sup> (2p<sub>1/2</sub>), Co<sup>2+</sup> (2p<sub>3/2</sub>), Co<sup>2+</sup> (2p<sub>1/2</sub>), and Co<sup>2+</sup> (2p<sub>3/2</sub>) spectra, respectively.<sup>41,42</sup>

Excellent thermal and chemical stabilities are crucial to catalytic applications. The superior thermal stability of V<sub>12</sub>B<sub>18</sub>-Co and V<sub>12</sub>B<sub>18</sub>-Ni is evidenced by the high decomposition temperature and variable-temperature powder X-ray diffraction (VT-PXRD). Thermogravimetric analyses (TGA) of V<sub>12</sub>B<sub>18</sub>-Co and  $V_{12}B_{18}$ -Ni were carried out, and the curve is shown in Figure S6. The TGA curve shows that the mass loss of  $V_{12}B_{18}$ -Co is 10.9% at 25-110 °C, which is mainly due to the free water molecules in the crystal, and the subsequent multistep weight loss at 218-420 °C is attributed to the decomposition of the ligand. Thus, we believe that V12B18-Co can be stabilized up to 200 °C. For V<sub>12</sub>B<sub>18</sub>-Ni, the TGA curve shows that the mass loss is divided into two steps, from 25 to 200 °C and 300 to 450 °C, and the corresponding mass loss is 9.8 and 8.4%, respectively. The former is due to the loss of physical water in the crystal, and the latter is attributed to the decomposition of the ligand. The thermal stability of V<sub>12</sub>B<sub>18</sub>-Co and V<sub>12</sub>B<sub>18</sub>-Ni has been further explored by the manual VT-PXRD measurements.<sup>43</sup> The manual VT-PXRD patterns



Figure 3. (a) Amount of CO,  $H_2$ , and  $HCOO^-$  produced from  $V_{12}B_{18}$ -Co,  $V_{12}B_{18}$ -Ni, and  $V_{12}B_{18}$  under visible-light irradiation. Recyclability of  $V_{12}B_{18}$ -Co (b) and  $V_{12}B_{18}$ -Ni (c) photocatalysts in five consecutive runs. (d) GC-mass result of the isotopic experiment under a  $^{13}CO_2$  atmosphere of  $V_{12}B_{18}$ -Co and (e) the  $^{13}C$  NMR and  $^{12}C$  NMR spectra of the liquid phase after catalysis. PXRD patterns of  $V_{12}B_{18}$ -Co (f) and  $V_{12}B_{18}$ -Ni (g) for simulated and after catalysis, presenting its stable structure during the reaction.

from 100 to 200 °C and 100 to 250 °C at intervals of 50 °C of crystals  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni, respectively, are matched well with the simulated one, which suggests that these two catalysts retain excellent thermal stability (Figures 2a and 2d). For chemical stability, we studied the stability of the sample in different organic solvents and aqueous solutions with different pH values. The PXRD patterns of  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni after 12 h of immersion in different solutions remained similar to the simulated PXRD patterns, which illustrate these two crystal samples possess good chemical stability in polar solvents, acids, and bases (Figures 2b,e and 2c,f).

3.2. Photochemical CO<sub>2</sub> Reduction Properties. Photocatalytic carbon dioxide reduction activity of V<sub>12</sub>B<sub>18</sub>-Co and  $V_{12}B_{18}$ -Ni was studied under a pure CO<sub>2</sub> atmosphere in the solution containing triethanolamine (TEOA) as a sacrificial reagent and  $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$  as a photosensitizer. Under visible-light irradiation, gaseous products of syngas (CO and  $H_2$ ) and liquid products of formic acid were detected for both V<sub>12</sub>B<sub>18</sub>-Co and V<sub>12</sub>B<sub>18</sub>-Ni. After 3 h of illumination, the amount of CO and  $H_2$  for  $V_{12}B_{18}$ -Co reaches 5.7 and 3.8 mmol  $g^{-1} h^{-1}$ , respectively (Figure 3a). The selectivity of CO over  $H_2$  is 60%. For the liquid HCOO<sup>-</sup>, the yield is 0.168 mmol  $g^{-1}$  h<sup>-1</sup> (Figure 3a). With V<sub>12</sub>B<sub>18</sub>-Ni as a catalyst, the generation amount of CO, H<sub>2</sub>, and HCOO<sup>-</sup> is 3.2, 0.3, and 0.260 mmol  $g^{-1} h^{-1}$ , respectively, under the same reaction time (Figure 3a). Comparing with that of  $V_{12}B_{18}$ -Co, the total gas reduction product declines by 2.7-fold, but the selectivity of CO rises to 91.43%. The high selectivity of CO in Ni-based materials over Co-based ones has been reported, which may be ascribed to stronger CO<sub>2</sub> adsorption energy and weaker H<sub>2</sub>O adsorption energy.<sup>11</sup> These results unambiguously illuminate the transition metals in these two POMs play an important role in CO<sub>2</sub> photoreduction. To further demonstrate this issue, the kernel of  $V_{12}B_{18}$ -Co without transition metals, that is  $V_{12}B_{18}$  $([V_{12}B_{18}O_{54}(OH)_6])$ ,<sup>44</sup> was synthesized. When it was used as a catalyst under the same CO<sub>2</sub> reduction conditions, only a small

amount of CO (0.47 mmol  $g^{-1}$  h<sup>-1</sup>) and H<sub>2</sub> (0.24 mmol  $g^{-1}$  h<sup>-1</sup>) was detected, and almost no HCOO<sup>-</sup> was detected (Figure 3a). In contrast to V<sub>12</sub>B<sub>18</sub>-Co and V<sub>12</sub>B<sub>18</sub>-Ni, the gas products of V<sub>12</sub>B<sub>18</sub> decrease by an order of magnitude. These results suggest the transition-metal sites might be active centers for CO<sub>2</sub> photoreduction.

The apparent quantum yield (AQY) of products could evaluate the utilization efficiency of one material to the irradiated light in photocatalysis. The AQY of  $V_{12}B_{18}$ —Co and  $V_{12}B_{18}$ —Ni is estimated at the wavelength at 420 nm (blue LED) and calculated based on eq S1 presented in the Supporting Information, and the value is up to 1.1% for  $V_{12}B_{18}$ —Co and 0.93% for  $V_{12}B_{18}$ —Ni. The value of  $V_{12}B_{18}$ —Co climbs to the top of the reported POMs that are under similar conditions (Table S3). These results reflect the outstanding light utilization ability of transition-metal-modified vanadoborate clusters in photocatalytic CO<sub>2</sub> reduction.

To detect the origin of the products, isotope tracer analysis is performed with <sup>13</sup>CO<sub>2</sub>. The gas products produced by the chemistry are analyzed by gas chromatography-mass spectrometry (GC-MS), and the liquid product is analyzed by <sup>13</sup>C NMR spectroscopy. The signal at m/z = 29 is observed rather than at m/z = 28 for both V<sub>12</sub>B<sub>18</sub>-Co and V<sub>12</sub>B<sub>18</sub>-Ni as catalysts (Figure 3d and Figure S7), verifying that the CO<sub>2</sub> molecules in these systems are the sources of generated CO. The results of <sup>13</sup>C NMR spectroscopy present the peaks at 164.8, 160.6, and 159.3 ppm (Figure 3e and Figure S8), which are determined to be H<sup>13</sup>COO<sup>-</sup>, <sup>13</sup>CO<sub>3</sub><sup>2-</sup>, and H<sup>13</sup>CO<sub>3</sub><sup>-</sup>, respectively, revealing HCOO<sup>-</sup> also originating from CO<sub>2</sub>.<sup>45</sup>

As photocatalytic stability is crucial for practical application, meanwhile, the stability of POM under photocatalytic CO<sub>2</sub> reduction has been a huge challenge. It is particularly important to investigate the stability of  $V_{12}B_{18}$ –Co and  $V_{12}B_{18}$ –Ni in photocatalysis. Recycling experiments were performed under the supply of fresh [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in each round. Five cyclic experiments (Figure 3b,c) show no pubs.acs.org/IC

entry	$V_{12}B_{18}$ -Co TON <sub>CO</sub> <sup>b</sup>	$V_{12}B_{18}$ -Co TON(H <sub>2</sub> ) <sup>c</sup>	$V_{12}B_{18}$ -Co TON <sub>HCOOH</sub> <sup>d</sup>	$V_{12}B_{18}$ -Ni TON <sub>CO</sub> <sup>b</sup>	$V_{12}B_{18}$ -Ni TON $(H_2)^c$	$V_{12}B_{18}$ -Ni TON <sub>HCOOH</sub> <sup>d</sup>
1	47.77	32.39	1.4	26.68	2.51	2.22
2 <sup>e</sup>	3.72	1.48	trace	3.72	1.48	trace
3 <sup>f</sup>	n.d.	n.d.	trace	n.d.	n.d.	trace
4 <sup>g</sup>	n.d.	n.d.	trace	n.d.	n.d.	trace
5 <sup>h</sup>	n.d.	n.d.	trace	n.d.	n.d.	trace
6 <sup><i>i</i></sup>	n.d.	n.d.	trace	n.d.	n.d.	trace
7 <sup>j</sup>	6.68	6.4	8.28	6.2	1.82	0.49

Table 1	1.	Various	Experimental	Conditions	of V	$V_{12}B_{18} - 0$	Co and	$V_{12}B_{18}$	–Ni
---------	----	---------	--------------	------------	------	--------------------	--------	----------------	-----

<sup>*a*</sup>Conditions:  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2\cdot 6\text{H}_2\text{O} (7 \text{ mg}), V_{12}B_{18}-\text{Co or } V_{12}B_{18}-\text{Ni} (1 \text{ mg}), \text{acetonitrile } (4 \text{ mL}), \text{TEOA} (1 \text{ mL}), \text{H}_2\text{O} (1 \text{ mL}), \text{CO}_2 (1 \text{ atm}), \lambda \geq 420 \text{ nm}, 20 ^{\circ}\text{C}, 3 \text{ h}.$  <sup>*b*</sup>Turnover number  $(\text{mol}_{\text{CO}}/\text{mol}_{\text{catalyst}})$ . <sup>*c*</sup>Turnover number  $(\text{mol}_{\text{H}_2}/\text{mol}_{\text{catalyst}})$ . <sup>*d*</sup>Turnover number  $(\text{mol}_{\text{HCOOH}})/(\text{mol}_{\text{catalyst}})$ . <sup>*c*</sup>Without the catalyst. <sup>*f*</sup>Without  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2\cdot 6\text{H}_2\text{O}$ . <sup>*g*</sup>Without TEOA. <sup>*h*</sup>In the dark. <sup>*i*</sup>Without CH<sub>3</sub>CN. <sup>*j*</sup>Without H<sub>2</sub>O.



Figure 4. (a) Charge decomposition analysis (CDA) of  $V_{12}B_{18}$ -Co. The value represents the charge transfer amount. (b) Calculated free energy diagram by the CO<sub>2</sub> conversion to  $V_{12}B_{18}$ -Co.

noticeable decline of CO, H<sub>2</sub>, and HCOO<sup>-</sup> in each cycle. In addition, PXRD patterns and IR spectra for  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni after the photocatalysis experiment are nearly the same as that of the fresh sample (Figure 3f,g and Figures S9 and S10). These results confirm that  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni are pretty stable during the photocatalytic reduction of carbon dioxide.

In order to illuminate the importance of each component in the CO<sub>2</sub> photocatalytic reduction system, a series of reference experiments are conducted and summarized in the results in Table 1. According to Table 1, we found that in the absence of  $V_{12}B_{18}$ -Co or  $V_{12}B_{18}$ -Ni (entry 2, Table 1), the turnover number decreases strongly to 5.2, suggesting the POM might be a cocatalyst in the photocatalysis. Without  $[Ru(bpy)_3]Cl_2$ (entry 3, Table 1) or TEOA (entry 4, Table 1) in the photocatalytic system, no CO or H<sub>2</sub> was detectable, demonstrating [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as a photosensitizer and TEOA as a sacrificial reagent are vital to the reduction. When the system is in the dark, no gas or liquid product was detected (entry 5, Table 1), indicating that the  $CO_2$  reduction reaction is powered by light. It is found that the reaction medium has a sharp influence on the catalytic effect. When only water is used as the reaction medium, the reaction does not occur (entry 6, Table 1). When only  $CH_3CN$  is employed as the reaction medium, reduction products are detected, but the amount is quite lower than that with CH<sub>3</sub>CN and water as the medium. These results illuminate CH<sub>3</sub>CN as the favorable medium for reducing carbon dioxide (entry 7, Table 1), and H<sub>2</sub>O might be the crucial donor of H protons.

3.3. Mechanism for Photocatalytic CO<sub>2</sub> Reduction. To reveal the rooted reasons behind the high activity of CO<sub>2</sub> photoreduction, the energy level of the catalysts is analyzed. The optical band gap  $(E_g)$  was measured by UV-vis diffuse reflectance spectroscopy and Tauc plots of  $(\alpha h \nu)^{1/2}$  versus photon energy  $(h\nu)$ . The values of  $E_{\rm g}$  evaluated from the absorption edge are 1.42 eV for V<sub>12</sub>B<sub>18</sub>-Co and 1.26 eV for  $V_{12}B_{18}$ -Ni (Figure S11). Meanwhile, their valence band (VB) energy  $(E_{VB})$  was examined through the VB XPS spectrum (Figure S12), and the  $E_{VB}$  of  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni is 0.28 and 0.62 eV, respectively. The conduction band (CB) energy  $(E_{CB})$  of  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni was calculated by the formula  $(E_{CB} = E_{VB}-E_g)$ ,<sup>46</sup> and the values of  $E_{CB}$  for  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni are determined to be -1.14 eV and -0.64 eV (Table S5). The  $E_{CB}$  of  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni is higher than the redox potential of  $E_{(CO_2/CO)} = -0.52$  V vs NHE<sup>47</sup> and  $E_{(CO,/HCOO^-)} = -0.61$  V vs NHE,<sup>48</sup> revealing that the transition-metal-modified VB-based POMs are a suitable catalyst for converting CO<sub>2</sub> into high-yield CO and HCOO<sup>-</sup>. The exhibited high  $E_{CB}$  value for  $V_{12}B_{18}$ -Co rather than V<sub>12</sub>B<sub>18</sub>-Ni may contribute to the superior catalytic activity of V<sub>12</sub>B<sub>18</sub>-Co. According to the previous literature, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> photosensitizer were 1.24 and -1.25 eV (vs NHE).<sup>49</sup> Since the  $E_{CB}$  value of -1.14 eV (vs NHE) for  $V_{12}B_{18}$ -Co and -0.64 eV (vs NHE) for  $V_{12}B_{18}$ -Ni is lower than that of the LUMO energy levels of  $[Ru(bpy)_3]Cl_2$ , the electrons on  $[Ru(bpy)_3]Cl_2$  preferentially transfer to the transition-metal-modified VB-based POMs.

Next, in order to determine the active site of CO<sub>2</sub>RR, the charge decomposition analysis (CDA) was carried out using Multiwfn3.8,<sup>50</sup> taking  $V_{12}B_{18}$ -Co as the example, and the results are summarized in Figure 4a. CDA calculation results show that the transfer of the injected electrons from the  $C_2H_4(NH_2)_2$  (en) ligand to  $Co^{2+}$  is favorable, with a number of 2.6853. Meanwhile, almost no electrons flow back to the en ligand. These processes are consistent with the classical chemical theory that the electrons of the coordination bond are contributed to by a pure ligand.<sup>51</sup> It is unfavorable for the electrons to continue to transfer from the Co<sup>2+</sup> to the inner  $V_{12}B_{18}$  core. It is worth noting that the amount of charge transferred from en to the inner V<sub>12</sub>B<sub>18</sub> core is very small and can be ignored. Therefore, it suggests that the photoinduced electrons from the photosensitizer move to the en ligand and then transfer to  $Co^{2+}$  instead of the  $V_{12}B_{18}$  core, so  $Co^{2+}$ probably serves as the active site of CO<sub>2</sub>RR.

Further, the deep understanding of the catalytic mechanism of CO<sub>2</sub>RR is revealed by density functional theory (DFT) calculations, and  $V_{12}B_{18}$ -Co is also taken as an example. Under light excitation, the adsorption energy of  $\text{CO}_2$  on V<sub>12</sub>B<sub>18</sub>-Co is -0.43 eV. The first step of hydrogenation of CO<sub>2</sub> can produce both HCOO\* and COOH\* intermediates as the proton–electron pairs  $(H^+ + e^-)$  can attack both C and O atoms of CO<sub>2</sub>. As can be seen from Figure 4b, the  $\Delta G$  (-1.06 eV) for the generation of HCOO\* from attacking the C atom is significantly lower than that for COOH\* (0.61 eV). However, the  $\Delta G$  for the hydrogenation process of HCOO\*  $+ e^- + H^+ \rightarrow HCOOH^*$  is very large (1.38 eV), which is thermodynamically unfavorable (the gray lines in Figure 4b). For COOH\* hydrogenation, the second proton-electron pair can either attack the O atom to obtain  $CO^* + H_2O$  (1) or attack the C atom to produce the HCOOH\* intermediate, with a  $\Delta G$  of -1.10 eV and -0.29 eV, respectively. It indicates that the CO<sub>2</sub>RR in the present work is more inclined to produce CO\*, which is consistent with the experimental result that the CO yield is much higher than that of HCOOH. The subsequent desorption processes of CO\* and HCOOH\* obtain CO and HCOOH products, respectively, leaving the catalyst for the next catalytic cycle. In conclusion, the possible mechanism of VB-based POMs in the CO<sub>2</sub> photocatalytic system is illustrated in Figure 5. Under visible light, the ground state photosensitizer [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> stimulates the excited state, and then the electron sacrificial agent TEOA combines with it to form a reduced photosensitizer. Next, the electrons from the reduced photosensitizer transfer to the transition metals of VB-based POMs and trigger the CO<sub>2</sub> reduction reaction.

### 4. CONCLUSION

In summary, two isolated transition-metal-modified vanadoborate clusters,  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni, have been synthesized under hydrothermal conditions. Both of them possess good thermal and chemical stabilities in a wide range of pH's of the aqueous solutions and polar solvents. As catalysts for CO<sub>2</sub>RR,  $V_{12}B_{18}$ -Co shows high efficiency under visible light with the yield of syngas and HCOO<sup>-</sup> up to 9.5 and 0.168 mmol g<sup>-1</sup> h<sup>-1</sup>, while the corresponding yield for  $V_{12}B_{18}$ -Ni is 3.5 and 0.260 mmol g<sup>-1</sup> h<sup>-1</sup>. The AQY of  $V_{12}B_{18}$ -Co and  $V_{12}B_{18}$ -Ni is estimated to be 1.1% and 0.93%. The value of  $V_{12}B_{18}$ -Co climbs to the top of the reported POM materials which are under similar conditions. The CDA suggests that transition metal is used as the active site of CO<sub>2</sub>RR, and DFT



Figure 5. Possible mechanism of the photocatalytic reduction of CO<sub>2</sub>.

calculations illustrate CO is the favorable product contrasted with HCOOH. This work provides novel insights into the design of stable, high-performance, and low-cost photocatalysts that convert carbon dioxide to high-value chemical feedstock.

#### ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00499.

Materials and methods, computational details, synthesis, characterization, and crystallographic data (PDF)

#### Accession Codes

CCDC 2060466–2060467 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## AUTHOR INFORMATION

#### **Corresponding Authors**

- Chun-Yi Sun Key Laboratory of Polyoxometalate Science of Ministry of Education, School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China; Email: suncy009@nenu.edu.cn
- Xin-Long Wang Key Laboratory of Polyoxometalate Science of Ministry of Education, School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China;
   orcid.org/0000-0002-5758-6351; Email: wangxl824@ nenu.edu.cn
- Li-Kai Yan Key Laboratory of Polyoxometalate Science of Ministry of Education, School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China; orcid.org/0000-0002-1352-4095; Email: yanlk924@ nenu.edu.cn

# Authors

Xiang Yu – Key Laboratory of Polyoxometalate Science of Ministry of Education, School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China

- Cong-Cong Zhao Key Laboratory of Polyoxometalate Science of Ministry of Education, School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China
- Jian-Xia Gu Key Laboratory of Polyoxometalate Science of Ministry of Education, School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China
- Hai-Yan Zheng Key Laboratory of Polyoxometalate Science of Ministry of Education, School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China
- Min Sun Key Laboratory of Polyoxometalate Science of Ministry of Education, School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China
- Zhong-Min Su Key Laboratory of Polyoxometalate Science of Ministry of Education, School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China; Jilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry, School of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun, Jilin 130022, P. R. China;
  orcid.org/0000-0002-3342-1966

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.1c00499

# Author Contributions

<sup>§</sup>X.Y. and C.-C.Z. contributed equally.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was financially supported by the NSFC of China (Nos. 21971032, 21801038, 21771035), the Fundamental Research Funds for the Central Universities (Nos. 2412016KJ041, 2412019QD009), and the Jilin Provincial Department of Science and Technology (No. 20190103018JH).

### REFERENCES

(1) Dalle, K. E.; Warnan, J.; Leung, J. J.; Reuillard, B.; Karmel, I. S.; Reisner, E. Electro- and Solar-Driven Fuel Synthesis with First Row Transition Metal Complexes. *Chem. Rev.* **2019**, *119*, 2752–2875.

(2) Dong, L. Z.; Zhang, L.; Liu, J.; Huang, Q.; Lu, M.; Ji, W. X.; Lan, Y. Q. Stable Heterometallic Cluster-Based Organic Framework Catalysts for Artificial Photosynthesis. *Angew. Chem., Int. Ed.* **2020**, *59*, 2659–2663.

(3) Dou, Y. B.; Zhou, A. W.; Yao, Y. C.; S, Y. L.; Li, J.-R.; Zhang, W. J. Suppressing hydrogen evolution for high selective CO<sub>2</sub> reduction through surface-reconstructed heterojunction photocatalyst. *Appl. Catal.*, B **2021**, 286, 119876.

(4) Zang, D.; Li, Q.; Dai, G.; Zeng, M.; Huang, Y.; Wei, Y. Interface engineering of Mo<sub>8</sub>/Cu heterostructures toward highly selective electrochemical reduction of carbon dioxide into acetate. *Appl. Catal., B* **2021**, *281*, 119426.

(5) Zhang, H. X.; Hong, Q. L.; Li, J.; Wang, F.; Huang, X.; Chen, S.; Tu, W.; Yu, D.; Xu, R.; Zhou, T.; Zhang, J. Isolated Square-Planar Copper Center in Boron Imidazolate Nanocages for Photocatalytic Reduction of  $CO_2$  to CO. *Angew. Chem., Int. Ed.* **2019**, *58*, 11752–11756.

(6) Zhou, J.; Wu, H.; Sun, C. Y.; Hu, C. Y.; Wang, X. L.; Kang, Z. H.; Su, Z. M. Ultrasmall C-TiO<sub>2-x</sub> nanoparticle/g-C<sub>3</sub>N<sub>4</sub> composite for CO<sub>2</sub> photoreduction with high efficiency and selectivity. *J. Mater. Chem. A* **2018**, *6*, 21596–21604.

(7) Xu, J.; Li, X.; Liu, W.; Sun, Y.; Ju, Z.; Yao, T.; Wang, C.; Ju, H.; Zhu, J.; Wei, S.; Xie, Y. Carbon Dioxide Electroreduction into Syngas Boosted by a Partially Delocalized Charge in Molybdenum Sulfide Selenide Alloy Monolayers. *Angew. Chem., Int. Ed.* **2017**, *56*, 9121–9125.

(8) Ettedgui, J.; Yael, D.-P.; Lev, W.; Ronny, N. Photoreduction of Carbon Dioxide to Carbon Monoxide with Hydrogen Catalyzed by a Rhenium(I) Phenanthroline-Polyoxometalate Hybrid Complex. *J. Am. Chem. Soc.* **2011**, *133*, 188–190.

(9) Hong, D. C.; Kawanishi, T. K. Y.; Tsukakoshi, Y. T.; Hiroaki, K. T.; Ishizuka, T. Y.; Kojima, T. K. H. K. Efficient Photocatalytic  $CO_2$ Reduction by a Ni(II)Complex Having Pyridine Pendants through Capturing a  $Mg^{2+}$  Ion as a Lewis-Acid Cocatalyst. *J. Am. Chem. Soc.* **2019**, 141, 20309–20317.

(10) Zhao, J.; Wang, Q.; Sun, C. Y.; Zheng, T. T.; Yan, L. K.; Li, M. T.; Shao, K. Z.; Wang, X. L.; Su, Z. M. A hexanuclear cobalt metalorganic framework for efficient  $CO_2$  reduction under visible light. *J. Mater. Chem. A* **2017**, *5*, 12498–12505.

(11) Han, B.; O, X.; Deng, Z.; Song, Y.; Tian, C.; Deng, H.; Xu, Y. J.; Lin, Z. Nickel Metal-Organic Framework Monolayers for Photoreduction of Diluted  $CO_2$ : Metal-Node-Dependent Activity and Selectivity. *Angew. Chem., Int. Ed.* **2018**, *57*, 16811–16815.

(12) Zhang, D.; Liu, T.; An, C.; Liu, H.; Wu, Q. Preparation of vanadium-substituted polyoxometalate doped carbon nitride hybrid materials POM/g- $C_3N_4$  and their photocatalytic oxidation performance. *Mater. Lett.* **2020**, *262*, 126954.

(13) Guo, L. Y.; Jagodic, M.; Zeng, S. Y.; Wang, Z.; Shi, Z. Q.; Wang, X. P.; Tung, C. H.; Sun, D. pH-Controlled assembly of two novel Dawson-sandwiched clusters involving the in situ reorganization of trivacant alpha- $[P_2W_{15}O_{56}]$ <sup>(12-)</sup> into divacant alpha- $[P_2W_{16}O_{57}]$ -(<sup>8-)</sup>. Dalton Trans. **2016**, 45, 8404–8411.

(14) Wang, M.-Y.; Ma, R.; He, L.-N. Polyoxometalate-based ionic liquids-promoted  $CO_2$  conversion. *Sci. China: Chem.* **2016**, *59*, 507–516.

(15) Du, J.; Lang, Z.-L.; Ma, Y.-Y.; Tan, H.-Q.; Liu, B.-L.; Wang, Y.-H.; Kang, Z.-H.; Li, Y.-G. Polyoxometalate-based electron transfer modulation for efficient electrocatalytic carbon dioxide reduction. *Chem. Sci.* **2020**, *11*, 3007–3015.

(16) Lei, J.; Yang, J.-J.; Liu, T.; Yuan, R.-M.; Deng, D.-R.; Zheng, M.-S.; Chen, J.-J.; Cronin, L.; Dong, Q.-F. Tuning Redox Active Polyoxometalates for Efficient Electron-Coupled Proton-Buffer-Mediated Water Splitting. *Chem. - Eur. J.* **2019**, *25*, 11432–11436.

(17) MacDonald, L.; McGlynn, J. C.; Irvine, N.; Alshibane, I.; Bloor, L. G.; Rausch, B.; Hargreaves, J. S. J.; Cronin, L. Using earth abundant materials for the catalytic evolution of hydrogen from electron-coupled proton buffers. *Sustain Energ Fuels.* **2017**, *1*, 1782–1787.

(18) Sullivan, K. P.; Wieliczko, M.; Kim, M.; Yin, Q.; Collins-Wildman, D. L.; Mehta, A. K.; Bacsa, J.; Lu, X.; Geletii, Y. V.; Hill, C. L. Speciation and Dynamics in the  $[Co_4V_2W_{18}O_{68}]^{10-}/Co(II)aq/CoO_x$  Catalytic Water Oxidation System. *ACS Catal.* **2018**, *8*, 11952–11959.

(19) Wang, M.-Y.; Song, Q.-W.; Ma, R.; Xie, J.-N.; He, L.-N. Efficient conversion of carbon dioxide at atmospheric pressure to 2-oxazolidinones promoted by bifunctional Cu(ii)-substituted poly-oxometalate-based ionic liquids. *Green Chem.* **2016**, *18*, 282–287.

(20) Gumerova, N. I.; Rompel, A. Polyoxometalates in solution: speciation under spotlight. *Chem. Soc. Rev.* **2020**, *49*, 7568–7601.

(21) Liu, R. J.; Zhang, G. J.; Cao, H. B.; Zhang, S. J.; Xie, Y. B.; Haider, A.; Kortz, U.; Chen, B. H.; Dalal, N. S.; Zhao, Y. S.; Zhi, L. J.; Wu, C.-X.; Yan, L.-K.; Su, Z. M.; Keita, B. Enhanced proton and electron reservoir abilities of polyoxometalate grafted on graphene for high-performance hydrogen evolution. *Energy Environ. Sci.* **2016**, *9*, 1012–1023.

(22) Han, X. B.; Li, Y. G.; Zhang, Z. M.; Tan, H. Q.; Lu, Y.; Wang, E. B. Polyoxometalate-based nickel clusters as visible light-driven water oxidation catalysts. *J. Am. Chem. Soc.* **2015**, *137*, 5486–5493. (23) Benseghir, Y.; Lemarchand, A.; Duguet, M.; Mialane, P.; Gomez-Mingot, M.; Roch-Marchal, C.; Pino, T.; Ha-Thi, M. H.; Haouas, M.; Fontecave, M.; Dolbecq, A.; Sassoye, C.; Mellot-Draznieks, C. Co-immobilization of a Rh Catalyst and a Keggin Polyoxometalate in the UiO-67 Zr-Based Metal-Organic Framework:

In Depth Structural Characterization and Photocatalytic Properties for CO<sub>2</sub> Reduction. J. Am. Chem. Soc. **2020**, 142, 9428–9438.

(24) Cai, L. X.; Li, S. C.; Yan, D. N.; Zhou, L. P.; Guo, F.; Sun, Q. F. Water-Soluble Redox-Active Cage Hosting Polyoxometalates for Selective Desulfurization Catalysis. *J. Am. Chem. Soc.* **2018**, *140*, 4869–4876.

(25) Shi, H. F.; Yu, Y. C.; Zhang, Y.; Feng, X. J.; Zhao, X. Y.; Tan, H. Q.; Khan, S. U.; Li, Y. G.; Wang, E. B. Polyoxometalate/ $TiO_2/Ag$  composite nanofibers with enhanced photocatalytic performance under visible light. *Appl. Catal., B* **2018**, *221*, 280–289.

(26) Ishizuka, T.; Ohkawa, S.; Ochiai, H.; Hashimoto, M.; Ohkubo, K.; Kotani, H.; Sadakane, M.; Fukuzumi, S.; Kojima, T. A supramolecular photocatalyst composed of a polyoxometalate and a photosensitizing water-soluble porphyrin diacid for the oxidation of organic substrates in water. *Green Chem.* **2018**, *20*, 1975–1980.

(27) Luo, Y.-H.; Dong, L.-Z.; Liu, J.; Li, S.-L.; Lan, Y.-Q. From molecular metal complex to metal-organic framework: The  $CO_2$  reduction photocatalysts with clear and tunable structure. *Coord. Chem. Rev.* **2019**, 390, 86–126.

(28) Zhou, W. H.; Li, N.; Cao, M. H.; Hu, C. W. Three-dimensional Ag/POM/Cu<sub>2</sub>O tricomponent nanohybrids with enhanced visiblelight photocatalytic activity. *Mater. Lett.* **2013**, *99*, 68–71.

(29) Li, N.; Liu, J.; Dong, B.-X.; Lan, Y.-Q. Polyoxometalate-Based Compounds for Photo/electrocatalytic Applications. *Angew. Chem., Int. Ed.* **2020**, *59*, 20779–20793.

(30) Bosch, G.-M.; Sarapulova, A.; Dsoke, S. Study of Polyoxometalates as Electrode Materials for Lithium-Ion Batteries: Thermal Stability Paves the Way to Improved Cycle Stability. *ChemElectroChem* **2021**, *8*, 656–664.

(31) Liu, X. X.; Zhang, D.; Li, L. Y.; Sun, X. J.; Zhang, L.; Yuan, H. M. Proton conduction in a new 3-D open-framework vanadoborate with an abundant hydrogen bond system. *Dalton Trans.* **2017**, *46*, 9103–9109.

(32) Zhou, J.; Liu, X.; Chen, R.; Xiao, H.-P.; Hu, F. L.; Zou, H. H.; Zhou, Y.; Liu, C.; Zhu, L. G. New 3-D polyoxovanadoborate architectures based on  $[V_{12}B_{18}O_{60}]^{16}$  clusters. *CrystEngComm* **2013**, 15, 5057–5063.

(33) Wang, Y.; Han, J.; Huang, J. B.; Yang, Z. H.; Pan, S. L.  $Al_8(BO_3)_4(B_2O_5)F_8$ : A F-containing aluminum borate featuring two types of isolated B-O groups. *Inorg. Chem.* **2020**, *59*, 810–817.

(34) An, L. T.; Zhou, J.; Xiao, H.-P.; Liu, X.; Zou, H. H.; Pan, C.-Y.; Liu, M. H.; Li, J. H. A series of new 3-D boratopolyoxovanadates containing five types of  $[K_xO_y]_n$  building units. *CrystEngComm* **2014**, *16*, 4236–4244.

(35) Wang, Z. J.; Sun, K.; Liang, C. Y.; Wu, L. N.; Niu, Z. Z.; Gao, J. M. Synergistic chemisorbing and electronic effects for efficient  $CO_2$  reduction using cysteamine-functionalized gold nanoparticles. *ACS Appl. Energy Mater.* **2019**, *2*, 192–195.

(36) Nam, D.; Huh, J.; Lee, J.; Kwak, J. H.; Jeong, H. Y.; Choid, K.; Choe, W. Cross-linking Zr-based metal-organic polyhedra *via* postsynthetic polymerization. *Chem. Sci.* **2017**, *8*, 7765–7771.

(37) Zhou, J.; Liu, X.; Hu, F. L.; Zou, H. H.; Li, R.; Li, X. J. One novel 3-D vanadoborate with unusual 3-D Na–O–Na network. *RSC Adv.* **2012**, *2*, 10937–10940.

(38) Yang, Y.; Zhang, C.; Huang, D.; Zeng, G.; Huang, J.; Lai, C.; Zhou, C.; Wang, W.; Guo, H.; Xue, W.; Deng, R.; Cheng, M.; Xiong, W. Boron nitride quantum dots decorated ultrathin porous g- $C_3N_4$ : Intensified exciton dissociation and charge transfer for promoting visible-light-driven molecular oxygen activation. *Appl. Catal., B* **2019**, 245, 87–99.

(39) Wang, M.; Che, Y. S.; Niu, C.; Dang, M. Y.; Dong, D. Effective visible light-active boron and europium Co-doped  $BiVO_4$  synthesized by sol-gel method for photodegradion of methyl orange. *J. Hazard. Mater.* **2013**, 262, 447–455.

(40) Xu, H.; Liu, X.-M.; Su, T.; Chen, W.-C.; Su, Z.-M. Two Ni/Cosubstituted sandwich-type germanomolybdates based on an unprecedented trivacant polyanion  $[\alpha$ -GeMo<sub>10</sub>O<sub>36</sub>]<sup>8–</sup>. *Dalton Trans.* **2020**, *49*, 977–982. (41) Chen, W. Y.; Han, B.; Tian, C.; Liu, X. M.; Liang, S. J.; Deng, H.; Lin, Z. MOFs-derived ultrathin holey  $Co_3O_4$  nanosheets for enhanced visible light  $CO_2$  reduction. *Appl. Catal., B* **2019**, *244*, 996–1003.

(42) Gulino, A.; Fiorito, G.; Fragalà, I. Deposition of thin films of cobalt oxides by MOCVD. J. Mater. Chem. 2003, 13, 861–865.

(43) Liu, J. W.; Fan, Y.-Z.; Li, X.; Wei, Z. W.; Xu, Y.-W.; Zhang, L.; Sun, C.-Y. A porous rhodium(III)-porphyrin metal-organic framework as an efficient and selective photocatalyst for CO<sub>2</sub> reduction. *Appl. Catal., B* **2018**, *231*, 173–181.

(44) Rijssenbeek, J. T.; Rose, D. J.; Haushalter, R. C.; Zubieta, J. Novel clusters of transition metals and main group oxides in the alkylamine/oxovanadium/borate system. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1008–1010.

(45) Guo, S.-H.; Qi, X.-J.; Zhou, H.-M.; Zhou, J.; Wang, X.-H.; Dong, M.; Zhao, X.; Sun, C.-Y.; Wang, X.-L.; Su, Z.-M. A bimetallic-MOF catalyst for efficient CO<sub>2</sub> photoreduction from simulated flue gas to value-added formate. *J. Mater. Chem. A* **2020**, *8*, 11712–11718.

(46) Guo, S.-H.; Zhou, J.; Zhao, X.; Sun, C.-Y.; You, S.-Q.; Wang, X.-L.; Su, Z.-M. Enhanced CO<sub>2</sub> photoreduction via tuning halides in perovskites. *J. Catal.* **2019**, *369*, 201–208.

(47) Prabhu, P.; Jose, V.; Lee, J. M. Heterostructured Catalysts for Electrocatalytic and Photocatalytic Carbon Dioxide Reduction. *Adv. Funct. Mater.* **2020**, *30*, 1910768.

(48) Li, X.; Yu, J.; Jaroniec, M.; Chen, X.-B. Cocatalysts for Selective Photoreduction of  $CO_2$  into Solar Fuels. *Chem. Rev.* **2019**, *119*, 3962–4179.

(49) Zhao, K.; Zhao, S. L.; Gao, C.; Qi, J.; Yin, H. J.; Wei, D.; Mideksa, M. F.; Wang, X.; Gao, Y.; Tang, Z.; Yu, R. Metallic Cobalt– Carbon Composite as Recyclable and Robust Magnetic Photocatalyst for Efficient CO<sub>2</sub> Reduction. *Small* **2018**, *14*, 1800762.

(50) Lu, T.; Chen, F. Multiwfn: a multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33, 580-592.

(51) Basolo, F.; Johnson, R. C. Coordination Chemistry. Study of Metal Complexes; 1964.