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## Efficient reduction of CO<sub>2</sub> and inhibition of hydrogen precipitation by polyoxometalate photocatalyst modified with the metal Mn†

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Photocatalytic reduction of CO<sub>2</sub> to chemical fuels is attractive for solving both the greenhouse effect and the energy crisis, but the key challenge is to design and synthesize photocatalysts with remarkable performance under visible light irradiation. Efficient catalytic carbon dioxide reduction (CO<sub>2</sub>RR) with light is considered a promising sustainable and clean approach to solve environmental problems. Herein, we found a new photocatalyst ((Mn(en)<sub>2</sub>)<sub>6</sub>[V<sub>12</sub>B<sub>18</sub>O<sub>54</sub>(OH)<sub>6</sub>]) (abbreviated as Mn<sub>6</sub>V<sub>12</sub>) based on the modifiability of polyoxometalates, in which Mn acts as a modifying unit to efficiently reduce CO<sub>2</sub> to CO and effectively inhibit the hydrogen precipitation reaction. This Mn modified polyoxometalate catalyst has a maximum CO generation rate of 4625.0 μmol g<sup>-1</sup> h<sup>-1</sup> and a maximum H<sub>2</sub> generation rate of 499.6 μmol g<sup>-1</sup> h<sup>-1</sup>, with a selectivity of 90.3% for CO generation and 9.7% for H<sub>2</sub> generation. This polyoxometalate photocatalyst can effectively reduce CO and inhibit the hydrogen precipitation reaction. It provides a new idea for the efficient photocatalytic carbon dioxide reduction (CO<sub>2</sub>RR) with polyoxometalate catalysts.

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### 1. Introduction

With the burning of large quantities of carbon containing fossil fuels and the anthropogenic emission of CO<sub>2</sub> into the atmosphere, the problem of global warming is worsening, threatening the safety of human society and the natural living environment.<sup>1</sup> The environmental problems brought about by the greenhouse effect, energy shortages and fossil energy consumption have become major challenges for the common future of mankind.<sup>2–4</sup> Therefore, Carbon Capture, Utilization and Storage (CCUS) is considered to be one of the most realistic ways to mitigate CO<sub>2</sub> concentration and slow down global warming.<sup>5,6</sup> Among various CO<sub>2</sub> utilization technologies, the conversion of CO<sub>2</sub> into chemicals and fuels through solar photocatalysis holds great promise for solving the global energy shortage and reducing the greenhouse effect.<sup>7,8</sup> The reduction of CO<sub>2</sub> to valuable hydrocarbon fuels also offers a

promising strategy for a carbon neutrality energy cycle.<sup>9</sup> The conversion of CO<sub>2</sub> into commercial chemicals and useful fuels, similar to that of plant photosynthesis by modelling plant photosynthesis, has a wide range of applications in the organic industry and in oxidation fuel cells.<sup>10–17</sup> This slows down energy consumption processes and reduces CO<sub>2</sub> concentrations.<sup>18,19</sup> The two-electron reduction products of syngas (from CO and H<sub>2</sub>) and formic acid are important raw materials and liquid fuels that are widely recognized as promising renewable fuels, which are also highly conducive to alleviating the energy crisis and climate change.<sup>20–22</sup>

Polyoxometalates (POMs) are a class of clusters formed by the coordination of early transition metals such as Mo, W, V, *etc.* in their highest oxidation states with oxygen atoms.<sup>23–26</sup> Which is an inorganic crystalline material with an oxygen-rich surface that has excellent physical and chemical properties.<sup>27</sup> It has been extensively studied in the fields of catalysis, medicine and materials science.<sup>28,29</sup> POMs can not only be structurally modified at the molecular level, but also have a good ability to carry and release electrons without changing their structural properties.<sup>30</sup> Driven by light, electrons in POMs can be excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the excited electrons are transferred from the valence band (VB) to the conduction band (CB) between the valence bands, resulting in the formation of electron–hole pairs in the valence and conduction bands, and the electron–hole pairs

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have a strong redox property and are used to catalyze the redox reactions.<sup>31,32</sup> These advantages give POMs unique properties for photocatalytic CO<sub>2</sub> reduction. In addition, the modifiability of the structure facilitates the introduction of functional groups and transition metals as active center to modulate the yield and selectivity of CO<sub>2</sub> reduction.<sup>33</sup> Transition metal modified polyoxometalates with redox pairs facilitate electron transfer and indicate structure–activity relationships in photochemical CO<sub>2</sub> reduction, exhibiting good photocatalytic activity for CO<sub>2</sub> reduction for more efficient solar-to-chemical energy conversion.<sup>34,35</sup> As a result, more and more attention has been paid to the potential applications in various fields. However, currently developed catalysts for photocatalytic CO<sub>2</sub> reduction still suffer from a number of limitations, including restricted use of visible light and poor selectivity.<sup>7</sup> Therefore, it is urgent and challenging to explore new transition metal modified polyoxometalate photocatalysts with high activity and selectivity.

In this paper, we present a new vanadium borate cluster based on modification with the metal Mn,<sup>36–38</sup> [Mn(en)<sub>2</sub>]<sub>6</sub>[V<sub>12</sub>B<sub>18</sub>O<sub>54</sub>(OH)<sub>6</sub>] (abbreviated as Mn<sub>6</sub>V<sub>12</sub>) can reduce CO<sub>2</sub> to CO with high efficiency and inhibit the hydrogen precipitation reaction effectively. The Mn modified vanadium borate clusters showed a maximum CO production rate of 4625.0 μmol g<sup>-1</sup> h<sup>-1</sup> and a maximum H<sub>2</sub> production rate of 499.6 μmol g<sup>-1</sup> h<sup>-1</sup>, with a selectivity of 90.3% for CO production and 9.7% for H<sub>2</sub> production. The high efficiency of CO reduction and the effective inhibition of hydrogen precipitation reaction were better than those of the same type of polyoxometalate catalysts. It provides a new way for the efficient photocatalytic carbon dioxide reduction (CO<sub>2</sub>RR) of transition metal modified polyoxometalate photocatalysts.



Jiangwei Zhang

Prof. Dr. Jiangwei Zhang is currently a “Steep plan High level Talents” Professor, “Grassland Talents” of Inner Mongolia Autonomous Region, Principle Investigator from College of Energy Material and Chemistry under leadership of Dean Academician Dongyuan Zhao, Inner Mongolia University. He received his Ph.D. from the Department of Chemistry, Tsinghua University (THU) in 2016. He has published 184

innovative publications with H-index = 45. Currently, His research focuses on the common key scientific issues “materials structure and reaction mechanism dynamically and precisely by visual detection and determination” and “Advanced characterization methodology and energy catalytic materials – Interdisciplinary”.

## 2. Experimental component

### 2.1. Synthesis of [Mn(en)<sub>2</sub>]<sub>6</sub>[V<sub>12</sub>B<sub>18</sub>O<sub>54</sub>(OH)<sub>6</sub>]

The synthesis was based on known literature and replaced with Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.623 g, 2.5 mmol), other reaction conditions were not changed.<sup>39</sup> Further details on the experimental methods and procedures are described in the ESI.†

### 2.2. Photocatalytic reactions

Prior to the reduction, 2 mL of triethanolamine (TEOA) was used as a sacrificial reagent, [Ru(bpy)<sub>3</sub>] Cl<sub>2</sub>·6H<sub>2</sub>O 11.6 mg as a photosensitizer, 8 mL of acetonitrile (CH<sub>3</sub>CN) and 2 mL of de-ionized water as solvents, and they were transferred into a 60 mL quartz glass reactor with a dispersed catalyst (2 mg) with a lid to carry out the photocatalytic reduction of CO<sub>2</sub> experiment. Afterwards, CO<sub>2</sub> gas was bubbled into the mixed solution for 15 min until the CO<sub>2</sub> concentration was saturated and oxygen was removed from the device to ensure that the system was carried out in a CO<sub>2</sub> atmosphere. The reaction was kept at ~20°C by condensing circulating water and irradiated under a 300 W xenon lamp with a 420 nm cut-off filter. After 1 h of illumination under visible light, the gaseous products (CO and H<sub>2</sub>) were collected with a 1 mL syringe and then immediately tested and analysed with a GC-2014C.

**XAFS measurements.** The X-ray absorption fine structure spectra V and Mn K-edge data were collected in transmission mode while the corresponding reference and the corresponding oxide reference sample were collected in transmission mode in TableXAFS-500A from Anhui Chuangpu Instrument Technology Co., Ltd. The sample were grinded and uniformly daubed on the special adhesive tape.

**XAFS analysis and results.** The acquired EXAFS data were processed according to the standard procedures using the ATHENA module of Demeter software packages.

The EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, the  $\chi(k)$  data of were Fourier transformed to real ( $R$ ) space using a hanging windows ( $dk = 1.0 \text{ \AA}^{-1}$ ) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of Demeter software packages

The following EXAFS equation was used:

$$\chi(k) = \sum_j \frac{N_j S_0^2 F_j(k)}{k R_j^2} \cdot \exp[-2k^2 \sigma_j^2] \cdot \exp\left[\frac{-2R_j}{\lambda(k)}\right] \cdot \sin[2kR_j + \phi_j(k)]$$

the theoretical scattering amplitudes, phase shifts and the photoelectron mean free path for all paths calculated.  $S_0^2$  is the amplitude reduction factor,  $F_j(k)$  is the effective curved-wave backscattering amplitude,  $N_j$  is the number of neighbours in the  $j^{\text{th}}$  atomic shell,  $R_j$  is the distance between the X-ray absorbing central atom and the atoms in the  $j^{\text{th}}$  atomic shell (backscattered),  $\lambda$  is the mean free path in  $\text{\AA}$ ,  $\phi_j(k)$  is the phase shift (including the phase shift for each shell and the

total central atom phase shift),  $\sigma_j$  is the Debye–Waller parameter of the  $j^{\text{th}}$  atomic shell (variation of distances around the average  $R_j$ ). The functions  $F_j(k)$ ,  $\lambda$  and  $\phi_j(k)$  were calculated with the *ab initio* code FEFF10. The additional details for EXAFS simulations are given below.

All fits were performed in the  $R$  space with  $k$ -weight of 2 while phase correction was also applied in the first coordination shell to make  $R$  value close to the physical interatomic distance between the absorber and shell scattered. The coordination numbers of model samples were fixed as the nominal values. While the  $S_0^2$ , internal atomic distances  $R$ , Debye–Waller factor  $\sigma^2$ , and the edge-energy shift  $\Delta$  were allowed to run freely.

**X-ray crystallography.** Data collections were performed by BL17B beamline of National Facility for Protein Science (NFPS), Shanghai Synchrotron Radiation Facility (SSRF) Shanghai. Data reduction, cell refinement and experimental absorption correction were performed with the software package of Bruker APEX5. The structures were solved by intrinsic phasing and refined against  $F^2$  by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. All the calculations were carried out by the program package of SHELX and Olex2 ver 1.2.10.

#### Crystal data and structure refinement for compound 1.

**Compound 1**  $[\text{Mn}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6]$ :  $\text{C}_{24}\text{H}_{96}\text{B}_{18}\text{Mn}_6\text{N}_{24}\text{O}_{60}\text{V}_{12}$ , trigonal, space group  $R\bar{3}$  (No. 148),  $a = b = 21.0608 \text{ \AA}$ ,  $c = 21.1268 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ,  $V = 8115.5 \text{ \AA}^3$ ,  $Z = 3$ , 3176 reflections measured,  $R_1 = 0.0640$ ,  $wR_2 = 0.0826$ .

CCDC 2324078 contains the supplementary crystallographic data for compound 1 respectively in this paper.†

## 3. Results and discussion

### 3.1. Catalyst structure

As shown in Fig. 1a and b,  $\text{Mn}_6\text{V}_{12}$  has a  $\text{B}_{18}\text{O}_{42}$  ring consisting of six  $\text{B}_3\text{O}_7$  ternary rings sharing oxygen atoms. The top of the ring consists of six  $\text{VO}_5$  quadrangular cones conjoined by the common side of the lid, and the bottom is two segments consisting of three  $\text{VO}_5$  quadrangular cones conjoined by the common side.<sup>40</sup> Overall there is a V12 cluster embedded in the B18 ring. In the  $[\text{B}_3\text{O}_7]$  unit, the B atom displays two different coordination geometries. Two B atoms are coordinated with four oxygen atoms to form a tetrahedral shape. One B atom is coordinated with three oxygen atoms to form a planar triangle. The oxygen atom on the periphery of the B18 ring is attached to the transition metal Mn and the ring is modified with six manganese ions. From the TEM image of  $\text{Mn}_6\text{V}_{12}$  (Fig. 1c), it is observed that  $\text{Mn}_6\text{V}_{12}$  is similar to spherical micron-sized plush clusters, and the plush edges are a lot of consisting of thin and long rod-like structures with a crystallographic spacing of  $d = 0.32 \text{ nm}$ . The extensive rod-like structure is supposed to be the active center of the cluster and serves to increase the active site.

In order to determine the valence and coordination structure of atoms at the atomic level, X-ray absorption fine structure (XAFS) measurements were performed.<sup>41,42</sup> The electronic structures and coordination environments of V and Mn in  $\text{Mn}_6\text{V}_{12}$  were analyzed using X-ray absorption spectroscopy (XAS), as well as Mn foil, MnO,  $\text{MnO}_2$ , MnPc, V foil, and  $\text{V}_2\text{O}_5$  as standard references. In Fig. 2a, X-ray measurements in terms of the K-edge of V in the absorption near edge structure

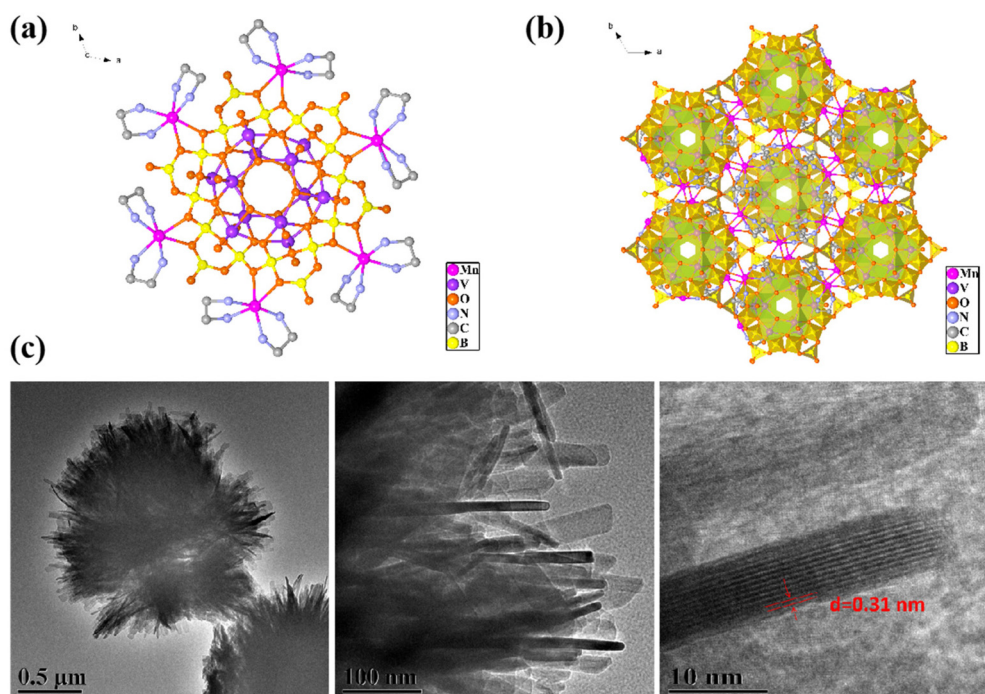
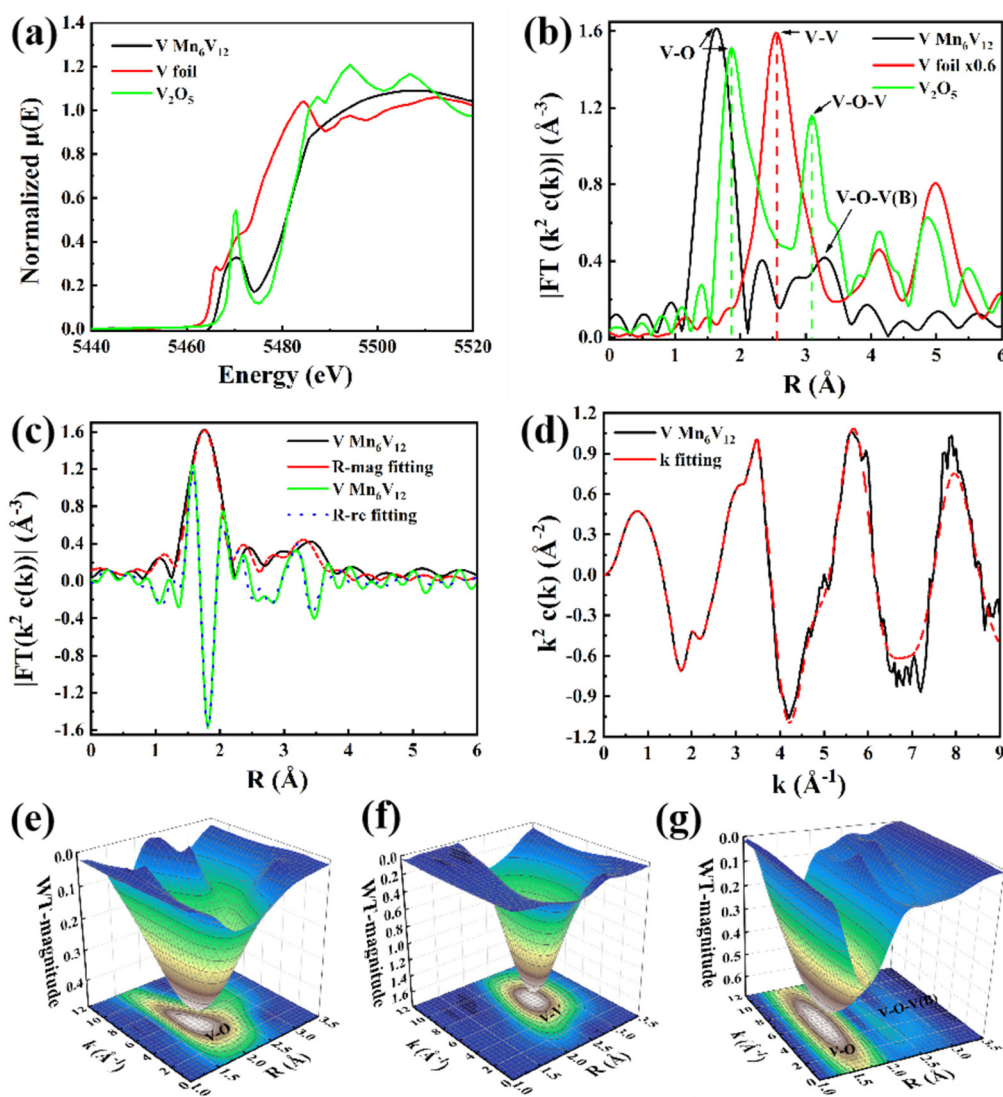


Fig. 1 (a) Schematic crystal structure of  $\text{Mn}_6\text{V}_{12}$ ; (b) crystal stacking diagram of  $\text{Mn}_6\text{V}_{12}$ ; (c) TEM image of  $\text{Mn}_6\text{V}_{12}$ .



**Fig. 2** (a) V K-edge normalized XANES spectra, (b) FT curves of V K-edge EXAFS spectra, (c) V K-edge EXAFS curve fitting at  $R$  space and  $q$  space, (d) V K-edge EXAFS curve fitting at  $k$  space, (e) wavelet transform EXAFS of  $V_2O_5$ , (f) Wavelet transform EXAFS of V foil, (g) wavelet transform EXAFS of  $Mn_6V_{12}$ .

(XANES) show that the absorption edge of  $Mn_6V_{12}$  is located between the absorption edges of V foil and  $V_2O_5$ .  $Mn_6V_{12}$  exhibits a V K-edge spectrum similar to that of  $V_2O_5$ , but the binding energy at the absorption edge of the V K-edge spectrum of  $Mn_6V_{12}$  is lower than that of  $V_2O_5$ , thus determining that the valence state of V is close to +5 and lower than +5. The leading edge peak at  $\sim 5470$  eV in Fig. 2a is attributed to the dipole-prohibited  $1s$  to  $3d$  electron jumps,<sup>43</sup> the decrease in the intensity of the leading edge peaks compared to  $V_2O_5$  indicates that the introduction of Mn atoms has resulted in an elevated local symmetry of  $Mn_6V_{12}$ . It is shown that  $Mn_6V_{12}$  is structurally stable around the V atom. The  $k^2$ -weighted Fourier transform EXAFS (FT-EXAFS) spectra (after phase correction) of standard V foil,  $V_2O_5$  and  $Mn_6V_{12}$  are shown in Fig. 2b. The corresponding specific fitting curves are shown in Fig. 2c and d, and the specific fitting parameters for  $Mn_6V_{12}$  on the V

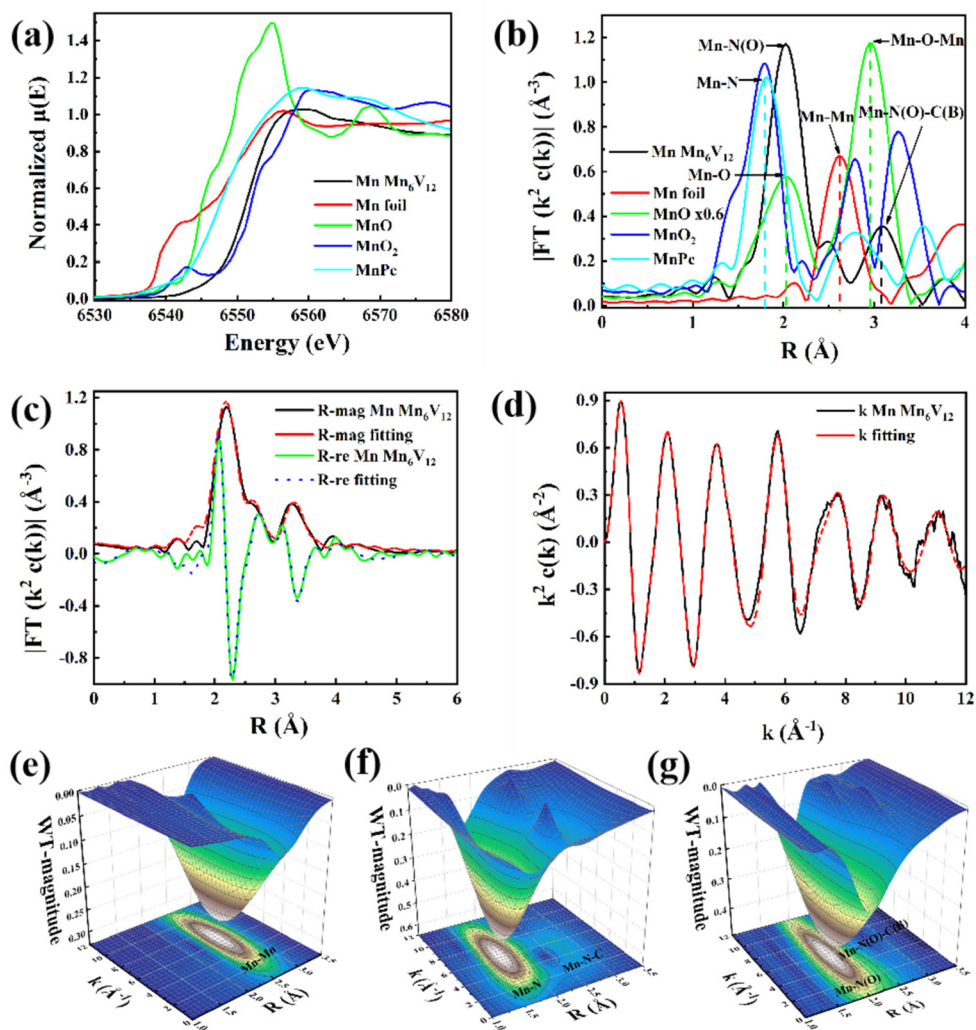
$k$ -side are shown in Table S1.† The absence of metal V–V scattering paths ( $2.55$  Å) in the V  $k$ -edge EXAFS spectrum of  $Mn_6V_{12}$  verifies the atomic dispersion of V (Fig. 2b). The first peak of  $Mn_6V_{12}$  is located at  $1.63$  Å, which is  $0.24$  Å shorter compared to the representative V–O coordination in  $V_2O_5$  ( $1.87$  Å). The peak of  $Mn_6V_{12}$  located at  $\sim 3.30$  Å is in the vicinity of the V–O–V of  $V_2O_5$  ( $3.10$  Å), which is broad and asymmetric, suggesting the presence of double coordination of V–O–V and V–O–B in  $Mn_6V_{12}$ , and in this way, further suggesting that due to the simultaneous presence of the two coordinating sites, there is a shortening of the V–O bond. The optimized model fitted well to the EXAFS spectra (Fig. 2c–d, and Table S1†), and the best-fit analysis clearly confirmed that the coordination numbers of V–O, V–O–B, and V–O–V were 5, 4, and 2, respectively. This means that the V center is connected to 5 O atoms, two of the V atoms are connected by 1 O atom

and the other 2 oxygen atoms are each connected to a B atom, a result that is consistent with the structure of the material. The wavelet transform (WT) (Fig. 2e–g) was applied to the  $k_2$ -weighted EXAFS data to further investigate the local environment of V on  $\text{Mn}_6\text{V}_{12}$ . As shown in Fig. 2g, two peaks exist for  $\text{Mn}_6\text{V}_{12}$  at 1.5 Å–1.75 Å and 2.25 Å–2.5 Å, corresponding to V–O and V–O–V(B). Compared to the WT data for  $\text{V}_2\text{O}_5$  (Fig. 2e), the V–O coordination in  $\text{Mn}_6\text{V}_{12}$  is significantly shortened, consistent with the results in Fig. 2b. In addition, there is no V–V coordination in  $\text{Mn}_6\text{V}_{12}$  compared to V foil (Fig. 2f), further illustrating the atomic dispersion of the V.

From the Mn K-edge X-ray absorption near edge structure (XANES) in Fig. 3a, it can be seen that the absorption edge of  $\text{Mn}_6\text{V}_{12}$  is intermediate between and close to Mn foil and  $\text{MnO}_2$ , which indicates that the valence state of Mn in  $\text{Mn}_6\text{V}_{12}$  is close to +4. The formation of Mn–N(O) and Mn–N(O)–C(B) coordination in  $\text{Mn}_6\text{V}_{12}$  was directly confirmed by phase-corrected Fourier transform (FT) extended X-ray absorption fine

structure (EXAFS) characterization (Fig. 3b). The first peak in the MnO standard sample is located at 2.0 Å and belongs to the Mn–O coordination. Therefore, the main peak at 2.02 Å in the FT-EXAFS spectrum of  $\text{Mn}_6\text{V}_{12}$  can be attributed to the Mn–N<sup>44,45</sup> or Mn–O double coordination environments. The second peak in the  $\text{Mn}_6\text{V}_{12}$  material is located at 3.10 Å, which is 0.15 Å longer compared to Mn–O–Mn (2.95 Å) in MnO, and can be considered as the scattering path of Mn–N(O)–C(B) in the higher shell. It is noteworthy that the Mn–Mn scattering path (2.6 Å) does not exist in this material, verifying the atomic dispersion of Mn.

A quantitative EXAFS curve-fitting analysis of the structural parameters of  $\text{Mn}_6\text{V}_{12}$  was carried out, and the best-fit analysis clearly confirms that the coordination numbers of Mn–N and Mn–N–C, and Mn–O–B are 4, 4, and 1, respectively, which implies that the Mn center is coordinated to four N atoms and one O atom, in accordance with the material structure (Fig. 3c and d; Table S1†). In contrast to Mn foil, MnPC, and  $\text{MnO}_2$



**Fig. 3** (a) Mn K-edge normalized XANES spectra, (b) FT curves of Mn K-edge EXAFS spectra, (c) Mn K-edge EXAFS curve fitting at  $R$  space and  $q$  space, (d) Mn K-edge EXAFS curve fitting at  $k$  space, (e) wavelet transform EXAFS of Mn foil, (f) wavelet transform EXAFS of MnPC, (g) wavelet transform EXAFS of  $\text{Mn}_6\text{V}_{12}$ .

shown in Fig. 3e–g, the wavelet transform (WT) results indicate the absence of Mn–Mn bonds (with a maximum bond value ( $K$ ) of  $7 \text{ \AA}^{-1}$ ), as well as the presence of Mn–N(O) and Mn–N(O)–C(B) bonds (with a maximum bond value ( $K$ ) of  $5.94 \text{ \AA}^{-1}$ ,  $6.0 \text{ \AA}^{-1}$ ) in this material. This result is consistent with the coordination environment exhibited in Fig. 3b and further illustrates the atomic dispersion of Mn.

Furthermore, the catalyst  $\text{Mn}_6\text{V}_{12}$  was characterized by Fourier transform infrared (FTIR) spectroscopy in the range of  $4000\text{--}500 \text{ cm}^{-1}$ . As shown in Fig. 4a, it is the characteristic peak of V–O bond in the range of  $700\text{--}1000 \text{ cm}^{-1}$ . The strong peaks at  $873$ ,  $811$ , and  $701 \text{ cm}^{-1}$  are due to the antisymmetric stretching vibration peaks of V–O–V (O is the bridging oxygen), and the peak at  $945 \text{ cm}^{-1}$  is the characteristic peak of V–O (O is the end-group oxygen). The peak at  $53\text{--}1045 \text{ cm}^{-1}$  belongs to the B–O antisymmetric stretching vibration peak belonging to the triangular coordination in the  $[\text{B}_3\text{O}_7]$  unit, and the peak at  $1060\text{--}1104 \text{ cm}^{-1}$  belongs to the B–O antisymmetric stretching vibration peak belonging to the tetrahedral coordination in the  $[\text{B}_3\text{O}_7]$  unit.<sup>46</sup> The appearance of the characteristic peak at  $2920 \text{ cm}^{-1}$  is a result of symmetric and asymmetric stretching of the C–H bond. The stretching vibrations of N–H have distinct peaks at  $1611\text{--}1635 \text{ cm}^{-1}$  and  $3394\text{--}3470 \text{ cm}^{-1}$ .<sup>47</sup> The characteristic peaks in the infrared spectra of the catalyst before and after the reaction were basically unchanged, indicating that the catalyst structure was relatively stable.

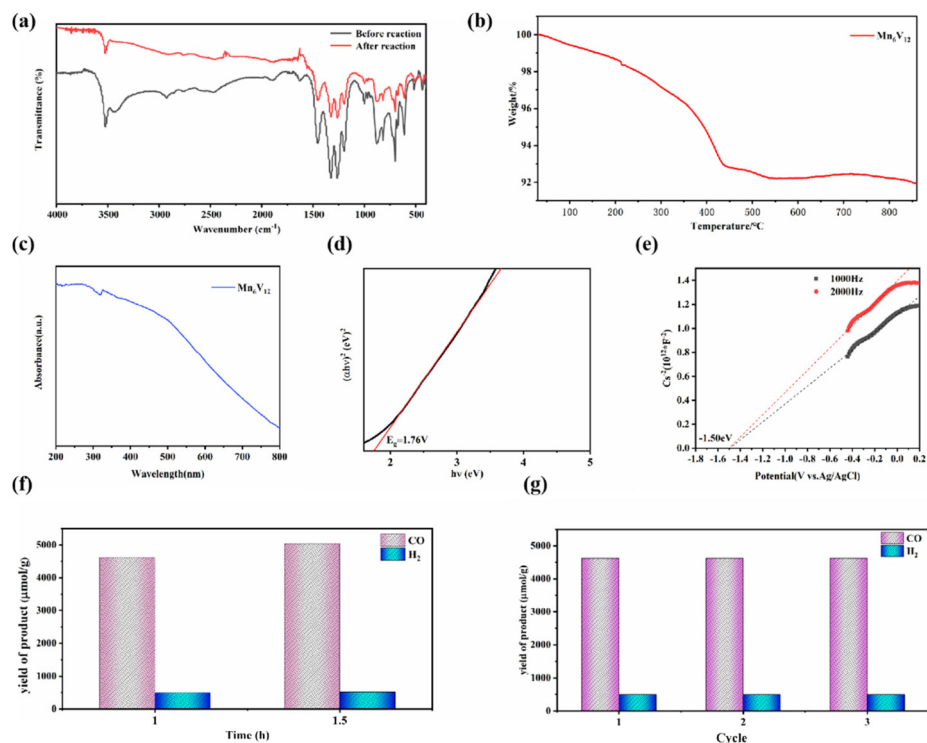
In order to further explore the thermal stability of  $\text{Mn}_6\text{V}_{12}$ , thermogravimetric analyses (TGA) were carried out in  $\text{N}_2$  atmo-

sphere in the temperature range from room temperature to  $800^\circ\text{C}$ . As shown in Fig. 4b, the TGA curve shows that the mass loss of  $\text{Mn}_6\text{V}_{12}$  is about 8% at  $0\text{--}800^\circ\text{C}$ , which is due to the decomposition of some free water molecules in the crystals, while the ligand does not collapse and decompose. Therefore, it can be assumed that  $\text{Mn}_6\text{V}_{12}$  can be stabilized at least up to  $800^\circ\text{C}$ . For the polyoxometalate photocatalysts  $[\text{Co}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6]$  and  $[\text{Ni}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6]$ , which were also modified with metals, the thermal stability was classified as  $200^\circ\text{C}$  and  $300^\circ\text{C}$ .<sup>39</sup> Therefore, the thermal stability of the polyoxometalate photocatalyst modified with metal Mn is better.

### 3.2. Photoreduction of $\text{CO}_2$

The photocatalytic potential of  $\text{Mn}_6\text{V}_{12}$  can be assessed based on the  $\text{Mn}_6\text{V}_{12}$  UV-vis diffuse reflectance spectra (Fig. 4c). Probably due to the effective charge migration between the metal Mn and the ligand, the catalyst exhibited a very broad absorption band in the range of  $200 \text{ nm}$  to  $700 \text{ nm}$ , indicating that the catalyst possesses a good light absorption capacity. Meanwhile, the band gap ( $E_g$ ) of the catalyst was estimated to be  $1.76 \text{ eV}$  by the Tauc plot method (Fig. 4d), which strongly suggests that  $\text{Mn}_6\text{V}_{12}$  has the potential to be a photo catalyst.

Mott–Schottky measurements under visible light irradiation show that the  $\text{Mn}_6\text{V}_{12}$  flat band potential is  $-1.50 \text{ eV}$  with respect to  $\text{Ag}/\text{AgCl}$  (Fig. 4e), suggesting that  $\text{Mn}_6\text{V}_{12}$  is an n-type semiconductor. For n-type semiconductors, the position of the conduction band (CB) is  $0.1 \text{ eV}$  lower than the position



**Fig. 4** (a) IR spectra of  $\text{Mn}_6\text{V}_{12}$ ; (b) TGA plot of  $\text{Mn}_6\text{V}_{12}$ ; (c) UV-visible diffuse reflectance spectra of  $\text{Mn}_6\text{V}_{12}$ ; (d) the Mott–Schottky plot of  $\text{Mn}_6\text{V}_{12}$  in  $0.2 \text{ M Na}_2\text{SO}_4$  aqueous solution; (e) the Mott–Schottky plot of  $\text{Mn}_6\text{V}_{12}$  in  $0.2 \text{ M Na}_2\text{SO}_4$  aqueous solution; (f) gas yield diagram of  $\text{Mn}_6\text{V}_{12}$  in photocatalytic system; (g) stability experiment of  $\text{Mn}_6\text{V}_{12}$  in the same catalytic system.

of the flat band, which is  $-0.77$  eV with respect to Ag/AgCl. According to the equation “( $E$ (vs. RHE) =  $E$ (vs. Ag/AgCl) +  $0.197$  V +  $0.0591 \times \text{pH}$ )”, the conduction band (CB) of  $\text{Mn}_6\text{V}_{12}$  is  $-0.77$  eV vs. RHE. The position of the  $\text{Mn}_6\text{V}_{12}$  conduction band (CB) is more negative than the potential for the reduction of  $\text{CO}_2$  to CO ( $-0.51$  eV vs. RHE,  $\text{pH} = 7$ ), suggesting that photo excited electrons can be transferred from the catalyst to the  $\text{CO}_2$  molecule. The valence band (VB) is  $0.99$  eV calculated by the equation  $E_g + E_{\text{CB}} = E_{\text{VB}}$ .

In the photocatalytic  $\text{CO}_2$  reduction system,  $\text{Mn}_6\text{V}_{12}$  was used as a photocatalyst, 2 mL of triethanolamine (TEOA) was used as a sacrificial reagent, 11.6 mg of  $[\text{Ru}(\text{bpy})_3] \text{Cl}_2 \cdot 6\text{H}_2\text{O}$  was used as a photosensitizer, and 8 mL of acetonitrile ( $\text{CH}_3\text{CN}$ ) and 2 mL of deionized water were used as solvents. Comparison test experiments were done to determine the source of the gaseous product CO. When photo catalysis was carried out for 1 h without passing  $\text{CO}_2$  gas but other catalytic reaction conditions were not changed, the yield of CO was found to be only  $183 \mu\text{mol g}^{-1}$ , whereas photo catalysis carried out with  $\text{CO}_2$  gas resulted in a higher yield of the product CO, which indicated that the carbon source of photo catalysis came from the passed  $\text{CO}_2$ , rather than acetonitrile ( $\text{CH}_3\text{CN}$ ) and triethanolamine (TEOA) in the catalytic system. As shown in Fig. 4f, after 60 min of light exposure, a large amount of CO was detected, and the production of  $\text{H}_2$  was detected to be much smaller than that of CO. The production rates of CO and  $\text{H}_2$  were  $4625.0 \mu\text{mol g}^{-1}$  and  $499.6 \mu\text{mol g}^{-1}$  respectively, and the production rates of CO and  $\text{H}_2$  were  $5048.1 \mu\text{mol g}^{-1}$  and  $520.0 \mu\text{mol g}^{-1}$  respectively, after the light exposure was continued for 30 min. With increasing light time, the yields of CO and  $\text{H}_2$  increased successively. The yield of  $\text{H}_2$  was much lower than that of CO, implying that the adsorption energy of  $\text{H}_2\text{O}$  on Mn ions and the high free energy of hydrogen precipitation could greatly inhibit the competing precipitation reaction. Comparing the product production rates at 1 h and 1.5 h, it was found that the rate of CO production was  $3365.4 \mu\text{mol g}^{-1} \text{h}^{-1}$  and the rate of  $\text{H}_2$  production was  $346.7 \mu\text{mol g}^{-1} \text{h}^{-1}$  for 1.5 h of light. The rate of product generation was higher for 1 h of light, with  $4625.0 \mu\text{mol g}^{-1} \text{h}^{-1}$  for CO and  $499.6 \mu\text{mol g}^{-1} \text{h}^{-1}$  for  $\text{H}_2$ . The selectivity for CO generation was 90.3%, and that for  $\text{H}_2$  generation was 9.7%. Fig. S1† displays the CO and  $\text{H}_2$  yield in the long reaction time of the  $\text{Mn}_6\text{V}_{12}$ , showing a gradually increased trend. However, the output of the yield per 0.5 h is steadily decreased with time, which can be attributed to the consumption of the photosensitizer agent. In addition, the same type of photocatalysts  $[\text{Co}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6]$  and  $[\text{Ni}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6]$ , after three hours of catalysis required in a similar catalytic system  $[\text{Co}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6]$  was catalyzed at a rate of  $5700 \mu\text{mol g}^{-1} \text{h}^{-1}$  for CO and  $3800 \mu\text{mol g}^{-1} \text{h}^{-1}$  for  $\text{H}_2$ .  $[\text{Ni}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6]$  has a CO production rate of  $3200 \mu\text{mol g}^{-1} \text{h}^{-1}$  and  $\text{H}_2$  production rate of  $300 \mu\text{mol g}^{-1} \text{h}^{-1}$ . By comparison, it was found that polyoxometalate catalyst modified with metal Mn could achieve efficient reduction of  $\text{CO}_2$  to CO in this photocatalytic system with only one hour of catalysis and could greatly inhibit the competitive hydrogen evolution

reaction (HER). The performance of the Mn modified polyoxometalate photocatalyst was superior to that of the Co and Ni modified polyoxometalate photocatalysts. Moreover, a comparison with the previously reported photocatalysts for this purpose in similar systems (Table S2†) reveals that  $\text{Mn}_6\text{V}_{12}$  exhibits comparatively better performance than other photocatalysts.

Control experiments were conducted to ensure the credibility of the experimental results (Fig. S2†). No observable products including CO and  $\text{H}_2$  were detected in the absence of either light or photocatalysts, indicating that both light and photocatalysts are crucial for photocatalytic  $\text{CO}_2$  reduction in this system.<sup>48</sup> Almost no product was detected in the absence of the Ru photosensitizer, suggesting that the photogenerated electrons came from Ru photosensitization. Removing TEOA from the system led to a conspicuous decline of catalytic activity, because it consumes the photogenerated holes and lessens the recombination rate of photogenerated carriers.<sup>49</sup> Furthermore, when pure  $\text{CO}_2$  was not introduced to the reactor, a notable drop of the amount of the products were detected, manifesting the carbon source of CO comes from  $\text{CO}_2$ .

In addition, in order to test the stability of the photocatalyst, the catalyst was photo catalyzed for 1 h under the same conditions, and the results after repeating the test three times showed a small difference, with no significant change in yield observed (Fig. 4g). This indicates that the catalyst has stable catalytic activity and can efficiently reduce  $\text{CO}_2$  to CO and effectively inhibit hydrogen precipitation.

### 3.3. Photocatalytic mechanism

According to the experimental results, the energy levels of  $\text{Mn}_6\text{V}_{12}$  at the highly occupied molecular orbital (HOMO) and the least occupied molecular orbital (LUMO) are  $-0.77$  eV and  $0.99$  eV, respectively, with respect to RHE. The energy levels of  $[\text{Ru}(\text{bpy})_3] \text{Cl}_2$  at the high occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) are  $1.24$  eV and  $-1.25$  eV, respectively. Since the  $E_{\text{CB}}$  value of  $\text{Mn}_6\text{V}_{12}$  is  $-0.77$  eV (vs. RHE) lower than the LUMO energy level of  $[\text{Ru}(\text{bpy})_3] \text{Cl}_2$ , electrons on  $[\text{Ru}(\text{bpy})_3] \text{Cl}_2$  are preferentially transferred to  $\text{Mn}_6\text{V}_{12}$ . In addition, the  $S_{\text{BET}}$  of  $\text{Mn}_6\text{V}_{12}$  is higher than that of  $[\text{Co}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6] \cdot 17\text{H}_2\text{O}$  (Fig. S3, S4 and Table S3†), suggesting  $\text{Mn}_6\text{V}_{12}$  may promote  $\text{CO}_2$  reduction to CO and restrain the HER process, compared to  $[\text{Co}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6] \cdot 17\text{H}_2\text{O}$ . Furthermore, the  $\text{Mn}_6\text{V}_{12}$  exhibits higher photocurrent and lower interfacial charge transfer resistance than that of  $[\text{Co}(\text{en})_2]_6[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6] \cdot 17\text{H}_2\text{O}$  (Fig. S5 and S6†), suggesting higher charge separation and transfer efficiency of  $\text{Mn}_6\text{V}_{12}$ , which directly influences the photocatalytic activity for  $\text{CO}_2$  reduction.

The possible mechanism of photocatalytic  $\text{CO}_2$  reduction to CO and  $\text{H}_2$  is that there are two photoelectron transfers in the photocatalytic process. The photosensitizer reaches its excited state under the irradiation of UV-visible light and receives electrons from the triethanolamine electron donor to form the intermediate in the reduced state, while the intermediate in

the reduced state then absorbs the visible light electrons to reach its excited state, and after that it transfers its electrons to the manganese metal ions on the POMs framework, which get the electrons to carry out a reduction reaction on the CO<sub>2</sub> to achieve the photocatalytic reduction of CO<sub>2</sub> to generate CO and H<sub>2</sub>. Moreover, according to the results of N<sub>2</sub> adsorption-desorption test, a larger BET surface area of Mn<sub>6</sub>V<sub>12</sub> may promote CO<sub>2</sub> reduction to CO and restrain the HER process.<sup>50</sup> Furthermore, combined with the measurements of photocurrent response and electrochemical impedance spectroscopy, a higher charge separation and transfer efficiency of Mn<sub>6</sub>V<sub>12</sub>, which directly influences the photocatalytic activity for CO<sub>2</sub> reduction, thus leading to more CO production.<sup>51</sup>

## 4. Conclusions

Polyoxometalate photocatalyst ([Mn(en)<sub>2</sub>]<sub>6</sub>[V<sub>12</sub>B<sub>18</sub>O<sub>54</sub>(OH)<sub>6</sub>]) (Mn<sub>6</sub>V<sub>12</sub>) with Mn as the modifying unit were synthesized by hydrothermal method, and the highest production rate of CO for catalytic CO<sub>2</sub> reduction was 4625.0 μmol g<sup>-1</sup> h<sup>-1</sup>, and the highest production rate of H<sub>2</sub> was 499.6 μmol g<sup>-1</sup> h<sup>-1</sup>. The selectivity of CO production was 90.3% and that of H<sub>2</sub> production was 9.7%. This polyoxometalate photocatalyst is good for efficient reduction of CO as well as effective inhibition of hydrogen precipitation reaction. The electronic structure and atomic coordination were elucidated using X-ray absorption near edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy. The study in this work provides new ideas and possibilities for future transition metal modified polyoxometalate for photocatalytic carbon dioxide reduction.

## Conflicts of interest

There are no conflicts to declare.

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