

### Article



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# Photocatalytic CO<sub>2</sub> Conversion of M<sub>0.33</sub>WO<sub>3</sub> Directly from the Air with High Selectivity: Insight into Full Spectrum Induced Reaction Mechanism

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KEYWORDS: Artificial photosynthesis; Conversion of CO<sub>2</sub> from air; Full spectrum light response; M<sub>0.33</sub>WO<sub>3</sub>.

**ABSTRACT:** The natural photosynthesis is a solar light-driven process utilized by plants to convert  $CO_2$  and water into carbohydrate molecules. The goal of artificial photosynthesis is the reduction of  $CO_2$  directly from air into high purity of value-added products at atmospheric pressure. However, its realization, combining with deeply mechanism investigation, is a huge challenge. Herein, we demonstrate that hexagonal tungsten bronze  $M_{0.33}WO_3$  (M=K, Rb, Cs) series with {010} facets, prepared by a peculiar "water-controllable releasing" solvothermal method, showed excellent full spectrum (UV, visible and NIR lights) induced photocatalytic  $CO_2$  reduction performance directly from the air at ambient pressure. Particularly, after 4 h near infrared light irradiation, ca. 4.32 %  $CO_2$  in the air could be converted into  $CH_3OH$  with 98.35 % selectivity for  $Rb_{0.33}WO_3$ . The experiments and theoretical calculations unveiled that the introduced alkali metal atom occupied the tunnel of hexagonal structure and donated more free electrons to reconstruct the electronic structure of  $M_{0.33}WO_3$ , which can enhance the polaron transition, modify the energy band structure, selectively adsorb  $CO_2$  rather than  $O_2$  from the air, decrease the activation energy of  $CO_2$  reaction, and finally make the effective  $CO_2$  reduction in the air a reality. This work may provide new possibility for the practical application of artificial photosynthesis.

#### INTRODUCTION

The dramatically boosting concentration of  $CO_2$  in the atmosphere seriously destructs the natural carbon balance, aggravates global warming and becomes a worldwide challenge and urgent issue.<sup>1,2</sup> Inspired by the nature photosynthesis, photocatalytic reduction of  $CO_2$  has been considered as one of the ideal solutions to address this issue since it can not only reduce the  $CO_2$  concentration environmental friendly but also enable to convert  $CO_2$  into renewable resources.<sup>3:8</sup> For widespread application of artificial photosynthesis, there are still some challenges to overcome. Many  $CO_2$  reduction systems demand relatively complicated reaction conditions.<sup>9-11</sup> Generally, high concentration of  $CO_2$  or special  $CO_2$ -capturing devices are required, because the low concentration of  $CO_2$  makes it very difficult to be

effectively adsorbed and activated on the surface of most photocatalysts,<sup>12-14</sup> and the anaerobic atmosphere is requisite to prevent the adverse oxidation reaction from happening.<sup>15-17</sup> In addition, the irradiation sources for photocatalytic carbon dioxide reduction (PCR) are usually ultraviolet (UV) and visible lights;<sup>18,19</sup> while near infrared (NIR) light is rarely utilized, which accounts for ca. 50 % of natural solar light. Moreover, the corresponding CO<sub>2</sub> conversion efficiency is extremely lower as compared to those of UV and visible lights induced ones.<sup>20-22</sup> Lastly, it is difficult to control the selectivity of PCR, and the products tend to be two or more of CO, HCOOH, HCHO, CH<sub>3</sub>OH and CH<sub>4</sub>, etc.<sup>23,24</sup>

Therefore, developing a photocatalyst, which can effectively reduce  $CO_2$  directly from air into value-added product of high selectivity under the irradiation of full spectrum (UV, visible and NIR lights) at ambient Environment

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condition, without the addition of any other special additive, sacrificial agent or  $CO_2$ -capturing device, and elucidating the corresponding  $CO_2$  reduction mechanism,<sup>25-28</sup> are grand challenges but extremely promising.

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Herein, we report a series of noble metal-free hexagonal tungsten bronze, M<sub>0.33</sub>WO<sub>3</sub> (M=K, Rb, Cs), as sole photocatalyst to achieve the above-expected effectively PCR directly from air at atmospheric pressure under the irradiation of full spectrum (UV, visible and NIR lights). Typically, under the irradiation of NIR light, Rb<sub>0.33</sub>WO<sub>3</sub> and Cs<sub>0.33</sub>WO<sub>3</sub> could present fascinating PCR performance in air with production selectivity above 98 % towards CH<sub>3</sub>OH. Besides, the  $CO_2$  and  $O_2$  temperatureprogrammed desorption (TPD), X-ray absorption nearedge spectroscopy (XANES) and calculation of energy loss function, etc. were employed to study the M<sub>0.33</sub>WO<sub>3</sub> series for the mechanism explanation. We found that the polaron transition induced short wavelength of NIR light played the predominant role in the outstanding NIR light induced PCR performance of the M<sub>0.33</sub>WO<sub>3</sub> series. Last but not least, the density functional theory (DFT) study of the reaction paths for PCR revealed that the existence of alkali metal atoms was remarkably beneficial for the high efficiency of full spectrum induced CO<sub>2</sub> reduction to CH<sub>3</sub>OH directly from the air.

#### **RESULTS AND DISCUSSION**

The  $M_{0,33}WO_3$  series were prepared by a peculiar "water-controllable releasing" solvothermal method using tungsten hexacarbonyl and nitrate salts as raw materials (see Supporting Information for more details), assisted by a H<sub>2</sub> reduction. The PCR performance of the samples was evaluated in a customized sealed quartz glass vessel under the irradiation of 300 W Xe lamp (350-2500 nm) with or without light filter (Figure S1, S2, S3). Noteworthily, the fresh air with standard atmospheric pressure was directly used as carbon source. Figure 1a show the corresponding PCR performance of the samples under the irradiation of full spectrum light of Xe lamp. The commercial WO<sub>2</sub> exhibited no observable PCR activity, and trace performances for heat-treated Rb<sub>0.33</sub>WO<sub>3.165</sub> and W<sub>18</sub>O<sub>49</sub> (Table S1). While ca. 17.50, 15.10 and 7.70 µmol of CH<sub>3</sub>OH product were respectively detected for per gram of the samples Cs<sub>0.33</sub>WO<sub>3</sub>, Rb<sub>0.33</sub>WO<sub>3</sub> and K<sub>0.33</sub>WO<sub>3</sub> after 4 h PCR that were much higher than the performance of sample Au@TiO<sub>2</sub> in the same scenario (Figure S<sub>4</sub>). In terms of full spectrum light irradiation, the main PCR products of the sample Rb<sub>0.33</sub>WO<sub>3</sub> consisted of ca. 21.59 % of HCHO and ca. 76.51 % of CH<sub>3</sub>OH (Figure 1b), with trace amount of CO and CH4. The total conversion rate for HCHO and CH<sub>3</sub>OH achieved about 4.78 µmol h<sup>-1</sup> g<sup>-1</sup> (Table S1), and the concentration of oxygen slightly increased as well (Table S<sub>2</sub>), but we did not detect the signal of hydrogen. Furthermore, the generation of different products of the sample Rb<sub>0.33</sub>WO<sub>3</sub> under full spectrum irradiation and in the pure CO<sub>2</sub> atmosphere are approximately stoichiometric (Table S<sub>3</sub>). The PCR stability of the sample Rb<sub>0.33</sub>WO<sub>3</sub> conducted in the air atmosphere was revealed

in Figure 1c. It is clear that the sample, which was simply washed using distilled water for next PCR test, still presented nice performance without obvious activity decrement after 7 times PCR tests in the air (4 h full spectrum light irradiation for each time). Besides, performance of the sample Rb<sub>0.33</sub>WO<sub>3</sub> in a prolonged run was displayed in the Figure S5, S6, indicating that the water content on the surface of the sample obviously affected the reaction performance. Moreover, the sample Rb<sub>0.33</sub>WO<sub>3</sub> kept nice stability in the air without light irradiation. The old sample Rb<sub>0.33</sub>WO<sub>3</sub>, which stored in plastic vessel in the air atmosphere for more than 5 months, still displayed nice performance (Figure S7, S8). More importantly, when PCR was conducted in the air under the irradiation of NIR light (>800 nm), the samples Cs<sub>0.33</sub>WO<sub>3</sub> and Rb<sub>0.33</sub>WO<sub>3</sub> still exhibited outstanding CH<sub>3</sub>OH production activity with the conversion rate of 1.27 and 2.33 µmol h<sup>-1</sup> g<sup>-1</sup> (Figure 1d), respectively. Figure 1e illustrate the variation of CO<sub>2</sub> in the air and the main products produced in PCR process referred to the sample  $Rb_{0,33}WO_3$  in above scenario. It is noticeable that the sample Rb<sub>0.33</sub>WO<sub>3</sub> displayed ca. 98.35 % PCR selectivity for CH<sub>3</sub>OH production and ca. 4.32 % conversion efficiency for  $CO_2$  after 4 h reaction (Table S4). Furthermore, as show in Tables S5, S6, it can be found out that the decrease of  $CO_2$  and the increase of gas products in PCR are stoichiometric under full spectrum light irradiation and NIR light irradiation, respectively.

To confirm that the production of CH<sub>2</sub>OH was really originated from PCR of the sample instead of other approaches, the PCR process was also conducted in pure N<sub>2</sub> atmosphere and various CO<sub>2</sub> concentrations. Under N<sub>2</sub> atmosphere, the sample Rb<sub>0.33</sub>WO<sub>3</sub> showed no detectable PCR activity (Figure 1f, S9). Meanwhile, the <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> labeling experiment reveal that the produced CH<sub>3</sub>OH stemmed from CO<sub>2</sub> photoreduction (Figure S10, Su). Fourier transform infrared (FTIR) spectrum of PCR reaction of the sample Rb<sub>0.33</sub>WO<sub>3</sub> also present the obviously new signals for the functional groups of C-H and O-H as compared to the fresh sample Rb<sub>0.33</sub>WO<sub>3</sub> and the no-light matched groups (Figure S12). Besides, when the PCR activity of the sample Rb<sub>0.33</sub>WO<sub>3</sub> was evaluated in various CO<sub>2</sub> concentrations, the sample presented increasing CH<sub>3</sub>OH production rate with rising CO<sub>2</sub> contents, so all that verified that the generating CH<sub>3</sub>OH was converted by CO<sub>2</sub>. Particularly, as PCR was tested in pure CO<sub>2</sub> atmosphere, the CH<sub>3</sub>OH production rate achieved ca. 26.50 µmol h-1 g-1 (Figure S9) under full spectrum light irradiation and ca. 15.48 µmol h<sup>-1</sup> g<sup>-1</sup> was reached for the NIR light induced one, which is much superior over most of the reported NIR light induced PCR (Table S7). More interestingly, it was found that the introduced water strongly influenced the process of PCR but no significant effect by H<sub>2</sub>, implying that under light irradiation, CO2 could directly react with water on the surface of Rb<sub>0.33</sub>WO<sub>3</sub>, rather than the common reduction process that water firstly was decomposed to H<sub>2</sub> and then CO<sub>2</sub> reacted with H<sub>2</sub> (Figure S13). More intriguing, the catalyst Rb<sub>0.33</sub>WO<sub>3</sub> can be used continuously in a flowing

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air and still demonstrated nice performance (Figure S<sub>3</sub> and Table S8).

2 Characterization of physical and chemical properties of 3 the samples is one of the best ways to shed light on the 4 superior PCR performance of M<sub>0.33</sub>WO<sub>3</sub> series over other 5 comparisons. It is well acknowledged that the crystal 6 structure, the adsorption of CO<sub>2</sub> and O<sub>2</sub> adsorption on the 7 surface of catalyst, and the light absorption capability as 8 well as activation energy are four key factors for high 9 efficiency of PCR activity in air atmosphere.<sup>29-32</sup> Thus, the 10 following discussion will be elaborated from above four 11 points. In this work, the M<sub>0.33</sub>WO<sub>3</sub> series were prepared by 12 "water-controllable above-mentioned releasing" 13 solvothermal method, in which the acetic acid and 14 ethanol mixed solutions were used as reaction solvent. With rising heating temperature, the acetic acid and 15 ethanol will gradually react to release water and then 16 control the hydrolysis of tungsten hexacarbonyl; 17 meanwhile, the ethanol could be used as reduction agent 18 to produce reduced W<sup>5+</sup>. In this case, the particle size, 19 morphology, light harvesting and alkali metal introducing 20 for tungsten bronze M<sub>0.33</sub>WO<sub>3</sub> series could be nicely 21 optimized. The XRD patterns and corresponding 22 structure information of the as-prepared samples were 23 shown in Figure 2a, 2b, S14 and Table S9. Commercial 24 WO3 and W18O49 were assigned to orthorhombic and 25 monoclinic systems, respectively, while all M<sub>0.33</sub>WO<sub>3</sub> were 26 well indexed to a peculiar hexagonal system. In this 27 unique hexagonal tungsten bronze crystal (Figure 2b), the 28 corner-sharing WO<sub>6</sub> octahedron built up the tungsten-29 oxygen framework to form uniformly dispersed trigonal 30 and hexagonal tunnels, and then large amounts of alkali 31 metal ions could be regularly introduced in the hexagonal 32 tunnel. In this condition, great numbers of reduced W5+ 33 would be produced in this unique M<sub>0.33</sub>WO<sub>3</sub> crystal 34 structure to keep charge balance.33 It is well known that 35 unsaturated transition metal and alkali metal introduced 36 in semiconductors are beneficial to light absorption and 37 CO<sub>2</sub> adsorption as well as activation.<sup>34-36</sup> So from the 38 viewpoint of structure, the employed M<sub>0.33</sub>WO<sub>3</sub> series are 39 promising candidates for PCR and the detailed effect of 40 unsaturated transition metal and introduced alkali metal 41 on PCR performance will be elucidated later.

42 Due to the small and similar specific surface area of the 43 samples (Table S10), the exposed facets should be key 44 point for gas adsorption.<sup>37</sup> Figure 2c, 2d, 2e, 2f present the 45 transmission electron microscopy (TEM), elementary 46 mapping, high-resolution transmission electron 47 microscopy (HRTEM) images and selected area electron 48 diffraction (SAED) pattern of the sample Rb<sub>0.33</sub>WO<sub>3</sub>. The 49 sample exhibited flower liked shape, consisted of nanorods, and the Rb, W and O atoms were uniformly 50 dispersed in the particles. In addition, the two closest 51 52 spots in SAED pattern were respectively attributed to the planes of (300) and (102), indicating the main exposed 53 facets in Rb<sub>0.33</sub>WO<sub>3</sub> was {010} facets and the minor 54 exposed facets on tips of nanorod should be {001} facets. 55 The other series of M<sub>0.33</sub>WO<sub>3</sub> particles also displayed 56 nanorod shape with dominant exposed {010} facets 57

(Figure S15, S16). Thus, the {010} and {001} facets were both considered as the candidates for CO<sub>2</sub> adsorption. The density functional theory (DFT) calculations confirmed that the CO<sub>2</sub> is much easier to be adsorbed on the {010} facets with much lower adsorption energy of -1.00 eV than that on the {001} facets with the adsorption energy of -0.38 eV (Table S11), and even the bond angle in  $CO_2$  has changed after adsorption on the {010} facets (Figure 3a, 3b). This advantage for {010} facets was partly due to that the {010} facets exposing cut open hexagonal tunnel and then much more alkali metal ions were exposed on surface to decrease adsorption energy, as compared to that of {001} facets exposing. Besides, CO2 adsorption capacities of Rb<sub>0.33</sub>WO<sub>3</sub> and W<sub>18</sub>O<sub>49</sub> are also different (Figure 3c) that the Rb<sub>0.33</sub>WO<sub>3</sub> has much higher  $\rm CO_2$  adsorption capacity than  $\rm W_{18}O_{49}.$  The  $\rm CO_2$ temperature programmed desorption (TPD) analysis confirms that the Rb<sub>0,33</sub>WO<sub>3</sub> sample exhibited two predominant desorption peaks around 100 and 300 °C, respectively (Figure 3d), which were probably owing to the desorption of CO<sub>2</sub> from various W sites on different exposed facets, while only weak desorption peak around 200 and 300 °C was observed for prepared W18O49. Furthermore, with increasing alkali metal ionic radius for K to Cs, the corresponding intensities for these two peaks increased (Figure S17), which were well indexed to the variation tendency of the calculated CO<sub>2</sub> adsorption energies (Table S11). Therefore, the alkali metal ion introducing on the surface of  $M_{0.33}WO_3$  series with {010} facets exposing is in favor of CO<sub>2</sub> adsorption over other samples. Besides, the adsorption of  $O_2$  over the samples should be considered for PCR performance since O<sub>2</sub> from air has competitive effect for CO<sub>2</sub> adsorption on the sample surface and is detrimental for CO<sub>2</sub> reduction owing to its oxidation property. The sample Rb<sub>0.33</sub>WO<sub>3</sub> represented very poor adsorption ability for O<sub>2</sub>, but the sample  $W_{18}O_{49}$  showed strong one for  $O_2$  (Figure 3e). Therefore, M<sub>0.33</sub>WO<sub>3</sub> series with {010} facets exposing has interesting adsorption selectivity for CO<sub>2</sub> over O<sub>2</sub> in the air, making PCR of M<sub>0.33</sub>WO<sub>3</sub> directly in the air possible.

To study full spectrum and NIR lights induced PCR performance, the light absorption capability of photocatalyst is a crucial factor. Figure 4a exhibit the diffuse reflectance spectroscopy (DRS) of the samples. All the samples displayed excellent intrinsic light absorption in the UV range. Moreover, with the increment of alkali metal ionic radius, the absorption edges of the samples were shifted to the long wavelength (Figure S18), indicating the narrowed band gap. More importantly,  $M_{0.33}WO_3$  series and  $W_{18}O_{49}$  presented interesting and very strong light absorption from 500 to 2200 nm, and the corresponding color images of particles were provided in Figure S19, while no detectable corresponding absorption for the sample  $Rb_{\scriptscriptstyle 0.33}WO_{\scriptscriptstyle 3.165}$  and weak intensity for commercial WO<sub>3</sub>. Therefore, M<sub>0.33</sub>WO<sub>3</sub> series could present excellent PCR performance under full spectrum light irradiation. On the other hand, the NIR light absorption shape of the samples was not symmetric, which is probably due to more reasons rather than sole

one. Some works explained that the intriguing NIR light absorption for WO3-x or W18O49 should be owing to the existence of oxygen vacancies.20 However, in this work, no hard evidences were observed for the existence of oxygen vacancies in the M<sub>0.33</sub>WO<sub>3</sub> sample by means of electron paramagnetic resonance (ESR) tests (Figure S20) and thermogravimetric analysis as well as poor adsorption ability for  $O_2$ . In addition, the reduced  $W^{5+}$  in  $M_{0,33}WO_3$ could be compensated by induced M<sup>+</sup> ions instead of oxygen vacancies, so the oxygen vacancies were not necessary for forming M<sub>0.33</sub>WO<sub>3</sub> crystal and the NIR light absorption of  $M_{0.33}WO_3$  samples was probably not induced by oxygen vacancies. The true mechanisms of NIR light absorption were further investigated by some measurement technologies. optical Firstly, the photoluminescence (PL) spectra of the samples were recorded in Figure S21. It is interesting that with the excitation wavelengths of 550 and 580 nm, the samples displayed two emission peaks at 825 and 870 nm, respectively. Since the PL spectra is a nice and indirect way to reflect the light harvesting mechanism of semiconductor, the strong NIR light harvesting of M<sub>0.33</sub>WO<sub>3</sub> series should be owing to two different mechanisms. Therefore, the dielectric functions and energy loss function of the sample Rb<sub>0.33</sub>WO<sub>3</sub> were calculated (Figure 4b, 4c). It is apparent in Figure 4b that a strong peak was appeared at ca. 3.8 eV in 22, which is assigned to the intrinsic transition from the valence to conduction band.<sup>38</sup> Notably, a relatively weak peak with asymmetrical profile at around 1.5 eV was observed in both  $\varepsilon_1$  and  $\varepsilon_2$ , which should be ascribed to the polaron absorption with the WO<sub>6</sub> octahedron as the host polarons induced by free electrons in crystal.38-40 Derived from the dielectric functions results, the energy loss function of the sample Rb<sub>0.33</sub>WO<sub>3</sub> presented two distinct peaks around 1.4 and 2.0 eV(Figure 4c), which should be attributed to the localized surface plasmon resonance (LSPR) and polarons,38,40 respectively. No such above phenomena were observed for bulk WO<sub>3</sub> (Figure S22).

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38 It is well recognized that the polaron transition and 39 LSPR are intimately related to the reduced W<sup>5+</sup> and free 40 electrons for W related system. Because the polaron 41 transition is caused by the hopping of small polarons 42 from W5+ to nearby W6+ positions or transferring from 43 localized levels, which is formed by localized free electrons, to conduction band, and the LSPR is originated 44 from large amounts of free electrons accumulated on the 45 conduction band.<sup>38,41</sup> W 4f XPS spectra (Figure 4d, and the 46 other elements of XPS spectra were supplemented in 47 Figure s23) and X-ray absorption near edge structure 48 (XANES) spectra (Figure 4e, S24) explicitly exhibited that 49 great amounts of reduced W5+ were really existed in the 50  $M_{0.33}WO_3$  series. It can also be seen from Figure 4f that, as 51 compared to WO<sub>3</sub>, the Fermi level of M<sub>0.33</sub>WO<sub>3</sub> series was 52 shifted to the conduction band, indicating the semi-53 metallic states of these the samples, and many free 54 electrons were existed in crystal. In addition, alkali metal 55 atoms all contributed to the over-all density of states 56 (DOS) in upper conduction band, implying that these 57

atoms were nicely ionized and then provided huge amounts of free electrons to the crystal. Therefore, polaron transition and LSPR effect were reasonably accounts for the strong NIR light absorption of  $M_{0.33}WO_3$  series.

To investigate the effect of polaron transition and LSPR induced NIR light absorption on the PCR performance in detail, the PCR activity of the samples as a function of irradiation wavelengths of NIR lights and reaction temperatures were studied (Figure S25, S26). As we all know, the harvesting of long wavelength of NIR light from LSPR leads to photothermal effect (Figure S27, S28). When PCR of the sample Rb<sub>0.33</sub>WO<sub>3</sub> was respectively performed at 60 and 150 °C, no product was detected without irradiation, and no big difference was observed under full spectrum and NIR lights irradiation, respectively. But much less activity was presented as PCR reaction temperature of the sample Rb<sub>0.33</sub>WO<sub>3</sub> was fixed at 10 °C, which should be owing to that at lower temperature, most of water in reaction vessel kept the liquid states rather than vapor, then no enough H<sub>2</sub>O vapor to contact with photocatalyst to conduct PCR. Obviously, the relatively high temperature did not have significant impact on the PCR performance. Besides, under the irradiation of NIR light with the wavelength above 800 nm and full spectrum light, the sample Rb<sub>0.33</sub>WO<sub>3</sub> presented prominent PCR performance; however, under the irradiation of light above 900 nm, no distinct activity was observed (Figure S25), and the detailed reason was described in the supporting information. Thus, it can be learned that the NIR light induced PCR performance of M<sub>0.33</sub>WO<sub>3</sub> series was mainly contributed by polaron transition induced by the short wavelength of NIR light rather than LSPR induced photothermal transition. And the corresponding band structure of Rb<sub>0.33</sub>WO<sub>3</sub> was shown in Figure S29, S30.

Finally, to shed light on the mechanism of whole process of artificial photosynthesis for various samples, two different models, hexagonal WO<sub>3</sub> and M<sub>0.33</sub>WO<sub>3</sub> with {010} exposed facets, were respectively established to clarify the effect of alkali metal on the PCR process in the air. The corresponding calculated stepwise Gibbs free energy diagrams for CO<sub>2</sub> reduction into CH<sub>3</sub>OH and relevant optimized structures were demonstrated in Figure 5, and all presented intermediate states had been optimized after considering various possibilities pathways with the lowest energies. To begin with, one CO<sub>2</sub> molecule was adsorbed into the nearby of W sites, and then one H<sub>2</sub>O molecule were adsorbed on the surface with minimized energies. Interestingly, after structure configuration optimization, we found that one hydrogen of H<sub>2</sub>O was automatically connected to the oxygen of CO<sub>2</sub> to form COOH\*(Step 2), which was well consistent with the results obtained above that only O<sub>2</sub> was observed in GC for PCR reaction but no H2 was detected. Combined with the FTIR spectra and in situ FTIR spectra (Figure S<sub>31</sub>, S<sub>32</sub>), the above interesting phenomenon indicated that W sites were possibly not only active for CO<sub>2</sub> adsorption and activation but also for H<sub>2</sub>O. After that, one more H<sub>2</sub>O was

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adsorbed on the surface (Step 3). Subsequently, COOH\* was further reacted to produce the sable intermediate  $C(OH)_2^*$ . The following two steps were the hydrogenation of C(OH)<sub>2</sub>\* to form HC(OH)<sub>2</sub>\*, H<sub>2</sub>COH\*, respectively. However, from HC(OH)<sub>2</sub>\* to H<sub>2</sub>COH\*, the hexagonal WO<sub>3</sub> exhibited increased energy of -2.10 eV while much favorable energy of -7.25 eV for hexagonal Rb<sub>0.33</sub>WO<sub>3</sub>; Finally, the intermediate H<sub>2</sub>COH\* was changed into the desirable CH<sub>3</sub>OH<sup>\*1</sup>. Notably, in the whole possible reaction steps, all showed negative energies, indicating they were favorable reaction channels. More importantly, 10 from the free energies of all the samples as presented in 11 Table S12, it could be found that the existence of alkali 12 metal in crystal was greatly favorable for CO<sub>2</sub> reduction 13 into CH<sub>3</sub>OH, and this effect was enhanced with the 14 increment of alkali metal ionic radius. Besides, the 15 possible reaction processes of CO<sub>2</sub> reduction into HCHO 16 over the sample Rb<sub>0.33</sub>WO<sub>3</sub> was also provided in Figure 17 S33. 18

Thus, from the viewpoint of reaction process (Table S12), 19 the sample  $Cs_{0,33}WO_3$  should present the best PCR 20 performance over other the samples. Nevertheless, as for 21 photocatalytic activity, in addition to reaction energies, 22 the light absorption, CO<sub>2</sub> adsorption capability, density 23 and separation ability of charge carries, etc. could also 24 affect the performance of PCR as well.<sup>42</sup> Figure 4a show 25 that the sample Rb<sub>0.33</sub>WO<sub>3</sub> exhibited the highest light 26 absorption from 200 to 900 nm. Meanwhile, the sample 27 Rb<sub>0.33</sub>WO<sub>3</sub> has stronger instantaneous photo-current than 28 the sample Cs<sub>0.33</sub>WO<sub>3</sub> under NIR light irradiation (Figure 29 S<sub>34</sub>), much superior over other the samples, but better 30 CO<sub>2</sub> adsorption capability for the sample Cs<sub>0.33</sub>WO<sub>3</sub> than 31 other ones. Under full spectrum light of Xe lamp 32 irradiation, the sample  $Cs_{0.33}WO_3$  presented the best PCR 33 performance in the air, indicating CO<sub>2</sub> adsorption 34 capability and reaction energies of CO<sub>2</sub> reduction played 35 dominant role in the superior PCR performance of the 36 samples. However, under the irradiation of NIR light, the 37 sample Rb<sub>0.33</sub>WO<sub>3</sub> showed the superior PCR performance 38 in the air over the sample Cs<sub>0.33</sub>WO<sub>3</sub>, and no distinct 39 activity was observed for other the samples. In this 40 scenario, light absorption made the main contribution to 41 the excellent PCR property of M<sub>0.33</sub>WO<sub>3</sub> series.

#### CONCLUSIONS

In summary, a series of hexagonal M<sub>0.33</sub>WO<sub>3</sub> nanorods with {010} exposed facets exhibited excellent PCR performance directly in the air with atmospheric pressure under the irradiation of full spectrum and NIR lights, respectively, much superior over W18O49, commercial WO3 and Au@TiO2. The experiments and theoretical calculations confirmed that the exposed {010} facets with large amounts of disclosed alkali metal and reduced W atoms on the surface for M<sub>0.33</sub>WO<sub>3</sub> series were beneficial for CO<sub>2</sub> adsorption, and detrimental on O<sub>2</sub> adsorption. It provided possibility for conversion of CO<sub>2</sub> directly from the air. Meanwhile, we found that the strong NIR light absorption ability of dark blue Mo.33WO3 series was originated from polaron transition and LSPR, and polaron

transition was mainly contributed to the high NIR light induced PCR performance. Finally, the DFT calculations found that the alkali metal in hexagonal tungsten bronze crystal was greatly in favor of CO<sub>2</sub> conversion into CH<sub>3</sub>OH. Our work may pave a new way for the PCR directly from the air to high selectivity of value-added product.

#### ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, characterization, theoretical calculation and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure 1. PCR performances of the  $M_{0.33}WO_3$  samples. (a)  $CO_2$  reduction activities of  $M_{0.33}WO_3$  series,  $Rb_{0.33}WO_{3.165}$  and  $W_{18}O_{49}$  as well as  $WO_3$  under full spectrum light irradiation; (b) the variation contents of  $CO_2$  and products during photocatalytic process over the sample  $Rb_{0.33}WO_3$  under full spectrum light irradiation; (c) photocatalytic stability of the sample  $Rb_{0.33}WO_3$  under full spectrum light irradiation for 4 h each time; (d)  $CO_2$  reduction activities of the samples under NIR light irradiation; (e) the variation contents of  $CO_2$  and product during photocatalytic process over the sample  $Rb_{0.33}WO_3$  under NIR light irradiation; and (f)  $CO_2$  reduction activities of the sample  $Rb_{0.33}WO_3$  under NIR light irradiation; and (f)  $CO_2$  reduction activities of the sample  $Rb_{0.33}WO_3$  with respect to divergence atmosphere and  $CO_2$  concentrations under NIR light irradiation.



Figure 2. (a) XRD patterns of samples, (b) crystal structure, (c) TEM, (d) element mapping, (e) HRTEM image and (f) SAED pattern of the sample Rb<sub>0.33</sub>WO<sub>3</sub>.



Figure 3. The optimized structure of  $CO_2$  adsorbed on the surface of {001} (a) and {010} (b) facets for the sample  $Rb_{0.33}WO_3$ , respectively. (c)  $CO_2$  adsorption isotherms; (d)  $CO_2$  TPD spectra of the samples conducted in simulated air without  $O_2$ ; and (e)  $O_2$  TPD spectra of the samples  $Rb_{0.33}WO_3$  and  $W_{18}O_{49}$ .



Figure 4. Optical properties and mechanism. (a), DRS spectra of the samples. (b), Calculated dielectric functions of the sample  $Rb_{0.33}WO_3$ . (c), Energy loss function derived from b. (d), W <sub>4f</sub>XPS spectra of the samples. (e), Magnified W L<sub>3</sub>-edge XANES spectra of the samples. (f), TDOS spectra of the samples.



Figure 5. PCR mechanism. Free energy diagrams for reduction of CO<sub>2</sub> to CH<sub>3</sub>OH over the sample Rb<sub>0.33</sub>WO<sub>3</sub> and comparison hexagonal WO<sub>3</sub> based on DFT calculation as well as corresponding structure models for every reaction steps from 1-7.



