### Heterogeneous Catalysis Hot Paper

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### **Elemental Boron for Efficient Carbon Dioxide Reduction under Light Irradiation**

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Abstract: The photoreduction of  $CO_2$  is attractive for the production of renewable fuels and the mitigation of global warming. Herein, we report an efficient method for CO<sub>2</sub> reduction over elemental boron catalysts in the presence of only water and light irradiation through a photothermocatalytic process. Owing to its high solar-light absorption and effective photothermal conversion, the illuminated boron catalyst experiences remarkable self-heating. This process favors CO<sub>2</sub> activation and also induces localized boron hydrolysis to in situ produce  $H_2$  as an active proton source and electron donor for  $CO_2$  reduction as well as boron oxides as promoters of CO<sub>2</sub> adsorption. These synergistic effects, in combination with the unique catalytic properties of boron, are proposed to account for the efficiency of the  $CO_2$  reduction. This study highlights the promise of photothermocatalytic strategies for  $CO_2$  conversion and also opens new avenues towards the development of related solar-energy utilization schemes.

Converting carbon dioxide (CO<sub>2</sub>), an abundant and inexpensive  $C_1$  feedstock as well as a potent greenhouse gas, into value-added carbon products provides an attractive and promising strategy to meet global energy demands and to simultaneously alleviate anthropogenic climate change.<sup>[1]</sup> The ideal route to achieve this goal is to reduce CO<sub>2</sub> catalytically by a photocatalyst with the utilization of solar light as the only input energy source.<sup>[2]</sup> However, despite having been studied

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for decades, such processes for  $CO_2$  conversion still remain very inefficient, largely owing to insufficient solar light utilization, the high energy barrier for  $CO_2$  activation, and the sluggish kinetics of the involved multiple  $e^-/H^+$  transfer processes.<sup>[1c,3]</sup> Therefore, aiming at promoting the reaction rate of  $CO_2$  conversion, increasing the utilization of solar energy, and also from the view of reducing  $CO_2$  emission, the development of more convenient and effective approaches to solar-light-driven  $CO_2$  reduction is urgently required.

The photothermal effect can be described as the conversion of photon energy into heat and has been considered as an emerging technology of great interest for solar energy harvesting.<sup>[4]</sup> As this technology can enable a remarkable and prompt increase in the local temperature at the nanometer scale, it has found a broad range of applications in various fields, including solar power generation, localized water heating, seawater desalination, and catalysis.  $^{[4a,b,5]}$  It is well known that thermodynamically stable CO<sub>2</sub> molecules are more reactive at high temperatures.<sup>[6]</sup> This thought made us aware of the benefits of the photothermal effect for CO<sub>2</sub> conversion. Particularly, in our recent work, the photoreduction of  $CO_2$  into CO and  $CH_4$  with  $H_2$  gas as the reductant proceeded at a remarkable reaction rate through a photothermocatalytic pathway, demonstrating the important role of the photothermal effect in CO<sub>2</sub> photoreduction.<sup>[3b]</sup> However, for this specific method, the employment of H<sub>2</sub> constitutes a major obstacle to potential applications owing to the wellrecognized problem of hydrogen storage and transportation, which is due to the intrinsically very low volumetric density of hydrogen.<sup>[7]</sup> New ideas are needed that make use of the photothermal effect for CO<sub>2</sub> conversion, which might lead to distinct new possibilities towards the integration of the efficient production of renewable fuels from CO2 and the utilization of solar energy even though this comes with huge challenges.

Boron has recently gained wide attention owing to its fascinating properties and various potential applications in photocatalysis, superconducting devices, neutron detectors, and hydrogen production from water splitting through self-hydrolysis.<sup>[8]</sup> Herein, we attempted to further extend the applicability of this promising material, and investigated the photothermal conversion over elemental boron particles for the first time. More importantly, it was found that upon light irradiation, the boron particles are heated by the photothermal effect, and enable the direct and efficient catalytic reduction of CO<sub>2</sub> into CO and CH<sub>4</sub>, with reaction rates outperforming most reported state-of-the-art photocatalysis systems (see the Supporting Information, Table S1). This was attributed to 1) the excellent photohermal effect of the boron

particles, which induces a high local temperature that facilitates  $CO_2$  activation; 2) self-hydrolysis of the boron particles driven by the photothermal effect, which in situ produces  $H_2$  as the active proton source and electron donor for  $CO_2$  reduction and boron oxides as promoters of  $CO_2$  adsorption; and 3) the unique catalytic properties of boron.

In this study, commercial amorphous boron powders were used as the starting materials. As boron has a strong capability to form stable covalently bonded molecular networks, even amorphous boron has previously been demonstrated to inevitably contain regular boron icosahedra.<sup>[9]</sup> Accordingly, as seen from our X-ray diffraction (XRD) patterns (Figure S1), some diffraction peaks belonging to β-rhombohedral boron (JCPDS 01-080-0323) were observed for the amorphous boron samples, which is consistent with previous reports.<sup>[9,10]</sup> The TEM image in Figure 1 a shows the network morphology of amorphous boron. The amorphous nature was confirmed by high-resolution TEM (HRTEM) imaging (Figure 1b) as no obvious lattice fringes were observed. It should be noted that in agreement with the XRD results, some crystalline boron particles were also found during our TEM studies.



**Figure 1.** a) TEM and b) HRTEM images and c) UV/Vis/NIR spectrum of the amorphous boron material. The inserted background in gray in (c) is a solar irradiation spectrum. d) The increase in temperature of amorphous boron samples under light irradiation at different light intensities.

Owing to the rather negative potential required for  $CO_2$  reduction and also the fairly positive potential needed for the oxidation of water or sacrificial agents,<sup>[3a,11]</sup> a photocatalyst that might enable photocatalytic  $CO_2$  reduction must possess a very large band gap (usually the photocatalyst presents in white or light yellow color),<sup>[1c,2c,12]</sup> thus significantly limiting the efficiency of solar light utilization (Figure S2). In sharp contrast, the amorphous boron catalyst employed here has a typical dark brown color (Figure S2 b), implying that it has a wide light absorption range. According to the absorption spectrum in Figure 1 c, the amorphous boron particles show excellent absorption features (absorbance > 1) in the UV and

visible regions of the solar spectrum that also tail even into the NIR region. The former absorption probably originates from the interband transitions, and the latter might be related to the absence of long-range order in the amorphous boron particles.<sup>[13]</sup> The intense absorption of amorphous boron implies its high capability for the utilization of solar energy.

Considering the benefits of high temperatures for CO<sub>2</sub> activation, we investigated the photothermal effect of this amorphous boron material. The changes in temperature upon light irradiation at different intensities are depicted in Figure 1 d. As expected, upon light irradiation, an instant and remarkable increase in the temperature of the sample was observed (reaching the maximum temperature within 10 min). Furthermore, a nearly linear relationship between the increase in temperature and the light intensity was observed for the present system (Figure S3). At a light intensity of 456 mW cm<sup>-2</sup> (full arc with a maximum input power of 300 W), the temperature of the sample increased up to 462 °C. Taken together, these results clearly demonstrate the good photothermal properties of the amorphous boron material, which should be beneficial for the activation of CO<sub>2</sub> and subsequent photoreduction.

Before investigating the  $CO_2$  photoreduction, the  $CO_2$ adsorption properties of the amorphous boron material were studied. For comparison, commercial TiO<sub>2</sub>, a widely used photocatalyst for CO<sub>2</sub> reduction, was also tested. As shown in Figure S4, although these two compounds possess nearly equal specific surface areas, the CO<sub>2</sub> uptake of the amorphous boron sample was more than twice as large than that of TiO<sub>2</sub>. This should be related to the presence of boron oxides on the surface of the boron material (Figure S5),<sup>[14]</sup> which are usually considered as trapping sites for CO<sub>2</sub>.<sup>[15]</sup> Considering the superior CO<sub>2</sub> adsorption capacity and excellent photothermal properties, this amorphous boron material was anticipated to display high CO<sub>2</sub> photoreduction activity.

In the CO<sub>2</sub> photoreduction measurements, water was used as the hydrogen source, and no additional sacrificial agents or metal cocatalysts were employed in the reaction system. These features should be advantageous for potential applications. As expected, full arc irradiation of the amorphous boron material led to continuous formation of CO and CH<sub>4</sub> by CO<sub>2</sub> photoreduction with reaction rates of 1.0 and 2.5 µmolh<sup>-1</sup>, respectively (Figure 2a). Even under visiblelight irradiation ( $\lambda > 400$  nm), the use of the amorphous boron catalyst still led to the formation of CO at 0.8 µmolh<sup>-1</sup> and  $CH_4$  at 1.9 µmol h<sup>-1</sup> (Figure 2b and Figure S6). To the best of our knowledge, this is the first example of CO<sub>2</sub> photoreduction over amorphous boron. Moreover, it should be noted that the boron material outperformed most photocatalysis systems for CO<sub>2</sub> photoreduction (Table S1). Under long-term irradiation, both CH4 and CO production increased in a nearly linear fashion (Figure S7). This suggests that the catalytic activity of the amorphous boron material for CO<sub>2</sub> photoreduction is fairly stable. When experiments were performed without light irradiation or in the absence of the boron material, CO and CH<sub>4</sub> were not detected (Figure 2b). This result indicates the necessity for light and boron in this CO<sub>2</sub> reduction. To further confirm the origin of the CO and CH<sub>4</sub> products, isotope tracer analyses were conducted with

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**Figure 2.** a) Gas evolution (CO and CH<sub>4</sub>) over the amorphous boron catalyst under full arc irradiation with a Xe lamp. b) Gas-evolution rates under different conditions. c) Time course of CO and CH<sub>4</sub> generation upon irradiation of the amorphous boron catalyst before and after the addition of water to the reaction system. d) High-resolution B 1s XPS spectra of an amorphous boron sample before and after CO<sub>2</sub> photoreduction.

<sup>13</sup>CO<sub>2</sub> and D<sub>2</sub>O as the substrates on a GC-MS system under identical catalysis conditions. As shown in Figures S8 and S9, we observed the formation of <sup>13</sup>CH<sub>4</sub>, <sup>13</sup>CO, and CD<sub>4</sub>. These results clearly demonstrate that the carbon and hydrogen sources of the formed reduction products are CO<sub>2</sub> and H<sub>2</sub>O. Additionally, apart from CD<sub>4</sub>, small amounts of CD<sub>x</sub>H<sub>4-x</sub> (x =3, 2, 1, or 0) products were also formed (m/z = 19, 18, 17, 16, 15, 14, 13, and 12), which should arise from surface-adsorbed H<sub>2</sub>O on boron.<sup>[16]</sup>

To investigate the mechanism of the  $CO_2$  photoreduction over the boron material, we first examined the CO<sub>2</sub> photoreduction in the absence of H<sub>2</sub>O. To rule out any effects from adsorbed water molecules, the boron material was intentionally pretreated in a long-term vacuum process (12 h) before irradiation. Although the absence of water could result in a higher temperature on the sample under irradiation (relative to the normal conditions with water) and thus benefit the activation of  $CO_2$  (Figure S10), only negligible amounts of CO had been formed after five hours (CH4 formation is not reasonable because of the absence of a hydrogen source in the reaction system; Figure 2b, c). This result suggests that the boron material is incapable of catalyzing CO<sub>2</sub> reduction in the absence of water under light irradiation. Indeed, once water had been introduced into the reaction system, both CO and CH4 were detected, and their amounts increased with irradiation time (Figure 2c). This phenomenon indicated the critical role of water in this boron-mediated CO<sub>2</sub> photoreduction while ambiguity still remained as to what reactions occurred over the illuminated boron material after water addition.

To answer this question, the gas products formed upon the addition of water and also the possible surface changes of the boron catalysts during the reaction were carefully explored. Aside from the CO and CH<sub>4</sub> obtained by CO<sub>2</sub> reduction, hydrogen was also detected during the test (Figure S11), which should result from the hydrolysis of boron under the high-temperature conditions induced by the photothermal effect.<sup>[8b,17]</sup> Accordingly, B(OH)<sub>3</sub>, the other product of boron hydrolysis, was also observed (Figures S12-S14). B(OH)<sub>3</sub> is a volatile compound,<sup>[8b, 17b, 18]</sup> and once it has formed on the surface of the illuminated boron sample, it will be gasified owing to the high temperature, thus keeping the boron catalyst surface exposed to the gaseous reaction species (e.g., H<sub>2</sub>O, CO<sub>2</sub>, or  $H_2$ ). Indeed, after the test,  $B(OH)_3$ was not observed on the boron powders (Figure 2d) but as a deposit on the walls of the reaction cell probably owing to the low surface temperature of the walls (Fig-

ure S12). Additionally, a comparison of the XPS spectra of boron samples recorded before and after CO<sub>2</sub> photoreduction also indicated the generation of some boron suboxide intermediates (BO and  $B_xO$  with x > 1) in the test (Figure 2d),<sup>[8d]</sup> further corroborating the occurrence of a hydrolysis reaction between boron particles heated by the photothermal effect and water with H<sub>2</sub> and gaseous B(OH)<sub>3</sub> as the products.

Based on these results and considering the high reactivity of  $H_2$  for  $CO_2$  reduction, we speculated that the  $CO_2$ photoreduction observed upon water addition to the system might depend on the presence of H<sub>2</sub>. However, using Al<sub>2</sub>O<sub>3</sub> as a reference substrate instead of boron, direct irradiation of a gaseous H<sub>2</sub>/CO<sub>2</sub> mixture (without boron) did not give rise to any CH<sub>4</sub> products (Figure S15; a 1000 W Xe lamp was employed to guarantee that the substrate temperature (396°C) is nearly equal to that (378°C) achieved under normal conditions with boron as the substrate and a 300 W Xe lamp as the light source; Figure S10). This result implies that the boron material is uniquely able to catalyze CO<sub>2</sub> reduction with the in situ generated  $H_2$  acting as the proton source and electron donor. To provide more evidence supporting this conclusion, a control CO2 photoreduction experiment was carried out with H<sub>2</sub> instead of water. In Figure S16, the continuous photoreduction of CO2 is shown, further suggesting the capability of the boron material to catalytically reduce  $CO_2$  in the presence of  $H_2$  and light irradiation. As this test was performed under water-free conditions, boron oxides or  $B(OH)_3$  will not be formed during the reaction, thus ruling out that they have an effect on the CO<sub>2</sub> reduction. Further-

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more, as shown in Figure S17, under identical irradiation conditions, a lower reaction temperature resulted in significantly decreased activity. This result emphasizes the profound contribution of the photothermal effect of the boron catalyst to efficient  $CO_2$  photoreduction.

To gain more insight into the details of the  $CO_2$  photoreduction over the boron particles, in situ FTIR experiments were conducted. Figure 3 shows IR spectra for  $CO_2$  photo-



Figure 3. In situ FTIR spectra of  $CO_2$  photoreduction over the amorphous boron material recorded after various irradiation times.

reduction over amorphous boron particles for various irradiation times; the band of the boron catalyst (in the presence of CO<sub>2</sub> and water) detected before illumination was used as the background. The bands at 2341 and 2360 cm<sup>-1</sup> are associated with adsorbed CO<sub>2</sub> (Figure 3 and Figure S18).<sup>[19]</sup> For longer irradiation times, these band intensities gradually increased, illustrating the increased adsorption of CO2 on the boron catalysts. This interesting phenomenon could be explained by the formation of boron oxides (Figure 2d), which have been shown to promote CO<sub>2</sub> adsorption.<sup>[15]</sup> Obviously, this enhanced CO<sub>2</sub> adsorption will benefit subsequent photoreduction. The band related to CO was detected at 2100 cm<sup>-1</sup>.<sup>[20]</sup> The increasing peak intensity indicates the gradual formation of CO over the illuminated boron catalysts. Meanwhile, the growing absorption band at 700–1700 cm<sup>-1</sup> was attributed to C=O, C-H, and C-OH vibrations, indicative of the formation of some intermediate products of CO<sub>2</sub> reduction, such as aldehydes and bidentate carbonates.<sup>[19,21]</sup>

On the basis of the discussion above, we propose the following mechanism for the efficient  $CO_2$  photoreduction over amorphous boron particles. As shown in Figure S19, under light irradiation, the boron particles are heated to a high temperature (378 °C) by photothermal conversion, which enables the localized hydrolysis of boron with water, leading to the in situ generation of H<sub>2</sub> and boron oxides. Then, the reduction of  $CO_2$  to CO and  $CH_4$  is catalyzed by the illuminated boron particles with the in situ formed H<sub>2</sub> as the proton source and electron donor. It is noteworthy that the high efficiency of the  $CO_2$  conversion might be due to several factors: 1) The excellent photothermal effect of the boron particles induces a high local temperature, which favors the activation of  $CO_2$ . 2) The high-temperature-induced localized

boron hydrolysis results in the in situ formation of boron oxides, which could act as promoters for  $CO_2$  adsorption onto the surface of the boron catalysts. 3) The in situ formed H<sub>2</sub> is a highly reactive proton source and electron donor for  $CO_2$ reduction. 4) The amorphous boron material is efficient in solar light utilization and possesses unique catalytic properties for  $CO_2$  reduction. Additionally, crystalline boron also showed good photothermocatalytic activity for  $CO_2$  reduction (Figures S20 and S21). The reason for the difference in activity between amorphous and crystalline boron is still under investigation.

In conclusion, we have shown that elemental boron enables the direct and efficient reduction of CO2 into CO and CH<sub>4</sub> in the presence of water and under light irradiation (without any additional sacrificial agents and cocatalysts). The strong absorption of the boron catalyst in the UV/Vis and even IR region causes a remarkable local photothermal effect, which not only favored the CO<sub>2</sub> activation, but also triggered localized self-hydrolysis of boron particles to produce H<sub>2</sub> as the active proton source and electron donor for CO<sub>2</sub> reduction as well as boron oxides as promoters of CO<sub>2</sub> adsorption. As a consequence of these synergistic effects as well as the unique intrinsic catalytic properties of the boron material, high CO<sub>2</sub> conversion efficiencies were realized. These findings highlight the great promise of elemental boron for CO<sub>2</sub> conversion through a one-step photothermocatalytic process, and might lead to new possibilities for the development of more efficient solar energy utilization schemes.

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#### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** boron materials  $\cdot$  CO<sub>2</sub> photoreduction  $\cdot$  energy conversion  $\cdot$  heterogeneous catalysis  $\cdot$  photothermocatalysis

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### **Communications**



# Communications

Heterogeneous Catalysis

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Elemental Boron for Efficient Carbon Dioxide Reduction under Light Irradiation



**Four in one**: Elemental boron is an efficient catalyst for direct  $CO_2$  reduction into CO and  $CH_4$  in the presence of water under light irradiation through a one-step photothermocatalytic process. The elemental boron material harvests the incident light, converts it into thermal energy, generates hydrogen, and catalyzes the overall process.

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