OPEN

SUBJECT AREAS:
ENERGY
RENEWABLE ENERGYReceived
16 January 2014Accepted
4 March 2014Published
28 March 2014Correspondence and
requests for materials
should be addressed to
F.M.J. (fmjin@sjtu.edu.
cn)Highly efficient and autocatalytic H₂O
dissociation for CO₂ reduction into
formic acid with zincFangming Jin¹, Xu Zeng¹, Jianke Liu², Yujia Jin², Lunying Wang³, Heng Zhong⁴, Guodong Yao¹
& Zhibao Huo¹¹School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan RD, Shanghai 200240, China,²College of Environmental Science & Engineering, Tongji University, 1239 Siping RD, Shanghai, 200092, China, ³School of Materials Science and Engineering, Tongji University, 200092 Shanghai, China, ⁴Research Center for Advanced Science and Technology, University of Tokyo, 153-8904 Tokyo, Japan.

Artificial photosynthesis, specifically H₂O dissociation for CO₂ reduction with solar energy, is regarded as one of the most promising methods for sustainable energy and utilisation of environmental resources. However, a highly efficient conversion still remains extremely challenging. The hydrogenation of CO₂ is regarded as the most commercially feasible method, but this method requires either exotic catalysts or high-purity hydrogen and hydrogen storage, which are regarded as an energy-intensive process. Here we report a highly efficient method of H₂O dissociation for reducing CO₂ into chemicals with Zn powder that produces formic acid with a high yield of approximately 80%, and this reaction is revealed for the first time as an autocatalytic process in which an active intermediate, ZnH[−] complex, serves as the active hydrogen. The proposed process can assist in developing a new concept for improving artificial photosynthetic efficiency by coupling geochemistry, specifically the metal-based reduction of H₂O and CO₂, with solar-driven thermochemistry for reducing metal oxide into metal.

By converting sunlight into chemical energy, artificial photosynthetic systems could potentially produce renewable, non-polluting fuels and chemicals. Although extensive attempts at developing a highly efficient solar-to-fuel conversion have been explored^{1–4}, a high efficiency conversion with a direct use of solar energy still remains extremely challenging. In contrast to direct solar-to-fuel conversion, an integrated technology can be expected to have a high potential for improving the efficiency of artificial photosynthetic systems. The electrochemical reduction of CO₂ can be regarded as a typical integrated technology to increase artificial photosynthetic efficiency because electricity generated from solar energy could be used. Some interesting integrated technologies have recently been reported, e.g., a solar two-step water-splitting thermochemical cycle based on metal/metal oxide redox reactions for hydrogen production^{5–10}. More recently, an attractive technology for the dissociation of CO₂ and H₂O into chemical fuel using certain redox reactions driven by a solar two-step process has also been reported^{11–12}. However, the product was limited to CO, and H₂ from H₂O cannot be used in the reaction.

On the other hand, the hydrogenation of CO₂ with gaseous hydrogen is currently regarded as the most commercially feasible method^{13–15}, and this research has also become increasingly active in both fundamental and industrial applications in China¹⁶. However, gaseous hydrogen is not easily obtained from low energy processes, and both high-purity hydrogen and hydrogen storage are required, which are regarded as energy-intensive process. Moreover, no matter what methods have been reported for the hydrogenation of CO₂, catalysts are essential for these processes^{13–15,17–18}. Thus, developing an autocatalytic, highly efficient and simple process for CO₂ reduction is highly desired.

Hydrothermal reactions have played an important role in the formation of fossil fuels, e.g. the abiotic conversion of dissolved CO₂ into hydrocarbons in the Earth's crust^{19–21}. In the abiotic synthesis of organics, the generally inferred pathway involves the reduction of CO₂ dissolved in water that accompanies the hydrothermal alteration of minerals, in which a primary role of minerals is to generate reducing conditions (H₂) through the reaction of ferrous Fe-bearing minerals with water^{19–21}. The abiotic synthesis of organics suggests that highly efficient dissociation of H₂O and subsequent reduction of CO₂ into organics could be achieved with metals under hydrothermal conditions. Thus, an integrated technology of interest for high-efficiency artificial photosynthesis could be developed by coupling the geochemical reactions involved in the dissociation of H₂O and the reduction

Figure 1 | The proposed integrated technology for improving artificial photosynthetic efficiency by coupling geochemistry for the metal-based reduction of H_2O and CO_2 into organics with solar-driven thermochemistry for reducing metal oxide into metal.

of CO_2 in the presence of metals with the solar-driven thermochemical reduction of metal oxides into metals, as described in Figure 1.

With this concept, the high-efficiency reduction of CO_2 by metals is crucial because the reduction of metal oxides with solar energy has been well studied and is nearing practical application^{5–10}. Among the candidate metals that have potential for reducing water into hydrogen in the hydrothermal reduction of CO_2 , Fe was tested, but almost no reductive products were observed without a catalyst, and the reduction products of CO_2 were very low even with a catalyst^{22–26}. Zn has a strong thermodynamic driving force for oxide formation, and ZnO is often used as a catalyst in the catalytic reduction of CO_2 with hydrogen; thus, the ZnO formed in situ by Zn oxidation in water might have an autocatalytic role and lead to a simple and highly efficient reduction of CO_2 without the need for complex material microstructure design. To the best of our knowledge, no study has reported autocatalytic CO_2 reduction. Here we present a highly efficient H_2O dissociation for reducing CO_2 into formic acid using a simple, commercially available Zn powder. We reveal for the first time that this reaction is autocatalytic.

Results

The reduction of CO_2 with Zn. The investigation started with the reaction of NaHCO_3 and Zn without the addition of any catalyst over a wide range of reaction conditions: the temperature was varied from 250°C to 325°C , and the reaction time was varied from 5 to 120 min. NaHCO_3 was used as a CO_2 source for simplicity. All the reaction products in the liquid samples were pure, and only formic acid was observed by the HPLC, GC, and IC analyses. An analysis of the gas samples by GC/TCD showed that only hydrogen, a small amount of CO_2 , and a trace amount of methane were produced for reaction times longer than 60 min. Further, the organic carbon in the liquid samples was determined by TOC analysis, and the amount of carbon

in the formic acid was comparable to the total carbon in the samples, which indicates that the selectivity for the production of formic acid was approximately 100%. As shown in Figure 2, the oxidation of Zn was rapid, and almost all the Zn was oxidised to ZnO after only 10 min. Additionally, the particle size of the newly formed ZnO was smaller than that of the initial Zn powder (Supporting Information Table S1). These results indicate that CO_2 can be easily and selectively reduced into formic acid with only Zn and without the addition of a catalyst.

Further, the free energy (ΔG) and the heat of reaction (ΔH) of water dissociation for the reduction of CO_2 into formic acid by Zn was calculated using available thermodynamic data, as expressed in Eq. 1.

$$\Delta G^\circ (298 \text{ K}) = -23.01 \text{ kJ/mol} \quad \Delta H^\circ (298 \text{ K}) = -114.75 \text{ kJ/mol}$$

Clearly, both the ΔG and ΔH values are negative; thus, from the thermodynamics point of view, the formation of formic acid from the dissociation of water in the presence of Zn is understandable.

The reaction characteristics and the optimisation of the parameters. Figure 3 shows the effects of reaction temperature and time on the yield of formic acid, which is defined as the percentage of formic acid formed divided by the initial amount of NaHCO_3 based on the carbon content. The yields were obtained from experiments performed at least in triplicate, and the relative error was less than 5%. The reduction of CO_2 into formic acid proceeded efficiently, and a high formic acid yield of 40–60% was obtained after only 5 min at above 300°C (Figure 3a), and an even higher formic acid yield of 78% was obtained after 60–90 min. Further experiments with longer reaction times were performed to determine if a yield greater than 78% at 250°C could be achieved, and these experiments indicated

Figure 2 | XRD patterns (a) and the conversion of Zn into ZnO (b) after the reactions for different reaction times (300°C , Zn 10 mmol, NaHCO_3 1 mmol).

Figure 3 | The effects of temperature (a) and reaction time at 250 °C (b) on the yield of formic acid.

that the highest formic acid yield after 90 min was only 59%, which occurred at 400 min (Figure 3b). These results suggest that a temperature greater than 250 °C is needed to achieve a high yield of formic acid. This observation is in agreement with results for the hydrothermal conversion of biomass in the literature, which is perhaps related to the maximal ion-product constant for subcritical water occurring between 280 and 300 °C^{23,27,28}.

The initial pH of the solution should be a key factor in the reduction of CO₂ to formic acid because pH can affect not only the decomposition of NaHCO₃ and the oxidation of Zn but also the decomposition of the resulting formic acid^{29–31}. Thus, the effect of the initial pH of the solution was subsequently investigated, and the initial pH was adjusted with NaOH or NaCl. As shown in Figure 4a, the initial pH strongly affects the yield of formic acid. The highest yield of formic acid was observed at an initial pH of 8.6, which was the natural pH value of aqueous NaHCO₃ before adjusting with NaOH. In the case of a lower, acidic pH of 4.0, the yield of formic acid decreased to 27.2%. These results indicate that a mildly alkaline pH was favourable for a high yield of formic acid, which suggests that the formation of formic acid may occur via HCO₃[−], as discussed later.

Figure 4b shows the effect of the amount of Zn and NaHCO₃ on the yield of formic acid. An increase in the amount of Zn

resulted in a significant increase in the yield of formic acid, which should be attributed to the promotion of CO₂ hydrogenation due to a higher hydrogen concentration. In addition, the inhibition of formic acid decomposition may have also contributed to the increase in the yield of formic acid because in the decomposition of formic acid, decarboxylation (HCOOH ↔ CO₂ + H₂) is the predominant pathway in high-temperature water^{29–31}. The decreased decomposition of formic acid was also supported by the observations that only a small amount of CO₂ and no CO were detected in the gas samples. As shown in Figure 3, although a high yield of formic acid was achieved, a higher Zn/NaHCO₃ ratio of 10/1 was used. Thus, 10 mmol Zn was reacted with various amounts of NaHCO₃ to find the optimal ratio of Zn/NaHCO₃ to obtain a high yield. As shown in Figure 4b, this ratio can be decreased to approximately 3:1 and still produce a yield of approximately 70%.

The effect of CO₂ on the conversion of H₂O and Zn. In the joint system that contains CO₂ or NaHCO₃ and Zn, CO₂ may provide the additional benefit of improving the H₂O and Zn conversions because the oxidation of Zn may be shifted to the right (products) due to the consumption of hydrogen (CO₂ hydrogenation) in the presence of CO₂, as explained in Eq. (2).

Figure 4 | Effect of the initial pH (a) and the amount of NaHCO₃ and Zn (b) on the yield of formic acid.

Table 1 | Effect of CO₂ on the production of hydrogen

Entry	NaHCO ₃ /mmol	The initial pH	H ₂ /mL	CO ₂ /mL	Total gas/mL
1	0	6.9	52	0	52
2 ^[a]	0	8.6	70	0	70
3	1	8.6	74	3.5	74
4	2	8.6	78	1.3	78

SUS316 reactor, Zn: 4 mmol, Temperature: 300°C, Reaction time: 120 min.

^[a] Adjustment of the initial pH with NaOH.

To investigate this topic, the production of hydrogen with and without NaHCO₃ was examined. As shown in Table 1, the amount of hydrogen produced in the presence of NaHCO₃ was significantly greater than that in the absence of NaHCO₃ (Table 1, entries 1, 3 and 4). In the oxidation of Zn in water to ZnO, Zn(OH)₂ may also form, which is an amphoteric oxide that can be dissolved in an alkaline solution to form Zn(OH)₄²⁻. Thus, the increase in hydrogen production in the presence of CO₂ or NaHCO₃ perhaps occurs because the addition of NaHCO₃ causes an increase in pH and can remove the passivating layer, enabling the subsequent reaction with water to produce hydrogen. This assumption was supported by a further experiment in which the initial pH value of the solution was adjusted to pH 8.6 using NaOH in the absence of NaHCO₃. The amount of hydrogen collected in this experiment was almost the same as the experiment in the presence of NaHCO₃ (Table 1, entry 2). Even so, CO₂ is clearly recognised as a promoter of hydrogen production because a large amount of formic acid was formed in the presence of CO₂. Additionally, the combined amount of hydrogen in the formic acid and gas samples in the presence of CO₂ must be higher than the amount of hydrogen in the gas samples without CO₂, i.e., some the hydrogen produced is consumed for producing formic acid in the presence of NaHCO₃.

Formation of formic acid with the use of gaseous CO₂. After understanding the reaction characteristics and attaining the optimised parameters, further experiments with gaseous CO₂ were conducted. As shown in Table 2, almost no formic acid was formed without the addition of NaOH (Table 2, entries 1–2). This near absence of formic acid is most likely due to low dissolution of CO₂ in water. Increasing the initial pH of the solution should lead to an increase in the dissolved CO₂ in water. Then, experiments with added NaOH to provide an alkaline solution were conducted. The yield of formic acid, as expected, increased with the increase in the initial pH (Table 2 entries 3–7). However, the yield of formic acid was not high when compared to yields obtained with NaHCO₃. Increasing the dissolution time of CO₂ before the reaction should lead to an increase in the formic acid yield. To further increase the solubility of CO₂ in the alkaline solution, the alkaline solution (pH 14) was maintained at 80°C for 2 h after the injection of CO₂, but before the hydrothermal reaction. As a result, the yield of formic acid increased to 38% and 55% for reactions with 6 and 10 mmol Zn, respectively (Table 2, entries 8–9). These results indicate that gaseous CO₂ can be directly used, but an alkaline solution is needed to improve the solubility of CO₂.

Discussion

Possible catalytic activity of the reactor wall. An intriguing finding in the present study is that an excellent yield of formic acid can be achieved without the addition of a catalyst. Some components play a catalytic role in the production of formic acid from CO₂ in the presence of Zn. To avoid effects from the reactor wall (SUS 316),

Table 2 | Yields of formic acid with gaseous CO₂

Entry	Yield/%	CO ₂ /mmol	The initial pH ^[b]	NaOH	Zn/mmol
1	0.02	2	6.7	Without	6
2	0.06	1	6.7	Without	10
3	0.03	2	8.8	With	6
4	0.74	2	11.4	With	6
5	5.90	2	13.0	With	6
6	16.60	2	14.0	With	6
7	7.40	1	14.0	with	10
8	38.00 ^[a]	1	14.0	With	6
9	55.00 ^[a]	1	14.0	With	10

300°C, 2 h.

^[a]The solution with the addition of NaOH and input of gaseous CO₂ was maintained for 2 h at 80°C before the hydrothermal reaction with Zn.^[b]at room temperature.

experiments with a Teflon-lined reactor were conducted at 250°C for 12 h. The temperature of 250°C was selected due to the temperature limitations of the Teflon material, and a longer reaction time of 12 h was used because of both the lower reaction temperature of 250°C and the slow heating rate of this reactor system that utilised an oven as a heater. As shown in Table 3 (entry 1), a high yield of formic acid can be obtained when using Zn without the addition of any catalyst, whereas the yield of formic acid was very low, only 1.8%, when using metallic iron (Fe) without the addition of Ni (Table 3, entry 2), and only slightly higher, 2.0%, when using Mg (Table 3, entry 3); however, a large amount of hydrogen was detected for these two cases. Further, the yield of formic acid greatly increased with the addition of a Ni catalyst when using either Fe or Mg (Table 3, entries 4–5). These results suggest that the reactor wall, composed of SUS 316, had no significant catalytic role, and the higher yield of formic acid when using Zn is attributed primarily to a catalytic role in the reduction of CO₂ to formic acid, i.e., some components play a catalytic role in the formation of formic acid from CO₂ in the presence of Zn.

Catalytic activity of the formed ZnO. ZnO is traditionally a good hydrogenation catalyst. After eliminating the possible catalytic effect of the reactor wall, the ZnO formed by the oxidation of Zn under hydrothermal conditions might have an autocatalytic role. To assess whether the formed ZnO acts as an autocatalyst, Zn was substituted with gaseous hydrogen and ZnO (hereafter called H₂ + ZnO). Reagent-grade ZnO, as well as both dry and wet ZnO collected after the Zn reactions were completed, was used in these experiments. The wet ZnO was collected to determine the loss in ZnO activity after the reactions with the dry ZnO. A two-step reaction was investigated for the experiments with wet ZnO. In the first step, Zn reacted with water, and H₂ and NaHCO₃ were added to the solution in the second step. Compared to the formic acid yields obtained without ZnO, the yield of formic acid with ZnO, particularly for wet ZnO collected after the Zn reaction, was slightly higher (Table 4), indicating that the added ZnO, even for the wet ZnO collected after the Zn reaction, only provides a very weak catalytic activity. Considering these results, a reasonable suggestion is that the added ZnO or the ZnO collected after the reactions has no significant catalytic activity in the reduction of CO₂ into formic acid. In other words, only the ZnO formed in situ has catalytic activity in the reduction of CO₂ into formic acid.

The activity of gaseous hydrogen (H₂) may be different from that of the hydrogen produced in situ in high-temperature water with Zn. Direct evidence that would confirm this assumption experimentally is difficult to obtain. Thus, experiments with Fe as a substitute for Zn in the presence and absence of ZnO were conducted. Fe was used as a substitute reducing agent for Zn because Fe can dissociate water and

Table 3 | Formic acid yields^[a] with a Teflon-lined reactor

Entry	Reductant	Reductant/ NaHCO_3 /mmol	Ni	Yield/%	Conditions	
					Temp./°C	Time/h
1	Zn	16/4	no	36.2	250	12
2	Fe	24/4	no	1.8	"	"
3	Mg	16/4	no	2.0	"	"
4	Mg	16/4	Ni	12.5	"	"
5	Fe	24/4	Ni	8.0	"	"

250°C, 12 h.
^[a]Formic acid yield is defined as the percentage of formic acid and the initial NaHCO_3 based on the carbon.

produce hydrogen, however, in the absence of a catalyst almost no reduction of NaHCO_3 occurred with this added Fe. The resulting yield of formic acid in the presence of Fe and ZnO was much lower than the yield with only Zn (Table 4, entries 6–11). Furthermore, the yield of formic acid with Mg and ZnO was also much lower than the yield with only Zn (Table 4). These results indicate that the hydrogen molecules generated by these metals have different activities and that only hydrogen from the oxidation of Zn in water is active for CO_2 reduction.

The autocatalytic mechanism. To study the autocatalytic mechanism of ZnO, we examined changes in the infrared (IR) absorption peaks of solid samples over the course of the reaction to identify whether an active intermediate structure was forming. As shown in Figure 5, no significant IR absorption peaks appeared for bulk ZnO. However, a peak at 3336.8 cm^{-1} caused by the stretching mode of the O–H complexes in ZnO^{32-35} was clearly observed in samples after the reaction, suggesting that the active intermediate structure likely involves species of $\text{H-Zn}\cdots\text{O-H}$. Then, the hydrogen in the ZnH^- complex could act as an active hydrogen due to the weak Zn–H bond. The ZnH^- complex has been reported as a possible source of active hydrogen for hydrogenation reactions, such as the Cu/ZnO-catalysed synthesis of methanol from a mixture of CO , CO_2 , and H_2 ³⁶ and the synthesis of the mononuclear alkyl Zn–H complex³⁷.

However, no IR absorption peak for a ZnH^- complex was observed. Interestingly, the two peaks observed at 1390 cm^{-1} and 1510 cm^{-1} corresponded respectively to the asymmetrical and symmetrical stretching of the absorbed HCOO^- ³⁸, and this result indicates that the IR absorption peak for ZnH^- is absent because the hydrogen in ZnH^- reacts with CO_2 to form formic acid. Furthermore, an ATR-FTIR experiment examining wet samples after reacting with only Zn (without NaHCO_3) revealed a clear peak for the ZnH^- complex at 1640 cm^{-1} . These results clearly indicate that the ZnH^- complex is formed and CO_2 hydrogenation occurs with the hydrogen in ZnH^- .

The key question in this discussion is then whether the active hydrogen in the Zn–H complex reacts with CO_2 or HCO_3^- . As mentioned before, almost no formation of formic acid was observed when using gaseous CO_2 in the absence of NaOH, and the yield of formic acid greatly increased in the presence of NaOH. From these results, hydrogenation can be concluded to occur mainly with HCO_3^- . Further, from Figure 4a, a mildly alkaline pH was favourable for a high yield of formic acid, and the highest yield of formic acid occurred at an initial pH of 8.6, which was the pH value of the NaHCO_3 solution prior to pH adjustment. Furthermore, an examination of the changes in pH of the solution after reaction times of 20–120 min indicated that the pH of the solution after the reaction was also 8.6–8.7, which was similar to the initial pH. Because HCO_3^- is the dominant anion at low temperatures and moderately alkaline pH, these observations suggest that HCO_3^- is the predominant species during these reactions, which is further evidence that the hydrogenation occurs with HCO_3^- . These results are in agreement with the calculated equilibrium distribution of CO_2 , HCO_3^- , CO_3^{2-} , and

HCOO^- at 300°C , 350 pars, which reported that HCO_3^- and HCOO^- were the predominantly dissolved carbon species at a moderately alkaline pH^{19,21}.

Based on these results, a possible mechanism can be explained as shown in Figure 6. Initially, ZnH^- complex 1 is generated from Zn oxidation in water (reaction I). In complex 1, both the electron-rich oxygen atom and electron-deficient Zn atoms of ZnO abstract a proton from the hydrogen moiety. The subsequent nucleophilic attack of the anionic proton of formed complex 1 on bicarbonate ion 2 yields the compound formate 4, along with zinc complex 5, and this complex then loses water to form ZnO 6.

The mechanism of H_2 absorption onto ZnO (reaction II) may also occur because a small amount of formic acid can be formed using $\text{H}_2 + \text{ZnO}$ (Table 1, entries 3–5). If reaction II occurs, then it would be favoured by a long reaction time. As expected, when using $\text{H}_2 + \text{ZnO}$, the yield of formic acid was significantly lower (0.6%) for a short reaction time of 10 min. However, the yield of formic acid increased to 7.4% after 30 min and to 23% after 120 min. Furthermore, the ratio of the yield of formic acid when using $\text{H}_2 + \text{ZnO}$ and only Zn clearly increased with increasing reaction time (Table S2). These results suggest that reaction II mainly occurred in the latter stage. From Figure 1 (a), the rate of formic acid formation before 10 min was much faster than that after 10 min. The rapid increase before 10 min should be responsible for reaction I, and the slow increase after 10 min for reaction II can be explained by the mass transfer limitations of H_2 because reaction II is a diffusion-limited reaction.

Zn cycle and assessment for energy conversion efficiency of solar energy to fuel with the proposed integrated technology. At present, our results show that CO_2 can be converted into formic acid with a

Table 4 | Formic acid yields with NaHCO_3 in the presence and absence ZnO

Run	Reductant	Reductant/ NaHCO_3 (mmol)	Additives	Yield/%
1	Zn	6/1	Without	57.5
2	H_2	6/1	Without	13.0
3	H_2	6/1	Reagent $\text{ZnO}^{[a]}$	16.0
4	H_2	6/1	Collected dry $\text{ZnO}^{[b]}$	15.5
5	H_2	6/1	Collected wet $\text{ZnO}^{[c]}$	23.0
6	Fe	4/1	Without	6.8
7	Fe	4/1	Reagent $\text{ZnO}^{[a]}$	5.5
8	Fe	4/1	Collected wet $\text{ZnO}^{[c]}$	5.1
9	Fe	6/1	Without	15.6
10	Fe	6/1	Reagent $\text{ZnO}^{[a]}$	6.7
11	Fe	6/1	Collected wet $\text{ZnO}^{[c]}$	9.6

The additive amount of ZnO in mole is the same as the reductant for all experiments.

^[a]Reagent ZnO: In power with 200-mesh size;

^[b]The solid residue collected after the reaction of using Zn and were treated by washing with deionized water several times, filtrating and drying in air;

^[c]see Supporting Information.

Figure 5 | FT-IR absorption spectra of wet sample after reactions with only Zn without NaHCO_3 (a) and bulk ZnO and solid samples after reactions with Zn and NaHCO_3 (b ~ f, NaHCO_3 1 mmol) (300°C , Zn 10 mmol).

high efficiency and selectively without the addition of a catalyst. As mentioned previously, ZnO can be reduced into Zn using concentrated solar energy^{10–15}. Additionally, a novel solar chemical reactor was developed in 1998³⁹, and recent research has shown much potential for the reduction of ZnO into Zn using concentrated solar energy at an industrial scale in the near future^{10,40}. Hence, a

highly efficient dissociation of H_2O for CO_2 reduction as shown in Figure 1 could potentially be achieved with Zn as a reductant under hydrothermal conditions combined with the reduction of the ZnO system using solar energy.

Further, on basis of the proposed integrated technology by coupling the proposed hydrothermal reduction of CO_2 with Zn and the

Figure 6 | Proposed mechanism of reduction of HCO_3^- into formic acid with Zn.

reduction of ZnO into Zn by solar energy as shown (see Figure 1), and a simple assessment of the energy efficiency of the solar to fuel (formic acid) process was performed.

Hydrothermal reduction of CO₂ with Zn can be written as:

Reduction of ZnO into Zn by solar energy can be written as:

Therefore, the solar-to-HCOOH energy conversion efficiency can be expressed as:

$$\eta_{\text{Zn to HCOOH}} = \eta_1 \times \eta_2 \quad (5)$$

where η_1 is the energy efficiency of Eq (3) and η_2 is the energy efficiency of Eq (4). Since Eq (3) is an exothermic reaction, and Zn is an energy input, η_1 can be expressed as:

$$\eta_1 = \frac{M_{\text{HCOOH}} \times \Delta H_{\text{HCOOH}}}{M_{\text{Zn}} \times \Delta H_{\text{Zn}}} \quad (6)$$

where M_{HCOOH} is the molar production of HCOOH, M_{Zn} is the molar consumption of Zn, and ΔH_{HCOOH} and ΔH_{Zn} are the higher heating values of formic acid and Zn, respectively. As discussed earlier (see Figure 4b), a 70% conversion efficiency from CO₂ to HCOOH was obtained for the condition NaHCO₃:Zn = 1:3, i.e., 3 mol Zn could yield 0.7 mol HCOOH. Thus, by substituting the higher heating values of formic acid and ZnO, Eq. (6) can be obtained as shown in Eq (7).

$$\eta_1 = \frac{0.7 \times (-254.34)}{3 \times (-350.46)} \% = 16.9\% \quad (7)$$

An energy efficiency (η) of 29–36% for ZnO-Zn-H₂ by solar energy has been achieved according to the literature¹⁰. If we use a lower energy efficiency such as 30% for ZnO-Zn-H₂ by solar energy, then the solar-to-HCOOH energy efficiency for Zn to HCOOH could achieve a value of ~5%.

The integrated technology from coupling the proposed hydrothermal reduction of CO₂ by Zn and the reduction of ZnO into Zn by solar energy can be compared with related technologies in the literature. Other researchers have proposed the production of hydrogen via metal oxide redox resulting from the solar-driven two-step dissociation of H₂O, but the hydrogen cannot be directly used to reduce CO₂. For the solar-driven two-step thermochemical dissociation of CO₂ and H₂O into chemical fuel using metal oxide redox, the product is limited to CO, and H₂ from water cannot be used to reduce CO₂.

In summary, we have developed a highly efficient and autocatalytic method of H₂O dissociation for the reduction of CO₂ into chemical fuel with commercially available Zn powder that produces formic acid with a high yield (70–80) from CO₂ and an exceptionally high selectivity of formic acid (ca. 100%). The mechanism of the autocatalytic reduction of CO₂ involves the formation of an active intermediate structure, Zn–H. The proposed process features multiple benefits, such as avoiding precious-metal catalysts and requiring neither high-purity hydrogen nor hydrogen storage, which are regarded as energy-intensive processes for conventional CO₂ hydrogenation. The proposed process can be linked to develop a new integrated technology for improving artificial photosynthetic efficiency by coupling geochemistry, specifically the metal-based reduction of H₂O and CO₂ into organics, with solar-driven thermochemistry for reducing metal oxide into metal. On the basis of this new integrated technology, a solar-to-fuel efficiency of approximately 5% can be achieved.

Methods

Materials and general procedure. Most experiments were conducted with sodium bicarbonate (NaHCO₃) as the CO₂ source for experimental convenience. In

particular cases, gaseous CO₂ and hydrogen were directly used. The zero-valent metals and metal oxides were in powder form with a particle size of 200 mesh without any further treatment. All the reagents were purchased from Sinopharm Chemical Reagent Co., Ltd, and were of analytical grade.

Experiments were conducted using a batch reactor that consisted of SUS 316 tubing with two end fittings, giving an inner volume of 5.7 mL. Details of the apparatus have been described previously^{41–42}. The typical reaction procedure was as follows: a desired amount of NaHCO₃, metal powders and 2 mL deionised water were loaded into the reactor and occupied 35% of the total reactor volume. After loading, the reactor was sealed and then immersed into a salt bath, which had been preheated to the desired temperature. The typical heating time required to raise the temperature of the reactor from 20 to 300 °C was approximately 30 s. After the predetermined reaction time, the reactor was removed from the salt bath and immediately immersed in a cold water bath. The reaction time was defined as the time period during which the reactor was kept in the salt bath.

A Teflon-lined stainless steel reactor with an inner volume of 22.8 mL was used to examine the possible catalytic effects of the 316 SUS reactor wall. Details of the apparatus and experimental procedure have been described elsewhere²³ and can also be found in the Supporting Information.

Sample analyses. After the reactors were cooled, the liquid, solid and gaseous samples were collected for analysis. Liquid samples were analysed via high-performance liquid chromatography (HPLC), gas chromatography/mass spectroscopy/flame ionisation detector (GC/MS/FID) and total organic carbon (TOC). A quantitative estimation of the formic acid concentration was based on the average value obtained from at least three samples via the HPLC analysis. Gas samples were analysed with a GC/TCD system. Details of the apparatus and analytical conditions of the GC/MS/FID/TCD have been described elsewhere^{41–42}, and can be found in the Supporting Information. Solid samples were washed with deionised water several times, dried in air and then characterised by X-ray diffraction (XRD) and infrared spectroscopy (IR). The particle size distribution (PSD) of the solid samples was determined using an EyeTech instrument. The details of the apparatus and analytical conditions for the solid samples with XRD, IR and PSD can also be found in the Supporting Information.

- Jessop, P. G., Joo, F. & Tai, C. C. Recent advances in the homogeneous hydrogenation of carbon dioxide. *Coord. Chem. Rev.* **248**, 2425–2442 (2004).
- Sakakura, T., Choi, J. C. & Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **107**, 2365–2387 (2007).
- Wang, W., Wang, S. P., Ma, X. B. & Gong, J. L. Recent advances in catalytic hydrogenation of carbon dioxide. *Chem. Soc. Rev.* **40**, 3703–3727 (2011).
- Yadav, R. K. *et al.* A photocatalyst-enzyme coupled artificial photosynthesis system for solar energy in production of formic acid from CO₂. *J. Am. Chem. Soc.* **134**, 11455–11461 (2012).
- Haueter, P., Moeller, S., Palumbo, R. & Steinfeld, A. The production of zinc by thermal dissociation of zinc oxide-solar chemical reactor design. *Sol. Energy* **67**, 161–167 (1999).
- Steinfeld, A. Solar thermochemical production of hydrogen—a review. *Sol. Energy* **78**, 603–615 (2005).
- Kodama, T. & Gokon, N. Thermochemical cycles for high-temperature solar hydrogen production. *Chem. Rev.* **107**, 4017–4048 (2007).
- Galvez, M., Loutzenhiser, P., Hischer, I. & Steinfeld, A. CO₂ splitting via two-step solar thermochemical cycles with Zn/ZnO and FeO/Fe₃O₄ redox reactions: thermodynamic analysis. *Energy Fuels* **22**, 3544–4550 (2008).
- Steinfeld, A. *et al.* Solar-processed metals as clean energy carriers and water-splitters. *Int. J. Hydrogen. Energy* **23**, 767–774 (1998).
- Steinfeld, A. Solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn/ZnO redox reactions. *Int. J. Hydrogen. Energy* **27**, 611–619 (2002).
- Chueh, W. C. *et al.* High-Flux Solar-Driven Thermochemical Dissociation of CO₂ and H₂O using Nonstoichiometric Ceria. *Science* **330**, 1797–1801 (2010).
- Chueh, W. C. & Haile, S. M. Ceria as a thermochemical reaction medium for selectively generating syngas or methane from H₂O and CO₂. *ChemSusChem* **2**, 735–739 (2009).
- Huff, C. A. & Sanford, M. S. Cascade Catalysis for the Homogeneous Hydrogenation of CO₂ to Methanol. *J. Am. Chem. Soc.* **133**, 18122–18125 (2011).
- Chan, B. & Radom, L. Design of Effective Zeolite Catalysts for the Complete Hydrogenation of CO₂. *J. Am. Chem. Soc.* **128**, 5322–5323 (2006).
- Hu, Y. H. Solid-solution catalysts for CO₂ reforming of methane. *Catal. Today* **148**, 206–211 (2009).
- Liu, C. J. Do we have a rapid solution for CO₂ utilization? A perspective from China. *Greenhouse Gas Sci Technol.* **2**, 75–76 (2012).
- Sun, Q. D., Ye, J. Y., Liu, C. J. & Ge, Q. F. In₂O₃ as a promising catalyst for CO₂ utilization: A case study with reverse water gas shift over In₂O₃. *Greenhouse Gas Sci Technol.* **4**, 140–144 (2014).
- Zhao, B. R., Pan, Y. X. & Liu, C. J. The promotion effect of CeO₂ on CO₂ adsorption and hydrogenation over Ga₂O₃. *Catal. Today* **194**, 60–64 (2012).
- McCammon, C. The Paradox of Mantle Redox. *Science* **308**, 807–808 (2005).
- Holm, N. G. & Charlou, J. L. Initial indications of abiogenic formation of hydrocarbons in the Rainbow ultramafic hydrothermal system, Mid-Atlantic Ridge. *Earth. Planet. Sci. Lett.* **191**, 1–8 (2001).

21. McCollom, T. M. & Seewald, J. S. A reassessment of the potential for reduction of dissolved CO₂ to hydrocarbons during serpentinization of olivine. *Geochim. Cosmochim. Acta*. **65**, 3769–3778 (2001).
22. Wu, B. *et al.* Catalytic conversion of NaHCO₃ into formic acid in mild hydrothermal conditions for CO₂ utilization. *Catal. Today* **148**, 405–410 (2009).
23. Jin, F. M. *et al.* High-yield reduction of carbon dioxide into formic acid by zero-valent metal/metal oxide redox cycles. *Energy. Environ. Sci.* **4**, 881–884 (2011).
24. Takahashi, H. *et al.* CO₂ reduction using hydrothermal method for the selective formation of organic compounds. *J. Mater. Sci.* **41**, 1585–1589 (2006).
25. Takahashi, H., Kori, T., Onoki, T., Tohji, K. & Yamasaki, N. Hydrothermal processing of metal based compounds and carbon dioxide for the synthesis of organic compounds. *J. Mater. Sci.* **43**, 2487–2491 (2008).
26. Tian, G. *et al.* Hydrothermal reactions from carbon dioxide to phenol. *ChemSusChem*. **3**, 323–324 (2010).
27. Franck, E. U. Thermophysical properties of supercritical fluids with special consideration of aqueous systems. *Fluid Phase Equilib.* **10**, 211–212 (1983).
28. Janecky, D. R. & Seyfried, W. E. Hydrothermal serpentinization of peridotite within the oceanic crust: Experimental investigations of mineralogy and major element chemistry. *Geochim. Cosmochim. Acta* **50**, 1357–1378 (1986).
29. Yasaka, Y., Yoshida, K., Wakai, C., Matubayasi, N. & Nakahara, M. Kinetic and equilibrium study on formic acid decomposition in relation to the water-gas-shift reaction. *J. Phys. Chem. A*. **110**, 11081–11090 (2006).
30. Jin, F. M. *et al.* Hydrothermal conversion of carbohydrate biomass into formic acid at mild temperatures. *Green Chem.* **10**, 612–615 (2008).
31. Peterson, A. *et al.* Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy. Environ. Sci.* **1**, 32–65 (2008).
32. Chauvin, C., Saussey, J., Lavalley, J. C. & Djega-Mariadassou, G. Definition of polycrystalline ZnO catalytic sites and their role in CO hydrogenation. *Appl. Catal.* **25**, 59–68 (1986).
33. Kokes, R. J., Dent, A. L., Chang, C. C. & Dixon, L. T. Infrared studies of isotope effects for hydrogen adsorption on zinc oxide. *J. Am. Chem. Soc.* **94**, 4429–4436 (1972).
34. Griffin, G. L. & Yates, J. T. Combined temperature-programmed desorption and infrared study of H₂ chemisorption on ZnO. *J. Catal.* **73**, 396–405 (1982).
35. Xiong, G., Pal, U., Serrano, J. G., Ucer, K. B. & Williams, R. T. Combined temperature-programmed desorption and infrared study of H₂ chemisorption on ZnO. *Phys. Stat. Sol.* **3**, 3577–3581 (2006).
36. Zapol, P., Jaffe, J. B. & Hess, A. C. Ab initio study of hydrogen adsorption on the ZnO (1010) surface. *Surf. Sci.* **422**, 1–7 (1999).
37. Sattler, W. & Parkin, G. Structure and reactivity of a mononuclear organozinc hydride complex: facile insertion of CO₂ into a Zn–H bond and CO₂-promoted displacement of siloxide ligands. *J. Am. Chem. Soc.* **133**, 9708–9711 (2011).
38. Tardio, J., Bhargava, S., Prasad, J. & Akolekar, D. B. Catalytic wet oxidation of the sodium salts of citric, lactic, malic and tartaric acids in highly alkaline, high ionic strength solution. *Top. Catal.* **33**, 193–199 (2005).
39. Steinfeld, A., Brack, M., Meier, A., Weidenkaff, A. & Wüthrich, D. *Energy* **23**, 803–814 (1998).
40. http://www.nrel.gov/hydrogen/pdfs/development_solar-thermal_zno.pdf.
41. Jin, F. M. *et al.* Controlling Hydrothermal Reaction Pathways To Improve Acetic Acid Production from Carbohydrate Biomass. *Environ. Sci. Technol.* **39**, 1893–1902 (2005).
42. Jin, F. M., Kishita, A., Moriya, T. & Enomoto, H. Kinetics of oxidation of food wastes with H₂O₂ in supercritical water. *J. Supercrit. Fluids.* **19**, 251–262 (2001).

Acknowledgments

We gratefully acknowledge financial support from the Natural Science Foundation of China (Grant No. 21077078, 21277091).

Author contributions

F.M.J. developed the idea, designed the experiments and wrote the paper. Y.J.J., J.K.L., X.Z., L.Y.W. performed the experiments and analyzed data. All authors contributed to analysis and discussion of the experimental data.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Jin, F.M. *et al.* Highly efficient and autocatalytic H₂O dissociation for CO₂ reduction into formic acid with zinc. *Sci. Rep.* **4**, 4503; DOI:10.1038/srep04503 (2014).

This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported license. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-nd/3.0>