View Article Online View Journal

Journal of Materials Chemistry A

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Zhao, Y. Gu, P. Chen, Z. Xin, H. Zhu, B. Wang, K. Zhu, S. C. Yan and Z. Zou, *J. Mater. Chem. A*, 2019, DOI: 10.1039/C9TA00562E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-a

Journal Name

ARTICLE



Highly Selective Electrochemical CO₂ Reduction to CO Using a Redox-Active Couple on Low-Crystallinity Mesoporous ZnGa₂O₄ Catalyst

Meiming Zhao^a, Yaliu Gu^a, Ping Chen^a, Zhenyu Xin^a, Heng Zhu^a, Bing Wang^{*a}, Kai Zhu^{*b}, Shicheng Yan^{*a} and Zhigang Zou^{ac}

Substantial overpotential of CO₂ activation, complex CO₂ reduction pathway, and the competitive H₂ evolution reaction (HER) limit the practical applications of CO₂-based electrochemical energy conversion and storage technology due to the low energy efficiency and product selectivity. Here, we proposed a strategy that combines mesopores and redox-active couple to effectively capture CO₂ and selectively generate CO product. As an example, we construct a redox-active couple, Zn^{2+}/Zn^+ , on the low-crystallinity mesoporous $ZnGa_2O_4$ electrocatalyst. The mesopores not only help to capture CO₂ effectively but also inhibit the H₂ evolution. The weak lattice constraint of low crystallinity benefits to formation of Zn^{2+}/Zn^+ redox couple to strongly interact with CO₂ molecule for subsequent activation and catalytic conversion, thus decreasing the activation energy of CO₂ to active species CO₂⁻ effectively and accelerating the proton transfer to form crucial COOH* intermediate. Consequently, this catalyst exhibited highly faradaic efficiency of 96% among Zn-based electrodes for CO generation at the relatively low applied potential of -1.4 V vs. Ag/AgCl (-0.8 V vs. RHE) and excellent stability during 10 h operation in 0.1 M KHCO₃ solution.

Introduction

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 20 March 2019. Downloaded by Tulane University on 3/23/2019 8:52:45 AM.

The unprecedented consumption of fossil fuels induced the energy shortage and potential global environmental crisis.^[1-3] In this scenario, CO_2 electrochemical reduction reaction (CO_2RR), converting chemical inert CO_2 molecule to fuels for a sustainable supply of electric energy, seems to be a promising solution to support environmental stability and to balance the use of natural resources.^[4, 5] CO, as one significant component of syngas (CO/H_2), is a common CO_2RR product exhibiting a

great potential to generate liquid fuels and synthetic petroleum through Fischer-Tropsch methods.^[6, 7] It is well established that the CO product from electrochemical CO₂ reduction mainly includes the following steps: ^[8] the activation of CO₂ by one electron *via* CO₂ + e⁻ \rightarrow CO₂⁻, proton reduction to generate COOH* (* is an indicative of adsorption site) by CO₂⁻ + * + H⁺ \rightarrow COOH*, converting COOH* to CO* by COOH* + H⁺ + e⁻ \rightarrow CO* + H₂O, and CO generation *via* CO* \rightarrow CO + *. In such reaction pathway, a challenge is to stably generate the important species CO₂⁻ and COOH* for selectively producing CO.

Several precious metals, such as Au,^[8] Ag,^[9] and Pd,^[10, 11] were demonstrated to exhibit the tightly binding with COOH* intermediate and weakly binding with CO*, thus affording high faradaic efficiency (generally > 90%) in CO generation.^[12] Similarly, metal Zn is also able to directly reduce CO₂ to CO.^{[13-} ^{15]} However, the faradaic efficiencies of Zn electrodes are still limited at 70~85%, even in the nanostructures such as nanoparticle, nanosheet, and nanodendrite.[13-15] A few of Zn atoms or ions-containing catalysts have been supposed to construct more effective active sites. For example, a zincnitrogen (Zn-N_x) ligand was constructed by coordinating the single Zn atom with N-doped graphene and achieved a high faradaic efficiency for CO up to 91~95% due to that the synergistic effect of Zn and N atoms could decrease the free energy barrier of COOH* formation and subsequently facilitate the desorption of CO*. [16, 17] The Zn-N ligand of organometallic complex was found as a Lewis base to activate inert CO₂ gas and successfully lowered the overpotential for CO₂ reduction approximately 0.6 V.^[18] CO₂ reduction on the Zn complex is

^a Jiangsu Key Laboratory of Artificial Functional Materials, Eco-materials and Renewable Energy Research Center (ERERC), National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, College of Engineering and Applied Sciences, Nanjing University, No. 22 Hankou Road, Nanjing, Jiangsu 210093, P. R. China. Email: yscfei@nju.edu.cn, bingwang@nju.edu.cn

^{b.} School of Information Science and Engineering, Nanjing University Jinling College, No. 8, Xuefu Road, Nanjing, Jiangsu 210089, People's Republic of China.Email: zhukai@jlxy.nju.edu.cn

^{c-} Jiangsu Key Laboratory for Nano Technology, National Laboratory of Solid State Microstructures, School of Physics, Nanjing University, No. 22, Hankou Road, Nanjing, Jiangsu 210093, People's Republic of China

t Electronic Supplementary Information (ESI) available: [XRD pattern of NaGaO₂. XRD patterns, N₂ adsorption-desorption isotherms, pore diameter, CO₂ adsorption-desorption isotherms, H₂ faradaic efficiency, partial current density and EPR signals of H-ZnGa₂O₄ and L-ZnGa₂O₄. Polarization curves on bare titanium sheet in N₂ or CO₂-saturated 0.1 M KHCO₃ solution. Oxidation peak of commercial ZnO, L-ZnGa₂O₄ and commercial Ga₂O₃ in CO₂-saturated 0.1 M KHCO₃ solution. Photograph of ZnO electrode and ZnGa₂O₄ electrode after CV scanning. XPS spectra of H-ZnGa₂O₄ at + 1.03V and -1.2 V. The cyclic voltammogram of the L-ZnGa₂O₄ in CO₂-saturated KCl, KHCO₃ solution (vs. RHE). Ultraviolet-visible (UV-vis) absorption spectrum of commercial ZnO, L-ZnGa₂O₄ after and before reaction. High-magnification TEM images and SAED patterns of L-ZnGa₂O₄ and H-ZnGa₂O₄ after reaction. See DOI: 10.1039/x0xx00000x

ARTICLE

expected to be achieved by a Zn redox couple, possibly Zn²⁺/Zn⁺ or Zn²⁺/Zn⁰. Monovalent Zn⁺ (3d¹⁰4s¹) has been proved to be a functional species in many cases due to the coordinatively unsaturated characteristic.^[19] For instance, the Zn⁺-V_o (oxygen vacancy) complexes in Zn-containing layered double hydroxide nanosheets are effective trapping sites for the CO₂ adsorption and significantly improve the activity of photocatalytic reduction of CO₂.^[20] However, to construct abundant and stable Zn redox couple on the inorganic catalysts is still a challenge due to their strong lattice constraint and limited specific surface area.

Here, we proposed a strategy that constructs surface abundant Zn²⁺/Zn⁺ redox-active couple on low-crystalline inorganic material with high specific area. The abundant redoxactive couple easily formed on the surface of the lowcrystallinity mesoporous $ZnGa_2O_4$ due to the weak lattice constraint and inherently exhibited strong interactions with carbon-based species. Moreover, the mesoporous structure of ZnGa₂O₄ may generate diffusion gradients through the local consumption of proton donor such as HCO3- to inhibit H2 evolution, offers high specific area to generate abundant Zn^{2+}/Zn^{+} redox-active couple and captures CO_2 molecule efficiently. The Zn^{2+}/Zn^{+} redox couple on $ZnGa_{2}O_{4}$ catalyst effectively activates the CO_2 to the active species CO_2^- and strongly coupled the electron and proton to form crucial COOH* intermediate. The inherently strong interaction between CO₂ and Zn^{2+}/Zn^{+} accompanied with the intrinsic advantage of mesoporous structure effectively suppressed the competitive H₂ evolution reaction, compared with other Zn-based electrodes, the L-ZnGa₂O₄ achieved the highest faradaic efficiency (96%) at the moderate applied potential of -1.4 V vs Ag/AgCl (-0.8 V vs. RHE), intuitively indicating the high selectivity and superior performance of L-ZnGa₂O₄.

Experimental section

Published on 20 March 2019. Downloaded by Tulane University on 3/23/2019 8:52:45 AM.

Synthesis of Mesoporous ZnGa₂O₄ Powders

Briefly, the porous ZnGa₂O₄ solid powders were prepared by ion exchange between $\ensuremath{\mathsf{NaGaO}}_2$ colloidal suspension and an aqueous solution of Zn(CH₃COO)₂. At first, in order to obtain the NaGaO₂ powders, Na₂CO₃ (1.07 g) and Ga₂O₃ (1.87 g) (molar ratio 1.01:1) were carefully ground in the mortar, then the mixed powders were transferred to an alumina crucible and heated at 1123K for 12h. Next, NaGaO₂ colloidal suspension (0.2 M, 10 mL) was prepared though dissolving the NaGaO₂ powder in deionized water. The pre-made suspension was added to Zn(CH₃COO)₂ aqueous solution(0.05 M, 20 mL) and the mixture was stirred for 3 h at room temperature. The mesoporous ZnGa₂O₄ was formed via a reaction of 2NaGaO₂ + Zn(CH₃COO)₂ \rightarrow ZnGa₂O₄ + 2CH₃COONa. After the reaction finished, the white sediment was separated by centrifugation and washed by deionized water for several times, then dried in air atmosphere at 343 K for 24 h. The high-crystallinity ZnGa₂O₄ powder was prepared by the same method with a heat treatment of the ionexchange sample under air in muffle furnace at 973K for 8h.

Preparation of Working Electrode

Journal Name

Compared with other electrocatalyst support, titanium is of high electrical conductivity and negligible $^{0.145}$ h $^{0.165}$ h $^{0.165}$ reduction. Because of its excellent properties, the as-prepared ZnGa₂O₄ powders were deposited on a titanium sheet (0.2 mm thickness, 99.5 % purity) via electrophoretic deposition (EPD). Before the preparation of working electrode, titanium sheets need to be chemically polished in a solution containing HF, HNO₃, H₂O (1:2:7 in volume) for 30s and cleaned with acetone, ethanol, deionized water under ultrasonic concussion in order to remove the compact oxidation layer. Just prior to EPD, 40 mg of ZnGa₂O₄ particles and 10 mg iodine were dispersed in 50 mL acetone solution by sonication for 30 min. Then, two titanium sheets were placed vertically at a 10 mm distance and immersed in the suspension followed by adding 20 V bias between them for 5 min. During the EPD process, insulating tapes were used in order to ensure the 1 cm² deposition area of the electrode.

Characterization of Mesoporous ZnGa₂O₄ Powders

The crystalline phases of the as-prepared ZnGa₂O₄ powders were determined by XRD (Rigaku Ultima III, CuKa radiation). The specific surface area of the ZnGa₂O₄ catalysts were obtained by nitrogen absorption at 77K on a surface area and porosity analyzer (Micromeritics ASAP 2020., USA) and calculated by BET method. CO₂ adsorption capacity was detected at 273 K based on the Brunauer–Emmett–Teller (BET) method at $P/P_0 = 0.03$. High-solution images and selected area electron diffraction (SAED) patterns of the ZnGa₂O₄ catalysts, were collected by transmission electron microscopy (TEM, FEI Tecnai G2 F30 S-Twin, USA) operated at 200 kV. UV-vis diffuse reflectance spectra (DRS) were obtained using a UV-vis spectrophotometer (UV-LAMBDA 950, PerkinElmer, USA) and were transformed into the absorption spectra according to the Kubelka-Munk relationship. The chemical state of ZnGa₂O₄ catalysts were investigated by X-ray photoelectron spectroscopy (XPS) on a PHI5000 Versa Probe (ULVAC-PHI, Japan) with monochromatized Al Ka X-ray radiation (1486.6 eV). The binding energy was corrected by reference to the C 1s line at 284.6 eV. The electron paramagnetic resonance (EPR) spectra were obtained using a Bruker (Model EMX-10/12 X-band, Bruker, Germany) electron paramagnetic resonance spectrometer at room temperature (298 K).

Electrochemical Measurements and Products Analysis

In order to evaluate the catalytic performance of the asprepared electrode, the measurements of CO_2 electrochemical reduction were conducted in a N gas-tight H-type cell separated by a piece of proton exchange membrane (Nafion 117) with a three-electrode system. The counter electrodes was a Pt sheet and an Ag/AgCl electrode filled with saturated KCl solution was used as the reference electrode. 0.1 M KHCO₃ or 0.1 M KCl solution was adopted as the electrolyte. Before the performing of 1 h controlled potential electrolysis, high purity CO_2 gas was purged through the catholyte and anolyte for 30 min to achieve saturate state. During the electrochemical measurements, the solution was stirred by a magnetic stirring apparatus in order to guarantee the CO_2 mass transfer process. Published on 20 March 2019. Downloaded by Tulane University on 3/23/2019 8:52:45 AM

Journal Name

After the reaction, 1mL gas was taken from the cathodic reaction cell for CO analysis by using a gas chromatograph (GC-2014, Shimadzu Corp., Japan) and H_2 analysis by another gas chromatograph (GC-8A, Shimadzu Corp., Japan). The solution was collected by a sealed bottle in order to detect the liquid product through a liquid chromatograph (CBM-20A, Shimadzu Corp., Japan).

Results and discussion

The NaGaO₂ precursor was first synthesized by heating the mixture of Na_2CO_3 and Ga_2O_3 with a mole ratio of 1.01:1 at 1123K for 12h. The 1% excess amount of Na₂CO₃ was added to compensate for the volatilization loss. The X-ray diffraction (XRD) indicated that single-phase NaGaO₂ was successfully prepared (Figure S1). Low-crystallinity ZnGa₂O₄ catalyst (denoted as L-ZnGa₂O₄) was synthesized by an ion-exchange reaction between NaGaO₂ and Zn(CH₃COO)₂ at room temperature. As well demonstrated in our previous report,^[21] the NaGaO₂ powders can be dissolved into water to form a colloidal suspension. The NaGaO2 colloid tends to form a mesoporous framework by flocculation due to a strong electrostatic attraction. After introducing Zn²⁺, the ion exchange reaction between Zn2+ and Na+ occurs and the mesoporous structure of NaGaO₂ colloidal template was copied and inherited into ZnGa₂O₄. For comparison, a high-crystallinity ZnGa₂O₄ (denoted as H-ZnGa₂O₄) was prepared by heating the low-crystallinity one at 973 K in air furnace. As illustrated in Figure S2, the X-ray diffraction (XRD) patterns of both asprepared samples can be well indexed to the cubic spinel ZnGa₂O₄ (JCPDS 38-1240). The broadening of XRD peaks with low intensity indicated the low crystallinity of the L-ZnGa₂O₄. In contrast, the sharp XRD peaks for H-ZnGa₂O₄ would demonstrate that the crystallinity of the L-ZnGa₂O₄ was evidently improved after heat treatment. Nitrogen adsorptiondesorption studies on L-ZnGa₂O₄ (Figure S3) show a type-IV isotherm, a typical mesoporous structure. The pore diameter calculated by the Barrett-Joyner-Halenda (BJH) method is 3.6 nm, specific surface area calculated from the Brunauer-Emmett-Teller (BET) plot ranging from $P/P_0 = 0.05$ to 0.29 is 153.7 m²g⁻¹. H-ZnGa₂O₄ exhibited a specific surface area of 26.8 m²g⁻¹ without obvious porous structure. The pore diameter for L-ZnGa₂O₄ calculated from the nitrogen adsorption isotherm by the Barrett-Joyner-Halenda (BJH) method was 3.8 nm. The L-ZnGa₂O₄ possess a CO₂ adsorption capacity of 17.64 mg g⁻¹, which is about 3 times as high as 5.92 mg g⁻¹ for H-ZnGa₂O₄ (Figure S4). The kinetic diameter of CO₂ is 0.33 nm, suggests that the ideal pore size seem to be 0.5 - 0.6 nm for the single molecule adsorption. In our case, the 3.8 nm pore would allow multimolecular adsorption to occur, probably due to the more basic sites (metal sites) on the surface of L-ZnGa₂O₄ with weak lattice constraint. Indeed, it has been demonstrated that the mesoporous SiO₂ molecular sieves with 3.5 nm pore after modification by basic groups such as hydroxyl or amino groups exhibited excellent CO₂ adsorption and followed а multimolecular adsorption model.^[22]

Transmission electron microscope (TEM) observations show that the L-ZnGa₂O₄ has a typical wormholes resulting from the aggregation of 5-10 nm crystals (**Figure 1a**), well corresponding with the BET results. Obviously, the 20-50 nm nanoplates were observed in H-ZnGa₂O₄ (**Figure 1b**), suggesting that the particle growth of L-ZnGa₂O₄ nanocrystals occurs during the heat treatment. The selected area electron diffraction (SAED) pattern presents single crystal characteristics, indicating that the ZnGa₂O₄ nanoplate is a single crystal.



Figure 1. a) TEM image of L-ZnGa₂O₄. Inset shows the high-resolution TEM (HRTEM) lattice image. White dashed line shows the profile of the nanocrystal. b) TEM image of H-ZnGa₂O₄. Inset shows the SAED pattern. c) Polarization curves on L-ZnGa₂O₄ (solid line) and H-ZnGa₂O₄ electrodes (dashed line) in N₂- or CO₂-saturated 0.1 M KHCO₃ solution. d) Faradaic efficiency for CO generation on ZnGa₂O₄ electrodes.

Due to the electrochemically inert CO₂ reduction on titanium sheet (Figure S5), the as-prepared ZnGa₂O₄ powders were electrophoretically deposited on a titanium sheet as a working electrode. CO₂ reduction on ZnGa₂O₄ electrodes was carried out in CO₂-saturated 0.1 M KHCO₃ solution in a gas-tight two-compartment electrolytic cell with a three-electrode system. Unless otherwise stated, all potentials were quoted versus a silver chloride electrode (Ag/AgCl). As shown in Figure 1c, the polarization curves of both H-ZnGa₂O₄ and L-ZnGa₂O₄ in CO₂-saturated 0.1 M KHCO₃ solution exhibited a cathodic current onset at approximately -1.3 V. Replacing CO₂ with N₂ will induce a 0.3 V negative shift of current onset potential for L-ZnGa₂O₄ and no obvious changes in potential-current relationship for H-ZnGa₂O₄, respectively. Only gaseous products, CO and H₂, were detected. The faradaic efficiency of CO and H₂ at various applied potentials were summarized in Figure 1d and Figure S6. We found that CO initially generated at -1.3 V, corresponding to an overpotential of 570 mV (theoretical redox potential at -0.73 V for CO₂/CO). For CO generation on L-ZnGa₂O₄, the faradaic efficiency (FE) significantly increased from 56% at -1.3 V to a peak value 96% at -1.4 V, and then maintained at 70-80% when potentials varied from -1.4 to -1.6 V. However, the FE of CO on H-ZnGa₂O₄ slightly varied at 28-37%

ARTICLE

Published on 20 March 2019. Downloaded by Tulane University on 3/23/2019 8:52:45 AM

from -1.3 to -1.6 V. As shown in **Table S1**, the performance of L-ZnGa₂O₄ surpasses the most Zn-based electrodes. The CO partial current densities on two ZnGa₂O₄ catalysts were calculated through multiplying their faradaic efficiencies by the polarization curves and then were plotted against the applied potentials. **Figure S7** clearly depicted that the L-ZnGa₂O₄ exhibited a higher partial current density over all the applied potentials, proving the high activity of L-ZnGa₂O₄ in CO₂ reduction.

The high activity of the L-ZnGa₂O₄ catalyst was further investigated by cyclic voltammogram scanning. Under N₂saturated 0.1 M KHCO₃ electrolyte, a board oxidation wave around -1.2 V during positive-going potential scanning and its corresponding reduction wave presented in the CV of the L-ZnGa₂O₄ electrode (Figure 2a). This evidence would originate from the redox reaction of Zn^{2+} , as demonstrated in the previous reports.^[14] However, the oxidation wave narrowed and positively shifted to the potential -1.03 V when used CO₂saturated 0.1 M KHCO₃ as electrolyte (Figure S8). This fact indicated that there are strong interactions between CO2 molecules and the Zn²⁺ species on L-ZnGa₂O₄. Indeed, such a strong interaction was only observed at -0.7 V on the ZnO electrode in CO₂-saturated 0.1 M KHCO₃ electrolyte (Figure S9a) but not on the Ga₂O₃ electrode (Figure S9b), indicating that the Zn species are mainly responsible for the CO₂ reduction. The difference in oxidation-wave potential would result from the different chemical environments for Zn in ZnO and ZnGa₂O₄. As depicted in Figure S10, after cyclic voltammetry scanning the white ZnO electrode turned to black because of the formation of metallic zinc while the ZnGa₂O₄ electrode still remained the initial colour, proving that the Zn2+ was not reduced to the metallic state but still the ionic state. Actually, the oxidation wave at -1.03 V and the reduction wave at -1.2 V of L-ZnGa₂O₄ were perfectly matched the redox behaviour of Zn^{2+}/Zn^{+} couple ZIF-8 catalyst in 0.5 M NaCl electrolyte, indicating the in existence of Zn²⁺/Zn⁺ redox couple in this system.^[23] Noting that the oxidation wave is obviously bigger than the reduction wave on L-ZnGa₂O₄. Similar irreversible reduction responses were reported for Zn complexes, which are attributed to the generation of rare, unstable, and low valent Zn⁺ species.^[24,25] As the generation of Zn⁺ requires an electron to enter the 4s orbital with high potentials since the 3d shell is already filled. In our case, the interactions between Zn⁺ and CO₂ may further enlarge this irreversibility due to the delayed reaction kinetics. In addition to the oxidation of Zn⁺ to Zn²⁺, the big anodic wave may include a contribution from carbon-containing species, such as CO_2^{-} , CO^* , and $COOH^*$, which are produced/adsorbed on the electrode surface. A similar anodic wave generation from adsorption of carbon-containing species was also observed on Ti³⁺/Ti⁴⁺ redox couple.^[26]



Figure 2. a) Cyclic voltammogram of the L-ZnGa₂O₄ in N₂- or CO₂-saturated 0.1 M KHCO₃ solution. Inset shows oxidation wave of L-ZnGa₂O₄ in CO₂-saturated 0.1 M KHCO₃ solution. b) Zn $2p_{3/2}$, c) Ga 3d, and d) C1s XPS spectra of L-ZnGa₂O₄ with and without electrochemical treatment.

The surface chemical states of catalyst during the $\ensuremath{\text{CO}_2}$ reduction were investigated by X-ray photoelectron spectroscopy (XPS). Clearly, as shown in Figure 2b, for the asprepared L-ZnGa₂O₄, the Zn 2p3/2 XPS spectrum was decomposed into two peaks: 1021.3 and 1019.5 eV. After constant potential electrolysis on L-ZnGa₂O₄ at -1.2 V, a reduction-current peak potential, in CO₂-satuared 0.1 M KHCO₃ solution for 1 h, the Zn 2p3/2 XPS spectrum was deconvoluted into two peaks at 1021.5 and 1019.2 eV. After 3 nm-depth ion milling for the as-prepared L-ZnGa₂O₄, the Zn 2p3/2 peak splitting disappeared and binding energy is 1021.9 eV, which is 0.9 eV higher than the binding energy of Zn-O bonds in H-ZnGa₂O₄ (1021.0 eV) due to the weak lattice constraint in lowcrystallinity L-ZnGa₂O₄. Therefore, the similar Zn 2p3/2 XPS peak splitting for L-ZnGa₂O₄ in air or CO₂-containing electrolyte is probably a result of the strong interactions between CO₂ and L-ZnGa₂O₄. The obvious binding energy splitting means that the Zn species exhibited a mixed valence states. The peak at 1021.3 eV for L-ZnGa₂O₄ or 1021.5 eV for L-ZnGa₂O₄ at -1.2 V would be assigned to the binding energy of Zn-O in ZnGa₂O₄.^[27] Correspondingly, the lower binding energy at 1019.5 eV for L-ZnGa₂O₄ or 1019.2 eV for L-ZnGa₂O₄ at -1.2 V may indicate that a low-valence Zn species was stabilized by carbon-containing species from CO₂ activation via an interaction between Zn species and CO₂.^[28] Indeed, the generation of low-valence Zn ions such as Zn⁺ requires to capture an electron into its 4s orbital because the 3d shell is fully filled. This evidence confirmed that under a negative potential Zn²⁺ on L-ZnGa₂O₄ tends to gain electrons to stay in a reduction state. The unstable low-valence Zn ions is able to transfer electrons to CO₂ molecules, thus decreasing the activation barrier of CO2. The strong interactions between CO₂ and Zn ions were also demonstrated at -1.03 V, an oxidation potential. At -1.03 V, the low Zn 2p3/2 binding energy at 1019.5 eV confirmed the strong interactions between CO₂ and Zn ions even at a relatively positive potential.

Journal Name

Journal Name

Ga 3d XPS spectrum of L-ZnGa₂O₄ was split into 19.7 eV for Ga^{3+} in ZnGa₂O₄ and a low-intensity peak at 17.7 eV (Figure 2c). After 3 nm-depth ion milling, a single-peak binding energy was observed at 19.9 eV. Therefore, the peak at 17.7 eV may originate from interactions between the Ga species and CO₂ from air. Indeed, the binding energy of 17.0 eV was only detected in L-ZnGa₂O₄ treated at -1.03 V, not at -1.2 V. This evidence supports that the Ga species on surface L-ZnGa2O4 seems to interact with CO_2 molecule due to the relatively high applied potential which is not enough to drive CO₂ conversion, as demonstrated in CV scanning. The binding energy at 18.4 eV occurs in both L-ZnGa₂O₄ treated at -1.03 and -1.2 V and is assigned to the Ga in metallic state from reduction of surface Ga ions, which probably suggests that the reduction of Ga species is an irreversible process.^[29] Although the Ga species is able to interact with CO₂, the CV scanning definitely supported the standpoint that the Zn species on ZnGa₂O₄ mainly contributed to the activation and reduction of CO₂ with the low overpotentials.

The C 1s XPS spectrum for L-ZnGa₂O₄ exhibited a peak at 284.6 eV for adventitious standard reference carbon and a peak at 288.4 eV for CO2⁻ (Figure 2d).^[30, 31] No peak at 288.4 eV was observed for L-ZnGa₂O₄ after 3 nm-depth ion milling, further verifying that the CO_2^- is from the activation of CO_2 on the surface of L-ZnGa₂O₄. Two peaks at 283.4 and 285.5 eV occur in both L-ZnGa₂O₄ treated at -1.03 and -1.2 V, were respectively assigned to the Zn-C bond in carbon-containing species and the C-O bonds.^[32-35] A peak at 288.8 eV on L-ZnGa₂O₄ at -1.03 V is assigned to the COOH*, resulting from the CO2⁻ species conversion by capturing proton.[36] This evidence means that the $CO_2^{\text{-}}$ species (288.5 eV) on L-ZnGa_2O_4 at -1.2 V is able to capture proton to form COOH* with assistance of Zn ions at a potential as low as -1.03 V. Although a low-intensity Ga-Ccontaining species at 282 eV was observed in L-ZnGa₂O₄ at -1.03 V, the existence of high-intensity Zn-C-containing species at both -1.03 and -1.2 V would mean that the CO₂ molecule is mainly activated by Zn species to CO2⁻, to COOH*, and to CO* for CO generation. Nevertheless, in the case of H-ZnGa₂O₄ catalyst (Figure S11), the low-content Zn-C-containing species (1019.0 eV) in Zn 2p XPS spectrum indicated that the lowcrystallinity L-ZnGa $_2O_4$ with high specific surface area could release Zn redox couple easily than high-crystallinity H-ZnGa₂O₄ with small specific surface area, and hence enhancing the ability of CO₂ conversion.

On the basis of the experimental evidences from the XPS and CV scanning, the CO₂ activation is expected to be achieved by Zn²⁺ capturing electrons to form Zn⁺, Zn²⁺ + e⁻ \rightarrow Zn⁺, and then Zn⁺ transfers electrons to activate CO₂ into CO₂⁻, Zn⁺ + CO₂ \rightarrow Zn²⁺ + CO₂⁻. This means that the surface lattice Zn²⁺ on L-ZnGa₂O₄ catalyst is first reduced into low-valence Zn species, Zn⁺. Subsequently, the Zn⁺ species interacted with CO₂ molecule to form adsorbed CO₂⁻ and thereby Zn²⁺ regenerated. It is well established that COOH^{*} is a critical intermediate during the generation of CO product. Theoretically, the formation of COOH^{*} intermediate during CO₂ electrochemical reduction was a result of coupled electron and proton transfer to the inert CO₂ molecule. The COOH^{*} species can be detected at a relatively positive potential, probably implied that the $Zn_{iel}^{2+}/Zn_{iel}^{+}$ edox couple on $ZnGa_2O_4$ did not only facilitate the generated CO_2^{-} but also accelerated the capture of proton significantly.

Figure 3. a) Cyclic voltammogram of the L-ZnGa₂O₄ in CO₂-saturated KHCO₃ solution. The inset shows the linear relationship between the peak potential and the concentration of KHCO₃ solution. b) Cyclic voltammogram of the L-ZnGa₂O₄ in CO₂-saturated KCl solution. The inset shows the relationship between the peak potential and the concentration of KCl solution. c) Cyclic voltammogram of L-ZnGa₂O₄ in CO₂-saturated KHCO₃ + EDTA-2Na solution. d) CO faradaic efficiency of the L-ZnGa₂O₄ in CO₂-saturated KHCO₃ + EDTA-2Na solution.

Usually, HCO3⁻-containing electrolyte was considered as a key proton transfer route for CO₂ reduction.^[1] Indeed, we discovery that the peak potential for oxidation wave on L-ZnGa2O4 electrode negatively shifted with increasing the concentration of HCO_{3}^{-} (Figure 3a). The peak potential $E_{p}(V)$ depends linearly on the concentration of HCO3⁻ (CHCO3⁻) and follows a formula of $E_p(V) = -1.026 - 0.17 \text{ CHCO}_3^-$ (mol L⁻¹). This linear relationship indicated that the HCO₃⁻ ion has a strong influence on the formation of COOH* by proton transfer. It is well known that the HCO₃⁻ ion could dissociate in the aqueous solution and release the H⁺ more easily than H₂O molecule due to the smaller dissociation constant for $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ (pKa = 10.33, 25 °C) than $H_2O \leftrightarrow H^+ + OH^-$ (pKa = 14, 25 °C).^[37] In order to further confirm that the HCO₃⁻ ion was the proton source instead of H_2O molecule, we performed the cyclic voltammogram of the L-ZnGa₂O₄ catalyst in CO₂-saturated KCl solution (pH = 6.55) with the same ion concentration as KHCO₃ electrolyte. The almost unchanged peak potential clearly demonstrated that the Zn²⁺/Zn⁺ redox couple nearly captured no proton from KCl solution, namely that Cl⁻ or H₂O nearly had no effect on the proton transfer process to the CO2intermediate (Figure 3b). To further confirm the HCO₃- is the source of protons, we converted the reference electrode from Ag/AgCl electrode to the pH-sensitive RHE electrode (Figure S12a, Figure S12b). The pH of KHCO₃, KCl electrolyte with different concentrations shown in Table S2 and the redox behavior of L-ZnGa₂O₄ were almost no change compare to the

This journal is © The Royal Society of Chemistry 20xx

Journal Name

Ag/AgCl electrode. By adding HCl to 0.1 M CO_2 -saturated KHCO₃ solution to adjust the pH value, the peak potential for oxidation wave on L-ZnGa₂O₄ electrode negatively shifted with decreasing the pH value (increasing the proton concentration)(**Figure S12c**), namely that increasing the concentration of proton produced the same phenomenon as increasing the concentration of HCO₃⁻, in other words, during the reaction the role of HCO₃⁻ can be analogized to proton. Thus, we can make a conclusion that the reduced Zn⁺ could not only facilitate the one-electron activation of inert linear CO₂ molecule but also interact with HCO₃⁻ ion to acquire proton for accelerating the CO₂ conversion.



Figure 4. Proposed CO₂ reduction mechanism over L-ZnGa₂O₄. (a) Reduction of Zn²⁺ driven by external circuit to form Zn⁺. (b) Oxidation of Zn⁺ by CO₂ to Zn²⁺ and formation of CO₂⁻ radical. (c) CO₂⁻ radical captures proton releasing by HCO₃⁻ to form COOH^{*}. (d) COOH^{*} captures the electron from external circuit and the H⁺ from HCO₃⁻ to generate CO.

Based on the above mentioned procedures, we proposed a brief schematic diagram for illustrating the reaction mechanism of L-ZnGa₂O₄ during CO₂ conversion catalysis (**Figure 4**). Firstly, the Zn²⁺ was reduced to Zn⁺ with applied potential, when the CO₂ molecule reached the surface of electrode, the Zn⁺ was oxidized to Zn²⁺ and transferred the electron to CO₂ molecule to form and stabilize the CO₂⁻ radical. Consequently, the CO₂⁻ radical captured the proton which dissociated from HCO₃⁻ ion to facilitate the formation of crucial COOH* intermediate, then the COOH* intermediate coupled with proton and electron continuously and produced CO molecule. Notably, the cyclic reduction and oxidation course of Zn²⁺/Zn⁺ redox couple keep the steady formation of CO₂⁻ radical.

To fully understand the key role of Zn²⁺/Zn⁺ on electrochemical reduction over L-ZnGa₂O₄ catalyst, we performed a poisoning test by adding 10 mΜ ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) into 0.1 M KHCO₃ solution (pH = 6.33). EDTA-2Na, as an excellent chelator for transition metal ions, is able to capture the zinc ions on L-ZnGa₂O₄.^[38, 39] As shown in Figure 3c, the oxidation peak at -1.03 V disappeared at all, indicating that the existence of EDTA-2Na can obviously suppress the interactions among L-ZnGa₂O₄, CO₂, and HCO₃⁻. Moreover, the onset potential of L-ZnGa₂O₄ catalyst in EDTA-2Na contained electrolyte shifted about 250 mV toward more negative potential. The FE of CO product provided further evidence to determine the critical function of Zn ion on ZnGa₂O₄ catalyst. Over the applied potentials, the FE of CO on L-ZnGa₂O₄ in EDTA-2Na contained electrolyte strikingly decreased compared with that in the electrolyte without EDTA-

2Na, and the FEs of CO are as low as 10-20 % (**Figure 3d**) The ultraviolet-visible absorption spectra (**Figure St3**)/Show (**Hat**, after the electrochemical reduction of CO₂, the L-ZnGa₂O₄ catalyst displayed an obvious absorption step of ZnO, indicating the presence of the high-activity zinc ions on L-ZnGa₂O₄ during CO₂ electrochemical reduction. The high-activity Zn^{2+}/Zn^+ will be immediately oxidized after electrolysis like the behavior of Cu^{2+} .^[40] In addition, for the sake of excluding the catalytic influence of oxygen vacancies that maybe present in the ZnGa₂O₄ catalysts, electron paramagnetic resonance (EPR) experiments were performed on both ZnGa₂O₄ specimens, however, it showed no signal of oxygen vacancy (**Figure S14**). These results further confirmed that the Zn ion was the main active species and responsible for the selective generation of CO from CO₂.



Figure 5. Nyquist impedance plots of as-prepared $ZnGa_2O_4$ catalysts in a) CO_2 -purged 0.1 M KHCO₃ solution and b) N₂-purged 0.1 M KHCO₃ solution. c) Tafel plots of as-prepared $ZnGa_2O_4$ catalysts. d) Stability test of L- $ZnGa_2O_4$ catalyst for current density measurement and faradaic efficiency of CO at - 1.4 V.

It is well known that both courses of CO₂RR and HER require the consumption of proton, thus a pH gradient would be created near the surface of electrode during the reaction. The mesoporous structure has been confirmed that exhibiting the special ability to increase alkalinity which produce within the porous network, therefore directly suppress the H₂ evolution through the depletion of proton donors during CO2RR process.^[41] Aiming to check the performance of L-ZnGa₂O₄ mesoporous structure on the alkalinity increase to inhibit the H₂ evolution, we conducted electrochemical impedance spectroscopy (EIS) on both L-ZnGa₂O₄ and H-ZnGa₂O₄ electrodes at -1.4 V. In the CO₂-saturated KHCO₃ electrolyte, the L-ZnGa₂O₄ exhibited a slightly smaller radius of the Nyquist plot, indicative of a slightly lower charge transfer resistance for L-ZnGa₂O₄ than H-ZnGa₂O₄ (Figure 5a). Interestingly, in N₂saturated KHCO₃ electrolyte, the L-ZnGa₂O₄ catalyst exhibited a much bigger impedance arc than the H-ZnGa₂O₄, meaning that the L-ZnGa₂O₄ catalyst has an enormous resistance for the hydrogen evolution reaction (HER) (Figure 5b). These facts

Published on 20 March 2019. Downloaded by Tulane University on 3/23/2019 8:52:45 AM

Published on 20 March 2019. Downloaded by Tulane University on 3/23/2019 8:52:45 AM

Journal Name

indicated that the L-ZnGa₂O₄ and H-ZnGa₂O₄ follow the similar interface reaction kinetics and the L-ZnGa₂O₄ suppressed HER effectively not only due to the strong interactions between CO₂ and the easily released Zn²⁺/Zn⁺ on low-crystallinity L-ZnGa₂O₄ but also on account of the mesoporous structure of ZnGa2O4 generates diffusional gradients through the local consumption of proton donor such as HCO_3^- to inhibit H_2 evolution. Tafel slope is also an effective parameter in evaluating the catalytic ability of catalyst in CO_2 electrochemical reduction. Theoretically, for CO₂ reduction, the Tafel slope of 118 mV dec⁻ ¹ stands for that the rate-limiting step is initial one-electron reduction of CO₂, while the Tafel slope of 59 mV dec⁻¹ implies that the rate-determining step is a chemical reaction step after the one-electron activation of inert CO₂ molecule.^[12] In our case, the calculated Tafel slopes of the L-ZnGa₂O₄ and H-ZnGa₂O₄ catalysts were 46 mV dec⁻¹ and 48 mV dec⁻¹, respectively (Figure 5c). The Tafel slopes of both catalysts were close to 59 mV dec⁻ ¹, pointing to a mechanistic pathway in which the coupled proton and electron transfer after the fast initial electron transfer step is rate-determining step.^[12] This proves that the Zn ions on L-ZnGa₂O₄ catalyst are able to activate CO₂ to the CO_2^{-} intermediate with a low energy barrier. Therefore, a more likely scenario was that the rate-determining step is the protonation of CO2- intermediate because of the first-order kinetic dependence of the concentration of HCO₃⁻ on oxidation peak potential. Meanwhile, in the case of same overpotential, the L-ZnGa₂O₄ exhibited a higher partial current density of CO than H-ZnGa₂O₄. These experiments successfully demonstrated the intrinsic advantage of the low-crystallinity material with porous structure on HER inhibition.

The stability of the L-ZnGa₂O₄ electrodes was evaluated in 0.1 M KHCO₃ electrolyte. For the current density measurement, the electrolyte was purged with CO₂ gas to maintain the constant pH value during the reaction. As shown in **Figure 5d**, the current density nearly stayed at 0.5 mA cm⁻² at -1.4 V for 10 h, suggesting the long-term stability of L-ZnGa₂O₄ catalyst. The FE was determined in a closed electrolytic cell with adding of CO₂ in a given interval. The L-ZnGa₂O₄ catalyst showed the high FEs at 70-96%. Although the FE of CO decreased with the consumption of CO₂ at the first cycle, the good repeatability of FE at the beginning of the second cycle confirmed the excellent durability of L-ZnGa₂O₄ catalyst. Moreover, the TEM image and SAED pattern (**Figure S15**) for L-ZnGa₂O₄ after 10 h electrochemical reaction showed no obvious change, further confirming the stability of the catalyst.

Conclusions

In summary, low-crystallinity mesoporous $ZnGa_2O_4$ was proposed as an effective electrocatalyst for selective reduction of CO_2 to CO. The low crystallinity makes the release of active Zn^{2+}/Zn^+ redox couple more easily than high-crystallinity one due to the weak lattice constraint. Mesoporous structure with high specific area is beneficial to the CO_2 adsorption, HER inhibition and offers more active Zn^{2+}/Zn^+ redox couple to activate CO_2 . As a result, CO product with 96 % faradaic efficiency was selectively produced at -1.4 V vs. Ag/AgCl. This study demonstrated that the low-crystallinity materials and be a family of great potential materials for selective COSPECULTER following a redox couple catalytic mechanism.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported primarily by the National Natural Science Foundation of China (51872135, 51572121, 21603098, and 21633004), the Natural Science Foundation of Jiangsu Province (BK20151265, BK20151383, and BK20150580) and the Fundamental Research Funds for the Central Universities (021314380133 and 021314380084).

Notes and references

- 1 Y. H. Chen, C. W. Li and M. W. Kanan, J. Am. Chem. Soc., 2012, 134, 19969.
- 2 J. L. Qiao, Y. Y. Liu, F. Hong and J. J. Zhang, Chem. Soc. Rev., 2014, 43, 631.
- 3 Y. H. Wang, J. L. Liu, Y. F. Wang, A. M. Al-Enizi and G. F. Zheng, Small, 2017, 13, 1701809.
- 4 K. P. Kuhl, E. R. Cave, D. N. Abram and T. F. Jaramillo, *Energy Environ. Sci.*, 2012, 5, 7050.
- 5 Z. Y. Zhang, M. F. Chi, G. M. Veith, P. F. Zhang, D. A. Lutterman, J. Rosenthal, S. H. Overbury, S. Dai and H. Y. Zhu, *ACS Catal.*, 2016, **6**, 6255.
- 6 T. Takeshita and K. Yamaji, *Energy Policy*, 2008, **36**, 2773.
- 7 J. L. DiMeglio and J. Rosenthal, J. Am. Chem. Soc., 2013, 135, 8798.
- 8 W. L. Zhu, R. Michalsky, O. Metin, H. F. Lv, S. J. Guo, C. J. Wright, X. L. Sun, A. A. Peterson and S. H. Sun, J. Am. Chem. Soc., 2013, 135, 16833.
- 9 M. Ma, K. Liu, J. Shen, R. Kas and W. A. Smith, ACS Energy Lett., 2018, 3, 1301.
- D. F. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. X. Wang, J. G. Wang and X. H. Bao, *J. Am. Chem. Soc.*, 2015, **137**, 4288.
- W. J. Zhu, L. Zhang, P. P. Yang, C. L. Hu, Z. B. Luo, X. X. Chang, Z. J. Zhao and J. L. Gong, *Angew. Chem. Int. Ed.*, 2018, 57, 11544.
- 12 D. D. Zhu, J. L. Liu and S. Z. Qiao, Adv. Mater., 2016, 28, 3423.
- 13 B. H. Qin, Y. H. Li, H. Q. Fu, H. J. Wang, S. Z. Chen, Z. L. Liu and F. Peng, ACS Appl. Mater. Interfaces., 2018, 10, 20530.
- 14 J. Rosen, G. S. Hutchings, Q. Lu, R. V. Forest, A. Moore and F. Jiao, ACS Catal., 2015, 5, 4586.
- 15 T. T. Zhang, X. F. Li, Y. L. Qiu, P. P. Su, W. B. Xu, H. X. Zhong and H. M. Zhang, J. Catal., 2018, 357, 154.
- 16 Z. P. Chen, K. W. Mou, S. Y. Yao and L. C. Liu, *ChemSusChem*, 2018, **11**, 2944.
- 17 F. Yang, P. Song, X. Z. Liu, B. B. Mei, W. Xing, Z. Jiang, L. Gu and W. L. Xu, Angew. Chem. Int. Ed., 2018, **130**, 12483.
- 18 E. S. Donovan, B. M. Barry, C. A. Larsen, M. N. Wirtz, W. E. Geiger and R. A. Kemp, *Chem. Commun.*, 2016, **52**, 1685.
- G. B. Chan, Y. F. Zhao, L. Shang, G. I. N. Waterhouse, X. F. Kang, L. Z. Wu, C. H. Tung and T. R. Zhang, *Adv. Sci.*, 2016, **3**, 1500424.
- 20 Y. F. Zhao, G. B. Chen, T. Bian, C. Zhao, G. I. N. Waterhouse, L. Z. Wu, C. H. Tung, L. J. Smith, D. O'Hare and T. R. Zhang, *Adv. Mater.*, 2015, **27**, 7824.
- 21 S. C. Yan, S. X. Ouyang, J. Gao, M. Yang, J. Y. Feng, X. X. Fan, L.

ARTICLE

Journal of Materials Chemistry A Accepted Manuscrip

Journal Name

View Article Online DOI: 10.1039/C9TA00562E

J. Wan, Z. S. Li, J. H. Ye, Y. Zhou and Z. G. Zou, *Angew. Chem. Int. Ed.*, 2010, **49**, 6400.

- 22 A. L. Chaffee, Fuel Process. Technol., 2005, 86, 1473.
- 23 Y. L. Wang, P. F. Hou, Z. Wang and P. Kang, *ChemPhysChem* 2017, **18**, 3142.
- 24 E. S. Donovan, B. M. Barry, C. A. Larsen, M. N. Wirtz, W. E. Geiger and R. A. Kemp, Chem. Commun., 2016, 52, 1685.
- 25 A. K. Gupta, A. Dhir and C. P. Pradeep, Inorg. Chem., 2016, 55, 7492.
- 26 D. B. Chu, G. X. Qin, X. M. Yuan, M. Xu, P. Zheng and J. Lu, ChemSusChem, 2008, 1, 205.
- 27 L. W. Lai and C. T. Lee, Mater. Chem. Phys., 2008, 110, 393.
- A. S. Alshammari, L. N. Chi, X. P. Chen, A. Bagabas, D. Kramer,
 A. Alromaeh and Z. Jiang, *RSC Adv.*, 2015, 5, 27690.
- 29 D. S. Li, M. Sumiya, S. Fuke, D. R. Yang, D. L. Que, Y. Suzuki and Y. Fukuda, *J. Appl. Phys.*, 2001, **90**, 4219.
- 30 X. Y. Deng, A. Verdaguer, T. Herranz, C. Weis, H. Bluhm and M. Salmeron, *Langmuir*, 2008, **24**, 9474.
- 31 Y. Li, P. F. Zhu and R. X. Zhou, Appl. Surf. Sci., 2008, 254, 2609.
- 32 J. M. Vohs and M. A. Barteau, Langmuir, 1989, 5, 965.
- 33 L. Jappinen, T. Jalkanen, B. Sieber, A. Addad, M. Heinonen, E. Kukk, I. Radevici, P. Paturi, M. Peurla, M. A. Shahbazi, H. A. Santos, R. Boukherroub, H. Santos, M. Lastusaari and J. Salonen, *Nanoscale Res. Lett.*, 2016, **11**, 413.
- 34 J. Q. Qin, X. Y. Zhang, C. W. Yang, M. Cao, M. Z. Ma and R. P. Liu, Appl. Surf. Sci., 2017, **392**, 196.
- 35 D. P. Dubal, N. R. Chodankar, Z. Caban-Huertas, F. Wolfart, M. Vidotti, R. Holze, C. D. Lokhande and P. Gomez-Romero, *J. Power Sources.*, 2016, **308**, 158.
- 36 M. T. Martinez, M. A. Callejas, A. M. Benito, M. Cochet, T. Seeger, A. Ansón, J. Schreiber, C. Gordon, C. Marhic, O. Chauvet, J. L. G. Fierro and W. K. Maser, *Carbon*, 2003, **41**, 2247.
- 37 Y. Hori, Modern Aspects of Electrochemistry, 2008, 42, 89.
- 38 H. Y. Jia, Z. Li, X. L. Wang and Z. Zheng, *J. Mater. Chem. A.*, 2015, **3**, 1158.
- 39 C. S. He, W. P. Zhu, Y. F. Xu, Y. Zhong, J. Zhou and X. H. Qian, J. Mater. Chem., 2010, 20, 10755.
- 40 D. Kim, C. S. Kley, Y. F. Li and P. D. Yang, Proc. Natl. Acad. Sci., 2017, 114, 10560.
- 41 A. S. Hall, Y. Yoon, A. Wuttig and Y. Surendranath, J. Am. Chem. Soc., 2015, 137, 14834.