# Spontaneous Atomic Sites Formation in Wurtzite CoO Nanorods for Robust CO<sub>2</sub> Photoreduction

Jishi Wei, Fan Lu Meng, Tongtao Li, Tianxi Zhang, Shibo Xi, Wei Li Ong, Xiao-Qiao Wang, Xinyue Zhang, Michel Bosman,\* and Ghim Wei Ho\*

Controlled incorporation of single atoms in a suitable host matrix can result in a radical transformation in catalytic properties. However, finding a straightforward synthetic strategy that offers a compelling combination of solution processing, atomic doping and a matching host is still a grand challenge. Here, a spontaneous heteroatom formation of atomic Zn sites in well-defined wurtzite CoO nanorods, delivering high photoreduction rates, reaching 86.7  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> for CO and 31.4  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> for CH<sub>4</sub> production is reported. Based on the validation of atomic Zn sites structures, catalytic process tracking via in situ/ex situ spectroscopic probes, and related structural simulations, a good description of the catalytic reaction kinetics for Zn/CoO as a function of applied potential is established, revealing how the single doping sites influence the CO<sub>2</sub> photoreduction.

# 1. Introduction

CO<sub>2</sub> reduction photocatalysts based on active atomic sites not only exhibit outstanding activity and stability due to their controllable coordination centers and distinct electronic structures, but also significantly reduce the consumption of catalytic species due to their atomic dispersion.<sup>[1]</sup> Combined with

```
J. S. Wei, F. L. Meng, T. T. Li, W. L. Ong, X.-Q. Wang, G. W. Ho
Department of Electrical and Computer Engineering
National University of Singapore
4 Engineering Drive 3, Singapore 117583, Singapore
E-mail: elehgw@nus.edu.sg
T. X. Zhang
Department of Chemical & Biomolecular Engineering
National University of Singapore
4 Engineering Drive 4, Singapore 117585, Singapore
S. B. Xi
Institute of Chemical and Engineering Sciences
A*STAR
1 Pesek Road, Jurong Island 627833, Singapore
X. Y. Zhang, M. Bosman, G. W. Ho
Department of Materials Science and Engineering
National University of Singapore
9 Engineering Drive 1, Singapore 117575, Singapore
E-mail: msemb@nus.edu.sg
M. Bosman, G. W. Ho
Institute of Materials Research and Engineering
A*STAR (Agency for Science, Technology and Research)
2 Fusionopolis Way, Singapore 138634, Singapore
     The ORCID identification number(s) for the author(s) of this article
     can be found under https://doi.org/10.1002/adfm.202109693.
```

```
DOI: 10.1002/adfm.202109693
```

a nanostructured architecture, the atomic active sites can also help to elucidate the reaction mechanisms and structureperformance relationships.<sup>[2]</sup> After all, the control of the surface structure of photocatalysts at the atomic level allows efficient surface charge separation.[3] For example, doped heteroatoms at the surface can induce an in-plane local electric field, which effectively inhibits the recombination of photogenerated electrons and holes on the catalyst surface.<sup>[1]</sup> Apart from the in-plane charge transfer pathway, the surface charge carrier separation can be projected into all directions by atomically loading active sites in 3D space.<sup>[1,4-6]</sup>

However, when atomic sites are intro-

duced into a mismatched host, phase instabilities will occur due to the large atomic size difference.<sup>[7]</sup> the distinct coordination numbers between guest atoms and host atoms,<sup>[8]</sup> or the polarization behavior and low separation efficiency of photoinduced e<sup>-</sup>-h<sup>+</sup> pairs.<sup>[9]</sup> In addition, the morphology and size of the host are also essential factors of a catalyst design, as they determine the exposed contact area.<sup>[10]</sup> The most significant considerations are the provision of efficient photon absorption, and the shortening of the charge migration distance and large contact area with reactants.<sup>[11]</sup> Therefore, building a catalyst with both nanoscale tailored geometry of the host and an atomic-scale optimal match between dopant sites and the host lattice, which can form a highly crystalline phase with minimal lattice disorder, is highly desired.<sup>[12,13]</sup> To this end, solutionbased thermal decomposition offers powerful opportunities to construct nano-catalysts with well-controlled morphologies and sizes, in a "bottom-up" manner.[14-16] Nevertheless, when incorporating a dopant precursor into a known host synthetic system, the morphology of the resultant product often changes drastically compared to its host counterparts,<sup>[17-20]</sup> and severe phase separation may even occur, due to the more complex thermodynamically controlled process.<sup>[21-23]</sup> This poses a huge challenge in using a solution-based strategy for well-defined single-atom catalysts with both surface and volumetric atomic doping, as well as maintaining the nanoscale structure.

Herein, we circumvent the common structural variation arising from the introduction of the foreign element into a crystalline host, and achieve homogeneous, surface and volumetric atomic-Zn doping in wurtzite CoO nanorods (Zn/CoO NRs), by virtue of the similar ionic radius of  $Co^{2+}$  (0.58 Å) and Zn<sup>2+</sup> (0.60 Å)<sup>[24]</sup> and their well miscible lattices,<sup>[25]</sup> based on a







**Figure 1.** A) Schematic diagram comparing the CoO NRs and the CoO NRs with single Zn sites. For 7.5 Zn/CoO NRs (optimal sample), we present a representative B) FESEM image and C) a HAADF STEM image and EDX maps, with Zinc mapped in red color and Cobalt in green color. Scale bar: 20 nm. D–E) Representative atomic-resolution HAADF STEM images of individual NRs. Scale bars: 5 nm.

one-pot thermal decomposition procedure. Benefiting from the similar nucleation and growth temperature of Co/Zn-oleate precursors,<sup>[26,27]</sup> the atomically dispersed Zn sites are spontaneously formed during the preparation in a liquid media, without affecting the overall morphology of the host CoO nanorods (CoO NRs) (Figure 1A). This in turn enables continuous and precise control of atomic doping, allowing the Zn-doping to be exclusively modulated without any other morphological or structural influences. The optimal Zn-doped CoO NRs in our work result in an optimized band structure and enhancement in CO<sub>2</sub> chemisorption, with the CoO host maintaining high densities of exposed photoactive surfaces and rapid interfacial charge carrier transport for heterogeneous reductions. The resulting structure exhibits highly efficient and stable photocatalytic activity toward CO<sub>2</sub> reduction without any sacrificial agents or photochemical sensitizers. This work demonstrates a well-engineered photocatalyst with atomic sites, which accounts for both physically and photochemically favorable advantages for robust CO<sub>2</sub> photoreduction. It also highlights the value of the adaptable decomposition synthesis strategy that will be

applicable to other metal-based catalysts as well, and may be exploited for designing rational catalytic models for various photochemical reactions.

## 2. Results and Discussion

#### 2.1. Structural Characterization and Analysis

The morphology of the as-prepared nanorods was identified with a series of techniques: field emission scanning electron microscopy (FESEM, Figure 1B and Figure S1, Supporting Information), high-resolution transmission electron microscopy (HRTEM, Figure S2, Supporting Information), and high-angle annular dark-field scanning transmission electron microscopy (Figure 1C–E). The images show that the monodispersed nanorods have fairly uniform, pencil-like shapes and a narrow size distribution with length 40–50 nm and diameter 6–10 nm.<sup>[28]</sup> Self-assembly of the uniform CoO NRs or Zn/CoO NRs was performed by slow evaporation of a few drops of the

nanorod suspensions on substrates. Figure 1B shows spontaneous local self-assembly of the nanorods to form short-range ordered cluster-like superlattice structures. The well-defined CoO or Zn/CoO NRs can be used as ideal structural models to understand the corresponding catalytic reaction mechanism and performance. As the Zn content increases (X Zn/CoO NRs, X = 2.5, 5, 7.5, and 10, where X represents the mole percentage of the Zn(Oleate)<sub>2</sub> precursor), the size uniformity remains wellpreserved (Figure S2, Supporting Information) but the color of the as-prepared nanorods changes gradually from dark green to emerald green (Figure S3, Supporting Information), indicating a composition variation over the entire series.<sup>[29]</sup> And this difference generated by Zn contents between different samples can also be directly distinguished by FESEM-energy dispersive X-ray spectroscopy (EDX) mapping results in Figure S4, Supporting Information.

We use 7.5 Zn/CoO NRs as a model for further observation. The uniform distribution of Zn dopants in the CoO hosts was confirmed by HAADF STEM imaging coupled with EDX (Figure 1C, Figures S5A-C and S6, Supporting Information) and also by electron energy loss spectroscopy (EELS) elemental mapping (Figure S5E-H, Supporting Information). The EDX and EELS elemental maps of 7.5 Zn/CoO NRs readily reveals the homogeneous distribution of Zn throughout the host matrix without any metallic Zn segregation or precipitation at the surface or bulk of the nanorods. These findings suggest that the as-prepared Zn/CoO NRs have uniform Zn dopant distribution, which is the result of a spontaneous process that uniformly distributes the dopant atoms in the CoO host during particle synthesis. High-resolution STEM images shown in Figure 1D,E, Supporting Information, reveal the typical hexagonal structure, viewed in (100), (002), and (101) orientations, respectively.<sup>[30]</sup> Their similar atomic number does not allow direct differentiation between the Co and Zn atoms from the STEM images. In view of the well-ordered lattice, it can be deduced that the Zn element have infused and doped the Co host lattice, hence does not affect the original wurtzite crystal of the CoO matrix.<sup>[31]</sup> This result attests that wurtzite-type CoO NRs serve as an ideal host structure for Zn atomic sites.<sup>[32]</sup> Similarly, TEM images (Figure S2, Supporting Information) of other Zn doping concentrations in CoO NRs also exhibit the same crystal growth behavior.

In order to understand the influence caused by Zn doping in the photocatalytic performance with objectivity, the possible effects generated by the differentiated aspect ratio of rod shape nano-catalysts or crystal growth orientation should be excluded. Using TEM images of all samples (Figure S7A–E, Supporting Information) as the basis for statistics, different samples show invariable aspect ratios (Figure S7F, Supporting Information) and shape without any visual structural defects, similar to the pure counterpart are observed. At the same time, the marked (002) plane denotes the preferential growth of the Zn/CoO nanorods is along the *c*-axis of the hexagonal cell (Figure S8, Supporting Information). As negligible changes in shape, morphology, structure, and preferred crystal orientation of the Zn/ CoO nanorods are noted, the associated change in the exposed crystal facets caused by Zn doping can be inconsiderable.

To gain deeper insight into the crystal structure of the Zn/CoO NRs, X-ray photoelectron spectroscopy (XPS), X-ray

diffraction (XRD) and X-ray absorption spectroscopy (XAS) were performed. The XPS results were used to further investigate the surfaces of these samples. All high-resolution XPS spectra presented in Figure 2A-C and Figure S9, Supporting Information, show typical Co-O and Zn-O bonds. In detail, the Co 2p band can be deconvoluted into two peaks, corresponding to Co 2p<sub>1/2</sub> (795.5 eV) and Co 2p<sub>3/2</sub> (779.6 eV).<sup>[33]</sup> The Zn 2p band can similarly be deconvoluted into two peaks at 1046.6 and 1023.6 eV, representing Zn 2p<sub>1/2</sub> and Zn 2p<sub>3/2</sub>, respectively.<sup>[34]</sup> The O 1s band contains a peak at 531.8 and one at 530.1 eV, attributed to Zn-O and Co-O, respectively.<sup>[35]</sup> The atomic ratio between Zn and Co increases from 2.5 to 9.8 at%, in accordance with the increase in the ratio of Zn(OL)2 and Co(OL)<sub>2</sub> precursors from 2.5 to 10 mol% for the 2.5 Zn/CoO to 10 Zn/CoO samples (Table S1, Supporting Information) and FESEM-EDX results (Figure S4, Supporting Information).

This clearly reflects the consistency and high controllability of the doping approach. The XRD patterns of the CoO nanorods, shown in Figure 2D, reveal that the peak positions are identical to the standard wurtzite CoO pattern (P6<sub>3</sub>mc).<sup>[36]</sup> The intense (002) peak denotes the preferential growth of the CoO nanorods along the c-axis, which is consistent with the STEM data. Noticeably, doping an appropriate amount of Zn element (2.5 Zn/CoO NRs to 7.5 Zn/CoO NRs, Figure S10, Supporting Information) still manifests as a homogeneous crystal phase without any phase separation, whereby the Zn/ CoO NRs shows a crystal structure consistent with that of the pristine CoO NRs. However, when more Zn dopants are introduced into the CoO matrix (10 Zn/CoO NRs), the peak intensity of the (002) plane decreased sharply. The excessive Zn dopants change the original crystal growth behavior and perturb the stable phase, leading to slight lattice distortions.<sup>[37]</sup> As such, it can be seen that the CoO matrix is capable of accommodating a high level of Zn doping (7.2 at% Zn contents (measured by XPS (Table S1, Supporting Information)) in the original CoO crystal structure, qualifying it as an ideal catalyst model for understanding the change generated by the introduced Zn atoms.

A more accurate coordination environment of the Zn dopant was further revealed by XAS analysis. The Fourier-Transformed Extended X-ray Absorption Fine Structure (FT-EXAFS) spectra acquired from Zn/CoO NRs (7.5 Zn/CoO NRs and 10 Zn/CoO NRs), reference samples (CoO NRs), standard Zn foil, and standard ZnO are presented in Figure 2E-L and Figures S11 and S12, Supporting Information. With increasing Zn incorporated, X-ray absorption near edge structure (XANES) spectra and FT-EXFAS curves of 10 Zn/CoO NRs diverge from those of CoO NRs. Accordingly, XRD shows a lower (002) peak for 10 Zn/CoO (Figure 2D). Moreover, it can also be found that 7.5 Zn/CoO NRs do not show a peak at 2.300 Å, related to the Zn-Zn bond that is explicitly observed in metallic Zn foil (Zn K-edge, R space, Figure S12B, Supporting Information).<sup>[38]</sup> Instead, a peak at 1.534 Å, corresponding to the Zn-O bond, is clearly detected in the Zn/CoO spectrum (Zn K-edge, R space, Figure 2L and Table S3, Supporting Information).<sup>[39]</sup> The first coordination shell peak is located at a position slightly different from the general Zn–O bonds, implying a Zn coordination environment that is different from the wurtzite ZnO (Figure S12C,D, Supporting Information). Compared with standard samples, the normalized XANES spectra of





www.advancedsciencenews.com



**Figure 2.** High-resolution XPS spectra of the A) Co, B) Zn, and C) O elements in 7.5 Zn/CoO NRs (Optimal sample). For 7.5 Zn/CoO NRs, 10 Zn/CoO NRs, and CoO NRs, D) XRD patterns, E) Normalized XANES spectra and F) FT-EXFAS curves of the Co K-edge. The corresponding EXFAS fitting curves of the 7.5 Zn/CoO NRs in G) Co k-space and H) Co R-space. I,J) Comparison of normalized XANES spectra and FT-EXAFS plots for 7.5 Zn/CoO NRs, Zn foil, and standard ZnO (Zn K-Edge). The corresponding EXFAS fitting curves of the 7.5 Zn/CoO NRs in K) Zn k-space. L) Zn R-space. (Inset figures in H and L) Schematic model of the 7.5 Zn/CoO NRs.

7.5 Zn/CoO NRs at Co K edge and Zn K edge show a resembling oscillation trend (Figure S12E,F, Supporting Information), and thus it is clear that a similar nearest neighbor atomic structure prevails between Zn and Co atoms in the CoO matrix.<sup>[40]</sup> In the Zn/CoO samples, we observe no peaks related to Zn–Zn in Zn metal or Zn–O in wurtzite ZnO, which would typically occur in the range 3.1–3.3 Å. This further excludes the presence of Zn metal and ZnO secondary phases in the samples, leaving the apparent scenario of Zn being distributed in the CoO host as single-site substitutions, not unlike the recently demonstrated  $Mo_1/Fe_2O_3$  catalyst.<sup>[41]</sup>

The light-harvesting capability, charge separation-transfer ability, and surface redox reactions of Zn/CoO NRs were studied to understand the influence of atomic Zn on their intrinsic photocatalytic properties. UV–vis diffuse reflectance spectra show that the CoO NRs have an absorption edge at  $\approx$ 552 nm (**Figure 3**A, Supporting Information). After Zn dispersion, a slight blue shift of all the absorption edges can be consistently observed from 2.5 Zn/CoO NRs to 10 Zn/CoO NRs (Figure S13, Supporting Information). Accordingly, the bandgap of CoO NRs was measured to be 1.85 eV, while Zn/ CoO NRs were measured to have bandgaps of 1.93, 1.96, 2.16, and 2.16 eV with increasing Zn concentration (Figure S14, Supporting Information), agreeing with previously reported work.<sup>[42]</sup> According to the Burstein–Moss effect, Zn doping can provide additional charge carriers that shift the energy gap toward the higher energy side.<sup>[43]</sup>

To gain insights into the band structure change with the Zn dispersion, the energy positions of the conduction band (CB) were calculated using Mott-Schottky plots at different frequencies (Figure 3B and Figure S15, Supporting Information). The CB of CoO NRs is found to be at -0.45 eV. With the increase in Zn doping, the CB edge gradually increases. This indicates that Zn doping induces a change in the CB, which could lead to an enlarged overall band gap in the doped materials. The CBs are derived to be -0.55, -0.58, -0.60, and -0.60 eV for 5 Zn/CoO NRs, 7.5 Zn/CoO NRs, and 10 Zn/CoO NRs, respectively, consistent with the obtained UV-vis results. Thus, it can be seen that Zn dopants can effectively change the electronic structures of the original CoO NRs, and the related band structure can be engineered to optimize the associated CO<sub>2</sub> photoreduction reactivity (Figure 3C and Figure S16, Supporting Information).<sup>[44]</sup> To further explore the crucial role of Zn-doping in tailoring the electronic structure at the atomic level, DFT calculations were performed. From Figure 3D,E, Supporting Information, the presence of the Zn dopant endows the CoO NRs with an increased density of states (DOS) in the CB and VB with respect to the pure CoO NRs. In addition, the

www.advancedsciencenews.com

IDVANCED

Ś

FUNCTIONAL MATERIALS www.afm-journal.de



Figure 3. A) UV–Vis spectra, B) Mott–Schottky plots at different frequencies, and C) band structures of different samples. DOS of D) CoO NRs and E) 7.5 Zn/CoO NRs. F) Nyquist plots (insert: related equivalent circuit) and G) photocurrent curves. H) Comparison of electronic transmission efficiency between CoO NRs (upper) and 7.5 Zn/CoO NRs (below, optimal sample) via XPS spectra.

spatial distribution of the orbital wave functions at the CB and VB (valence band) reveal that the d-orbitals from Zn dopants (purple line in Figure 3E) contribute greatly to this change.<sup>[45]</sup> Together with the previous characterizations, it can be concluded that the addition of Zn sites can effectively change the original electronic structure of CoO NRs, which leads to variations in potential positions that affect the thermodynamics of the CO<sub>2</sub> photoreduction process.<sup>[46]</sup>

The surface charge transfer efficiencies were measured by electrochemical impedance spectroscopy (EIS) (Figure 3F; Figure S17 and Table S4, Supporting Information). The charge transfer resistance simulated by equivalent circuit follow the sequence 7.5 Zn/CoO NRs (904  $\Omega$ ) < 10 Zn/CoO NRs (966  $\Omega$ ) < 5 Zn/CoO NRs (1222  $\Omega$ ) <2.5 Zn/CoO NRs (1228  $\Omega$ ) < CoO NRs (2084  $\Omega$ ), inferring that the lowest interfacial charge-transfer resistance is the 7.5 Zn/CoO NRs samples. All these results confirm that Zn doped CoO NRs, especially the 7.5 Zn/

CoO NRs, show good interfacial charge carrier transfer.<sup>[47]</sup> To further explore the photogenerated charge-separation efficiency, photocurrent, and fluorescence (FL) characterizations were also conducted. As shown in Figure 3G and Figure S18, Supporting Information, the charge transfer process was investigated by transient photocurrent responses. The 7.5 Zn/CoO NRs sample is observed to possess a higher photocurrent density than the CoO NRs, likely pertaining to Zn effectively suppressing the electron-hole recombination. Also considering that the result is obviously higher than other CoO samples with lower Zn content, it suggests that an optimal amount of Zn atoms is an essential factor to enhance the surface reaction kinetics of photocatalytic reactions.<sup>[48]</sup> This is further supported by FL spectra (Figure S19, Supporting Information) where pure CoO NRs display a relatively high intensity peak caused by the intrinsic carrier recombination. A significantly quenched photoluminescence emission is observed for Zn/CoO NRs, indicating its enhanced electron trapping ability and charge carrier separation compared with the pure CoO. Thus, an adequate supply of electrons is realized by CoO with dispersed Zn atoms, optimizing the elementary process of photocatalytic CO<sub>2</sub> reduction.<sup>[49]</sup> Besides, this phenomenon is further investigated using time-resolved transient photoluminescence (PL). The emission decay curves of both samples (Figure S20, Supporting Information) are fitted by the exponential kinetics function where two-lifetime values were derived. And the average emission lifetime reflects the overall emission decay, where lifetimes prolong from 11.90 ns (CoO NRs) to 34.20 ns (7.5 Zn/CoO NRs) for different samples. For photocatalytic materials with a single component, the significantly increased carriers lifetime confirmed the function of atomic Zn sites in the separation of the photogenerated electron and hole, thus, achieving the provision of long-lived electrons for CO<sub>2</sub> reduction.<sup>[50-54]</sup>

The appreciable difference in photoelectric properties brought forth by the Zn dispersion within the CoO host is directly reflected by the quantitative comparison of charge transfer efficiency. Apart from the difference in charge transfer characteristics between Zn/CoO NRs and CoO NRs as distinguished by EIS tests, FL spectra, decay lifetime, or photocurrent measurements shown above, a more direct approach can be employed. In this regard, photoreduction capability comparison between CoO NRs and Zn/CoO NRs through the formation of metallic Pt from [H<sub>3</sub>O]<sub>2</sub>[PtCl<sub>6</sub>].4H<sub>2</sub>O will help to single out the role played by Zn dopants.<sup>[55]</sup> In Figure 3H, three sets of Pt 4f XPS peaks can be assigned to metallic Pt<sup>0</sup>, partially oxidized Pt<sup>2+</sup> and Pt4+ species. The percentage of Pt0 is determined to account for 48.2 at% from the sum of Pt species for all Pt-contained samples. Comparatively, the percentage of Pt<sup>0</sup> in Pt-7.5 Zn/CoO NRs can reach 73.4 at% (Table S5, Supporting Information). Moreover, for Pt-CoO NRs, the binding energies of Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  are observed respectively at 74.3 and 70.6 eV, lower than those of the Pt-7.5 Zn/CoO NRs (Pt  $4f_{7/2} = 74.5$  eV and Pt  $4f_{5/2} =$ 71.1 eV). This is because the electron transfer occurs from the CoO to the Pt particles with higher work function.<sup>[56]</sup> When Zn sites are introduced into CoO NRs, the binding energy of Pt  $4f_{7/2}$  shifts toward higher values (71.1 eV), which is close to that of metallic Pt (71.2 eV), indicating that the energy required for electron transfer from Zn/CoO is lower.[57] This demonstrates that the electron transfer efficiency can be greatly improved with the Zn dopants distributed in the CoO matrix.

#### 2.2. Photocatalytic Performance and Simulation

Before validating the CO<sub>2</sub> photocatalytic performance, we first identify whether the CO<sub>2</sub> photoreduction process might come from the other carbon source (oleate acid) on the surface. Labeled <sup>13</sup>CO<sub>2</sub> generated by Na<sub>2</sub><sup>13</sup>CO<sub>3</sub> was used as the tracer to test the carbon source of CO and CH<sub>4</sub>, and general <sup>12</sup>CO<sub>2</sub> gas was also taken for the related contrast experiment. The photoreduction products were analyzed by gas chromatographymass spectrometry, and the experimental results are shown in Figure S21, Supporting Information. Compared with the unlabeled CO<sub>2</sub>, the m/z values of CH<sub>4</sub> and CO produced from <sup>13</sup>C-labeled CO<sub>2</sub> molecules were 17 and 29, respectively, which confirms that the carbon source of CO and CH<sub>4</sub> originates from

the photoreduction process of  $CO_2$ .<sup>[58]</sup> Besides the <sup>13</sup>C isotope labeling experiments, <sup>18</sup>O isotope labeling was also conducted to confirm the half-reaction of oxidation. Shown as Figure S21, Supporting Information, the presence of <sup>16</sup>O<sup>18</sup>O and <sup>18</sup>O<sub>2</sub> in the <sup>18</sup>O labeling experiment verifies that O<sub>2</sub> originated from water oxidation.<sup>[59]</sup>

Further CO<sub>2</sub> photoreduction of all prepared photocatalysts was also performed under simulated sunlight irradiation in a high pressure (10 atm) reactor system. The main gaseous products of H<sub>2</sub>, CO, and CH<sub>4</sub> were detected in the photocatalytic reduction system (Shown as the GC profile in Figure S22, Supporting Information). Besides the identification of gas products, liquid <sup>1</sup>H NMR was also employed to detect the presence of the liquid products. The result reveals that there is no peak associated with any liquid product, this ensures the reliability of following comparison and analysis (Figure S23, Supporting Information). Figure 4A and Figure S24, Supporting Information, display the CO and CH<sub>4</sub> yields of various photocatalysts under the same irradiation conditions. After 1 h of irradiation time, the 7.5 Zn/CoO nanorods yielded  $\approx$ 86.7 and 31.4 µmol g<sup>-1</sup> of CO and CH<sub>4</sub>, respectively. The optimally doped 7.5 Zn/CoO NRs outperforms other reported CoOx-based photocatalysts (Table S6, Supporting Information).<sup>[60-65]</sup> In comparison, the pure CoO NRs catalyst shows that the natural reduction efficiency of CO<sub>2</sub> under sunlight irradiation is negligible. This corroborates with our earlier findings that the CB position of CoO NRs (-0.45 eV shown in Figure 3B) is incapable of CO<sub>2</sub> reduction. Furthermore, Zn/CoO NRs with fewer atomic Zn sites (2.5 Zn/CoO NRs and 5 Zn/CoO NRs) show lower CO<sub>2</sub> photoreduction performance. And such differences are also proven by their poor ability in charge transfer, electron trapping ability and charge carrier separation through the photocurrent and FL characterizations (Figure S17-S20, Supporting Information).

The contrast between different samples in catalytic ability can be better reflected by the product selectivity. In Figure S25, Supporting Information, the single product selectivity of the CoO NRs samples toward H<sub>2</sub> correlates to their band structures as shown in Figure 3A-E. The selectivity for CO<sub>2</sub> reduction products of CoO NRs is dependent on Zn doping concentration. The overall selectivity of CO2-reduced products for the 7.5Zn/CoO NRs can reach 80.3% (59.0% for CO and 21.3% for CH<sub>4</sub>, respectively). With an overly increase in Zn contents, the 10 Zn/CoO NRs shows a relatively lower selectivity in carbonaceous products (71.2%), and higher product selectivity in H<sub>2</sub>. Furthermore, with increasing amount of Zn incorporated, XANES spectra and FT-EXFAS curves of 10 Zn/CoO NRs is observed to deviate from those of CoO NRs (Figure 2E,F, Supporting Information). This suggests that the overdoped Zn species have affected the original CoO matrix. According to previous studies, over doping of Zn will result in amalgamation of metal oxides to form minute amounts of binary metal oxides. This reduces the accessible Zn atomic sites and adversely affects the related catalytic performance.[66,67]

The apparent quantum efficiency (AQE) of  $CO_2$  photoreduction process over 7.5 Zn/CoO NRs at different wavelengths is then studied. As shown in Figure S26, Supporting Information, the AQE increases at shorter wavelengths, which is in accordance with the optical absorption spectrum. Impressively, the AQE of 7.5 Zn/CoO NRs can reach 2.23% in the visible light





**Figure 4.** A)  $CO_2$  photoreduction performance of different samples. B) Cycle stability of 7.5 Zn/CoO NRs (optimal sample) in the  $CO_2$  photoreduction process. C) In situ DRIFTS of the 7.5 Zn/CoO NRs during the photoreduction process. D)  $CO_2$ -TPD curves of CoO NRs and 7.5 Zn/CoO NRs. E) Side view of  $CO_2$  adsorption models of I. CoO NRs and 7.5 Zn/CoO NRs with Zn site in the II) inner layer and III) surface layer (Grey balls represent C atoms, pink balls represent O atoms, green balls represent Co atoms, and red balls represent Zn atoms).

range (at 400 nm), which is comparable to many other highly efficient CO<sub>2</sub> photocatalysts.<sup>[68–70]</sup> Long-term stability of the optimal CoO NRs with Zn sites is particularly important for practical applications. The sample exhibits stable reactivity for a durable photoreduction process over 18 h without noticeable deterioration (Figure 4B). Further, unchanged XRD patterns (Figure S27, Supporting Information) and surficial elements (based on XPS results, Figure S28, Supporting Information) of 7.5 Zn/CoO NRs before and after the photocatalytic process (18 h) imply their stable crystal structure and composition. Moreover, by comparing the HRTEM images of 7.5 Zn/CoO NRs before and after photocatalytic process, the morphology, lattice plane, and lattice spacing of the sample remained unchanged before and after the photocatalytic process, also proving their structural stability (Figure S29, Supporting Information).

To disclose the CO<sub>2</sub> photoreduction process, in situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) studies of optimal Zn/CoO NRs (7.5 Zn/CoO NRs) were conducted to detect their intermediates during CO<sub>2</sub> photoreduction (Figure 4C). Based on the in situ DRIFTS result, it can be concluded that CO<sub>2</sub> molecules are first adsorbed on the surface of Zn/CoO NRs and then converted into various intermediate species, such as CO<sup>2-</sup> (1566 cm<sup>-1</sup>), C–H (1329 cm<sup>-1</sup>), HCO<sub>3</sub><sup>-</sup> (1211 and 1678 cm<sup>-1</sup>), and CO<sub>3</sub><sup>2-</sup> (1361, 1382, 1520, 1541, and 1618 cm<sup>-1</sup>),<sup>[71]</sup> and eventually transformed into CO and other carbon reductants upon illumination. As shown in the inset of Figure 4C, the augmented peak at 2142 cm<sup>-1</sup> is attributed to the stretching vibration of CO, which gradually increases with

the irradiation time.<sup>[72]</sup> It demonstrates that CO<sub>2</sub> molecules are continuously converting into CO molecules. Furthermore, from the results of in situ DRIFTS, a possible photocatalytic reaction pathway is proposed in Figure S30, Supporting Information. The photogenerated electrons from the Zn/CoO NRs are captured rapidly by  $CO_2$  and yield  $\cdot CO_2$  radicals, due to the better CO<sub>2</sub> binding ability on the surface. At the same time, the photogenerated holes are captured by H<sub>2</sub>O to initiate the photooxidation process, yielding protons (H<sup>+</sup>) and hydroxyl radicals  $(\cdot OH)$ .<sup>[73]</sup> Then, unstable  $\cdot CO_2$  radicals subsequently transfer to surface carbon anions ( $CO_3^{2-}$ ) or react with above  $\cdot OH$  and generate the other intermediate radicals such as HCO3-.[74] All these carbon species can be clearly observed in in situ DRIFTS in the range of 1300–1700 cm<sup>-1</sup> in Figure 4C. They will continue to combine with  $H^+$  from water vapor (H<sub>2</sub>O) and  $e^-$  from the catalysts to form CO molecules,<sup>[73]</sup> where gradually enhanced peaks at 2142 cm<sup>-1</sup> reflected by in situ DRIFTS prove the formation of CO molecules. Furthermore, CO molecules can now become intermediates for further hydrogenation reduction into CH<sub>4</sub> molecules.<sup>[74]</sup> During the above processes, the efficiency of photocatalytic CO<sub>2</sub> reduction is significantly enhanced by the atomically dispersed Zn within the CoO NRs.

 $CO_2$ -TPD is another crucial characterization to understand the differences in catalytic performance caused by Zn dopants. As shown in Figure 4D, at low-temperature (50–200 °C), CoO NRs and 7.5 Zn/CoO NRs exhibit almost the same  $CO_2$ desorption peaks, which can be ascribed to physical adsorption. This result is related to the apparent geometrical shape,

FUNCTIONAL

www.afm-journal.de



which corroborates with our observation that Zn doping does not result in an obvious morphological change between CoO NRs and Zn/CoO NRs. The 7.5 Zn/CoO NRs show two strong peaks at 475 and 552 °C, in contrast to the two relatively weaker peaks at 453 and 513 °C of the CoO NRs. Hence, stronger CO<sub>2</sub> chemical desorption occurs at the surfaces of 7.5 Zn/CoO NRs, which demonstrates that more active sites are formed with Zn dopants incorporated within the CoO matrix.<sup>[75]</sup> Combined with simulation results of the CO<sub>2</sub> adsorption energy (Figure 4E), the presence of Zn dopants will change the CO<sub>2</sub> adsorption energy from -0.100 to -0.519 to -0.652 eV (with different positions of Zn sites), translating into a favorable coupling of free CO<sub>2</sub> molecules with the Zn/CoO NRs, similar to what was recently observed for a Cu-Fe catalyst.<sup>[76]</sup> Thus, Zn dopant active sites resulting from the substitution of original Co atoms in the CoO crystals can change the surface adsorption energy and will accelerate the reactions between CO2 molecules and the catalyst. This reflects the valid contribution of atomic Zn dopants in the kinetics of the CO<sub>2</sub> photoreduction process.

# 3. Conclusions

We have demonstrated a photocatalyst from wurtzite type CoO nanorods with atomic Zn sites for efficient CO<sub>2</sub> reduction. The good lattice match and atomic homogeneity ensure a suitable band structure and robust CO<sub>2</sub> chemisorption. Accordingly, the production rate of CO reaches a high value of 86.7  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, exceeding other cobalt oxide-based catalysts for CO<sub>2</sub> photoreduction. Collectively, the characterization and theoretical calculations results show strong electronic coupling, modulated DOS and appropriate CO<sub>2</sub> adsorption energy of the judiciously chosen and well-constructed host-dopant catalyst. This work provides an effective avenue for the spontaneous synthesis of highly active, singly dispersed dopant photocatalysts, toward efficient CO<sub>2</sub> conversion.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

The authors acknowledge support from the Ministry of Education (MOE) Singapore, under AcRF Tier 2 (MOE2019-T2-1-179) and A\*STAR under its 2019 AME IRG & YIRG Grant Calls, A2083c0059.

# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.



## Keywords

atomic zinc, band structure engineering,  $\mathsf{CO}_2$  photoreduction, doped heterostructures

Received: September 24, 2021 Revised: December 6, 2021 Published online: December 22, 2021

- B. Xia, Y. Zhang, J. Ran, M. Jaroniec, S. Z. Qiao, ACS Cent. Sci. 2021, 7, 39.
- [2] Y. Pan, Y. Qian, X. Zheng, S.-Q. Chu, Y. Yang, C. Ding, X. Wang, S.-H. Yu, H.-L. Jiang, *Natl. Sci. Rev.* **2021**, *8*, nwaa224.
- [3] L. Zeng, C. Xue, Nano Res. 2020, 14, 934.
- [4] J. Di, C. Chen, S. Z. Yang, S. Chen, M. Duan, J. Xiong, C. Zhu, R. Long, W. Hao, Z. Chi, H. Chen, Y. X. Weng, J. Xia, L. Song, S. Li, H. Li, Z. Liu, *Nat. Commun.* **2019**, *10*, 2840.
- [5] H. B. Zhang, J. Wei, J. C. Dong, G. G. Liu, L. Shi, P. F. An, G. X. Zhao, J. T. Kong, X. J. Wang, X. G. Meng, J. Zhang, J. H. Ye, *Angew. Chem., Int. Ed.* **2016**, *55*, 14310.
- [6] H. B. Zhang, Y. Wang, S. W. Zuo, W. Zhou, J. Zhang, X. W. D. Lou, J. Am. Chem. Soc. 2021, 143, 2173.
- [7] Y. Chen, J. Xu, S. Xie, Z. Tan, R. Nie, Z. Guan, Q. Wang, J. Zhu, Materials 2018, 11, 821.
- [8] Y. Xu, G. Wang, G. Ma, H. Wu, X. Wang, L. Shi, H. Zhang, L. Jin, X. Ma, Y. Zou, J. Yin, *Phys. Status Solidi B* **2019**, *256*, 1800753.
- [9] J. Hu, J. Liu, Z. Chen, X. Ma, Y. Liu, S. Wang, Z. Liu, C. Huang, Phys. Chem. Chem. Phys. 2020, 22, 22349.
- [10] R. He, R. K. Hocking, T. Tsuzuki, Mater. Chem. Phys. 2012, 132, 1035.
- [11] K. Zhang, G. Zhang, J. Qu, H. Liu, Small 2020, 16, 1907001.
- [12] X. Su, X. F. Yang, Y. Huang, B. Liu, T. Zhang, Acc. Chem. Res. 2019, 52, 656.
- [13] S. Chen, S. Ma, Z. P. Liu, J. Phys. Chem. Lett. 2021, 12, 3328.
- [14] T. Hyeon, S. S. Lee, J. Park, Y. Chung, H. Bin Na, J. Am. Chem. Soc. 2001, 123, 12798.
- [15] D. S. Wang, Y. D. Li, Adv. Mater. 2011, 23, 1044.
- [16] Z. Y. Jiang, Q. Kuang, Z. X. Xie, L. S. Zheng, Adv. Funct. Mater. 2010, 20, 3634.
- [17] C. Zhou, H. Y. Yuan, P. Hu, H. F. Wang, Chem. Commun. 2020, 56, 15201.
- [18] H. Q. Liu, D. Moronta, L. Y. Li, S. Y. Yue, S. S. Wong, Phys. Chem. Chem. Phys. 2018, 20, 10086.
- [19] A. K. Guria, N. Pradhan, Chem. Mater. 2016, 28, 5224.
- [20] D. Cardillo, K. Konstantinov, T. Devers, *Mater. Res. Bull.* 2013, 48, 4521.
- [21] P. C. Chen, M. Y. Gao, S. Yu, J. B. Jin, C. Y. Song, M. Salmeron, M. C. Scott, P. D. Yang, *Nano Lett.* **2021**, *21*, 6684.
- [22] S. Y. Tang, D. R. G. Mitchell, Q. B. Zhao, D. Yuan, G. L. Yun, Y. X. Zhang, R. R. Qiao, Y. L. Lin, M. D. Dickey, W. H. Li, *Matter* 2019, 1, 192.
- [23] M. Schmitt, J. N. Zhang, J. Lee, B. Lee, X. Ning, R. Zhang, A. Karim, R. F. Davis, K. Matyjaszewski, M. R. Bockstaller, *Sci. Adv.* 2016, 2, e1601484.
- [24] S. Narasimman, L. Balakrishnan, Z. C. Alex, RSC Adv. 2018, 8, 18243.
- [25] C. C. Ma, A. Navrotsky, Chem. Mater. 2012, 24, 2311.
- [26] Z. C. Yan, S. FitzGerald, T. M. Crawford, O. T. Mefford, J. Phys. Mater. 2021, 4, 034013.
- [27] H. M. Wang, Z. F. Lu, D. Z. Lu, C. H. Li, P. F. Fang, X. Wang, Solid State Sci. 2016, 55, 69.
- [28] H. X. Wang, M. X. Tang, F. L. Shi, R. M. Ding, L. C. Wang, J. B. Wu, X. K. Li, Z. Liu, B. L. Lv, ACS Appl. Mater. Interfaces 2020, 12, 38140.
- [29] M. R. Buck, A. J. Biacchi, R. E. Schaak, Chem. Mater. 2014, 26, 1492.

### **ADVANCED** SCIENCE NEWS

www.advancedsciencenews.com



- [30] K. An, N. Lee, J. Park, S. C. Kim, Y. Hwang, J. G. Park, J. Y. Kim, J. H. Park, M. J. Han, J. J. Yu, T. Hyeon, *J. Am. Chem. Soc.* **2006**, *128*, 9753.
- [31] C. Song, K. W. Geng, F. Zeng, X. B. Wang, Y. X. Shen, F. Pan, Y. N. Xie, T. Liu, H. T. Zhou, Z. Fan, *Phys. Rev. B* 2006, 73, 024405.
- [32] H. Zhang, Y. Wang, S. Zuo, W. Zhou, J. Zhang, X. W. D. Lou, J. Am. Chem. Soc. 2021, 143, 2173.
- [33] A. Jena, T. R. Penki, N. Munichandraiah, S. A. Shivashankar, J. Electroanal. Chem. 2016, 761, 21.
- [34] J.-S. Wei, Z.-Y. Zhu, X. Zhao, T.-B. Song, J.-H. Huang, Y.-X. Zhang, X. Liu, L. Chen, X.-Q. Niu, Y.-G. Wang, H.-M. Xiong, *Chem. Eng. J.* 2021, 425, 130660.
- [35] H. B. Li, Y. F. Qiao, J. Li, H. L. Fang, D. H. Fan, W. Wang, Biosens. Bioelectron. 2016, 77, 378.
- [36] K. M. Nam, W. S. Seo, H. Song, J. T. Park, NPG Asia Mater. 2017, 9, e364.
- [37] L. M. C. Pereira, U. Wahl, S. Decoster, J. G. Correia, L. M. Amorim, M. R. da Silva, J. P. Araújo, A. Vantomme, *Phys. Rev. B* 2011, *84*, 125204.
- [38] B. W. Yuan, Z. H. Yao, C. L. Qiu, H. Y. Zheng, Y. L. Yan, Q. Q. Zhang, X. Sun, Y. Gu, X. Zhong, J. G. Wang, J. Energy Chem. 2020, 51, 312.
- [39] A. Patlolla, J. Zunino, A. I. Frenkel, Z. Iqbal, J. Mater. Chem. 2012, 22, 7028.
- [40] M. H. Chu, G. Martinez-Criado, J. Segura-Ruiz, S. Geburt, C. Ronning, Appl. Phys. Lett. 2013, 103, 141911.
- [41] W. Y. Qu, X. N. Liu, J. X. Chen, Y. Y. Dong, X. F. Tang, Y. X. Chen, Nat. Commun. 2020, 11, 1532.
- [42] H. Sutanto, S. Wibowo, E. Hidayanto, Mater. Res. Express 2017, 4, 076409.
- [43] J. S. Manser, P. V. Kamat, Nat. Photonics 2014, 8, 737.
- [44] S. Chen, C. Pei, J. Gong, Energy Environ. Sci. 2019, 12, 3473.
- [45] N. Ali, B. Singh, Z. A. Khan, A. R. Vijaya, K. Tarafder, S. Ghosh, *Sci. Rep.* **2019**, *9*, 2461.
- [46] W. A. Thompson, E. S. Fernandez, M. M. Maroto-Valer, ACS Sustainable Chem. Eng. 2020, 8, 4677.
- [47] K. Q. Lu, Y. H. Li, F. Zhang, M. Y. Qi, X. Chen, Z. R. Tang, Y. M. A. Yamada, M. Anpo, M. Conte, Y. J. Xu, *Nat. Commun.* 2020, *11*, 5181.
- [48] F. Zhao, Y. Feng, Y. Wang, X. Zhang, X. Liang, Z. Li, F. Zhang, T. Wang, J. Gong, W. Feng, Nat. Commun. 2020, 11, 1443.
- [49] D. Liu, C. Wang, Y. Yu, B.-H. Zhao, W. Wang, Y. Du, B. Zhang, Chem 2019, 5, 376.
- [50] H. X. Zhang, Q. L. Hong, J. Li, F. Wang, X. S. Huang, S. M. Chen, W. G. Tu, D. S. Yu, R. Xu, T. H. Zhou, J. Zhang, *Angew. Chem.*, *Int. Ed.* **2019**, *58*, 11752.
- [51] G. L. Xu, H. B. Zhang, J. Wei, H. X. Zhang, X. Wu, Y. Li, C. S. Li, J. Zhang, J. H. Ye, ACS Nano 2018, 12, 5333.
- [52] X. Wu, H. B. Zhang, J. C. Dong, M. Qiu, J. T. Kong, Y. F. Zhang, Y. Li, G. L. Xu, J. Zhang, J. H. Ye, *Nano Energy* **2018**, *45*, 109.
- [53] S. Gao, B. C. Gu, X. C. Jiao, Y. F. Sun, X. L. Zu, F. Yang, W. G. Zhu, C. M. Wang, Z. M. Feng, B. J. Ye, Y. Xie, J. Am. Chem. Soc. 2017, 139, 3438.

- [54] L. Liang, F. C. Lei, S. Gao, Y. F. Sun, X. C. Jiao, J. Wu, S. Qamar, Y. Xie, Angew. Chem., Int. Ed. 2015, 54, 13971.
- [55] Y. Wang, X. Shang, J. Shen, Z. Zhang, D. Wang, J. Lin, J. C. S. Wu, X. Fu, X. Wang, C. Li, *Nat. Commun.* **2020**, *11*, 3043.
- [56] M. Hatanaka, N. Takahashi, N. Takahashi, T. Tanabe, Y. Nagai, A. Suda, H. Shinjoh, J. Catal. 2009, 266, 182.
- [57] W. Ye, Z. Sun, C. Wang, M. Ye, C. Ren, R. Long, X. Zheng, J. Zhu, X. Wu, Y. Xiong, *Nano Res.* **2018**, *11*, 3313.
- [58] S. Wang, X. Hai, X. Ding, S. Jin, Y. Xiang, P. Wang, B. Jiang, F. Ichihara, M. Oshikiri, X. Meng, Y. Li, W. Matsuda, J. Ma, S. Seki, X. Wang, H. Huang, Y. Wada, H. Chen, J. Ye, *Nat. Commun.* **2020**, *11*, 1149.
- [59] J. Q. Xu, Z. Y. Ju, W. Zhang, Y. Pan, J. F. Zhu, J. W. Mao, X. L. Zheng, H. Y. Fu, M. L. Yuan, H. Chen, R. X. Li, *Angew. Chem., Int. Ed.* **2021**, 60, 8705.
- [60] L. Wang, J. W. Wan, Y. S. Zhao, N. L. Yang, D. Wang, J. Am. Chem. Soc. 2019, 141, 2238.
- [61] Y. W. Ma, J. Du, Y. X. Fang, X. C. Wang, ChemSusChem 2021, 14, 946.
- [62] W. J. Sun, X. Y. Meng, C. J. Xu, J. Y. Yang, X. M. Liang, Y. J. Dong, C. Z. Dong, Y. Ding, *Chin. J. Catal.* **2020**, *41*, 1826.
- [63] K. T. Liu, X. D. Li, L. Liang, J. Wu, X. C. Jiao, J. Q. Xu, Y. F. Sun, Y. Xie, Nano Res. 2018, 11, 2897.
- [64] F. F. Mei, J. F. Zhang, C. H. Liang, K. Dai, Mater. Lett. 2021, 282, 128722.
- [65] T. Wang, L. Shi, J. Tang, V. Malgras, S. Asahina, G. G. Liu, H. B. Zhang, X. G. Meng, K. Chang, J. P. He, O. Terasaki, Y. Yamauchi, J. H. Ye, *Nanoscale* **2016**, *8*, 6712.
- [66] X. Wang, S. Shen, S. Q. Jin, J. X. Yang, M. R. Li, X. L. Wang, H. X. Han, C. Li, Phys. Chem. Chem. Phys. 2013, 15, 19380.
- [67] H. B. Zhang, X. F. Lu, Z. P. Wu, X. W. D. Lou, ACS Cent. Sci. 2020, 6, 1288.
- [68] Y. B. Shi, G. M. Zhan, H. Li, X. B. Wang, X. F. Liu, L. J. Shi, K. Wei, C. C. Ling, Z. L. Li, H. Wang, C. L. Mao, X. Liu, L. Z. Zhang, *Adv. Mater.* **2021**, *33*, 2100143.
- [69] A. Raza, H. L. Shen, A. A. Haidry, L. H. Sun, R. Liu, S. S. Cui, J. CO<sub>2</sub> Util. 2020, 37, 260.
- [70] H. J. Yu, F. Chen, X. W. Li, H. W. Huang, Q. Y. Zhang, S. Q. Su, K. Y. Wang, E. Y. Mao, B. T. Mei, G. D. Mul, T. Y. Ma, Y. H. Zhang, *Nat. Commun.* **2021**, *12*, 4594.
- [71] L. Z. Liu, H. W. Huang, Z. S. Chen, H. J. Yu, K. Y. Wang, J. D. Huang, H. Yu, Y. H. Zhang, Angew. Chem., Int. Ed. 2021, 60, 18303.
- [72] L. Hao, L. Kang, H. W. Huang, L. Q. Ye, K. L. Han, S. Q. Yang, H. J. Yu, M. Batmunkh, Y. H. Zhang, T. Y. Ma, *Adv. Mater.* **2019**, *31*, 1900546.
- [73] N. X. Li, B. B. Wang, Y. T. Si, F. Xue, J. C. Zhou, Y. J. Lu, M. C. Liu, ACS Catal. 2019, 9, 5590.
- [74] Y. P. Liu, D. Y. Shen, Q. Zhang, Y. Lin, F. Peng, Appl. Catal. B 2021, 283, 119630.
- [75] W. H. Li, G. H. Zhang, X. Jiang, Y. Liu, J. Zhu, F. S. Ding, Z. M. Liu, X. W. Guo, C. S. Song, ACS Catal. 2019, 9, 2739.
- [76] B. W. Zhou, P. F. Ou, N. Pant, S. B. Cheng, S. Vanka, S. Chu, R. T. Rashid, G. Botton, J. Song, Z. T. Mi, *Proc. Natl. Acad. Sci. USA* 2020, 117, 1330.