# Journal of Materials Chemistry A



View Article Online

## PAPER



Cite this: DOI: 10.1039/d0ta07196j

# What is the better choice for Pd cocatalysts for photocatalytic reduction of CO<sub>2</sub> to renewable fuels: high-crystallinity or amorphous?<sup>†</sup>

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Solar-driven photocatalytic conversion of CO<sub>2</sub> to renewable fuels represents an appealing approach to remedy environmental damage and address the energy crisis. Recently, the photocatalytic conversion efficiency has been improved with the implantation of cocatalysts into semiconductor photocatalysts. However, catalytic activity and selectivity are often limited by the uncontrollable charge trapping and surface reactivity behaviors of cocatalysts. Herein, for the first time, we reveal that engineering the crystallinity of cocatalysts offers an efficient route to tune both the interfacial charge kinetics and surface reaction dynamics. With Pd nanosheets as model cocatalysts, the influence of the degree of crystallinity of Pd on the photocatalytic performance is systematically investigated. When integrated with CdS quantum dots, it is found that high-crystallinity Pd with prefect lattice periodicity and fewer bulk and interfacial defects is conducive to the electron transfer from CdS to Pd, which thus yields more effective inhibition of  $H_2$  evolution on the CdS surface and achieves the highest selectivity of 100% for  $CO_2$ reduction. In contrast, low-crystallinity Pd provides large numbers of surface unsaturated atoms and defects as highly active sites for highly efficient CO2-to-CO/CH4 conversion. The combination of experimental analysis with theory simulation suggests that the amorphous Pd outperforms the highcrystallinity one in the adsorption and activation of CO<sub>2</sub> molecules. As a result, the CdS-Pd sample with the largest percentage of amorphous domains of Pd achieves the highest CO and  $CH_4$  evolution rates, 10.3 and 5.9 times higher than those of pristine CdS, respectively. This work opens a new avenue to tune the photocatalytic activity and selectivity in solar driven CO<sub>2</sub> conversion through regulating the crystallinity of cocatalysts.

Received 23rd July 2020 Accepted 22nd September 2020

DOI: 10.1039/d0ta07196j

rsc.li/materials-a

## 1. Introduction

The extensive consumption of fossil fuels has increased the atmospheric carbon dioxide concentration and escalated the greenhouse effect. Solar driven conversion of  $CO_2$  into useful renewable fuels using semiconductor based photocatalysts represents a green and sustainable approach to relieve the energy crisis and resolve the concomitant global warming.<sup>1-3</sup> Hitherto, various semiconductor photocatalysts have been studied for their feasibility and efficiency in the  $CO_2$  reduction reaction.<sup>4-7</sup> Nevertheless, the photocatalytic performance of pristine semiconductors is often limited by serious electron–

hole recombination or sluggish surface reaction kinetics.<sup>8,9</sup> Several approaches have been explored to improve the photocatalytic properties, including the integration of semiconductors with cocatalysts.<sup>10–12</sup> Metal such as Pd,<sup>13</sup> Pt,<sup>14</sup> Ru<sup>15</sup> and Ag<sup>16</sup> as reduction cocatalysts not only trap photogenerated electrons from light-harvesting semiconductors and promote the charge separation, but also provide surface active sites and facilitate the adsorption and activation of CO<sub>2</sub> molecules. In spite of the considerable progress, the developed semiconductor–metal photocatalytic systems often suffer from uncontrollable electron trapping ability and surface reactivity of cocatalysts, leading to limited enhancement in the catalytic activity and product selectivity.

Rational surface and interface design of cocatalysts is a promising route to improve the electron capture ability and promote the catalytic reactivity.<sup>17-19</sup> Various parameters of cocatalysts, such as the crystalline phase,<sup>20</sup> exposed facets<sup>21</sup> and surface defects,<sup>22</sup> have been optimized to tune the  $CO_2$  conversion efficiency and tailor the product selectivity. Crystallinity, usually specified as a percentage of the volume of the material that is crystalline, is another important parameter in

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<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ta07196j

photocatalytic systems. Generally, highly crystalline semiconductors with periodic lattices and fewer bulk defects are beneficial for charge transfer and separation,<sup>23–25</sup> while amorphous structures offer abundant unsaturated atoms as highly active sites for surface reactions.<sup>26,27</sup> Nevertheless, the studies on the effects of the crystallinity of cocatalysts on the photocatalytic performance are still lacking as of now.

Considering the effects of crystallinity on the charge transfer and surface reactivity in semiconductor photocatalysts, it is anticipated that crystallinity engineering on cocatalysts would also provide an efficient way to adjust the photocatalytic activity and product selectivity. The question is whether a highcrystallinity or amorphous one is a better choice? Inspired by this, with Pd nanosheets as model cocatalysts, the effects of crystallinity on the photocatalytic CO<sub>2</sub> reduction performance are investigated. Herein, crystallinity tunable Pd nanosheets are integrated with CdS quantum dots to form hybrid photocatalysts. It is found that both the catalytic activity and selectivity change regularly with the variation in the crystallinity of Pd. Highly crystalline Pd facilitates electron capture from lightharvesting CdS, which thus prevents H<sub>2</sub> evolution from occurring on CdS more effectively and achieves high selectivity for CO2 reduction. On the other hand, poorly crystalline Pd provides highly active sites for the adsorption and activation of CO<sub>2</sub> molecules, maximizing the efficiency of the conversion of CO<sub>2</sub> to CO and CH<sub>4</sub>.

## 2. Experimental

#### 2.1. Synthesis of Pd and CdS-Pd samples

In a typical synthesis of Pd-48 nanosheets,<sup>28</sup> 20 mg of Pd(acac)<sub>2</sub> and 260 mg of TOPO were added into 16 mL of octanoic acid in a 50 mL round-bottom flask with magnetic stirring under Ar bubbling for 30 min. When the temperature was increased to 48 °C, 20 mg of Mo(CO)<sub>6</sub> and 3 mL of DMF were added into the aforementioned mixture and the reaction was maintained for 100 min. The color of the solution changed from yellow to dark blue within 30 min. The final product was obtained by centrifugation at 9000 rpm for 5 min, washed with hexane three times, and then dispersed in 4 mL hexane. Pd-60, Pd-80 and Pd-100 nanosheets with different crystallinities can be obtained by using the same synthetic method at different temperatures, *i.e.*, 60, 80 and 100  $^\circ\mathrm{C},$  respectively. In a typical procedure for the synthesis of CdS-Pd, a 2 mL suspension of Pd nanosheets (1.5 mg mL<sup>-1</sup> in hexane) was mixed with a 2 mL suspension of CdS quantum dots (4.0 mg mL<sup>-1</sup> in chloroform/ethanol) and were further sonicated for 3 min. The as-obtained sample was centrifuged, washed with ethanol three times, and dried at 45 °C in a vacuum.

## 2.2. Photocatalytic CO<sub>2</sub> reduction measurements

15 mg of the photocatalysts were dispersed on a flat glass plate at the bottom of a 100 mL reactor purchased from Beijing Perfectlight Company (China). And 1 mL H<sub>2</sub>O was added, which surrounded the plate. Prior to the test, the reactor loaded with the catalyst was first purged with high purity  $CO_2$  (0.15 MPa) for

20 min. Then the light-irradiation experiment was performed by using a 300 W Xe lamp (PLS-SXE300D/300DUV, Beijing Perfectlight, China) with visible light as the illumination source. Visible light (420 <  $\lambda$  < 780 nm) was used as the illumination source, which was realized using both a 420 nm cutoff filter (long-wave-pass) and a 780 nm cutoff filter (short-wave-pass). The power density of the visible light was measured to be 100 mW cm<sup>-2</sup> using a radiometer (FZ-A, China). The photocatalytic reaction was performed under visible light irradiation with stirring at 400 rpm for 4 h. After completion of the reaction, the products were analyzed using a gas chromatograph (GC-2014, Shimadzu) with Ar as the carrier gas. The amount of H<sub>2</sub> was determined using a thermal conductivity detector (TCD). The amount of CH4 was measured by using a flame ionization detector (FID). CO was converted to CH<sub>4</sub> using a methanation reactor and then analyzed using a FID. After the reaction was completed, the sample was collected via centrifugation at 8000 rpm for 5 min. During the stability test, the photocatalysts were collected after each run and then reused for CO<sub>2</sub> photoreduction. The samples were also tested in 0.15 MPa fresh Ar instead of CO2 but in the presence of H2O and showed no activity for generation of carbon products and thus confirmed that our measurements were free of any carbon contaminants.

#### 2.3. Photoelectrochemical measurements

4.0 mg of the as-synthesized products were dispersed in a mixture of 15 µL of ethanol and 15 µL of Nafion, which was then uniformly spin-dropped onto a 1 cm  $\times$  1 cm indium tin oxide (ITO)-coated glass using a spin coater (SC-1B, China). Subsequently, the ITO-coated glass was heated at 60 °C in a vacuum oven for 3 h. The photocurrents were measured on a CHI 760E electrochemical station (Shanghai Chenhua, China) under ambient conditions under irradiation from a 300 W Xe lamp (PLS-SXE300D/300DUV, Beijing Perfectlight, China). Visible light (420 <  $\lambda$  < 780 nm) with a power density of 100 mW cm<sup>-2</sup> was used as the illumination source. A three-electrode cell was used to perform the electrochemical measurements. The working electrode was the ITO-coated glass. A Ag/AgCl electrode and Pt foil were used as the reference electrode and counter electrode, respectively. The three electrodes were inserted in a quartz cell filled with a 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. The photoresponse of the prepared photoelectrodes (i.e., I-t) was obtained by measuring the photocurrent density under chopped light irradiation (light on/off cycles: 30 s) at a bias potential of 0.1 V vs. Ag/AgCl for 600 s. Electrochemical impedance spectroscopy (EIS) was performed in the  $10^{-1}$  to  $10^{5}$  Hz frequency range with an AC voltage amplitude of 10 mV at an applied potential of 0.1 V vs. Ag/AgCl. The transient open-circuit voltage decay (OCVD) was measured for a total of 800 s under visible light irradiation, and the light was switched on and off 100 and 400 s from the start, respectively. The average lifetime of the photogenerated carriers  $(\tau_n)$  was obtained according to the OCVD using the following equation:

$$\tau_{\rm n} = \frac{K_{\rm B}T}{q} \left(\frac{{\rm d}V_{\rm oc}}{{\rm d}t}\right)^{-1} \tag{1}$$

where  $K_{\rm B}$  is the Boltzmann constant, *T* is the temperature (in Kelvin), and *q* is the unsigned charge of an electron.

#### 2.4. Electrochemical measurements

Electrochemical measurements were performed in a threeelectrode system using an electrochemical workstation (CHI 760E). The working electrode was the glassy carbon electrode, and a platinum column and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. In a typical preparation procedure of the working electrode, 6 µL of the homogeneous ink, which was prepared by dispersing 4 mg sample and 60 µL Nafion solution (5 wt%) in 1 mL waterethanol solution with a volume ratio of 3:1, was loaded onto a glassy carbon electrode with a 3 mm diameter. For CO<sub>2</sub> reduction experiments, linear sweep voltammetry (LSV) of the Pd nanosheets was carried out in an Ar-saturated and CO2saturated 0.5 M KHCO<sub>3</sub> solution (40 mL, pH = 7.3) with a scan rate of 10 mV s<sup>-1</sup>, based on the above electrolysis cell, respectively. All potentials in this study were measured against the Ag/ AgCl reference electrode and converted to the RHE reference scale based on the following equation: E(vs. RHE) = E(vs. Ag/AgCl) + 0.21 V + 0.0591  $\times$  pH.

#### 2.5. Computational details

All the density functional theory (DFT) and first-principles molecular dynamics (MD) computations were performed by using the DMol3 code.<sup>29</sup> The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional of the generalized gradient approximation (GGA) was employed to describe the electron interactions.<sup>30</sup> The double numerical plus polarization (DNP) basis set was used for all elements.<sup>31</sup> Self-consistent field (SCF) computations were performed with a convergence criterion of  $10^{-6}$  a.u. on the total energy and electronic computations. The core electrons were treated by the effective core potentials method. The Nosé-Hoover heat bath scheme was used for the MD simulation. Grand canonical Monte Carlo (GCMC) simulations were performed with the sorption module to search for the possible location of CO<sub>2</sub> on the surface of high-crystallinity and amorphous Pd.29 All GCMC simulations were carried out with the Metropolis Monte Carlo method and universal force field at a temperature of 298 K.32,33 The simulation processes included an equilibration period  $(10^7 \text{ steps})$  and a production period  $(10^7 \text{ steps})$ .

The initial geometry of high-crystallinity Pd was obtained from the sample structure file of Materials Studio 8.0.<sup>29</sup> Supercells consisting of  $5 \times 5 \times 5$  unit cells were employed for the optimization and MD simulation. The initial geometry of amorphous Pd was extracted from the MD result of highcrystallinity Pd at 5000 K. The optimized geometries of highcrystallinity Pd and amorphous Pd are shown in Table S1.<sup>†</sup> Based on the experimental results, the (111) surface was used for the interface reaction simulation of high-crystallinity Pd. For amorphous Pd, the same method was performed to obtain an exposed side, recorded as the amorphous Pd(111) surface. The surface slab was cleaved from the optimized structure of highcrystallinity and amorphous Pd. The vacuum region is >12 Å along the *z*-axis to avoid the interactions between two periodic images. The Monkhorst–Pack *k* point sampling was set as  $3 \times 3 \times 1.^{34}$  All the possible structures for the (111) surface of high-crystallinity Pd and amorphous Pd, CO<sub>2</sub> and their adsorption systems were optimized for calculating the single-point energy (*E*) and Hirshfeld atomic charge (Table S1–S3<sup>†</sup>).<sup>35</sup> The interaction energies (*E*<sub>int</sub>) between the Pd(111) surface and CO<sub>2</sub> were evaluated as:

$$Pd(111) + CO_2 \rightarrow Pd(111) - CO_2$$
(2)

$$E_{\rm int} = E_{\rm Pd-CO_2} - (E_{\rm Pd} + E_{\rm CO_2})$$
 (3)

According to this definition, a more negative  $E_{int}$  indicates a more favorable adsorption.

## 3. Results and discussion

## 3.1. Sample synthesis and characterization

In the proof-of-concept design, Pd nanosheets with different degrees of crystallinity were first synthesized by reducing  $Pd(acac)_2$  with CO released by the decomposition of  $Mo(CO)_6$  at various temperatures according to previous literature.28 The reason for choosing the nanosheet structure is that the high surface-to-volume ratio of two-dimensional structures maximizes the number of reaction sites exposed on the surface and guarantees a large interfacial area in contact with semiconductors.36 The Pd nanosheets obtained at 48, 60, 80 and 100 °C (named Pd-48, Pd-60, Pd-80 and Pd-100, respectively) exhibit similar morphologies of a wrinkled paper-like structure with nanoscale thickness and micrometer-sized edge length (Fig. S1<sup>†</sup>). Highresolution transmission electron microscopy (HRTEM) images show that a typical nanosheet is composed of crystalline and amorphous domains (Fig. 1a-d). For clarity, the crystalline domains are marked by the yellow curves (Fig. 1a and b), while the amorphous domains are marked by the blue curves (Fig. 1c and d). With the increase of the synthetic temperature, the area of crystalline domains gradually increases while that of amorphous domains decreases from Pd-48 to Pd-100. The percentages of the crystalline areas in Pd-48, Pd-60, Pd-80 and Pd-100 are estimated to be 12.2%, 46.4%, 83.0%, and 97.0%, respectively. The lattice spacing of 2.2 Å in the crystalline domains suggests the exposed (111) facet of Pd (Fig. 1a-d). Our previous report has revealed that the Pd(111) surface is a preferable exposed facet of the cocatalyst for CO<sub>2</sub> photoreduction compared with the Pd(100) one.<sup>37</sup>

In the second step, monodisperse CdS quantum dots, which have a narrow size distribution with an average diameter around 3.8 nm (Fig. S2†), were then deposited on the surface of Pd nanosheets at room temperature to obtain the CdS–Pd samples. It should be noted that *in situ* growth of CdS on Pd nanosheets through the heating process is not suitable here given that high temperature would alter the degree of crystallinity of Pd. The as-obtained samples based on different Pd nanosheets are denoted as CdS-Pd-48, CdS-Pd-60, CdS-Pd-80 and CdS-Pd-100, respectively. As shown in Fig. 1e–h (also Fig. S3†), CdS quantum dots are uniformly distributed over the surface of Pd nanosheets in all the samples. There is no obvious



Fig. 1 (a-d) HRTEM images of Pd nanosheets with different degrees of crystallinity: (a) Pd-48, (b) Pd-60, (c) Pd-80 and (d) Pd-100; (e-h) TEM images of CdS-Pd samples: (e) CdS-Pd-48, (f) CdS-Pd-60, (g) CdS-Pd-80 and (h) CdS-Pd-100; (i) STEM image and (j-l) EDS mapping profiles of CdS-Pd-48 showing the elements (j) Pd, (k) Cd and (l) S.

difference in the morphology between the different samples. The elemental distribution in the supported nanostructures can be obtained from the scanning TEM (STEM) image of CdS-Pd-48 (Fig. 1i) as well as the corresponding energy-dispersive spectroscopy (EDS) mapping (Fig. 1j–l).

The detailed structure and composition information of the as-obtained samples are then characterized using the X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) techniques, respectively. As shown in Fig. 2a, in the XRD pattern of pristine quantum dots, all the peaks can be indexed to cubic hawleyite  $\beta$ -CdS (JCPDS 10-0454). In comparison with CdS, CdS-Pd-48 exhibits a similar pattern without the obvious peaks of Pd, further suggesting the low degree of crystallinity of Pd. In contrast, additional peaks attributed to the face-centered cubic (fcc) Pd (JCPDS 46-1043) can be observed in CdS-Pd-60, the intensities of which gradually increase from CdS-Pd-60 to CdS-Pd-80 and then to CdS-Pd-100, further implying the gradual increase in the degree of crystallinity of Pd. The survey XPS spectra further indicate the presence of Cd, S and Pd elements in the CdS-Pd samples (Fig. S4<sup>†</sup>). In the highresolution Cd 3d spectra (Fig. 2b), doublets located at 405.5 and 412.3 eV can be assigned to the Cd  $3d_{5/2}$  and Cd  $3d_{3/2}$  binding energies of CdS, respectively.38 The S 2p spectra can be divided into S  $2p_{3/2}$  and S  $2p_{1/2}$  peaks occurring at binding energies of 161.8 and 163.0 eV, respectively (Fig. 2c).<sup>38</sup> In the Pd 3d spectra, the main peaks at 335.3 eV (Pd 3d<sub>5/2</sub>) and 340.6 eV (Pd 3d<sub>3/2</sub>) are in agreement with the zero valence of Pd, while trace amounts of Pd(II) chemical states are also shown as doublets (336.7 eV

and 342.0 eV), which are typical features of solution-phase synthesized Pd nanocrystals (Fig. 2d).<sup>39</sup> Notably, from CdS-Pd-48 to CdS-Pd-100, both Cd 3d and S 2p core-levels exhibit slight positive shifts, while Pd 3d peaks gradually shift to lower binding energies, suggesting more electron loss and accumulation in CdS and Pd, respectively.<sup>40</sup> These results suggest that free electrons transfer from CdS to Pd upon the hybridization between them, and the charge re-distribution is more obvious when the degree of crystallinity of Pd is higher.

#### 3.2. Photocatalytic performance analysis

Upon acquiring detailed sample information, the photocatalytic activities were evaluated in the mixed vapor of CO<sub>2</sub> and H<sub>2</sub>O under visible light irradiation. As shown in Fig. 3a, bare CdS produces a relatively high amount of H<sub>2</sub> and low amount of CO as well as a trace amount of CH<sub>4</sub>, suggesting the occurrence of the following CO<sub>2</sub> reduction reactions:  $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$  and  $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$  and side reaction:  $2H^+ + 2e^- \rightarrow H_2$ , which is in agreement with previous reports.<sup>41,42</sup> Given the competition between targeted CO<sub>2</sub> reduction and side water splitting, the selectivity for CO<sub>2</sub> reduction is determined to be 31.6%, which is calculated according to the average evolution rates of the reduction products as well as the electrons required to generate products using the following equation:

Selectivity (%) = 
$$[2\nu(CO) + 8\nu(CH_4)]/[2\nu(H_2) + 2\nu(CO) + 8\nu(CH_4)] \times 100\%$$
 (4)



Fig. 2 (a) XRD patterns of CdS based samples; (b–d) XPS spectra of CdS–Pd samples: (b) Cd 3d, (c) S 2p and (d) Pd 3d high-resolution spectra.

where  $\nu$ (CO),  $\nu$ (CH<sub>4</sub>) and  $\nu$ (H<sub>2</sub>) stand for the formation rates of CO, CH<sub>4</sub> and H<sub>2</sub>, respectively, and 2, 8 and 2 electrons are required for CO, CH<sub>4</sub> and H<sub>2</sub> production according to the above reaction equations.

With further loading of CdS on Pd nanosheets, the photocatalytic performance obviously changed. H<sub>2</sub> generation is notably depressed, while CO and CH<sub>4</sub> yields increase remarkably, which should be related to the functions of cocatalysts. With the same loading amount of CdS, the product yield shows a strong correlation with the crystallinity of Pd. Among the four CdS-Pd samples, CdS-Pd-48 achieves the highest average CO  $(23.93 \ \mu mol \ g_{cat}^{-1} \ h^{-1})$  and  $CH_4$   $(0.35 \ \mu mol \ g_{cat}^{-1} \ h^{-1})$ production rates, 10.3 and 5.9 times higher than those of pristine CdS, respectively. The enhancements of Pd-48 to the CO and CH<sub>4</sub> evolution rates of CdS as well as the selectivity for CO<sub>2</sub> reduction also surpass those of reported cocatalysts in combination with CdS (Table S4<sup>†</sup>).<sup>43-46</sup> With the increase in the crystallinity of Pd from CdS-Pd-48 to CdS-Pd-100, both the average CO and CH<sub>4</sub> production rates gradually decrease. Meanwhile, H<sub>2</sub> yield also experiences a decline with no H<sub>2</sub> detected in CdS-Pd-100. Consequently, the selectivity toward CO<sub>2</sub> reduction

gradually increases from 95.8% for CdS-Pd-48 to 97.1% for CdS-Pd-60, and then to 98.3% for CdS-Pd-80 and 100% for CdS-Pd-100. The CdS-Pd samples also exhibit excellent durability (Fig. 3b). Taking CdS-Pd-48 as an example, there is no obvious drop in both the yield and selectivity of carbonaceous products in five 4 h cycles, which can be ascribed to the well-maintained structure and composition of the catalyst during the photocatalytic process (Fig. S5 and S6<sup>†</sup>).<sup>47</sup> The morphologies of CdS-Pd-60, CdS-Pd-80 and CdS-Pd-100 are also well-maintained after the photocatalytic reactions, suggesting the high stabilities of the CdS-Pd photocatalysts are independent on the crystallinity degree of Pd (Fig. S7<sup>†</sup>). It should be noted that no lowcarbon product was detected in the absence of catalysts, a CO2 atmosphere or light illumination, confirming that CO and CH<sub>4</sub> actually originated from photoreduction of CO2. To further confirm this, the <sup>13</sup>C isotope labeling experiment was performed over CdS-Pd-48 using <sup>13</sup>CO<sub>2</sub> as the source of carbon. The strong signals at m/z = 29 and m/z = 17 can be assigned to <sup>13</sup>CO and <sup>13</sup>CH<sub>4</sub>, respectively, suggesting that the carbon source is derived from used CO<sub>2</sub> (Fig. 3c and d). Moreover, the formation of O2 is also detected during the photocatalytic processes,

H,

а 30





-Selectivity

b 30

со сн

Fig. 3 (a) Average production rates of H<sub>2</sub>, CO and CH<sub>4</sub> in photocatalytic CO<sub>2</sub> reduction with CdS based samples as catalysts under visible light irradiation as well as their selectivities for CO2 reduction; (b) average production rates of CO and CH4 in five cycles with CdS-Pd-48 as the catalyst under visible light irradiation as well as the selectivities for  $CO_2$  reduction; (c and d) mass spectra of (c)  ${}^{13}CO$  (m/z = 29) and (d)  ${}^{13}CH_4$  (m/z = 17) produced over CdS-Pd-48 in the photocatalytic reduction of  $^{\overline{13}}$ CO<sub>2</sub>.

indicating the occurrence of the oxidation half reaction:  $H_2O$  +

#### 3.3. Photocatalytic mechanism studies

To gain insight into the crystallinity sensitive photocatalytic performance, the light-harvesting behaviors of the samples were first evaluated using the ultraviolet-visible (UV-vis) diffuse reflectance spectra. As shown in Fig. 4a, pure CdS exhibits an absorption edge at around 550 nm. Based on the curve plots for  $(\alpha h\nu)^2$  versus  $h\nu$  (inset of Fig. 4a), the bandgap of CdS is calculated to be 2.52 eV by using the equation:

$$(\alpha h\nu)^n = A(h\nu - E_g) \tag{5}$$

where  $\alpha$  is the absorption coefficient,  $h\nu$  is the light energy, A is a constant,  $E_g$  is the optical bandgap, and *n* is equal to 2 for direct bandgap CdS. With the further loading of CdS on Pd nanosheets, the bandgap of CdS does not change, while additional broad background absorption can be observed in the region ranging from 550 to 800 nm, which can be ascribed to the interband transition of bound electrons in Pd to highenergy levels as well as the light scattering of CdS closely packed on the nanosheets.48,49 It should be noted that as a nonplasmonic metal, black Pd nanosheets exhibit no plasmonic absorption band in the visible region (Fig. S8†). The comparable light absorption of the CdS-Pd samples in the visible region guarantees the approximative charge generation abilities. Then photocurrent measurements were employed to elucidate the

charge migration and separation behaviors.<sup>50,51</sup> As revealed by Fig. 4b, the couple of Pd significantly improves the photocurrent response of pristine CdS under visible light irradiation, implying the cocatalyst role of Pd in enhancing the photogenerated electron-hole separation. The CdS-Pd-48, CdS-Pd-60, CdS-Pd-80 and CdS-Pd-100 achieve 3.1, 5.0, 6.1 and 7.2-fold increases in the photocurrent density, respectively, revealing the ever-increasing electron capture abilities of Pd cocatalysts with the improvement of the degree of crystallinity. The enhancement is mainly ascribed to the disordered nature of amorphous Pd domains.52,53 On one hand, the contact between CdS and surface defect enriched amorphous Pd induces the formation of interfacial defects between them, which act as electron-hole recombination centers during the interfacial charge transfer. On the other hand, the disordered arrangement of atoms disfavors the diffusion of photogenerated electrons, while the bulk defects act as scattering centers for electron transfer, both of which increase the possibility of charge loss. Thus high-crystallinity Pd cocatalysts with a lower percentage of amorphous domains display superior electron trapping capability in comparison with low-crystallinity ones. The crystallinity-dependent charge kinetic behaviors are also confirmed by the reduced radii of electrochemical impedance spectroscopy (EIS) Nyquist plots in the same sequence (Fig. 4c). Furthermore, the photoluminescence (PL) spectrum of CdS is quenched more significantly by Pd with higher crystallinity, further implying the more effective prevention of charge recombination through radiative pathways (Fig. 4d). As revealed



Fig. 4 (a) UV-vis diffuse reflectance spectra of CdS based samples; the inset is the corresponding Tauc plots; (b) photocurrent vs. time (I-t) curves at 0.1 V vs. Ag/AgCl under visible light irradiation; (c) EIS Nyquist plots at 0.1 V vs. Ag/AgCl; (d) PL spectra excited at 370 nm; the inset is the magnification of the PL peaks; (e) transient OCVD measurements after exposure to visible light; (f) average lifetimes of the photogenerated charge carriers ( $\tau_n$ ) obtained from transient OCVD measurements.

by transient open-circuit voltage decay (OCVD) measurements, the improved charge separation contributes to prolonged carrier lifetimes. According to the open-circuit voltage ( $V_{oc}$ ) decay in the dark (Fig. 4e), average lifetimes of photogenerated charge carriers ( $\tau_n$ ) are estimated as electron-hole recombination gradually occurs when light illumination is turned off. The prolongation of average carrier lifetimes of CdS–Pd with the increasing crystallinity of Pd is clearly shown in Fig. 4f.

According to the above discussion, the charge separation behaviors of the samples and the yields of low-carbon products are in the reverse order, suggesting that surface reactivity plays a critical role in the photocatalytic  $CO_2$  reduction process. Given that the introduction of Pd into CdS significantly prevents  $H_2$ production but accelerates CO and  $CH_4$  generation, it can be inferred that the surface of CdS mainly drives  $H_2$  evolution, while Pd cocatalysts offer surface reactive sites for the conversion of  $CO_2$  to CO and  $CH_4$ . The charge transfer from CdS to Pd decreases the number of electrons accumulated on the surface of CdS, leading to a sharp drop in  $H_2$  generation. Moreover, owing to the enhanced CdS $\rightarrow$ Pd interfacial electron transfer with the increase of the crystallinity of Pd, the number of photoinduced electrons used for  $H_2$  evolution gradually decreases. Thus, CdS–Pd samples experience a gradual decline in  $H_2$  yield, giving rise to the increase of selectivity toward CO<sub>2</sub> reduction.

Then the question is why high-crystallinity Pd cocatalysts with better electron trapping ability exhibit lower CO and CH<sub>4</sub> production. To further elucidate the mechanistic details behind the results, the performance of Pd nanosheets in electrocatalytic CO2 reduction was evaluated. Given the functions of the cocatalyst in accepting electrons and providing reaction sites are much similar to those of electrocatalysts, the electrocatalytic properties enable an in-depth understanding of the photocatalytic activities among different cocatalysts.54 The electrocatalytic properties were examined with a CO2-saturated and Ar-saturated KHCO3 solution as the electrolyte, respectively. As revealed by the linear sweep voltammetry (LSV) results in Fig. 5a, the current densities of the electrode grafted with Pd nanosheets under a CO<sub>2</sub> atmosphere are higher than those under Ar bubbling. This increased current can be assigned to the cathodic current generation of the reduction of CO<sub>2</sub>



Fig. 5 (a) Linear sweep voltammetry (LSV) curves of Pd nanosheets with different degrees of crystallinity recorded in CO<sub>2</sub>-saturated and Arsaturated 0.5 M KHCO<sub>3</sub>; (b) partial current densities and corresponding (c) Tafel plots of CO<sub>2</sub> reduction for Pd nanosheets with different degrees of crystallinity.

molecules induced by Pd.55,56 With the increase of crystallinity from Pd-48 to Pd-100, the current difference narrows gradually, confirming that the poorly crystalline Pd nanosheets act as more effective electrocatalysts for CO<sub>2</sub> reduction. This suggests that the disordered atomic arrangement in the amorphous domains of Pd boosts the density of unsaturated surface atoms and surface structural defects, which act as highly active sites for the CO<sub>2</sub> reduction reaction and thus elevate the efficiency for CO and CH<sub>4</sub> formation.<sup>60,61</sup> To further confirm this, the partial current densities of CO<sub>2</sub> reduction were calculated by multiplying the total current density by the corresponding faradaic efficiencies determined using a gas chromatograph for CO and CH4.57-59 As shown in Fig. 5b, the current density of Pd-48 reaches  $-14.7 \text{ mA cm}^{-2}$  at -0.9 V vs. RHE, which is around 3.1, 7.4 and 14.7 times higher than those of Pd-60, Pd-80 and Pd-100, respectively. Also the corresponding Tafel plots were investigated based on the partial current densities of CO<sub>2</sub> reduction and, as presented in Fig. 5c, it can be seen that a decline in the resulting Tafel slope is observed with the decrease of the crystallinity of Pd, further suggesting a reduced kinetic barrier for CO<sub>2</sub> reduction.<sup>62</sup>

To further analyze the crystallinity degree-dependent surface reaction kinetics in CO2 reduction, adsorption behaviors of CO2 molecules on the surface of high-crystallinity and amorphous Pd were simulated, respectively. As the crystal surface of the high-crystallinity Pd nanosheet was proved to be the (111) facet from the HRTEM images, the (111) surface was used for the interface reaction simulation of high-crystallinity Pd to ensure the consistency of the theoretical model with the experimental sample. For amorphous Pd, the same method was performed to obtain the exposed side, recorded as the amorphous Pd(111)surface. For the adsorption of CO<sub>2</sub> on the high-crystallinity Pd(111) surface, there are totally 3 different interaction modes (Table S2<sup>†</sup>). When the C atom of CO<sub>2</sub> directly connects with the Pd atom in high-crystallinity Pd (Pd<sub>crys</sub>), the adsorption system shows the most negative energy with an interaction energy  $(E_{int})$ of -12.41 kcal mol<sup>-1</sup>. When the disordered arrangement of Pd atoms in the amorphous Pd is taken into consideration, 10 possible adsorption systems obtained by GCMC were optimized

(Table S3 and Fig. S9†). Similarly, when C of CO<sub>2</sub> directly connects with the Pd atom, the adsorption system is more energetically favorable, while the connection of O of CO<sub>2</sub> with the Pd atom will increases the system's energy. The calculated  $E_{int}$  values for the adsorption on amorphous Pd are in the range of -12.06 kcal mol<sup>-1</sup> (the 2<sup>nd</sup> adsorption site)  $\sim$ -15.28 kcal mol<sup>-1</sup> (the 7th adsorption site), among which 8 values are more negative than that for the high-crystallinity Pd. As indicated by the  $E_{int}$  values, the adsorption of CO<sub>2</sub> is more favorable on the amorphous Pd surface in comparison with the high-crystallinity one.

All the possible adsorption interactions mentioned above were simulated, but only the most favorable ones are detailed here. The structures and atomic charges (q) of the relevant adsorption systems are shown in Fig. 6. The C-Pd distances are 2.65 Å and 2.38 Å for the adsorption on  $Pd_{crvs}$  and the 7<sup>th</sup> adsorption site of the amorphous Pd(111) surface (Pd<sub>amor7</sub>), respectively. As indicated by the q values of  $CO_2$  in the adsorption system of high-crystallinity Pd (-0.29e) and amorphous Pd (-0.31e), intermolecular electron transfer from the connected Pd and its surrounding Pd atoms to CO<sub>2</sub> occurred during the formation of C-Pd bonds. Additionally, the C-Pd bond formed on the surface of amorphous Pd is more stable, which is consistent with the calculation results of Eint. After the adsorption interaction, the average bond length of C-O in CO2 is elongated from 1.20 Å to 1.28 Å for high-crystallinity Pd and 1.30 Å for amorphous Pd, suggesting the more significant weakening of the C-O bond in amorphous Pd. Furthermore, the q values of the atoms C and O in CO<sub>2</sub> changed from 0.20e and -0.10e to -0.00e and -0.14e for high-crystallinity Pd and to -0.01e and -0.16e for amorphous Pd, respectively. The electrons on C and O atoms increase more significantly in the case of amorphous Pd, making them easier to undergo CO<sub>2</sub>-to-CO/ CH<sub>4</sub> conversion. Thus, amorphous Pd performs better than the high-crystallinity one in adsorbing and activating CO<sub>2</sub>, which is consistent with the experimental results that CdS-Pd-48 with the lowest crystallinity of Pd achieves the highest CO and CH<sub>4</sub> evolution rates.

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Fig. 6 Optimized geometries for the  $Pd(111)-CO_2$  adsorption systems with the lowest energy: (a) high-crystallinity and (b) the amorphous Pd(111) surface. *q* stands for the atomic charge. Peacock blue: Pd; dark gray: C; red: O.



Scheme 1 Schematic illustrating the photocatalytic processes of CdS–Pd with (a) highly crystalline and (b) poorly crystalline Pd nanosheets as cocatalysts.

Based on the above discussion, the crystallinity-dependent photocatalytic processes can be illustrated in Scheme 1. With the visible-light excitation of CdS, some of the photo-excited electrons migrate to the surface of CdS for H<sub>2</sub> evolution, while others transfer to the Pd surface for the conversion of CO<sub>2</sub> to CO and CH<sub>4</sub>. When highly crystalline Pd nanosheets with excellent electron capture capability are used as cocatalysts, smooth electron transfer from CdS to Pd decreases the number of electrons accumulated on the CdS surface and thus prevents the H<sub>2</sub> evolution, contributing to higher selectivity for CO<sub>2</sub> reduction (Scheme 1a). In contrast, poorly crystalline Pd nanosheets as cocatalysts boost the density of highly active sites on the surface for CO<sub>2</sub>-to-CO/CH<sub>4</sub> conversion despite the relatively lower electron capture efficiency, thus endowing CdS-Pd with improved CO and CH<sub>4</sub> evolution (Scheme 1b). It can be inferred that the surface reactivity rather than the charge transfer is the rate-determining step in CO<sub>2</sub> reduction on the Pd cocatalyst.

## 4. Conclusions

In conclusion, we have demonstrated that the photocatalytic performance in CO<sub>2</sub> reduction can be modulated by tailoring the crystallinity of cocatalysts. With Pd nanosheet supported CdS quantum dots as model photocatalysts, it is found that both the yields of reduction products and selectivity for CO<sub>2</sub> reduction have a strong correlation with the crystallinity of Pd cocatalysts. In particular, CdS-Pd-100 with high-crystallinity Pd achieves 100% selectivity for CO<sub>2</sub> reduction, while CdS-Pd-48 with the lowest crystallinity of Pd exhibits superior CO and CH<sub>4</sub> evolution rates of 23.93 and 0.35 µmol  $g_{cat}^{-1}$  h<sup>-1</sup>, 10.3 and 5.9 times higher with respect to those of bare CdS, respectively. It is found that highly crystalline Pd cocatalysts facilitate the charge transfer from CdS to Pd, which thus prevents the side reaction of H<sub>2</sub> production occurring on the surface of CdS. On the other hand, the experimental and calculation results

indicate that the adsorption and activation of  $CO_2$  are more favorable on the amorphous Pd surface. Consequently, the increasing density of highly active sites enables more efficient conversion of  $CO_2$  to CO and  $CH_4$  along with the decrease of Pd crystallinity. This work offers a crystallinity engineering approach to optimize the activity and selectivity in photocatalytic  $CO_2$  reduction.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21603191, 21775138, and 21806144), Zhejiang Provincial Natural Science Foundation of China (No. LQ16B010001, LQ18B070003, and LY20B030003), Public Welfare Technology Application Research Plan Project of Zhejiang Province (Analysis Test Item, No. 2017C37024) and Foundation of Science and Technology Bureau of Jinhua (No. 20204185, 20204186).

## Notes and references

- 1 T. Inoue, A. Fujishima, S. Konishi and K. Honda, *Nature*, 1979, 277, 637.
- 2 S. C. Roy, O. K. Varghese, M. Paulose and C. A. Grimes, *ACS Nano*, 2010, 4, 1259.
- 3 W. Tu, Y. Zou and Z. Zhou, Adv. Mater., 2014, 26, 4607.
- 4 J. L. White, M. F. Baruch, J. E. Pander III, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev and A. B. Bocarsly, *Chem. Rev.*, 2015, **115**, 12888.
- 5 S. N. Habisreutinger, L. Schmidt-Mende and J. K. Stolarczyk, *Angew. Chem., Int. Ed.*, 2013, **52**, 7372.
- 6 K. Li, B. S. Peng and T. Y. Peng, ACS Catal., 2016, 6, 7485.
- 7 T. Xia, R. Long, C. Gao and Y. Xiong, *Nanoscale*, 2019, **11**, 11064.
- 8 S. Bai, J. Jiang, Q. Zhang and Y. Xiong, *Chem. Soc. Rev.*, 2015, 44, 2893.
- 9 A. Dhakshinamoorthy, S. Navalon, A. Corma and H. Garcia, *Energy Environ. Sci.*, 2012, 5, 9217.
- 10 J. Yang, D. Wang, H. Han and C. Li, *Acc. Chem. Res.*, 2013, **46**, 1900.
- 11 X. Li, J. Yu, M. Jaroniec and X. Chen, *Chem. Rev.*, 2019, **119**, 3962.
- 12 J. R. Ran, M. Jaroniec and S. Z. Qiao, *Adv. Mater.*, 2018, **30**, 1704649.
- 13 Y. Zhu, Z. Xu, W. Jiang, S. Zhong, L. Zhao and S. Bai, *J. Mater. Chem. A*, 2017, **5**, 2619.
- 14 W. N. Wang, W. J. An, B. Ramalingam, S. Mukherjee, D. M. Niedzwiedzki, S. Gangopadhyay and P. Biswas, *J. Am. Chem. Soc.*, 2012, **134**, 11276.
- 15 F. Ye, F. Wang, C. Meng, L. Bai, J. Li, P. Xing, B. Teng, L. Zhao and S. Bai, *Appl. Catal.*, *B*, 2018, 230, 145.

- 16 K. Iizuka, T. Wato, Y. Miseki, K. Saito and A. Kudo, J. Am. Chem. Soc., 2011, 133, 20863.
- 17 S. Bai, W. Yin, L. Wang, Z. Li and Y. Xiong, *RSC Adv.*, 2016, 6, 57446.
- 18 S. Zhong, Y. Xi, S. Wu, Q. Liu, L. Zhao and S. Bai, J. Mater. Chem. A, 2020, 8, 14863.
- 19 S. Zhong, Y. Xi, Q. Chen, J. Chen and S. Bai, *Nanoscale*, 2020, 12, 5764.
- 20 S. Bai, C. Gao, J. Low and Y. Xiong, Nano Res., 2019, 12, 2031.
- 21 S. Bai, L. Wang, Z. Li and Y. Xiong, *Adv. Sci.*, 2017, 4, 1600216.
- 22 S. Bai, N. Zhang, C. Gao and Y. Xiong, *Nano Energy*, 2018, 53, 296.
- 23 T. N. Ye, M. Xu, W. Fu, Y. Y. Cai, X. Wei, K. X. Wang,
  Y. N. Zhao, X. H. Li and J. S. Chen, *Chem. Commun.*, 2014,
  50, 3021.
- 24 J. Wang, Y. Shen, Y. Li, S. Liu and Y. Zhang, *Chem.-Eur. J.*, 2016, **22**, 12449.
- 25 M. Alsawat, T. Altalhi, J. G. Shapter and D. Losic, *Catal. Sci. Technol.*, 2014, 4, 2091.
- 26 Y. Kang, Y. Yang, L. Yin, X. Kang, G. Liu and H. Cheng, *Adv. Mater.*, 2015, **27**, 4572.
- 27 X. Hai, W. Zhou, K. Chang, H. Pang, H. Liu, L. Shi, F. Ichihara and J. Ye, *J. Mater. Chem. A*, 2017, 5, 8591.
- 28 N. Yang, H. Cheng, X. Liu, Q. Yun, Y. Chen, B. Li, B. Chen,
  Z. Zhang, X. Chen, Q. Lu, J. Huang, Y. Huang, Y. Zong,
  Y. Yang, L. Gu and H. Zhang, *Adv. Mater.*, 2018, 30, 1803234.
- 29 Accelrys Materials Studio, Version 8.0, Accelrys Inc, San Diego, USA, 2015.
- 30 J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2008, **100**, 136406.
- 31 D. R. Hamann, M. Schlüter and C. Chiang, *Phys. Rev. Lett.*, 1979, **43**, 1494.
- 32 W. K. Hastings, Biometrika, 1970, 57, 97.
- 33 A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024.
- 34 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Solid State*, 1976, 13, 5188.
- 35 F. L. Hirshfeld, Theor. Chim. Acta, 1977, 44, 129.
- 36 Y. Zhu, Z. Xu, W. Jiang, W. Yin, S. Zhong, P. Gong, R. Qiao, Z. Li and S. Bai, *RSC Adv.*, 2016, 6, 56800.
- 37 X. Zhang, Z. Zhao, W. Zhang, G. Zhang, D. Qu, X. Miao, S. Sun and Z. Sun, *Small*, 2016, **12**, 793.
- 38 X. Cai, Q. Chen, R. Wang, A. Wang, J. Wang, S. Zhong, Y. Liu, J. Chen and S. Bai, *Adv. Mater. Interfaces*, 2019, 6, 1900775.
- 39 S. Bai, X. Wang, C. Hu, M. Xie, J. Jiang and Y. Xiong, *Chem. Commun.*, 2014, **50**, 6094.
- 40 Y. Xia, B. Cheng, J. Fan, J. Yu and G. Liu, *Small*, 2019, 15, 1902459.
- 41 H. L. Wu, X. B. Li, C. H. Tung and L. Z. Wu, *Adv. Mater.*, 2019, **31**, 1900709.
- 42 C. Chen, T. Wu, H. Wu, H. Liu, Q. Qian, Z. Liu, G. Yang and B. Han, *Chem. Sci.*, 2018, **9**, 8890.
- 43 Z. Zhu, J. Qin, M. Jiang, Z. Ding and Y. Hou, *Appl. Surf. Sci.*, 2017, **391**, 572.

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- 44 J. Yu, J. Jin, B. Cheng and M. Jaroniec, J. Mater. Chem. A, 2014, 2, 3407.
- 45 C. Bie, B. Zhu, F. Xu, L. Zhang and J. Yu, *Adv. Mater.*, 2019, **31**, 1902868.
- 46 Z. Zhu, Y. Han, C. Chen, Z. Ding, J. Long and Y. Hou, *ChemCatChem*, 2018, **10**, 1627.
- 47 W. Song, P. Ge, Q. Ke, Y. Sun, F. Chen, H. Wang, Y. Shi, X. Wu, H. Lin, J. Chen and C. Shen, *Chemosphere*, 2019, 221, 166.
- 48 H. Sakamoto, T. Ohara, N. Yasumoto, Y. Shiraishi, S. Ichikawa, S. Tanaka and T. Hirai, J. Am. Chem. Soc., 2015, 137, 9324.
- 49 S. Sarina, H. Y. Zhu, Q. Xiao, E. Jaatinen, J. Jia, Y. Huang,
   Z. Zheng and H. Wu, *Angew. Chem., Int. Ed.*, 2014, 53, 2935.
- 50 H. Zhang, J. Lin, Z. Li, T. Li, X. Jia, X. Wu, S. Hu, H. Lin, J. Chen and J. Zhu, *Catal. Sci. Technol.*, 2019, 9, 502.
- 51 P. Xiao, J. Lou, H. Zhang, W. Song, X. Wu, H. Lin, J. Chen, S. Liu and X. Wang, *Catal. Sci. Technol.*, 2018, **8**, 201.
- 52 P. Dagenais, L. J. Lewis and S. Roorda, *J. Phys.: Condens. Matter*, 2015, 27, 345004.

- 53 A. Zhu, G. J. Shiflet and S. J. Poon, *Metall. Mater. Trans. A*, 2012, **43**, 3501.
- 54 W. Bi, L. Zhang, Z. Sun, X. Li, T. Jin, X. Wu, Q. Zhang, Y. Luo, C. Wu and Y. Xie, ACS Catal., 2016, 6, 4253.
- 55 G. Yin, M. Nishikawa, Y. Nosaka, N. Srinivasan, D. Atarashi, E. Sakai and M. Miyauchi, *ACS Nano*, 2015, **9**, 2111.
- 56 T. E. Rosser, C. D. Windle and E. Reisner, *Angew. Chem., Int. Ed.*, 2016, 55, 7388.
- 57 F. Lei, W. Liu, Y. Sun, J. Xu, K. Liu, L. Liang, T. Yao, B. Pan, S. Wei and Y. Xie, *Nat. Commun.*, 2016, 7, 12697.
- 58 D. Gao, H. Zhou, F. Cai, J. Wang, G. Wang and X. Bao, *ACS Catal.*, 2018, **8**, 1510.
- 59 F. Pan, B. Li, E. Sarnello, Y. Fei, Y. Gang, X. Xiang, Z. Du, P. Zhang, G. Wang, H. T. Nguyen, T. Li, Y. H. Hu, H. C. Zhou and Y. Li, *ACS Nano*, 2020, 14, 5506.
- 60 J. Xie and Y. Xie, ChemCatChem, 2015, 7, 2568.
- 61 J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2013, 135, 17881.
- 62 I. Merino-Garcia, J. Albo, J. Solla-Gullón, V. Montiel and A. Irabien, *J. CO2 Util.*, 2019, **31**, 135.