Electrocatalysis



# Achieving the Widest Range of Syngas Proportions at High Current Density over Cadmium Sulfoselenide Nanorods in CO<sub>2</sub> Electroreduction

Rong He, An Zhang, Yilun Ding, Taoyi Kong, Qing Xiao, Hongliang Li, Yan Liu, and Jie Zeng\*

Electroreduction of CO<sub>2</sub> is a sustainable approach to produce syngas with controllable ratios, which are required as specific reactants for the optimization of different industrial processes. However, it is challenging to achieve tunable syngas production with a wide ratio of CO/H<sub>2</sub>, while maintaining a high current density. Herein, cadmium sulfoselenide (CdS<sub>x</sub>Se<sub>1-x</sub>) alloyed nanorods are developed, which enable the widest range of syngas proportions ever reported at the current density above 10 mA cm<sup>-2</sup> in CO<sub>2</sub> electroreduction. Among CdS, Se1\_, nanorods, CdS nanorods exhibit the highest Faradaic efficiency (FE) of 81% for CO production with a current density of 27.1 mA cm<sup>-2</sup> at -1.2 V vs. reversible hydrogen electrode. With the increase of Se content in CdS<sub>x</sub>Se<sub>1-x</sub> nanorods, the FE for  $H_2$  production increases. At -1.2 V vs. RHE, the ratios of CO/H<sub>2</sub> in products vary from 4:1 to 1:4 on  $CdS_xSe_{1-x}$  nanorods (x from 1 to 0). Notably, all proportions of syngas are achieved with current density higher than  $\approx 25$  mA cm<sup>-2</sup>. Mechanistic study reveals that the increased Se content in CdS<sub>x</sub>Se<sub>1-x</sub> nanorods strengthens the binding of H atoms, resulting in the increased coverage of H\* and thus the enhanced selectivity for H<sub>2</sub> production in CO<sub>2</sub> electroreduction.

As the mixture of CO and H<sub>2</sub>, syngas serves as an important feedstock in the petroleum industry for synfuel production.<sup>[1]</sup> In practical applications, specific ratios of CO/H<sub>2</sub> in syngas are required for the optimization of different industrial processes.<sup>[2]</sup> Typically, a CO/H<sub>2</sub> ratio of 1:2 is desired for Fischer-Tropsch synthesis, whereas the hydroformylation process holds the optimal CO/H<sub>2</sub> ratio of 1:1. Currently, syngas with tunable compositions is mainly produced by two mature technologies, including coal gasification and natural gas reforming.<sup>[3]</sup> The dependence on nonrenewable fossil fuels drives researchers to explore sustainable alternatives for tunable syngas production.<sup>[ $\bar{4}$ ,5]</sup> Owing to the abundance and nontoxicity, CO<sub>2</sub> and water serve as ideal carbon and hydrogen sources of syngas, respectively.<sup>[6,8]</sup> Given the combination of CO<sub>2</sub> reduction and water splitting, electroreduction of CO<sub>2</sub> into syngas in aqueous electrolyte is particularly appealing, because this process

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proceeds under the ambient reaction condition and can be driven by intermittent electricity produced by renewable energy sources.<sup>[9–20]</sup>

Recently, a vast variety of catalysts have been developed to produce syngas via the electroreduction of  $CO_2$ .<sup>[21–31]</sup> For example, carbon supported palladium (Pd/C) was demonstrated to convert CO<sub>2</sub> to syngas with CO/H<sub>2</sub> ratios ranging from 1:2 to 1:1 by manipulating the applied potential from -0.5 to -0.6 V vs. reversible hydrogen electrode (RHE).<sup>[32]</sup> As another example, through the variation of potential from 0.07 to -0.33 V vs. RHE, tunable CO/H<sub>2</sub> ratios in a large range between 2:1 and 1:4 were achieved over Cu/ZnO catalysts via the photoassisted electrochemical conversion of  $CO_2$ .<sup>[33]</sup> In the above cases, tunable ratios of syngas was achieved through the change of applied potential, thus syngas with certain ratios was inevitably produced under low overpotential.

Unfortunately, the current density of syngas at low overpotential was commonly on the scale of 1 mA cm<sup>-2</sup>. As a metric relevant to solar fuel synthesis, the current density of 10 mA cm<sup>-2</sup> is required for syngas production.<sup>[34]</sup> Therefore, it is of significant importance to develop catalysts for tunable syngas production with a wide ratio of CO/H<sub>2</sub> above such current density, which remains as a grand challenge.

Herein, we developed cadmium sulfoselenide ( $CdS_xSe_{1-x}$ ) alloyed nanorods, which enabled the widest range of syngas proportions ever reported at the current density above 10 mA cm<sup>-2</sup> in CO<sub>2</sub> electroreduction. Among CdS<sub>x</sub>Se<sub>1-x</sub> nanorods, CdS nanorods exhibited the highest Faradaic efficiency (FE) of 81% for CO production with a current density of 27.1 mA cm<sup>-2</sup> at -1.2 V vs. RHE. The decrease of x value in  $CdS_xSe_{1-x}$  nanorods enhanced the FE for H<sub>2</sub> production. At -1.2 V vs. RHE, the ratios of CO/H<sub>2</sub> in syngas varied from 4:1 to 1:4 with the x value switching from 1 to 0 in  $CdS_xSe_{1-x}$ nanorods. In particular,  $CdS_{0.43}Se_{0.57}$  and  $CdS_{0.22}Se_{0.78}$  nanorods produced syngas with CO/H<sub>2</sub> ratios of 1:1 and 1:2, respectively. Notably, all proportions of syngas were achieved with current density higher than  $\approx 25$  mA cm<sup>-2</sup>. During the potentiostatic tests, CdS<sub>x</sub>Se<sub>1-x</sub> nanorods exhibited excellent long-term stability. Mechanistic study revealed that the increased Se content in  $CdS_xSe_{1-x}$  nanorods strengthened the binding of H atoms, leading to the increased coverage of H\* and thus the enhanced selectivity for H<sub>2</sub> production in CO<sub>2</sub> electroreduction.

R. He, A. Zhang, Y. Ding, T. Kong, Q. Xiao, H. Li, Y. Liu, Prof. J. Zeng Hefei National Laboratory for Physical Sciences at the Microscale Key Laboratory of Strongly-Coupled Quantum Matter Physics of Chinese Academy of Sciences Department of Chemical Physics University of Science and Technology of China Hefei, Anhui 230026, P. R. China E-mail: zengj@ustc.edu.cn



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In a typical synthesis of  $CdS_xSe_{1-x}$  nanorods, different molar ratio of S/Se powder and a certain amount of hydrazine hydrate  $(N_2H_4)$  were added into ethylenediamine (EDA) solution containing CdCl<sub>2</sub> precursor in sequence. The mixture was then transferred into a Teflon-lined stainless steel autoclave and maintained at 140 °C for 12 h. Here, x was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). As shown in the scanning electronic microscopy images, all the products took the nanorod morphology (Figure S1, Supporting Information). Transmission electron microscopy (TEM) images of individual nanorods were provided to analyze the influence of Se content on the size of nanorods (Figure S2, Supporting Information). Regardless of the Se content in  $CdS_xSe_{1-x}$  nanorods, the width of nanorods was ≈6 nm (Table S1, Supporting Information). In contrast, due to the different binding energy of EDA molecules on the crystal facets of CdS and CdSe, the rod length and aspect ratio decreased with the increase of Se content in  $CdS_xSe_{1-x}$  nanorods.<sup>[35]</sup> Figure 1a-c shows the high-resolution TEM (HRTEM) images of CdS<sub>0.75</sub>Se<sub>0.25</sub>, CdS<sub>0.5</sub>Se<sub>0.5</sub>, and  $CdS_{0.25}Se_{0.75}$  nanorods, demonstrating that  $CdS_xSe_{1-x}$ nanorods were crystalline. In addition, as indicated by HRTEM images in Figure S3 (Supporting Information), pure CdS and CdSe nanorods possessed a lot of defects as well, suggesting the defects in nanorods were not attributed to the alloyed structure. As shown by the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of  $CdS_xSe_{1-x}$  nanorods, the arrangement of Cd atoms clearly exhibited wurtzite structure without surface migration (Figure 1d–f). Along the [002] directions in HAADF-STEM images, the intensity profiles clearly demonstrated the increased interplanar spacings of (002) facets with the increase of Se content in the alloyed nanorods (Figure 1g–i).

In order to validate the alloyed structure of  $CdS_xSe_{1-x}$  nanorods, we performed the elemental analysis. **Figure 2a**–c shows the HAADF-STEM images and the corresponding energy-dispersive X-ray (EDX) elemental mapping of individual  $CdS_xSe_{1-x}$  nanorod. Regardless of the Se content in  $CdS_xSe_{1-x}$  nanorods, the Cd, S, and Se elements completely overlapped the nanorods. The compositions of  $CdS_xSe_{1-x}$  nanorods were further confirmed by the EDX spectra (Figure S4, Supporting Information). Figure 2d–i shows the line-scanning profiles along the center and terminal of the  $CdS_xSe_{1-x}$  nanorods, which further demonstrated that Cd, S, and Se were homogenously distributed in the whole  $CdS_xSe_{1-x}$  nanorods without spatial segregation.



**Figure 1.** a–c) HRTEM images of typical CdS<sub>0.75</sub>Se<sub>0.25</sub>, CdS<sub>0.5</sub>Se<sub>0.5</sub>, and CdS<sub>0.25</sub>Se<sub>0.75</sub> nanorods. d–f) HAADF-STEM images of the parts marked in panel a–c. g–i) Intensity profiles recorded from the rectangular boxes along [002] directions in panel d–f.





Figure 2. a-c) HAADF-STEM and STEM-EDX elemental mapping images of  $CdS_{0.75}Se_{0.25}$ ,  $CdS_{0.5}Se_{0.5}$ , and  $CdS_{0.25}Se_{0.75}$  nanorods. d-i) Line-scanning profiles of Cd, S, and Se along the center and terminal of  $CdS_{0.75}Se_{0.25}$ ,  $CdS_{0.5}Se_{0.75}$  nanorods. The recorded directions are marked by orange lines in panel a-c.

To further investigate the structure and composition of  $CdS_xSe_{1-x}$  nanorods, we carried out a series of characterizations. As evidenced by X-ray diffraction (XRD) patterns, all the CdS<sub>x</sub>Se<sub>1-x</sub> nanorods exhibited similar characteristic peaks of wurtzite nanocrystals, indicating the homogeneously alloyed structures of  $CdS_xSe_{1-x}$  nanorods (Figure 3a).<sup>[36]</sup> With the increase of Se content in  $CdS_xSe_{1-x}$  nanorods, all the diffraction peaks shifted to smaller diffraction angles because of the increased lattice constant of  $CdS_xSe_{1-x}$  nanorods. On the basis of the XRD data, we calculated the interplanar spacings of  $CdS_xSe_{1-x}$  nanorods for different facets (Figure 3b). Quasi linear relations were observed between the atomic ratio of Se and the lattice spacings for all the facets, which was in accordance with the Vegard's law.<sup>[37]</sup> This result further demonstrated the homogeneously alloyed structure of  $CdS_xSe_{1-x}$  nanorods. Figure 3c shows the Raman spectra of  $CdS_xSe_{1-x}$  nanorods. The peaks at 205 and 302 cm<sup>-1</sup> were assigned to the longitudinal modes of CdS and CdSe, respectively. Due to the high miscibility gap of CdS<sub>x</sub>Se<sub>1-x</sub> system, the peaks for both CdS and CdSe were clearly observed on  $CdS_xSe_{1-x}$  (0 < x < 1) alloyed nanorods.<sup>[38]</sup> When x value varied from 1 to 0 in  $CdS_xSe_{1-x}$  nanorods, the peak for CdS shifted to lower wavenumber, together with the peak for CdSe shifting to higher wavenumber. This result was consistent with the standard two-mode behavior induced by the composition of  $CdS_xSe_{1-x}$  alloy.<sup>[39]</sup> Figure S5 (Supporting Information) shows the X-ray photoelectron spectroscopy (XPS) survey spectra of  $CdS_xSe_{1-x}$  nanorods. The signals of Cd, S, and Se were clearly recorded in  $CdS_xSe_{1-x}$  nanorods. Figure 3d shows the XPS spectra of CdS<sub>x</sub>Se<sub>1-x</sub> nanorods in S 2s and Se 3s region. The peaks at 225.7 and 228.9 eV were attributed to S 2s and Se 3s, respectively. The variation in relative intensity of the two peaks clearly indicates the tunable ratios of S to Se in  $CdS_xSe_{1-x}$  nanorods. In Cd 3d XPS spectra of  $CdS_xSe_{1-x}$ 

nanorods, both the Cd  $3d_{3/2}$  and  $3d_{5/2}$  peaks shifted to lower binding energies with the increase of Se content, due to the larger electronegativity of S than that of Se (Figure S6, Supporting Information).

To elucidate the formation mechanism of alloyed  $CdS_xSe_{1-x}$ nanorods, we characterized the products obtained at different reaction time in the standard synthetic procedure of CdS<sub>0.5</sub>Se<sub>0.5</sub> nanorods. The morphology evolved from lamellar nanocrystals into nanorods with the prolonging of reaction time (Figure S7, Supporting Information). As shown by the XRD spectra of the products obtained at different time points, the main peak narrowed without the alternation of peak position as reaction proceeded. As such, the degree of crystallinity increased during the synthesis of CdS<sub>0.5</sub>Se<sub>0.5</sub> nanorods, whereas the compositions kept unchanged (Figure S8, Supporting Information). The ICP-AES analysis also confirmed the unchanged stoichiometry (Table S2, Supporting Information). Based on these results, we established some rationale for the formation of alloyed structure. At the beginning of the reaction, the S and Se powders were quickly reduced to  $S^{2-}$  and  $Se^{2-}$  by the N<sub>2</sub>H<sub>4</sub>. The large amounts of anion gave rise to a fast nucleation process, resulting in the formation of alloyed  $CdS_xSe_{1-x}$ nanocrystals. As the reaction proceeded, the lamellar  $CdS_xSe_{1-x}$ nanocrystals were folded into nanorods due to the dissociation of the adsorbed EDA molecules on the surface of  $CdS_xSe_{1-x}$ nanocrystals.<sup>[40]</sup>

The as-prepared  $CdS_xSe_{1-x}$  nanorods were uniformly loaded on carbon papers of  $1 \times 0.5$  cm<sup>2</sup> in area for the electroreduction of CO<sub>2</sub>. As indicated by the geometrical current densities at applied overpotentials, all the  $CdS_xSe_{1-x}$  nanorods exhibited similar catalytic activity towards CO<sub>2</sub> reduction despite of the varied *x* value (Figure S9, Supporting Information). **Figure 4**a shows the partial current densities for CO production (*j*<sub>CO</sub>)







**Figure 3.** a) XRD patterns of the  $CdS_xSe_{1-x}$  nanorods. b) The calculated interplanar spacings of different facets in  $CdS_xSe_{1-x}$  nanorods. c) Raman spectra of the  $CdS_xSe_{1-x}$  nanorods. d) XPS spectra of the  $CdS_xSe_{1-x}$  nanorods in the S 2s and Se 3s region.



**Figure 4.** a) Current densities for CO production at selected potentials on  $CdS_xSe_{1-x}$  nanorods. b) Faradaic efficiencies for CO production at selected potentials on  $CdS_xSe_{1-x}$  nanorods. c) Geometrical current densities and the corresponding proportions of syngas at -1.2 V vs. RHE on  $CdS_xSe_{1-x}$  nanorods. d) Plot of current density (*j*) vs. time for the CdS,  $CdS_{0.5}Se_{0.5}$ , and CdSe nanorods at a constant potential of -1.2 V vs. RHE.



on  $CdS_xSe_{1-x}$  nanorods. Among the  $CdS_xSe_{1-x}$  nanorods, CdS nanorods exhibited the highest  $j_{CO}$  at applied overpotentials. At -1.2 V vs. RHE, CdS exhibited a  $j_{CO}$  of 21.9 mA cm<sup>-2</sup>, with the geometrical current density of 27.1 mA cm<sup>-2</sup>. With the increase of Se content in  $CdS_xSe_{1-x}$  nanorods, the current density for H<sub>2</sub> production increased (Figure S10, Supporting Information). These results were further supported by the linear sweep voltammetry (LSV) curves of CdS, CdS<sub>0.5</sub>Se<sub>0.5</sub>, and CdSe nanorods in N2-saturated and CO2-saturated KHCO3 electrolytes (Figure S11, Supporting Information). Figure 4b shows the FE for CO production on  $CdS_xSe_{1-x}$  nanorods at applied overpotentials. The FE for CO production significantly decreased with the rise of x in  $CdS_xSe_{1-x}$  nanorods. Specifically, CdS nanorods showed the highest FE of 81% for CO production among the  $CdS_xSe_{1-x}$  nanorods at -1.2 V vs. RHE, whereas CdSe nanorods exhibited the lowest FE of 20%. Compared with the commercial CdS and CdSe powders, the CdS and CdSe nanorods exhibited similar FE for gaseous products, demonstrating that the selectivity of the  $CdS_rSe_{1-r}$  system was mainly relevant to the composition, rather than the morphology (Figure S12, Supporting Information).

The variable selectivity for the CO and H<sub>2</sub> production on CdS<sub>x</sub>Se<sub>1-x</sub> nanorods provides an opportunity for the production of syngas with tunable proportions. By adjusting x value from 1 to 0 in  $CdS_xSe_{1-x}$  nanorods, the ratios of CO/H<sub>2</sub> in syngas varied from 4:1 to 1:4 at -1.2 V vs. RHE (Figure 4c). Notably, all proportions of syngas were produced with current density higher than  $\approx 25$  mA cm<sup>-2</sup>. Moreover, because the most useful CO/H<sub>2</sub> ratios in syngas were 1:1 and 1:2, we explored the suitable  $CdS_xSe_{1-x}$ nanorods for achieving such proportions of syngas. As shown in Figure S13 (Supporting Information), CdS<sub>0.43</sub>Se<sub>0.57</sub> nanorods produced the CO/H<sub>2</sub> ratio of 1:1 with a current density of 25.9 mA cm<sup>-2</sup>, whereas  $CdS_{0.22}Se_{0.78}$  nanorods got the CO/H<sub>2</sub> ratio of 1:2 with a current density of 26.5 mA cm<sup>-2</sup>. In addition, the durability of CdS, CdS<sub>0.5</sub>Se<sub>0.5</sub>, and CdSe nanorods as representatives of CdS<sub>x</sub>Se<sub>1-x</sub> nanorods was tested by scanning at a constant potential of -1.2 V vs. RHE (Figure 4d). During a 10 h potentiostatic test, all the  $CdS_xSe_{1-x}$  nanorods exhibited less than 5% decay in current density with stable FE for gaseous products (Figure S14, Supporting Information). Therefore,  $CdS_xSe_{1-x}$  nanorods served as promising catalysts for persistently producing a wide proportion of syngas with considerable current density during CO<sub>2</sub> reduction process.

Motivated by the variable selectivity of  $CdS_xSe_{1-x}$  nanorods, we analyzed the relevant reaction kinetics in CO<sub>2</sub> reduction. As shown in Figure 5a, CdSe and CdS<sub>0.5</sub>Se<sub>0.5</sub> nanorods exhibited Tafel slopes of 135 and 99 mV dec-1, respectively. As such, the conversion of CO2 into COOH\* is determined as the rate-limiting step in CO<sub>2</sub> reduction for the two catalysts.<sup>[41]</sup> In contrast, a lower Tafel slope of 69 mV dec<sup>-1</sup> was observed on CdS nanorods, indicating that the transformation of COOH\* into CO\* served as the rate-limiting step. Figure 5b shows the Nyquist plots and the corresponding equivalent circuit of the three nanorods. Based on the diameter of semicircular Nyquist plot, the charge-transfer resistance  $(R_{CT})$  of CdS nanorods was calculated to be 5.0  $\Omega$ , which was lower than that (6.0  $\Omega$ ) of  $CdS_{0.5}Se_{0.5}$  and that (8.0  $\Omega$ ) of CdSe nanorods. Accordingly, the Faradaic process was faster on CdS nanorods than that on the other two nanorods during the electroreduction of CO<sub>2</sub>.

The dramatic differences in reaction kinetics of  $CdS_xSe_{1-x}$ nanorods inspired us to further analyze the mechanism for  $CO_2$  reduction. The double-layer capacitances ( $C_{dl}$ ) of CdS, CdS<sub>0.5</sub>Se<sub>0.5</sub>, and CdSe nanorods were similar, ranging from 11.4 to 12.4 mF cm<sup>-1</sup> (Figure S15, Supporting Information). The negligible difference in  $C_{dl}$  values indicates that the variation of electrochemical active surface area (ECSA) of  $CdS_xSe_{1-x}$ nanorods could be neglected. We further normalized the  $j_{CO}$ on the basis of  $C_{dl}$  values, demonstrating that the slightly decreased ECSA was not the main reason for the decreased  $j_{CO}$  with the increase of Se content (Figure S16, Supporting Information). Figure 5c shows the IR-compensated oxidative LSV scans for OH<sup>-</sup> adsorption on CdS, CdS<sub>0.5</sub>Se<sub>0.5</sub>, and CdSe nanorods. The peaks for OH<sup>-</sup> adsorption on CdS, CdS<sub>0.5</sub>Se<sub>0.5</sub>, and CdSe nanorods were all located at 0.18 V vs. RHE, indicating that  $CdS_rSe_{1-r}$  nanorods possessed the same binding strength for OH<sup>-</sup>. Given that the binding strength for CO<sub>2</sub> is positively correlated with the binding strength for OH-,  $CdS_xSe_{1-x}$  nanorods exhibited the same ability for the activation of  $CO_2$ .<sup>[42]</sup> Figure 5d shows the Tafel plots of the three nanorods in N2-saturated KHCO3 electrolyte. Based on the intercept of the linear region in Tafel plots, the exchange current density (i<sub>0</sub>) for HER at the thermodynamic redox potential ( $\eta = 0$ ) was calculated. The  $j_0$  increased from 29 to 48 and 59  $\mu$ A cm<sup>-2</sup> for CdS, CdS<sub>0.5</sub>Se<sub>0.5</sub>, and CdSe nanorods, respectively. Due to the weak adsorption of H atoms in  $CdS_xSe_{1-x_2}$ the binding strength for H atoms is positively correlated with the  $j_0$  value of  $CdS_xSe_{1-x}$  nanorods.<sup>[43]</sup> As such, the binding strength for H atoms was enhanced with the Se content in  $CdS_xSe_{1-x}$  nanorods.

To further investigate the interaction between intermediates and catalysts in CO<sub>2</sub> electroreduction, we conducted the galvanostastic step experiments. When the applied current density switched from -2 mA cm<sup>-2</sup> to 0.5  $\mu$ A cm<sup>-2</sup>, the adsorbed intermediates were oxidized, accompanied with the formation of platforms in the plots of potential versus time.<sup>[44]</sup> Figure 5e shows the galvanostastic step experiments in N2-saturated and CO2saturated KHCO3 electrolyte on CdS nanorods. In N2-saturated electrolyte, a characteristic platform was observed at 0.22 V vs. RHE, which can be attributed to  $H^*$  oxidation. After  $CO_2$  was introduced into the electrolyte, a new platform emerged at 0.05 V vs. RHE, corresponding to COOH\* oxidation. Figure 5f shows the galvanostatic step experiments on CdS, CdS<sub>0.5</sub>Se<sub>0.5</sub>, and CdSe nanorods in CO2-saturated KHCO3 electrolyte. The platforms of the three nanorods for COOH\* oxidation were located at the same potential, whereas the potential of the platform for H\* oxidation gradually increased from 0.22 V of CdS to 0.32 V of CdSe. This result was consistent with the enhanced binding strength for H atoms by the introduction of Se atoms in  $CdS_xSe_{1-x}$  nanorods. Moreover, with the increase of Se content in  $CdS_xSe_{1-x}$  nanorods, the platform for H\* oxidation gradually extended, accompanied with the shortening of platform for COOH\* oxidation. Accordingly, the coverage of COOH\* decreased with the increased coverage of H\* in CO<sub>2</sub> electroreduction, resulting in the declined ratios of CO/H<sub>2</sub> in products.

In conclusion, we developed a highly active catalyst composed of  $CdS_xSe_{1-x}$  nanorods, which enabled the production of syngas with widest compositions in  $CO_2$  electroreduction. Among  $CdS_xSe_{1-x}$  nanorods, CdS nanorods exhibited the







**Figure 5.** a) Tafel plots of the CdS,  $CdS_{0.5}Se_{0.5}$ , and CdSe nanorods in CO<sub>2</sub>-saturated KHCO<sub>3</sub> electrolyte. b) Nyquist plots of the three nanorods in CO<sub>2</sub>-saturated KHCO<sub>3</sub> electrolyte. c) IR-compensated oxidative LSV scans in N<sub>2</sub>-saturated KOH for the three nanorods. d) The Tafel plots of the three nanorods in N<sub>2</sub>-saturated KHCO<sub>3</sub> electrolyte. The exchange current densities ( $j_0$ ) for HER were derived from the intercept of the linear region in Tafel plots. e) The galvanostatic step experiments for CdS nanorods in N<sub>2</sub>-saturated and CO<sub>2</sub>-saturated KHCO<sub>3</sub> electrolyte. f) Galvanostatic step experiments for the three nanorods in CO<sub>2</sub>-saturated and CO<sub>2</sub>-saturated KHCO<sub>3</sub> electrolyte. f) Galvanostatic step experiments are experiments for the three nanorods in CO<sub>2</sub>-saturated KHCO<sub>3</sub> electrolyte. Two steps were involved in the experiments. The current densities of two steps were set as  $-2 \text{ mA cm}^{-2}$  and 0.5  $\mu$ A cm<sup>-2</sup>, respectively. The switch of two steps was set at 30 s.

highest FE of 81% for CO production with a current density of 27.1 mA cm<sup>-2</sup> at -1.2 V vs RHE. With the increase of Se content in CdS<sub>x</sub>Se<sub>1-x</sub> nanorods, the FE for H<sub>2</sub> production increased. At -1.2 V vs. RHE, the ratios of CO/H<sub>2</sub> varied from 4:1 to 1:4 on CdS<sub>x</sub>Se<sub>1-x</sub> nanorods, with current density higher than  $\approx$ 25 mA cm<sup>-2</sup> for all proportions of syngas. In addition, CdS<sub>x</sub>Se<sub>1-x</sub> nanorods exhibited excellent long-term stability during the potentiostatic tests. Mechanism study revealed that the variable selectivity of CO<sub>2</sub> reduction on CdS<sub>x</sub>Se<sub>1-x</sub> nanorods originated from the differences in binding strength for H atoms. This work not only developed CdS<sub>x</sub>Se<sub>1-x</sub> nanorods as promising catalysts for CO<sub>2</sub> electroreduction, but also provided a strategy for tunable syngas production.

## Supporting Information

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

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# **Conflict of Interest**

The authors declare no conflict of interest.

### **Keywords**

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