

Letter

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# Electrocatalytic CO<sub>2</sub> Reduction to Alcohols with High Selectivity over Two-Dimensional Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> Nanosheet

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**ABSTRACT:** Electrochemical conversion of CO<sub>2</sub> into alcohols provides an attractive path toward achieving a carbon-neutral cycle, while its efficiency is challenged by identifying active electrocatalysts for the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). In this work, we report Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet acts as an efficient CO<sub>2</sub>RR electrocatalysts toward highly selective hydrogenation of CO<sub>2</sub> to alcohols. This catalyst is capable of achieving a high total Faradaic efficiency (FE<sub>methanol</sub> + ethanol) of 88.3%, with a FE<sub>methanol</sub> up to 65.2% at -0.20 V vs. reversible hydrogen electrode in 0.5 M KHCO<sub>3</sub> solution, much higher than most reported CO<sub>2</sub>RR electrocatalysts. Density functional theory calculations indicate that Fe atom on the Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> surface can be regared as the active site for alcohol formation.

**KEYWORDS:** *Fe*<sub>2</sub>*P*<sub>2</sub>*S*<sub>6</sub> *nanosheet, CO*<sub>2</sub> *reduction reaction, electrocatalysts, alcohols, density functional theory* 

#### INTRODUCTION

Over the past few decades, the overcombustion of fossil fuels emits large amount of CO<sub>2</sub> to the atmosphere, causing serious global concerns.<sup>1,2</sup> Electrocatalytic conversion of CO<sub>2</sub> to valuable chemicals has been an attractive route to fix the issue of growing energy demand and environmental problems.<sup>3-6</sup> CO<sub>2</sub> can be electrochemically converted into gaseous carbon products (CO,<sup>7-11</sup> CH<sub>4</sub>,<sup>12-14</sup> and C<sub>2</sub>H<sub>4</sub>)<sup>15-17</sup>) and liquids like HCOOH<sup>18,19</sup> and alcohols.<sup>20-26</sup> However, the electroreduction of CO<sub>2</sub> to alcohols suffers from intricate six or more electron/proton coupling steps and sluggish kinetics, and thus it is highly urgent to identify efficient electrocatalysts for CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) toward selective production of alcohols.

Among alcohols, methanol and ethanol as hydrogen carriers are widely used to feed the direct alcohols fuel cells because of easy storage and rather high mass energy density (methanol: 6.1 kWh kg<sup>-1</sup>; ethanol: 8.0 kWh kg<sup>-1</sup>).<sup>27-29</sup> Encouragingly, some recent progress has been made to design and develop CO<sub>2</sub>RR electrocatalysts for methanol and/or ethanol production in aqueous media.<sup>21,30-34</sup> Zhang et al. synthesized hierarchical Pd/SnO<sub>2</sub> nanosheets with a Faradaic efficiency for methanol (FE<sub>methanol</sub>) of 54.8±2%.<sup>21</sup> Lu group reported several noble metal-containing CO2RR electrocatalysts, including [PYD]@Pd (FE<sub>methanol</sub>: 35%),<sup>30</sup> [PYD]@Cu-Pt (FE<sub>methanol</sub>: 37%),<sup>31</sup> and [PYD]@Cu-Pd (FE<sub>ethanol</sub>: 12±1%).<sup>32</sup> Cu nanowire array is also active for CO2-to-ethanol conversion but with a low FE<sub>ethanol</sub> of 5.0%,33 and Cu<sub>4</sub>Zn catalyst gives a much higher FE<sub>ethanol</sub> of 29.1%.<sup>34</sup> Given that Fe is the cheapest and one of the most abundant transition metals, Fe-based material would offer us a most economical CO<sub>2</sub>RR electrocatalyst for alcohol production, which however has rarely been explored.

Here, we focus our attention on  $Fe_2P_2S_6$  nanosheet as a 2D catalyst toward highly selective hydrogenation of CO<sub>2</sub> to alcohols. At -0.20 V vs. reversible hydrogen electrode (RHE), this catalyst attains a total  $FE_{methanol} + ethanol$  of 88.3% with a high  $FE_{methanol}$  up to 65.2% in 0.5 M KHCO<sub>3</sub>, outperforming most reported CO<sub>2</sub>RR electrocatalysts. It also exhibits strong electrochemical stability with a slight deterioration during 30-h continuous electrocatalysis. Density functional theory (DFT) calculations reveal that Fe atom acts as favorable CO<sub>2</sub>RR active site and the thermodynamically favored process promotes methanol production.

#### **RESULTS AND DISCUSSION**

Figure 1a shows the whole fabrication process of  $Fe_2P_2S_6$ nanosheet (see Supporting Information for preparative details). X-ray diffraction (XRD) patterns for the samples before and after exfoliation are displayed in Figure 1b. It can be observed that all the peaks are compatible with the JCPDF pattern (No. 74-1501) after exfoliation treatment, indicating the crystallinity is preserved in the Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet. Energy dispersive X-ray spectrum (Figure S1) and inductively coupled plasma mass spectrometry analysis both show that atomic ratio for Fe/P/S of the sample is nearly 1:1:3. Besides, the relative intensity of the peaks is weakened after exfoliation, which comes from the different orientations of Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> before and after exfoliation treatment.<sup>35,36</sup> The scanning electron microscopy (SEM) image (Figure S2a) reveals that bulk  $Fe_2P_2S_6$  is flat with sizes of 20-40 µm. As shown in Figure S2b, Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> owns dense layer structure from the edge position. Transmission electron microscopy (TEM) image for the exfoliated Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> reveals a sheet-shaped structure (Figure 1c) confirming the formation of nanosheet after exfoliation. High-resolution TEM (HRTEM) image for

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 $Fe_2P_2S_6$  nanosheet shows that interplanar spacing is 0.293 nm corresponding with the (130) plane of  $Fe_2P_2S_6$ , as shown in Figure 1d. Atomic force microscopic (AFM) image manifests that the average thickness of the exfoliated  $Fe_2P_2S_6$  nanosheet is about 1.3 nm (Figure 1e). All these above characterizations reveal that the successful synthesis of  $Fe_2P_2S_6$  nanosheet by liquid exfoliation of bulk counterpart.



Figure 1. (a) Schematic illustration of the procedures to fabricate  $Fe_2P_2S_6$  nanosheets. (b) XRD patterns of bulk  $Fe_2P_2S_6$  and  $Fe_2P_2S_6$  nanosheets. (c) TEM, (d) HRTEM and (e) AFM images of  $Fe_2P_2S_6$  nanosheets.



Figure 2. (a) XPS survey spectrum of  $Fe_2P_2S_6$  nanosheet. XPS spectra for  $Fe_2P_2S_6$  nanosheet in regions of (b) Fe 2p, (c) P 2p, and S 2p.

X-ray photoelectron spectroscopy (XPS) survey spectrum of  $Fe_2P_2S_6$  is presented in Figure 2a, which evidences the presence of Fe, P, and S elements as well as O and C elements arising from surface oxidation/contamination.<sup>37</sup> As indicated by Fe 2p region in Figure 2b, the peaks can be fitted at 709.5 and 722.8 eV corresponding to  $2p_{3/2}$  and  $2p_{1/2}$  of  $Fe^{2+.38}$  Another two peaks at 713.9 and 729.4 eV reveal the existence of  $Fe^{3+.38}$  The spectra of P 2p (Figure 2c) exhibits binding energies at 133.1 and 133.9 eV attributed to P  $2p_{3/2}$  and P  $2p_{1/2}$ .

respectively, corresponding to P–S bonds in  $P_2S_6$  unit.<sup>39</sup> The peak at 134.5 eV is ascribed to the P–P bond.<sup>39</sup> For the region of S 2p (Figure 2d), only a pair of peaks are found, confirming only one form of sulfur exists in the  $Fe_2P_2S_6$ , which consistent with crystal structure.



**Figure 3.** (a) LSV curves of  $Fe_2P_2S_6$  nanosheet/CP. (b) Chronoamperometry curves. (c) FEs of CO<sub>2</sub>RR products on  $Fe_2P_2S_6$  nanosheet/CP at different potentials. (d) <sup>1</sup>H NMR spectra of <sup>12</sup>C methanol standard sample and the electrolysis product using <sup>13</sup>CO<sub>2</sub> as feeding gas.

We evaluated the catalytic CO<sub>2</sub>RR performance of the Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet using a three-electrode system. Figure 3a presents linear sweep voltammetry (LSV) curves over Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet/CP in Ar- and CO2-saturated electrolyte solution. A higher cathodic current density can be clearly seen in CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub>, revealing occurrence of CO<sub>2</sub>RR. Thus, we choose the potential window from -0.20 to -0.50 V for CO<sub>2</sub>RR by the LSV curves. As depicted in Figure 3b, the current density begins high and falls to a steady state, which may be attributed to the decrease in local concentration of CO<sub>2</sub> and H<sup>+</sup> near working electrode surface and double layer charging.40-43 The steady current densities at a series of applied potentials suggest good electrochemical stability of  $Fe_2P_2S_6$  during CO<sub>2</sub>RR tests. On-line gas chromatography (GC) and headspace GC (HS-GC) analyses were performed to identify and quantify the reduction products (Figure S3 and S4). Figure 3c shows FEs at different working potentials. As observed, no H<sub>2</sub> was produced and the FE of alcohols achieves the maximum value of 88.3% (FE<sub>methanol</sub>: 65.2%; FE<sub>ethanol</sub>: 23.1%) at -0.20 V (Figure 3c). Of note, Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet compares favorably to the behaviors of bulk  $Fe_2P_2S_6$  (Figure S5) and most reported CO<sub>2</sub>RR catalysts (Table S1). Combining GC, <sup>1</sup>H nuclear magnetic resonance (NMR) data (Figure S6) and ion chromatography (IC) analysis (Figure S7), it is safely to conclude that electrocatalytic CO<sub>2</sub>RR over  $Fe_2P_2S_6$  nanosheet only produces methanol, ethanol, and  $H_2$ without the formation of HCOOH, CH<sub>4</sub>, and CO.

Control experiments were performed to confirm that methanol and ethanol were indeed generated by electrochemical reduction of  $CO_2$  over  $Fe_2P_2S_6$  nanosheet. In Ar-saturated 0.5 M KHCO<sub>3</sub>, there is no methanol and ethanol at different potentials (Figure S8a). Also note that we failed to detect methanol and ethanol when no potential was applied to  $CO_2$ -saturated electrolyte (Figure S8b). Isotope labeled  ${}^{13}CO_2$  was also used as feeding gas to trace the origin of carbon source. As we can see in Figure 3d, the incorporation of  ${}^{13}C$ 

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label into methanol was proved by the peak splitting shown in <sup>1</sup>H NMR, which provides direct evidence to manifest that methanol in the system stemmed only from electrochemical CO<sub>2</sub>RR over Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet. Stability of catalyst is critical to practical use. Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet/CP shows no obvious attenuation in yield during successive recycling tests at -0.50 V for 5 times (Figure S9). Furthermore, under sustained CO<sub>2</sub> gas flow in cathode, there is a a slight decline in current density during 30-h electrolysis at -0.50 V (Figure S10). The  $Fe_2P_2S_6$  still maintains its nanosheet morphology (Figure S11) after a long electrochemical measurement. And there is almost no change in XPS spectra of Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> (Figure S12) after long-term CO<sub>2</sub>RR electrolysis confirming it has strong robustness against CO2RR electrolysis. After long-term electrolysis, the yields of methanol and ethanol for  $Fe_2P_2S_6$ nanosheet/CP (Figure S13) shows no significant drop compared with initial one, demonstrating that the excellent eletrochemical stability of Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet.



**Figure 4.** (a) Optimized geometry of  $CO_2$  over  $Fe_2P_2S_6$  surface and corresponding charge distribution differences (red and blue regions represent positive and negative charges, respectively). Fe, bluish violet; P, pink; S, orange; O, red; C, gray. (b) Reaction energy profile from DFT calculations for methanol and ethanol production via  $CO_2$  reduction over  $Fe_2P_2S_6$  surface (the asterisk symbol (\*) denotes the adsorption site). (c) Density of states of p orbital of C atom in each species during the process of  $CO \rightarrow CH_3OH^1$ .

We conducted DFT calculations to gain further insight into catalytic mechanism involved. The possible adsorption sites including Fe, P, and S atoms are considered to locate the CO<sub>2</sub> molecule (Figure S14). Full geometry optimization indicates that CO<sub>2</sub> tends to be strongly adsorbed at the bridge site above two Fe atoms via end-on pattern with a binding energy of -2.20 eV, which is significantly larger than the values for other catalysts.44-46 As a result, the nearby S atom is pushed outwards and bond to the carbon atom with the length of 1.83 Å, as shown in Figure 4a. Charge density differences are shown in Figure 4b, where electrons accumulate at the region between Fe and bottom O atoms, as well as between C and adjacent S atoms, verifying the strong binding interactions between CO<sub>2</sub> and the electrocatalyst. The Löwdin charge analysis shows that there is 0.49 e transfer from the surface to CO<sub>2</sub>, indicating that the Fe atom on the surface donate electrons to CO<sub>2</sub> molecule. Subsequently, as shown in Figure 4b, the adsorbed  $CO_2$  can be feasibly reduced during the hydrogenation process, indicated by the general downhill profile of the Gibbs free energy change ( $\Delta G$ ). Three different pathways are compared to verify the selectivity of the catalyst, including the production of CH<sub>3</sub>OH molecule in two different configurations and C<sub>2</sub>H<sub>5</sub>OH (Table S2). As for the reduction process represented by the red line, the potential determining

step (PDS) is \*HCOH $\rightarrow$ \*H<sub>2</sub>COH, with a uphill free energy change of 0.36 eV. On the black line pathway, the value of PDS is 0.22 eV, occurring at the step of  $*H_3CO \rightarrow CH_3OH$ . As for the pathway to produce C<sub>2</sub>H<sub>5</sub>OH, the PDS is rather high for the first step of  $*CO \rightarrow 2(*CO)$ , with an uphill free energy change of 0.35 eV. Although the reaction goes spontaneously after the second CO molecule adsorbed, the first step hinders such reaction pathway producing C<sub>2</sub>H<sub>5</sub>OH. Density of States (DOS) of the C-2p orbitals of all the steps during the reduction process to produce CH<sub>3</sub>OH are analyzed, as shown in Figure 4c. There is a distinct PDOS peak locating around -6.00 eV, splitting into several small peaks and shifting to lower energy levels while the first H appears. H atom promotes even distribution of the electronic state of C atom, and the corresponding  $\Delta G$  is -1.90 eV. Furthermore, the PDOS peaks increase in strength obviously with the second H adsorbed, agreeing well with the relatively large changes in  $\Delta G$  (-1.18) eV). It should be noted that the distinct peak of \*OCH<sub>3</sub> is similar with the state of \*CO, with strength increased and energetic more stable (locating around -9.37 eV), indicating the electronic state of C atom has reached a relatively stable state. Detailed reaction energy profiles of Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet to convert CO<sub>2</sub> to alcohols rather than HCOOH, CH<sub>4</sub> are shown in Figures S15-S18.

#### CONCLUSION

In summary, Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> nanosheet is successfully developed as a high-efficiency CO<sub>2</sub>RR electrocatalyst to convert CO<sub>2</sub> to alcohols. It achieves a FE<sub>methanol</sub> + ethanol of 88.3% with a FE<sub>methanol</sub> of 65.2% at -0.20 V vs. RHE in 0.5 M KHCO<sub>3</sub>. Density functional theory calculations suggest that Fe atom on the Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> surface serves as the active site for alcohols formation. This work not only offers a cost-effective catalyst for electrochemical conversion of CO<sub>2</sub> to alcohols, but would provide a novel outlook on future investigations of Fe-based nanomaterials as advanced CO<sub>2</sub>RR catalysts for alcohols product.

#### ASSOCIATED CONTENT

#### **Supporting Information**

Experimental details; <sup>1</sup>H NMR and XPS spectra; SEM and TEM images; energy dispersive X-ray, GC and IC data; calibration and chronopotentiometry curves; yields and FEs; active sites; reaction energy profiles; Tables S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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### Table of Contents Graphic



 $Fe_2P_2S_6$  nanosheet acts as a 2D catalyst toward highly selective electroreduction of  $CO_2$  to alcohols. In 0.5 M KHCO<sub>3</sub> solution, this catalyst is capable of achieving a high total Faradaic efficiency ( $FE_{methanol + ethanol}$ ) of 88.3%, with a  $FE_{methanol}$  up to 65.2% at -0.20 V vs. reversible hydrogen electrode, much higher than most reported  $CO_2RR$  electrocatalytst. Density functional theory calculations reveal that Fe atom on the  $Fe_2P_2S_6$  surface serves as the active site for alcohol formation.