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# A composite heterogeneous catalyst C-Py-Sn-Zn for selective electrochemical reduction of CO<sub>2</sub> to methanol

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#### ARTICLE INFO

*Keywords:* Electroreduction of CO<sub>2</sub> Bimetallic catalyst Organic catalyst Heterogeneous catalyst Methanol ABSTRACT

By using electrochemical oxidation and electrodeposition methods, 4-aminopyridine (Py) and bimetallic Sn-Zn were successfully immobilized on the surface of pure carbon paper to construct a composite heterogeneous catalyst (C-Py-Sn-Zn), which could effectively catalyse electrochemical reduction of CO<sub>2</sub> to selectively form CH<sub>3</sub>OH. The experimental results reveal that the synergic effect between Sn and Zn as well as bimetallic Sn-Zn and organic catalyst Py plays a very important role in catalyzing CO<sub>2</sub> electroreduction. With C-Py-Sn-Zn electrocatalyst, the maximum Faradaic efficiency of CH<sub>3</sub>OH formation could reach 59.9% at the potential -0.5 V vs. RHE, and the catalytic activity could maintain stability during a 26-hour-electrolysis period.

## **1. Introduction**

The excessive use of fossil fuels has greatly increased the level of carbon dioxide emission in the atmosphere, causing a series of environmental issues such as global warming [1]. How to convert and utilize  $CO_2$  confronts a great challenge. On the other hand,  $CO_2$  is a cheap, abundant and renewable C1-feedstock, which can be converted into chemicals and fuels by chemical [2], electrochemical [3–5], and photochemical methods [6,7]. Among various routes, the electrochemical reduction of carbon dioxide is particularly attractive due to its distinctive advantages [8,9].

Some studies have indicated that the main products of electrochemical reduction of carbon dioxide are formic acid, hydrocarbons, alcohols, CO, etc. Among these reduction products, methanol has a relatively high economic value owning to storage easily at atmospheric pressure, so that it can be directly used as raw materials, fuels or solvent [10–12]. In recent years, the electrochemical reduction of CO<sub>2</sub> to CH<sub>3</sub>OH has drawn great attention of researchers all over the world. For instance, Jia et al. prepared novel nanostructured Cu-Au alloy electrocatalysts through electrochemical deposition with a nano-porous Cu film (NCF) as the template to catalyze electrochemical reduction of CO<sub>2</sub>, and the results reveal that Faradic efficiencies of alcohols (methanol and ethanol) are greatly dependent on the nanostructures and compositions of Cu-Au alloys [13]. Albo et al. developed Cu/Bi metal-organic framework-based electrocatalyst systems for electrochemical transformation of CO<sub>2</sub> to alcohols, and the maximum Faradaic efficiencies of methanol and ethanol are 8.6% and 28.3%, respectively [14]. Lu and Wang et al. successfully prepared pyridine derivative (PYD) doped metal composite electrocatalysts such as [PYD] @ Pd [15], [PYD] @ Cu-Pt [16] and [PYD] @ Cu-Pd [17] for electroreduction of CO<sub>2</sub> to methanol, obtaining Faradic efficiency of 35%, 37% and 26% for methanol under low potential electrolysis, respectively. In addition, Ensafi et al. reported a new electrocatalyst (selfassembled monolayer electrode of 2-pyridinethiol@Pt-Au nanoparticles) for reducing of CO2 to CH3OH, with a Faradic efficiency of 39% at a polarization potential of -0.20 V (vs. Ag/AgCl) [18]. Up to now, although much progress has been made in the electroreduction of CO<sub>2</sub> to methanol, there are still some shortcomings on electrocatalysts, such as poor selectivity, low Faradic efficiency, short catalytic life, using expensive noble metal as the catalysts and so on. Therefore, it is still very necessary to develop a highly efficient and cheap catalytic system for CO<sub>2</sub> electrochemical reduction.

Recently, more and more alloys or bimetallic materials have been used in the carbon dioxide electroreduction [13,19–21]. Pyridine derivatives were also applied to electro-catalyze carbon dioxide reduction. Bocarsly et al. [22,23] found that pyridine could effectively catalyze  $CO_2$  electroreduction to selectively

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efficiency of 30%. However, pyridine and its derivatives as homogeneous electrocatalysts are not favorable to the separation and purification of products and recycling, which greatly limit their practical application. In this work, 4-aminopyridine (organic catalyst, denoted with Py) and Sn-Zn (bimetallic catalyst) were immobilized on the surface of carbon paper electrode by electrooxidation modification [24,25] and electrodeposition methods [26,27], to construct a bifunctional heterogeneous catalytic system C-Py-Zn-Sn for electroreduction of CO2 to CH<sub>3</sub>OH. This bifunctional heterogeneous catalyst not only could overcome the drawbacks of homogeneous catalysis but also could more effectively catalyze CO<sub>2</sub> electroreduction to selectively form CH<sub>3</sub>OH through the synergic effect between different metal catalysts as well as organic and bimetallic catalysts. Compared with homogeneous or composite catalysts containing noble metals [13,15–18,22], this heterogeneous non-noble metal catalytic system seems to be more attractive in the practical application of CO<sub>2</sub> electroreduction.

## 2. Experimental

#### 2.1 Catalysts preparation



**Scheme 1.** Illustration process of 4-aminopyridine immobilized on the surface of carbon paper electrode (CPE) [24,25].

Preparation of C-Py catalyst by an electrochemical oxidation method. According to the literature [24,25], 4aminopyridine can be bonded to the surface of pure carbon paper electrode via electrochemical oxidation in anhydrous ethanol solution, as shown in Scheme 1. In our experiment, the electrochemical oxidation was carried out in an undivided cell containing 0.01 mol  $L^{-1}$  4-aminopyridine and 0.1 mol  $L^{-1}$  LiClO<sub>4</sub> ethanol solution, with pure carbon paper anode and Pt foil cathode within the potential range 0 to 1.6 V vs. Ag/AgCl. After the anodization for 5 min, the anode was extracted from the cell, washed with ethanol and deionized water in turn, and then dried at room temperature. The prepared electrocatalyst is denoted by C-Py.

Preparation of C-Sn-Zn (C-Sn and C-Zn) catalysts by electrodeposition method. Sn-Zn catalyst was an electrodeposited on carbon paper electrode in an undivided electrolytic cell using a QJ-3005T DC regulated power under galvanostatic mode with 15 mA  $cm^{-2}$  for 5 min at 25 °C. The electroplating solution consists of 0.1 mol  $L^{-1}$  SnSO<sub>4</sub>, 0.1 mol  $L^{-1}$  ZnSO<sub>4</sub>·7H<sub>2</sub>O, 0.4 mol  $L^{-1}$  C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O, 0.4 mol  $L^{-1}$  (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 4 g  $L^{-1}$  L-ascorbic acid, 0.1 g  $L^{-1}$  sodium dodecyl sulfonate and 1 g  $L^{-1}$  PEG-600. The pH value of the electroplating solution was adjusted to 5~6 with 1:1 NH<sub>3</sub>·H<sub>2</sub>O aqueous solution. After the electrodeposition, the obtained electrocatalyst was washed several times with ethanol and deionized water in turn, and then dried at room temperature. The prepared electrocatalyst was marked by C-Sn-Zn. The C-Zn or C-Sn was prepared by the similar electrodeposition method.

## $SnSO_4$ was used as the corresponding metal salt.

Preparation of C-Py-Sn-Zn electrode. With the prepared C-Py as the cathode and graphite as the anode, Sn-Zn was further electrodeposited on the surface of C-Py electrode. The obtained electrode catalyst was called C-Py-Sn-Zn. The electrodeposition procedure is the same as that of C-Sn-Zn catalyst.

#### 2.2 Catalysts characterization

X-ray diffraction (XRD) patterns were recorded by using a D8 Advance Bruker AXS with a Cu-K<sub> $\alpha$ </sub> radiation ( $\lambda$ = 0.15406 nm) source operating at 40 kV and 40 mA. The morphologies of the samples were analyzed by using a field-emission scanning electron microscope (FE-SEM, Zeiss Merlin, Germany). X-ray photoelectron spectrum (XPS) was determined by a Kratos Axis Ulra DLD spectrometer (England Krotads Company) with 0.48 eV energy resolution and 3 microns imaging spatial resolution.

#### 2.3 Electrochemical measurements and electrolysis

Electrochemical measurements were performed in a three-electrode system at a CHI660C electrochemical workstation. The electrocatalytic reduction of CO<sub>2</sub> was carried out in the H-type cell with 50 mL of electrolyte in the cathodic and anodic compartment separated by Nafion 117 membrane, under a continuous flow of CO<sub>2</sub>. Before the electrolysis, the KHCO<sub>3</sub> electrolyte solution was saturated with CO2 for 30 min. The prepared electrocatalyst (such as C-Py-Sn-Zn, C-Sn-Zn, C-Sn or C-Zn) was used as the working electrode, and platinum foil and Ag/AgCl (saturated KCl) were served as the counter electrode and reference electrode, respectively. The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were conducted in 0.1 mol L<sup>-1</sup> KHCO<sub>3</sub> aqueous solution at a scan rate of 50 mV s<sup>-1</sup>. The potentials involved in the CV, LSV and electrolysis were all transformed to reversible hydrogen electrode (RHE), based on the formula E (vs. RHE) = E (vs. Ag/AgCl) +  $0.197 \text{ V} + \text{pH} \times 0.059 \text{ V}.$ 

The liquid products were quantitatively analyzed by <sup>1</sup>H NMR spectra (Bruker Advance 400 MHz), in which 500  $\mu$ L of electrolyte was mixed with 100  $\mu$ L of D2O containing 1 mmol L<sup>-1</sup> of dimethyl sulfoxide (DMSO) as an internal standard. A series of the known concentrations of methanol solutions were used as the standard solutions. The linear regression curve was obtained from the peak area of the NMR and the known standard concentration of methanol. Based on the standard curve and the NMR peak area ratio of methanol to DMSO, the concentration of the target product CH<sub>3</sub>OH could be quantitatively determined. The calculation of the product Faraday efficiency (FE) is based on the formula FE=6nF/Q, where *n* is the number of moles for methanol is quantified by NMR spectra, 6 is the number of electrons transferred for CO<sub>2</sub> electroreduction to methanol, F is the Faraday constant (96485 C  $mol^{-1}$ ), and Q is the total electric amount applied in the electrolysis. Moreover, the gaseous products were detected by using a gas chromatograph (GC) with a packed column, a thermal conductivity detector and a



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## 3. Results and discussion (a) С ntensity (a.u.) C-Py C-Zn C-Sn-Zn C-Py-Sn-Zn C-Sn 70 50 60 20 30 40 80 90 20 (degree) (d) 2 µm (h) 2 µm

**Fig. 1.** XRD patterns (a) and SEM images of pure carbon paper (b) and the as-prepared catalysts C-Zn (c, d), C-Sn (e, f), C-Sn-Zn (g, h), and C-Py-Sn-Zn (i, j).

The crystalline structures of the as-prepared electrocatalysts were characterized by using X-ray diffractions. In Fig. 1a, it was found that the presence of Sn element can greatly weaken the diffraction intensity of carbon fiber. Compared with pure carbon paper (C), the prepared C-Py does not generate new diffraction peaks, probably because the loading amount of 4-aminopyridine (Py) on the carbon paper surface is too low to reach the detection limit of XRD. For the C-Sn, C-Zn, C-Sn-Zn and C-Py-Sn-Zn electrocatalysts, the diffraction peaks corresponding to the tetragonal  $\beta$ -Sn and hexagonal Zn phases could be observed, which are consistent with that reported in the literature [28]. The XRD results indicated

successfully electrodeposited on the surface of pure carbon paper. According to the phase diagram of Sn and Zn, their mutual solubility is very limited. Sn-Zn is generally considered as a mechanical alloy in which Sn and Zn do not form a solid-solution or an intermetallic compound. Our XRD results further support this viewpoint.



**Fig. 2.** (a) CV curves of pure carbon paper electrode with or without 4-aminopyridine in 0.1 mol  $L^{-1}$  LiClO<sub>4</sub> ethanol solution; (b) the corresponding energy dispersive spectrometer (EDS) of C-Py-Sn-Zn electrocatalyst.

Fig. 1b-j show SEM images of pure carbon paper and the prepared C-Zn, C-Sn, and C-Py-Sn-Zn electrode catalysts. From Fig. 1b, it can be clearly observed that the pure carbon paper has a porous fiber structure. This kind of fiber structure is favorable for the adsorption and diffusion of CO<sub>2</sub> gas. In addition, carbon paper has a good electric conductivity, so carbon paper fiber is very suitable as the substrate to load active organic catalyst (4aminopyridine) and metal catalysts (such as Zn, Sn or Sn-Zn) for the electrocatalytic reduction of CO<sub>2</sub>. The SEM results (Fig. 1b-j) further demonstrate that the metal Zn, Sn or bimetallic Sn-Zn has been successfully electrodeposited on the surface of carbon paper fiber, respectively. From the high magnification SEM images (Fig. 1d, 1f, 1h and 1j), it could be seen that the electrodeposited metal films all consist of irregular nanoparticles. Compared with C-Sn (Fig. 1f), C-Zn (Fig. 1d) has smaller nanoparticles and smoother surface. The C-Sn-Zn and C-Py-Sn-Zn electrocatalysts were obtained under the same electrodeposition conditions, thus having the similar microstructures (Fig. 1g-1). In the following investigation, the effect of their microstructures on the catalytic activity could be almost neglected for CO<sub>2</sub> electroreduction.

Fig. 2a shows CV curves of pure carbon paper

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0.01 mol L <sup>1</sup> 4-aminopyridine (red line) and without 4aminopyridine (black line). In the absence of 4aminopyridine, no oxidization peaks could be observed within the potential range of 0 to 1.6 V vs. Ag/AgCl, while an obviously irreversible oxidation peak appeared at 1.3 V in the presence of 4-aminopyridine. This oxidation peak is attributed to the oxidization of 4-aminopyridine to the corresponding ammonia cation free radical, which could further react with the carbon paper to immobilize the surface of carbon paper electrode (Scheme 1) [24,25]. In order to further determine whether 4-aminopyridine (Py) was well immobilized on the surface of carbon paper fiber, the energy dispersive X-ray spectrum (EDS) test was carried out for C-Py-Sn-Zn electrocatalyst, as shown in Fig. 2b. It was found that the C-Py-Sn-Zn material contains tin, zinc, oxygen, nitrogen, and carbon elements. This result confirms that Py was succesfully immobilized on the surface of carbon paper fiber.



Fig. 3. XPS spectra of C-Py and C-Py-Sn-Zn for N 1s (a), and survey spectra for C-Py-Sn-Zn catalyst (b).

In addition, XPS can also be used to qualitatively identify the amine-containing compounds immobilized on the surface of glass carbon electrode or carbon fibers [22,25,29,30]. In C-Py and C-Py-Sn-Zn samples, the XPS peak corresponding to N 1s at 399.7 eV could be observed (Fig. 3), further proving that 4-aminopyridine was indeed

by the electrooxidation method. Compared with C-Py, C-Py-Sn-Zn displays slightly low intensity of N 1s, which may be due to the electrodeposited bimetallic Sn-Zn covering a part of 4-aminopyridine immobilized on the electrode surface. In addition, the Sn  $3d_{5/2}$  peak (486.07 eV) and Zn  $2p_{3/2}$  (1020.74 eV) peak were observed in C-Py-Sn-Zn sample, which further confirmed the existence of Sn and Zn on the carbon paper surface.

In order to evaluate catalytic activity of the prepared electrode catalysts, we made LSV experiments. Fig. 4a shows the LSV curves of various catalysts in N2- and  $CO_2$ -saturated 0.1 mol L<sup>-1</sup> KHCO<sub>3</sub> aqueous solutions at a scan rate of 50 mV s<sup>-1</sup>. Within the potential range -0.1 to -0.9 V, the reduction peaks were occurred in all the examined electrodes, which were attributed to the reduction of metal oxides (such as ZnO or SnO<sub>x</sub>) on the electrode surface. With the same electrode (C-Py-Sn-Zn), the increase of current density in CO<sub>2</sub>-saturated solution is much greater than that in N<sub>2</sub>-saturated solution within the potential range -0.9 to -1.2 V, which is ascribed to electroreduction of CO<sub>2</sub> or H<sub>2</sub> evolution because of CO<sub>2</sub>saturated solution having lower pH value. Notably, the current density corresponding to bimetallic C-Sn-Zn electrode is higher than that of single metal C-Zn or C-Sn electrodes within the range -0.9 to -1.2 V, indicating that the combination of Sn with Zn metal may be favorable to electroreduction of CO<sub>2</sub>. In particular, the cathodic current density in C-Py-Sn-Zn catalytic system is much larger than that in C-Sn-Zn electrode, in the potential range from -0.9 to -1.2 V. This means that the synergic effect between bimetallic Sn-Zn and organic catalyst Py may play a very important role in catalyzing  $CO_2$ electroreduction.

The catalytic activity of electrode catalysts is related with their electrochemical active surface area (ECSA), and the ECSA is proportional to the double layer capacitance. To further evaluate the catalytic activity of the prepared electrode catalysts, the double layer capacitance was determined by CV experiments with different scan rates. Based on the CV results, the double layer capacitance could be obtained by the corresponding relationship between the current density and scan rate, as shown in Fig. 4b. Notably, C-Py-Sn-Zn has the highest double layer capacitance (402.8  $\mu$ F cm<sup>-2</sup>) among the examined electrode catalysts (C-Py-Sn-Zn, C-Sn-Zn, C-Sn and C-Zn). Thus, it is reasonable to expect that C-Py-Sn-Zn may have better catalytic activity than C-Sn-Zn or C-Sn and C-Zn.

Table 1 Electrochemical reduction of  $CO_2$  to methanol with different electrodes at -0.5 V vs. RHE.

Entry	Electrode catalyst	Methanol (FE%)	CO (FE%)	H <sub>2</sub> (FE%)
1	C-Sn	24	13	32
2	C-Zn	33	50	10
3	C-Sn-Zn	52	14	29
4	C-Py-Sn-Zn	59.9	11	21



**Fig. 4.** (a) LSV curves of the as-prepared catalysts in N<sub>2</sub>- (dashed line) and CO<sub>2</sub>-saturated (solid line) 0.1 mol  $L^{-1}$  of KHCO<sub>3</sub> aqueous solution; (b) The double layer capacitance of the as-prepared catalysts; (c) Faradaic efficiencies of methanol obtained with C-Sn-Zn and C-Py-Sn-Zn electrodes at various potentials; (d) The stability of C-Py-Sn-Zn electrode in electrolyzing CO<sub>2</sub>-saturated 0.1 mol  $L^{-1}$  of KHCO<sub>3</sub> aqueous solution at -0.5 V vs. RHE.

Table 2	Comparison	of the electrochemic	al reduction of	$CO_2$ to methanol	with different	catalytic systems.
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Electrocatalysts	Electrolyte	Potential (V)	MeOH (EtOH) FE (%)	Ref.
PD-Zn/Ag foam	$0.1 \text{ mol } L^{-1} \text{ KHCO}_3$	-1.38 V vs. RHE	10.5	[11]
Cu <sub>63.9</sub> Au <sub>36.1</sub>	$0.5 \text{ mol } \text{L}^{-1} \text{ KHCO}_3$	-1.1 V vs. SCE	15.9 (12)	[13]
Cu/Bi-MOF <sup>a</sup>	$0.5 \text{ mol } \text{L}^{-1} \text{ KHCO}_3$	-0.21 V vs. RHE	8.6 (28.3)	[14]
[PYD]@Pd	$0.5 \text{ mol } L^{-1} \text{ KCl}$	-0.6 V vs. SCE	35	[15]
[PYD]@Cu–Pt	$0.5 \text{ mol } \text{L}^{-1} \text{ KCl}$	-0.6 V vs. SCE	37	[16]
[PYD]@Cu–Pd	$0.5 \text{ mol } \text{L}^{-1} \text{ KCl}$	-0.6 V vs. SCE	26	[17]
2-pyridinethiol@Pt-Au	$0.1 \text{ mol } L^{-1} \text{ KNO}_3$	-0.2 V vs. Ag/AgCl	39	[18]
Pyridine/Pd	$0.5 \text{ mol } \text{L}^{-1} \text{ NaClO}_4$	-	30	[22]
Pyridine/Pt or Pd	$0.5 \text{ mol } \text{L}^{-1} \text{ KCl}$	-	22±2	[23]
4-Aminopyridine/Pt	$0.5 \text{ mol } \text{L}^{-1} \text{ KCl}$	-	$39 \pm 4$	[31]
Pt@adenine-rGO <sup>b</sup>	$0.1 \text{ mol } L^{-1} \text{ KNO}_3$	-0.3 V vs. Ag/AgCl	85	[32]
Pt@histamine-rGO	$0.1 \text{ mol } \text{L}^{-1} \text{ KNO}_3$	-0.3 V vs. Ag/AgCl	37	[33]
Mo-Bi BMC <sup>c</sup>	$0.5 \text{ mol } \text{L}^{-1}$ [Bmim]BF <sub>4</sub> in MeCN	-0.7 V vs. RHE	71.2	[34]
Pd <sub>83</sub> Cu <sub>17</sub> aerogel	[Bmim][BF <sub>4</sub> ]:H <sub>2</sub> O (1:3)	-2.1 V vs. Ag/Ag <sup>+</sup>	80	[35]
Pd/SnO <sub>2</sub>	$0.1 \text{ mol } \text{L}^{-1} \text{ NaHCO}_3$	-0.24 V vs. RHE	54.8	[36]
CoPc-CNT <sup>d</sup>	$0.1 \text{ mol } \text{L}^{-1} \text{ KHCO}_3$	-0.94 V vs. RHE	44	[37]
BP <sup>e</sup>	$0.1 \text{ mol } \text{L}^{-1} \text{ KHCO}_3$	-0.5 V vs. RHE	92	[38]
C-Py-Sn-Zn	$0.1 \text{ mol } \text{L}^{-1} \text{ KHCO}_3$	-0.5 V vs. RHE	59.9	This work

<sup>a</sup> MOF: Metal-organic framework; <sup>b</sup> r-GO: Reduced graphene oxide; <sup>c</sup> BMC: Bimetallic chalcogenide; <sup>d</sup> Cobalt phthalocyanine-carbon nanotube; <sup>e</sup>BP: Boron phosphide nanoparticles.

Table 1 gives the results of electroreduction of  $CO_2$  to methanol with different electrodes at -0.5 V vs. RHE. With C-Sn or C-Zn as the electrode catalyst, the electrolysis of CO<sub>2</sub>-saturated KHCO<sub>3</sub> aqueous solution (0.1 mol L<sup>-1</sup>) could only give a relatively low Faraday efficiency (FE) of CH<sub>3</sub>OH formation (24% and 33%,

respectively, Table 1, entries 1 and 2). Notably, the FE of CH<sub>3</sub>OH formation is greatly enhanced to 52% in the C-Sn-Zn catalyst case (entry 3). Obviously, the bimetallic catalyst (C-Sn-Zn) is superior to the single metal one (C-Sn or C-Zn) for CO<sub>2</sub> electroreduction. The similar results were observed in the previous investigations [13,16]. Compared with single metal catalysts, bimetallic (mixed-

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structure around the active sites or centers, which could modulate the relative binding energy of different reaction intermediates in the electrocatalytic surface and the local atomic arrangement at the active sites. Moreover, the change of the edge atoms in the bimetallic catalytic systems may favor to improve CO<sub>2</sub> adsorption on the active sites and suppress the competitive the hydrogen evolution reaction (HER). In the C-Sn-Zn catalytic system, the synergic effect between Sn and Zn catalyst is beneficial to improving the electrocatalytic reduction of CO<sub>2</sub> to selectively form CH<sub>3</sub>OH. Compared with C-Sn-Zn catalyst, C-Py-Sn-Zn displays a higher FE of CH<sub>3</sub>OH formation under the same electrolytic conditions (59.9%, entry 4 and Fig. 4c). These results indicate that the synergic effect between bimetallic Sn-Zn and 4aminopyridine (Py) could further enhance  $CO_2$ electroreduction to form CH<sub>3</sub>OH. In addition, the gaseous products (CO and  $H_2$ ) could also be detected by using GC. The presence of 4-aminopyridine may inhibit the hydrogen evolution reaction (HER) because of 4aminopyridine containing alkaline groups.

For an electrode catalyst, in addition to its catalytic activity, its stability is important as well. As shown in Fig 4d, the catalytic activity of C-Py-Sn-Zn electrode could basically keep stable during the electrolysis process of 26 h without obvious attenuation. Electrolyzed at -0.5 V vs. RHE in CO<sub>2</sub>-saturated KHCO<sub>3</sub> aqueous solution (0.1 mol L<sup>-1</sup>), the Faraday efficiency of methanol formation could maintain 59.9%. The comparison results with different catalytic systems were listed in Table 2. The present catalytic system C-Py-Sn-Zn is wholly comparable with that reported in the literature [11,13–18,22,23, 31–38].

## 4. Conclusions

In summary, we have developed a novel electrocatalyst C-Py-Sn-Zn by modifying carbon paper electrode with bimetallic Sn-Zn and 4-aminopyridine. This bifunctional heterogeneous catalyst could overcome the inherent drawbacks of homogeneous catalysis. More importantly, it could more effectively catalyze CO<sub>2</sub> electroreduction to selectively form CH<sub>3</sub>OH via the synergic effect between different metals as well as the organic and the bimetallic catalysts. Compared with C-Sn-Zn, C-Sn and C-Zn electrode catalysts, C-Py-Sn-Zn has the best catalytic performance in the conversion of CO<sub>2</sub> to methanol and the maximum Faradaic efficiency for methanol quantified by NMR spectra could reach 59.9%. Moreover, it is worth mentioning that C-Py-Sn-Zn catalyst has a good stability, continuously electrolyzing over 26 h without loss of its activity. Consequently, this stable and low-cost heterogeneous catalyst has a potential application in catalyzing CO<sub>2</sub> electroreduction to methanol.

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- [1] S. Chun, A. Majumdar, Nature 488 (2012) 294-303.
- [2] X.D. Xu, J.A. Mouliji, Energy Fuels 10 (1996) 305-325.
- [3] S. Gao, Y. Lin, X.C. Jiao, Y.F. Sun, Q.Q. Luo, W.H. Zhang, D.Q. Li, J.L. Yang, Y. Xie, Nature 529 (2016) 68–71.
- [4] S.Y. Choi, S.K. Jeong, H.J. Kim, Il-H. Baek, K.T. Park, ACS Sustain. Chem. Eng. 4 (2016) 1311–1318.
- [5] J.L. Qiao, P. Jiang, J.S. Liu, J.J. Zhang, Electrochem. Commun. 38 (2014) 8–11.
- [6] P. Usubharatana, D. McMartin, A. Veawab, P. Tontiwachwuthikul, Ind. Eng. Chem. Res. 45 (2006) 2558–2568.
- [7] Y.G. Wang, X. Bai, H.F. Qin, F. Wang, Y.G. Li, X. Li, S.F. Kang, Y.H. Zuo, L.F. Cui, ACS Appl. Mater. Interfaces 8 (2016) 17212–17219.
- [8] J.P. Jones, G.K.S. Prakash, G.A. Olah, Isr. J. Chem. 54 (2014) 1451–1466.
- [9] D.T. Whipple, Paul J.A. Kenis, J. Phys. Chem. Lett. 1 (2010) 3451–3458.
- [10] J.L. Qiao, Y.Y. Liu, F. Hong, J.J. Zhang, Chem. Soc. Rev. 43 (2014) 631–675.
- [11] Q.H. Low, N.W.X. Loo, F. Calle-Vallejo, B.S. Yeo, Angew. Chem. Int. Ed. 58 (2019) 2256–2260.
- [12] J. Albo, M. Alvarez-Guerra, P. Castaño, A. Irabien, Green Chem. 17 (2015) 2304–2324.
- [13] F. Jia, X.X. Yu, L.Z. Zhang, J. Power Sources 252 (2014) 85–89.
- [14] J. Albo, M. Perfecto-Irigaray, G. Beobide, A. Irabien, J. CO<sub>2</sub> Utilization 33 (2019) 157–165.
- [15] H.P. Yang, S. Qin, H. Wang, J.X. Lu, Green Chem. 17 (2015) 5144–5148.
- [16] H.P. Yang, Y.N. Yue, S. Qin, H. Wang, J.X. Lu, Green Chem. 18 (2016) 3216–3220.
- [17] H.P. Yang, S. Qin, Y.N. Yue, L. Liu, H. Wang, J.X. Lu, Catal. Sci. Technol. 6 (2016) 6490–6494.
- [18] A.A. Ensafi, H.A. Alinajafi, M. Jafari-Asl, B. Rezaei, J. Electroanal. Chem. 804 (2017) 29–35.
- [19] X. Guo, Y.X. Zhang, C. Deng, X.Y. Li, Y.F. Xue, Y.M. Yan, K. Sun, Chem. Commun. 51 (2015) 1345–1348.
- [20] G.O. Larrazábal, A.J. Martín, S. Mitchell, R. Hauert, J. Pérez-Ramírez, J. Catal. 343 (2016) 266–277.
- [21] Q. Lai, N. Yang, N., G.Q. Yuan, Electrochem. Commun. 83 (2017) 24–27.
- [22] G. Seshadri, C. Lin, A.B. Bocarsly, J. Electroanal. Chem. 372 (1994) 145–150.
- [23] E.B. Cole, P.S. Lakkaraju, D.M. Rampulla, A.J. Morris, E. Abelev, A.B. Bocarsly, J. Am. Chem. Soc., 132 (2010) 11539–11551.
- [24] R.S. Deinhammer, M. Ho, J.W. Anderegg, M.D. Porter, Langmuir 10 (1994) 1306–1313.
- [25] B. Barbier, J. Pinson, G. Desarmot, M. Sanchez, J. Electrochem. Soc. 137 (1990) 1757–1764.
- [26] H. Kazimierczak, P. Ozga, A. Jalowiec, R. Kowalik, Surf. Coat. Technol. 240 (2014) 311–319.
- [27] M. Esfahani, J. Zhang, Y.C. Wong, Y. Durandet, J. Wang, J. Electroanal. Chem. 813 (2018) 143–151.
- [28] Z. Liu, A.M. Elbasiony, S.Z. El Abedin, F. Endres, ChemElectroChem 2 (2015) 389–395.
- [29] A.J. Downard, A.B. Mohamed, Electroanalysis 11 (1999) 418–423.
- [30] S. Antoniadou, A.D. Jannakoudakis, R.D. Jannakoudakis, E. Theodoridou, J. Appl. Electrochem. 22 (1992) 1060–1064.
- [31] E.E.B. Cole, M.F. Baruch, R.P. L'Esperance, M.T. Kelly, P.S. Lakkaraju, E.L. Zeitler, A.B. Bocarsly, Top. Catal. 58 (2015) 15–22.
- [32] H.A. Alinajafi, A.A. Ensafi, B. Rezaei, Int. J. Hydrogen Energy 43 (2018) 23262–23274.
- [33] R.F. Zarandi, B. Rezaei, H.S. Ghaziaskar, A.A. Ensafi, Int. J. Hydrogen Energy 44 (2019) 30820–30831.

#### Journal Pre-proof

- Znang, B.X. Han, Angew. Cnem. Int. Ed. 55 (2016) 1-6.
- [35] L. Lu, X.F. Sun, J. Ma, D.X. Yang, H.H. Wu, B.X. Zhang, J.L. Zhang, B.X. Han, Angew. Chem. Int. Ed. 57 (2018) 14149– 14153.
- [36] W.Y. Zhang, Q. Qin, L. Dai, R.X. Qin, X.J. Zhao, X.M. Chen, D.H. Ou, J. Chen, T.T. Chuong, B.H. Wu, N.F. Zheng, Angew.

## Author Statement

## Credit

- 1. All authors have read the manuscript (Title: A composite heterogeneous catalyst C-Py-Sn-Zn for selective electrochemical reduction of  $CO_2$  to methanol) and agreed about the submission to *Electrochemistry Communications*.
- 2. The original and unpublished manuscript is not being considered for publication elsewhere.
- **3.** Gaoqing Yuan as a supervisor instructed the whole experimental work and revised this manuscript.
- 4. Wenjing Huang made all experiments and wrote the initial manuscript.

There is no conflict of interest statement.

## Highlights

- A novel heterogeneous catalyst C-Py-Sn-Zn was successfully prepared via electrochemical methods.
- The synergic effect between Sn and Zn or 4aminopyridine and Sn-Zn catalysts plays a key role.
- With C-Py-Sn-Zn catalyst, the Faradaic efficiency of CH<sub>3</sub>OH formation could reach 59.9%.
- C-Py-Sn-Zn catalyst has a good catalytic stability, continuously catalyzing 26 h without attenuation.

- [57] Y.S. WU, Z. Jiang, X. Lu, Y.Y. Liang, H.L wang, Nature 575 (2019) 639–642.
- [38] S.Y. Mou, T.W. Wu, J.F. Xie, Y. Zhang, L. Ji, H. Huang, T. Wang, Y.L. Luo YL, Xiong, B. Tang, X.P. Sun, Adv. Mater. 31 (2019) 1903499.



## A composite heterogeneous catalyst C-Py-Sn-Zn for selective electrochemical reduction of CO<sub>2</sub> to methanol

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## **Graphical abstract**

A heterogeneous catalyst (C-Py-Sn-Zn) consisting of 4-aminopyridine (Py) and bimetallic Sn-Zn could effectively catalyze electroreduction of CO<sub>2</sub> to selectively form CH<sub>3</sub>OH.



<sup>[34]</sup>