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# Exclusive formation of formic acid from CO<sub>2</sub> electroreduction by tunable Pd-Sn alloy

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Abstract: Conversion of carbon dioxide (CO2) into fuels and chemicals via electroreduction has attracted significant interest derived from renewable energy storage and environmental sustainability, although it suffered from large overpotential and low selectivity. Here, we report a Pd-Sn alloy electrocatalyst for the exclusive conversion of CO<sub>2</sub> into formic acid in an aqueous solution. This catalyst showed a nearly perfect faradaic efficiency toward formic acid formation at the very low overpotential of -0.26 V, where both CO formation and hydrogen evolution were completely suppressed. Density functional theory (DFT) calculations suggested that the formation of the key reaction intermediate HCOO\* as well as the product formic acid was the most favourable over the Pd-Sn alloy catalyst surface with an atomic composition of PdSnO<sub>2</sub>, consistent with our experiments. This indicates the great potential of the tunable Pd-Sn alloy catalyst for the efficient conversion of CO2 into valuable products.

CO<sub>2</sub> is widely considered to be responsible for the climate change, and its utilization as an alternative carbon feedstock may be a viable approach for its remedy. Consequently, there is significant interest in the electrochemical conversion of CO2 into value-added chemicals or fuels driven by low-grade renewable electricity, which means to store the intermittent electric energy in high-energy-density fuels.<sup>[1-3]</sup> Although numerous metallic electrodes were extensively investigated for catalyzing CO<sub>2</sub> electroreduction,<sup>[4,5]</sup> most of them suffered from large overpotential, low faradaic efficiency (FE) and poor product selectivity due to the competitive hydrogen evolution reaction (HER). An effective strategy is to design bimetallic or multimetallic alloy electrocatalysts,<sup>[6-9]</sup> which can benefit from the synergy between different metallic components to form superlattice structures, compressive lattice strains, and/or unique shapes/morphologies, leading to enhanced electrocatalytic performance. Specially, the exquisite surface oxide formation would change the surface electronic structures

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of alloy nanoparticles (NPs), which was believed to enhance their electrocatalytic activities<sup>[10,11]</sup>, and determine the favourable intermediates and final products. However, it is still a great challenge to exclusively produce certain product via  $CO_2$  electroreduction.<sup>[12]</sup>

Here, we report that by virtue of tuning surface electronic structures of Pd-Sn alloy electrocatalysts, CO2 can be exclusively converted to formic acid with nearly 100% FE at an overpotential as low as -0.26 V. We demonstrated that systematically varying the Pd/Sn composition in the alloy NPs resulted in the valley-shaped curve of Pd(0)/Pd(II), which was found to be correlated with the CO<sub>2</sub> electrocatalytic activity and selectivity. First principles DFT calculations further suggested that the optimal surface Pd-Sn-O configuration with the highest oxygen occupancy facilitated the formation of the key reaction intermediate HCOO\* and the generation of the only product of formic acid by the second proton-electron transfer, whereas both CO formation and HER were suppressed. These findings offer the scenario that alloy surface metal-oxide configurations are highly sensitive to electrocatalytic performance, which is unexpected from the previous perception on how alloy  $\ensuremath{\mathsf{NPs}}^{\ensuremath{^{[13-15]}}}$ should function in electrochemical reactions.

Activated carbon (AC) supported Pd-Sn alloy NPs were synthesized via a modified wetting chemistry reduction method with sodium citrate as a stabilizing agent and sodium borohydride as a reductive agent (See Supporting Information (SI) for details). The composition of Pd-Sn NPs was controlled by varying the molar ratio of the precursors PdCl<sub>2</sub> and SnCl<sub>2</sub>, and their particle sizes were preserved as similar as possible by maintaining the ratio of the stabilizing/reductive agents. The obtained samples were denoted as Pd<sub>x</sub>Sn/C. The subscript x represents the molar ratio of Pd/Sn. For comparison, single-component Pd and Sn catalysts supported on AC were also prepared, and these samples were denoted as Pd/C and Sn/C, respectively.

Transmission electron microscopy (TEM) images reveal that the NPs in Pd/C,  $Pd_xSn/C$  and Sn/C are homogeneously dispersed on the AC spherical supports (Figure 1A, B and Figure S1). Size distribution histograms show that over 90% of NPs in these catalysts possess a very narrow size range of 1–5 nm. The particle with the d-spacing of 2.24 Å corresponds to the (111) lattice fringe of metallic Pd (the inset in Figure 1A), while the spacing of 2.25 Å is consistent with the alloy PdSn (121) plane (the inset in Figure 1B). A large number of NPs in Pd/C and PdSn/C were imaged randomly and the results showed that all particles had very similar lattice spacing. The individual phase compositions were further confirmed by mapping and X-ray diffraction (XRD) analyses (vide infra). Figure 1C shows the formation of PdSn alloy NPs on AC in PdSn/C by scanning TEM (STEM) mapping. The corresponding elemental maps of Pd, Sn,

C and their overlap indicate that Pd and Sn elements are evenly distributed in PdSn NPs supported on AC spheres.

Figure 1D displays the XRD patterns of monometallic Pd/C, Sn/C and PdxSn/C alloy catalysts in the range of  $15^{\circ}$ – $85^{\circ}$  (20). The diffraction peaks corresponding to metallic Pd (111), (200), (220), (311) and (222) planes (JCPDS# 050681) were detected along with the broad characteristic (002) peak of AC in Pd/C (Figure 1Da). The alloy catalysts Pd<sub>x</sub>Sn/C (Figure 1Db-g) possess broadened diffraction peaks, which exhibit stepwise broadening and slight shift with decreasing Pd/Sn ratios. The intense peak around 40° in Pd<sub>4</sub>Sn/C (Figure 1Db) downshifts by 0.1° and the full width half maximum (FWHM) increases by 0.7° compared to the Pd (111) peak in Pd/C. With the decrease in Pd content, such intense peaks continuously downshift and broaden. Exhaustive analyses for the intense peaks from 35° to 50° in Pd<sub>x</sub>Sn/C (Figure 2B and Table S2) indicate that the apparently broadened peaks were actually composed of multiple overlapping peaks from different allov phases. The Pd<sub>x</sub>Sn/C catalysts have the corresponding alloy phase compositions in accordance with initial feeding ratios. This shows that bimetallic alloy phases Pd<sub>3</sub>Sn, Pd<sub>2</sub>Sn, PdSn, PdSn<sub>2</sub>, PdSn<sub>4</sub> were formed, as evidenced by HRTEM investigations (the insets in Figure S1), implying that the bulk phase compositions of Pd<sub>x</sub>Sn NPs were well controlled to the desired alloy phases through the accurate wetting chemistry processes. With respect to Sn/C (Figure 1Dh), the peaks of both metallic Sn and SnO<sub>2</sub> phases were detected, in agreement with the HRTEM image (Figure S1H), where the Sn NPs were adjacent to the SnO<sub>2</sub> ones.



Figure 1. Microstructural analysis and bulk compositions of the catalysts. TEM images and size distributions of the NPs in (A) Pd/C and (B) PdSn/C. The insets show the high resolution TEM (HRTEM) images of corresponding NPs. (C) STEM-EDS element mapping of PdSn/C. Scale bars in the maps represent 2 nm unless noted otherwise. (D) XRD patterns of the catalysts. Single-metallic (a) Pd/C, (h) Sn/C and alloy PdxSn/C (b–g): (b) Pd<sub>4</sub>Sn/C, (c) Pd<sub>3</sub>Sn/C, (d) Pd<sub>2</sub>Sn/C, (e) PdSn/C, (f) Pd<sub>0.5</sub>Sn/C, and (g) Pd<sub>0.25</sub>Sn/C.

The surface electronic states of Pd/C, Sn/C and Pd<sub>x</sub>Sn/C alloys were studied by X-ray photoelectron spectroscopy (XPS). The Pd 3d spectrum in Pd/C (Figure 2Aa) was fitted with two components, and the  $3d_{5/2}$  peak located at a binding energy of 335.1 eV was the characteristic of metallic Pd (0) while that at 336.8 eV was assigned to Pd(II) in the PdO state. The catalyst PdSn/C (Figure 2Ab) also consists of two components with Pd

3d<sub>5/2</sub> peaks centred at 335.1 and 336.8 eV, corresponding to Pd (0) and Pd (II), respectively. Oxide species were verified in both Pd/C and Pd<sub>x</sub>Sn/C by XPS spectra (Figure S3 and Tables S3, S4). However, XRD and HRTEM characterizations show only metallic Pd and Pd-Sn alloy phases as bulk compositions in Pd/C and Pd<sub>x</sub>Sn/C, implying that the surface oxide layers evidenced by XPS are too thin to be detectable. The surface of metal NPs is intrinsically prone to getting oxidized when exposed to air, while the bulk remains metallic because of the kinetic limit of surface oxidation.<sup>[16]</sup> The intense Sn 3d<sub>5/2</sub> peaks of PdSn/C (Figure 2Bb) at 485.0 and 486.7 eV correspond to the metallic Sn(0) state and the Sn(IV) state in SnO<sub>2</sub>, respectively. While for Sn/C (Figure 2Bc), only Sn(IV) is present, and metallic Sn(0) was not detected, whose existence was confirmed by XRD patterns. This implies that the metallic Sn phase was enwrapped by surface SnO<sub>2</sub> layer.

Variation of the relative intensity ratios of Pd(0)/Pd(II) and Sn(0)/Sn(IV) with respect to the molar ratios of Pd/Sn in Pd, Sn and allov PdxSn NPs can also be clearly seen in Figure 2C. The Pd(0)/Pd(II) ratio in Pd/C is 2.33, comparable of the previously reported values.<sup>[17,18]</sup> However, it decreases rapidly when the Pd content in NPs gradually decreases, and the Pd(0) was minimum in PdSn/C with the lowest Pd(0)/Pd(II) ratio of 1.47. Interestingly, the Pd(0)/Pd(II) ratios rise again when further decreasing the Pd/Sn molar ratios, leading to the valley-shaped variation of Pd(0)/Pd(II) with bulk Pd/Sn molar ratios. In contrast, the Sn(0)/Sn(IV) ratios monotonically decrease with decreasing Pd/Sn molar ratios. It has been known that noble metal Pd has relatively high electron negativity and low oxygen affinity,<sup>[19]</sup> while Sn is considered as an oxophilic metal.<sup>[20,21]</sup> The proportions of the low oxidation state Pd(0) and Sn(0) are relatively higher when Pd is dominant. When more Sn is present a substantive amount of SnO2 generate on the surface, which in turn prevents Pd from being oxidized resulting in the increasing Pd(0)/Pd(II) ratios again. Therefore, the distinct oxygen affinities of Pd and Sn combined with the variation of their compositions in NPs led to the valley-shaped curve with a unique bottom located at PdSn/C, which comprises the bulk PdSn alloy and the surface Pd-O-Sn layer with the Pd(0)/Pd(II) ratio of 1.47 and the Sn(0)/Sn(IV) ratio of 0.18. In contrast to the bulk composition, the surface electronic states of catalysts can exert significant influence on the adsorption/desorption capacity as well as the catalytic performance.<sup>[22]</sup> The largest amount of CO<sub>2</sub> was observed to desorb at lower temperature on PdSn/C than on other catalysts in the temperature-programmed desorption experiments (Figure S4), indicating the distinct interaction of CO2 with the optimal Pd-O-Sn configuration, which will significantly influence the adsorption/activation of CO<sub>2</sub>.



**Figure 2.** Surface analysis of the electrocatalysts. XPS spectra of (A) the Pd 3d level and (B) the Sn 3d level of the catalysts (a) Pd/C, (b) PdSn/C, (c) Sn/C. (C) The relatively intensity ratios of Pd(0)/Pd(II) and Sn(0)/Sn(IV) versus the molar ratios of Pd/Sn.

The potentiostatic CO<sub>2</sub> electrolysis was performed in a CO<sub>2</sub>saturated KHCO<sub>3</sub> aqueous solution (See SI for details), and the results are shown in Figure 3. CO<sub>2</sub> electroreduction on these catalysts reproducibly yielded CO and formic acid with a substantial amount of hydrogen from HER. The reaction on the non-supported Pd<sub>2</sub>Sn catalyst was dominated by hydrogen production (51% FE) with CO and HCOOH as minor products at an overpotential of -0.86 V. However, it was reversed with carbon-supported catalysts, indicating that activated carbon suppress the HER, in agreement with previous findings.<sup>[23,24]</sup> Pd/C and Sn/C delivered similar HCOOH FE about 50%. With respect to the alloy catalysts, it was found that their HCOOH and CO FEs were highly dependent on the surface configurations at the respective cathodic peak potentials, where CO<sub>2</sub> electroreduction reaction rates were maximum (Figure S5). The less-Sn substituted catalyst Pd<sub>4</sub>Sn/C gave relatively low HCOOH FE (43%), resulting from the metallic Sn on the surface.<sup>[25,26]</sup> With increasing Sn content, the HCOOH FE increases to 54% over Pd<sub>3</sub>Sn/C and further up to 63% over Pd<sub>2</sub>Sn/C. Surprisingly, the highest FE of >99% for producing HCOOH was obtained over the PdSn/C catalyst at the lowest overpotential of -0.26 V. We note that negligible H<sub>2</sub> (FE less than 0.3%) was produced from the HER, and CO formation was completely suppressed over PdSn/C. Subsequently, HCOOH FE decreased gradually to 73% over  $Pd_{0.5}Sn/C$  and 42% over  $Pd_{0.25}Sn/C$  when further increasing the Sn content. At the same potential of -0.43 V (vs. RHE), the HCOOH FEs over all other alloy catalysts were far lower than that over PdSn/C (Figure S6). In contrast, the CO FEs followed the opposite variation trend to the HCOOH FEs, suggesting that the productions of CO and HCOOH are competing routes during CO2 electroreduction. Note that the changes in the HCOOH FE and overpotential are synchronous with those of Pd(0)/Pd(II) in Pd<sub>x</sub>Sn NPs, indicating that the activity of producing HCOOH is sensitive to the surface oxide species on alloy NPs. Recently, Luc et al. reported that an optimal SnO<sub>x</sub> layer in the Ag-Sn bimetallic catalyst was obtained via tuning the molar ratio of Sn and Ag, exhibiting a high HCOOH FE of ~80% at -0.8 V (vs. the reversible hydrogen electrode, RHE).<sup>[27]</sup> In comparison, the catalyst PdSn/C delivered the HCOOH FE over 99% at the lower potential of -0.43 V (vs. RHE). By tuning the electronic state via Sn alloying, the largest amount of palladium oxide species were formed on the surface of the catalyst PdSn/C, as indicated by the XPS results, resulting in superior performance to produce HCOOH in the electrocatalytic reduction of CO2. The catalysts with Pd/Sn ratio close to one also resulted in relatively high HCOOH FEs compared to other alloy catalysts (Table S5). In addition, PdSn/C delivered rather stable potentiostatic electrolysis at the potential of -0.43 V (vs. RHE), showing the negligible decay in the current density after electrolysis for 5 h (Figure S8). The post-reaction XPS analyses showed that the ratios of Pd(0)/Pd(II) and Sn(0)/Sn(IV) of the catalysts after the reaction (Figure S9 and Tables S6, S7) were almost same to those before the reaction, implying the surface oxide species in these catalysts were stable.



**Figure 3.** Faradaic efficiency and overpotential of Pd/C, Sn/C and alloy  $Pd_xSn/C$  at the applied potentials (0.5 M KHCO<sub>3</sub> saturated by CO<sub>2</sub>). The non-supported Pd<sub>2</sub>Sn was compared as reference. The faradaic efficiency is stated as an average and calculated at the steady-state current and product concentration.

To further shed light on the origin of the exclusive formation of formic acid over the PdSn alloy electrocatalyst, we performed DFT calculations to investigate the energetics of the key reaction intermediates involved in the different pathways in CO2 electroreduction over characteristic alloy surface configurations (see SI for details). Starting from bicarbonate (HCO3\*) species, which was demonstrated as the primary carbon source on electrode surface for CO2 electroreduction, [28-30] we examined the possible pathways of stepwise electrocatalytic hydrogenations on the surfaces composed of Pd<sub>3</sub>O, Pd<sub>2</sub>SnO, PdSnO<sub>2</sub> and Sn<sub>2</sub>O<sub>2</sub>. From the energy profiles in Figure 4 and Figures S11-S13, we can see that the preferred intermediates and most favourable pathways are highly dependent on the surface configurations. For Pd<sub>3</sub>O, Pd<sub>2</sub>SnO, PdSnO<sub>2</sub> and Sn<sub>2</sub>O<sub>2</sub>, the calculated reaction energies for the intermediates HCOO\* and COOH\* via the first proton-electron transfer are -0.17 eV/-0.65 eV, -0.79 eV/-0.41 eV, -1.23 eV/-0.37 eV and -1.52 eV/-0.88 eV, respectively. The reaction energies for the further formation of the adsorbed products HCOOH\* and CO\*/H2O\* via the second proton-electron transfer are -1.68 eV/-1.12 eV, -1.55 eV/-1.69 eV, -1.44 eV/-0.73 eV and -2.10 eV/-1.64 eV, respectively. Thus, the energy differences between the intermediates ( $\Delta E_1$ ) and the adsorbed products ( $\Delta E_2$ ) are -0.48 eV/0.56 eV, 0.38 eV/-0.14 eV, 0.86 eV/0.71 eV and 0.64 eV/0.46 eV, respectively. Both  $\Delta E_1$  and  $\Delta E_2$  reach the maximum over the surface composed of PdSnO<sub>2</sub>, where the most favourable pathway involves the HCOO\* intermediate and leads to formic acid formation. Over surfaces of other Pd-Sn-O compositions, Pd<sub>3</sub>O, Pd<sub>2</sub>SnO and Sn<sub>2</sub>O<sub>2</sub>, it is unfavourable to form either HCOO\* or HCOOH\*, resulting in reduced formic acid formation.

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**Figure 4.** Calculated reaction energy profiles for  $CO_2$  electroreduction to form CO (top) and HCOOH (bottom) on the PdSnO<sub>2</sub> surface. PdSnO<sub>2</sub> represents the configuration with almost half Pd atoms are substituted by Sn atoms, in which the surface composition of palladium oxide reach the maximum (for more detials, see SI computational section).

Our results indicated that the preferred intermediates and most favourable pathways during  $CO_2$  electroreduction reaction were highly dependent on the surface configurations of alloy catalysts. The alloy catalyst PdSn/C with a Pd/Sn molar ratio of one possessed the lowest Pd(0)/Pd(II) ratio, leading to the exclusive formation of formic acid. On the basis of our DFT calculations, we concluded that only on the PdSnO<sub>2</sub> surface does HCOO<sup>\*</sup> and HCOOH<sup>\*</sup> remain the most favoured species, which is consistent with the experimental findings.

In conclusion, a simple strategy is illustrated for selective synthesis of formic acid from  $CO_2$  electroreduction, which is attributed to the tuning of surface electronic structures of supported Pd-Sn alloy NPs. The electrocataytic activity and selectivity are highly dependent on the surface configurations, in which formic acid with nearly 100% FE at the lowest overpotential of -0.26 V was produced on the PdSn alloy surface with optimal surface Pd, Sn and O configuration. Our findings are important for the further development of low cost, high activity and high selectivity alloy catalysts for  $CO_2$  electrochemical conversion, with the potential for the efficient utilization of  $CO_2$ .

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**Keywords:** CO<sub>2</sub> conversion • electrochemical reduction • Pd-Sn alloy • formic acid

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The Pd-Sn alloy supported electrocatalysts were synthesized for the electrochemical conversion of  $CO_2$  in an aqueous solution. A nearly perfect faradaic efficiency toward formic acid formation at the very low overpotential of -0.26 V was achieved over PdSn/C, which was attributed to the optimal surface oxide configuration.