High Active PdSn Binary Alloyed Catalysts Supported on B and N Codoped Graphene for Formic Acid Electro-Oxidation

Dan Chen 1,2, Shien Pei 1, Zhishun He 1, Haibo Shao 1, Jianming Wang 1,*, Kai Wang 2, Yong Wang 2 and Yanxian Jin 2,*

1 Department of Chemistry, Zhejiang University, Hangzhou 310027, China; chendan824@tzc.edu.cn (D.C.); shienpei@zju.edu.cn (S.P.); zshe@zju.edu.cn (Z.H.); shaohb@zju.edu.cn (H.S.)
2 School of Pharmaceutical and Materials Engineering, Taizhou University, Taizhou 318000, China; wangkai0914@zju.edu.cn (K.W.); wangyong@tzc.edu.cn (Y.W.)
* Correspondence: wjm@zju.edu.cn (J.W.); shirleyj@tzc.edu.cn (Y.J.); Tel.: +86-571-87951513 (J.W.); +86-576-88660356 (Y.J.); Fax: +86-571-87951895 (J.W.); +86-576-88660177 (Y.J.)

Received: 10 June 2020; Accepted: 30 June 2020; Published: 7 July 2020

Abstract: A series of PdSn binary catalysts with varied molar ratios of Pd to Sn are synthesized on B and N dual-doped graphene supporting materials. The catalysts are characterized by X-ray diffraction (XRD) and Transmission electron microscopy (TEM). Formic acid electro-oxidation reaction is performed on these catalysts, and the results reveal that the optimal proportion of Pd:Sn is 3:1. X-ray photoelectron spectroscopy (XPS) measurements show that when compared with 3Pd1Sn/graphene, B and N co-doping into the graphene sheet can tune the electronic structure of graphene, favoring the formation of small-sized metallic nanoparticles with good dispersion. On the other hand, when compared with the monometallic counterparts, the incorporation of Sn can generate oxygenated species that help to remove the intermediates, exposing more active Pd sites. Moreover, the electrochemical tests illustrate that 3Pd1Sn/BN-G catalyst with a moderate amount of Sn exhibits the best catalytic activity and stability on formic acid electro-oxidation, owing to the synergistic effect of the Sn doping and the B, N co-doping graphene substrate.

Keywords: PdSn binary catalysts; B and N dual-doped graphene; formic acid electro-oxidation; synergistic effect

1. Introduction

With the development of renewable energy resources, fuel cells as portable power sources have been enormously studied. Among the different varieties of fuel cells, direct formic acid fuel cells (DFAFCs), which possess low toxic, high energy conversion efficiency and ease of handling, have attracted considerable attention [1,2]. The development of the active anode catalysts for the oxidation of formic acid plays an important role in the DFAFCs’ technologies. Nowadays, compared with Pt, Pd-based catalysts are considered as a good candidate for anode catalysts because of their high power density and anti-poisoning ability [3,4]. However, the high cost and the low stability of Pd-based catalysts limit their practical application.

In order to improve the electrocatalytic activity and reduce the usage of the Pd catalysts, one feasible strategy is to form Pd-based alloys by incorporating non-precious metals. PdCo, PdFe, PdCu, PdNiPdSn and PdBi binary electrocatalysts have shown higher catalytic activities and stabilities for the electro-oxidation of small molecules (e.g., alcohol and formic acid) as well as oxygen reduction reaction (ORR), than commercial Pd/C catalysts [5–10]. For example, Du et al. presented Pd86Sn14 showing much enhanced current densities and durability toward ethanol oxidation reaction among...
Three carbon-supported Pd-Sn catalysts [11], while Adam suggested that Pd$_{1.5}$Sn shows the best electro-catalytic activity [12]. Brouzgou et al. exhibited that the optimum Pd$_3$Sn$_2$ supported on carbon black has the desirable activity for glucose electro-oxidation [13]. Zhang [14] and Liu [15] found that PdSn/C (2:1) shows better electrocatalytic activity for formic acid oxidation, while Tu showed that the optimal ratio of Pd to Sn is 3:1 [16]. Although the above investigations have been conducted, the optimum atomic ratio between Pd and Sn varies according to different catalytic systems, and even in the same catalytic system the optimum Sn composition is rather controversial.

Another efficient way is to select suitable support with large surface area and good electrical conductivity for loading metal catalysts. The metal–support interaction can strongly influence the physicochemical and electrochemical properties of the metal catalysts [17]. Carbonaceous materials such as carbon blacks [18], carbon nanotubes [19] and graphene [20] are often used as catalyst supports. Nowadays, graphene has been extensively studied as a promising support material for the electrooxidation of alcohols and formic acid due to its high specific surface area and easy modulation [21]. Particularly, functionalizing or heteroatom doping into the graphene architectures can easily tune the electronic structures and improve the electrochemical reactivity [22,23]. Many research groups have made efforts to synthesize doped graphene as metal supports for enhancing the electrocatalytic performance toward the electro-oxidation of alcohol and formic acid [24–26].

Up to now, some researchers focused on the PdSn bimetallic catalysts supporting on carbon blacks or carbon nanotubes [12,27,28], and other researchers aimed at various Pd nanoparticles supporting on modified graphene [20,29]. However, the synergistic effect of PdSn alloys and functional and/or doped graphene nanocomposites still needs to be illuminated. Moreover, recent studies showed that dual-doped graphene can combine the advantages of two different heteratoms and lead to further enhanced catalytic performance [24]. In this work, a series of PdSn bimetallic catalysts supported on B-N dual-doped graphene is prepared by a chemical reduction method, and their electrocatalytic properties on the electro-oxidation of formic acid are investigated. Based on the improvement of the microstructures and electrocatalytic performance of the PdSn bimetallic catalysts, the optimum atom ratio of Sn/Pd and the effect of B, N co-doping graphene substrate are discussed in detail.

2. Results and Discussion

2.1. Structural Analysis

The phase structures of the Pd-based catalysts were analyzed by XRD, and the results are given in Figure 1. The broad diffraction peak at about $2\theta = 26^\circ$ is attributed to the C (002) reflection of the graphene or its derivatives. It is noted that the C (002) peak intensities of 4Pd$_1$Sn BN-G and Pd/BN-G samples are relatively low, which could result from the higher Pd contents on the carbon surface. The diffraction peaks at approximately $2\theta = 39.5^\circ$, $45.4^\circ$, $66.4^\circ$ and $79.6^\circ$ are assigned to the typical Pd face-centered cubic (fcc) crystal structure patterns of the (111), (200), (220) and (311) planes, respectively [30]. It is obvious that the Pd diffraction peaks of all the PdSn/BN-G samples slightly shift to the low-angle region, compared with that of Pd/BN-G, reflecting that the Sn atoms are incorporated into Pd lattice and the alloyed Pd-Sn nanomaterials are formed [12,15,27]. The small peak around $41.5^\circ$ for xPdySn/BN-G may be ascribed to the partial oxidation of Sn [31]. The crystallite sized and the lattice parameter $\alpha$ can be estimated from the Pd (111) diffraction data using the Debye–Scherrer formula and Bragg’s law, and the crystallite size thus obtained and other physicochemical parameters are summarized in Table 1. It can be clearly seen that the average crystallite size decreases in the order: Pd/G $<$ 3Pd1Sn/G $<$ Pd/BN-G $<$ 1Pd1Sn/BN-G $<$ 2Pd1Sn/BN-G $<$ 4Pd1Sn/BN-G $<$ 3Pd1Sn/BN-G. Moreover, the lattice structure of Pd crystal is expanded by the incorporation of Sn to Pd. Moreover, the alloying degree ($\chi$, mole fraction of Sn, at.%) can be determined by the following equation [32].

$$\chi \left(1 - \frac{r_{\text{Sn}}}{r_{\text{Pd}}}\right) = 1 - \frac{\alpha_{\text{alloy}}}{\alpha_{\text{Pd}}}$$  (1)
where the element radii $r_{\text{Sn}}$ and $r_{\text{Pd}}$ are 1.41 and 1.37 Å, respectively, and $\alpha_{\text{alloy}}$ and $\alpha_{\text{Pd}}$ are the lattice parameters of PdSn alloys and Pd. The atomic ratios of Pd to Sn determined by ICP analysis (Table 1) are similar to the nominal ones, implying that most of the metal ions in the reactants are reduced to the metals.

The morphology and microstructure of the 3Pd1Sn/BN-G catalyst were investigated by TEM. As is shown in Figure 2a, most of the alloy particles homogenously distribute on the supporting materials except for some degree of aggregation. According to the statistical size distribution histograms in the inset of Figure 2a, the average particle size is about 5.61 nm. In contrast, the metal particles in 3Pd1Sn/G are heterogeneously decorated on the graphene with much more agglomerates, as displayed in Figure S1a,b (the Supporting Information), and the alloy particles have larger sizes, around 9.94 nm. This means that with the heteroatom doping of B and N into the graphene architecture, the dispersion of metal on the graphene support can be improved and the combination of metal nanoparticles with graphene may also be enhanced [33]. In addition, as is seen from Figure S1c–h, the average particle size in 1Pd1Sn/BN-G, 2Pd1Sn/BN-G and 4Pd1Sn/BN-G is 6.8 nm, 5.7 nm and 5.65 nm, respectively. The results are close to the XRD data. The HRTEM images in Figure 2b reveal that the lattice fringe with a crystal plane distance of 0.23 nm is attributed to the d-spacing of the PdSn (111) plane [34]. Further inspection by elemental mapping in Figure 2c–h indicates that the catalyst contains C, N, B, Pd and Sn as the main components, and these elements are evenly dispersed throughout the selected region. This shows that the catalytic PdSn alloy particles with smaller size are well dispersed and effectively anchored onto the supporting materials. The EDS results from TEM are summarized in Table S1 (the Supporting Information) and it is revealed that the doping amount of B and N in graphene is about 6.16% and 1.83% (wt%).

![Figure 1](image_url)  
Figure 1. XRD patterns of xPdySn/BN-G, Pd/BN-G and Pd/G catalysts.
of the Pd nanoparticles, regarding the number of electrochemically active sites per unit mass of catalyst \[20,37\]. As depicted in Figure 3b, the ECSA values follow the sequence: 3Pd1Sn/BN-G (136.5 m² g⁻¹) > 4Pd1Sn/BN-G (99.1 m² g⁻¹) > 2Pd1Sn/BN-G (70.3 m² g⁻¹) > 1Pd1Sn/BN-G (50.9 m² g⁻¹) > Pd/BN-G (21.1 m² g⁻¹) > 3Pd1Sn/G (15.2 m² g⁻¹) > Pd/G (14.2 m² g⁻¹). 3Pd1Sn/BN-G catalyst exhibits the largest ECSA value, which is most likely due to the good dispersion of metal nanoparticles immobilized on supporting materials.

The electro-catalytic performances towards formic acid electro-oxidation for all the samples were tested by the CV at a scan rate of 50 mV s⁻¹ in 1 M HCOOH with 0.5 M H₂SO₄, and the results are illustrated in Figure 4. It is generally accepted that the electrooxidation of formic acid follows a dual-pathway mechanism \[8,38\]. One is a dehydrogenation path which directly produces CO₂ by reaction (2), and the other is a dehydration path which makes CO₂ by multi-step reactions (3)–(5).

(I) Dehydrogenation path

\[
Pd + HCOOH \rightarrow Pd + CO_2 + 2H^+ + 2e^- \quad (2)
\]
It is worth noting that the 3Pd1Sn/BN-G (64.41 mA cm\(^{-2}\)) catalysts mainly oxidize formic acid through the direct pathway, and only a small amount of formic acid is oxidized by the indirect pathway, which leads to CO\(_{\text{ads}}\) accumulated on the surface of catalysts [8,40,41]. Generally, the peak current density in the cathodic scan, the broad oxidation peak is related to the re-oxidation of HCOOH [18,39]. Obviously, the current densities for the direct oxidation of all the samples are much higher than those of the indirect one. This suggests that these Pd-based catalysts mainly oxidize formic acid through the direct pathway, and only a small amount of formic acid is oxidized by the indirect pathway, which leads to CO\(_{\text{ads}}\) accumulated on the surface of catalysts [8,40,41]. Generally, the peak current density in the forward scan is used to measure the electro-activity of the catalysts. As shown in Figure 4a, by comparing with Pd/BN-G, all the PdSn/BN-G samples display better electrocatalytic activity, and the specific activity of these samples follows the order: 3Pd1Sn/BN-G (86.23 mA cm\(^{-2}\)) > 4Pd1Sn/BN-G (73.65 mA cm\(^{-2}\)) > 2Pd1Sn/BN-G (64.41 mA cm\(^{-2}\)) > 1Pd1Sn/BN-G (58.76 mA cm\(^{-2}\)) > Pd/BN-G (54.14 mA cm\(^{-2}\)). This indicates that the addition of Sn into the catalysts may improve the electrocatalytic performance toward the electrochemical oxidation of HCOOH. Furthermore, as presented in Figure 4b, the electrocatalytic current of 3Pd1Sn/BN-G is about 1.9 times as large as that of 3Pd1Sn/G (46.18 mA cm\(^{-2}\)), while the electrocatalytic activity of Pd/BN-G is 1.3 times higher than that of Pd/G (42.20 mA cm\(^{-2}\)). Based on the above results, it is clear that the B, N dual-doping graphene can promote the activity of the catalysts. It is worth noting that the 3Pd1Sn/BN-G catalyst has the largest current density, that is, it shows the

(II) Dehydration path

\[
Pd + HCOOH \rightarrow Pd-CO + H_2O \quad (3)
\]

\[
Pd + H_2O \rightarrow Pd-OH + H^+ + e^- \quad (4)
\]

\[
Pd-CO + Pd-OH \rightarrow Pd + CO_2 + H^+ + e^- \quad (5)
\]
best electrocatalytic performance on the electrochemical oxidation of HCOOH, resulting from the synergistic effect of Sn addition and B, N dual-doping graphene.

The stability of the catalysts is an important factor to evaluate the application of the fuel cells. Chronoamperometry tests were used to estimate the stability of all the samples at 0.4 V for 1 h in a solution of 1 M HCOOH + 0.5 M H2SO4. As is shown in Figure 5, the current densities of all the catalysts rapidly decrease at the initial stage, and then they gradually decay and reach a pseudo-steady state. This phenomenon is quite similar to those of other Pd-based catalysts [38,42], suggesting the same poisoning mechanism of the intermediate species accumulated on the catalysts toward the electrochemical oxidation of HCOOH. The pseudo-steady current density of 3Pd1Sn/BN-G reaches 12.00 mA cm−2, which is much larger than the counterpart catalysts 4Pd1Sn/BN-G (8.87 mA cm−2), 2Pd1Sn/BN-G (7.57 mA cm−2), 1Pd1Sn/BN-G (6.63 mA cm−2), Pd/BN-G (4.87 mA cm−2), 3Pd1Sn/G (4.01 mA cm−2) and Pd/G (2.49 mA cm−2). The electrocatalytic activity of 3Pd1Sn/BN-G at different time intervals (0 s, 500 s, 3600 s) during the stability test is illustrated in Figure S2; it can be seen that within and even after the stability test, the electrocatalytic activity is almost the same as that before the stability test. Figure S3 shows the TEM images of 3Pd1Sn/BN-G before and after the chronoamperometric test; it can be found that there is no significant change in the structural integrity of the 3Pd1Sn/BN-G catalyst and most of the alloy particles retain homogenously dispersed on the supporting materials except for some degree of aggregation after the stability test, which is responsible for its relatively high catalytic activity. By considering the cyclic voltammograms and stability results, it is obvious to find that 3Pd1Sn/BN-G has the highest electrocatalytic for formic acid oxidation, which results from an appropriate incorporation amount of Sn in the alloy phase and the addition of B and N into the graphene as the supporting material.

![Figure 5. Chronoamperometric curves of all the catalysts in the solution with 1 M HCOOH + 0.5 M H2SO4 solution at 0.4 V.](image)

2.3. XPS Analysis

In order to gain further insight into the promoting effect of 3Pd1Sn/BN-G catalyst toward formic acid oxidation, the XPS measurements were carried out to analyze the surface composition and the valent state of the elements in the catalysts. As displayed by the survey spectrum of XPS in Figure 6a, it is clear that C, B, N, Pd, Sn and O elements exist in 3Pd1Sn/BN-G catalyst. Percentages of the related fitting species are listed in Table 2. As depicted in Figure S4, N 1s spectrum can be divided into five peaks as B-N type, pyridinic N, pyrrolic N, graphitic N and oxidized N, and B 1 s pattern can be convoluted into three species, named as BC3(B-N), BC2O and BCO2 [43].

As is shown in Figure 6b,c, the splitting patterns of the Pd 3d band of 3Pd1Sn/G and 3Pd1Sn/B-N-G contains three pairs of doublets. The intensive doublet (335.6, 340.8 eV) is related to Pd0, the doublet
at 336.8 and 342.1 eV may be assigned to Pd(II) in PdO, while another doublet at 338.2 and 343.6 eV corresponds to the Pd(IV) in PdO₂ [20,44]. The contents of Pd⁰, Pd(II) and Pd(IV) in 3Pd1Sn/G are 57%, 25% and 18%, respectively (Table 2). In contrast, the proportion of metallic Pd in 3Pd1Sn/B-N-G is increased to 61%, whereas, the proportions of Pd(II) and Pd(IV) are 26% and 13%, respectively. Additionally, in our previous work, compared with Pd/G, Pd/BN-G also possesses the increased metallic Pd [43]. Many investigations illustrated that N doping benefits the nucleation of metal particles [45,46] and the B atom with low electronegativity increases the electron density of Pd [33]. This indicates that B, N co-doping into the framework of graphene can combine the advantages of B and N to tune the electronic structure of graphene, thus favoring the formation and good dispersion of metallic nanoparticles.

![Figure 6.](image-url)

Figure 6. (a) XPS spectra of 3Pd1Sn/BN-G, Pd 3d region in 3Pd1Sn/G (b) and 3Pd1Sn/BN-G (c), (d) Sn 3d region in 3Pd1Sn/BN-G.

Sn 3d signal can be deconvoluted into two symmetrical peaks, as illustrated in Figure 6d. The two peaks at 485.1 and 493.5 eV are ascribed to metallic Sn, and the other peaks at 486.9 and 495.3 eV belong to oxidized Sn species, mainly in the form of SnO₂ [11]. The proportions of two components are 5% for Sn⁰ and 95% for Sn⁴⁺. So it is reasonable to believe that the Sn element in the surface layer of the 3Pd1Sn/BN-G catalyst mainly exists in the form of SnO₂. SnO₂ can provide OH species that aid the removal of CO-like intermediate poisonous species [47]. With the incorporation of Sn to Pd, the oxophilic character of Sn atoms are likely to be present at the surface of Pd metals to generate oxygenated species, which can help re-oxidize the intermediates, such as CO₂ads, thus preventing the accumulation of poisoning-species and leaving more active Pd sites available for the electrochemical oxidation of HCOOH. This is responsible for the improvement of the catalytic activity and stability of the PdSn catalysts. According to the XRD results, the alloyed Pd-Sn nanomaterials are formed in the xPdySn/BN-G catalysts, while in the XPS analysis Sn in the surface layer of these catalysts mainly exists in the form of SnO₂. Combined with XRD and XPS data, we conclude that xPdySn/BN-G catalysts are homogeneous alloys with Pd and Sn, while the Sn atoms on the surface with most of the surface Sn oxidized into SnO₂. Considering that Sn itself has no catalytic activity toward formic
acid oxidation [15], it not only acts as a co-catalyst, but also a sacrificial component in the alloy, so a moderate amount of Sn is a key factor affecting the catalytic performance of Pd. According to the above results, it is found that the optimal ratio of Pd to Sn is 3:1, which is consistent with other functionalized carbon-supported PdSn catalysts [31,48].

| Samples       | B.E. of Pd3d_{5/2}/eV | B.E. of Pd3d_{3/2}/eV | Species | at% | B.E. of Sn3d_{5/2}/eV | B.E. of Sn3d_{3/2}/eV | Species | at% |
|---------------|------------------------|------------------------|---------|-----|------------------------|------------------------|---------|-----|
| 3Pd1Sn/G      | 335.71                 | 340.96                 | Pd0     | 57  | 485.06                 | 493.46                 | Sn0     | 10  |
|               | 337.61                 | 342.86                 | Pd(II)  | 25  | 486.86                 | 495.31                 | Sn(II)  | 90  |
|               | 338.46                 | 343.96                 | Pd(IV)  | 18  | -                      | -                      | -       | -   |
| 3Pd1Sn/BN-G   | 335.66                 | 340.91                 | Pd0     | 61  | 485.21                 | 493.66                 | Sn0     | 5   |
|               | 336.81                 | 342.16                 | Pd(II)  | 26  | 486.91                 | 495.36                 | Sn(II)  | 95  |
|               | 338.26                 | 343.61                 | Pd(IV)  | 13  | -                      | -                      | -       | -   |

3. Materials and Methods

3.1. Synthesis of BN-G Supporting Materials

BN-G was produced by a two-step hydrothermal method as described in our previous work [43]. Briefly, graphene oxide (GO) was firstly prepared by the Hummers’ liquid phase oxidation method [49], using graphite powder (<20 µm, Sigma-Aldrich, Shanghai, China) as a raw material, and B-G was synthesized using boric acid (analytical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) as the B source. An amount of 200 mg GO was ultrasonically dispersed in 20 mL distilled water, and boric acid (4 wt%) (analytical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) was added. The as-obtained suspension was put into a 100 mL Teflon-lined stainless steel autoclave and maintained at 200 °C for 5 h, and then the intermediate product was centrifuged, washed and dried in a vacuum oven at 80 °C overnight. The intermediate product was placed in a tube furnace and heated at 400 °C for 4 h in Ar atmosphere, and then B-G sample was obtained. Then, 200 mg B-G and 50 mL of 25 wt% aqueous ammonia (analytical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were thoroughly mixed under ultrasonic vibration. The resulting slurry was transferred to an autoclave as the same condition as B-G, and then the product BN-G was prepared.

3.2. Synthesis of PdSn/BN-G Binary Catalysts

A series of xPdySn/BN-G binary alloyed catalysts were synthesized, with the x/y ratios varying from 1:1 to 4:1 and the total-metal loading of 20 wt% in each sample. A typical synthesis of 3Pd1Sn/BN-G catalyst was as follows. First, 80 mg BN-G was uniformly dispersed in 30 mL distilled water with ultrasonic stirring. Subsequently, 2.741 mL 0.05 M PdCl₂ (analytical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and 10.31 g SnCl₂·2H₂O (analytical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were mixed with the above slurry and stirred for 30 min. The resultant suspension solution was transferred to a three-neck bottle, and potassium borohydride solution (KBH₄, 316 mg in 120 mL water) (analytical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) was added drop by drop, and this reaction was conducted at 60 °C for 6 h. Finally, the product was filtered and dried overnight. Other samples including 1Pd1Sn/BN-G, 2Pd1Sn/BN-G and 4Pd1Sn/BN-G were also synthesized by the same method. For comparison, 3Pd1Sn/G and Pd/BN-G were prepared by a similar process.

3.3. Materials Characterization

The crystalline structures of synthesized samples were measured by powder X-ray diffraction (XRD) analyses (Bruker D8, Germany). The morphologies of materials were investigated by transmission electron microscopy (TEM, FEI F20, USA). An Escalab 250Xi X-ray photoelectron spectrometer (XPS, USA) operating at 500 W and 15 kV with Mg Kα radiation was used to record XPS spectra,
where binding energies were referred to the adventitious C 1s peak at 284.6 eV. The XPS spectra were analyzed using XPS PEAK 4.1 software. Metal contents of all the samples were obtained by inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 725, USA).

3.4. Electrocatalytic Measurements

The electrocatalytic properties of the catalysts were conducted on a CHI760d electrochemical workstation (Shanghai, China) using a three electrode system, with the catalysts’ modified glass carbon electrodes (4 mm in diameter) as the working electrode, a Pt foil as the counter electrode and the saturated calomel electrode (SCE) as the reference electrode. All the electrochemical tests were carried out in a N₂-saturated electrolyte at 25 °C. The working electrode was obtained by the following procedure. First, 5 mg catalysts, 30 µL 5 wt% Nafion solution and 1.1 mL ethanol (analytical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were mixed together with ultrasonic stirring, and then 5 µL as-obtained slurry was spread onto the pre-polished glass carbon disk, where the loading amount of the catalysts was 0.175 mg cm⁻².

4. Conclusions

PdSn binary alloyed catalysts have been successfully prepared on B, N co-doping graphene substrate by a chemical reduction procedure. The heteroatom doping of B and N into the graphene substrate modify the electronic structure of graphene, thus improving the deposition of PdSn alloys and enhancing the metal–support interaction. The doping of Sn in Pd may promote the removal of the accumulated CO-like residues, thus exposing more free active Pd sites for formic acid electro-oxidation. 3Pd1Sn/BN-G with an optimal proportion of Sn shows more active and stable electro-catalytic performance, benefiting from its small particle size and good dispersion. The above promising results may shed new light on the design of active Pd-based catalysts in the direct formic acid fuel cells.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/7/751/s1, Figure S1: (a) TEM image of 3Pd1Sn/G and (b) its corresponding particle size distribution; (c) TEM image of 1Pd1Sn/BN-G and (d) its corresponding particle size distribution; (e) TEM image of 2Pd1Sn/BN-G and (f) its corresponding particle size distribution; (g) TEM image of 4Pd1Sn/BN-G and (h) its corresponding particle size distribution. Figure S2: Cyclic voltammograms of 3Pd1Sn/BN-G in the solution with 1 M HCOOH + 0.5 M H₂SO₄ solution during the stability test at different time intervals (0, 500, 3600s), scan rate: 50 mV s⁻¹. Figure S3: TEM images of 3Pd1Sn/BN-G before (a) and after (b) the electrocatalytic stability test toward the electrochemical oxidation of HCOOH.

Author Contributions: Conceptualization, D.C. and Y.J.; software, Z.H. and Y.W.; resources, H.S. and K.W.; data curation, S.P.; writing—original draft preparation, D.C.; writing—review and editing, J.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of Zhejiang Province, grant number LTY20B03002; Zhejiang Provincial Department of Education of China, grant number Y201840358; Scientific research project of Taizhou University, grant number Z2020044.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Yu, X.; Pickup, P.G. Recent advances in direct formic acid fuel cells (DFAFC). J. Power Sources 2008, 182, 124–132. [CrossRef]
2. Meng, H.; Zeng, D.R.; Xie, F.Y. Recent development of Pd-based electrocatalysts for proton exchange membrane fuel cells. Catalysts 2015, 5, 1221–1274. [CrossRef]
3. Qiu, X.Y.; Zhang, H.Y.; Dai, Y.X.; Zhang, F.Q.; Wu, PS.; Wu, P.; Tang, Y.W. Sacrificial template-based synthesis of unified hollow porous palladium nanospheres for formic acid electro-oxidation. Catalysts 2015, 5, 992–1002. [CrossRef]
4. Ding, J.; Liu, Z.; Liu, X.R.; Liu, B.; Liu, J.; Deng, Y.D.; Han, X.P.; Hu, W.B.; Zhong, C. Tunable periodically ordered mesoporosity in palladium membranes enables exceptional enhancement of intrinsic electrocatalytic activity for formic acid oxidation. Angew. Chem. Int. Ed. 2020, 132, 5130–5139. [CrossRef]
Catalysts 2020, 10, 751

5. Mondal, S.; Raj, C.R. Electrochemical dealloying-assisted surface-engineered Pd-based bifunctional electrocatalyst for formic acid oxidation and oxygen reduction. ACS Appl. Mater. Interfaces 2019, 11, 14110–14119. [CrossRef]

6. Cai, B.F.; Ma, Y.R.; Wang, S.Z.; Yi, N.; Zheng, Y.; Qiu, X.Y.; Tang, Y.W.; Bao, J.C. Facile synthesis of PdFe alloy tetrahedrons for boosting electrocatalytic properties towards formic acid oxidation. Nanoscale 2019, 11, 18015–18020. [CrossRef]

7. Zhang, L.Y.; Gong, Y.Y.; Wu, D.B.; Wu, G.L.; Xu, B.H.; Bi, L.; Yuan, W.Y.; Cui, Z.M. Twisted palladium-copper nanochains toward efficient electrocatalytic oxidation of formic acid. J. Colloid Interface Sci. 2019, 537, 366–374. [CrossRef]

8. Zhang, Y.; Huang, B.L.; Shao, Q.; Feng, Y.G.; Xiong, L.K.; Peng, Y.; Huang, X.Q. Defect engineering of palladium-tin nanowires enables efficient electrocatalysts for fuel cell reactions. Nano Lett. 2019, 19, 6894–6903. [CrossRef]

9. Xu, H.; Zhang, K.; Yan, B.; Wang, J.; Wang, C.Q.; Li, S.M.; Gu, Z.L.; Du, Y.K.; Yang, P. Ultra-uniform PdBi nanodots with high activity towards formic acid oxidation. J. Power Sources 2017, 356, 27–35. [CrossRef]

10. Tu, D.D.; Wu, B.; Wang, B.X.; Deng, C.; Gao, Y. A highly active carbon-supported PdSn catalyst for formic acid electrooxidation. Int. J. Hydrog. Energy 2019, 44, 20368–20378. [CrossRef]

11. Brouzgou, A.; Song, S.; Tsiakaras, P. Carbon-supported PdSn and Pd3Sn4 anodes for glucose electrooxidation in alkaline media. Appl. Catal. B Environ. 2014, 158–159, 209–216. [CrossRef]

12. Liu, Z.H.; Ge, J.J.; Ma, L.; Xiao, J.H.; Lu, T.H.; Xing, W. Highly active carbon-supported PdSn catalysts for formic acid electrooxidation. Fuel Cells 2009, 9, 114–120. [CrossRef]

13. Liu, Z.L.; Zhang, X.H. Carbon-supported PdSn nanoparticles as catalysts for formic acid oxidation. Electrochem. Commun. 2009, 11, 1667–1670. [CrossRef]

14. Asgardi, J.; Calderón, J.C.; Alcaide, F.; Quequera, A.; Calvillo, L.; Lázaro, M.J.; García, G.; Pastor, E. Carbon monoxide and ethanol oxidation on PtSn supported catalysts: Effect of the nature of the carbon support and Pt:Sn composition. Appl. Catal. B Environ. 2015, 168–169, 33–41. [CrossRef]

15. Juárez-Marmolejo, L.; Perea-Rodríguez, S.; Montes de Oca-Yemha, M.G.; Palomar-Pardavé, M.; Romero-Romó, M.; Ezeta-Mejía, A.; Morales-Gil, P.; Martínez-Huerta, M.V.; Lázaro, M.J. Carbon supported PdM (M=Fe, Co) electrocatalysts for formic acid oxidation. Influence of the Fe and Co precursors. Int. J. Hydrog. Energy 2019, 44, 1640–1649. [CrossRef]

16. Mazurkiewicz-Pawlicka, M.; Malolepszy, A.; Mikolajczuk-Zychora, A.; Mierzwa, B.; Borodziński, A.; Stobinski, L. A simple method for enhancing the catalytic activity of Pd deposited on carbon nanotubes used in direct formic acid fuel cells. Appl. Surf. Sci. 2019, 476, 806–814. [CrossRef]

17. Kankla, P.; Limtrakul, J.; Green, M.L.H.; Chanlek, N.; Luksirikul, P. Electrooxidation of formic acid enhanced by surfactant-free palladium nanocubes on surface modified graphene catalyst. Appl. Surf. Sci. 2019, 471, 176–184. [CrossRef]

18. Liu, M.M.; Zhang, R.Z.; Chen, W. Graphene-supported nanoelectrocatalysts for fuel cells: Synthesis, properties, and applications. Chem. Rev. 2014, 114, 5117–5160. [CrossRef]

19. Li, X.; Chen, J.Z.; Zuo, H.B.; Liu, X.T.; Shi, Z.Y. Electrochemical characterization and design principles of heteroatom-doped graphene catalysts for oxygen-reduction reaction. J. Phys. Chem. C 2017, 121, 14434–14442. [CrossRef]

20. Chai, G.L.; Qiu, K.P.; Qiao, M.; Titirici, M.M.; Shang, C.X.; Guo, Z.X. Active sites engineering leads to exceptional ORR and OER bifunctionality in Pd codoped graphene frameworks. Energy Environ. Sci. 2017, 10, 1186–1195. [CrossRef]

21. Zhang, X.; Zhang, X.; Zhu, J.X.; Tiwary, C.S.; Ma, Z.Y.; Huang, H.J.; Zhang, J.F.; Lu, Z.Y.; Huang, W.; Wu, Y.P. Palladium nanoparticles supported on nitrogen and sulfur dual-doped graphene as highly active electrocatalysts for formic acid and methanol oxidation. ACS Appl. Mater. Interf. 2016, 8, 10858–10865. [CrossRef] [PubMed]

22. Yang, H.L.; Li, S.W.; Feng, F.; Ou, S.Y.; Li, F.; Yang, M.; Qian, K.L.; Jin, J.; Ma, J.T. Palladium nanoparticles with surface enrichment of palladium oxide species immobilized on the aniline-functionalized graphene as an advanced electrocatalyst of ethanol oxidation. ACS Sustain. Chem. Eng. 2019, 7, 14621–14628. [CrossRef]
25. Chowdhury, S.R.; Maiyalagan, T. Enhanced electro-catalytic activity of nitrogen-doped reduced graphene oxide supported PdCu nanoparticles for formic acid electro-oxidation. *Int. J. Hydrog. Energy* 2019, 44, 14808–14819. [CrossRef]
26. Zhu, F.C.; Wang, M.; He, Y.W.; Ma, G.S.; Zhang, Z.H.; Wang, X.G. High activity of carbon nanotubes supported binary and ternary Pd-based catalysts for methanol, ethanol and formic acid electro-oxidation. *J. Power Sources* 2013, 242, 610–620. [CrossRef]
27. Fontes, E.H.; Ramos, C.E.D.; Nandenh, J.; Piasentin, R.M.; Neto, A.O.; Landers, R. Structural analysis of PdRh/C and PdSn/C and its use as electrocatalysts for ethanol oxidation in alkaline medium. *Int. J. Hydrog. Energy* 2019, 44, 937–951. [CrossRef]
28. Yang, Y.; Huang, H.J.; Shen, B.F.; Jin, L.; Jiang, Q.G.; Yang, L.; He, H.Y. Anchoring nanosized Pd on three-dimensional boron- and nitrogen-codoped graphene aerogels as a highly active multifunctional electrocatalyst for formic acid and methanol oxidation reactions. *Inorg. Chem. Front.* 2020, 7, 700–708. [CrossRef]
29. Geraldes, A.N.; Silva, D.F.; Silva, J.C.M.; Sá, O.A.; Spinacé, E.V.; Neto, A.O.; Santos, M.C. Palladium and palladium-tin supported on multi wall carbon nanotubes or carbon for alkaline direct ethanol fuel cell. *J. Power Sources* 2015, 275, 189–199. [CrossRef]
30. Wang, W.; Kang, Y.M.; Yang, Y.; Liu, Y.Q.; Chai, D.; Lei, Z.Q. PdSn alloy supported on phenanthroline-functionalized carbon as highly active electrocatalysts for glycerol oxidation. *Int. J. Hydrog. Energy* 2016, 41, 1272–1280. [CrossRef]
31. Suo, Y.G.; Zhuang, L.; Lu, J.T. First-principles considerations in design of Pd-alloy catalysts for oxygen reduction. *Angew. Chem. Int. Ed.* 2007, 46, 2862–2864. [CrossRef] [PubMed]
32. Sun, Y.R.; Du, C.Y.; Han, G.K.; Qu, Y.T.; Du, L.; Wang, Y.J.; Chen, G.Y.; Gao, Y.Z.; Yin, G.P. Boron, nitrogen co-doped graphene: A superior electrocatalyst support and enhancing mechanism for methanol electro-oxidation. *Electrochim. Acta* 2016, 212, 313–321. [CrossRef]
33. Zhu, F.C.; Wang, M.; He, Y.W.; Ma, G.S.; Zhang, Z.H.; Wang, X.G. A comparative study of elemental additives (Ni, Co and Ag) on electrocatalytic activity improvement of PdSn-based catalysts for ethanol and formic acid electro-oxidation. *Electrochim. Acta* 2014, 148, 291–301. [CrossRef]
34. Zhang, H.X.; Wang, C.; Wang, J.Y.; Zhai, J.J.; Cai, W.B. Carbon-supported Pd-Pt nanoalloy with low Pt content and superior catalysis for formic acid electro-oxidation. *J. Phys. Chem. C* 2010, 114, 6446–6451. [CrossRef]
35. Xu, H.; Yan, B.; Li, S.M.; Wang, J.; Wang, C.Q.; Guo, J.; Du, Y.K. One-pot fabrication of N-doped graphene supported dandelion-like PtRu nanocrystals as efficient and robust electrocatalysts towards formic acid oxidation. *J. Colloid Interface Sci.* 2018, 512, 96–104. [CrossRef]
36. Salomé, S.; Ferraria, A.M.; Rego, A.M.B.; Alcaide, F.; Savadogo, O.; Rego, R. Enhanced activity and durability of novel activated carbon-supported PdSn heat-treated cathode catalyst for polymer electrolyte fuel cells. *Electrochim. Acta* 2016, 192, 268–282. [CrossRef]
37. Zhang, W.Y.; Yao, Q.S.; Wu, X.D.; Fu, Y.S.; Deng, K.M.; Wang, X. Intimately coupled hybrid of graphitic carbon nitride nanoflakelets with reduced graphene oxide for supporting Pd nanoparticles: A stable nanocatalyst with high catalytic activity towards formic acid and methanol electro-oxidation. *Electrochim. Acta* 2016, 200, 131–141. [CrossRef]
38. Liu, X.; Bu, Y.F.; Cheng, T.; Gao, W.; Jiang, Q. Flower-like carbon supported Pd-Ni bimetal nanoparticles catalyst for formic acid electrooxidation. *Electrochim. Acta* 2019, 324, 134816. [CrossRef]
39. Zhang, L.Y.; Zhao, Z.L.; Li, C.M. Formic acid-reduced ultrasmall Pd nanocrystals on graphene to provide superior electrocatalytic activity and stability toward formic acid oxidation. *Nano Energy* 2015, 11, 71–77. [CrossRef]
40. Zhang, H.X.; Wang, S.H.; Jiang, K.; André, T.; Cai, W.B. In situ spectroscopic investigation of CO accumulation and poisoning on Pd black surfaces in concentrated HCOOH. *J. Power Sources* 2012, 199, 165–169. [CrossRef]
41. Hu, S.Z.; Munoz, F.; Noborikawa, J.; Haan, J.; Scudiero, L.; Ha, S. Carbon supported Pd-based bimetallic and trimetallic catalyst for formic acid electrochemical oxidation. *Appl. Catal. B Environ.* 2016, 180, 758–765. [CrossRef]
42. Zhang, J.W.; Chen, M.S.; Li, H.Q.; Li, Y.J.; Cao, Z.M.; Fang, M.L.; Kuang, Q.; Zheng, J.; Xie, Z.X. Stable palladium hydride as a superior anode electrocatalyst for direct formic acid fuel cells. *Nano Energy* 2018, 44, 127–134. [CrossRef]
43. Jin, Y.X.; Han, D.M.; Jia, W.P.; Huang, G.B.; Li, F.; Chen, X.Y.; Li, R.R.; Zheng, M.M.; Gao, W.Y. B-N codoped graphene as a novel support for Pd catalyst with enhanced catalysis for ethanol electrooxidation in alkaline medium. J. Electrochem. Soc. 2017, 164, F638–F644. [CrossRef]

44. Wu, Y.R.; Wang, C.M.; Zou, L.L.; Huang, Q.H.; Yang, H. Incorporation of cobalt into Pd$_2$Sn intermetallic nanoparticles as durable oxygen reduction electrocatalyst. J. Electroanal. Chem. 2017, 789, 167–173. [CrossRef]

45. Perini, L.; Durante, C.; Favaro, M.; Perazzolo, V.; Agnoli, S.; Schneider, O.; Granozzi, G.; Gennaro, A. Metal-support interaction in platinum and palladium nanoparticles loaded on nitrogen-doped mesoporous carbon for oxygen reduction reaction. ACS Appl. Mater. Interfaces 2015, 7, 1170–1179. [CrossRef] [PubMed]

46. Jiang, H.; Liu, L.; Zhao, K.; Liu, Z.; Zhang, X.S.; Hu, S.Z. Effect of pyridinic- and pyrrolic-nitrogen on electrochemical performance of Pd for formic acid electrooxidation. Electrochim. Acta 2020, 337, 135758. [CrossRef]

47. Zhu, M.Y.; Sun, G.Q.; Xin, Q. Effect of alloying degree in PtSn catalyst on the catalytic behavior for ethanol electro-oxidation. Electrochim. Acta 2009, 54, 1511–1518. [CrossRef]

48. Feng, Y.; Bin, D.; Zhang, K.; Ren, F.F.; Wang, J.; Du, Y.K. One-step synthesis of nitrogen-doped graphene supported PdSn bimetallic catalysts for ethanol oxidation in alkaline media. RSC Adv. 2016, 6, 19314–19321. [CrossRef]

49. Hummers, W.S.; Offeman, R.E. Preparation of graphitic oxide. J. Am. Chem. Soc. 1958, 80, 1339. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).