1. Introduction

The development of fuel cells is one of the important ways to achieve carbon neutrality [1–5]. A direct formic acid fuel cell (DFAFC), with the following advantages, a high theoretical energy density, a low operating temperature and easy management, are attracting a lot of interest [6–10].

Palladium (Pd) has a good catalytic performance for DFAFC [11–14]. Various Pd-based bimetallic alloy catalysts (e.g., PdCu [15], PdMn [16], PdW [17], PdCO [18], PdIr [19], PdSn [20], PdNi [21]) have been prepared to improve the inert FAOR because these alloys exhibited the ability to get rid of OH species. Among them, the PdCo-alloys have attracted great attention. Zhang et al. fabricated a PdCo Nds-RGO catalyst exhibiting the excellent peak current density toward the FAOR [22]. Li et al. prepared a PdCo0.70/C catalyst showing an enhanced mass activity toward the FAOR [23]. Hence, PdCo-based catalysts have the great potential in a DFAFC. However, the instability of the catalysts caused by the dissolution of metal, the Ostwald ripening, and the corrosion of the carbon carrier have not been solved [22,24,25]. Therefore, how to improve the electrochemical catalytic activity and stability of the PdCo-based catalysts are the current focus of researchers’ efforts.

Doping [17,26–28] is considered to be the most effective method to improve the stability and activity of Pd-alloy catalysts because the doped metal can change the electronic state around the Pd atom, affecting the adsorption of the toxic intermediates and weakening the dissolution of Pd. Tang et al. doped Co into Pd to form an alloy, which significantly improved the activity and stability of the catalyst [29]. In addition, Pd can also form alloy catalysts with other metals (Cu, Ni, Ru) by doping, which is characterized by the improved intrinsic activity and stability toward the FAOR [30–32].

It is well known that increasing the loading rate of metal nanoparticles on a support is an effective method to improve the activity of the catalysts. With these advantages, a good electrical conductivity, thermal stability, electrochemical stability, a negligible vapor
pressure, non-toxicity and biodegradability, DES [33–35] was used as a green solvent to prepare catalysts. In our previous study, a series of Pt- and Pd-based high-performance catalysts were prepared using DES as the reaction solvent [36–40]. Fan et al. prepared the alloy catalysts (PdSn [20], PtCo [34], PtCu [33], PtV [41], PtLa [42]) by a chemical reduction or electrochemistry method in DES, that plays an important role in controlling the shape of these nanocrystallines. These catalysts showed an excellent mass activity in the fuel cell. Zhuo et al. electrochemically synthesized the AuPt nanopowers in DES and applied them for the organic electrooxidation [43]. Wei et al., prepared concave cubic PtSm alloy nanocrystals [44], concave-disdyakis triacontahedral Pd nanocrystals [45] and cubic Pt$_{93}$Ir$_7$ [46] with high-index facets that exhibit a higher electrocatalytic activity and stability. Hammons et al. prepared Pd nanoparticles electrodeposited from DES and revealed the interaction between the particles and the solvent, showing that this special solvent can stabilize these electrodeposited Pd nanoparticles [47]. Therefore, the high-performance PdCo catalysts are expected to be prepared in DES.

MWCNTs, with a unique morphology and excellent properties, have attracted much more interest in a variety of fields [48–51]. Therefore, in DES, we doped the Co element into Pd to form the PdCo alloy structure and then loaded it on MWCNTs (Pd$_3$Co$_1$/CNTs) (Scheme 1). The electrochemical tests showed that this catalyst shows an excellent electrocatalytic performance. This study provides a new strategy for the development of a high-performance PdCo alloy FAOR catalyst.

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MWCNTs (OD: 8 nm, Length: 10–30 mm, Purity 1/4 95 wt%) were purchased from the Xianfeng Nanomaterials Technology Co., Ltd., Nanjing, China. Nafion solution (5 wt%) was purchased from Sigma-Aldrich, Saint Louis, MO, USA. Choline chloride [HOC$_2$H$_4$N(CH$_2$)$_2$Cl], Urea [CO(NH$_2$)$_2$], C$_2$H$_5$OH, PdCl$_2$, Co(NO$_3$)$_2$, NaBH$_4$, H$_2$SO$_4$, HCOOH and HNO$_3$ were purchased from Shanghai Chemical Reagent Co., Ltd., Shanghai, China. All of the reagents used were analytically pure.
2.2. Materials Synthesis

Concretely, DES (mole ratio of the urea/choline chloride is 2) was stirred at 80 °C until a homogeneous, colourless liquid developed and was sealed at 60 °C, for later use [37]. All solutions are configured with DES instead of water. Then, the untreated 200 mg MWCNTs were functionalized by an acidification treatment (V\(_{\text{H}_{2}\text{SO}_{4}}\)/V\(_{\text{HNO}_{3}}\) = 3/1) (referred to CNTs-AO) and sealed at room temperature, for later use. A 10 mg CNTs-AO, 0.33 mL PdCl\(_2\) /DESs solution (10 mg/mL), and 0.11 mL Co(NO\(_3\))\(_2\) /DESs solution (10 mg/mL) were added in 20 mL DES with an appropriate proportion (mole ratio of Pd/Co is 3). Then, 60 mg NaBH\(_4\) was added and stirred at 60 °C for three hours at room temperature. The product was washed three times with distilled water and anhydrous ethanol, repeatedly. The material was centrifuged in a centrifugal machine, and dried in a vacuum drying oven at 60 °C all night (referred to Pd\(_3\)Co\(_1\)/CNTs). In the control experiment, the Pd\(_1\)Co\(_1\)/CNTs and Pd\(_1\)Co\(_3\)/CNTs catalysts were prepared following the same steps, as above, except for the change in the amount of Co(NO\(_3\))\(_2\). Pd/CNTs were prepared following the same steps, as above, except for the addition of Co(NO\(_3\))\(_2\).

2.3. Materials Characterization

The XRD patterns were obtained using an X-ray diffractometer (Rigaku D/MAX 2500 v/pc, Japan) with a Cu Kα radiation source (l = 1.5406 Å). The XPS measurements were carried out using a Physical Electronics PHIQuantum 2000 system with an Al Kα radiation source, and all of the XPS spectra were calibrated with the C1s line at 284.5 eV. The surface morphologies and the microstructures of the prepared catalysts were analyzed using (SEM, LEO-1530) and (HRTEM, JEOL JEM-2100) with an accelerating voltage of 200 kV. An Agilent 720 inductively coupled plasma-optical emission spectrophotometer (ICP-OES, USA) was used to determine the Pd contents of Pd/C (20%), Pd/CNTs (17.5%), Pd\(_1\)Co\(_1\)/CNTs (18.3%), Pd\(_1\)Co\(_3\)/CNTs (18.6%) and Pd\(_3\)Co\(_1\)/CNTs (19.1%) (Table S1: Supporting Information).

2.4. Electrochemical Measurements

According to our previously published protocol, the catalyst-modified glassy carbon electrodes (GC, 5 mm in diameter) were prepared [37]. Using a traditional three-electrode system in an electrochemical workstation (CHI 830b05049, Shanghai Chenhua Instrument Co., Ltd., Shanghai, China) at 25 °C, all of the electrochemical measurements were performed. The counter electrode and the reference electrode were a platinum foil and a saturated calomel electrode (SCE), respectively. The working electrode was modified as follows: 0.05, 0.3, and 1.0 µm alumina powder was used to polish the GC. With the existence of redistilled water (950 µL) and a Nafion solution (0.5 wt%, 50 µL), the catalysts (2 mg) were dispersed in this solution above (1000 µL). A suspension (10 µL) was trickled over the GC electrode at room temperature. The Pd loading of Pd/C, Pd/CNTs, Pd\(_1\)Co\(_1\)/CNTs, Pd\(_1\)Co\(_3\)/CNTs and Pd\(_3\)Co\(_1\)/CNTs were 23.8, 24.2, 24.3, 24.5, and 24.9 µg cm\(^{-2}\).

In a N\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\) solution, we studied the electrochemical behaviors of all catalysts. The corresponding formic acid electrocatalytic properties of all catalysts were studied in 1.0 M HCOOH + 0.5 M H\(_2\)SO\(_4\) solution. Furthermore, we used CO stripping experiments to investigate the CO toxicity of all catalysts, in terms of the following steps. Firstly, to remove the dissolved O\(_2\) in the solution, we degassed the electrolyte by purging with a pure N\(_2\) airflow for 15 min. Secondly, to allow the saturated adsorption of CO, we degassed the pure CO airflow bubbling for 15 min at a scan rate of 50 mV s\(^{-1}\) while maintaining the potential sweep in the range of −0.2 and 0.0 V. Then, to remove the dissolved CO and to avoid the disturbance of O\(_2\) in the air, we degassed the electrolyte by purging with pure N\(_2\) for 30 min. Finally, to oxidize the preadsorbed CO on the surface of the catalysts, we executed the CO stripping voltammograms in the range of −0.2 V and 1.0 V. All of the currents in the electrochemical experiments were expressed by the normalized current per milligram of the Pd metal loading on the working electrode. The electrolyte was purged with pure N\(_2\) for 15 min before each measurement, and impeded the disturbance of O\(_2\) in the air with a flux of N\(_2\) flow over the electrolyte.
3. Results and Discussion

Figure 1 shows the XRD patterns of the Pd$_3$Co$_1$/CNT and Pd/CNT catalysts. The $2\theta$ (26.2$^\circ$) is attributed to C(002) of MWCNTs-AO [37]. The Pd(111), (200), (220) and (311) diffraction peaks of Pd/CNTs at 39.0$^\circ$, 44.3$^\circ$, 66.1$^\circ$ and 79.8$^\circ$, while all corresponding Pd peaks of Pd$_3$Co$_1$/CNTs shifted to higher $2\theta$ values of 39.2$^\circ$, 44.6$^\circ$, 66.3$^\circ$ and 80.1$^\circ$, suggesting the formation of the Pd$_3$Co$_1$ alloy [18,52,53]. Meanwhile, (Figure S1: Supporting Information) shows the XRD patterns of the Pd$_1$Co$_1$/CNT and Pd$_1$Co$_3$/CNT catalysts. The Pd(111), (200), (220) and (311) diffraction peaks still appear, which indirectly indicates that Co doped into the interior of Pd to form an alloy.

![Figure 1. XRD patterns of the Pd/CNT and Pd$_3$Co$_1$/CNT catalysts.](image)

Figure 2 shows the TEM (a), HRTEM (b–c) images and the HAADF-STEM element mapping (d–g) results (Pd, Co) and elements of Pd$_3$Co$_1$/CNTs. Figure 2a,b shows Pd$_3$Co$_1$ nanoclusters successfully loaded on the surface of MWCNTs. As shown in Figure 2c, the spacings of Pd(111) crystal planes in Pd$_3$Co$_1$/CNTs to be 0.206 nm, which is different from the Pd(111)(0.222 nm) of Pd/CNTs (Figure S2: Supporting Information). This may be attributed to the doping of Co atoms with a small radius and compressed in the lattice constant of Pd [22]. Figure 2d–g shows that Pd and Co atoms are evenly distributed in the nanoclusters, which also indirectly proves the formation of alloys. In addition, in order to further determine the formation of the alloy structure, the TEM and HRTEM images and the HAADF-STEM element mapping of Pd$_3$Co$_1$/CNTs were also re-performed in another region, and the results showed that Pd and Co formed an alloy structure (Figure S3: Supporting Information). Figures S4 and S5: Supporting Information show the EDX line-profiles and the spot scanning of the Pd$_3$Co$_1$ nanoparticle (where Pd is in red and Co in blue), which further proved the existence of the alloy and the molar ratio of Pd and Co is (3.07/1). The average nanoparticles’ sizes of Pd$_3$Co$_1$/CNTs (Figure 2a), Pd$_3$Co$_1$/C (Figure S6: Supporting Information), Pd$_3$Co$_1$/CNTs (Figure S7: Supporting Information), Pd$_1$Co$_1$/CNTs (Figure S7: Supporting Information) and Pd/CNTs (Figure S8: Supporting Information) are 4.3, 4.5, 4.9, 5.3 and 7.5 nm (200 particles). Furthermore, in order to explore the carrier’s influence on the catalysts, Figure S9: Supporting Information shows the TEM and HRTEM images of Pd$_3$Co$_1$/C. It can be seen that there is no significant change in the size of the nanoparticles when carbon black is used as the carrier.

Figure 3a shows the XPS survey spectra of Pd$_3$Co$_1$/CNTs. The signals corresponding to C 1s (284.6 eV), O 1s (531.2 eV), Pd 3d (338.2 eV), and Co 2p (783.2 eV) are observed. The two splitting peaks of C 1s (C-C, C-O) are attributed to MWCNTs-AO (Figure 3b) [38]. Figure 3c shows the peaks of Co (0) and Co (+2), which are the evidence of Co. Figure 3d and Table S2: Supporting Information show a slight positive change (0.3 eV) in the Pd (0) peak position from Pd/CNTs to Pd$_3$Co$_1$/CNTs, indicating the strong charge transfer
interaction between the Co and Pd atoms to form the PdCo bond [54,55], which was the important reason for improving the stability and anti-CO toxicity. Furthermore, the presence of Co (+2) and Pd (+2) is attributed to the oxidation of oxygen in the air [36].

Figure 2. TEM and HRTEM images (the corresponding particle size distribution); HAADF-STEM elements.

Figure 3. (a) XPS survey spectra, (b) C (1s) spectrum, (c) Co (2p) spectrum of Pd₃Co₁/CNTs, (d) Pd (3d) spectrum of Pd₃Co₁/CNTs and Pd/CNTs.

Figure 4a shows the cyclic voltammograms (CV) of the Pd₃Co₁/CNTs, Pd/CNTs and Pd/C catalysts in the 0.5 M H₂SO₄ solution. The associated ECSA was calculated by integrating the area associated with the hydrogen adsorption region [56], according to:

\[
\text{ECSA} = \frac{Q_H}{210 \, (\mu\text{C cm}^{-2})} / W_{\text{Pd}}
\]

wherein \(Q_H\) is the integrated charge within the hydrogen adsorption area in the CV curves after subtracting the charge from the double-layer region. It should be noted that the data were obtained from the CV curves with 210 (µC/cm²) as the conversion factor. \(W_{\text{Pd}}\) is the mass of Pd. Therefore, the ECSA of Pd₃Co₁/CNTs was calculated to be 41.2 m² g⁻¹, which is higher than those of Pd/CNTs (33.4 m² g⁻¹) and Pd/C (31.1 m² g⁻¹). The larger
ECSA of Pd₃Co₁/CNTs is attributed to the smaller Pd₃Co₁ particles. In order to explore the effect of the atomic ratio on the catalyst performance, we tested the catalytic performance of different Pd/Co catalysts for the FAOR (Figure 4b). In the forward scan, the anodic peak was assigned to the formic acid oxidation, and another anodic peak in the reverse scan was associated with the oxidation of the intermediate carbonaceous species formed during the forward scan [57,58]. For Pd₃Co₁/CNTs, the peak current density in the forward scan is 2410.1 mA mg⁻¹, higher than Pd₁Co₁/CNTs (1752.3 mA mg⁻¹), Pd₃Co₃/CNTs (1255.1 mA mg⁻¹), Pd/CNTs (1262.8 mA mg⁻¹) and Pd/C (819.2 mA mg⁻¹) (Figure 4b,c). In order to investigate whether the high activity is achieved by the alloying effect or the supporting effect, we tested the catalytic activity of the carbon-supported Pd₃Co₁ alloy catalyst (Pd₃Co₁/C) towards the FAOR (Figure S10: Supporting Information). The peak current density of Pd₃Co₁/C is 1919.2 mA mg⁻¹, higher than Pd₁Co₁/CNTs (1752.3 mA mg⁻¹), Pd₃Co₃/CNTs (1255.1 mA mg⁻¹), Pd/CNTs (1262.8 mA mg⁻¹) and Pd/C (819.2 mA mg⁻¹), but lower than Pd₃Co₁/CNTs (2410.1 mA mg⁻¹), which revealed that the high activity was achieved through the synergistic effect of the alloy effect and the support effect. The alloy effect is beneficial to enhance the toxicity resistance of the catalyst and the addition of MWCNTs is beneficial to improve the electron transport. To evaluate the long-term performance of all catalysts, the chronoamperometric (CA) measurements were performed at +0.3 V for 7200 s. As shown in Figure 4d, in the initial period, all curves showed a fast current decay that indicated the poisoning of the electrocatalysts, due to the formation of intermediate species [26]. Then, after 7200 s, the Pd₃Co₁/CNT catalyst, still maintaining higher current density (95.1 mA mg⁻¹), was almost 2.6 and 29.7 times greater than Pd/CNTs (36.3 mA mg⁻¹) and Pd/C (3.2 mA mg⁻¹), which illustrated that Pd₃Co₁/CNTs exhibit a better stability.

![Figure 4](image_url)

**Figure 4.** (a,c) Cyclic voltammograms and (d) current-time curves of Pd₃Co₁/CNTs, Pd/CNTs and Pd/C; (b) cyclic voltammograms curves of Pd₃Co₁/CNTs, Pd₁Co₁/CNTs and Pd₁Co₃/CNTs in 0.5 M H₂SO₄/1.0 M HCOOH + 0.5 M H₂SO₄ solution.

We used CO stripping experiments to investigate the CO toxicity of all catalysts. Figure 5 shows the CO stripping voltammograms and the subsequent CV curves. The hydrogen adsorption/desorption were completely suppressed in the low potential region due to the CO_ads species on the active sites of the catalysts [59]. Following the removal of
CO_{ads}, the peaks associated with hydrogen adsorption/desorption reappeared. The onset potential of the adsorbed CO oxidation of Pd_{3}Co_{1}/CNTs was negatively shifted to 0.36 V, and the corresponding potentials were 0.55 and 0.67 V for Pd/CNTs and Pd/C, indicating that Pd_{3}Co_{1}/CNTs have an excellent CO oxidation ability.

![Figure 5. CO stripping voltammograms of Pd/C, Pd/CNT and Pd_{3}Co_{1}/CNT catalysts in 0.5 M H_{2}SO_{4} solution.](image)

In conclusion, compared with Pd/C, Pd/CNTs, Pd_{3}Co_{1}/CNTs and Pd_{1}Co_{3}/CNTs, Pd_{3}Co_{1}/CNTs exhibited 1.38-, 1.92-, 1.91- and 2.94-fold enhancement in mass activity toward the FAOR, respectively. The onset potential of the adsorbed CO oxidation of Pd_{3}Co_{1}/CNTs was negatively shifted to 0.36 V and the corresponding potentials were 0.55, and 0.67 V for Pd/CNTs, and Pd/C. Furthermore, after 7200 s, the Pd_{3}Co_{1}/CNT catalyst still maintained a higher current density (95.1 mA mg_{Pd}^{-1}) that was 2.6-, and 29.7- times greater than Pd/CNTs (36.3 mA mg_{Pd}^{-1}) and Pd/C (3.2 mA mg_{Pd}^{-1}). The excellent catalytic performance and stability of Pd_{3}Co_{1}/CNTs can be attributed to the bi-functional mechanism and the obtained Pd_{3}Co_{1} alloy nanoclusters. In the bifunctional mechanism, Pd is responsible for the adsorption and oxidative dehydrogenation of formic acid and Co provides the adsorbed hydroxyl group (OH_{ads}) at a more negative potential, in comparison with Pd to oxidize the intermediate [22,60]. Moreover, the special Pd_{3}Co_{1} alloy nanoclusters can provide abundant catalytic active sites, reduce the charge-transfer impedance, improving the efficiency of the material transfer and further improve the catalytic activity and stability. Furthermore, the Pd_{3}Co_{1}/CNT catalyst presents the better FAOR mass activity, in comparison with the recent research works on Pd-based bimetallic catalysts [22,26,57,61–67] (Table S3: Supporting Information).

4. Conclusions

Herein, with the assistance of DES, the obtained Pd_{3}Co_{1}/CNT catalyst exhibited the excellent electrocatalytic performance towards the FAOR. The doping of Co atoms changed the electron configuration of Pd to form a new Pd-Co bond, thus affecting the adsorption of the toxic intermediates and weakening the dissolution of Pd, which were the important reasons for improving the stability and anti-CO toxicity. Furthermore, these doped Co atoms provided more co-catalytic active sites to obtain more OH^{-} from the H_{2}O molecule, which could further interact with the toxic intermediates generated on the Pd active sites to further improve performance. This research provides a new strategy to obtain the Pd-alloy high-performance catalysts for DFAFC.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12234182/s1, Figure S1. XRD patterns of Pd$_3$Co$_1$/CNT (a) and Pd$_2$Co$_3$/CNTs(b) catalysts; Figure S2. TEM and HRTEM images of the Pd/CNT catalyst; Figure S3. TEM and HRTEM images; HAADF-STEM elements mapping; the corresponding elements of Pd and Co of Pd$_3$Co$_1$/CNTs (another region); Figure S4. EDX line-profiles (a,b), spot scanning (c,d) of a Pd$_3$Co$_1$ nanoparticle (where Pd is in red and Co in blue) of Pd$_3$Co$_1$/CNTs. Figure S5. EDX-spot scanning and element content ratio (b,c) of a Pd$_3$Co$_1$ nanoparticle in Pd$_3$Co$_1$/CNTs. Figure S6. The corresponding particle size distribution of a Pd$_3$Co$_1$/C catalyst. Figure S7. TEM and HRTEM images and the corresponding particle size distribution of Pd$_3$Co$_1$/CNT (a–c) and Pd$_2$Co$_3$/CNT (d–f) catalysts. Figure S8. The corresponding particle size distribution of Pd/CNTs. Figure S9. TEM and HRTEM images of a Pd$_3$Co$_1$/C catalyst. Figure S10 Cyclic voltammograms curve of Pd$_3$Co$_1$/C in 0.5 M H$_2$SO$_4$ + 1.0 M HCOOH. Table S1: Elemental composition of the samples obtained from ICP; Table S2: Pd 3d peaks of Pd$_3$Co$_1$/CNTs and Pd/CNTs; Table S3: A recent literature survey of the activity of the FAOR electrocatalysts.

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References

1. Li, Z.; Chen, Y.; Ji, S.; Tang, Y.; Chen, W.; Li, A.; Zhao, J.; Xiong, Y.; Wu, Y.; Gong, Y.; et al. Iridium Single-Atom Catalyst on Nitrogen-Doped Carbon for Formic Acid Oxidation Synthesized Using a General Host-Guest Strategy. *Nat. Chem.* 2020, 12, 764–772. [CrossRef] [PubMed]

2. Lv, F.; Huang, B.; Feng, J.; Zhang, W.; Wang, K.; Li, N.; Zhou, J.; Zhou, P.; Yang, W.; Du, Y.; et al. A Highly Efficient Atomically Thin Curved PdIr Bimetallene Electrocatalyst. *Nat. Sci. Rev.* 2021, 8, nwab019. [CrossRef]

3. Ding, J.; Liu, Z.; Liu, X.; Liu, B.; Liu, J.; Deng, Y.; Han, X.; Hu, W.; Zhong, C. Tunable Periodically Ordered Mesoporosity in Palladium Membranes Enables Exceptional Enhancement of Intrinsic Electrocatalytic Activity for Formic Acid Oxidation. *Angew. Chem.* 2020, 132, 5130–5139. [CrossRef]

4. Shi, Y.; Schimmenti, R.; Zhu, S.; Venkatraman, K.; Chen, R.; Chi, M.; Shao, M.; Mavrikakis, M.; Xia, Y. Solution-Phase Synthesis of PdH$_{0.706}$ Nanocubes with Enhanced Stability and Activity toward Formic Acid Oxidation. *J. Am. Chem. Soc.* 2022, 144, 2556–2568. [CrossRef] [PubMed]

5. Yang, P.; Yang, X.; Liu, W.; Guo, R.; Yao, Z. Graphene-Based Electrocatalsysts for Advanced Energy Conversion. *Green Energy Environ.* 2022. [CrossRef]

6. Xi, Z.; Li, J.; Su, D.; Muzzio, M.; Yu, C.; Li, Q.; Sun, S. Stabilizing CuPd Nanoparticles via CuPd Coupling to WO$_{2.72}$ Nanorods in Electrochemical Oxidation of Formic Acid. *J. Am. Chem. Soc.* 2017, 139, 15191–15196. [CrossRef]

7. Li, H.; Zhang, Y.; Wan, Q.; Li, Y.; Yang, N. Expanded Graphite and Carbon Nanotube Supported Palladium Nanoparticles for Electrocatalytic Oxidation of Liquid Fuels. *Carbon* 2018, 131, 111–119. [CrossRef]

8. Zhang, L.Y.; Wang, F.; Wang, S.; Huang, H.; Meng, X.; Ouyang, Y.; Yuan, W.; Guo, C.X.; Li, C.M. Layered and Hierostructrued Pd/PdWCr Sheet-Assembled Nanoflowers as Highly Active and Stable Electrocatalysts for Formic Acid Oxidation. *Adv. Funct. Mater.* 2020, 30, 2003933. [CrossRef]

9. Li, Y.H.; Deng, H.C.; Zhou, Z.H.; Yang, P.P.; Fei, J.J.; Xie, Y.X. Pd$_{12}$Ag$_1$ Nanosialloy on Dendritic CNFs Catalyst for Boosting Formic Acid Oxidation. *Appl. Surf. Sci.* 2023, 608, 155131. [CrossRef]

10. Qian, H.; Wu, J.; Guo, Y.; Fang, W. PdAgPt Corner-Satellite Nanocrystals in Well-Controlled Morphologies and the Structure-Related Electrocatalytic Properties. *Nanomaterials* 2021, 11, 340. [CrossRef] [PubMed]
11. Liu, X.; Li, Z.; Wang, K.; Zhou, L.; Zhao, X.; Jiang, W.; Li, Q.; Deng, Y. Facile Synthesis of Pd Nanocubes with Assistant of Iodide and Investigation of Their Electrocatalytic Performances Towards Formic Acid Oxidation. *Nanomaterials* 2019, 9, 375. [CrossRef] [PubMed]

12. Zheng, F.; Kwong, T.L.; Yung, K.F. Surfactant-Free Monodispersed Pd Nanoparticles Template for Core-Shell Pd@PdPt Nanoparticles as Electrocatalyst towards Methanol Oxidation Reaction (MOR). *Nanomaterials* 2022, 12, 260. [CrossRef]

13. Kim, J.; Jang, J.S.; Peck, D.H.; Lee, B.; Yoon, S.H.; Jung, D.H. Methanol-Tolerant Platinum-Palladium Catalyst Supported on Nitrogen-Doped Carbon Nanofiber for High Concentration Direct Methanol Fuel Cells. *Nanomaterials* 2016, 6, 148. [CrossRef]

14. Su, S.; Shi, Y.; Zhou, Y.; Wang, Y.B.; Wang, F.B.; Xia, X.H. Tailoring the Electron Density of Pd Nanoparticles through Electronic Metal-Support Interaction for Accelerating Electrocatalysis of Formic Acid. *Electrochem. Commun.* 2019, 107, 106540. [CrossRef]

15. Li, X.; Liu, Y.; Zhang, J.J.; Yan, B.; Jin, C.; Dou, J.; Li, M.; Feng, X.; Liu, G. No Annealing Synthesis of Ordered Intermetallic PdCu Nanocatalysts for Boosting Formic Acid Oxidation. *Chem. Mater.* 2022, 34, 1385–1391. [CrossRef]

16. Zhong, L.; Zeng, T.; Ling, M.; Wang, Y.; Yuan, W.; Zhang, L.Y. Electrocatalytic Activity Enhancement of Palladium-Manganese Nanosheet Assembled Nanobuds by Tuning Electronic Structure. *Appl. Surf. Sci.* 2022, 505, 154634. [CrossRef]

17. Zhang, L.Y.; Meng, X.; Zhang, W.; Zeng, T.; Yuan, W.; Zhao, Z. Synthesis of Palladium–Tungsten Metallene-Constructed Sandwich-Like Nanosheets as Bifunctional Catalysts for Direct Formic Acid Fuel Cells. *ACS Appl. Energy Mater.* 2021, 4, 12336–12344. [CrossRef]

18. Juárez-Marmolejo, L.; Pérez-Rodríguez, S.; de Oca-Yemha, M.M.; Palomar-Pardavé, M.; Romero-Romo, M.; Ezeta-Mejía, A.; Morales-Gil, F.; 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. Hydrogen Energy* 2019, 44, 1640–1649. [CrossRef]

19. Zhang, L.Y.; Li, Z. Graphene Decorated with PdIr Nanocrystals: Ultrasound-Assisted Synthesis, and Application as a Catalyst for Oxidation of Formic Acid. *J. Colloid Interf. Sci.* 2017, 505, 783–788. [CrossRef]

20. Wang, R.X.; Fan, Y.J.; Liang, Z.R.; Zhang, J.M.; Zhou, Z.Y.; Sun, S.G. PdSn Nanocatalysts Supported on Carbon Nanotubes Synthesized in Deep Eutectic Solvents with High Activity for Formic Acid Electrooxidation. *RSC Adv.* 2016, 6, 60400–60406. [CrossRef]

21. Bao, Y.; Zha, M.; Sun, P.; Hu, G.; Feng, L. PdNi/N-Doped Graphene Aerogel with Over Wide Potential Activity for Formic Acid Electrooxidation. *J. Energy Chem.* 2021, 59, 748–754. [CrossRef]

22. Zhang, L.Y.; Gong, Y.; Wu, D.; Li, Z.; Li, Q.; Zheng, L.; Chen, W. Palladium-Cobalt Nanodots Anchored on Graphene: In-Situ Synthesis, and Application as an Anode Catalyst for Direct Formic Acid Fuel Cells. *Appl. Surf. Sci.* 2019, 469, 305–311. [CrossRef]

23. Li, X.; Peng, X.; Wang, Y.; Xi, B.; Dou, J.; Zhang, J.J.; Liu, Y.; Jin, C.; Dou, J.; Li, M.; Feng, X.; Liu, G. No Annealing Synthesis of Ordered Intermetallic PdCu Nanocatalysts for Boosting Formic Acid Oxidation. *Chem. Mater.* 2022, 34, 1385–1391. [CrossRef]

24. Zhang, L.Y.; Meng, X.; Zhang, W.; Zeng, T.; Yuan, W.; Zhao, Z. Synthesis of Palladium–Tungsten Metallene-Constructed Sandwich-Like Nanosheets as Bifunctional Catalysts for Direct Formic Acid Fuel Cells. *ACS Appl. Energy Mater.* 2021, 4, 12336–12344. [CrossRef]

25. Yao, B.; Wang, C.; Xu, H.; Zang, K.; Li, S.; Du, Y. Facile Synthesis of a Porous Pd/Cu Alloy and Its Enhanced Performance toward Methanol and Formic Acid Electrooxidation. *ChemPluschem* 2017, 82, 1211–1218. [CrossRef]

26. Zhang, L.Y.; Gong, Y.; Wu, D.; Wu, G.; Xu, B.; Bi, L.; Yuan, W.; Cui, Z. Twisted Palladium-Copper Nanocubes toward Efficient Electrocatalytic Oxidation of Formic Acid. *J. Colloid Interf. Sci.* 2019, 537, 366–374. [CrossRef]

27. Wang, F.; Wang, S.; Wu, D.; Huang, H.; Yuan, W.; Zhang, L.Y. Layered PdW Nanosheet Assemblies for Alcohol Electrooxidation. *Appl. Surf. Sci.* 2021, 531, 147860. [CrossRef]

28. Selepe, C.T.; Gwebu, S.S.; Matthews, T.; Mashola, T.A.; Sikeyi, L.L.; Zikhali, M.; Maxakato, N.W. Effect of Sn Doping on Pd Electro-Catalysts for Enhanced Electro-Catalytic Activity towards Methanol and Ethanol Electro-Oxidation in Direct Alcohol Fuel Cells. *Nanomaterials* 2021, 11, 2725. [CrossRef]

29. Ma, Y.; Li, T.; Chen, H.; Chen, X.; Deng, S.; Xu, L.; Sun, D.; Tang, Y. A General Strategy to the Synthesis of Carbon-Supported PdM (M = Co, Fe and Ni) Nanodendrites by High-Performance Electrocatalysts for Formic Acid Oxidation. *J. Energy Chem.* 2017, 26, 1238–1244. [CrossRef]

30. Zeng, T.; Meng, X.; Huang, H.; Zheng, L.; Chen, H.; Zhang, Y.; Yuan, W.; Zhang, L.Y. Controllable Synthesis of Web-Footed PdCu Nanosheets and Their Electrocatalytic Performance. *Small* 2022, 18, 2107623. [CrossRef] [PubMed]

31. Wang, W.; He, T.; Yang, X.; Liu, Y.; Wang, C.; Li, J.; Xiao, A.; Zhang, K.; Shi, X.; Jin, M. General Synthesis of Amorphous PdM (M = Cu, Fe, Co, Ni) Alloy Nanowires for Boosting HCOOH Dehydrogenation. *Nan Lett.* 2021, 21, 3458–3464. [CrossRef]

32. Zhang, X.J.; Zhang, J.M.; Zhang, P.Y.; Li, Y.; Xiang, S.; Tang, H.G.; Fan, Y.J. Highly Active Carbon Nanotube-Supported Ru@Pd Core-Shell Nanostructure as an Efficient Electrocatalyst toward Ethanol and Formic Acid Oxidation. *Mol. Catal.* 2017, 436, 138–144. [CrossRef]

33. Zhong, J.; Li, L.; Waqas, M.; Wang, X.; Fan, Y.; Qi, J.; Yang, B.; Rong, C.; Chen, W.; Sun, S. Deep Eutectic Solvent-Assisted Synthesis of Highly Efficient PtCu Alloy Nanoclusters on Carbon Nanotubes for Methanol Oxidation Reaction. *Electrochim. Acta* 2019, 322, 134677. [CrossRef]

34. Zhang, J.M.; Sun, S.N.; Li, Y.; Zhang, X.J.; Zhang, P.Y.; Fan, Y.J. A Strategy in Deep Eutectic Solvents for Carbon Nanotube-Supported PtCo Nanocatalysts with Enhanced Performance toward Methanol Electrooxidation. *Int. J. Hydrogen Energy* 2017, 42, 26744–26751. [CrossRef]

35. Wagle, D.V.; Zhao, H.; Baker, G.A. Deep Eutectic Solvents: Sustainable Media for Nanoscale and Functional Materials. *Acc. Chem. Res.* 2014, 47, 2299–2308. [CrossRef] [PubMed]
36. Yang, P.; Devasenathipathy, R.; Xu, W.; Wang, Z.; Chen, D.H.; Zhang, X.; Fan, Y.; Chen, W. Pt0.5CeO2 Nanoparticles Supported on Multiwalled Carbon Nanotubes for Methanol Electro-Oxidation. ACS Appl. Nano Mater. 2021, 4, 10884–10891. [CrossRef]
37. Yang, P.P.; Zhao, F.C.; Luo, N.; Li, Y.H.; Wang, C.; Zhang, L.; Xie, Y.X.; Fei, J.J. A ‘Special’ Anhydrous System for the Preparation of Alloyed Pd0.5Ce0.5 Nanonetworks Catalyst Supported on Carbon Nanotubes with High Electrochemical Oxidation Activity for Formic Acid. Int. J. Hydrogen Energy 2021, 46, 18857–18865. [CrossRef]
38. Yang, P.; Zhou, Z.; Zheng, T.; Gu, C.; Gong, X.; Zhang, Y.; Xie, Y.; Yang, N.; Fei, J. A Novel Strategy to Synthesize Pt/CNTs Nanocatalyst with Highly Improved Activity for Methanol Electrooxidation. J. Electroanal. Chem. 2021, 897, 115557. [CrossRef]
39. Yang, P.; Wei, L.; Xiao, X.; Zhou, Z.; Li, J.; Zhang, Y.; Xie, Y.; Yang, N.; Fei, J. Electrocatalytic Oxidation of Formic Acid on Pt/CNTs Nanocatalysts Synthesized in Special ‘Non-Aqueous’ System. J. Electroanal. Chem. 2022, 906, 115980. [CrossRef]
40. Yang, P.; Li, Y.; Chen, S.; Li, J.; Zhao, P.; Zhang, L.; Xie, Y.; Fei, J. One-Step Synthesis in Deep Eutectic Solvents of PtSn-CeO2 Alloy Nanopore on Carbon Nanotubes for Enhanced Electro-Catalytic Methanol Oxidation. J. Electroanal. Chem. 2021, 887, 115164. [CrossRef]
41. Zhang, J.M.; He, J.J.; Wang, X.Q.; Fan, Y.J.; Zhang, X.J.; Zhong, J.P.; Chen, W.; Sun, S.G. One-Step Synthesis in Deep Eutectic Solvents of PtV Alloy Nanonetworks on Carbon Nanotubes with Enhanced Methanol Electrooxidation Performance. Int. J. Hydrogen Energy 2019, 44, 28709–28719. [CrossRef]
42. Xiang, S.; Wang, L.; Huang, C.C.; Fan, Y.J.; Tang, H.G.; Wei, L.; Sun, S.G. Concave Cubic PtLa Alloy Nanocrystals with High-Index Facets: Controllable Synthesis in Deep Eutectic Solvents and Their Superior Electrocatalytic Properties for Ethanol Oxidation. J. Power Sources 2018, 399, 422–428. [CrossRef]
43. Azevedo, R.S.; de Sousa, J.R.; Araujo, M.T.; Martins Filho, A.J.; de Alcantara, B.N.; Araujo, F.; Queiroz, M.G.; Cruz, A.C.; Vasconcelos, B.H.B.; Chiang, J.O.; et al. In Situ Immune Response and Mechanisms of Cell Damage in Central Nervous System of Fatal Cases Microcephaly by Zika Virus. Sci. Rep. 2018, 8, 1. [CrossRef]
44. Wei, L.; Mao, Y.J.; Liu, F.; Sheng, T.; Wei, Y.S.; Li, J.W.; Fan, Y.J.; Zhao, X.S. Concave Cubic Pt–Sm Alloy Nanocrystals with High-Index Facets and Enhanced Electrocatalytic Ethanol Oxidation. ACS Appl. Energy Mater. 2019, 2, 7204–7210. [CrossRef]
45. Wei, L.; Xu, C.-D.; Huang, L.; Zhou, Z.-Y.; Chen, S.-P.; Sun, S.-G. Electrochemically Shape-Controlled Synthesis of Pd Concave-Disyndyakis Triacantahedra in Deep Eutectic Solvent. J. Phys. Chem. 2015, 120, 15569–15577. [CrossRef]
46. Mao, Y.J.; Wei, L.; Chen, S.; Zhang, X.S.; Chen, Y.; Sheng, T.; Zhu, F.C.; Tan, N.; Zhou, Z.Y.; Sun, S.G. Excavated Cubic Platinum-Iridium Alloy Nanocrystals with High-Index Facets as Highly Efficient Electrocatalysts in N2 Oxidation to NH3. Chem. Commun. 2019, 55, 9335–9338. [CrossRef]
47. Hammons, J.A.; Muselle, T.; Ustarroz, J.; Tzedaki, M.; Raes, M.; Hubin, A.; Terryn, H. Stability, Assembly, and Particle/Solvent Interactions of Pd Nanoparticles Electrodeposited from a Deep Eutectic Solvent. J. Phys. Chem. 2013, 117, 14381–14389. [CrossRef]
48. Luo, S.-X.L.; Liu, R.Y.; Lee, S.; Swagger, T.M. Electrocatalytic Isoxazoline-Nanocarbon Metal Complexes. J. Am. Chem. Soc. 2021, 143, 10441–10453. [CrossRef]
49. Qi, Z.; Xiao, C.; Liu, C.; Goh, T.W.; Zhou, L.; Maligal-Ganesh, R.; Pei, Y.; Li, X.; Curtiss, L.A.; Huang, W. Sub-4 Nm PtZn Intermetallic Nanoparticles for Enhanced Mass and Specific Activities in Catalytic Electrooxidation Reaction. J. Am. Chem. Soc. 2017, 139, 4762–4768. [CrossRef]
50. Zhang, L.; Li, J.; Wang, C.; Bang, J.; Chen, X.; Li, Y.; Shi, J.; Zhao, P.; Xie, Y.; Fei, J. A Novel Kaemperlo Electrochemical Sensor Based on Glass Carbon Electrode Modified by Poly (3, 4-Ethlenedioxythiophene) Decorated with Green Synthesized MIL-100(Fe)-Multi-Walled Carbon Nanotubes Composites. Sensors 2017, 17, 129484. [CrossRef]
51. Hu, Y.; Wang, C.; Zhao, P.; Zhang, L.; Li, J.; Xie, Y. A Novel Catechin Electrochemical Sensor Based on a Two-Dimensional MOFs Material Derivative Zn Doped Carbon Nanosheets and Multi-Walled Carbon Nanotubes Composite Film. Talanta 2022, 246, 123520. [CrossRef][PubMed]
52. Cazares-Avila, E.; Ruiz-Ruiz, E.J.; Hernandez-Ramirez, A.; Rodriguez-Varela, F.J.; Morales-Acosta, M.D.; Morales-Acosta, D. Effect of OMC and MNWTC Support on Mass Activity of PdCo Catalyst for Formic Acid Electro-Oxidation. Int. J. Hydrogen Energy 2017, 42, 30349–30358. [CrossRef]
53. Gunji, T.; Wakabayashi, R.H.; Noh, S.H.; Han, B.; Matsumoto, F.; DiSalvo, F.J.; Abruna, H.D. The Effect of Alloying of Transition Metals (M = Fe, Co, Ni) with Palladium Catalysts on the Electrocatalytic Activity for the Oxygen Reduction Reaction in Alkaline Media. Electrochem. Acta 2018, 283, 1045–1052. [CrossRef]
54. Zuluaga, S.; Stolbov, S. Factors Controlling the Energetics of the Oxygen Reduction Reaction on the Pd-Co Electro-Catalysts: Insight from First Principles. J. Chem. Phys. 2011, 135, 134702. [CrossRef]
55. Suy, Y.; Zhuang, L.; Lu, J. First-Principles Considerations in the Design of Pd-Alloy Catalysts for Oxygen Reduction. Angew. Chem. Int. Edit. 2007, 46, 2862–2864. [CrossRef]
56. Yang, B.; Zhang, W.; Hu, S.; Liu, C.; Wang, X.; Fan, Y.; Jiang, Z.; Yang, J.; Chen, W. Bidirectional Controlling Synthesis of Branched PdCu Nanoalloys for Efficient and Robust Formic Acid Oxidation Electrocatalysis. J. Colloid Interf. Sci. 2021, 600, 503–512. [CrossRef]
57. Zhang, Z.; Gong, Y.; Wu, D.; Li, Z.; Li, Q.; Zheng, L.; Chen, W.; Yuan, W.; Zhang, L.Y. Facile Fabrication of Stable PdCu Clusters Uniformly Decorated on Graphene as an Efficient Electrocatalyst for Formic Acid Oxidation. Int. J. Hydrogen Energy 2019, 44, 2731–2740. [CrossRef]
58. Zhang, L.Y.; Meng, X.; Wu, H.; Wang, F.; Huang, H.; Ouyang, Y.; Yuan, W.; Guo, C.X.; Li, C.M. Tungsten-Induced Synthesis of Defective Palladium–Copper–Tungsten Trimetallic Nanochains to Highly Enhance Activity for Formic acid Electrooxidation. *Mater. Today Energy* 2020, 18, 100558. [CrossRef]

59. Chen, Y.; Yang, Y.; Fu, G.; Xu, L.; Sun, D.; Lee, J.M.; Tang, Y. Core–Shell CuPd@Pd Tetrahedra with Concave Structures and Pd-Enriched Surface Boost Formic Acid Oxidation. *J. Mater. Chem. A* 2018, 6, 10632–10638. [CrossRef]

60. Gong, Y.; Liu, X.; Gong, Y.; Wu, D.; Xu, B.; Bi, L.; Zhang, L.Y.; Zhao, X. Synthesis of Defect-Rich Palladium-Tin Alloy Nanochain Networks for Formic Acid Oxidation. *J. Colloid Interf. Sci.* 2018, 530, 189–195. [CrossRef]

61. Zheng, J.; Zeng, H.; Tan, C.; Zhang, T.; Zhao, B.; Guo, W.; Wang, H.; Sun, Y.; Jiang, L. Coral-like PdCu Alloy Nanoparticles Act as Stable Electrocatalysts for Highly Efficient Formic Acid Oxidation. *ACS Sustain. Chem. Eng.* 2019, 7, 15354–15360. [CrossRef]

62. Zhang, L.Y.; Zhao, Z.L.; Yuan, W.; Li, C. M Facile one-pot surfactant-free synthesis of uniform Pd₆Co nanocrystals on 3D graphene as an efficient electrocatalyst toward formic acid oxidation. *Nanoscale* 2016, 8, 1905–1909. [CrossRef] [PubMed]

63. Wang, L.; Zhai, J.J.; Jiang, K.; Wang, J.Q.; Cai, W.B. Pd–Cu/C electrocatalysts synthesized by one-pot polyol reduction toward formic acid oxidation: Structural characterization and electrocatalytic performance. *Int. J. Hydrogen Energy* 2015, 40, 1726–1734. [CrossRef]

64. Sun, D.; Si, L.; Fu, G.; Liu, C.; Sun, D.; Chen, Y.; Tang, Y.; Lu, T. Nanobranched porous palladium–tin intermetallics: One-step synthesis and their superior electrocatalysis towards formic acid oxidation. *J. Power Sources* 2015, 280, 141–146. [CrossRef]

65. Yang, F.; Zhang, Y.; Liu, P.F.; Cui, Y.; Ge, X.R.; Jing, Q.S. Pd–Cu alloy with hierarchical network structure as enhanced electrocatalysts for formic acid oxidation. *Int. J. Hydrogen Energy* 2016, 41, 6773–6780. [CrossRef]

66. Feng, A.; Bai, J.; Shao, W.; Hong, W.; Tian, Z.Q.; Xiao, Z. Surfactant-free Pd–Fe nanoparticles supported on reduced graphene oxide as nanocatalyst for formic acid oxidation. *Int. J. Hydrogen Energy* 2017, 42, 15196–15202. [CrossRef]

67. Zhu, F.; Ma, G.; Bai, Z.; Hang, R.; Tang, B.; Zhang, Z.; Wang, X. 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]