

Pd-Sn alloy nanoparticles for electrocatalytic methanol oxidation: Phase evolution from solid solution to intermetallic compounds

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© Tsinghua University Press 2022 Received: 1 April 2022 / Revised: 12 May 2022 / Accepted: 20 May 2022

ABSTRACT

Developing efficient catalysts with high activity and durability via alloying strategy is essential to the energy conversion in various electro-catalytic reactions. Among the different alloy structures, intermetallic compounds (IMCs) have received much attention recently due to the special geometric and electronic effects and outstanding activity and durability, endowed by their ordered structure. Herein, A series of hollow-structured nanocrystals of Pd-Sn alloy, including face-centered cubic solid solution of Pd(Sn), IMCs of Pd₂Sn, and IMCs of Pd₃Sn₂, are fabricated via a solvothermal strategy by varying the precursor ratio of Pd and Sn. The structure difference of the nanocrystals has been investigated via combined electron microscopy and spectroscopy, assisted by local elemental separation analysis and X-ray spectroscopy. Among all, Pd₃Sn₂ IMCs show outstanding methanol oxidation reaction (MOR) activity in terms of mass activity (1.3 A·mg_{Pd}⁻¹) and specific activity (5.03 mA·cm⁻²). Through density functional theory (DFT) simulation calculations on three different Pd-Sn alloy models, the performance has been well understood. As compared with Pd(Sn) and Pd₂Sn, the high MOR kinetics on Pd₃Sn₂ is featured by its weaker CO adsorption and favorable CO–OH co-adsorption.

KEYWORDS

Pd-Sn alloy, intermetallic compound, hollow structure, electrocatalysis, methanol oxidation reaction

1 Introduction

Noble metal-based nanomaterials have attracted much attention in the past decades for their irreplaceable role in catalyzing many important reactions [1–3]. The catalytic performance is driven by the reaction kinetics, which can be determined by the activation energy of the reaction and described by the adsorption energy of the intermediates [4, 5]. Meanwhile, the adsorption energy is in turn dependent on the electronic structure of the catalyst, which is correlated with its physical structure and especially the surface structure [6]. While Pt-group metals have long been demonstrated as superior electrocatalysts for processes likes hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and methanol oxidation reaction (MOR) [7–9], the limited activity and low abundance still call for new synthetic innovation in their alloys with precise control, enhanced activity, higher durability, and insightful understanding of mechanism [10–12].

The structure of binary alloys usually falls into three categories, including heterostructure, solid solution, and intermetallic compound (IMC) [13–15]. The choice of structure is thermodynamically determined by the interaction between the like and unlike atoms, but experimentally dependent on the synthetic protocols and requires great expertise [16–18]. Among them, IMC has been proven to be an effective candidate to form highly active and durable alloy catalysts, as it is driven by the favorable interaction between the unlike atoms [14, 19]. Huang's group reported the synthesis of ultrathin nanowires (NWs) of A1-phase palladium-copper alloy, which was transformed into an

intermetallic B2 phase (PdCu-B2 NWs) by electrochemical treatment at room temperature [20]. For the reduction reaction (HER), the PdCu nanostructures with the intermetallic B2 phase show enhanced electrocatalytic activity in both acidic and basic media as compared to the A1 phase. The density functional theory (DFT) calculation results indicate that the B2 phase nanostructure has more "suitable" hydrogen binding energies and lower water dissociation activation energies than the disordered counterparts. Jeong et al. prepared disordered Pt₃Co alloy nanowires (D-Pt₃Co NWs) and fully ordered Pt₃Co intermetallic nanowires (O-Pt₃Co NWs) catalysts by confined nano-spatial orientation using mesoporous silica templates [21]. O-Pt₃Co NWs exhibit superior oxygen reduction activity and stability over D-Pt₃Co NWs and Pt/C. Combining DFT calculation results and experimental evidence, it is found that the excellent intrinsic catalytic activity of ordered intermetallic compounds can be attributed to the enhanced ligand effect in the subsurface. Importantly, the membrane electrode assembly (MEA) test indicates the excellent durability of O-Pt₃Co NWs in proton exchange membrane fuel cell (PEMFC) single-cell.

The Pd-Sn system has received special attention as Sn forms a large library of IMCs and solid solution with palladium, providing plenty of room for the study of structure–control and structure–performance relationship. The incorporation of Sn not only reduces the use of the expensive Pd but also improves the electronic structure of the noble metal [22–25]. In addition, the oxygen affinity of Sn effectively removes the intermediate

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adsorbed on the surface and reduces the Pd poisoning, thereby improving the catalytic activity and durability [26-28]. In the study of Du and co-workers, a series of grid-like PdSn nanomaterials prepared by the modified polyol method were employed as efficient anode catalysts for direct alcohol fuel cells [29]. The X-ray photoelectron spectroscopy (XPS) results clearly indicated that the introduction of Sn changed the electronic structure of Pd, which played an important role in improving the MOR activity. Huang et al. synthesized wavy Pd₄Sn nanowires, which exhibited high activity and stability in ORR and MOR [30]. The improvement of MOR activity and stability comes from the vacancy structure (especially the Sn vacancy structure) caused by surface defects, which reduces the activation energy of the MOR process and increases the energy barrier of the CO poisoning process. While various alloys of Pd-Sn have been studied as promising electrocatalysts for MOR, there is still huge room for improvement.

Herein, a series of Pd-Sn alloy nanoparticles (NP) with hollow structure were obtained via a solvothermal method. The alloy structure evolves from Pd-Sn solid solution to Pd₃Sn₂ and Pd₂Sn IMCs with the increase of Sn/Pd ratio. The catalytic evaluation manifests that the hollow Pd₃Sn₂ IMC possesses the best electrocatalytic activity and durability for MOR in alkaline medium, as compared with the other two catalysts, i.e., Pd₂Sn and Pd(Sn) solid solution. The proper spatial distribution of Pd and Sn in Pd₃Sn₂ has led to suitable electronic structure and favorable coadsorption of CO and OH, which weakened the adsorption of CO and contribute to the excellent performance.

2 Experimental

2.1 Materials and chemicals

All the reagents were of analytical grade and used without further purification. Palladium(II) acetylacetonate (Pd(acac)₂) was purchased from Aldrich Chemistry; tin(II) chloride dihydrate (SnCl₂·2H₂O) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); polyvinylpyrrolidone (PVP, K 29-32) was purchased from Macklin; N,N-dimethylformamide (DMF) was purchased from Tianjin Yuanli Chemical industry Co., Ltd. (Tianjin, China). Vulcan XC-72R carbon was supplied by Cabot Corp. Potassium hydroxide (KOH, 95%) was purchased from Meryer. Methanol solution was purchased from Shanghai Aladdin Biochemical Technology. Nafion (5 wt.%) was purchased from Sigma-Aldrich. Ar (99.999%) was purchased from Tianjin Yekong High-Tech Gas Co., Ltd.

2.2 Synthesis of Pd_xSn_y NP catalysts

The Pd_xSn_v alloy nanoparticles were prepared by reference to the synthesis of excavated cubic platinum-tin alloy [31]. Pd₃Sn₂ was synthesized with a precursor Sn/Pd ratio of 1:1. In a hydrothermal synthesis reactor, 12 mL of DMF was added, followed by 0.02 mmol of Pd(acac)₂, 0.02 mmol of SnCl₂·2H₂O, and 0.3 g of PVP. After stirring and dissolving, the autoclave was transferred into a 200 °C oven and reacted for 6 h. The resulting solution was centrifuged and washed with deionized water, and then dried in vacuum. Pd(Sn), Pd₂Sn, and Sn(Pd) were synthesized by similar methods with Sn/Pd ratio of 1:4 (0.008 mmol of SnCl₂·2H₂O and 0.032 mmol of Pd(acac)₂), 2:3 (0.016 mmol of SnCl₂·2H₂O and 0.024 mmol of Pd(acac)₂), and 4:1 (0.032 mmol of SnCl₂·2H₂O and 0.008 mmol of Pd(acac)₂), respectively, with all the other conditions unchanged. The synthesis of pure Pd (or Sn) was to remove the precursor of Sn (or Pd) under the same other conditions.

2.3 Materials characterization

Transmission electron microscopy (TEM, JEOL-1230) was used to characterize the morphology of the products. High-resolution TEM (HRTEM), high-angle annular dark field scanning TEM (HAADF-STEM), and energy dispersive X-ray spectroscopy (EDS) mapping were performed on a JEOL JEM-F200 transmission electron microscope. The crystal structure of the sample was analyzed by X-ray diffractometry (XRD) at room temperature using a D8-Focus diffractometer (Bruker AXS) with a Cu K α radiation source (40 kV, 40 mA, and λ = 1.5418 Å). The XPS was performed using an ESCALAB-250Xi spectrometer (Thermo Fisher Scientific) with Al K α X-ray. The amount of three Pd-Sn samples for the electro-catalytic reaction was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720).

2.4 Electrochemical measurements

The electrochemical analysis was performed on a CHI-660 potentiostat (CH Instruments, Austin, TX, USA). A typical threeelectrode system was used in the measurement, with a glassycarbon (GC, diameter of 4 mm) electrode as the working electrode, a platinum foil as the counter electroche, and a Hg/HgO electrode as the reference electrode. For electrochemical test, the carbon black powder (Vulcan XC-72R, Cabot) was used as the support for all the as-obtained alloy nanoparticles. The loading of metals in the carbon-supported catalyst was 20%: 2 mg of the alloy and 8 mg of the carbon were dispersed in 1 mL of isopropanol and mixed with 990 μ L of pure water. Then 10 μ L of Nafion (5.0 wt.%) was added before ultrasonication for 1 h to form a uniformly dispersed suspension. The ink was cast onto the GC electrode to form an even film, with a metal loading of 40 μ g·cm⁻².

For electrochemical test, cyclic voltammetry (CV) was performed in argon-saturated 1.0 M KOH and 1.0 M KOH added with 1.0 M methanol solution respectively, at a sweep rate of 50 mV·s⁻¹. The electrochemically active surface area (ECSA) of the catalysts was calculated by integrating the oxidation charge of CO stripping on the CV in the 1.0 M KOH solution. For CO stripping test, first, CO was bubbled into 1.0 M KOH for 20 min, followed by another 10 min with the potential held at 0.08 V. Argon gas was then introduced for 30 min to remove the excess CO. Finally, CO was stripped by scanning CV from 0.05 to 1.2 V at a sweep rate of 10 mV·s⁻¹.

3 Results and discussion

In the presence of Pd(acac)₂, SnCl₂·2H₂O, PVP, and DMF, Pd-Sn nanoparticles with different compositions were obtained through a solvothermal method at 200 °C for 6 h. Three types of hollow Pd-Sn nanocrystals were obtained by tuning the ratio of SnCl₂·2H₂O and Pd(acac)₂ at 1:4, 2:3, and 1:1. The actual atomic ratio of Sn to Pd was determined by the EDS and ICP-OES (Fig. S1 and Table S1 in the Electronic Supplementary Material (ESM)). The results obtained by the two analytical methods are similar and very close to the theoretical feed ratio.

As shown in the XRD pattern (Fig. S2 in the ESM), the products obtained with a molar ratio of Sn/Pd = 1/4 (blue line) retain a typical face-centered cubic (fcc) structure, just as pristine Pd. The diffraction angle shifts to a lower end to that of Pd (JCPDS: 46-1043) as the doping of larger Sn (metallic radius: 140 pm) expands the crystal lattice of Pd (131 pm) [22]. A clear hollow structure can be identified from the TEM and HRTEM images (Figs. 1(a) and 1(b)), which could be attributed to the Kirkendall effect [32–34]. It is reasonable as Pd is more easily reduced from its precursor as compared to Sn. Hence, Pd nanoparticles will be generated in the reaction and act as the



Figure 1 (a) TEM image, (b) HRTEM image (inset: enlarged view of local area), (c) HAADF image, and (d) EDS mapping of nanoparticles with Sn/Pd molar ratio of 1:4. TEM, HRTEM, HAADF, and EDS images of Sn to Pd of 2:3 ((e)–(h)) and 1:1 ((i)–(l)), respectively. The scale bars in TEM ((a), (e), and (i)) and HRTEM ((b), (f), and (j)) images are 50 and 5 nm, respectively. The scale bars in the insets of (b), (f), and (j) are 1 nm.

template for the hollow structure, with Pd out-diffusing against the inward-diffusing Sn. In comparison, the TEM image of the product obtained with only Pd precursor shows solid nanoparticles (Fig. S3 in the ESM), while the XRD diffraction peaks show clear shift to the lower angle (black line in Fig. S2 in the ESM), due to the formation of palladium hydride. The peak size in the TEM-based histogram of the hollow nanoparticles is around 25 nm (Fig. S4(a) in the ESM). The HRTEM image (Fig. 1(b)) confirms the crystalline feature of the hollow structure, which shows a lattice spacing of 0.237 nm, slightly larger than that of fcc Pd (111) (0.225 nm) and consistent with the XRD shift. The EDS mapping of the product confirms the mixing of the two elements although slight enrichment of Sn at the surface can be identified (Fig. 1(d)). It supports the above hypothesis that the Sn was grown on the preformed Pd nanoparticles and the structure underwent incomplete mixing.

When more Sn is introduced into the host, the alloy structure underwent further transformation into an ordered one. As shown in the XRD pattern (green line in Fig. S2 in the ESM) of the products obtained from Sn/Pd = 2/3, an IMC phase of Pd₂Sn (JCPDS: 52-1515) can be identified. The particle size is smaller (12 nm, Fig. S4(b) in the ESM) but the hollow feature is retained (Figs. 1(e)–1(g)). The lattice spacing in Fig. 1(f) (0.229 nm) can be attributed to the {013} crystal plane of Pd₂Sn IMC while the mixing of Pd and Sn is more uniform with less element enrichment.

When the Sn/Pd ratio increases to 1, the XRD pattern (red line in Fig. S2 in the ESM) can be indexed to Pd_3Sn_2 IMC (JCPDS: 04-0801). The peak size sampled from the TEM images is around 13 nm (Fig. S4(c) in the ESM). The lattice fringes in Fig. 1(j) (0.227 nm) are consistent with the interplanar spacing of {102} planes in the hexagonal Pd_3Sn_2 . A darker ring can be identified in the center part of the hollow structure. It is clearer in the highcontrast region of the HAADF-STEM image (Fig. 1(k)). The central part should be attributed to the unalloyed Pd, which has a density (12.0 g·cm⁻²) much higher than that of Pd_3Sn_2 (10.2 g·cm⁻²). The EDS elemental mapping clearly indicates the near-uniform mixing of Pd and Sn in the nanoparticles, with some residue Sn left between the nanoparticles (Fig. 1(l)). It makes up for the difference between the stoichiometry of the crystalline phase and the ICP-EDS results. The Pd and Sn distribution is further investigated by the local element separation (LES) method developed by us recently. The heatmap of the LES matrix was derived from the EDS mapping signal of Pd and Sn (Figs. 2(a) and 2(b)). As shown in Fig. 2(c), the yellow regions indicate a Pd/Sn ratio higher than average (Pd-rich) and the blue regions lower than average (Sn-rich). The bright yellow pixels in the heatmap match well with the high-brightness part in the HAADF-STEM image, confirming the enrichment of Pd in the center of the nanoparticles. The residual Sn around the alloy nanoparticles could be easily identified in the navy regions of the heatmap.

While the series of hollow structured nanoparticles can be obtained with the element ratio as in the precursor, we will use Pd(Sn), Pd_2Sn , and Pd_3Sn_2 to indicate the samples with Sn/Pd feed ratio of 1:4, 2:3, and 1:1 for the following discussion, respectively. Although more IMC types can be identified from the phase diagram (Fig. S5 in the ESM), they were not obtained under the experimental conditions, as confirmed by the single Pd_3Sn_2 crystalline phase in the sample obtained with Sn/Pd ratio of 4 (Fig. S2 in the ESM).

The hollow structure is featured by large surface area, which is beneficial to catalysis by exposing more active sites. The MOR activity of the series of Pd-Sn catalysts was evaluated in alkaline media. As shown in the CV in a 1 M KOH electrolyte (Fig. S6 in the ESM), the hydrogen adsorption peak can be observed in the range of 0.05–0.4 V vs. reversible hydrogen electrode (RHE) while the peak between 0.4–1.2 V (vs. RHE) can be attributed to the hydroxyl adsorption/desorption. Pd₃Sn₂ exhibits lower OH desorption potential (0.722 V) than Pd₂Sn and Pd(Sn), corresponding to high OH binding energy (BE).

The electrochemical MOR for the Pd-Sn alloy catalysts was conducted by CV measurement in an Ar-saturated solution containing 1 M KOH and 1 M CH₃OH. Here, the current density was normalized by the ECSA calculated from CO stripping which is 25.8 m²g⁻¹ for Pd₃Sn₂, 25.8 m²·g⁻¹ for Pd₂Sn, and 21.7 m²g⁻¹ for Pd(Sn), as shown in Fig. 3(a) and Fig. S7 in the ESM. Pd₃Sn₂ has the lowest onset potential and the highest peak current density in term of specific activity (Fig. 3(b)). This could be explained by the most negative CO desorption potential of Pd₃Sn₂ as compared to the other samples (Fig. 3(a)). As shown in Fig. 3(c), Pd₃Sn₂ has



Figure 2 (a) and (b) EDS mapping of Pd and Sn in the alloy nanoparticles with Sn/Pd ratio of 1, and (c) the local elemental separation heatmap derived from the EDS mapping.



Figure 3 Electrochemical evaluation of Pd_3Sn_2 , Pd_2Sn , and Pd(Sn). (a) CO stripping in Ar-saturated 1.0 M KOH at a scan rate of 10 mV·s⁻¹. (b) Methanol oxidation in aqueous solution containing 1.0 M KOH and 1.0 M methanol (scan rate: 50 mV·s⁻¹). (c) Comparison of the mass activities and specific activities of different catalysts towards methanol oxidation.

the highest mass activity (1.3 A·mg_{Pd}⁻¹) and specific activity (5.03 mA·cm⁻²), which are 1.6 and 1.5 times those of Pd₂Sn, respectively. The superior performance of Pd₃Sn₂ was also consolidated via chronoamperometry. After holding the potential at 0.74 V (vs. RHE) for 7,200 s, the residual mass activity of Pd₃Sn₂ (50.3 A·g_{Pd}⁻¹) is 1.4 and 2.2 times those of the Pd₂Sn (36.3 A·g_{Pd}⁻¹) and fcc Pd(Sn) (23.3 A·g_{Pd}⁻¹), respectively, illustrating the excellent stability of Pd₃Sn₂ (Fig. S8 in the ESM). Therefore, the results demonstrate that the Pd₃Sn₂ phase exhibits superior MOR performance in both activity and durability.

To investigate the relationship between the structure and performance in these Pd-Sn alloy, XPS was used to probe the difference in their electron structure. In all the samples, the peak area for Sn in the oxidized state is clearly larger than that of Sn in the metallic state (Figs. 4(a)-4(c)). The calculated ratio of Sn^o to Sn^{2+/4+} is 29.2:70.8 in Pd(Sn), 21.6:78.4 in Pd₂Sn, and 24.2:75.8 in Pd₃Sn₂. It should be noted that Sn is easily oxidized and not all Sn is alloyed with Pd or forming Pd-Sn IMC. In this regard, the XPS of Pd is more informative than that of Sn. The Pd 3d spectra indicate that the majority of Pd in Pd(Sn), Pd₂Sn, and Pd₃Sn₂ is in metallic state, as is shown in Figs. 4(d)-4(f). Both the Pd $3d_{3/2}$ and 3d_{5/2} peaks of Pd₂Sn (Fig. 4(e)) can be fitted by three peaks, indicating the presence of Pd in three different oxidation states. The Pd $3d_{5/2}$ peaks typically have BE of 335.1, 335.7, and 336.2 eV. The peak at 336.2 eV is attributed to surface oxidation while the other two peaks are related to the two different Pd atoms in the crystal structure of Pd_2Sn and Pd_3Sn_2 . The diminishment of peak at 335.1 eV in Pd_3Sn_2 is related to the reduced ratio of Pd species in the channels of the crystal structure (1/3 as compared to 1/2 in Pd_2Sn), as is shown in Fig. S9 in the ESM.

Further understanding of the activity difference in the Pd-Sn alloy can be consolidated by the DFT calculation. Based on the bifunctional mechanism [35], CO and OH adsorption energies are efficient descriptor for the MOR activity. To find the spatial distribution of CO and OH adsorption, the difference in CO and OH adsorption energy between different sites of the catalyst models was studied, including Pd₃Sn₂, Pd₂Sn, and Pd(Sn) with 25% Sn doping (simplified model for the Pd(Sn) solid solution). As shown in Fig. S10 in the ESM, the green and orange points were stable or meta-stable CO (green) and OH (orange) adsorption sites in the Pd-Sn alloy surface. CO tends to adsorb on the Pd sites and OH tends to adsorb on the Sn sites or Pd/Sn bridge sites. Hence, the synergetic effects of Pd and Sn exhibit as different adsorption preference in the CO and OH. Moreover, CO and OH tend to be distantly dispersed in Pd₂Sn and closely dispersed in Pd₃Sn₂ and Pd(Sn) models. Because the adsorbed CO molecules were lastly oxidized by the adjacent OH group, the spatial proximity of CO and OH was able to highly influence the kinetics of surface CO removal. To further understand the influence of CO and OH distribution, the most stable CO/OH coadsorption configuration is shown in Fig. 5(a) and the C-O partial pair distribution function (PDF) of different models is plotted in



Figure 4 XPS of ((a)-(c)) Sn 3d and ((d)-(f)) Pd 3d for ((a) and (d)) Pd₃Sn₂, ((b) and (e)) Pd₂Sn, and ((c) and (f)) Pd(Sn). The Sn²⁺ and Sn⁴⁺ species are very close in BE to be differentiated.



Figure 5 (a) The most stable CO and OH co-adsorption configuration on Pd-Sn alloy models including Pd(Sn) with 25% doping, Pd₂Sn, and Pd₃Sn₂. (b) C–O partial pair distribution function of the models. (c) Adsorption energy of CO and OH in the Pd(Sn), Pd₂Sn, and Pd₃Sn₂ models. (d) RESP charge of C (in CO molecule) and O (in OH group) adsorbed on the Pd(Sn), Pd₂Sn, and Pd₃Sn₂ surface.

Fig. 5(b). The distances of the second and third shells O in the catalyst models are 2.6 and 3.2 Å for Pd(Sn), 3.1 and 3.2 Å for Pd₃Sn₂, and 4.0 and 4.1 Å for Pd₂Sn. Among them, the Pd₂Sn model has the longest CO–OH distance while Pd(Sn) the shortest.

On the other hand, the adsorption energy was compared to distinguish the difference in adsorption energy among the catalyst models. As shown in Fig. 5(c), the CO adsorption shows big difference in different Pd-Sn models while the OH adsorption is almost unaffected. The CO adsorption energy in the Pd₃Sn₂ model is +0.69 eV, which indicates greater anti-poisoning characteristics. The Pd(Sn) model has the most negative CO adsorption energy and the most surface sites of Pd due to the low doping level. Hence, a large part of Pd(Sn) surface could be poisoned because the adsorbed OH cannot convert all the adjacent strongly-bonded CO molecules. The charge feature was also studied to unveil the interaction between CO and the substrate. The restrained electrostatic potential (RESP) charges of C (in CO molecule) and O (in OH group) were fitted (Fig. 5(d) and Fig. S10 in the ESM). The C atoms have more positive charge in the Pd₃Sn₂ model, which indicates less electron transfer from Pd, while the transfer in Pd(Sn) and Pd₂Sn models is more significant. To sum up, Pd₃Sn₂ is featured by weaker CO adsorption and favorable CO-OH coadsorption, which contributes to its high MOR kinetics as compared with Pd(Sn) and Pd₂Sn.

4 Conclusions

To summarize, a facile approach has been developed to synthesize a novel class of binary Pd-Sn alloy nanoparticles with a hollow structure. The increased doping of Sn leads to the evolution from Pd-Sn solid solution to Pd-Sn IMCs of Pd₂Sn and Pd₃Sn₂. IMC of higher Sn/Pd ratio cannot be obtained with this method, even with excess Sn addition. The structure difference after Sn introduction effectively modifies the electronic structure of the alloy, which further regulates the absorption energy of the reaction intermediate. When the Sn/Pd feed ratio is 1/1, the resultant Pd₃Sn₂ IMC shows the highest catalytic MOR activity (1.3 A·mg_{Pd}⁻¹ and 5.03 mA·cm⁻²) among all. Based on the DFT calculation results, the change in the electronic structure has led to weakened adsorption of CO and favorable co-adsorption of CO and OH, which contributes to the excellent performance of Pd₃Sn₂.

Acknowledgements

The authors acknowledge support from the Natural Science Foundation of Tianjin, China (No. 18JCYBJC20600) and Institute of Energy, Hefei Comprehensive National Science Center (No. 19KZS207).

Electronic Supplementary Material: Supplementary material (detailed supporting figures of TEM, XRD, XPS, electrocatalytic MOR measurement, and DFT calculation information) is available in the online version of this article at https://doi.org/10.1007/s12274-022-4565-2.

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